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Corrosion Protection under Thermal Insulation

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Submission date: June 2013
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NATURVITENSKAPELIGE UNIVERSITET
INSTITUTT FOR PRODUKTUTVIKLING
OG MATERIALER

MASTEROPPGAVE VÅR 2013
FOR
STUD.TECHN. KAREN SIGBJØRNSEN

KORROSJONSBESKYTTELSE UNDER TERMISK ISOLERING
Corrosion protection under thermal insulation

Korrosjon under termisk isolasjon på rør er et stort problem i kjemisk og petrokjemisk industri. Den høye temperaturen under isolasjonen gjør at stålet i røret kan korrodere raskt hvis vann trenger gjennom mantlingen over isolasjonen. På grunn av mantling og isolasjon er det også svært vanskelig å inspisere for korrosjon. Alt må fjernes før man har tilgang til røret og kan inspisere korrosjonstilstand. Dette gjør at inspeksjon og vedlikehold blir svært komplisert og dyrt. Det finnes ingen enkel løsning på problemet, men det er flere ting man kan gjøre for å redusere omfanget. En av disse tingene er å sørge for at de korrosjonsbeskyttende beleggene som benyttes er av tilstrekkelig god kvalitet. For det trenger man en test og en testprosedyre som kan skille mellom dårlige og gode belegg. Oppgaven vil gå ut på å implementere og evaluere en slik test.

Innhold i oppgaven:
- Litteraturstudie på korrosjon under isolasjon og korrosjonsbeskyttelse med maling under isolasjon
- Sette sammen testapparatur basert på publisert metode
- Teste et antall belegg
- Evaluere prøvene og sammenligne med andre resultater
- Analyse av beleggene i SEM for å undersøke nedbrytningsmekanismer

Besvarelsen skal ha med signert oppgavetekst, og redigeres mest mulig som en forskningsrapport med et sammendrag på norsk og engelsk, konklusjon, litteraturliste, innholdsfortegnelse, etc. Ved utarbeidelse av teksten skal kandidaten legge vekt på å gjøre teksten oversiktlig og velskrevet. Med henblikk på lesning av besvarelsen er det viktig at de nødvendige henvisninger for korresponderende steder i tekst, tabeller og figurer anføres på begge steder. Ved bedømmelse legges det stor vekt på at resultater er grundig bearbeidet, at de oppstilles tabellarisk og/eller grafisk på en oversiktlig måte og diskuteres utførlig.

Senest 3 uker etter oppgavestart skal et A3 ark som illustrerer arbeidet leveres inn. En mal for dette arket finnes på instituttets hjemmeside under menyen masteroppgave (http://www.ntnu.no/ipm/masteroppgave). Arket skal også oppdateres en uke før innlevering av masteroppgaven.

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Ole Øystein Knudsen
Faglærer

Preface

This master's thesis is written at the Department of Engineering Design and Materials, at the Norwegian University of Science and Technology.

I would like to thank my supervisor Ole Øystein Knudsen for all the help and guidance throughout the thesis. I would also like to thank Peter Aidan von Bonin for all the help with sample preparation and SEM training, Synnøve Åldstedt for the help with the grinding, Wilhelm Dall for helping me out with the SEM and Nils-Inge Nilsen for all the help during set-up and execution of the testing.

Trondheim 13.06.2013

Karen Sigbjørnsen

Abstract

Corrosion under insulation (CUI) is an extensive and costly problem for the petrochemical and chemical industry. Both good coatings to mitigate the problem and test methods to ensure the quality of these coatings are needed. In this thesis, four coatings; standard epoxy coating, epoxy phenolic coating, titanium modified inorganic copolymer (TMIC) and thermally sprayed aluminium (TSA), were tested for their ability to mitigate the problem. To simulate the CUI conditions, several test methods may be used, as there is no consensus on which method that best represents the CUI conditions. The cyclic pipe test developed by Halliday et al. [1] were used and evaluated in this work.

In this test method, the coatings were applied at carbon steel pipes with outer diameter of 6 cm and length of 60 cm. Calcium silicate insulation covered by aluminium foil was wrapped around the pipes and this was placed in casseroles and put on hot plates. 30 cycles with cyclic temperatures and wet/dry conditions were performed. 1 cycle ran for 24 hours and consisted 8 hours of heating at 450^{o}C followed by 16 hours of natural cooling at ambient temperature. Before and after each heating period, 1 litre of 1% NaCl solution was poured into the insulation.

The results showed that best protection was achieved by the TMIC coating with no degradation up to 300^{o}C. Second came the TSA with no degradation up to 190^{o}C. The epoxy phenolic had the lowest temperature tolerance with blistering and poor adhesion at 160^{o}C and failure by rusting and blistering at 220^{o}C. The testing of the standard epoxy was not completed due to lack of time.

The cyclic pipe test proved to be an overall good test method for comparing coatings for CUI protection. All the major problems as thermal cycling with high temperatures, wetting and drying period, intermittent immersion and thermal shock are included in the test. It is also relatively easy to set up and not very demanding concerning equipment.

Some improvements could be made for the test method regarding more constant testing conditions between tests. These are:

- A test set-up with a horizontally placed pipe with a heat source in one of the ends could be developed to create equal immersion conditions along the length of the test pipe.
- To set additional fixed terms to minimize variations between tests and improve the temperature control.

Sammendrag

Korrosjon under isolasjon er et omfattende og kostbart problem for petrokjemisk og kjemisk industri. Både gode belegg for å redusere problemet og testmetoder for å sikre kvaliteten på disse beleggene er nødvendig. I denne oppgaven er fire belegg; standard epoksybelegg, fenolepoksy belegg, titan modifisert uorganisk kopolymer (TMIC) og termisk sprøytet aluminium (TSA), testet for sin evne til å redusere korrosjon under isolasjon. Flere testmetoder kan benyttes for å simulere korrosjon under isolasjon, men det er ingen enighet om hvilken metode som best representerer dette. I denne oppgaven ble den sykliske rørtesten utviklet av Halliday et al. [1] brukt og evaluert.

I denne testmetoden ble beleggene påført på karbonstålrør med ytre diameter 6 cm og lengde 60 cm. Kalsiumsilikat isolasjon dekket av aluminiumsfolie ble plassert rundt rørene og dette ble deretter plassert i gryter og satt på varmeplater. 30 sykluser med syklisk temperatur og skiftende våte og tørre forhold ble utført. En syklus varte i 24 timer og besto av oppvarming til 450^{o}C i 8 timer og deretter naturlig avkjøling i 16 timer ved omgivelsestemperatur. Før og etter hver oppvarmingsperiode ble 1 liter med 1% NaCl-løsning helt over isolasjonen.

Resultatene viste at den beste beskyttelsen for røret ble oppnådd med TMIC belegg. Ingen nedbrytning av belegget ble sett for temperaturer opp til 300^{o}C. Nest best beskyttelse gav TSA som ikke hadde noen nedbrytning opp til 190^{o}C. Epoksyfenol hadde den laveste temperaturtoleransen med blemmer og dårlig heft fra temperaturer høyere enn 160^{o}C og fullstendig nedbrytning av belegget med rust og blemmer ved 220^{o}C. Testingen av standard epoksy ble ikke fullført på grunn av tidsmangel.

Den sykliske rørtesten viste seg generelt sett å være en god testmetode for å sammenligne belegg for CUI beskyttelse. Alle de viktigste problemene som termisk sykling ved høy temperatur, våte og tørre perioder, sporadisk nedsenkning i elektrolytisk løsning og termisk sjokk, er inkludert i testen. Den er i tillegg relativt enkelt å sette opp og ikke veldig krevende med tanke på utstyr.

Noen forbedringer kan gjøres ved testmetoden for å få mer konstante testforhold mellom testene. Disse er:

- Et testoppsett med et horisontalt plassert rør med en varmekilde i en av endene kan utvikles for å få periodisk nedsenkning i hele testrørets lengderetning.
- Angi flere faste betingelser for å minimere variasjoner mellom testene og oppnå bedre temperaturkontroll.

Contents

Nomenclature

CSCC	Chloride stress corrosion cracking
CUI	Corrosion under insulation
DFT	Dry film thickness
MIO	Micaceous iron oxide
SEM	Scanning electron microscope
TMIC	Titanium modified inorganic copolymer
TSA	Thermally sprayed aluminium

1 Introduction

1.1 Background

Already in the 1950's corrosion under insulation (CUI) was reported, but it was not before the 1980's there was an increased effort to mitigate CUI [2]. Today it is a widespread problem in the petrochemical industry counting for 60 to 80% of all pipe maintenance costs [3]. In a study conducted from 1999 to 2001 by Koch et al. [4], the direct cost of corrosion in USA was estimated to $276 billion dollars a year, i.e. about 3% of the gross domestic product. $121 billion dollars were spent on preventing corrosion, and 88.3% these were spent on organic coatings. Coatings under the insulation is the best solution to mitigate CUI [5]. These coatings need to withstand several harsh conditions, and improvements are made continuously. A very aggressive corrosive environment may occur under the insulation but the insulation will hide the corrosion, and the damage might not be discovered until serious injury occurs. As inspection or non-destructive on-stream examination is difficult and almost as costly as re-painting the field [3], very high demands are set for the coatings.

1.2 Problem

Organic coatings and thermally sprayed aluminium (TSA) have already proven to be useful in mitigation of CUI. However, TSA has very strict application requirements and organic coatings do not withstand very high temperatures that may occur in the petrochemical or refinery processes. To deal with these issues, high-temperature silicone coatings have been developed. Four coatings; standard epoxy, epoxy phenolic, thermally sprayed aluminium (TSA) and titanium modified inorganic copolymer (TMIC), were tested. To ensure the quality of the coatings, tests simulating the CUI conditions have been developed, but there is no consensus on which method is to be used. The test should also represent accelerated conditions as the testing is done over a limited time period.

1.3 Objective with this work

The objective with this work is to:

- Test four coatings and compare them to each other and to other test results to see how they perform in CUI conditions.
- Implement and evaluate the cyclic pipe test developed by Halliday et al. [1].

2 Theoretical background

2.1 Insulation of pipes

When containing hot or cold fluid in a tank, pipe or other equipment, insulation will be important to avoid heat loss or condensation. These are the main reasons to insulate, but there are also other reasons such as protection of personnel and noise reduction.

However, due to the temperature difference between the insulation and the steel, condensation may occur. This is the root cause of corrosion under insulation (CUI) [6]. If there is water present, depending on temperature cycling and chemical composition of the water phase, it may develop a very aggressive corrosive environment at the steel surface. The most destructive CUI temperature range is from 60 to 120^{o}C, as the water evaporates at higher temperatures [7]. However, in a closed system corrosion may occur also at higher temperatures as the vapour may be hindered to escape the insulation by the jacketing. The vapour may condensate at the inside of the jacketing and maintains the moist environment. **Figure 2.1** shows the corrosion rate (CR) as a function of temperature in an open and a closed system. The closed system shows similar corrosion rate as is measured for CUI [2]. It is observed that while the CR decreases at higher temperatures for the open system, it increases for the closed system, which is also the case for CUI.

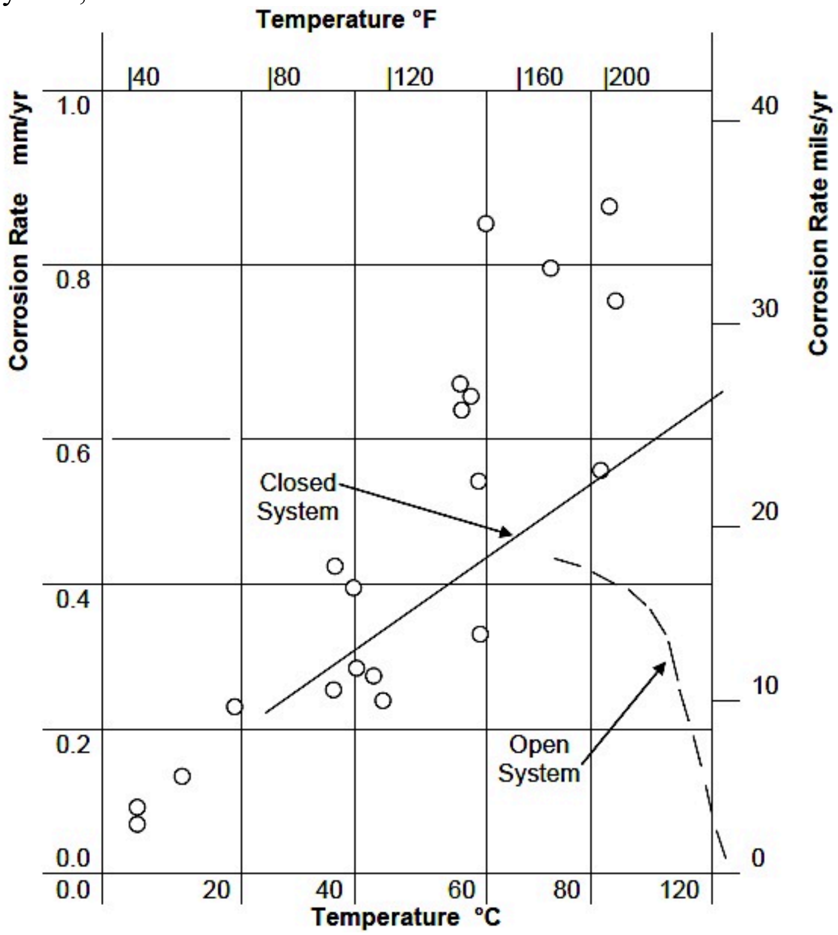

Figure 2.1 Corrosion rate of steel in water at different temperatures, open and closed systems. The plotted circles represent field values measured for CUI [2].

To protect the insulation from mechanical damage, weather conditions and to prevent water from penetrating the insulation, a weather barrier or a jacketing is installed outside the insulation, as in **Figure 2.2**. Nevertheless, this will not hinder the water permanently, and sooner or later the water will slip through the barrier and enter the insulation [8]. Therefore, coatings are used on the steel surface to mitigate CUI.

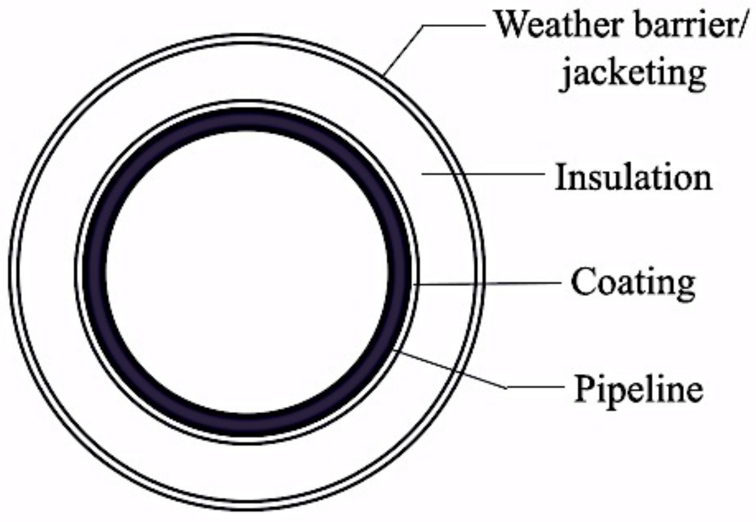

Figure 2.2 Typical cross section of an insulated pipe.

It was during the 1970s, when the energy costs increased, pipes were insulated to save energy [9]. This caused unknown corrosion problems, because it was hidden under the insulation. Today, it is still a hidden problem, as the insulation is typically only removed every 15-20 years [9]. Therefore, several measures are taken to deal with the problem; immersion grade coatings, proper insulation and risk based inspection [6]. For better inspection without removing the insulation, Gassco have developed an inspection method where dogs are used to detect corrosion under insulation [10]. Air samples are taken from underneath the insulation, and presented for trained dogs. Due to their good sense of smell, the dogs will detect if the sample is taken from an area with corrosion. Testing so far has shown very good results.

2.2 The CUI cycle

The cycle causing the CUI is described by Bock [11] as shown in **Figure 2.3**. When the pipe or vessel is cold, water may penetrate the weather barrier or jacketing as well as the insulation, and the steel surface will become wet, as shown in **Figure 2.3**a). When the temperature of the steel or equipment increases, the water will start to evaporate, but the jacketing will prevent most of the moisture to escape, **Figure 2.3**b). As the temperature decreases, the vapour trapped under the cladding will condensate and penetrates the insulation, **Figure 2.3**c). Again the steel is moist and corrosion may occur if there is no coating to prevent it. Contaminants from the wet insulation and the thermal cycling may concentrate and strengthen electrolytes found in the water, and the corrosion rate may increase dramatically.

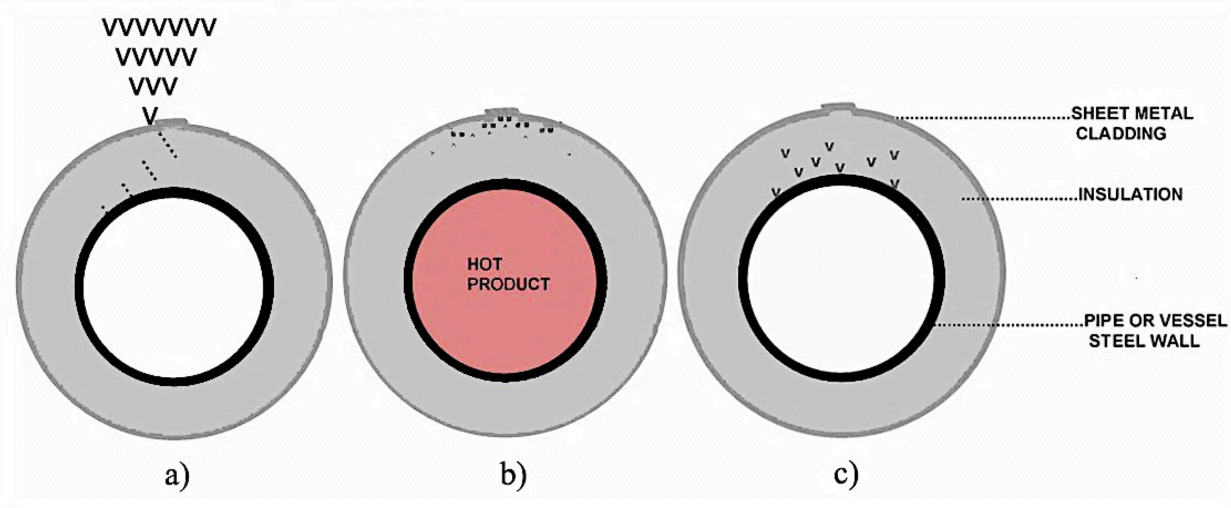

Figure 2.3 The CUI cycle [11].

2.2.1 Corrosion types

The type of corrosion that occurs under thermal insulation depends on which type of steel is used. Also the shape of the pipe or vessel will influence the corrosion type. At temperatures 0 to 150°C, carbon and low alloy steel will suffer significantly from general (uniform) corrosion. However, at some locations, for instance hollows and corners where the water will accumulate, pitting corrosion may occur. At 60 to 205°C, the main problems for austenitic and duplex stainless steels, are pitting corrosion and chloride stress corrosion cracking (CSCC) [12]. For more information about different corrosion types, see [12].

2.3 Influence of insulation on CUI

The choice of insulation does not only affect the ability to maintain the temperature. Also the corrosion rate may be affected. Today, calcium silicate, expanded pearlite, man-made mineral fibres, cellular glass, organic foams and ceramic fibres are common insulation material used by the industry [5]. Some insulation types, such as phenolic foam and polyurethane foam, will contain chlorides and bromide ions that dissolve when the insulation is wetted. This will decrease the pH of the water, which may accelerate the corrosion rate [12]. There are also large differences in the wicking properties of insulations. Calcium silicate may absorb up to 400% of its own weight of water, while cellular glass (foamglass) is a non-wicking insulation that will not absorb water provided that the cell structure is still intact [13]. Also, wet calcium silicate has a pH of 9 to 10, which will create an unfavourable corrosive environment for coatings such as alkyds and inorganic zinc [5]. When choosing insulation for austenitic and duplex stainless steels, the chloride content should be carefully considered due to susceptibility to CSCC.

Williams et al. [14] performed testing of different types of insulation to study the influence of insulation on CUI. Laboratory tests focusing on effectiveness of corrosion inhibitors, hydrophobe durability, maximum water uptake and time to dry out were executed. Also, the insulation was exposed to outdoor conditions in 12 weeks on a bare-steel rig. The results are summarized in

Table 2.1. Altogether, the water absorbent materials; calcium silicate and mineral wool, performed worst and Pyrogel XT, a flexible aerogel blanket material, had excellent results in all of the categories.

Table 2.1 Results from CUI testing performed by Williams et al. [14]. Score 1 represents poor, 5 represents excellent and "–" indicates no testing was done in this category. [14]

	Calcium silicate	Expanded perlite	Pyrogel XT	Cellular glass	WRG mineral wool	Mineral wool	Pyrogel XT over mineral wool
Durability of corrosion inhibitors	1	2	5	-	-	-	-
Water repellency within CUI range	1	4	5	5	4	1	5
Thermal durability of hydrophobe	-	2	5	-	1	-	5
Water repellency above CUI range	-	2	5	5	1	-	5
Maximum water uptake	1	1	5	5	3	1	2
Time to dry out	1	1	5	-	3	1	-
External pipe stand tests	2	5	5	1	3	2	5

As wet insulation is essential for CUI to occur, attempts have been made to prevent contact between the insulation and the steel. Haraldsen [15] performed tests where the effect of a distance insulation system, **Figure 2.4**, was compared to a normal insulation system. The distant insulation system gave a positive result for all of the coatings tested. However, the perforated aluminium plate used beneath the insulation was not suited for the task, as there were corroded holes and loss of locking hinges.

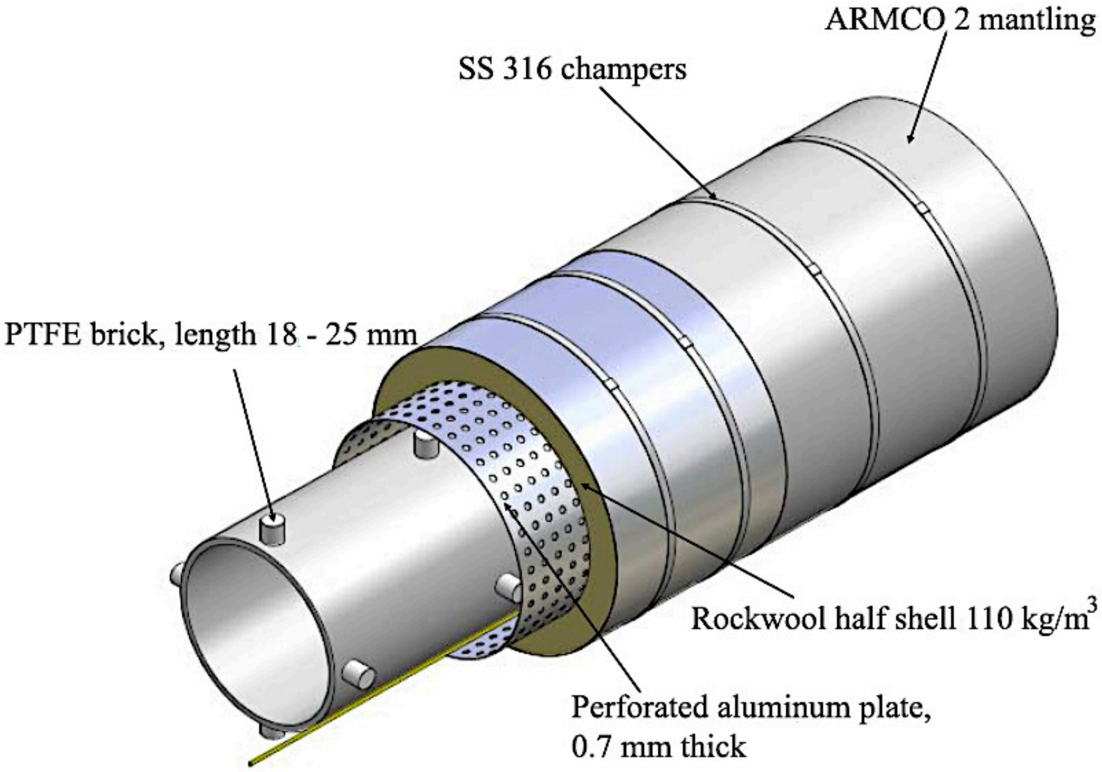

Figure 2.4 Distant insulation system [15].

2.4 Coatings to protect against CUI

Coatings under insulation are effectively used to prevent the contact between the water and the steel and hence hinder corrosion. However, the coatings will not have an indefinite lifetime and there are several limitations to the conditions under which they should be used. A large variety of coatings are available to count for different requirements, but they will also have various limitations. To choose a coating, several conditions need to be taken into account; the operating temperature, weather and loading conditions, availability to maintenance and the lifetime of the coating, which depends on surface preparation, application and curing. [16]. The most common coating systems used for mitigation of CUI are the phenolic epoxies and novolac epoxies [9]. However, process temperatures are increasing, and where 150°C was used before, 205°C might be used today [9]. This imposes higher requirements for the coatings, and new high temperature coatings are therefore developed.

2.4.1 Organic Coatings

Epoxy coatings are widely used to mitigate CUI. The epoxy provides good barrier properties, adhesion and chemical resistance. On the other hand, it must be protected against light due to degradation by UV light [16]. Sa 2.5 or SSPC-SP 10 near-white blast cleaning is recommended as surface preparation, which is defined as:

> A near-white metal blast cleaned surface, when viewed without magnification, shall be free of all visible oil, grease, dust, dirt, mill scale, rust, coating, oxides, corrosion products, and other foreign matter, except for staining as noted in Section 2.2. [17].

In Section 2.2, random staining is limited to 5% of a unit area at the surface, which is approximately 5776 mm^2. This surface preparation is also recommended for the phenolic epoxy coating.

Phenolic epoxies are also frequently used and the coating tested has a maximum operating temperature of 230^oC [1]. At higher temperatures, the coating will become brittle and crack. Phenolic epoxies normally have a narrow dry film thickness (DFT) range [11], and it must not exceed 300 μm (12 mils) to avoid cracking. Typically, two coats of 100 μm (4 mils) each are used. The application temperature should not be less than 3^oC, and temperatures lower than 10^oC results in longer curing times.

2.4.2 Metallic Coatings

Thermally sprayed aluminium (TSA) is a very common metallic coating used for CUI. TSA has a maximum operating temperature of 595^oC [5], and it has no limit to the surface temperature when it is applied, as it is arc or flame applied. SSPC-SP10, near-white blast cleaning is needed as surface preparation [11]. The application and surface preparation are crucial for the corrosion resistant properties of the TSA, but when correctly applied, it has demonstrated a lifetime of 20 year with no maintenance [7]. In rural areas it will not function as a sacrificial anode, but in marine environments containing chlorides it will have this effect. A protective layer of Al_2O_3 is formed at the surface and slows down the corrosion rate [18]. However, TSA has a porosity of 5 to 15% and therefore sealer paints are often applied as a final coat, as the porous surface forms a good base for the paint [12].

Zinc has a slimmer passive film area in a chloride containing environment, see **Figure 2.5**, and will therefore often be an active layer, which implies higher corrosion rate. When using zinc as protection against corrosion, the film will thus corrode away after much shorter time than the aluminium coating. Also, Shih [19] found that for temperatures higher than approximately 60^oC, the corrosion potential for zinc increases more than iron. There is no reversal in the standard electrochemical potential between zinc and iron, but in closed circuit conditions corrosion products will form at the zinc surface, but not on the iron surface and the corrosion potential for the zinc will become greater than for the iron. This implies that zinc will transform from sacrificial anode to cathode for the carbon steel. However, this is dependant of the presence of dissolved oxygen, temperature and the composition of the water. This should be taken into account when using zinc as cathodic protection. For an insulated surface, NORSOK M-501 [20] recommends that zinc should not be used at temperatures higher than 60^oC.

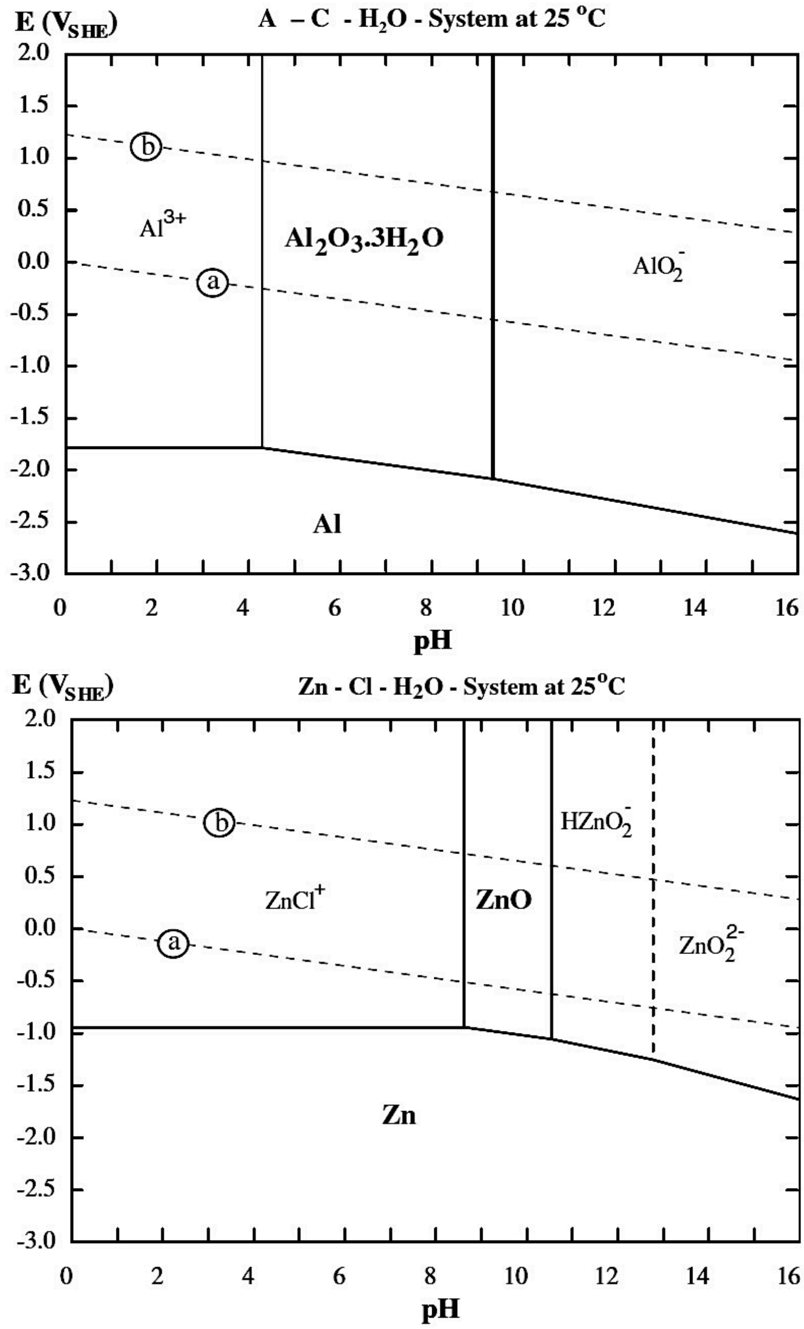

Figure 2.5 Pourbaix diagram for pure Al and Zn in 1M NaCl solution (0.67 activity of Cl^-) in Cl^- – H_2O system at 25°C [21].

2.4.3 Silicon-based coatings

Silicone-based coatings are formed when inorganic silicone pigments are added to a coating. They have high operation temperature limit and high resistance against moisture and weathering. However, they are somewhat expensive and will not withstand acids and alkalis [18]. Several types of silicone-based coatings have been developed. Inorganic zinc silicate coating can endure temperatures up to 400°C, but due to unsatisfactory long-term corrosion resistance it is not used for CUI [22]. The maximum dry film thickness of many zinc silicates are 75 μm (3 mils), which are not sufficient for protection against CUI [7]. Despite showing excellent protection against corrosion in atmospheric environment, the harsh corrosion conditions under insulation accelerate the corrosion rate of zinc such that the coating will only provide corrosion protection for a few years [7]. If steel is primed with an inorganic zinc-rich coating, it should be top-coated to extend the service life [9]. Also the thermal cycling and shock properties of these early silicon-based coatings are poor [7]. NACE SP0198-2010 recommends that inorganic zinc-rich coatings should not be used by itself for mitigation of CUI at temperatures 50 to 175°C in a closed and often wet system as it presents inadequate corrosion resistance. [5].

Titanium modified inorganic copolymer (TMIC) coatings will survive temperatures up to 400°C in cyclic operation and 650°C in continuous operation in a CUI environment [22]. It consists of cross-linked inorganic film formers and contains aluminium flake pigments. During thermal cycling, the pipe will have thermal expansion and contraction. The coating also needs to follow this cycle in order to have good adhesion and hence good corrosion protection. The overlapping aluminium flake pigments will make it possible for the coating to endure the stresses that arise during a heat cycle due to mechanical toughening of the coating [22]. TMIC can be applied by brush and roller techniques or by airless or conventional spray [7]. Furthermore, the minimum surface pre-treatment is only SSPC-SP6, commercial blasted surfaces. O'Donoghue et al. [22] tested a TMIC coating, which performed excellent corrosion protection up to 400°C. It was noted that the cross-linking was not fully achieved until it was heated above 100°C. TMIC may also be used to seal the porosity of the TSA, and this combination of coatings will extend the lifetime of the TSA with 25-30 years [7].

2.5 Test methods

2.5.1 Cyclic pipe test

The cyclic pipe test was developed by Halliday et al. [1]. A coated pipe is insulated with calcium silicate, sealed with aluminium foil and placed upon a hot plate, see **Figure 2.6**. Calcium silicate represents the worst-case scenario, as it is very wicking. The temperature at the hot plate is 450°C, and at the opposite end of the pipe the temperature is approximately 60°C. This system is cycled 30 times with 8 hours of heating followed by 16 hours of natural cooling. Before and after each heating cycle the insulation is wetted with 1 litre 1% NaCl solution, as would have been the case if there were a break in the insulation.

Figure 2.6 Assembly of cyclic pipe test [7].

The coatings are evaluated with respect to rusting (ISO 4628-3:2003) [23], blistering (ISO 4628-2:2003) [24] and cracking (ISO 4628-4:2003) [25]. The rusting is categorized according to **Table 2.2** and the blistering is evaluated with respect to both density and size of the blisters on a scale from 0 to 5. The rating of cracking is characterized in terms of size, density and depth of the cracks. Also here the size and density are rated from 0 to 5. The depth of the crack are divided in three categories; surface cracks that does not penetrate the top coat, cracks that only penetrates the top coat, not affecting the underlying coat(s) and cracks that penetrates the whole coating system.

Table 2.2 Classification of rusting according to ISO 4628-3:2003 [23].

Degree of rusting	Rusted area %
Ri 0	0
Ri 1	0.05
Ri 2	0.5
Ri 3	1
Ri 4	8
Ri 5	40 to 50

Collins et al. [26] performed a similar cyclic testing of coatings in 1985. Only the highest temperature was 315°C and instead of NaCl solution, 1 litre of water was poured into the insulation once a day. The pipe was suspended over a propane burner, see **Figure 2.7**, and calcium silicate was used as insulation on the bottom two-thirds of the pipe, while fire retardant polyurethane foam covered the top third. Water running through fire retardant polyurethane foam has an acid pH, which creates a corrosive environment. However, water running through calcium silicate is alkaline and this combination provides severe test conditions. Also in this test the pipes were cycled 30 times with 8 hours heating and 16 hours natural cooling. The coatings were evaluated by visual inspection and it was found that those coatings that failed to some extent under the calcium silicate, failed catastrophically beneath the fire retardant polyurethane foam, which presented the most corrosive environment.

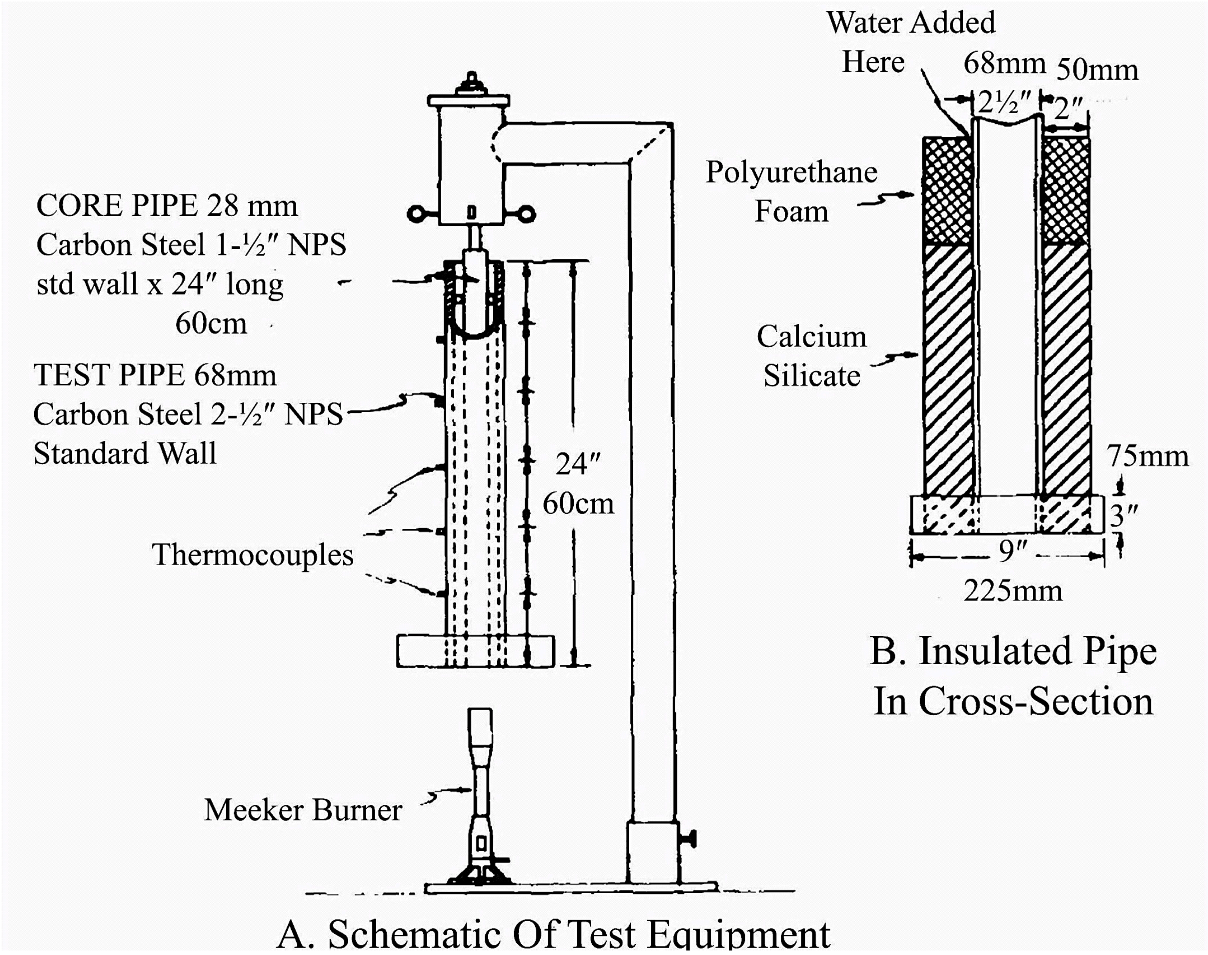

Figure 2.7 Testing equipment used by Collins et al. [26].

2.5.2 Laboratory simulation of CUI

ASTM G189-07 describes a standard guide for laboratory simulation of CUI [27]. This method consists of a CUI cell with three to six test specimens and non-conductive spacers, but with electrical contact between the three specimens on each side of the large spacer, see **Figure 2.8**. This cell was first used by Abavarathna et al. [2]. The large seal is used under the insulation to separate the specimens in two environments. One of the sides is used as a control environment where no corrosion protection is used. In the other half, the specimens may be coated or inhibitors added to compare the results with the control condition. The specimens used should have a nominal diameter of 2 inches (50.8 mm), 4.75 mm thickness and 6.35 mm width. An immersion heater is placed inside the pipe to regulate the temperature. Also thermocouples are placed beneath the insulation at the surface of the innermost ring specimen for monitoring of the temperature. As shown in **Figure 2.9**, one half of the circumference is covered by insulation with holes for fluid feed and drain. The fluid suggested consists of water containing 1 ppm NaCl that is acidified with H_2SO_4 to achieve a pH of 6.

Different types of environments may be simulated, but in order to simulate a wet/dry environment with cyclic temperatures, the insulation should be wetted for 20 hours and then be allowed to dry for 4 hours. The temperature should be held at the lowest temperature for 20 hours, and then 4 hours at the highest temperature. This should be done for at least 72 hours. To measure the amount of corrosion, mass loss information or electrochemical dynamic polarization resistance measurements are used.

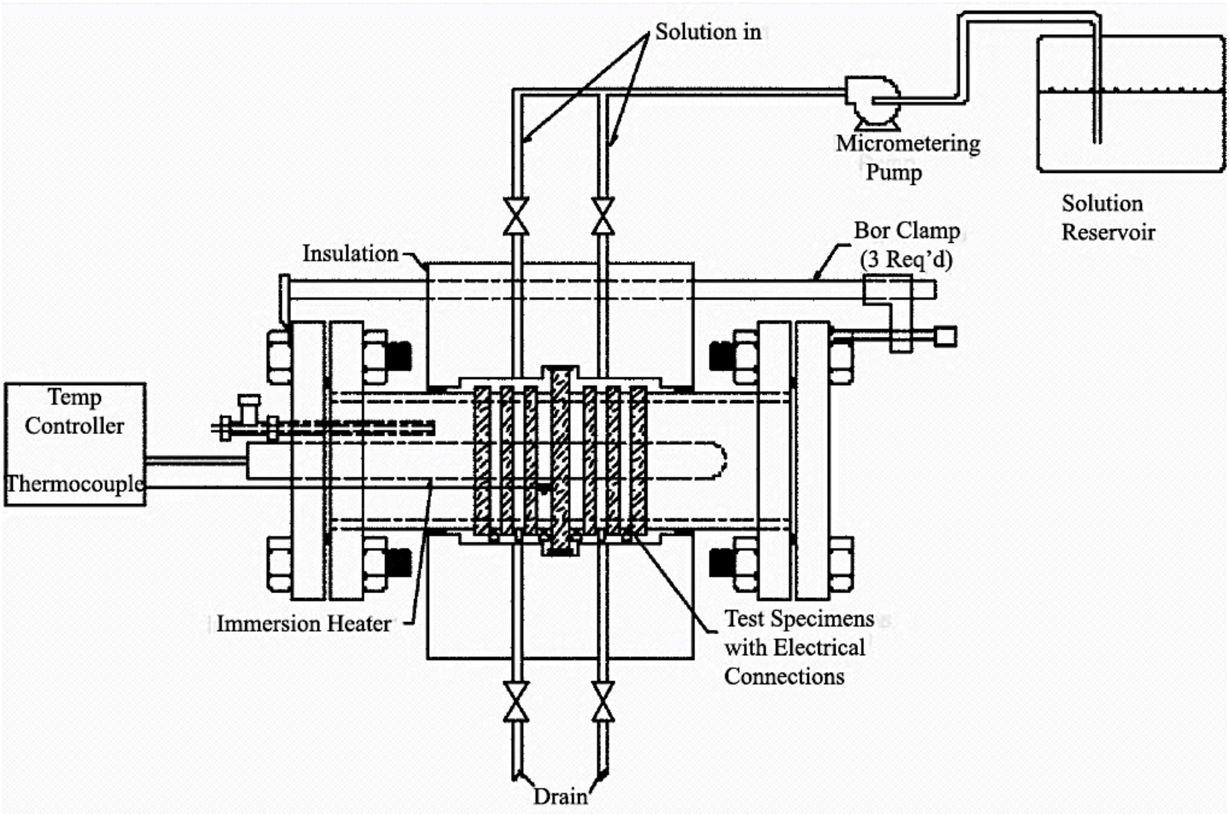

Figure 2.8 Cell for laboratory simulation of CUI [27].

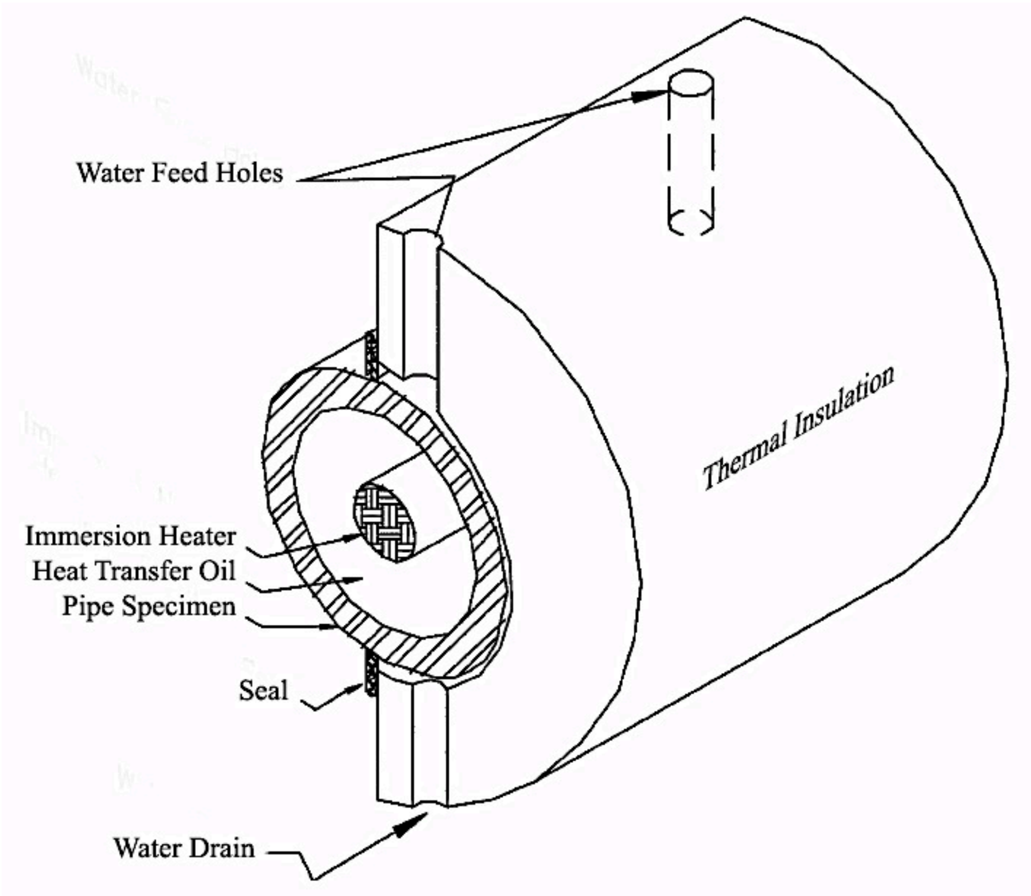

Figure 2.9 Cross section of CUI cell [27].

2.5.3 Pilot scale accelerated testing

Haraldsen [15] performed testing by an accelerated test method which turned out to present very harsh conditions for the steel. A planned inspection was made after two months of testing and due to the large rate of corrosion the test was then terminated.

The test cell consisted of test spools of carbon steel tube sections flanged together in open containers, see **Figure 2.10**. The containers were filled with seawater and drained immediately after the spools were fully submerged, which lasted for approximately 20 minutes. This was done three times a week. Steam was lead through the pipes to provide an internal temperature of 140°C. The ambient temperature was 15 to 20°C with 30-80% relative humidity.

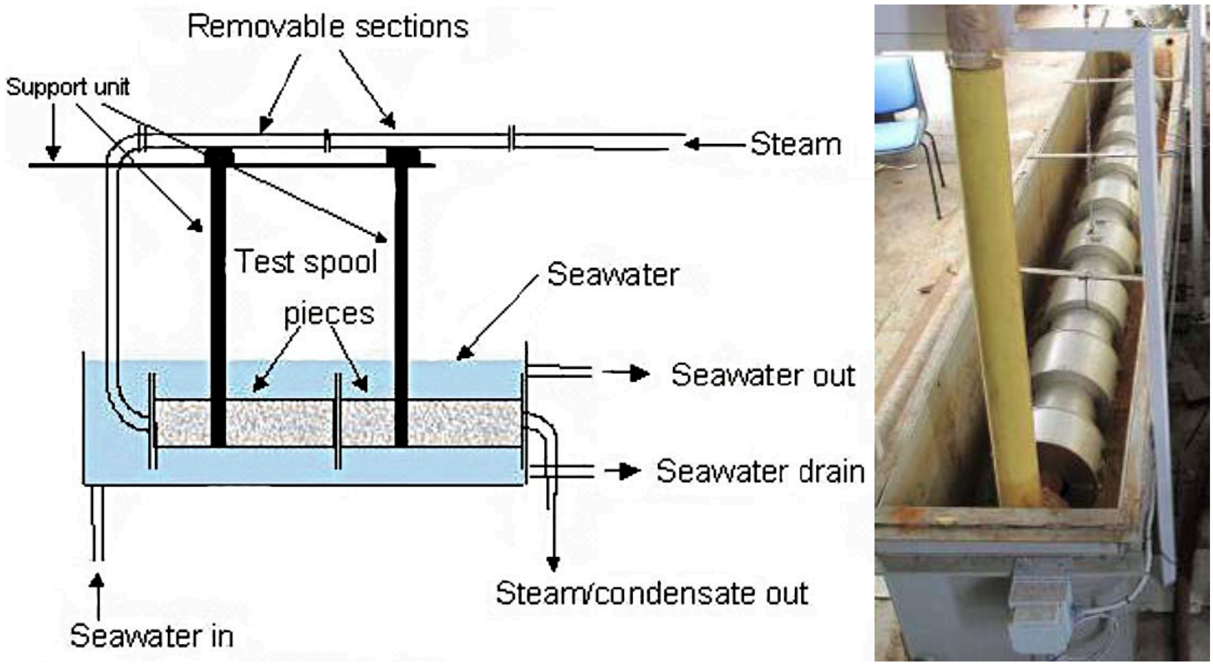

Figure 2.10 Sketch and photo of test rig used by Haraldsen [15].

The test spools were 410 mm long and had an outer diameter of 115 mm and were coated with two different coatings with an un-coated area in the middle, see **Figure 2.11**. They had been used for CUI testing before and corrosion products and remains of old coating were present at the surface, as is the situation when maintenance is performed for a CUI system. Different surface pre-treatment were used to evaluate their effect on the coating performance. Mineral wool was used for insulation and both distance insulation system and insulation applied directly at the coating was tested. After the test was ended, the coatings, insulations, surface pre-treatment and application method and temperature were evaluated and divided into four categories; no, slight, medium or heavy. The evaluation was based on several criteria; disbonded area, visual impression, surface condition, and degree of blistering, cracking and corrosion creep.

Figure 2.11 Test spool with two different coatings separated by a masked, un-coated area in the middle [15].

3 Experimental procedure

3.1 Coatings

An overview of the four coating tested is shown in **Table 3.1**

Table 3.1 Overview of tested coatings

Coating	Maximum operating temperature (^{o}C)		Application temperature of steel surface	Surface pre-treatment	Dry film thickness (DFT) (μm)	Number of coats
	Continuous	Cyclic				
Standard epoxy	120	150	Ambient	Sa 2 ½	100-200	2
Epoxy phenolic	200	230	Ambient	Sa 2 ½	200	2
Thermally sprayed aluminium (TSA)	480 [28]	595 [5]	Ambient	Sa 3	200-400	1
Titanium modified inorganic copolymer (TMIC)	650	450	Ambient	Sa 2 ½	175-200	2

3.2 Cyclic pipe test

3.2.1 Equipment

Four carbon steel pipes with outer diameter of 6 cm and length of 60 cm were coated with different coatings. Asbestos free calcium silicate insulation with a thickness of 5 cm was used and thin aluminium wrapping covered the insulation. During testing, the pipes were placed upon a hot plate for regulating the temperature. The test set-up is shown in **Figure 3.1**a) and the cross section of the pipe is shown in **Figure 3.1**b). A casserole was placed at the bottom of the pipe to hinder the electrolyte to get in contact with the hot plate, see **Figure 3.2**. At the top of the insulation, a 1-2 cm deep radial pit was cut out to drain the fluid homogeneously into the insulation, see **Figure 3.3**. Also, small holes were made every 5 cm along the length of the insulation to allow temperature measurements with thermocouples, see **Figure 3.4**. At the bottom of the pipe, the casserole covered two of the holes, and therefore an angled hole was made in order to be able to place a thermocouple near the pipe bottom, see **Figure 3.6**.

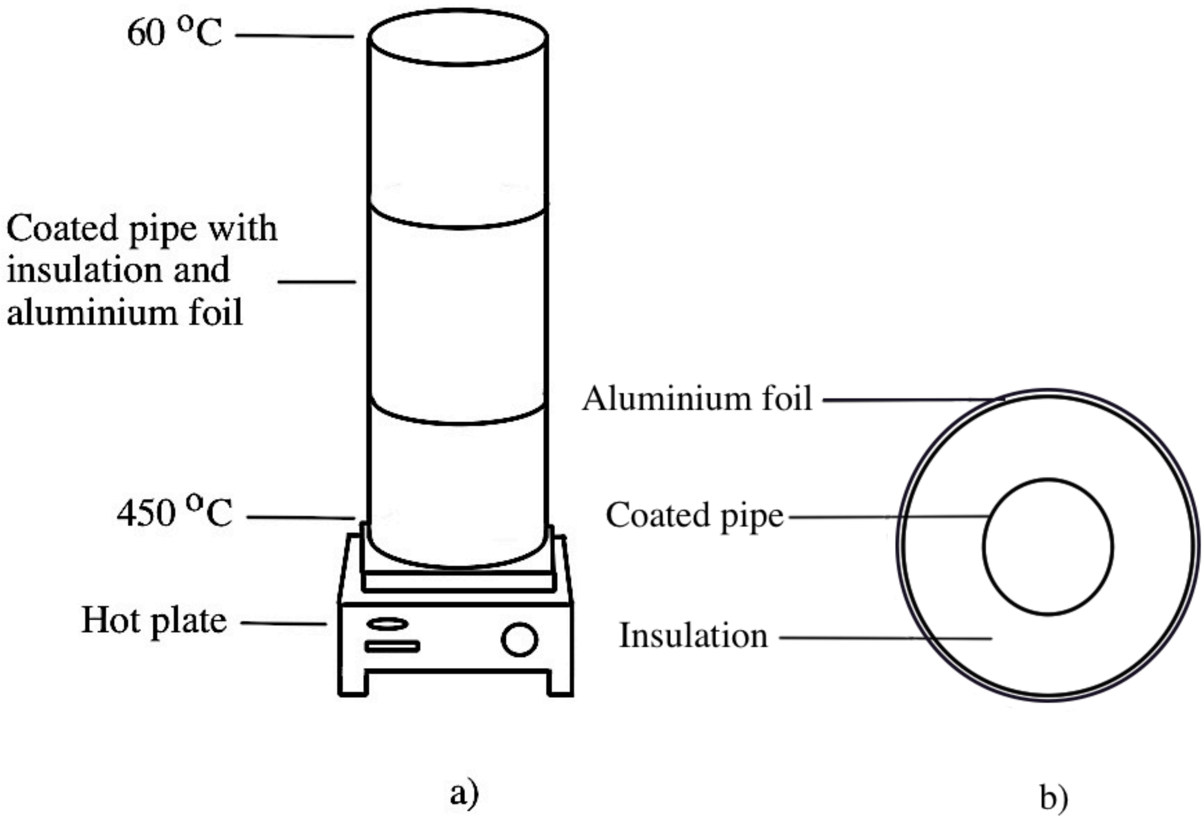

Figure 3.1 Detailed overview of test set-up. After [1].

Figure 3.2 Test set-up with hot plate, casserole and insulated pipe.

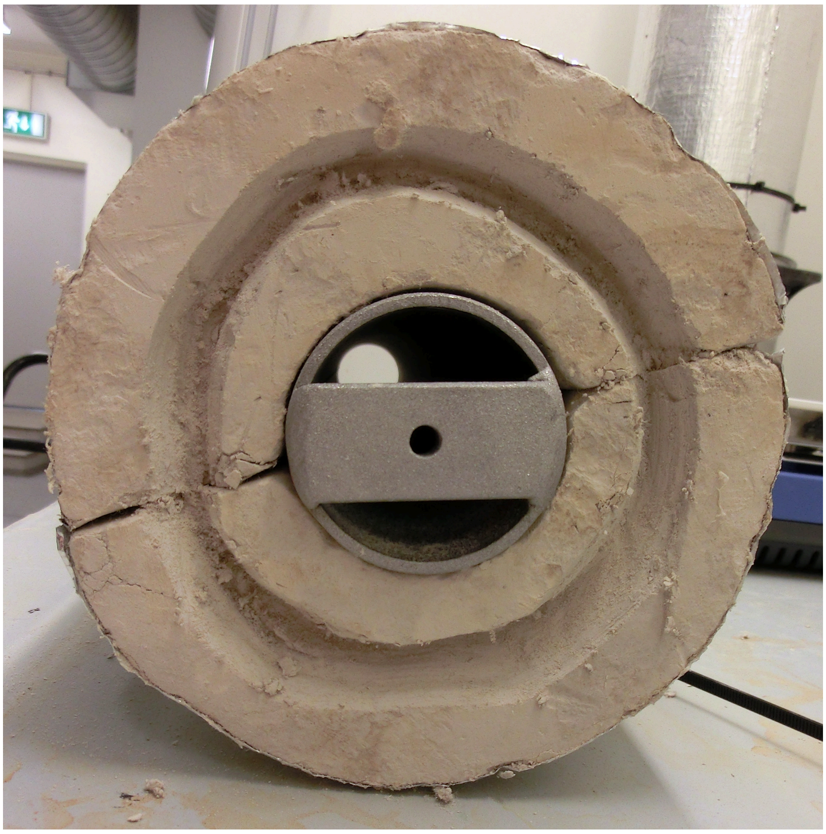

Figure 3.3 Pit carved out at the top of the insulation.

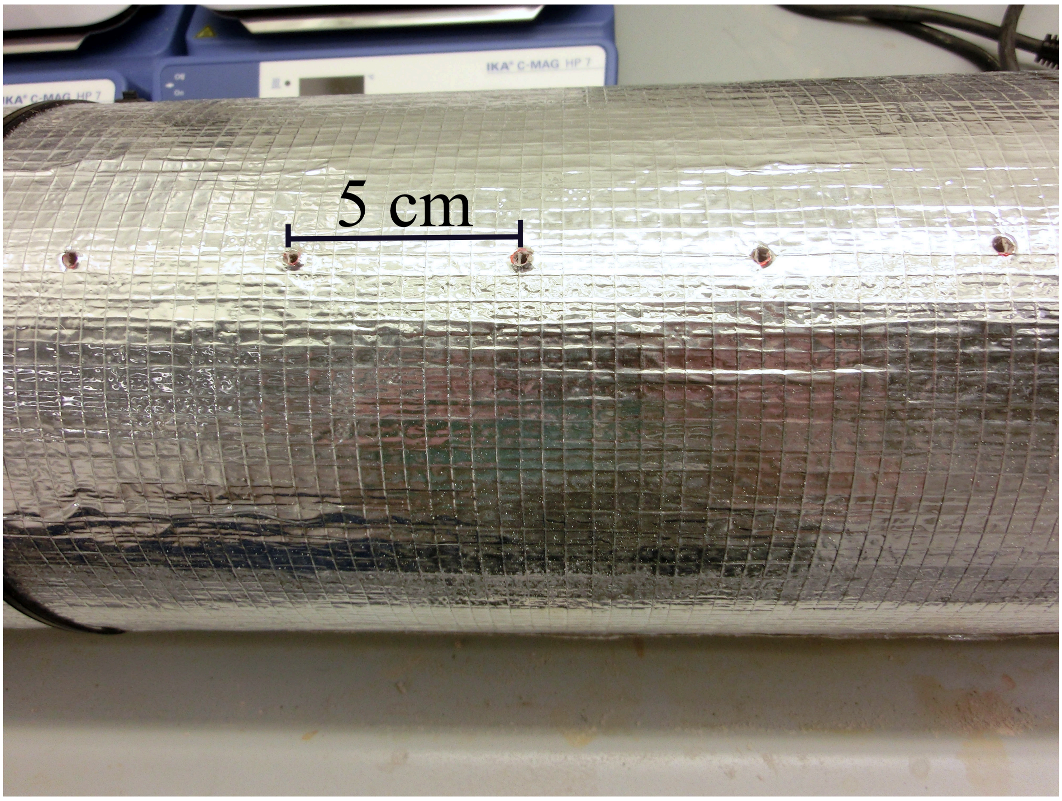

Figure 3.4 Holes for thermocouples.

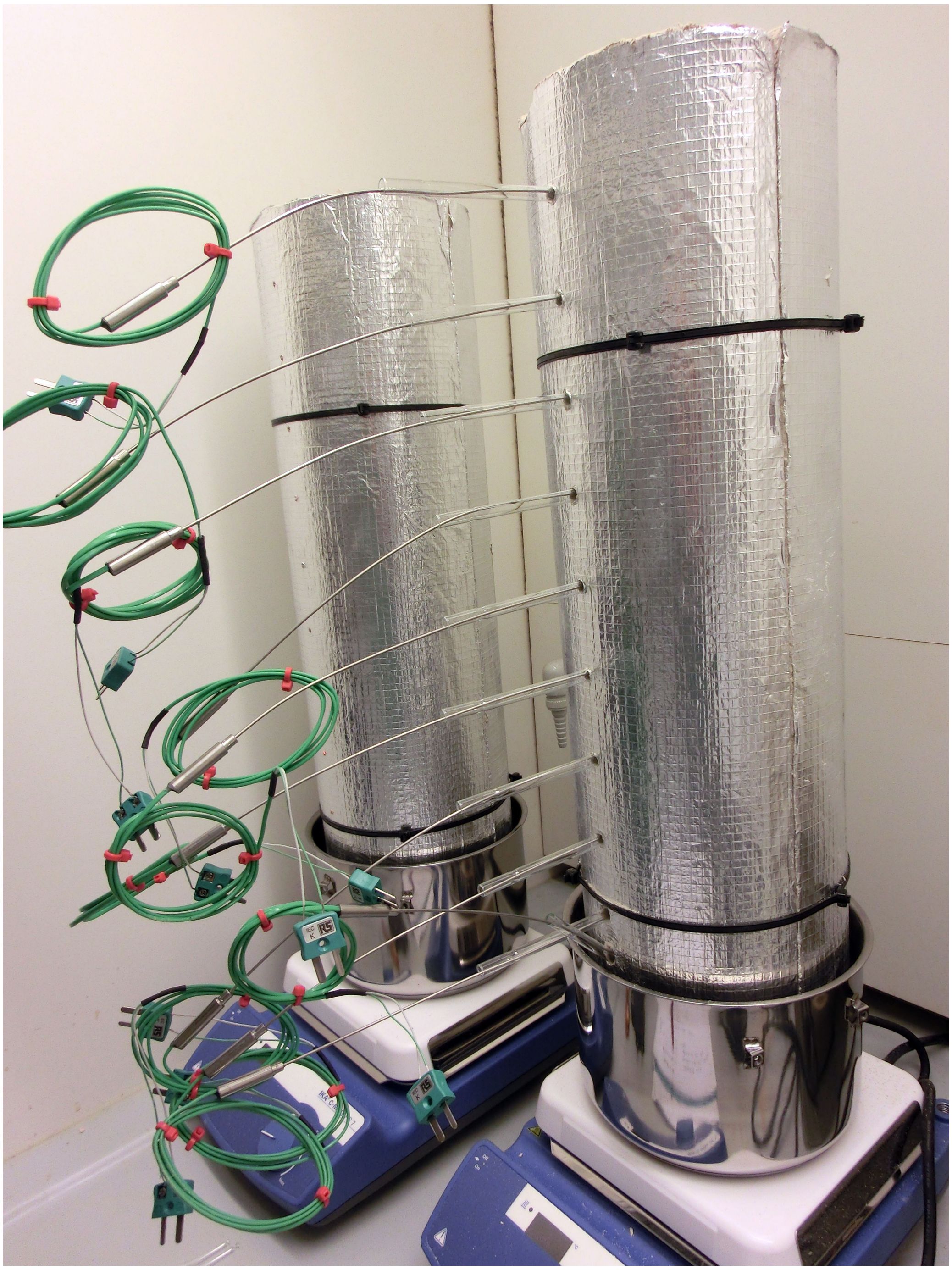

Figure 3.5 Thermocouples installed in insulation.

Figure 3.6 Angled thermocouple at the bottom of the pipe due to coverage by the casserole. Glass tubes were used to hinder corrosion of the thermocouple.

3.2.2 Methods

The cyclic pipe test developed by Halliday et al. [1] is used to evaluate the coatings. Cyclic heating was performed 30 times with 8 hours of heating and 16 hours of natural cooling. Every 5^{th} cycle there was a break of two days where the hot plates were turned off and no fluid was poured into the insulation. During the heating period, the hot plate was turned on $450^{o}C$. The temperature was logged continuously for one of the pipes (the TMIC coated pipe). For the other pipes, the temperature was measured once a day, approximately after 7.5 hours. Before and after each heating cycle 1 litre 1% NaCl solution was poured into the groove at the top of the insulation. After 15 cycles, the insulation was removed and new insulation installed. This was due to the uneven degradation of the insulation. The bottom end absorbs more fluid since this end will be immersed until the fluid has evaporated.

3.2.3 Evaluation

After testing, the coatings were first visually examined according to ISO 4628, part 2, 3 and 4, blistering, rusting and cracking, respectively. Then samples with approximately length of 2.5 cm each were cut from the areas with coating failure for all of the coatings. For the TSA, six samples were cut out along the pipe from the bottom. Two samples from the bottom of the TMIC coated pipe and one sample from where the degradation started for the epoxy phenolic were also prepared. These samples were moulded in conductive resin in a cross sectional view and grinded down to P2400. Three samples with TSA, two samples with TMIC and one sample with epoxy phenolic were also polished with 3 microns diamond polish to get a better view in the scanning electron microscope (SEM).

First, all of the samples were examined in a Leica optical microscope to determine thickness of the coating and also to get an overview of the adhesion and porosity in the coating. Then a selection of the samples was examined in SEM to further study the degradation, porosity and adhesion of the coatings. Due to an error in one of the SEM, two SEM were used. FESEM characterization with both Zeiss Ultra 55 and Hitachi SU-6600 were performed with secondary electron detector.

4 Results

4.1 Results after 15 cycles

4.1.1 Temperature measurements

Temperature measurements were done daily at ten sites along the samples, see **Figure 4.1**. For the TMIC coating, the temperature was logged continuously throughout the test period. **Figure 4.2** displays the first heating period for the TMIC followed by the cooling period shown in **Figure 4.3**. Here, the heat loss due to the glass tubes covering the thermocouples is not taken into account, and the temperatures are therefore assumed to be slightly higher. For complete temperature measurements during the testing for the TMIC coating, see Appendix A. After measuring the temperatures without glass tubes, the maximum temperatures were calculated for the first cycle, see **Figure 4.4**.

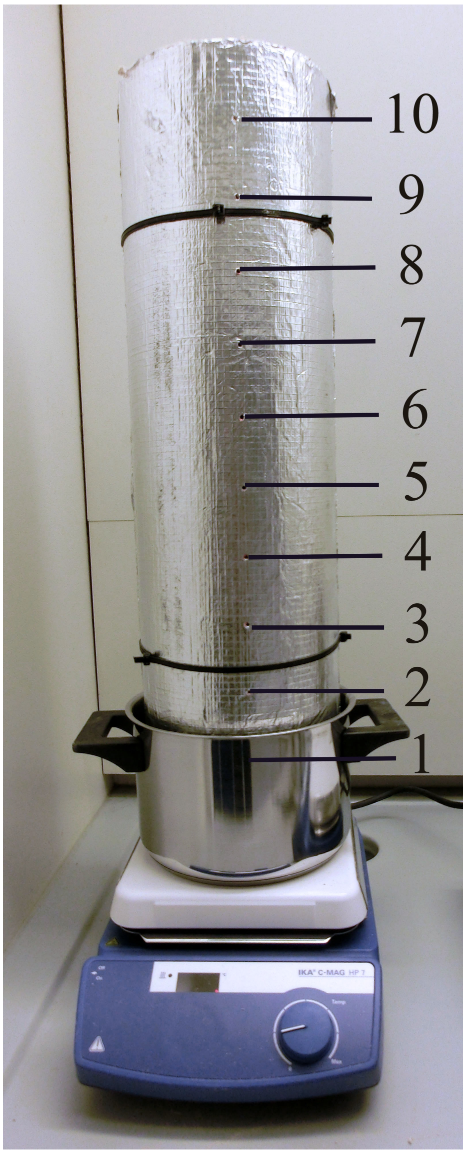

Figure 4.1 Numbering of temperature measurement holes.

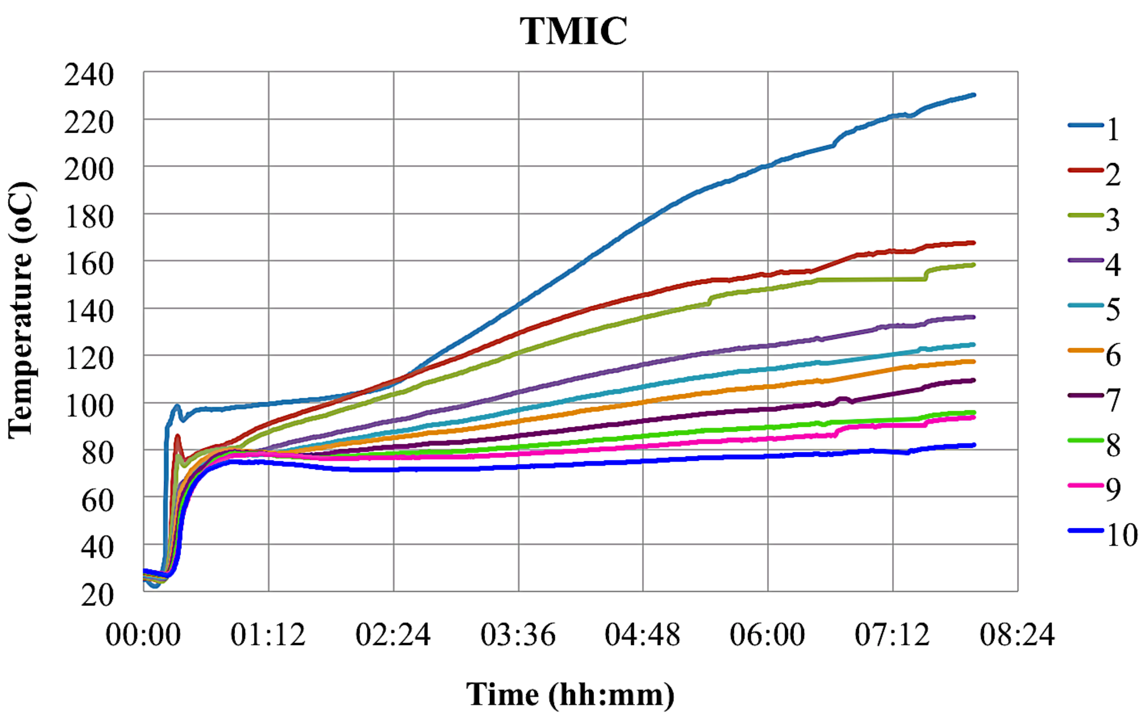

Figure 4.2 Temperature variation over time during the heating period of 8 hours, cycle 1. No correction of heat loss due to the glass tubes covering the thermocouple has been done.

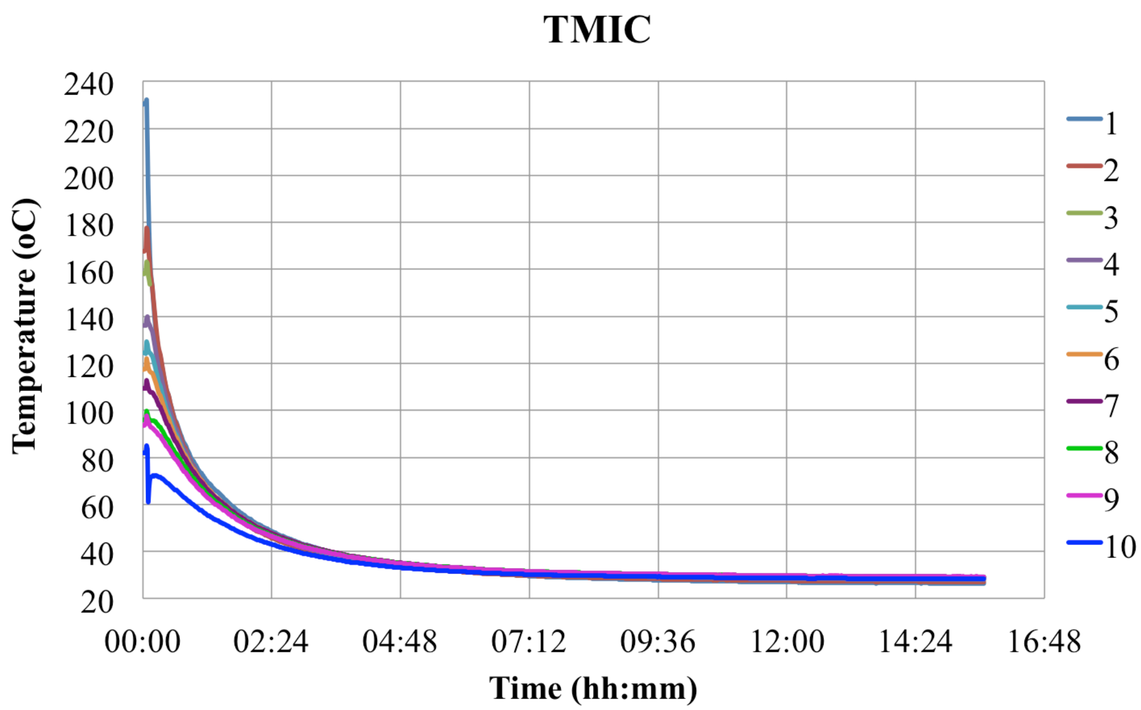

Figure 4.3 Temperature variation over time during the cooling period of 16 hours, cycle 1.

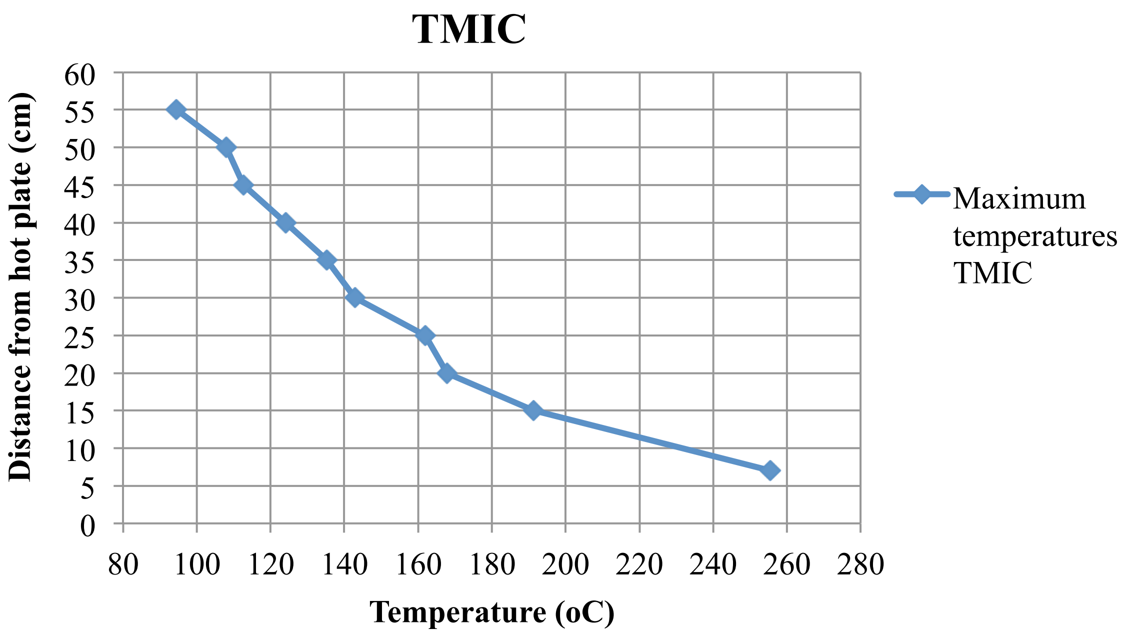

Figure 4.4 Maximum temperatures for TMIC coating during cycle 1. Correction for heat loss due to the glass tubes covering the thermocouple has been done.

The temperatures decreased with each cycle. During the first cycle, it was estimated that all coatings reached temperatures close to 300°C. An exception was the standard epoxy, which only reached about 200°C. The manual temperature measurements were done approximately 30 minutes before the maximum temperature was reached, and hence the maximum temperature after 7.5 h was 240°C for TMIC, epoxy phenolic and TSA, and 180°C for the standard epoxy. At the top of the pipes, the maximum temperature varied between the coatings from 60°C (standard epoxy) to 90°C (TMIC). As the insulation degraded and was saturated with water, the temperatures decreased, especially closest to the hot plate, see **Figure 4.5**, **Figure 4.6**, **Figure 4.7** and **Figure 4.8**.

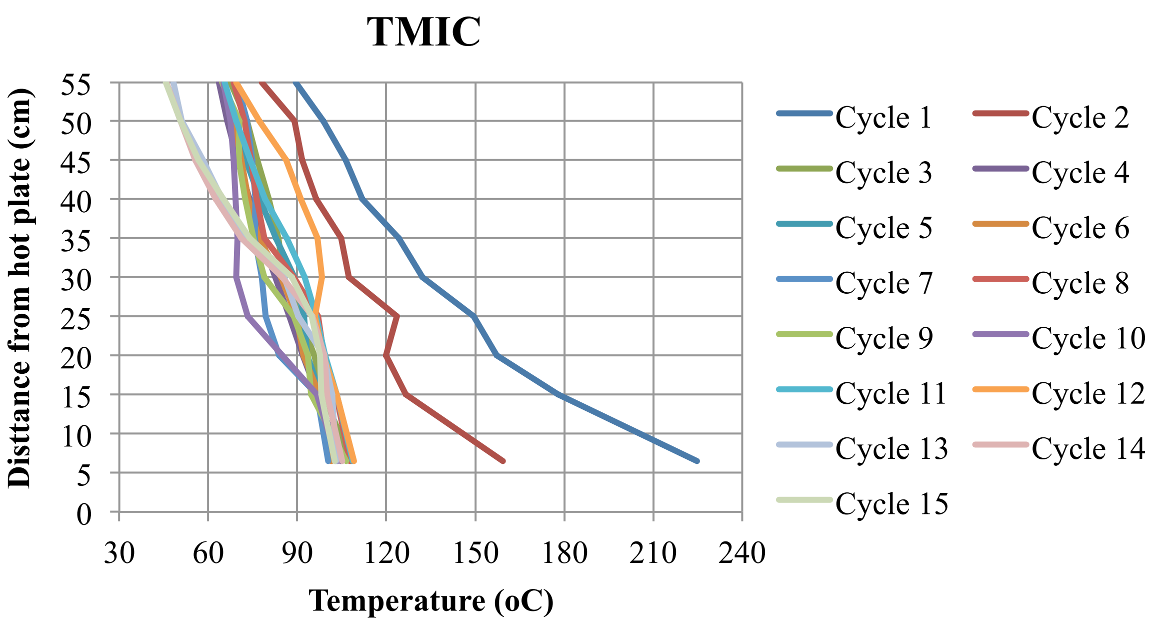

Figure 4.5 Temperature range for TMIC coating after approximately 7.5 h of heating. Correction for heat loss due to the glass tubes covering the thermocouple has been done.

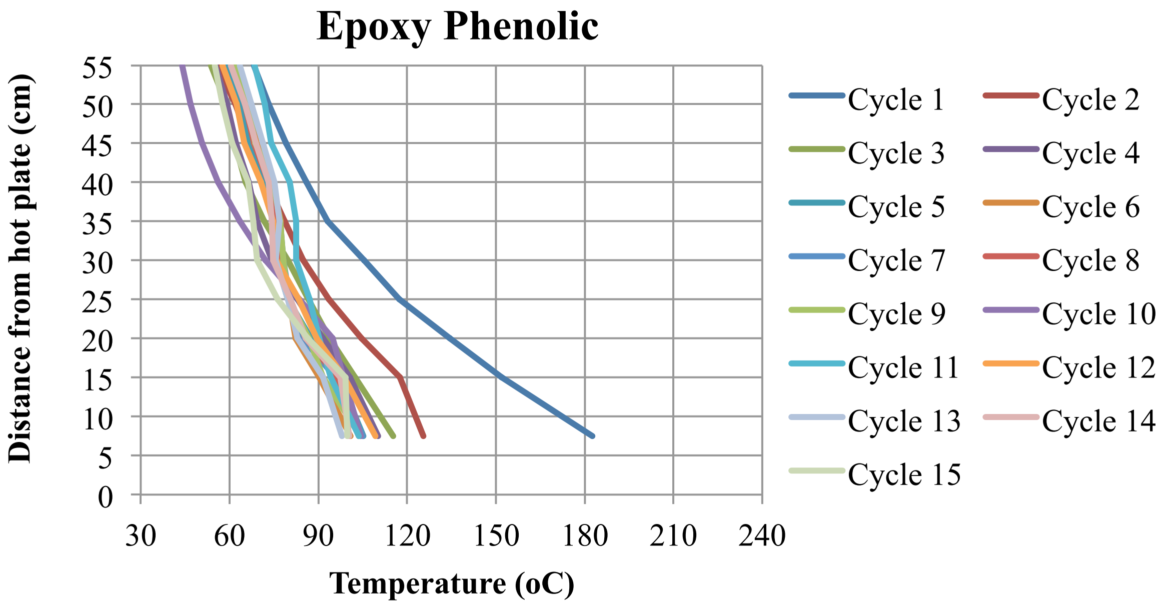

Figure 4.6 Temperature range for epoxy phenolic coating after approximately 7.5 h of heating.

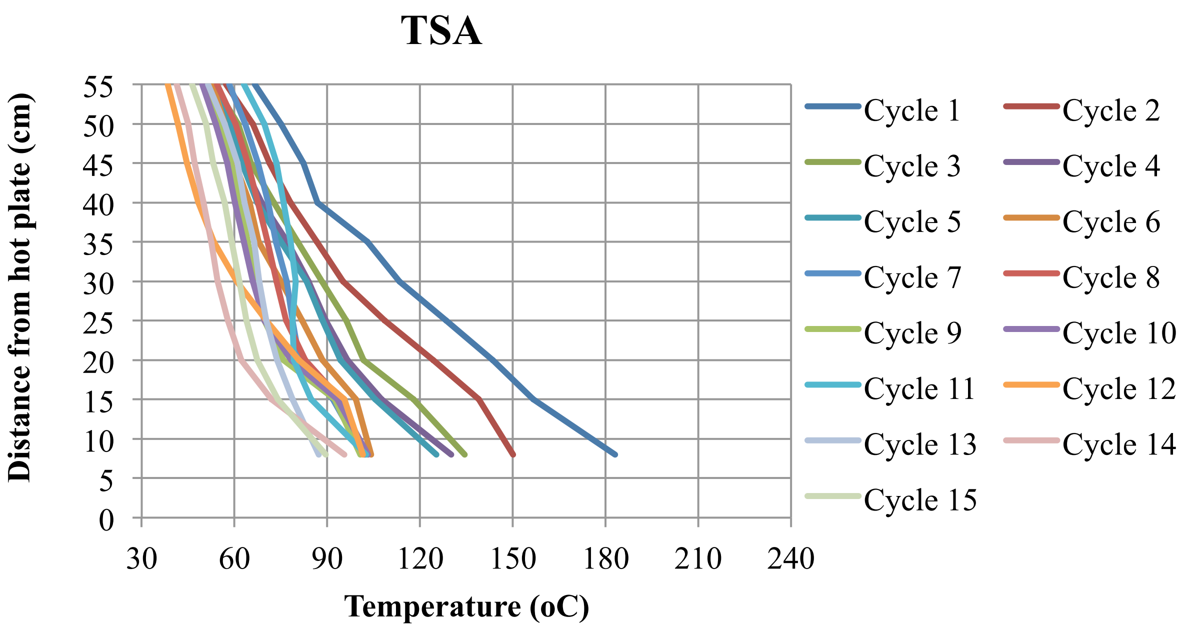

Figure 4.7 Temperature range for TSA after approximately 7.5 h of heating.

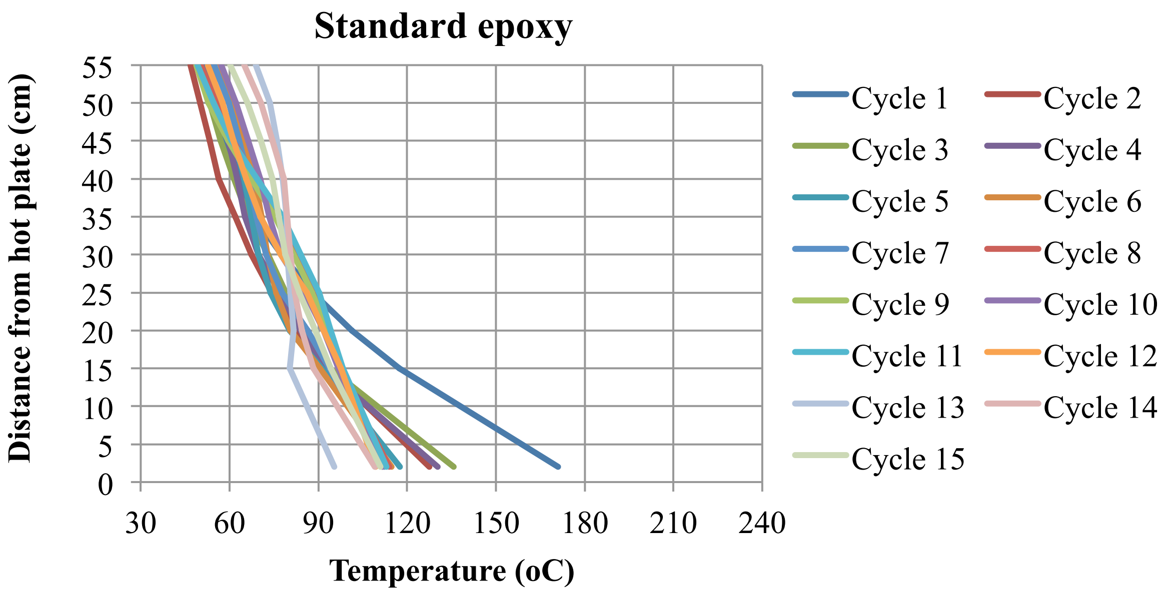

Figure 4.8 Temperature range for standard epoxy coating after approximately 7.5 h of heating.

4.1.2 Evaluation of coatings

After 15 cycles, the insulation was removed and new insulation was installed. Marks and scratches in the coating were observed at the locations where thermocouples were used to measure the temperature see **Figure 4.9**. For the TSA, rust was seen at the marks but for the TMIC only the scratches closest to the hot plate had visible rust. The epoxy phenolic and standard epoxy had almost no marks after the thermocouples, and no rust was seen. When removing the insulation, the surface of the pipes was damp and a lot of remnants of the insulation and corrosion products were attached to the pipes especially at the bottom. For the highest temperature range, the epoxy phenolic and standard epoxy had also discolouring and slight blistering.

Figure 4.9 Coating after 15 cycles. Highest temperature at the bottom.

4.2 Final results

Due to a defected hot plate, the testing of the standard epoxy coating started 15 cycles after the other coatings. Therefore, testing of this coating was not finished during the period this thesis was written and hence the standard epoxy will not be included in the final results.

4.2.1 Temperature measurements

Some changes in the temperatures were observed for cycle 16 compared to cycle 1, even though the insulation was new and dry at the start of both cycles, see **Figure 4.10**, **Figure 4.11** and **Figure 4.12**. From cycle 1 to cycle 16, the TMIC had a decrease in maximum temperature after 7.5 h of heating from 240 to 210^{o}C, the epoxy phenolic did not change from 240^{o}C and the TSA decreased from 240 to 170^{o}C. For the last 15 cycles, holes were made closer to the hot plates and higher temperatures were therefore measured. However, this was not done to the TMIC as the thermocouples were placed in glass tubes and these were difficult to place further down due to the kettle the samples were placed inside. During the evaluation of the coatings, the highest temperature is assumed to be 300^oC. This estimate is based on temperature measurements further up from the hot plate and also the fact that the manual temperature measurements were conducted 30 minutes before the heating time was finished. Maximum temperatures from the TMIC coating were found after approximately 8 hours of heating and they indicated temperatures up to 300^oC close to the hot plate for cycle 1.

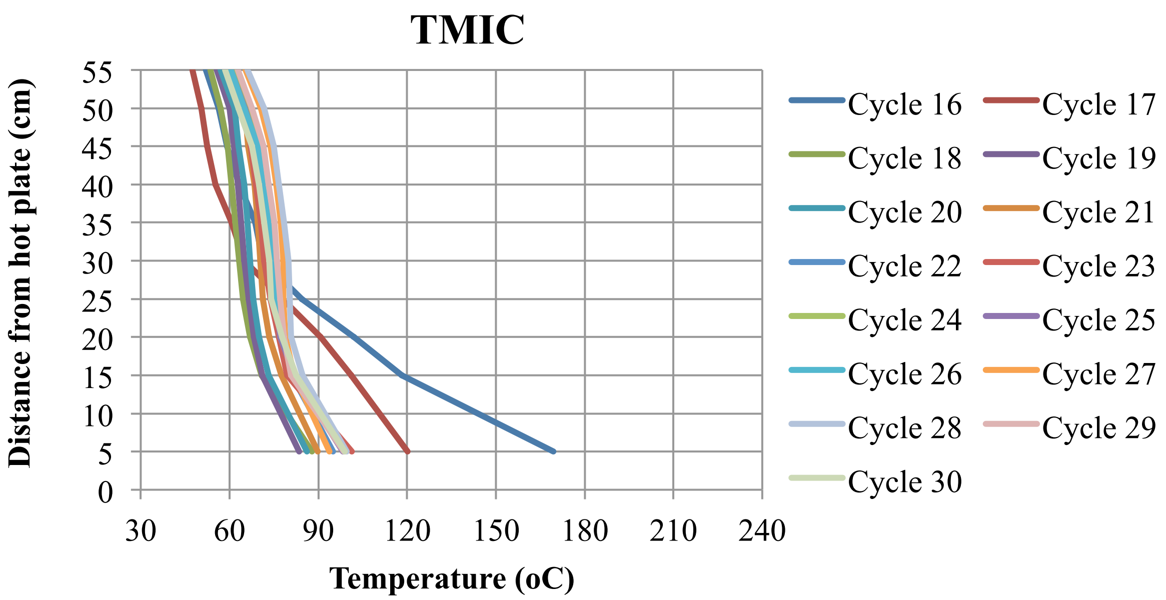

Figure 4.10 Temperature range for TMIC coating after approximately 7.5 h of heating. Correction for heat loss due to the glass tubes covering the thermocouple has been done.

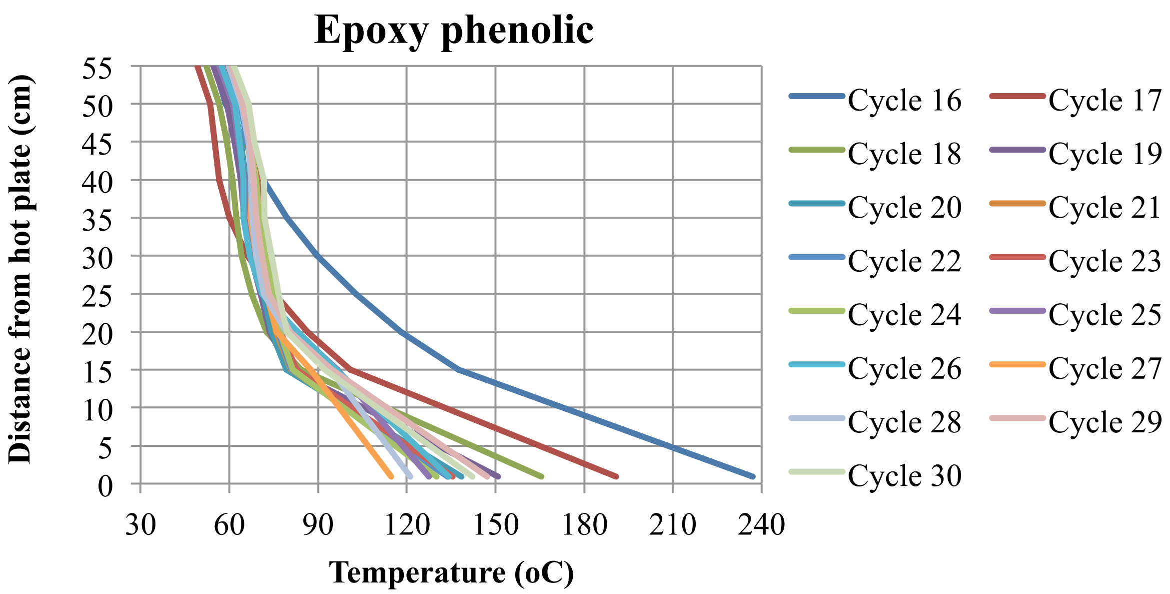

Figure 4.11 Temperature range for epoxy phenolic coating after approximately 7.5 h of heating.

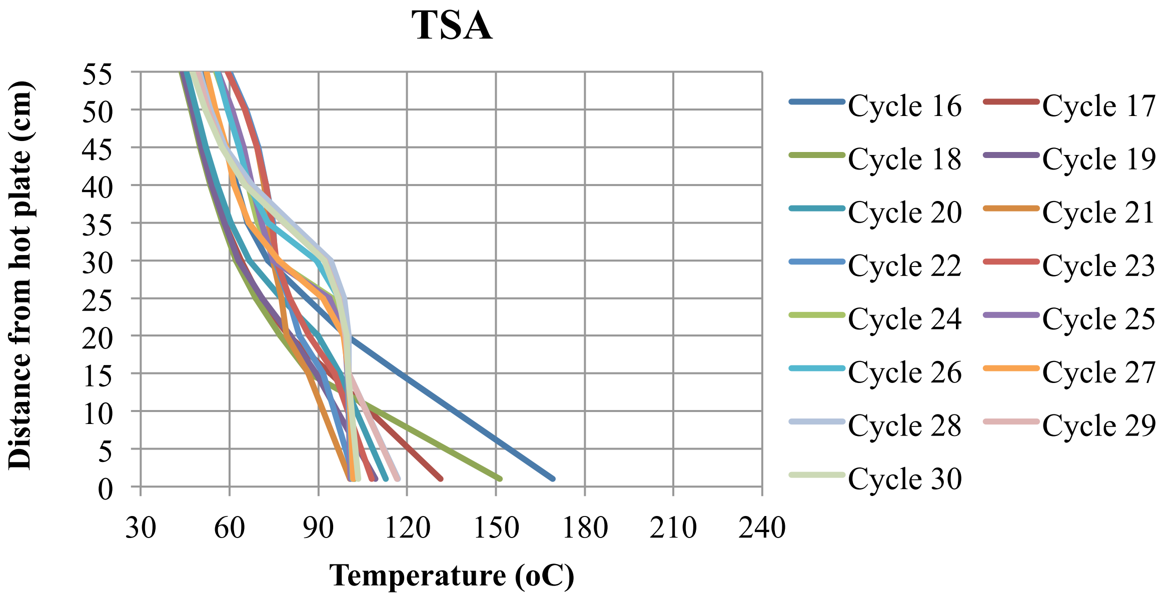

Figure 4.12 Temperature range for TSA coating after approximately 7.5 h of heating.

4.2.2 Evaluation of coatings after 30 cycles

The coatings were first examined visually and photographs are shown in Appendix B. Then cross sectional samples from each pipe were examined in microscope. Images from SEM are found in Appendix C. A visual overview of the tested coatings is presented in **Figure 4.13**. The corrosion at the top of the TSA coated pipe is due to lack of coating and it is a good illustration of how the pipes would have looked if they were uncoated.

TMIC | Epoxy Phenolic | TSA

Figure 4.13 Coatings after 30 cycles of the cyclic pipe test. Highest temperature at the bottom.

Visual examination of the coatings displayed good results for the TMIC coating with only slight degradation and rusting at the bottom, see **Figure 4.14**. At one spot, 2 mm in diameter and close to the bottom of the pipe, the coating had failed and rusting was seen. No blisters or cracks were found at the coating surface. Markings after the thermocouples were clearly visible, see **Figure 4.15**, and slightly rusting was seen at the markings closest to the hot plate.

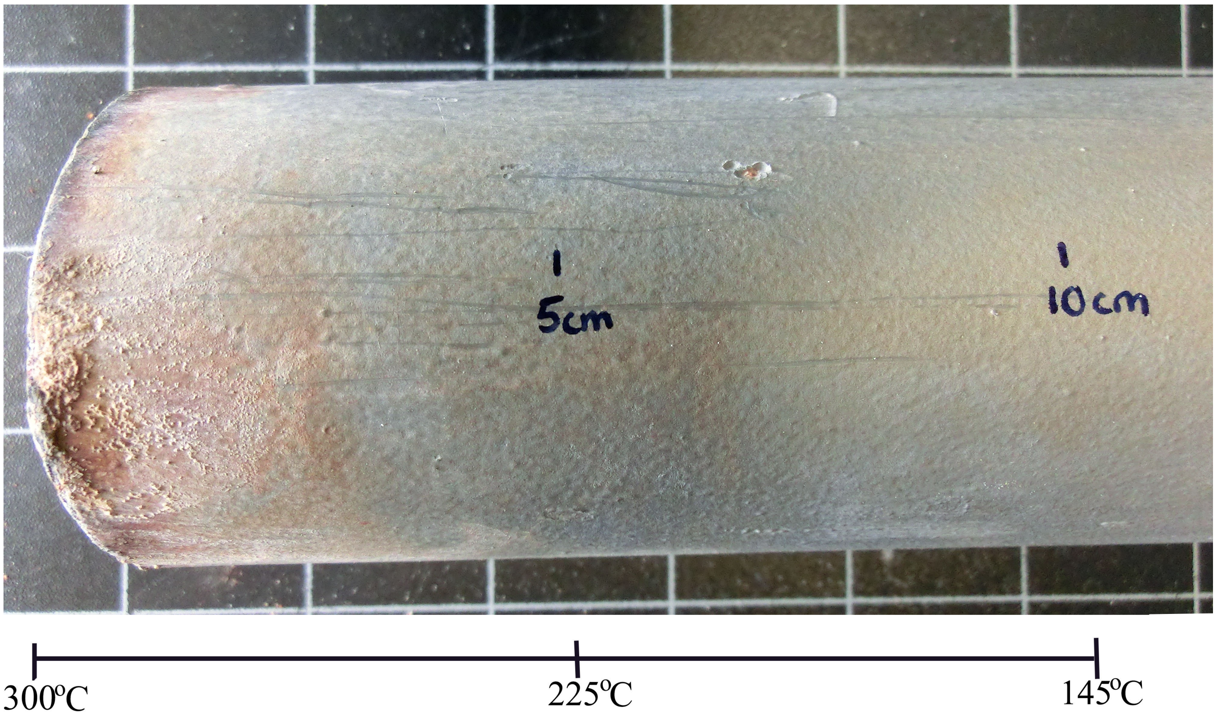

Figure 4.14 TMIC coating closest to hot plate after 30 cycles.

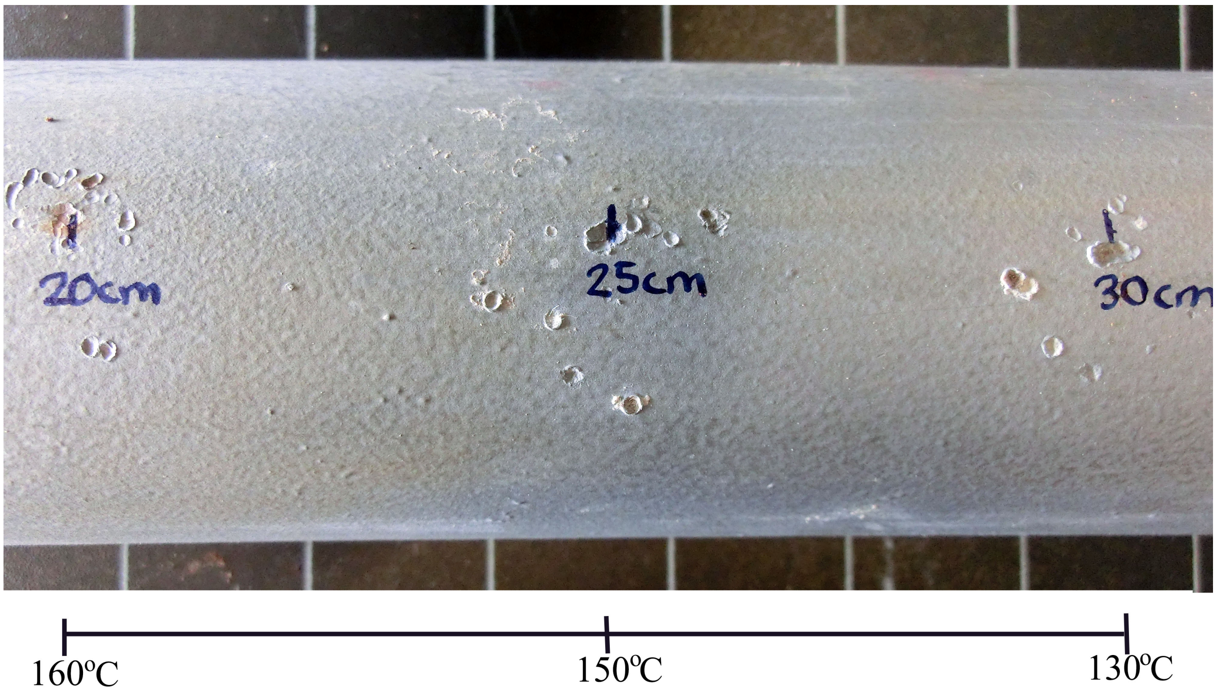

Figure 4.15 Visible markings after thermocouples in TMIC coating.

Examination in optical microscope showed a slight thinning of the coating closest to the hot plate. Here the coating was measured to approximately 220 µm and increasing to 260 µm in the 225°C tempered zone. Further it increased to approximately 280 µm in the 145°C-tempered region. Pictures from the examination in SEM indicated some pores and also some areas with poor adhesion. However, this is uncertain, as it was difficult to determine due to both conductive and non-conductive contents in the coating. **Figure 4.16** presents an overview of the coating in the 250^{o}C-tempered area. The aluminum pigments are seen as dark lines in the matrix, and an area of what seems to be poor adhesion is seen to the left. The coating was intact all the way down to the bottom of the pipe, see **Figure 4.17**.

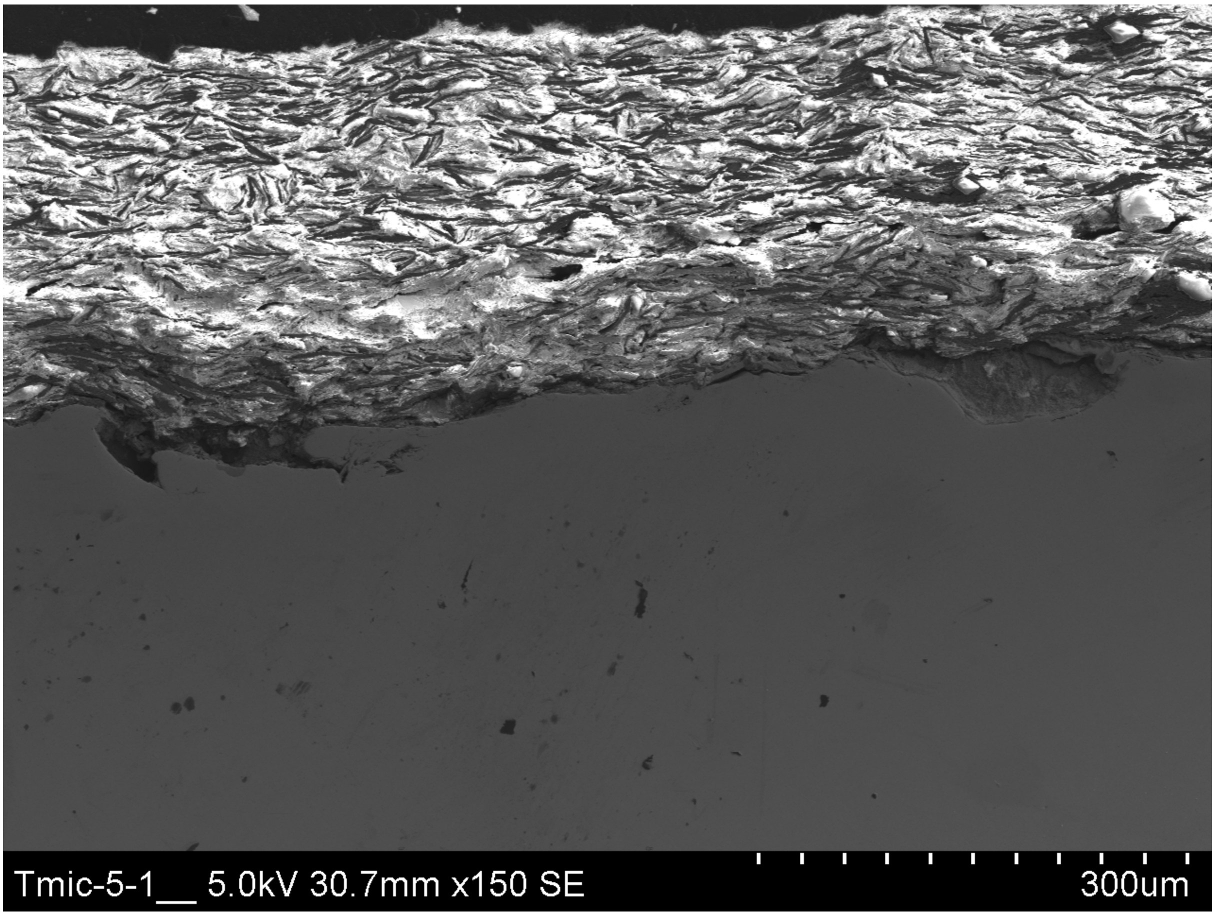

Figure 4.16 TMIC coating, imaged in Hitachi SU-6600 from approximately the 250^{o}C-tempered area.

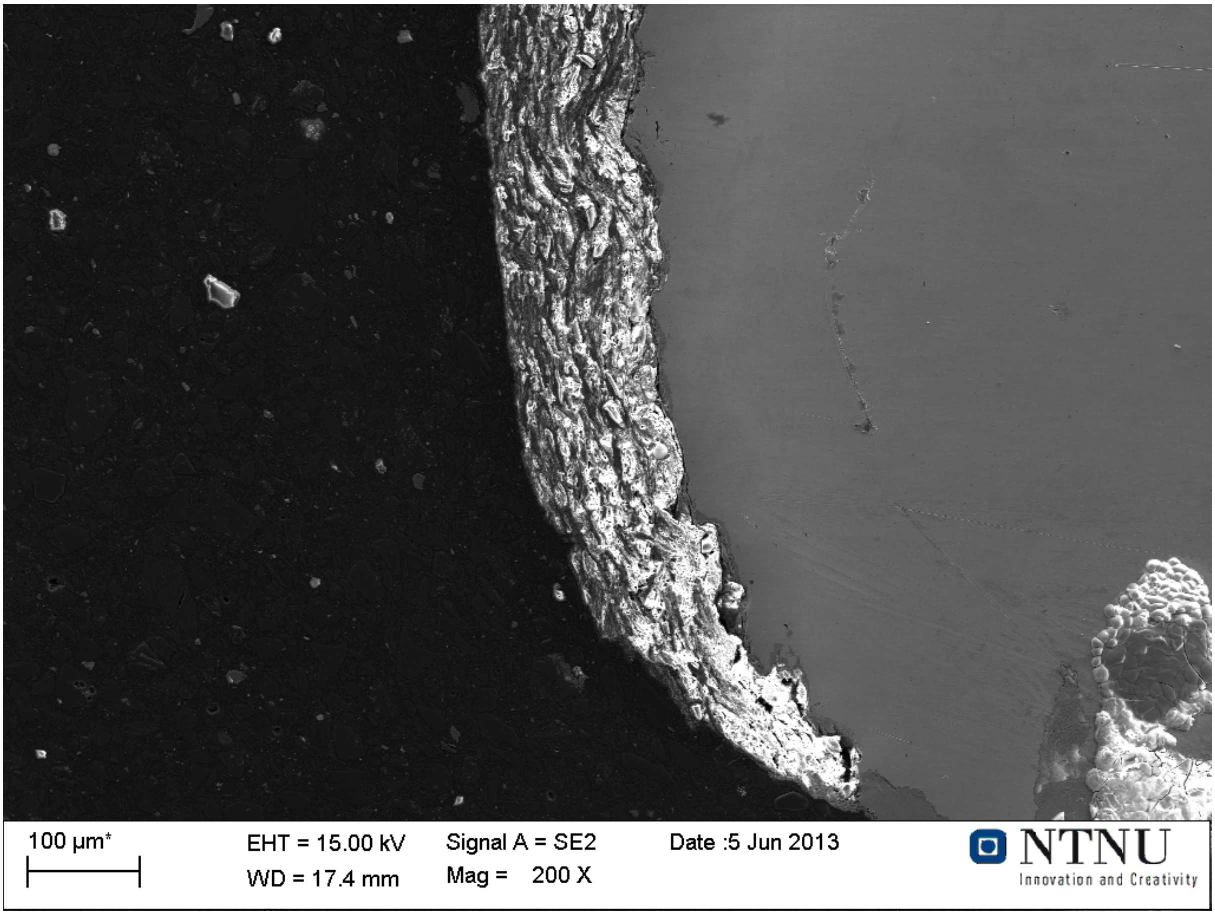

Figure 4.17 TMIC coating closest to the hot plate (at the bottom), imaged in Zeiss Ultra 55.

The epoxy phenolic coating failed for the highest temperatures, with blistering and rusting. Blisters were found in the 150 to 175°C area, see **Figure 4.18**, as well as in the area closest to the hot plate. According to ISO 4628-2, the degree of blistering was evaluated to be 4(S3) for the 150 to 175°C area and 4(S4) in the hottest area. Also rusting degree Ri 4 according to ISO 4628-3 was found closest to the hot plate, see **Figure 4.19**. The coating was clearly discoloured from approximately 140°C. However, almost no marks were seen after the thermocouples.

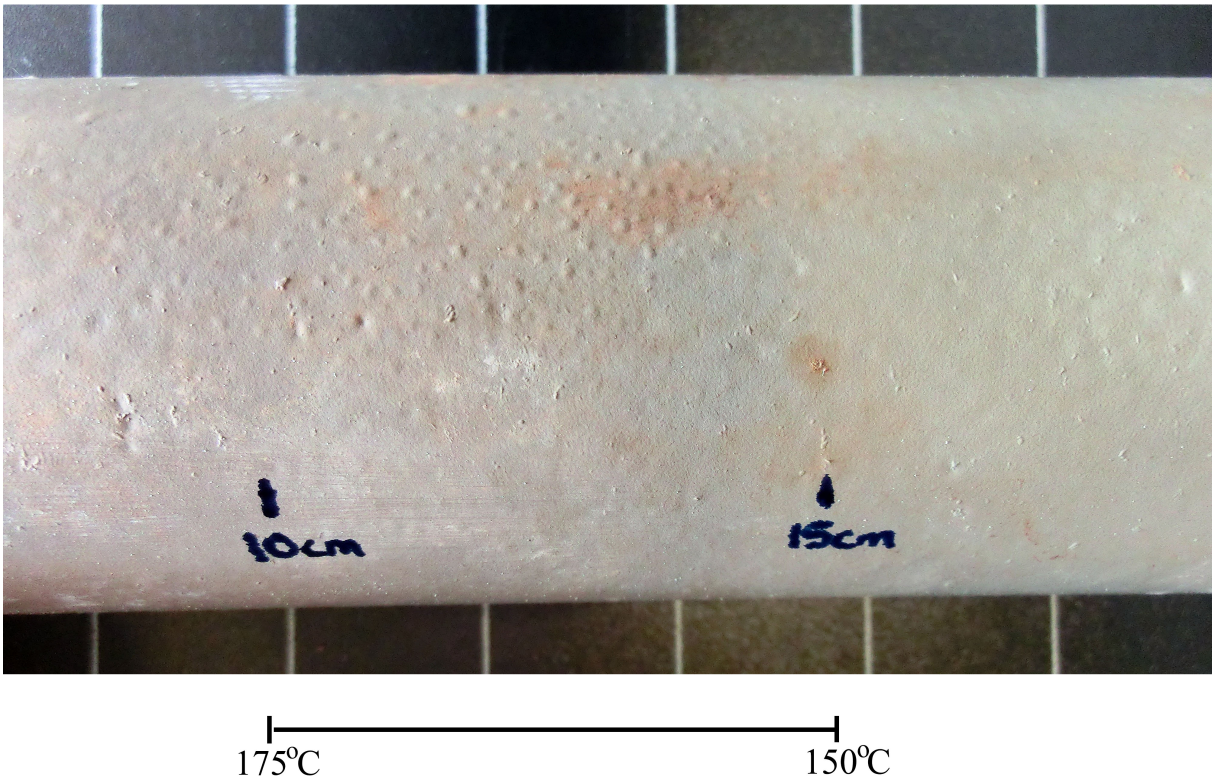

Figure 4.18 Blistering of epoxy phenolic coating.

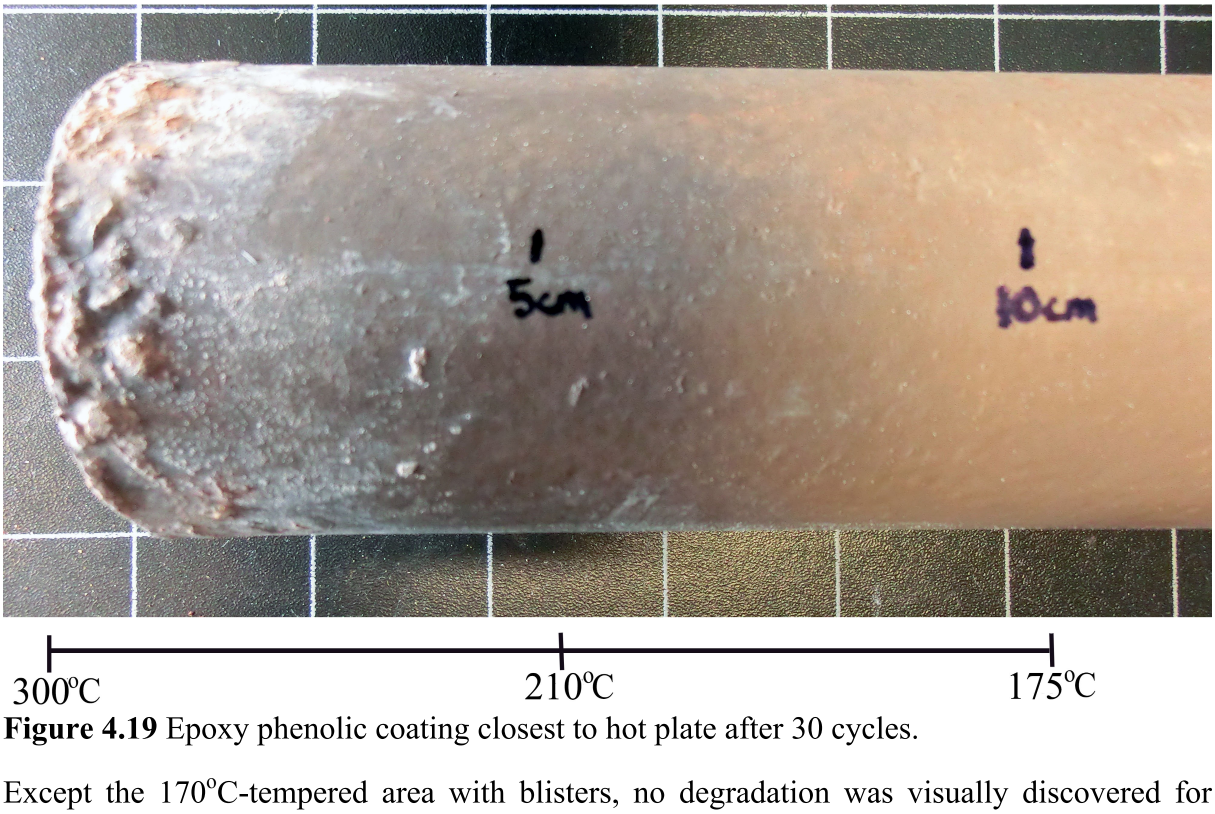

Figure 4.19 Epoxy phenolic coating closest to hot plate after 30 cycles.

Except the 170°C-tempered area with blisters, no degradation was visually discovered for temperatures lower than approximately 220°C. In the 170°C-tempered blistered area, the thickness of the coating was found by optical microscope to be approximately 200 μm and areas with poor adhesion were seen. Better images of the areas with poor adhesion were taken in SEM, see **Figure 4.20**. Poor adhesion was seen for large areas of the coating in this region, however, the adhesion improved at temperature lower than approximately 160°C. Little porosity was found for the coating, but this was difficult to determine since the coating was non-conductive, which led to charging problems in the SEM.

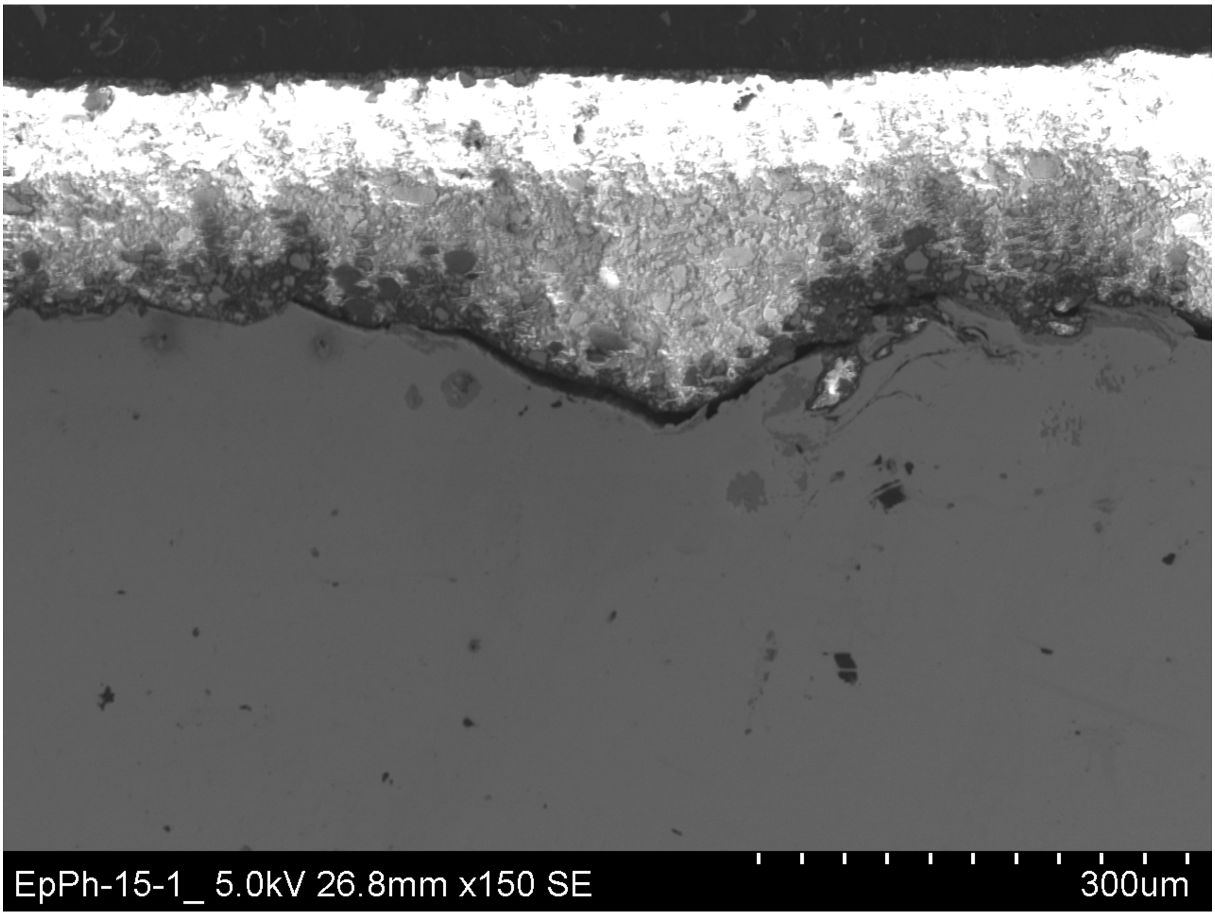

Figure 4.20 Epoxy phenolic coating approximately in the 170^{o}C-tempered area with poor adhesion. Imaged in Hitachi SU-6600.

The TSA also performed well, but for temperatures higher than 190^{o}C, the coating started to degrade and rusting was seen at the bottom, **Figure 4.21**. At some areas no coating was left and rusting on the bare steel was seen. Other areas only had rusting degree Ri 1. No cracking or blistering was seen. Large amounts of white deposits, presumably aluminium oxide, were found at the coating and at the insulation, see **Figure 4.22**. Also here some marks were seen after the thermocouples.

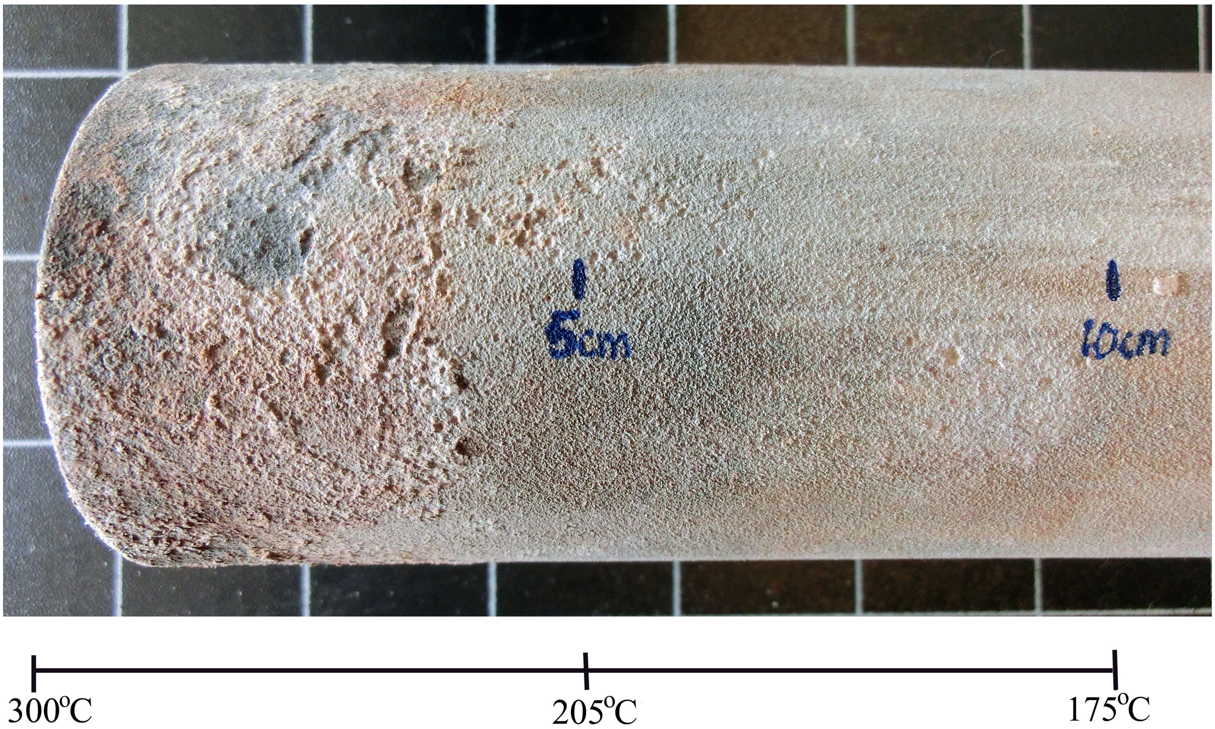

Figure 4.21 TSA coating closest to hot plate after 30 cycles.

Figure 4.22 White deposit of presumably aluminium oxide at the insulation.

Examination in optical microscope showed that almost no coating was left for temperatures higher than approximately 220°C. For the 190 to 220°C range, the coating was intact except a few areas with significantly degraded coating and reduced thickness, see **Figure 4.23**. The coating between these areas with degraded coating was intact, and the thickness was measured to 206 μm. From 190°C and lower, thickness above 300 μm, good adhesion and some porosity was found. Images from SEM also show that the adhesion was very good between the areas with degraded coating in the 205°C-tempered area, see **Figure 4.24**.

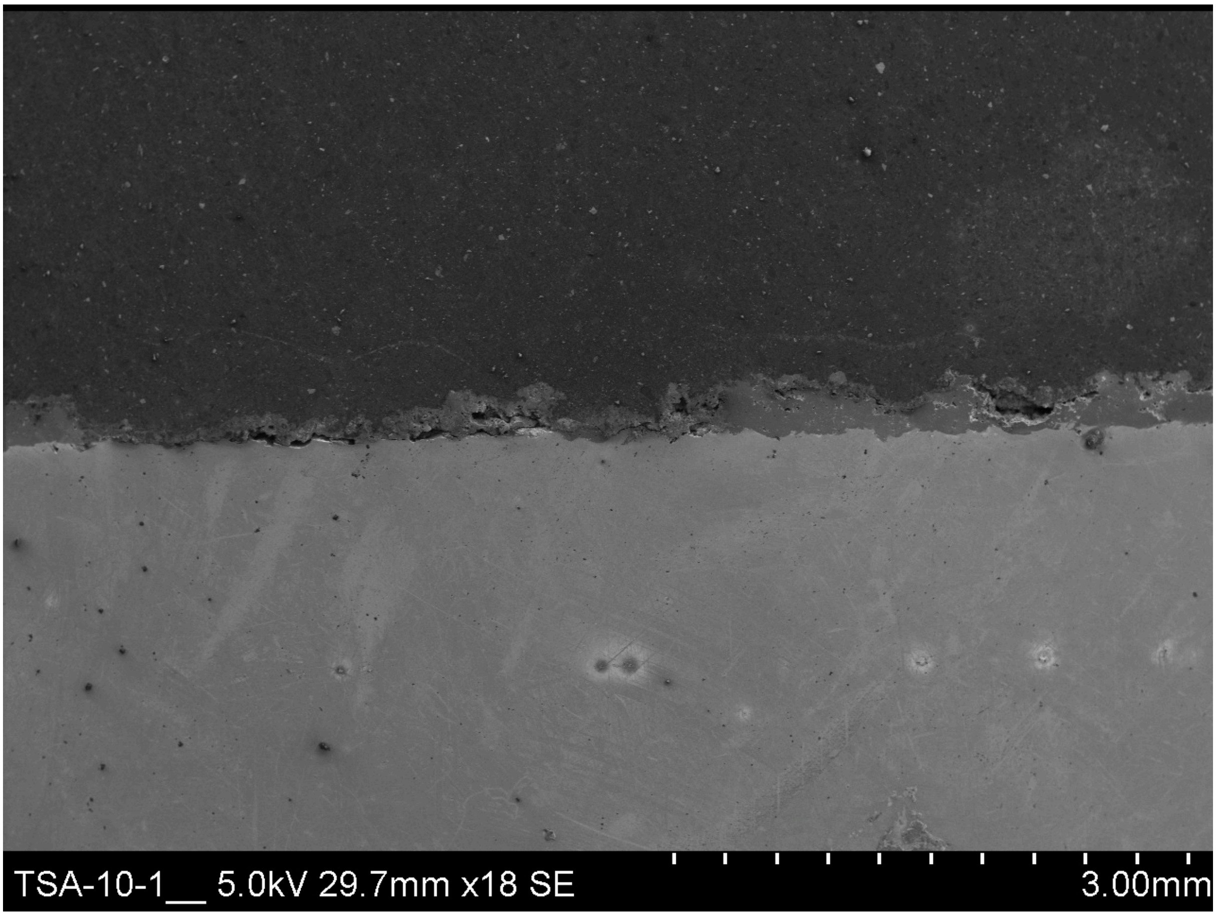

Figure 4.23 Damaged and degraded TSA coating in the 210^{o}C-tempered area. The resin is the darkest grey at the top and the carbon steel is the brightest grey at the bottom. A thin line of TSA coating is seen in the middle. Imaged in Hitachi SU-6600.

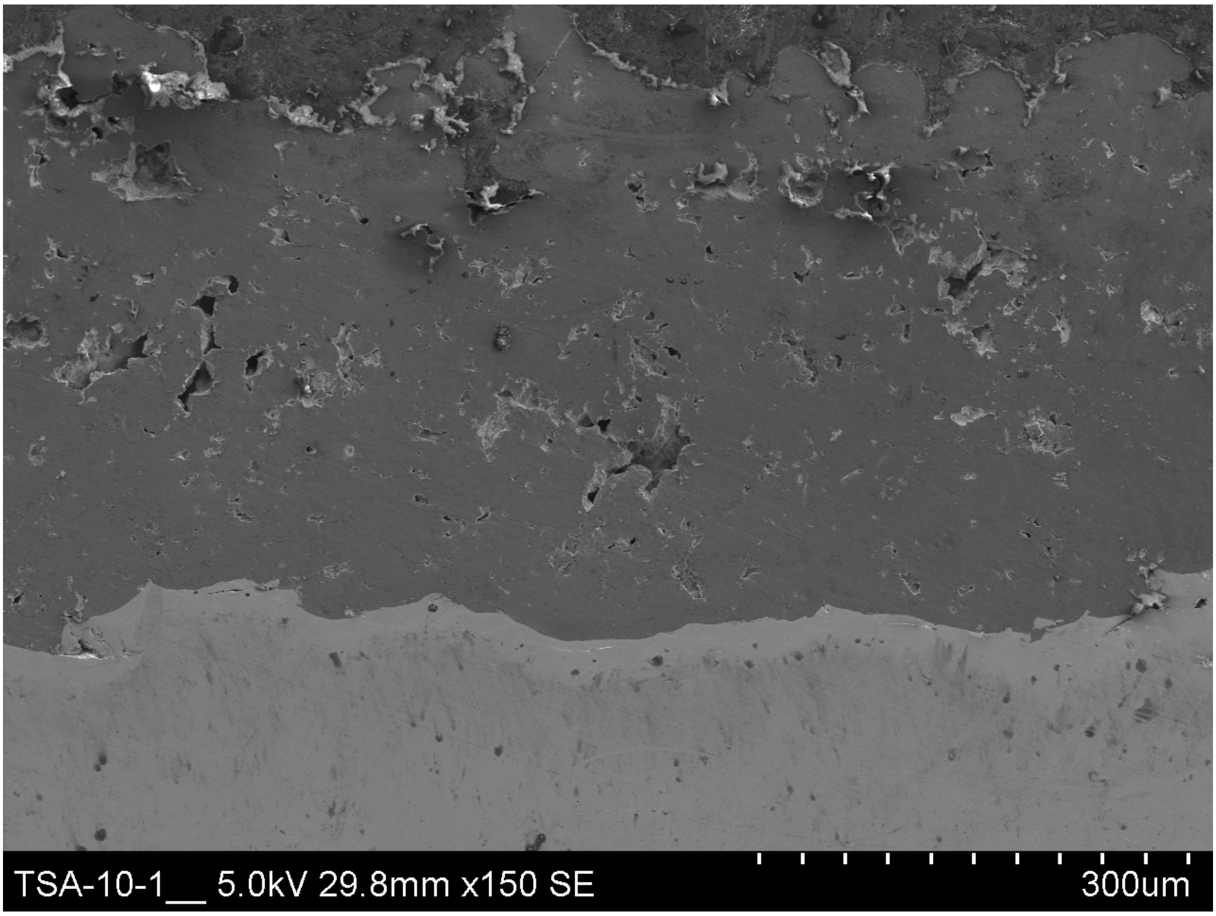

Figure 4.24 TSA coating in the 205°C-tempered area. Carbon steel is the brightest grey at the bottom with porous TSA above. Imaged in Hitachi SU-6600.

5 Discussion

5.1 Coatings

The temperatures used in this evaluation are only an estimate based on the temperature measurements. There are mainly two sources of errors concerning the measurements. A few degrees difference were also observed between the multimeter used for the manual temperature measurements and a conventional thermometer. Also, the holes made in the insulation were larger than the diameter of the thermocouples, and air might have cooled down the surface of the pipe in the area.

5.1.1 TMIC

The TMIC coating provided very good protection against corrosion. Closer examination of the rust at the bottom of the pipe showed that most of it probably was corrosion creep from the bare steel edge of the pipe. The coating itself was intact and showed no sign of degradation down to 300^{o}C. The single spot of coating failure and rust is likely to have occurred due to mechanical damage of the coating as no other degradation of the coating is seen visually or in SEM for the area. However, adhesion and porosity was difficult to evaluate in SEM, but a few areas with poor adhesion and a few pores were seen. The pores might also have been aluminium pigments, as they appear as dark lines and holes in the coating. The areas where poor adhesion is found are very few, and whether this is due to the application of the coating or coating degradation is not known.

What seems to be a crack in the coating along the steel surface is barely visible on the pictures from the SEM. This line is found from the bottom and along the sample up to the area where a clip fixing the sample in the right position during the moulding is situated. Where the clip is installed the crack is not visible. The next sample, which is from the area above the clip of the first sample, the crack is again visible and runs in the middle of the coating in the direction along the steel surface. Again, when the crack reaches the clip in this sample, it disappears. It is possible that this crack occurred during the sample preparation, but it might also be poor adhesion between the two layers of coatings.

Testing by O'Donoghue et al. [22], supports the good performance of TMIC in this investigation. As in this thesis, they used the cyclic pipe test to evaluate TMIC coating. The performance was good with no blistering, flaking or cracking, and no breakdown of the coating microstructure up to 335^{o}C. In the temperature area 335 to 445^{o}C rusting grade Ri 0 and Ri 1 was seen, but the stain was easily removed, as it was probably corrosion products from the uncoated end of the pipe. Some dulling and slight loss of luster was seen above 190^{o}C. It was compared to TSA, a modified silicone copolymer and an inorganic polymer with micaceous iron oxide (MIO). The results showed that TMIC and TSA had the best protection for CUI.

TMIC coating was also tested in another investigation by O'Donoghue et al. [7]. This test concluded that TMIC performs up to 450^{o}C without breakdown and offers better protection than both a modified silicone copolymer and an inorganic polymer with MIO. The testing performed in this work did not reach higher temperatures than 300^{o}C, but up to this temperature the results supports each other.

Haraldsen [15] also tested a high temperature inorganic copolymer in a pilot scale accelerated testing. This coating degraded heavily, but the test conditions were very harsh and the pipes had already been used for similar testing and residual coating and corrosion product was present at the surface. The test simulated therefore a situation where maintenance of pipes used in CUI conditions was done. This is a different situation than what was the case for the cyclic pipe test performed in this work, and differences in the results are therefore expected.

The marks after the thermocouples were seen very clearly for the TMIC. For this coating, permanent glass tubes were installed in the insulation, and occasionally also manual temperature measurements were done to calibrate the temperatures due to the heat loss from the glass tubes. This is seen from the marks, as one larger and several small marks are found for each site. This might indicate poor mechanical resistance for the coating, especially since the marks after the glass tubes were not moved during the testing. However, they had to be installed twice due to the re-installation of the insulation. The temperature does not seem to influence the mechanical resistance of the coating, since the marks were as clearly at the top as at the bottom. When scratching the coatings after testing, marks are easily made at the TMIC, a little bit harder at the TSA and hardly any marks at all were seen for the epoxy phenolic.

5.1.2 Epoxy phenolic

Almost no marks after the thermocouples were seen on the coating, which indicates good resistance against mechanical damage. Discolouring was seen, but this does not affect the anti-corrosive performance of the coating.

Blisters were seen in the 150 to 1575°C area. The epoxy phenolic coating is expected to resist temperatures higher than 175°C, which might indicate that the blistering was due to low film thickness in this area. However, the coating thickness was measured to approximately 200 µm, which is the specified thickness specified by the manufacturer. The coating failed by rusting and blistering in the 220 to 230°C tempered area. The coating should provide corrosion protection for cyclic service with intermittent temperatures up to 230°C, which is a somewhat higher temperature than what was seen during the testing. If the 150 to 175°C-tempered area of blisters is disregarded, the results agrees very well with the given temperature limit. Due to the fact that no blisters were seen in the 175 to 220°C-tempered area, the some aspects with the application of the coating may have influenced the blistering at 150 to 175°C.

Haraldsen [15] tested an epoxy phenolic coating during the accelerated pilot testing. This coating performed generally well, but the highest temperature during this test was 140°C, which is considerably lower than the temperatures achieved during the testing in this thesis. Also, the accelerated pilot test has a higher degree of immersion and the good results for the epoxy phenolic in this test might indicate better barrier properties than the TMIC. As the TMIC performed better for the cyclic pipe test, this might indicate better resistance against thermal cycling at higher temperatures.

5.1.3 TSA

TSA performed well for temperatures up to approximately 190°C. The 190 to 220°C-tempered zone that was examined in microscope contained some areas with degraded coating in the region where the thermocouples were used. As the quality of the coating between these areas was good, it is very likely that the areas with degraded coating are due scratches in the coating by the thermocouples. However, visual inspection of the 190 to 220°C-tempered region showed that coating degradation were also visible in areas where the thermocouples were not used. Therefore, the degradation of the coating seemed to start in the 190°C-tempered area. This is considerably lower than expected, as TSA is claimed to withstand temperatures up to 595°C in cyclic service [5]. However, MacDonald et al. [29] found that for temperatures higher than 150°C, aluminium in high temperature aqueous systems has an increasing region of corrosion in alkaline environments. This is due to increased formation of AlO_2^- instead of Al_2O_3. Calcium silicate contains high levels of sodium silicate, which is alkaline, and hence the test method includes both immersion, higher temperatures than 150°C and alkaline environments. This combination will generate increased corrosion for the TSA, as seen in the test.

Some porosity was seen in the coating, which is typical for arc sprayed TSA. This did not seem to affect the corrosion protection in the areas were the coating was still intact and good adhesion was found.

O'Donoghue et al. [22] used the cyclic pipe test to evaluate TSA and reported of no blistering, flaking or cracking, but Ri 2 was found in the 390 to 445°C range. Also, minute pinpoints of rust were found from 140 to 390°C. In the testing performed in this work, no degradation was seen until 190°C. Here the coating was visibly thinner with areas with rust stains.

Accelerated testing performed by Haraldsen [15] included more immersion than the cyclic pipe test, but the temperatures only reached 140°C and mineral wool was used as insulation, so the environment was not alkaline. These conditions are much better for the TSA, and as expected it performed well and was rated among the best of the tested coatings.

Testing of TSA has also been performed with the ASTM G189 test method. Kane et al. [30] performed cyclic testing with temperatures varying from 82°C during the wet period and 110°C during the dry period. When calcium silicate insulation was used, the corrosion rate was measured from 0.003 to 0.03 mm/y and no sacrificial reduction was found for the coating. Visual examination also confirmed that no pitting had occurred. This is a satisfying result and it agrees with the fact that there was no coating degradation in the 110°C region for the cyclic pipe test. However, TSA is not expected to corrode in this temperature range [5] and it would have been more interesting to compare results from a higher temperature range where degradation is more likely to occur.

5.1.4 Comparison of coatings

The coatings can be compared for temperatures up to 300°C in CUI conditions, see **Table 5.1**. The worst performance in each category is listed. The temperature where the degradation of the coating started has been added the most weight when choosing the best protective coating for CUI conditions up to 300°C. Overall, TMIC was rated the best coating, followed by TSA and then the phenolic epoxy. If the temperature where the coatings failed is considered, the epoxy phenolic almost performed as well as the TSA. Also, from the marks after the thermocouples, the epoxy phenolic had the best resistance against mechanical damage.

Table 5.1 Comparison of the tested coatings.

	TMIC	Epoxy phenolic	TSA
Adhesion	Intermediate	Worst	Best
Rusting	Ri 0	Ri 4	Rusted steel surface area with no coating left
Blistering	None	4(S4)	None
No degradation up to:	300°C	160°C	190°C

It is expected that the epoxy phenolic coating should perform worst under this conditions as the temperature range exceeds its limits. However, TMIC and TSA should withstand these temperatures and conditions, and therefore the poor performance of the TSA was surprising.

5.2 Test method

As ASTM G189 [27] is the only test method for CUI that is specified in a standard, it is reasonable to compare the test method used in this thesis to the one described in ASTM G189. During testing with the cyclic pipe test, both good and bad aspects of the test method were revealed. The ASTM method is elaborate and requires special equipment. The method has some weaknesses when it comes to testing of coatings, as will be discussed later, so building the apparatus and testing the method was beyond the scope of this work. Additional positive and negative aspects concerning ASTM G189 might be found during testing. Aspects discussed here are based on the description of the method in the ASTM standard and experiences with this method found by others.

First of all there are differences in specimens between the two tests. ASTM G189 uses three to six ring specimens with a nominal diameter of 50.8 mm (2 in.), 4.75 mm (0.187 in.) thickness and 6.35 mm (0.25 in.) wide, i.e. a rather small coated area. Three specimens with the same coating may be tested at the same time, but only half of the outer surface of the specimens is tested. While the cyclic pipe test uses 600 mm long pipes with outer diameter of 60 mm, which is considerably larger than for the ASTM test method. Kane et al. [30] used ASTM G189 to test a TSA coating in a CUI environment. They had to increase the width of the ring specimens from 6.35 mm (0.25 in.) to 12.7 mm (0.5 in.) to accommodate the application and evaluation of the coating.

Also the evaluation of the samples is different and related to the selection of test specimens. As the specimens for ASTM G189 are so small that visual evaluation of the coating is difficult, corrosion rate is used instead for evaluation. Corrosion rate is a good indication of susceptibility to corrosion of a metal, but the degradation of a coating might not always correspond to the metal corrosion rate. A coating full of blisters and little adhesion might still be able to provide corrosion protection for a while, but it will be classified as failed in a visual evaluation. Kane et al. [30] visually examined the specimens in addition to use the corrosion rate, hence it was more convenient to use larger specimens. Corrosion rate seems therefore not to be the best evaluation form for the corrosion protection of coatings.

Bock [11] listed some requirements for the ideal CUI system, among them the ability to survive damp surface exposure and immersion in chemicals from insulation and environment for lengths of time when the surface is under 100°C. It should also withstand steam when the temperature rises above 100°C and cyclic service. Both of the test methods include large amount of electrolyte to create immersion and steam exposures. The insulation used in ASTM G189 has holes both for leading the water in and for drainage. Here the solution is pumped continuously through the CUI cell during the cooling period, leaving the insulation saturated with electrolyte and creating an immersed condition for the length of the pipe. During the cyclic pipe test, water will gather at the bottom of the casserole for a while after each wetting, creating immersed conditions for the pipe, before the water evaporates. However, this will only happen for the bottom part of the pipe, and hence the conditions will not be the same along the length of the pipe. Moreover, this immersed condition means that the insulation degrades much faster at the bottom of the pipe than at the top and the water will cool down the steel surface, causing larger heat loss and lower temperatures at the bottom. This is not ideal, as the only parameter that should vary along the length of the pipe is the temperature. The immersed condition creates an uncertainty of the actual condition the coating has gone through. Therefore, the ASTM G189 test method seems to represent these conditions best, as some parts of the specimens used in the cyclic pipe test will not experience immersion.

The cyclic pipe test runs for 30 cycles with 8 h heating and 16 h cooling, while ASTM G189 suggests a minimum duration of three cycles with 4 h heating and 20 h cooling. Three cycles and 72 h is a short time for testing coatings, even though the conditions are harsh. However, testing with ASTM G189 has been performed with initial aging treatment for both insulation and specimens before the testing was started [30]. Abavarathna et al. [2] found that for wet/dry 66/121°C cycling, the efficiency of the coated pre-corroded specimens decreased 10 % compared to the specimens with no initial treatment. This indicates that aging the specimens prior to testing may be a good way to compensate for the short test period. Nevertheless, CUI is a problem that evolves over time, and 72 hours seems a very short time for coating degradation to develop.

The cyclic pipe test has a fixed set of parameters that ensures the same conditions for each test. However, some parameters that affect the test conditions and might influence the reproducibility of the test are not specified. No restrictions are set for these factors to make the conditions as equal as possible.

First of the non-specified parameters is the pause during testing. During the cyclic pipe test, addition of electrolyte and cyclic heating are stopped during weekends and holidays. The pipes are left in ambient temperature and the aggressiveness of the corrosive environment is reduced. However, some corrosion will continue during these breaks and hence the length of the breaks will influence the results to some degree. If results from a test run with a two-week break and weekend breaks are compared to a test with only weekend breaks, it might be reasonable to take this into account. As the test is now, this is not considered and the effect of the breaks is neglected.

Second is the variation in immersion conditions, which is highly affected by the size of the casseroles. In this work, relatively small casseroles were initially used, but as the insulation was saturated with electrolyte the casseroles were filled up and found to be too small. Larger casseroles were then used and then the electrolyte only covered the bottom of the pipe by a couple of centimetres. To establish more constant conditions, it will be helpful to set some requirements concerning the level of immersion that will determine the casserole size.

Finally the variation in temperatures between each pipe in different tests is important. This is a complex factor influenced by a lot of other aspects with the test that is difficult to control. **Figure 5.1** and **Figure 5.2** compare the temperatures of the coatings during the first cycle and the temperature range for cycle 16. After the insulation was changed, the conditions should be the same as for cycle 1. Differences up to approximately 50^{o}C were seen between the pipes during cycle 1. From cycle 1 to cycle 16, the temperature for the epoxy phenolic coating increased 20^{o}C at some places. The saturation of the insulation with the electrolyte decreased the temperature from cycle to cycle. This may be compensated by turning the insulation around, i.e. take it off, and flip it so that the insulation at the top then is exposed at the bottom of the sample. As new insulation was available and this seemed the best way to prevent uneven degradation of the insulation, new insulation was installed instead in this test. However, whether the old insulation is flipped, new is installed or nothing is done concerning the degradation of the insulation, this will influence the temperature of the sample significantly. The variation in temperature is also influenced by how much of the electrolyte that gathers in the insulation and how much that runs quickly through gaps and cracks. It was observed differences between the insulation half-shells regarding the speed at which the electrolyte penetrated the insulation.

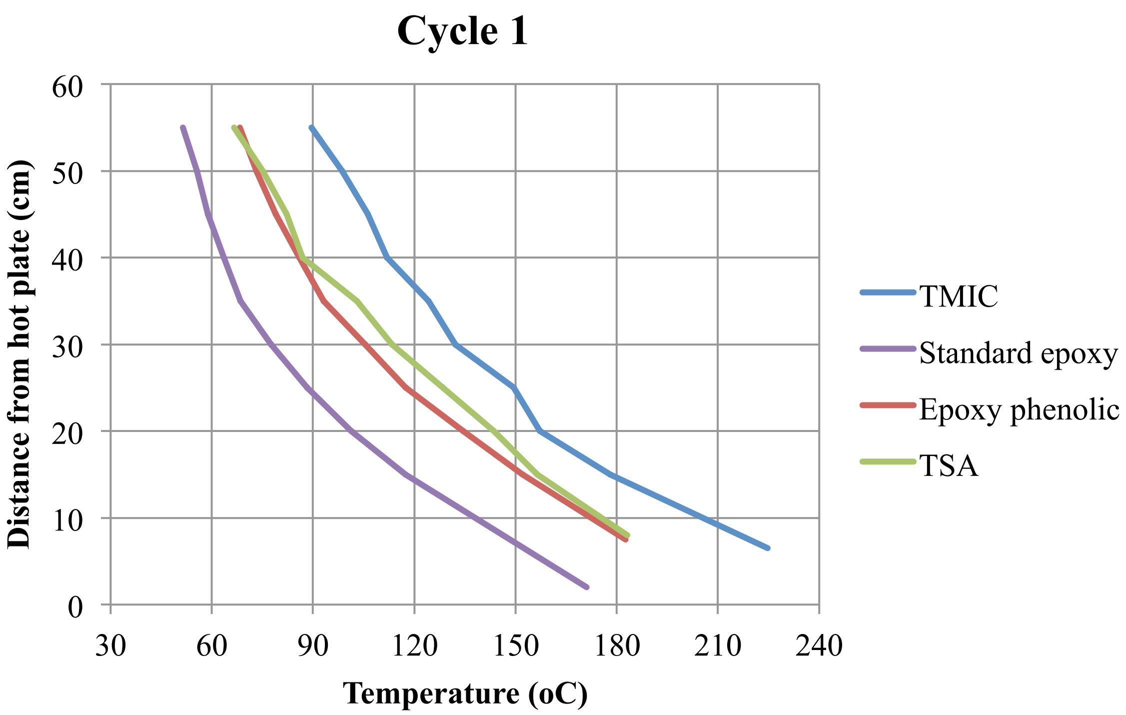

Figure 5.1 Temperature range after 7.5 h heating during cycle 1

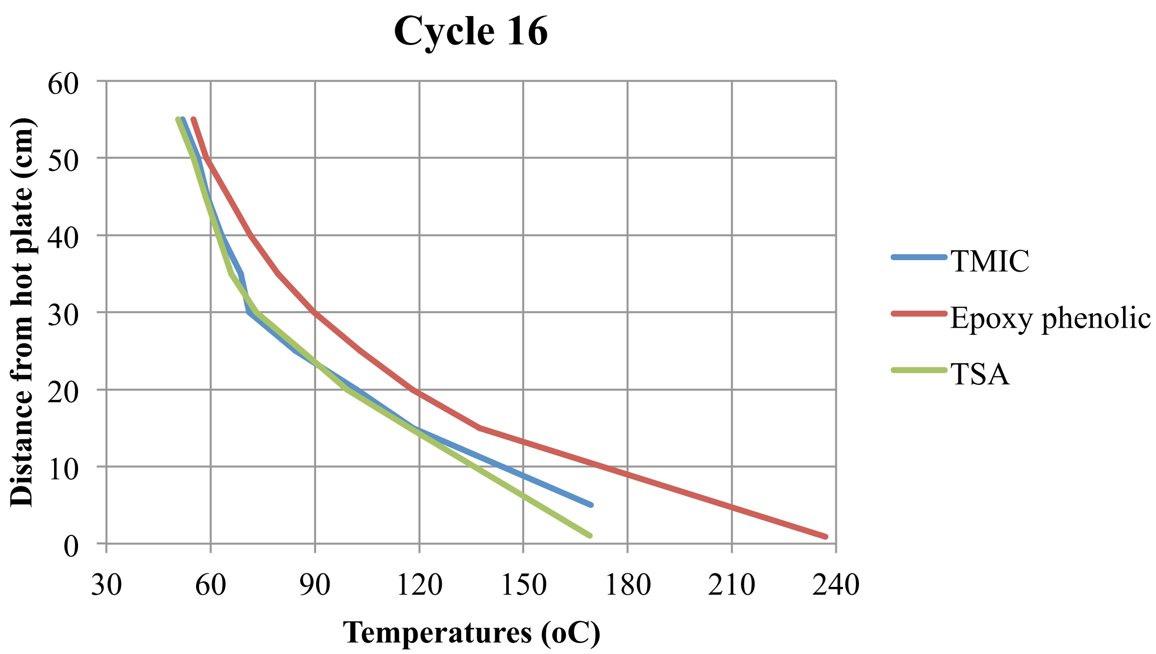

Figure 5.2 Temperature range after 7.5 h heating during cycle 16.

Also, the temperature along the pipe represents an uncertainty. The time when the measurements were performed varied, different coatings have different thickness and thermal conductivity, and the distances from the hot plate were not very precise. The temperature gradient is large along the pipe near the bottom, so it is difficult to accurately determine the temperatures along the pipe. In earlier tests conducted with the cyclic pipe test, [7, 22], the temperature was measured on an uncoated pipe during a temperature cycle with no fluid involved. Since the water cools down the pipes, the temperatures achieved in this work are lower than what was found in previous investigations. Hence, the temperatures seem to vary from test to test.

ASTM G189 testing includes spacers between the steel specimens. The outer diameter of these spacers is 63.5 mm (2.5 in.) and the nominal diameter of the test specimens is 50.8 mm (2 in.). The difference is not large, but as the specimens are quite thin (6.35 mm), this is enough to separate the specimens and the insulation. Haraldsen [15] has documented the efficiency of spacing between insulation and metal surface, so this will influence the test conditions significantly. The environment will be much less aggressive, allowing the surface of the specimens to dry completely between the wettings.

The temperature varied significantly throughout the test. During the first cycle, the highest temperature was estimated to be approximately up to 300^{o}C for all of the coatings except the standard epoxy, which only reached a maximum temperature of approximately 200^{o}C. As the insulation became more saturated with electrolyte and started to degrade, the temperatures decreased from cycle to cycle until the highest temperature was found to be about 100^{o}C for cycle 15. After replacement of the insulation, the temperatures again rose up to 240^{o}C for the epoxy phenolic and TMIC, but the TSA only reached approximately 180^{o}C. Again they all slowly decreased for each cycle until the highest temperature was approximately 100^{o}C. After testing, the temperature range used in the evaluation of the coating is based on the highest temperatures experienced during the first cycle. But already during the second cycle the temperatures decreased considerably. The highest temperatures indicated in the evaluation are only reached one or two times during the complete test period. This means that a coating said to be good for temperatures up to 200°C has only experienced this temperature for very short time periods. The time spent at the maximum temperature is probably important, so this aspect needs more attention if this test is to be developed into a standard method

For the ASTM G189 test method, a temperature controller and thermocouples are used to maintain the high temperatures even when the insulation absorbs water and degrades. Then the temperatures given in the results have been used throughout the testing period. However, to find the maximum temperature for the coating, several tests must be carried out as only one temperature is tested each time. For the cyclic pipe test, one test gives the results for a large range of temperatures, which is an advantage.

As described above, both negative and positive aspects were found with the test method. But overall the test includes all of the major issues concerning CUI. The test is also quite easy to set up, as no special test apparatus has to be built. Only standard laboratory equipment and materials are used: hot plates, casseroles or other equipment that hinder water from getting in contact with the hot plates, insulation, electrolyte and pipes with coating are needed.

The TSA coating seems to perform worse than expected for the cyclic pipe test. This is due to the harsh conditions of the test with immersion, alkaline environment and higher temperatures than 150°C. However, these conditions might also occur in CUI conditions in reality, and the test should represent the worst-case scenario.

The most negative aspect of the test must be the different level of immersion along the length of the pipe. Intermittent immersion should be experienced for all of the temperature ranges, as will be the case for the most severe CUI conditions.

6 Conclusions

6.1 Coatings

From the results, some conclusions can be drawn concerning the coatings:

- Best protection against CUI up to 300°C was achieved by the TMIC coating. No blistering, cracking or rusting was seen for this coating.
- TSA had the second best performance with no degradation of the coating to 190°C.
- The epoxy phenolic coating had the lowest temperature limit and blistering and poor adhesion were found at 160°C. At temperatures higher than 220°C the coating failed completely by rusting and blistering.

The standard epoxy was only tested for 15 cycles. The coating should be tested to 30 cycles and compared to the other coatings.

6.2 Further improvements to test method

The cyclic pipe test displayed both positive and negative aspects, but all in all, the method has demonstrated that all the major threats to the coating like thermal cycling, high temperatures, wetting and drying period, some immersion and thermal shock are included in the tests. It is not a very demanding test concerning equipment and skills, and it is easy to set up.

Improvements that would contribute more constant testing conditions between tests should be made. Especially changes that would improve temperature control and wetting along the test pipe should be considered. To solve the problem with varying immersion conditions along the length axis, a test set-up with a horizontally placed pipe with a heat source in one of the ends could be developed and tested.

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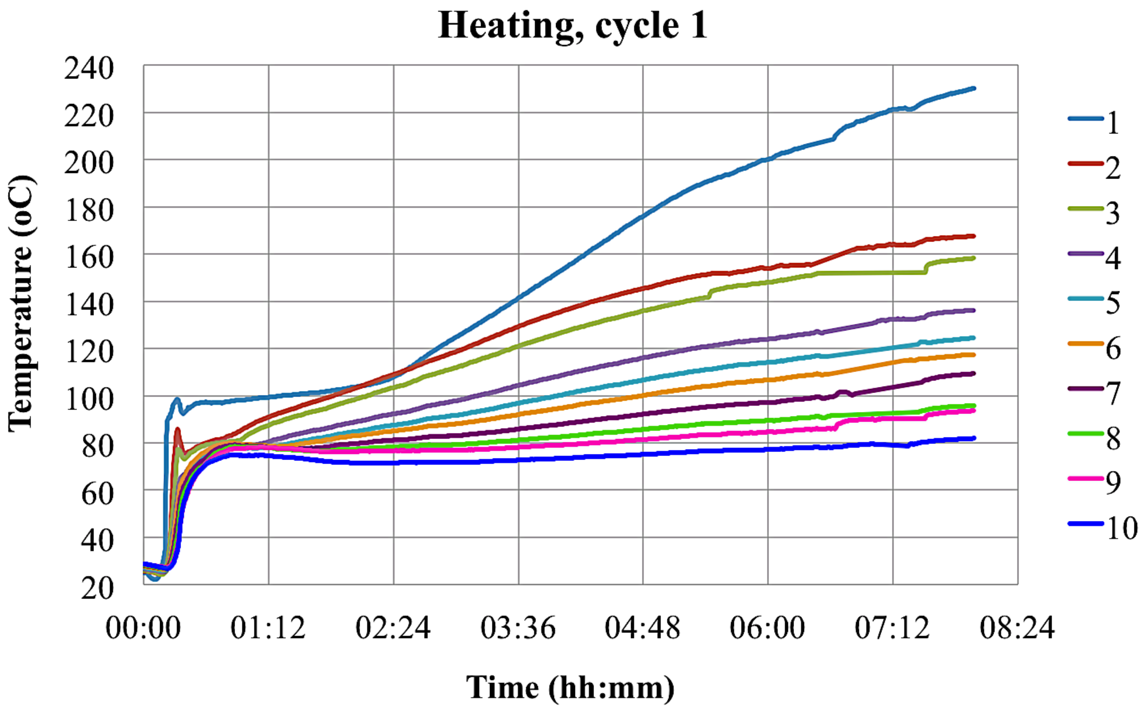
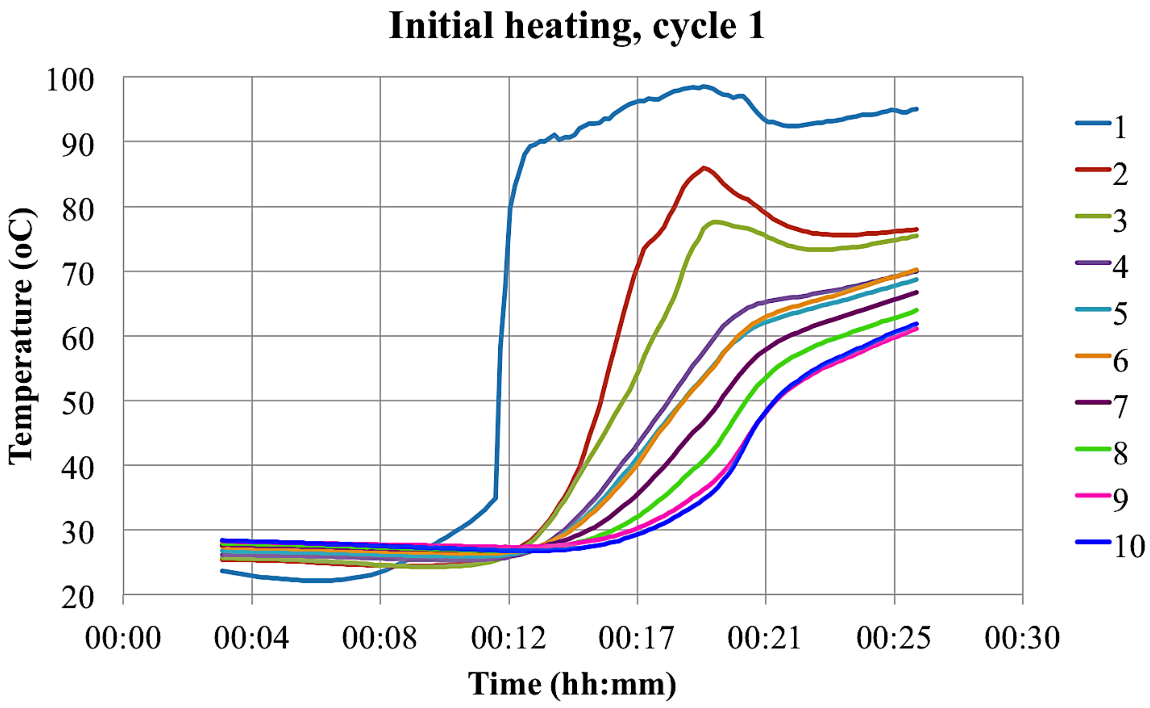
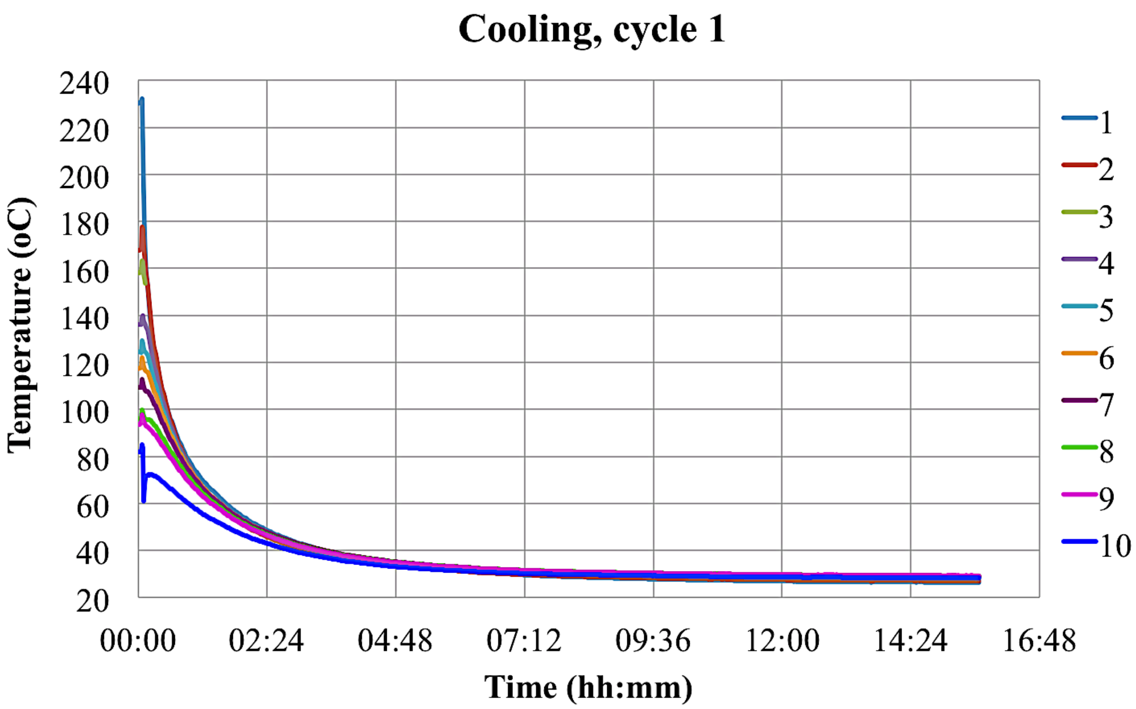
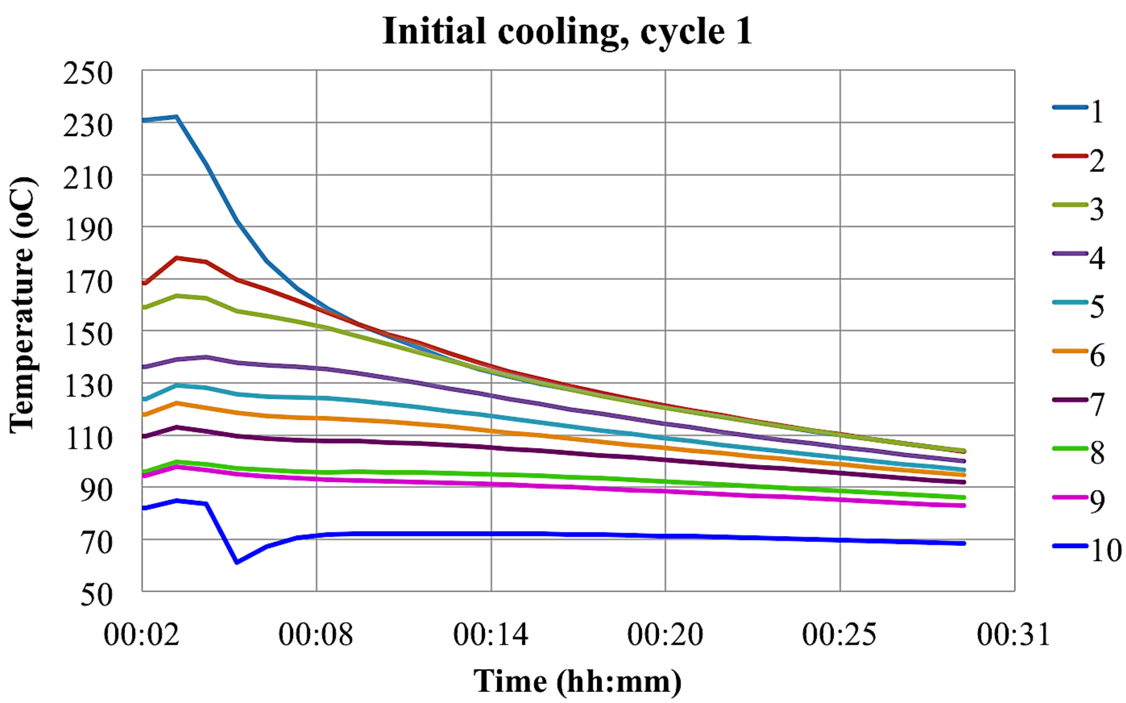
Appendix A: Temperature measurements

A.1 Cycle 1






Cooling, cycle 1
Temperature (oC)
240
220
200
180
160
140
120
100
80
60
40
20
00:00
02:24
04:48
07:12
09:36
12:00
14:24
16:48
Time (hh:mm)
1
2
3
4
5
6
7
8
9
10


Initial cooling, cycle 1
Temperature (oC)
250
230
210
190
170
150
130
110
90
70
50
00:02
00:08
00:14
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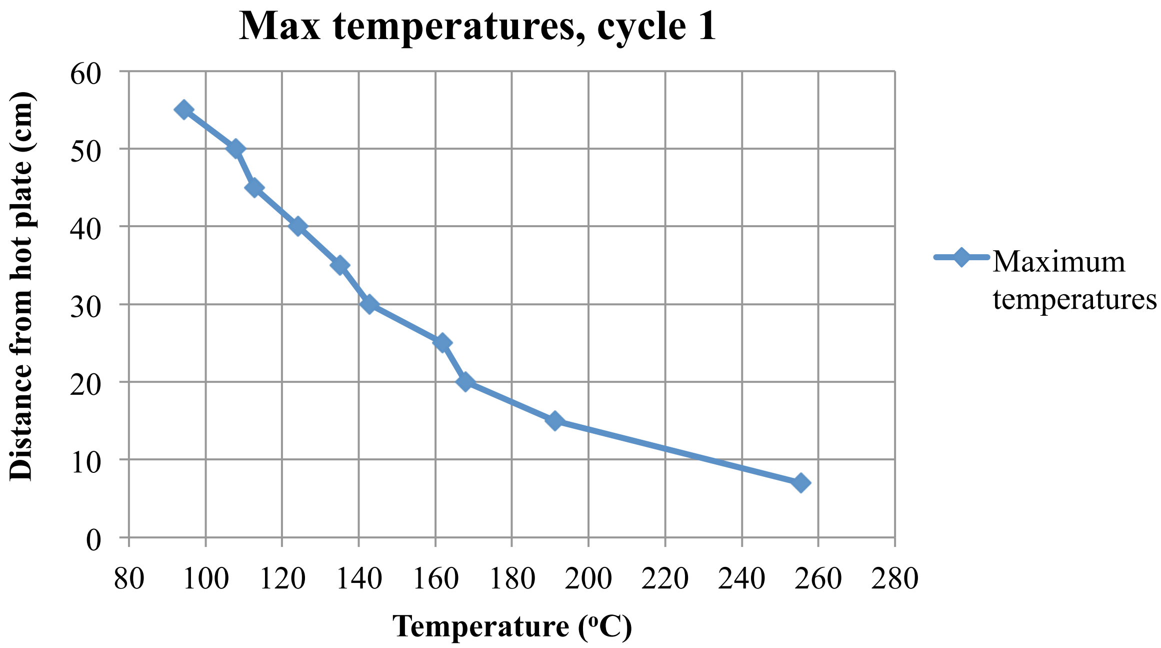
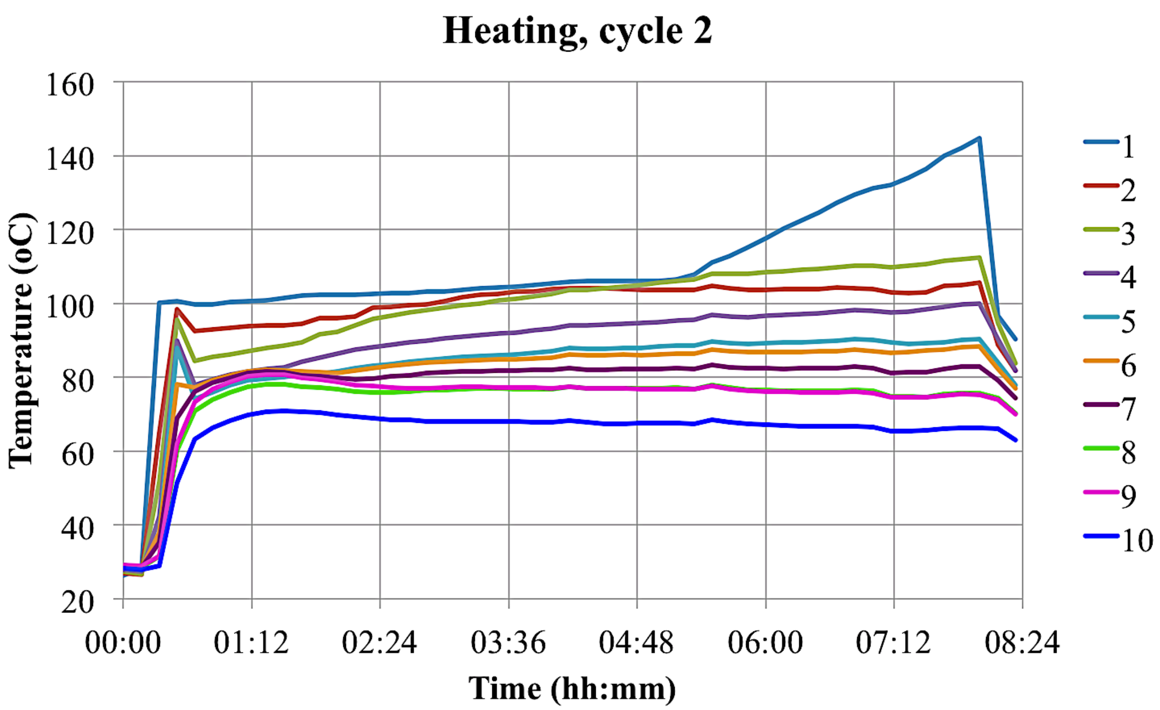
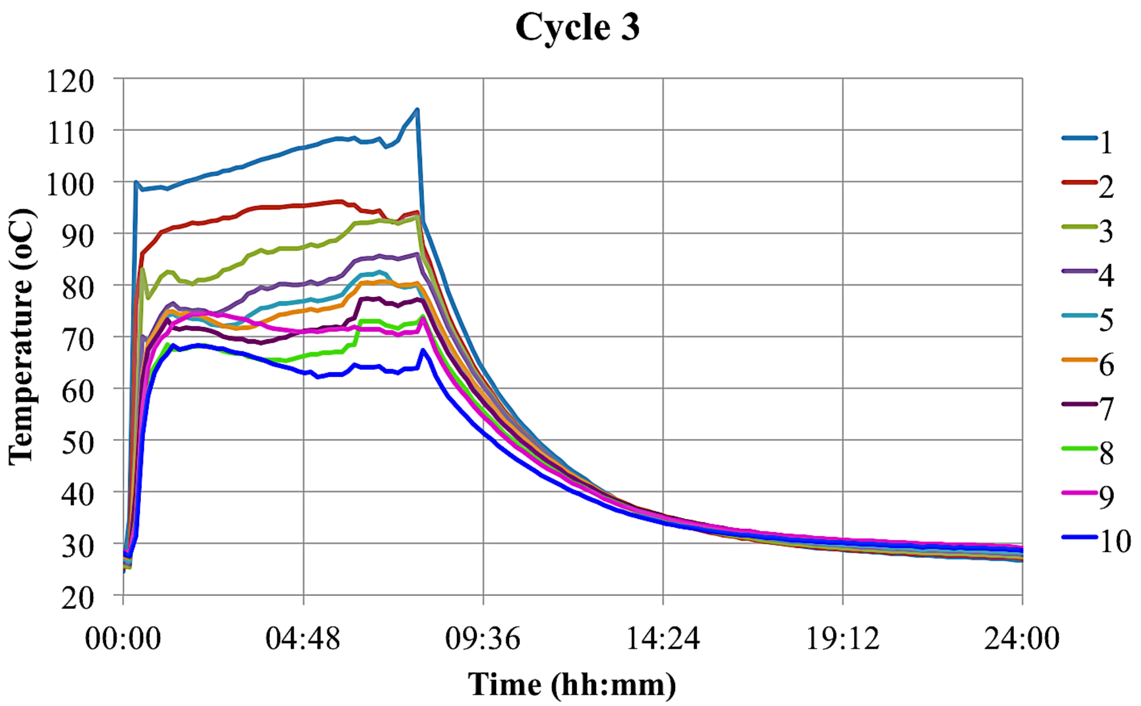
00:25
00:31
Time (hh:mm)
1
2
3
4
5
6
7
8
9
10


Max temperatures, cycle 1
Distance from hot plate (cm)
0
10
20
30
40
50
60
80
100
120
140
160
180
200
220
240
260
280
Temperature (°C)
Maximum temperatures

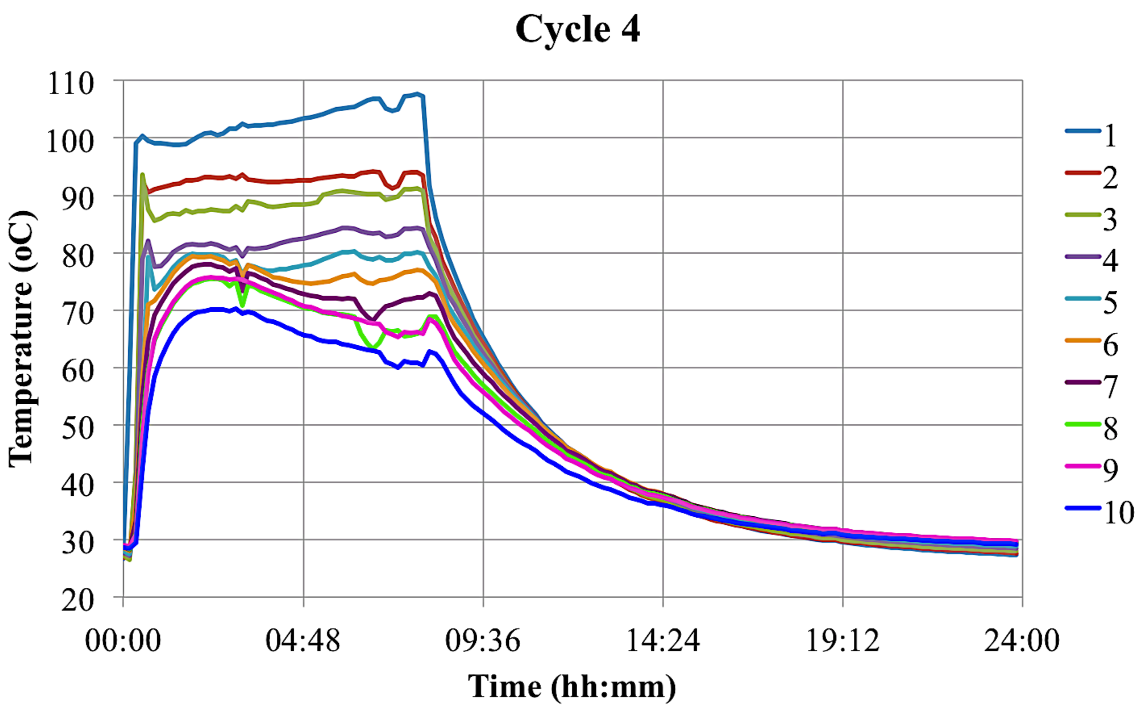
A.2 Cycle 2


Heating, cycle 2
Temperature (oC)
20
40
60
80
100
120
140
160
00:00
01:12
02:24
03:36
04:48
06:00
07:12
08:24
Time (hh:mm)
1
2
3
4
5
6
7
8
9
10

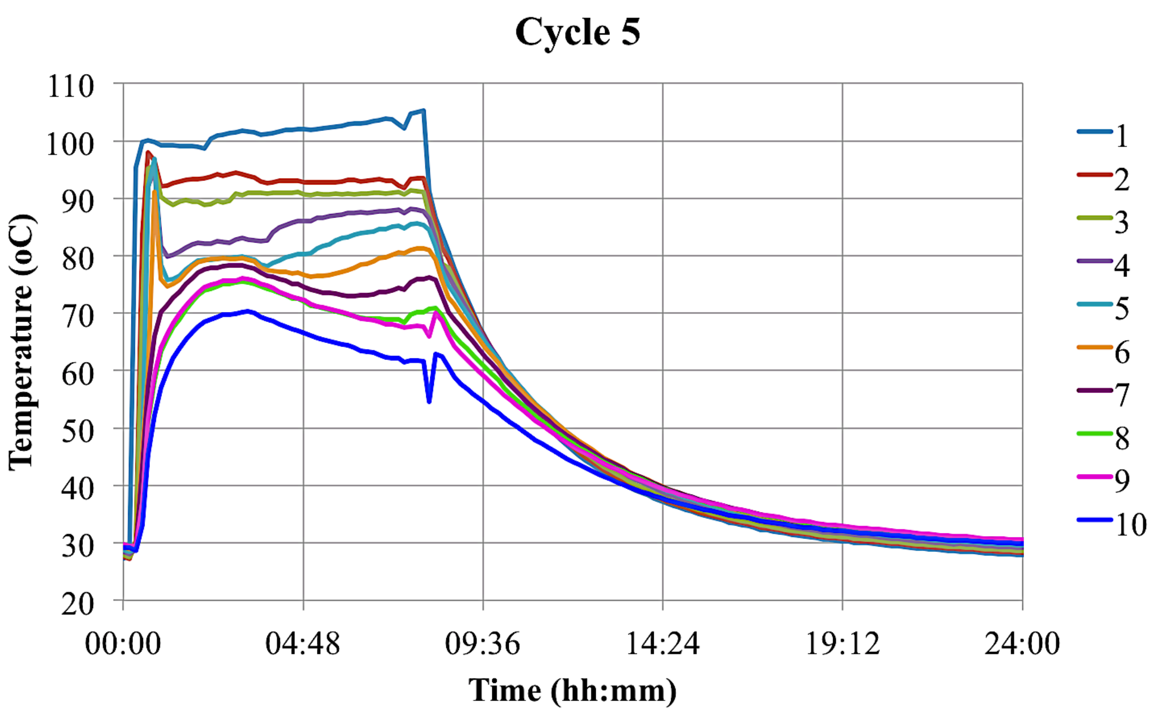
A.3 Cycle 3



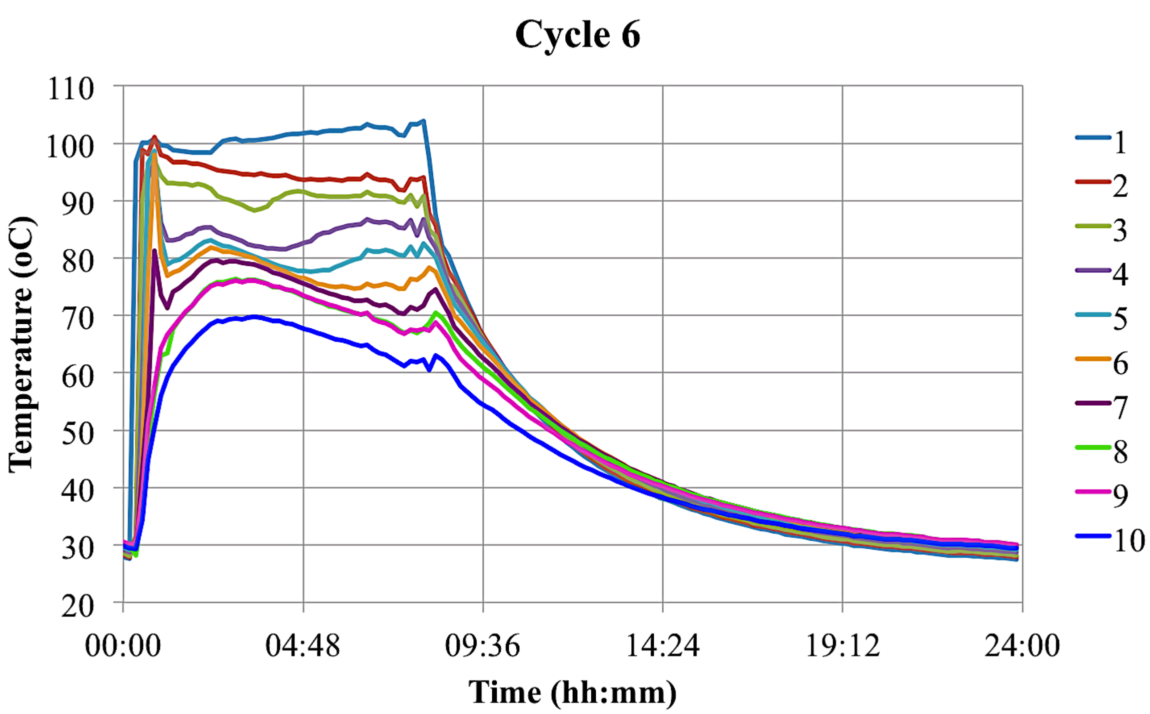
A.4 Cycle 4



A.5 Cycle 5



A.6 Cycle 6



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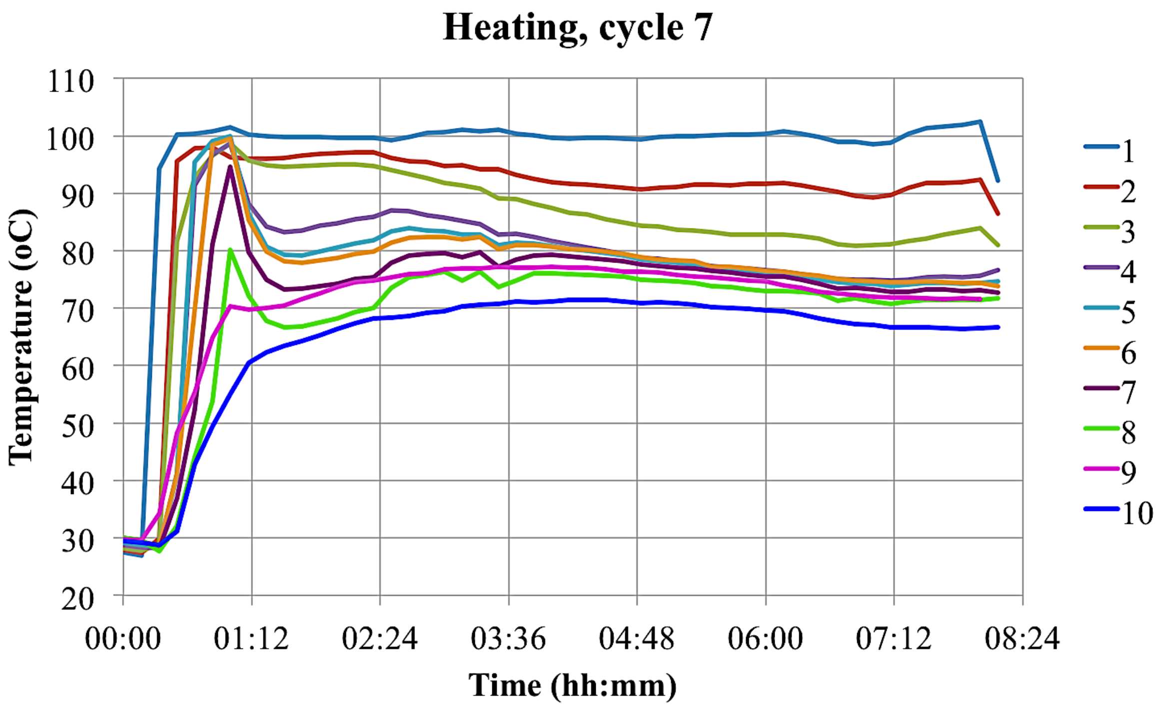
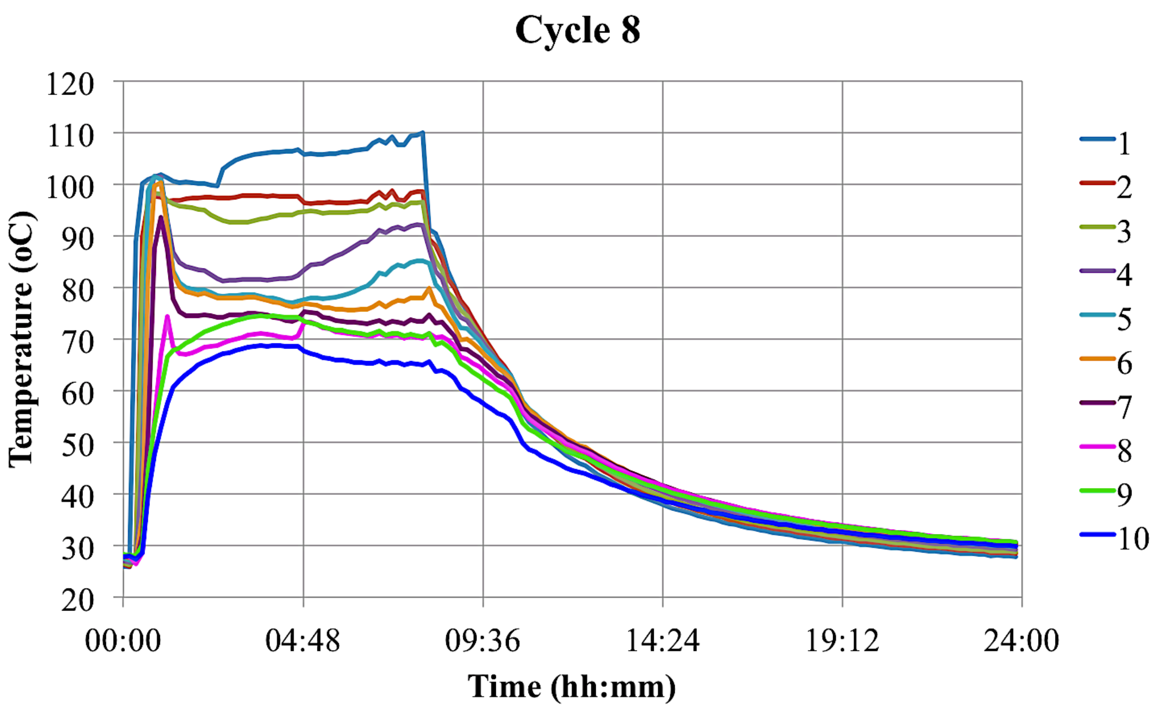
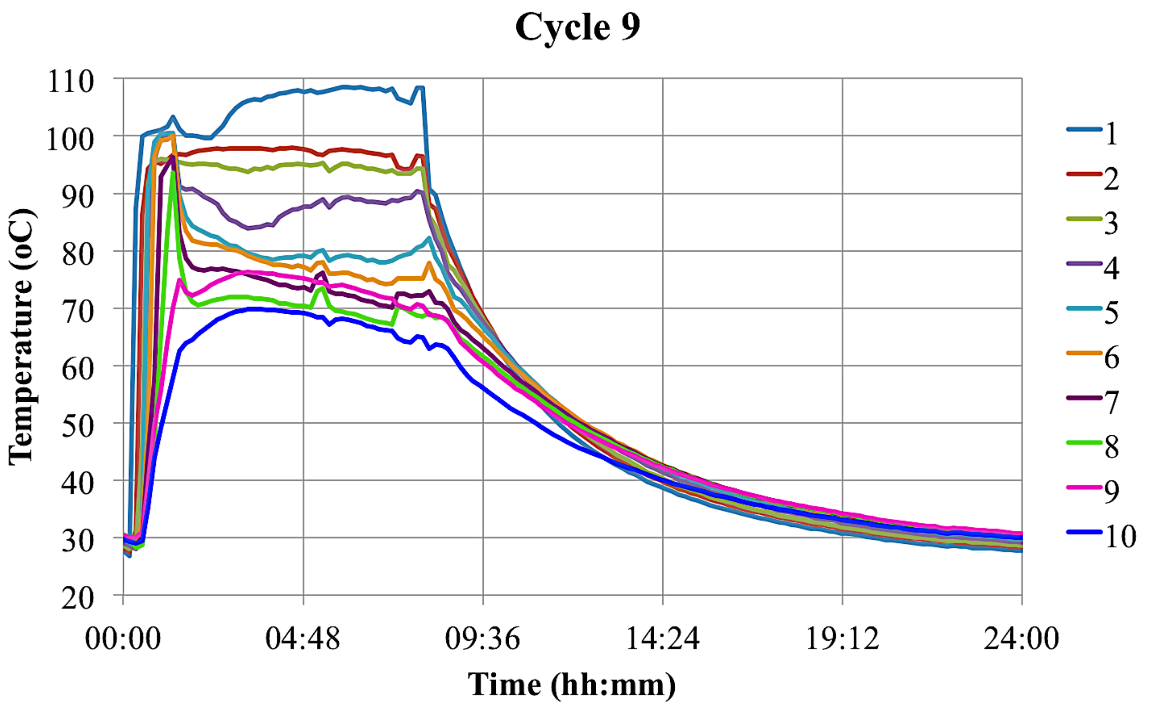


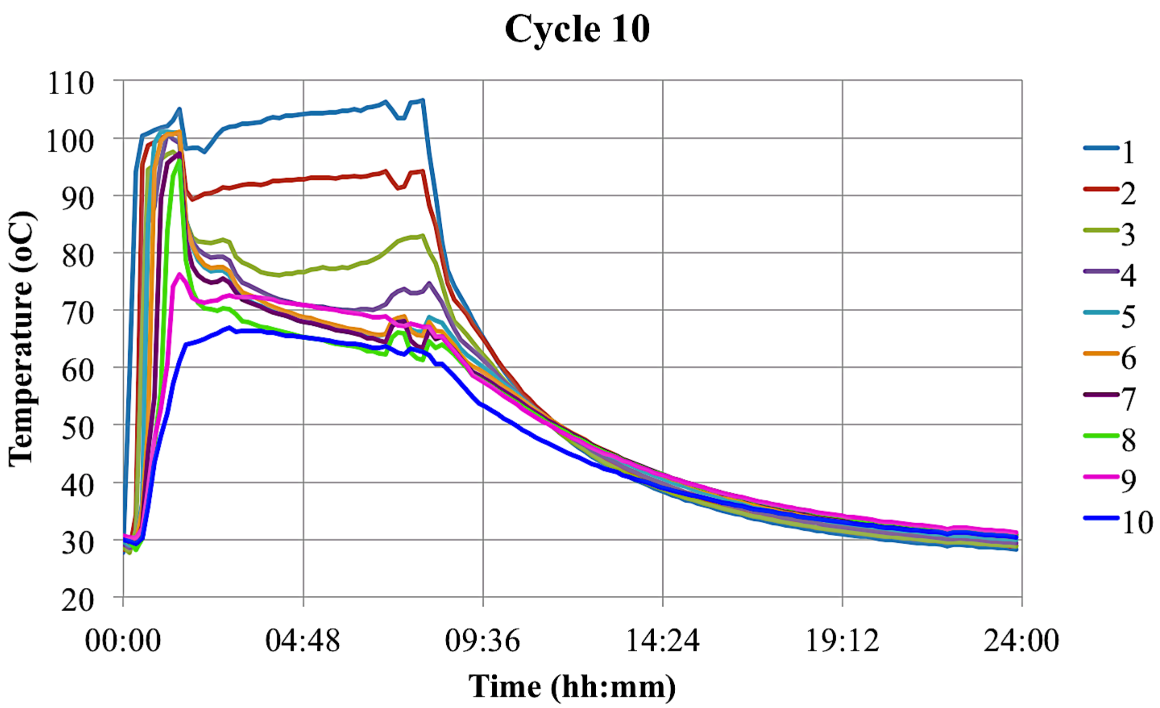
A.8 Cycle 8



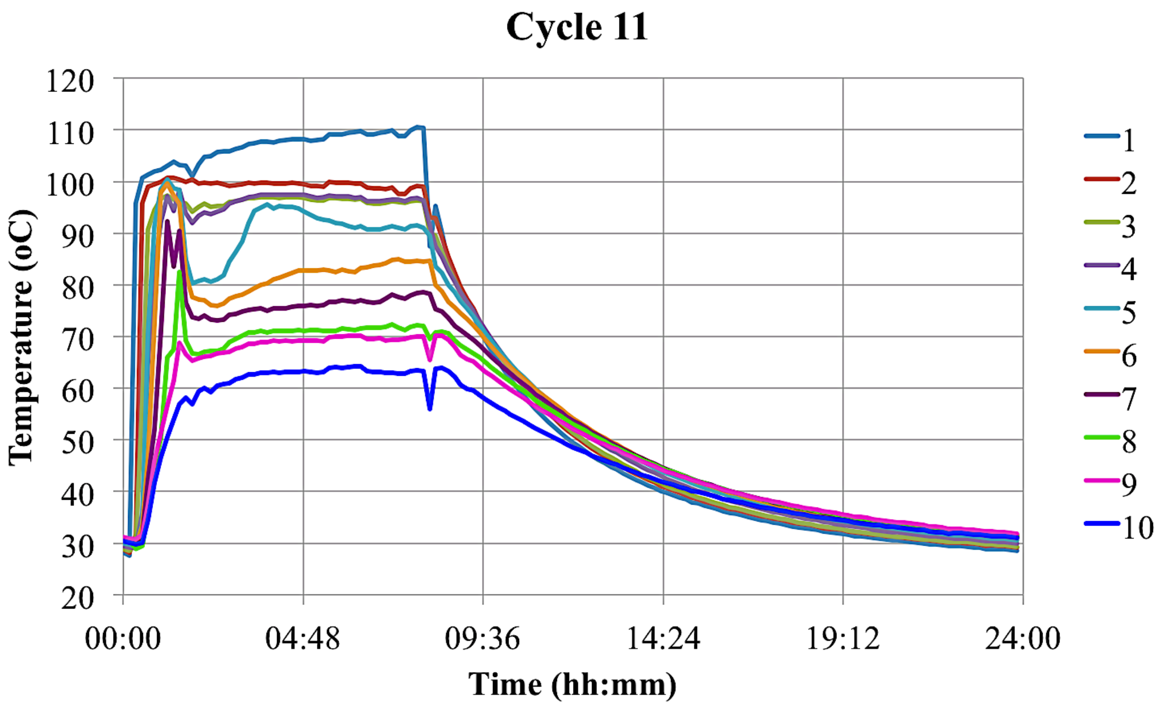
A.9 Cycle 9



A.10 Cycle 10



A.11 Cycle 11



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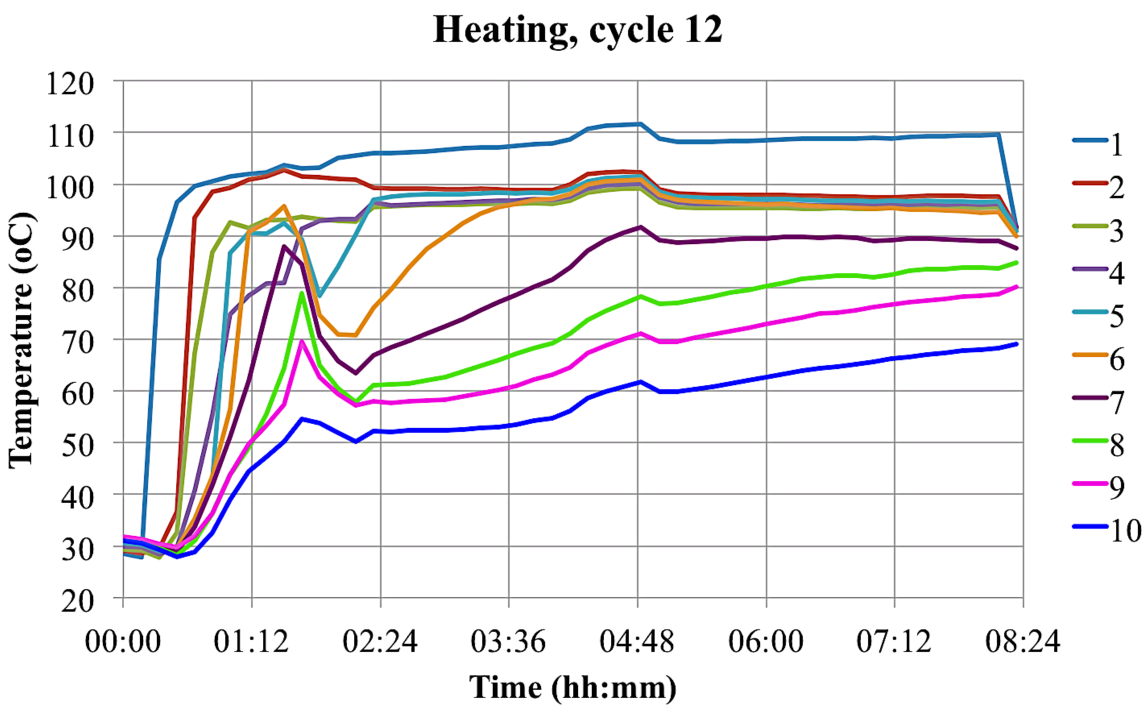
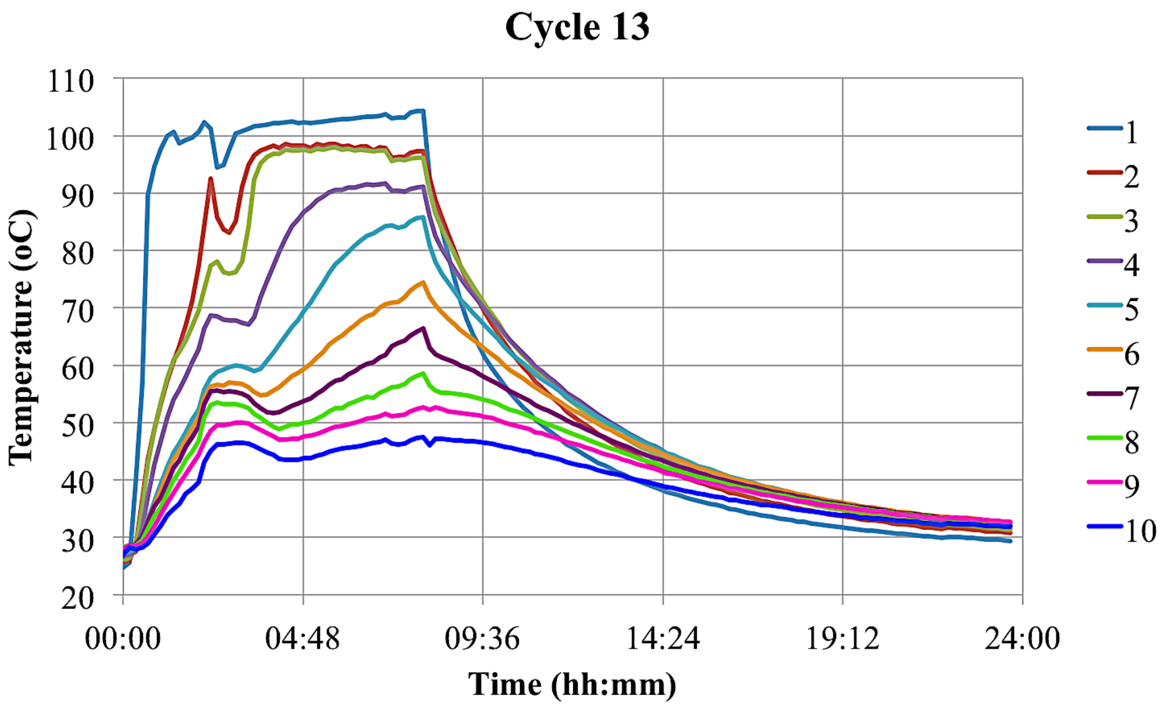
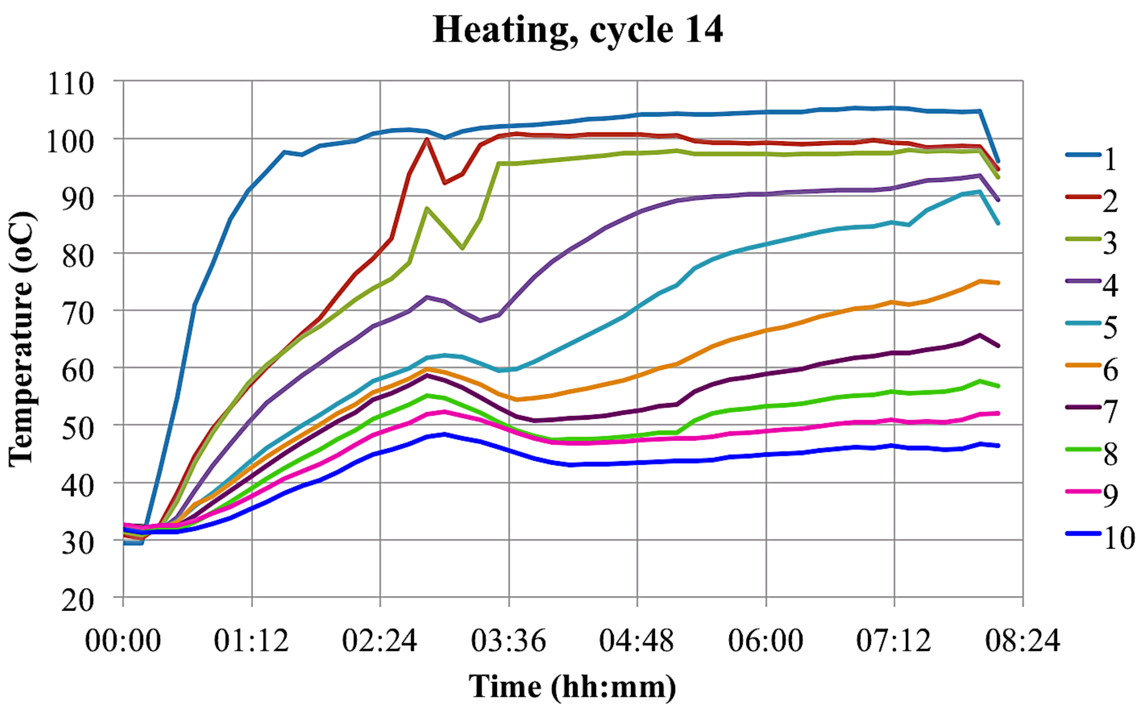


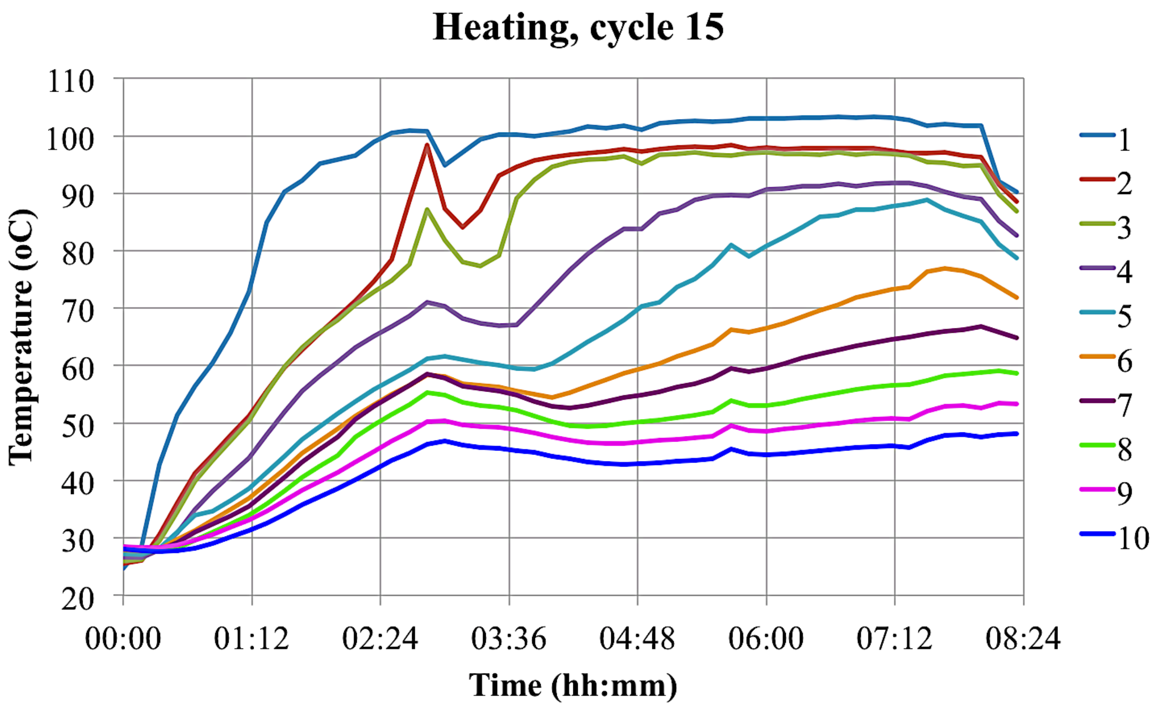
A.13 Cycle 13



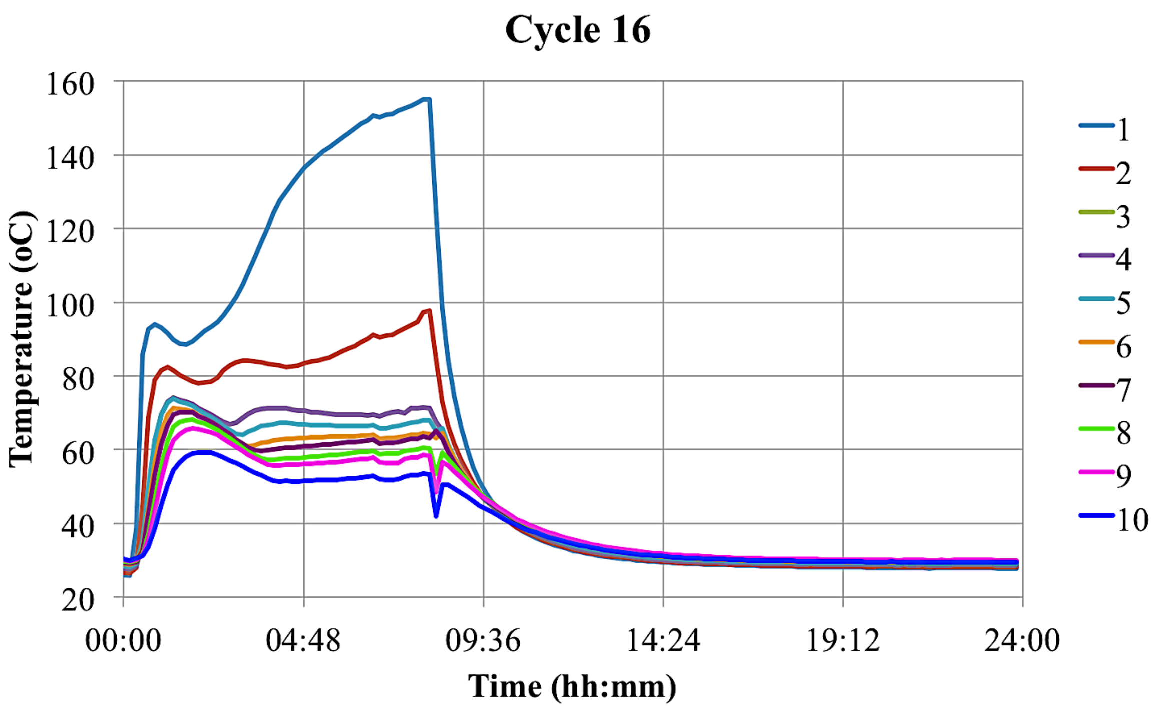
A.14 Cycle 14



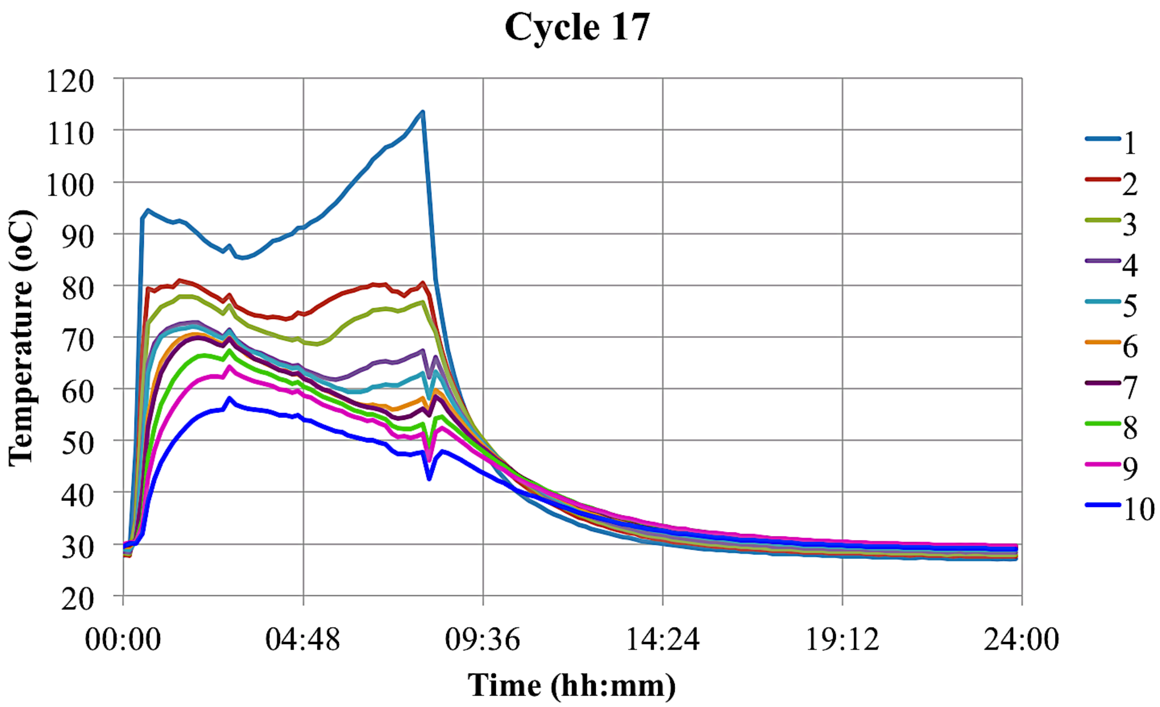
A.15 Cycle 15



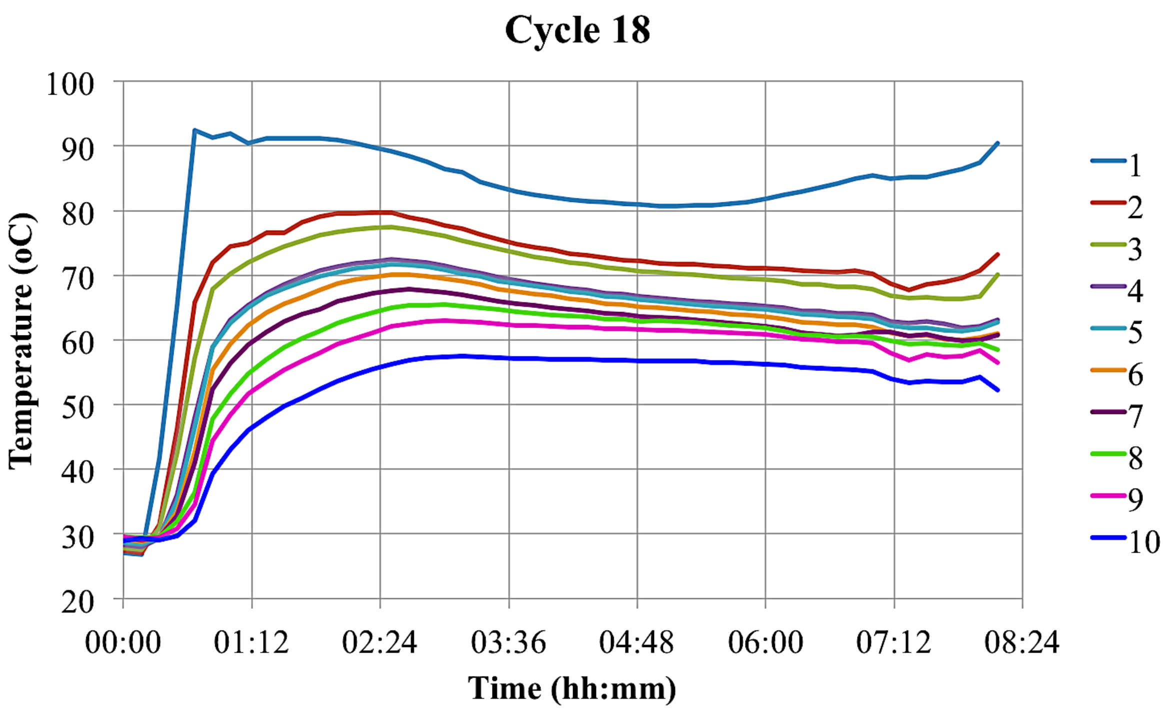
A.16 Cycle 16



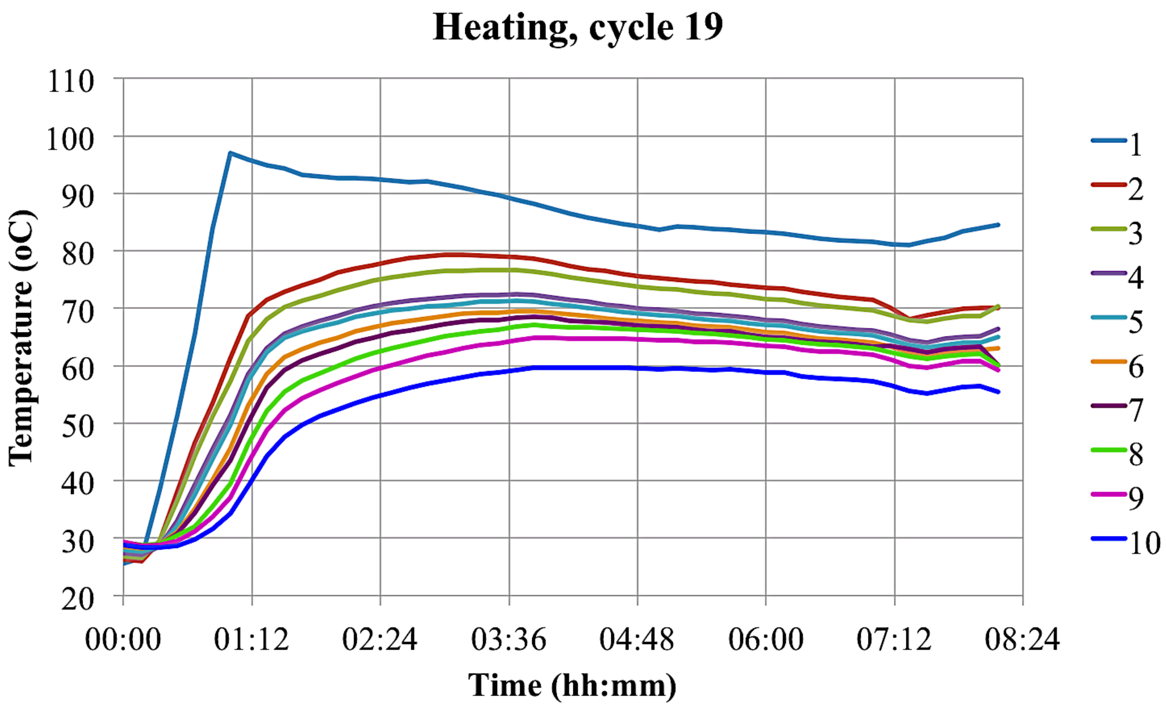
A.17 Cycle 17



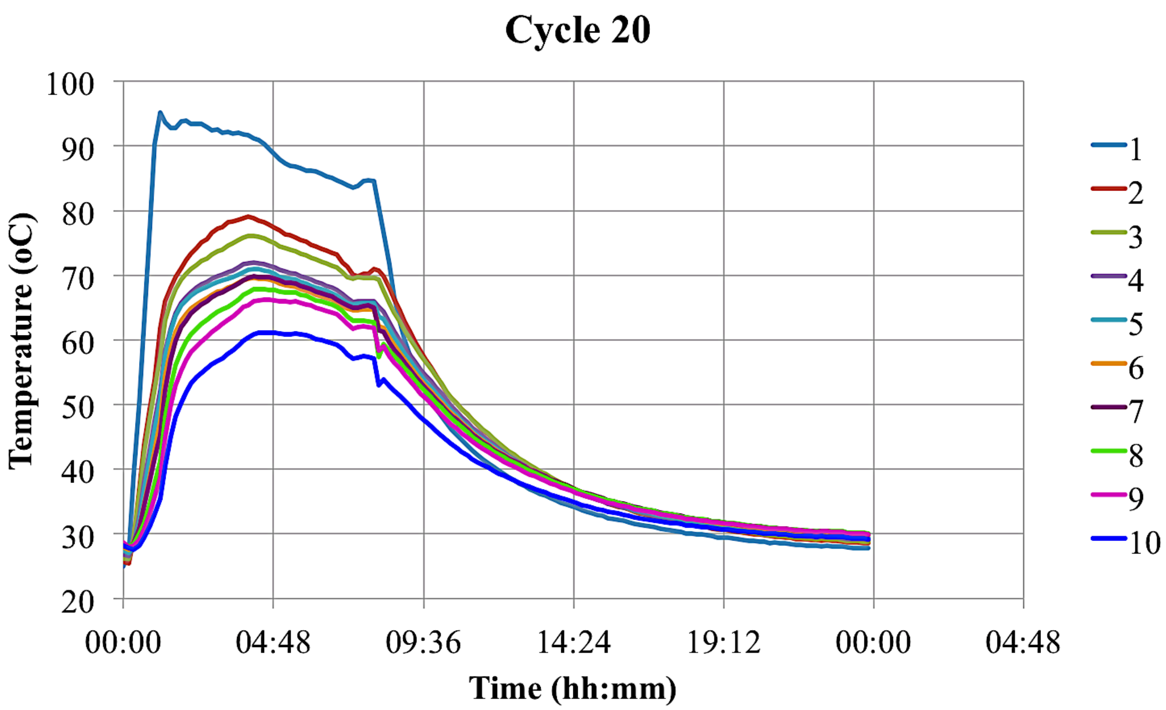
A.18 Cycle 18



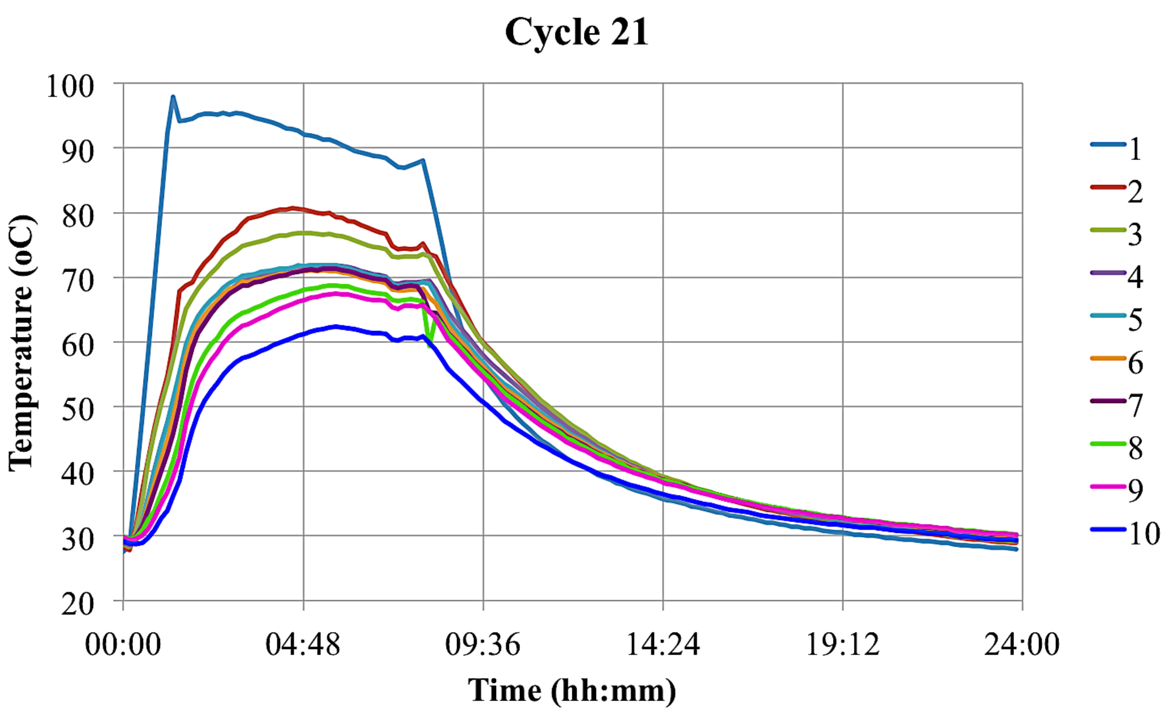
A.19 Cycle 19



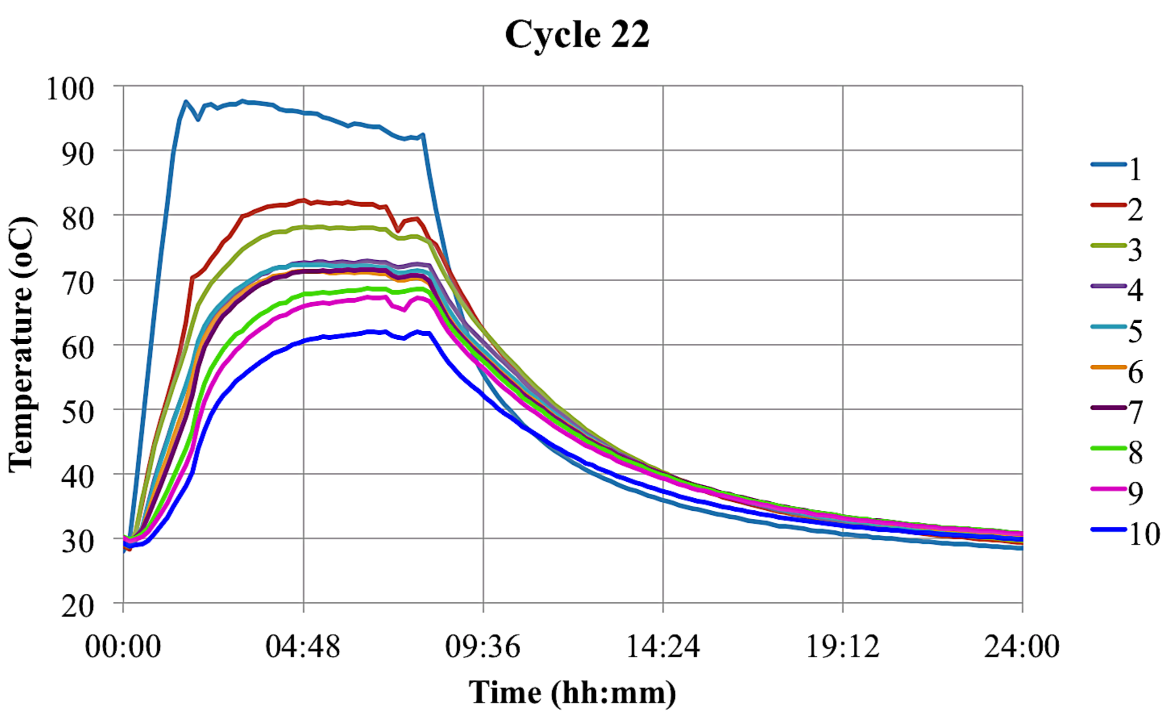
A.20 Cycle 20



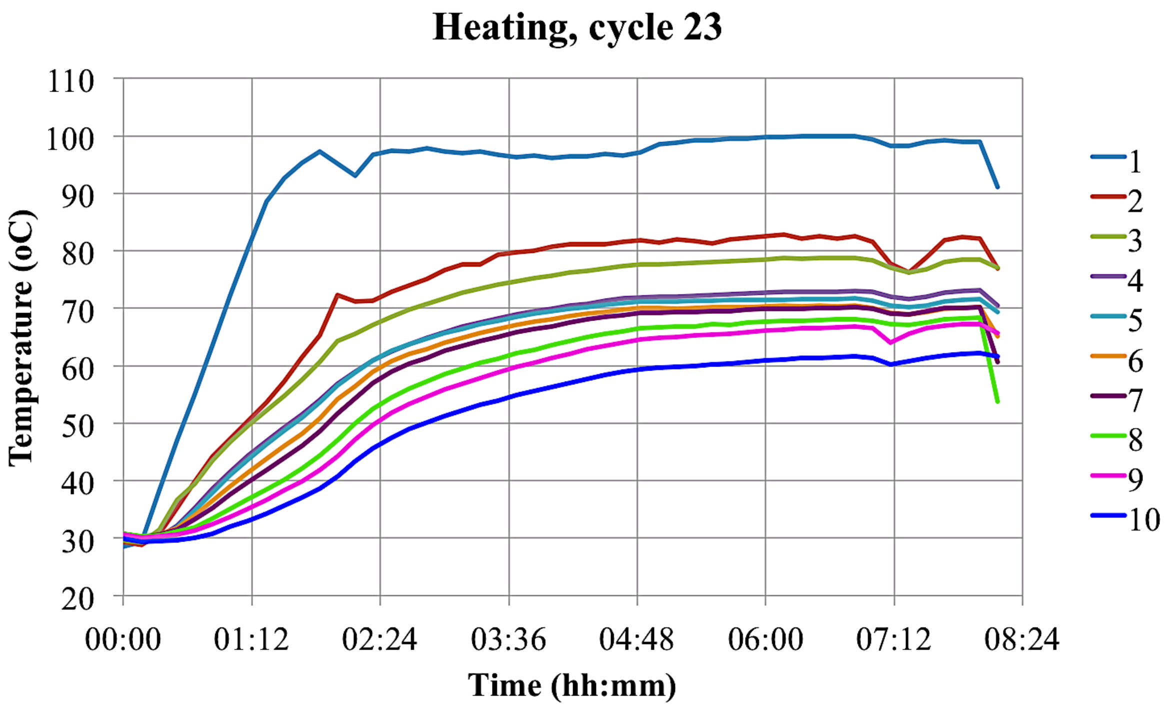
A.21 Cycle 21



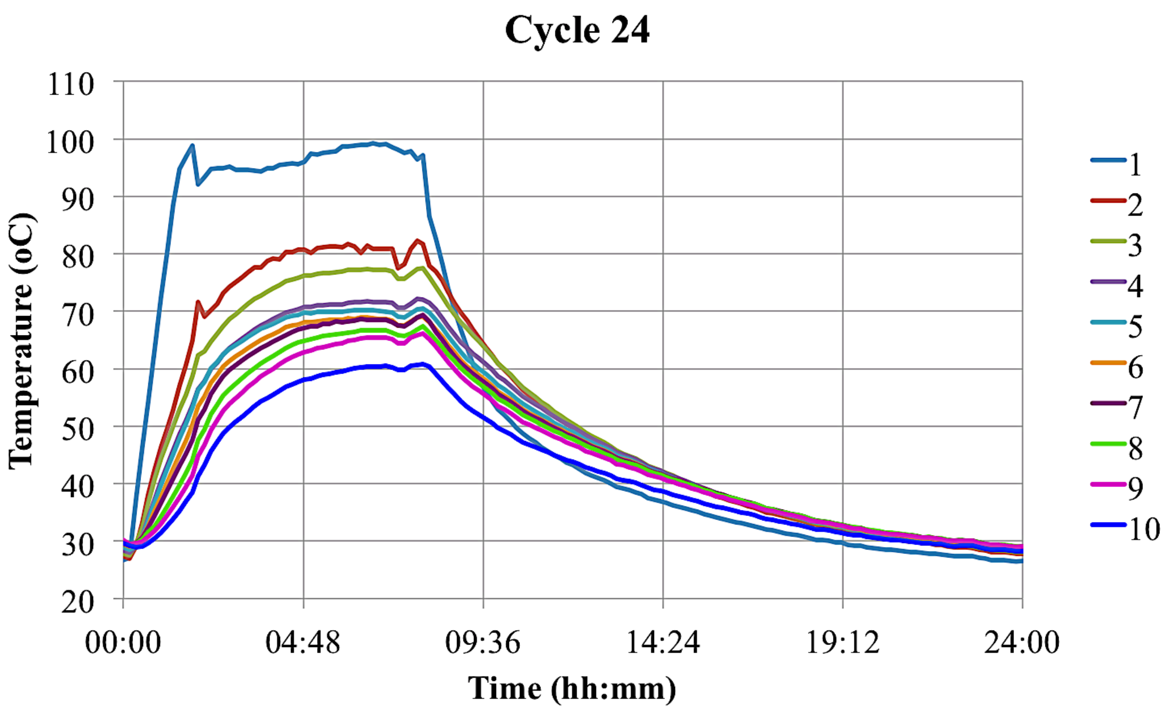
A.22 Cycle 22



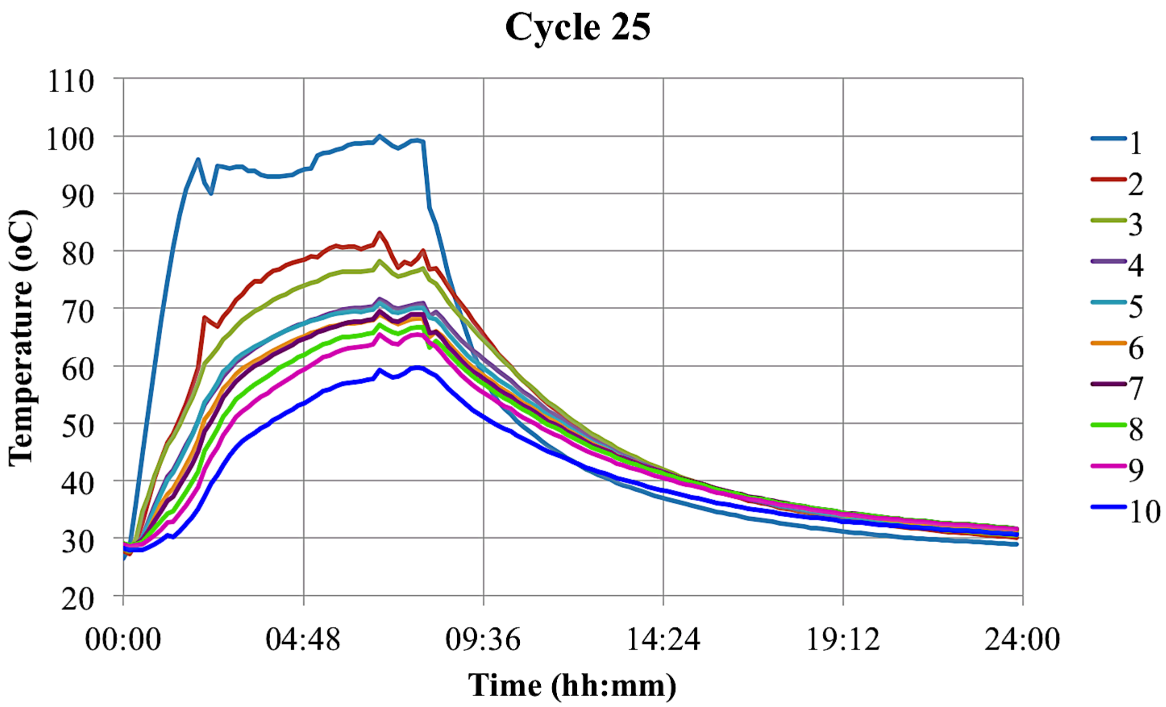
A.23 Cycle 23



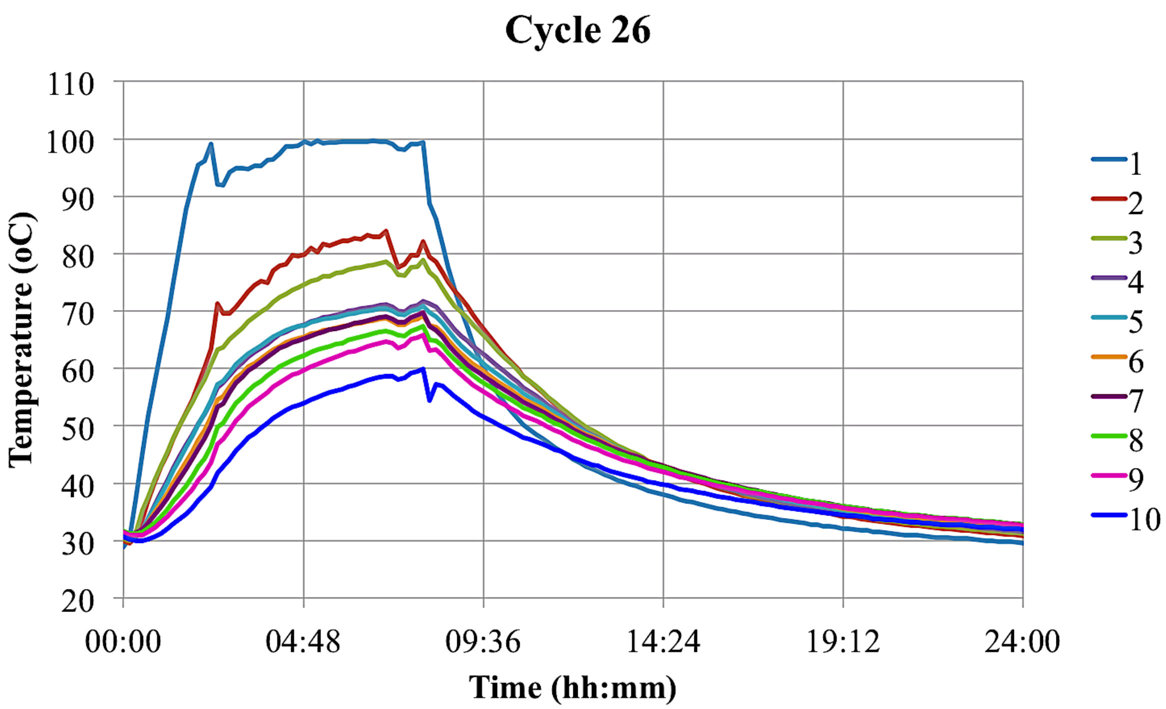
A.24 Cycle 24



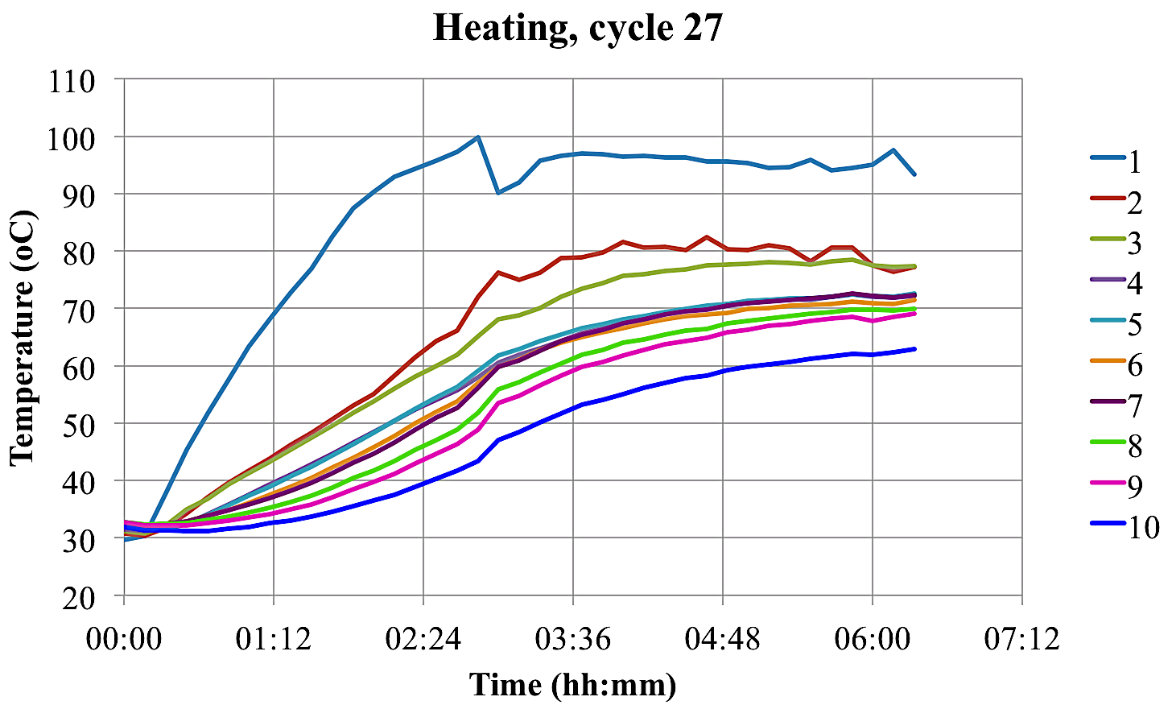
A.25 Cycle 25



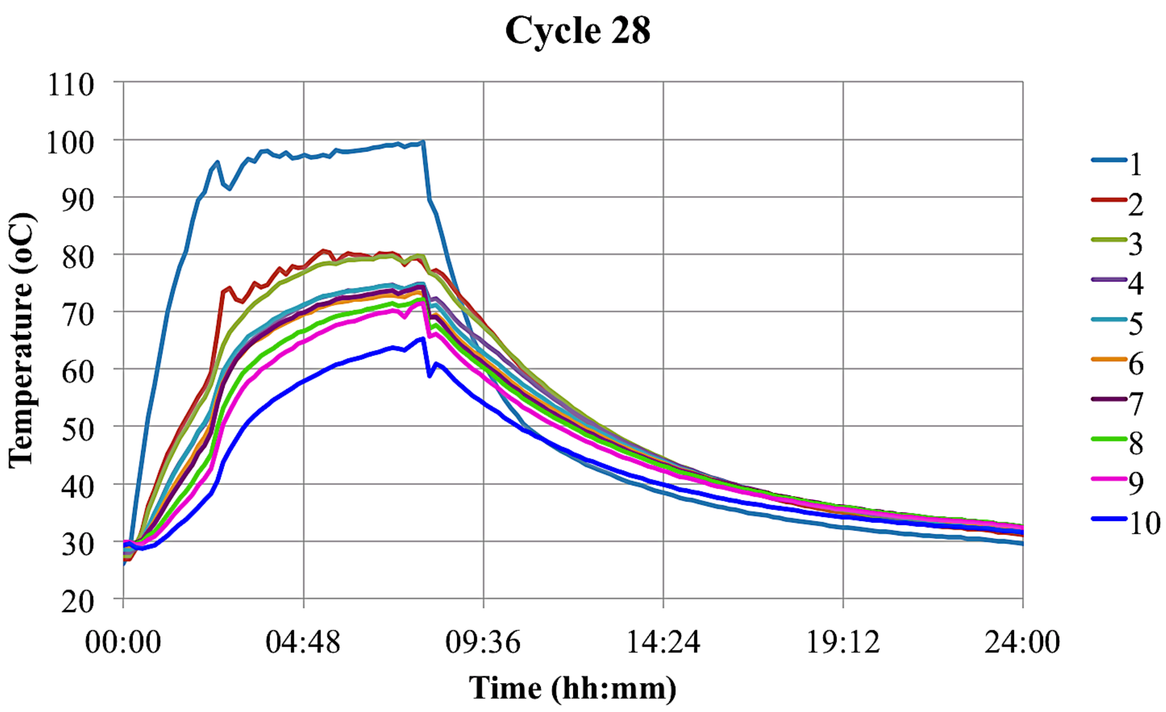
A.26 Cycle 26



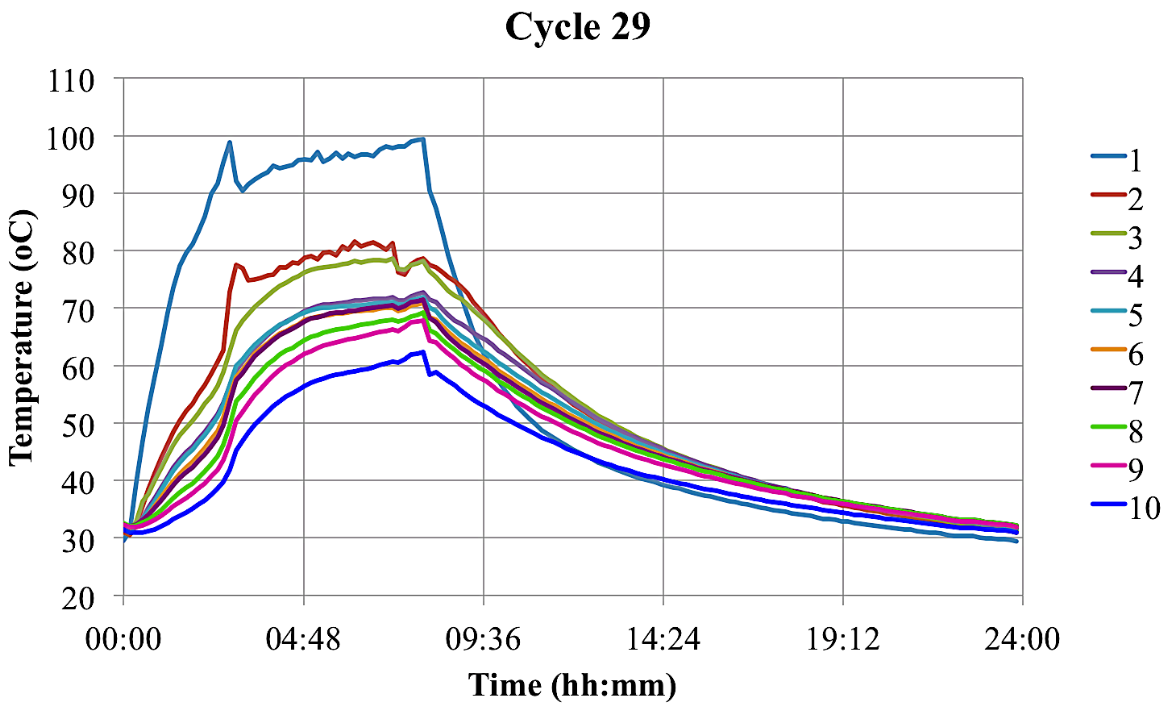
A.27 Cycle 27



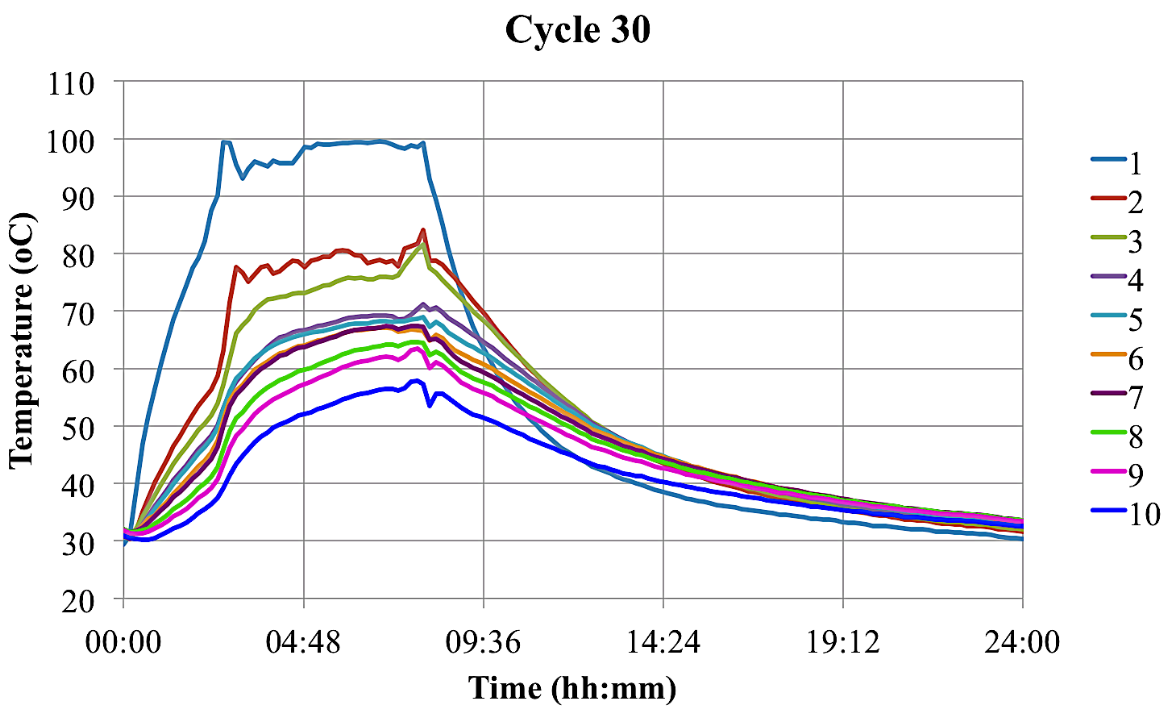
A.28 Cycle 28



A.29 Cycle 29

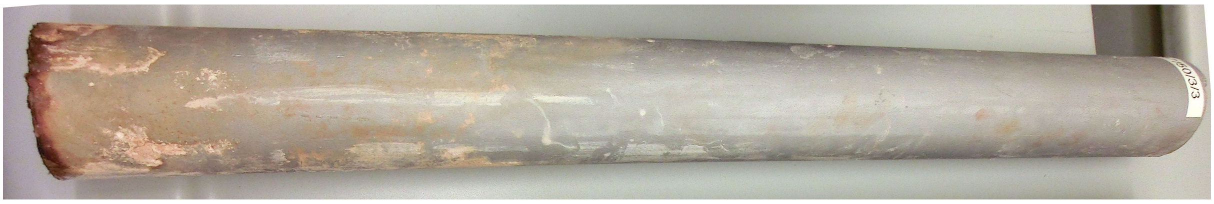


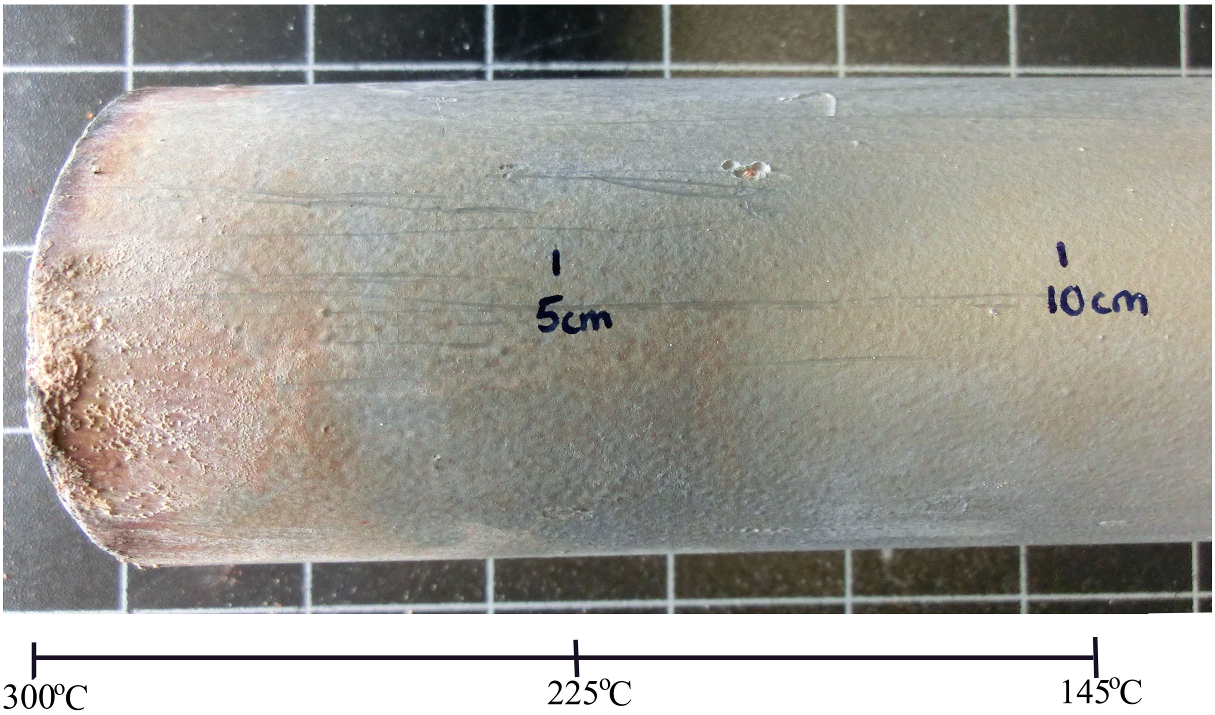
A.30 Cycle 30

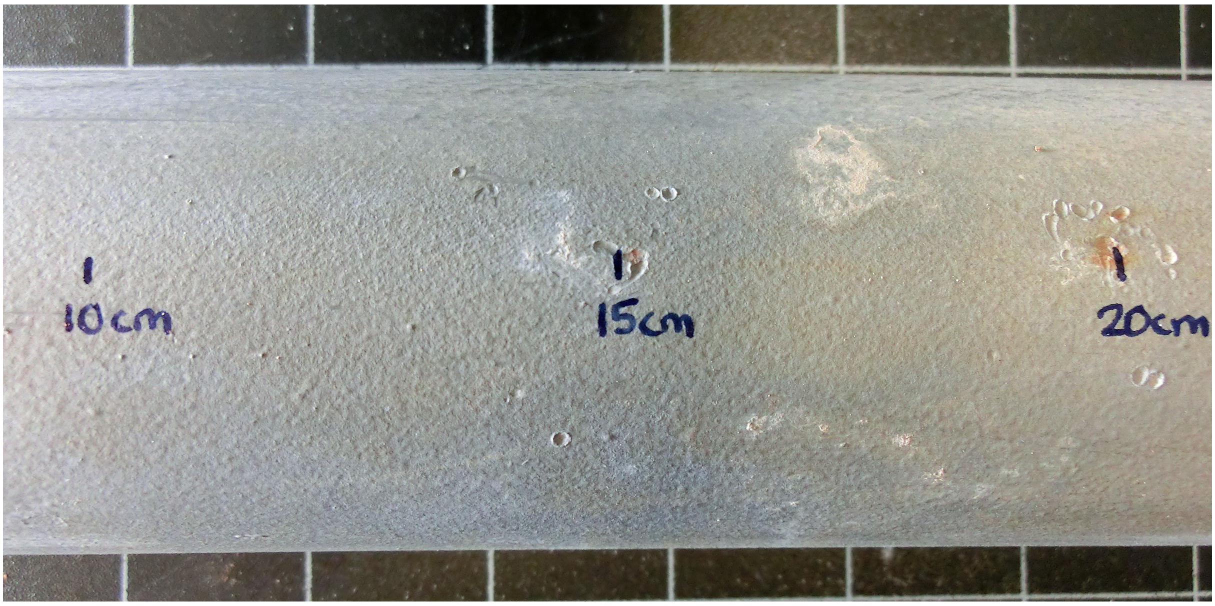


Appendix B: Pictures of coatings after testing

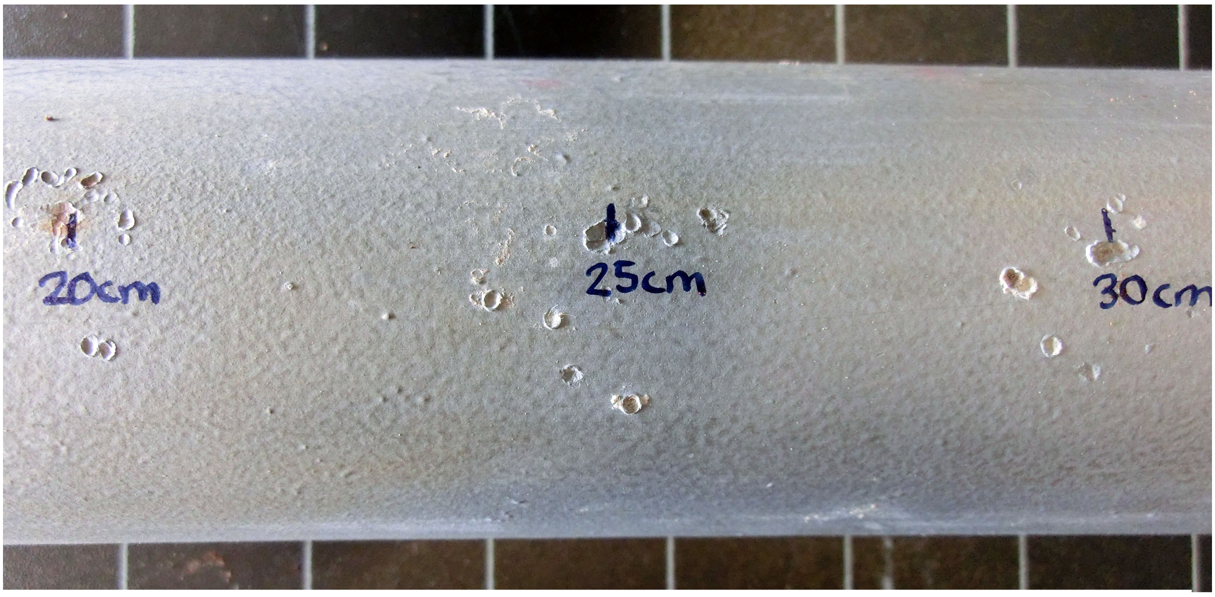
B.1 TMIC



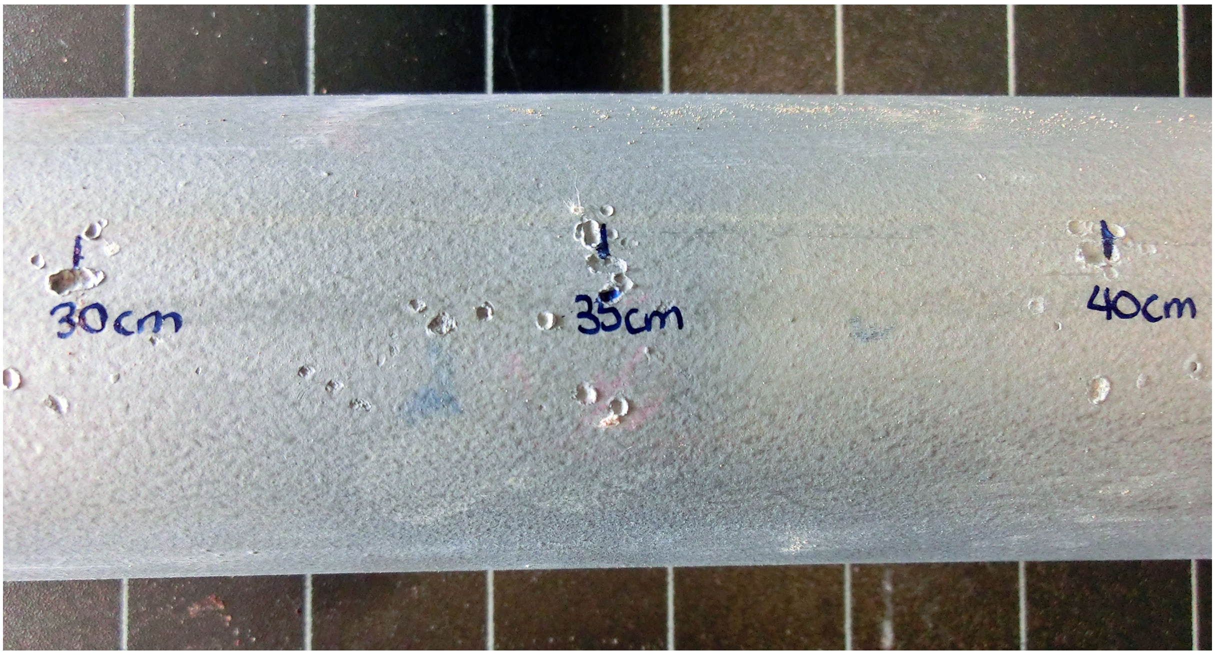




205ºC 180ºC 160ºC



160ºC 150ºC 130ºC

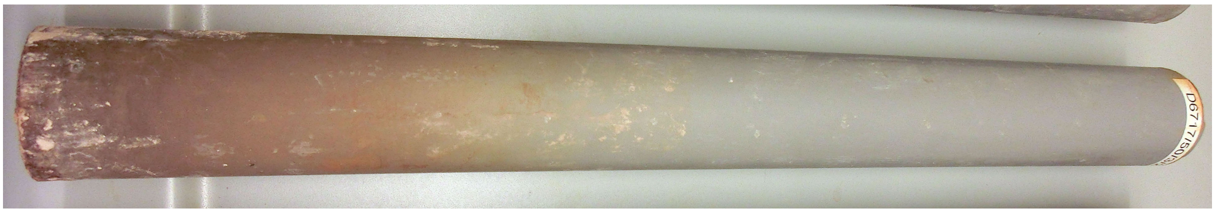


130ºC 125ºC 110ºC

110ºC 105ºC 100ºC

100ºC 90ºC

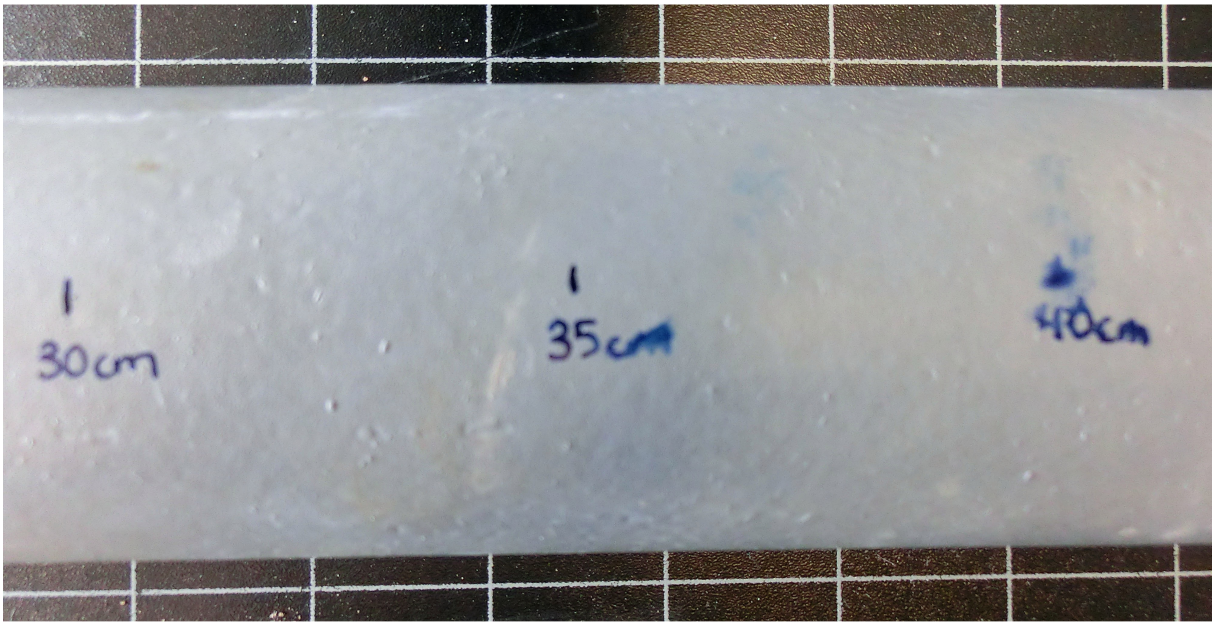
B.2 Epoxy phenolic



300ºC 210ºC 175ºC

175ºC 150ºC 135ºC

135ºC 115ºC 105ºC



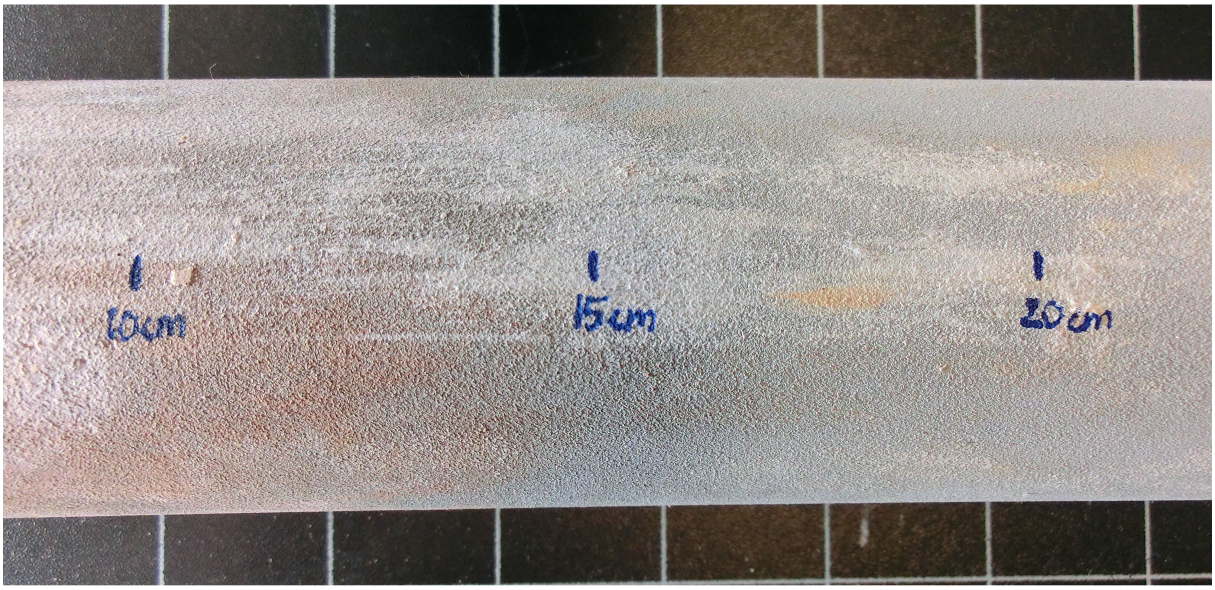
105ºC 95ºC 85ºC

85ºC 80ºC 75ºC

75ºC 70ºC

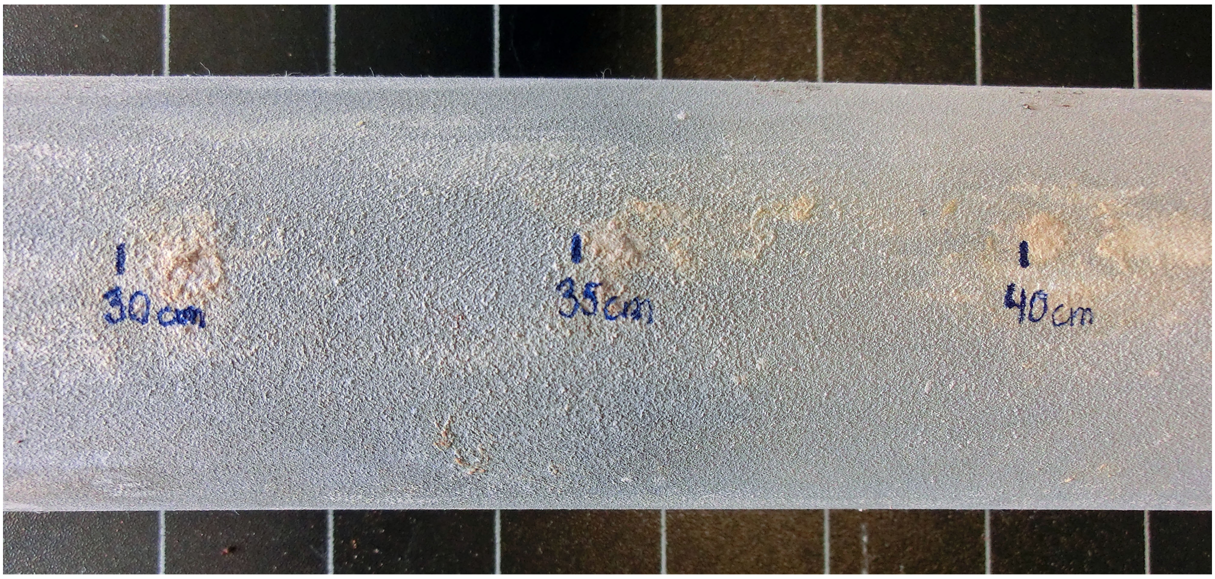
B.3 TSA

300ºC 205ºC 175ºC

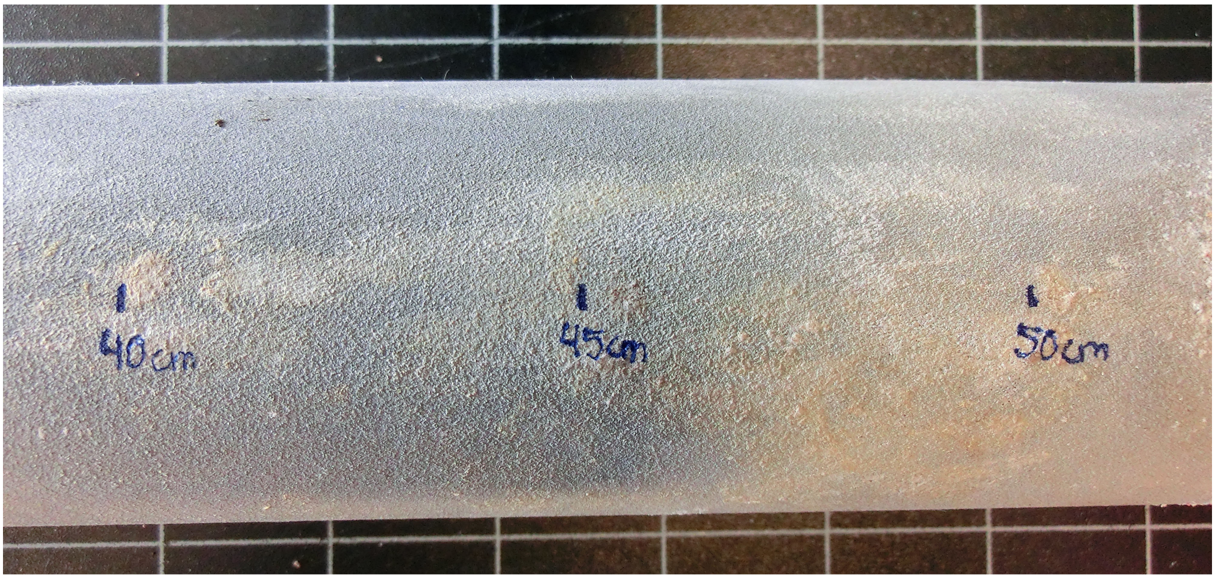


175ºC 155ºC 145ºC

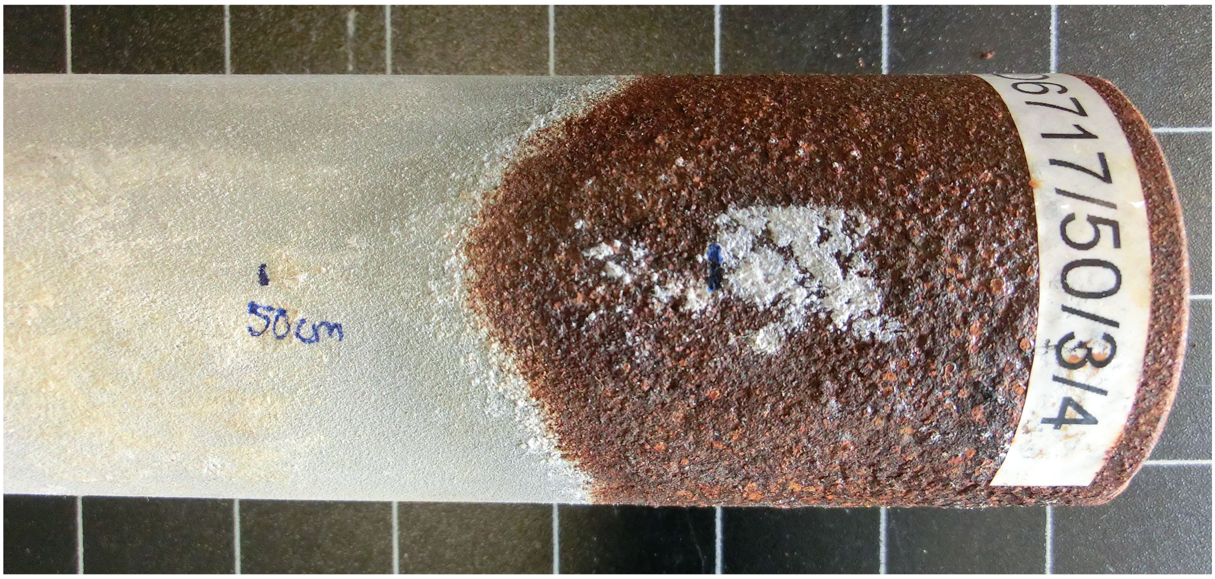
145ºC 130ºC 115ºC



115°C 105°C 85°C



85°C 80°C 75°C



75ºC 65ºC

Appendix C: Images from SEM

C.1 TMIC

C.1.1 Images from Hitachi SU-6600

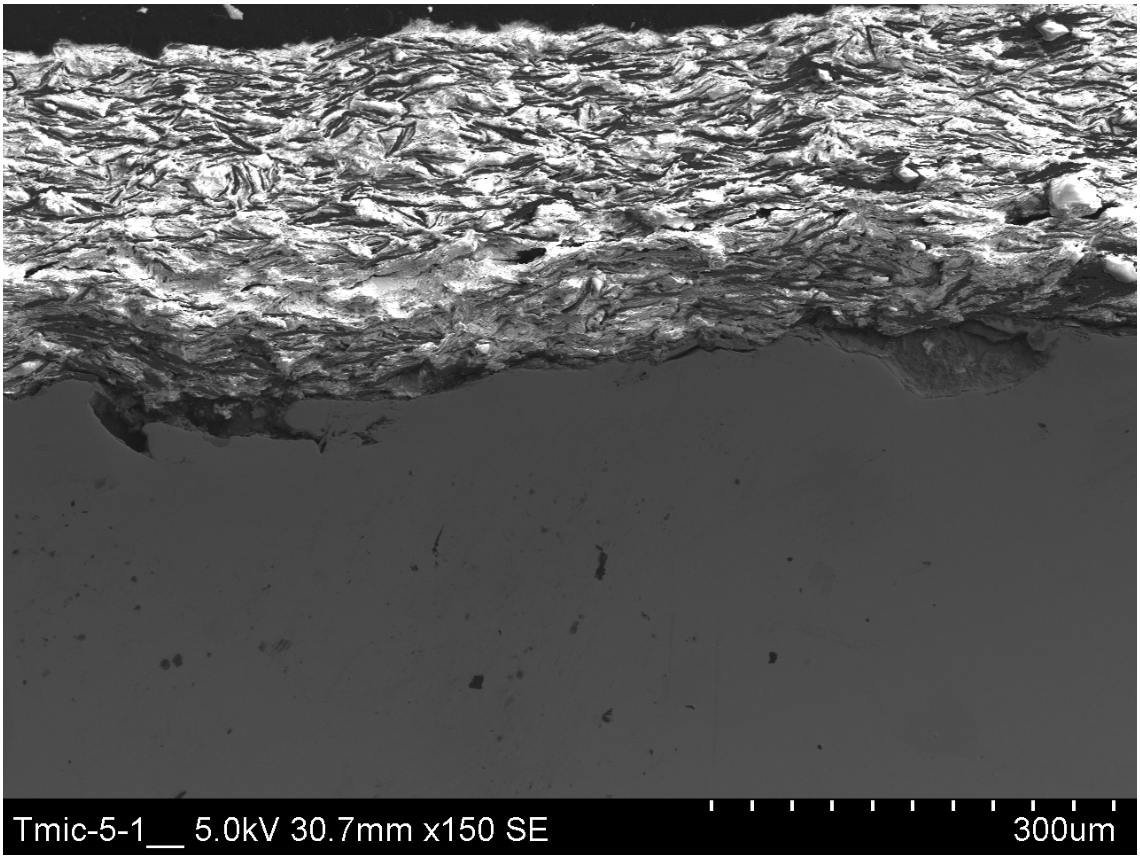


Figure C.1 Image approximately from the 280^{o}C-tempered area.

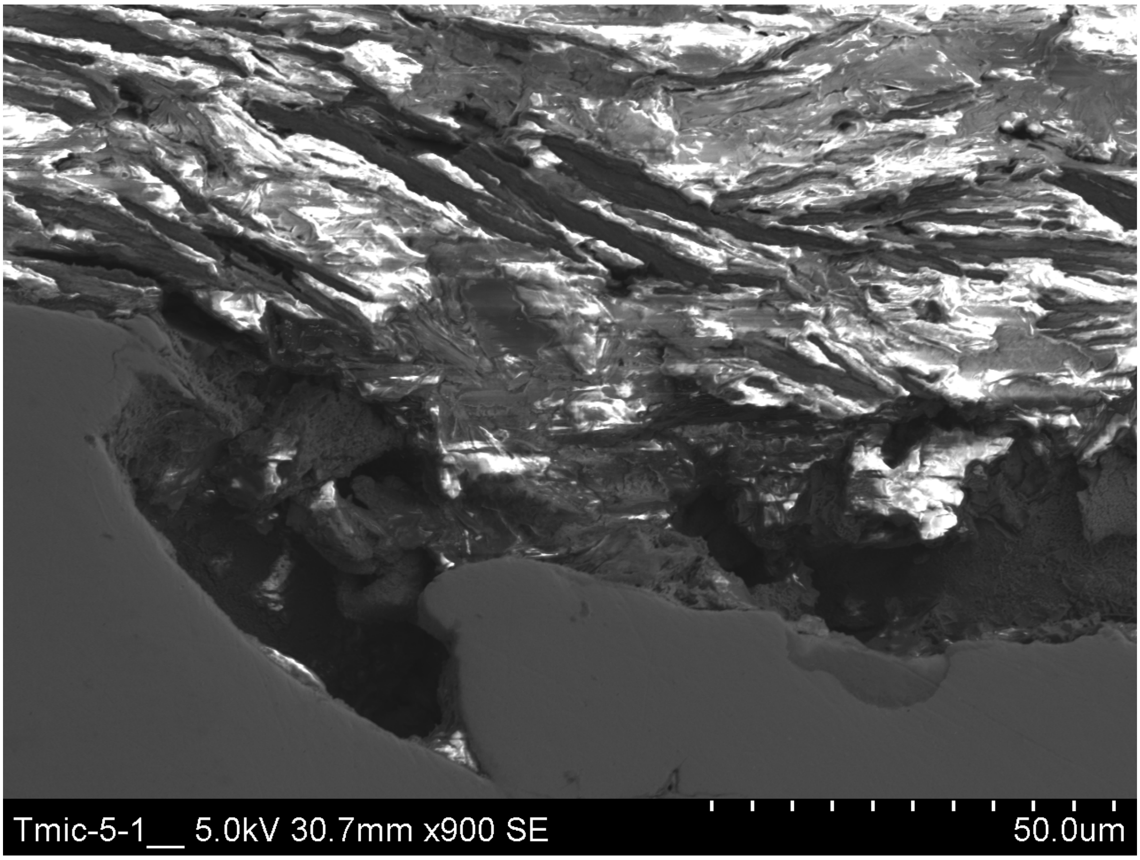


Figure C.2 Image approximately from the 280^{o}C-tempered area.

C.1.2 Images from Zeiss Ultra 55

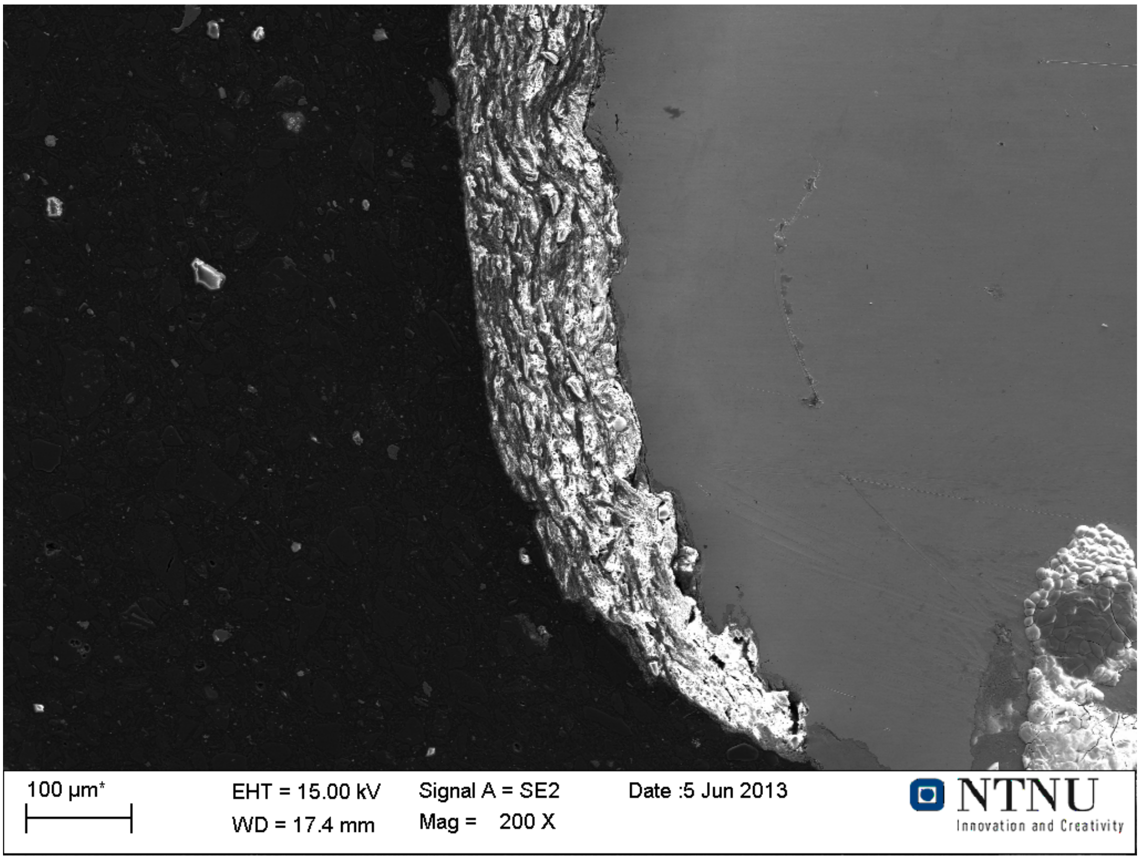


Figure C.3 Image from the bottom of the pipe, in the 300°C-tempered area.

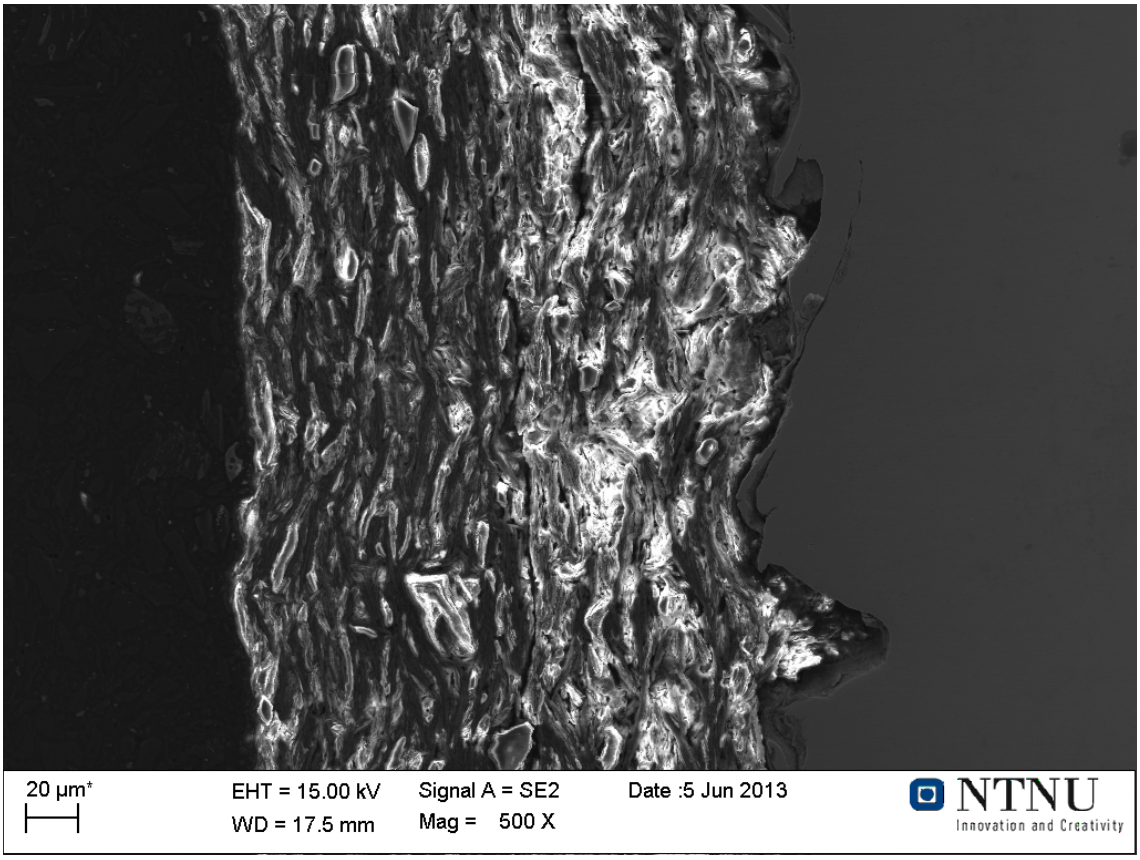


Figure C.4 Image approximately from the 250°C-tempered area.

C.2 Epoxy phenolic

C.2.1 Images from Hitachi SU-6600

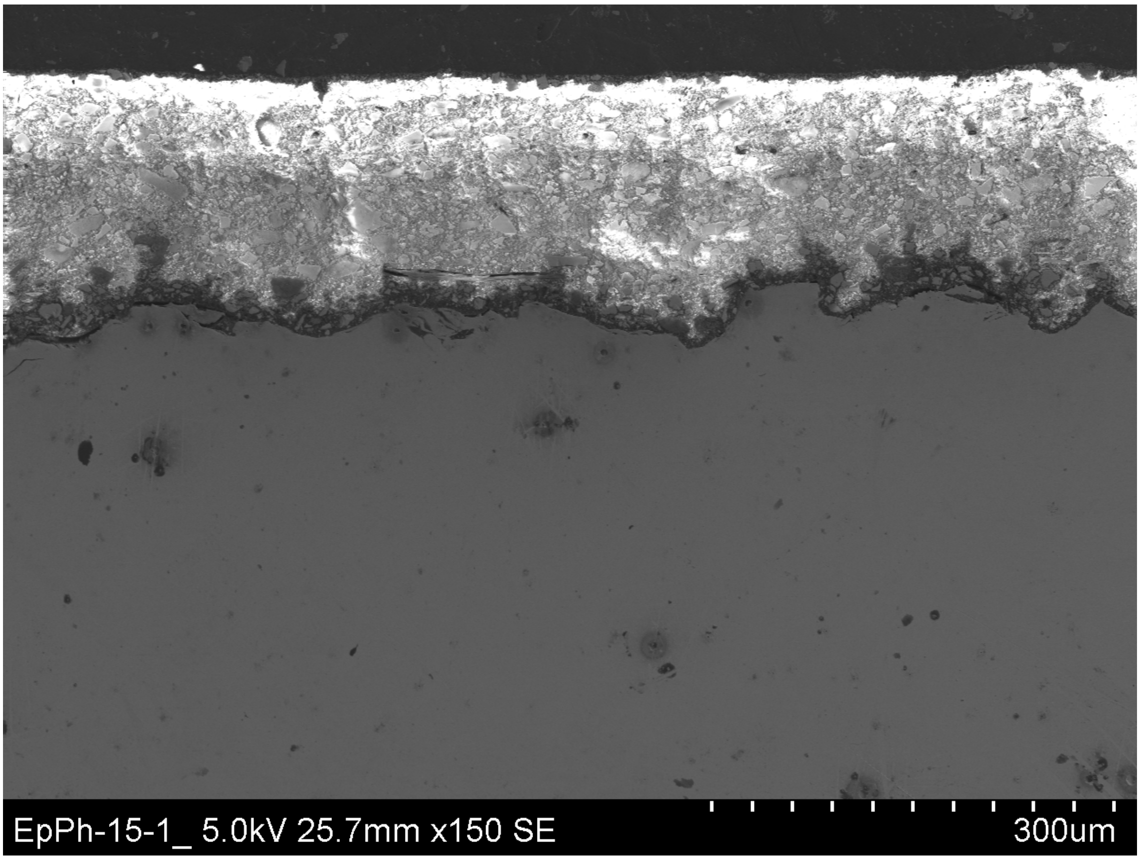


Figure C.5 Image approximately from the 175^{o}C-tempered area.

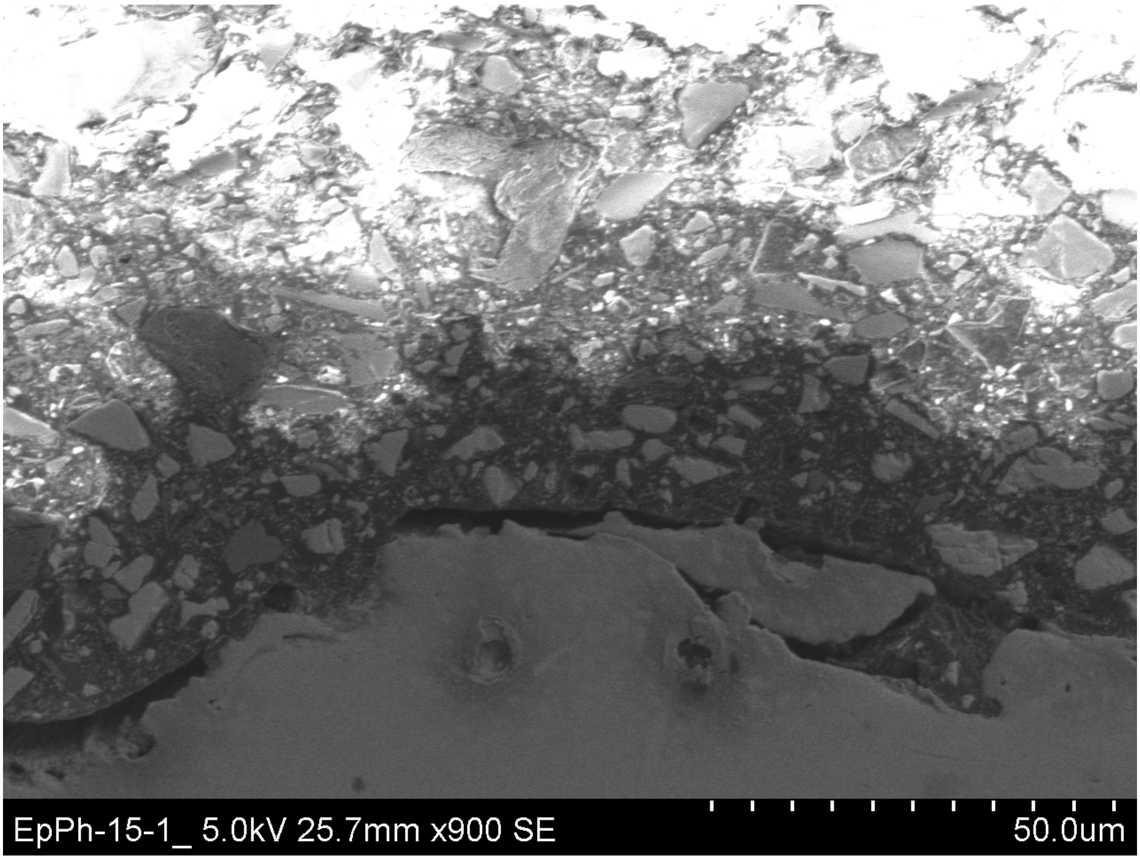


Figure 6 Image approximately from the 175°C-tempered area.

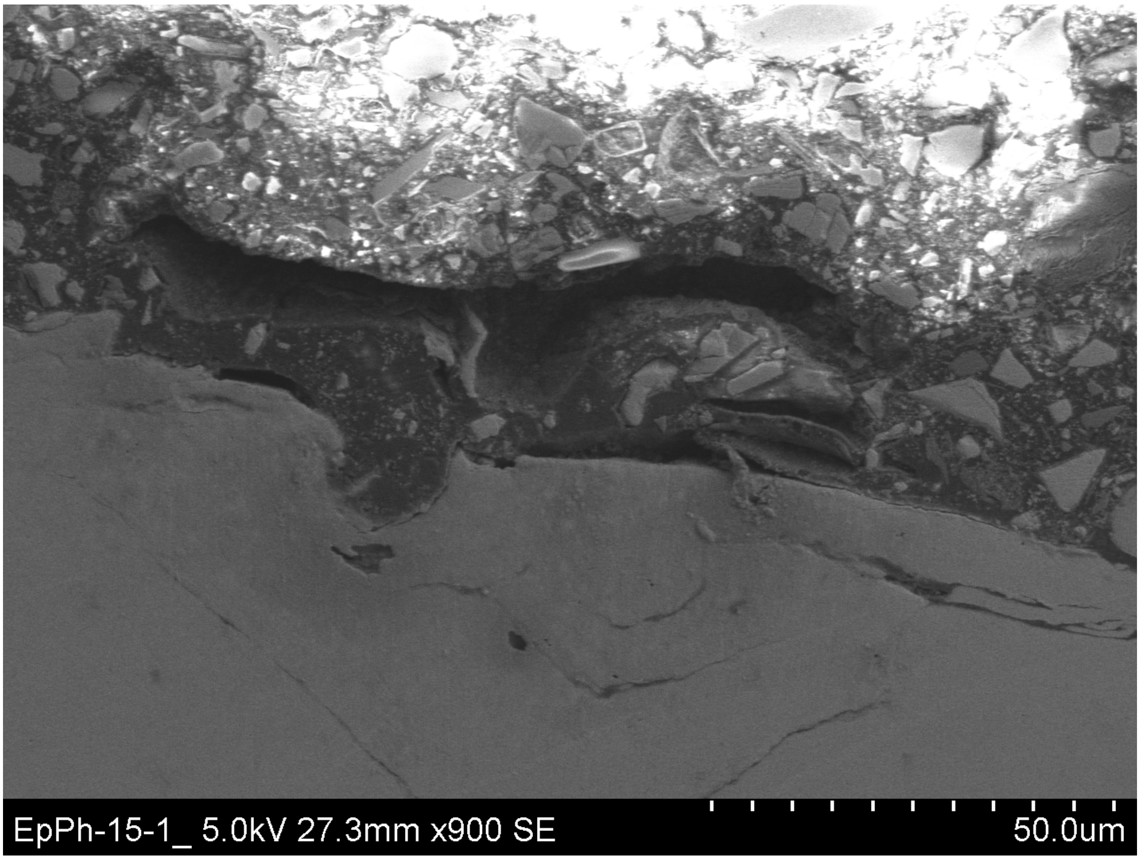


Figure 7 Image approximately from the 165°C-tempered area.

C.2.2 Images from Zeiss Ultra 55

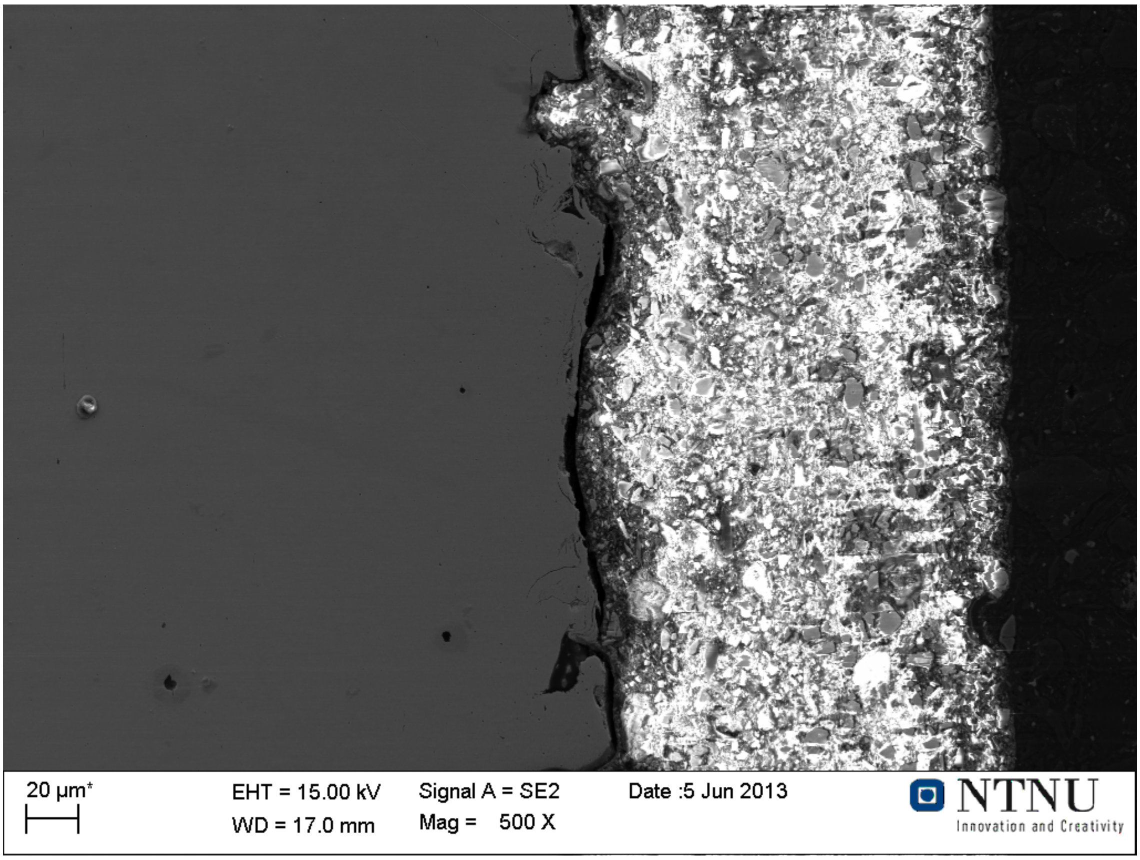


Figure 8 Image approximately from the 170°C-tempered area.

C.3 TSA

C.3.1 Images from Hitachi SU-6600

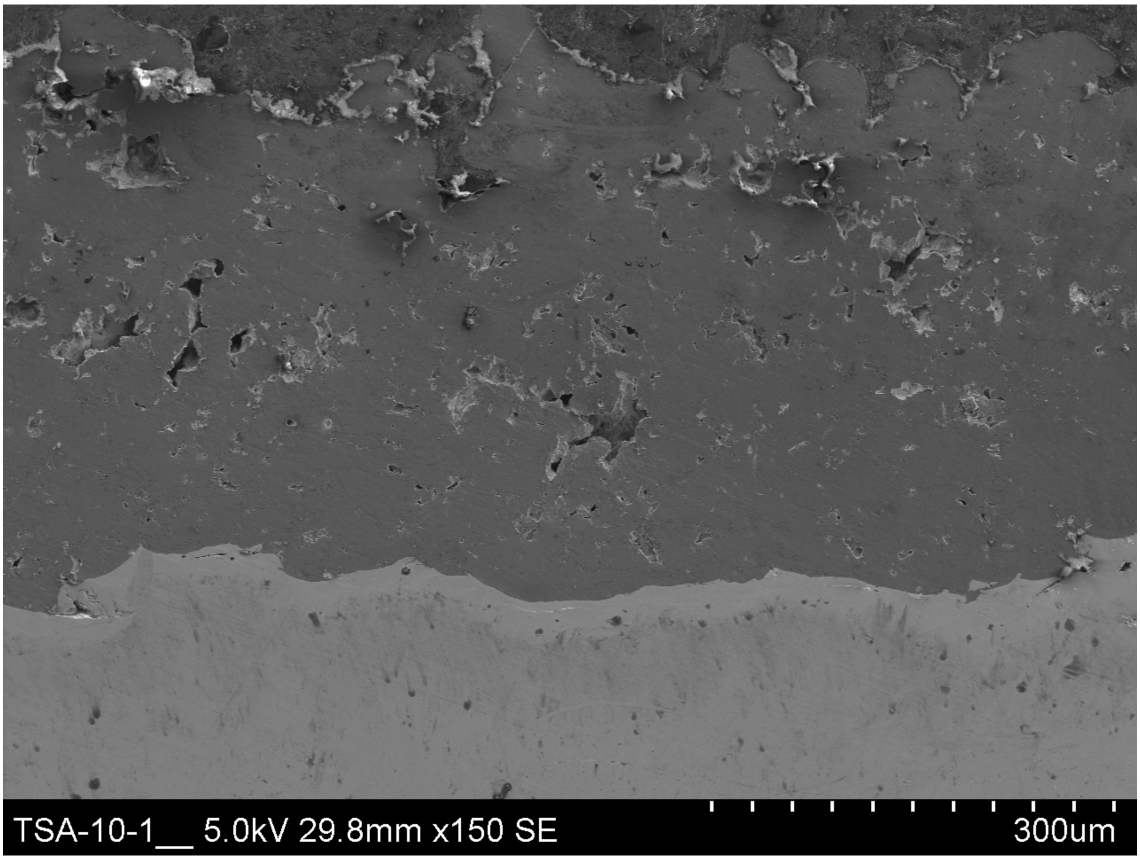


Figure 9 Image approximately from the 170°C-tempered area.

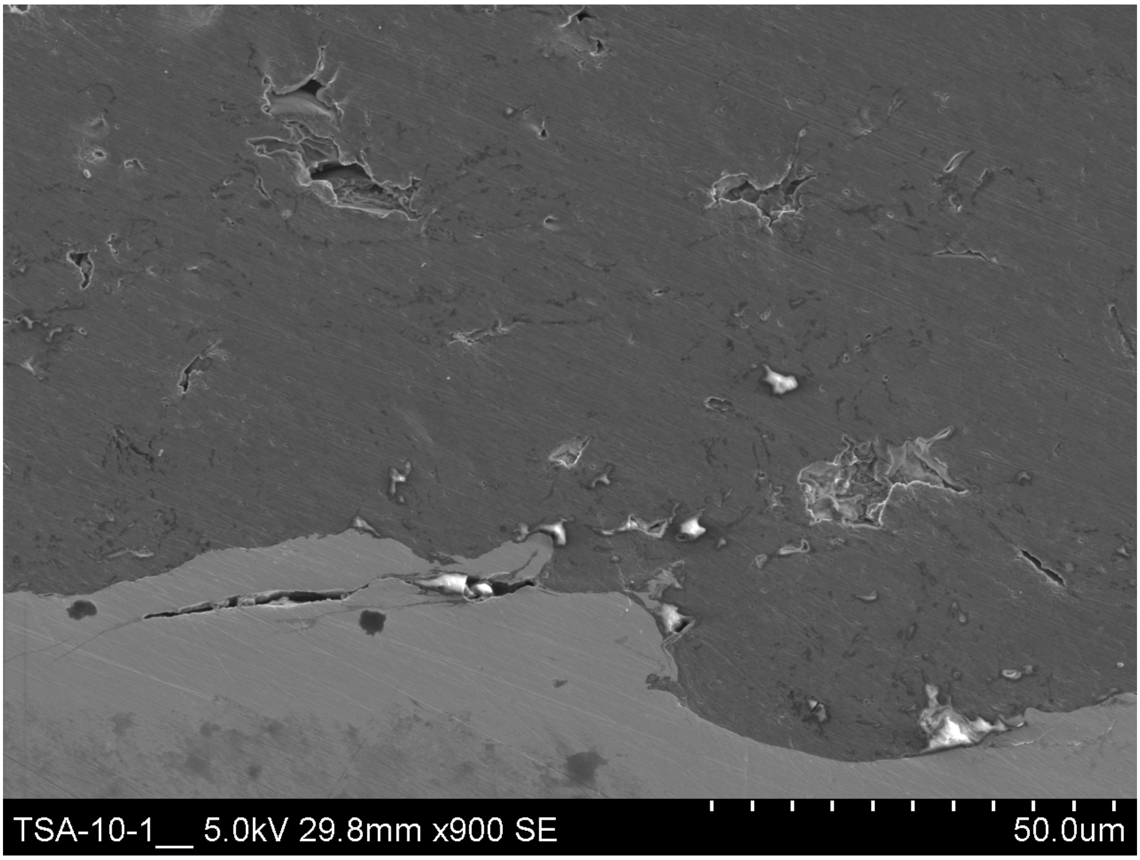


Figure 10 Image approximately from the 170^{o}C-tempered area.

C.3.2 Images from Zeiss Ultra 55

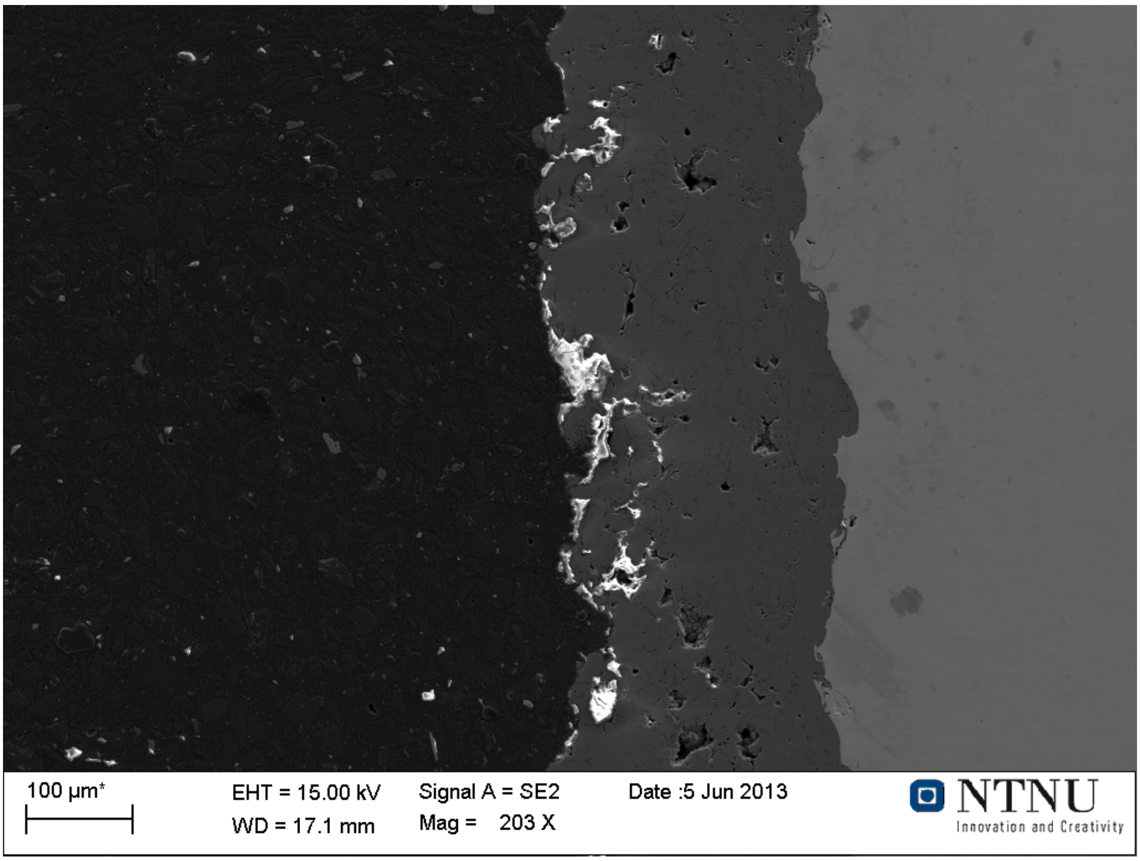


Figure 11 Image approximately from the 205^{o}C-tempered area.

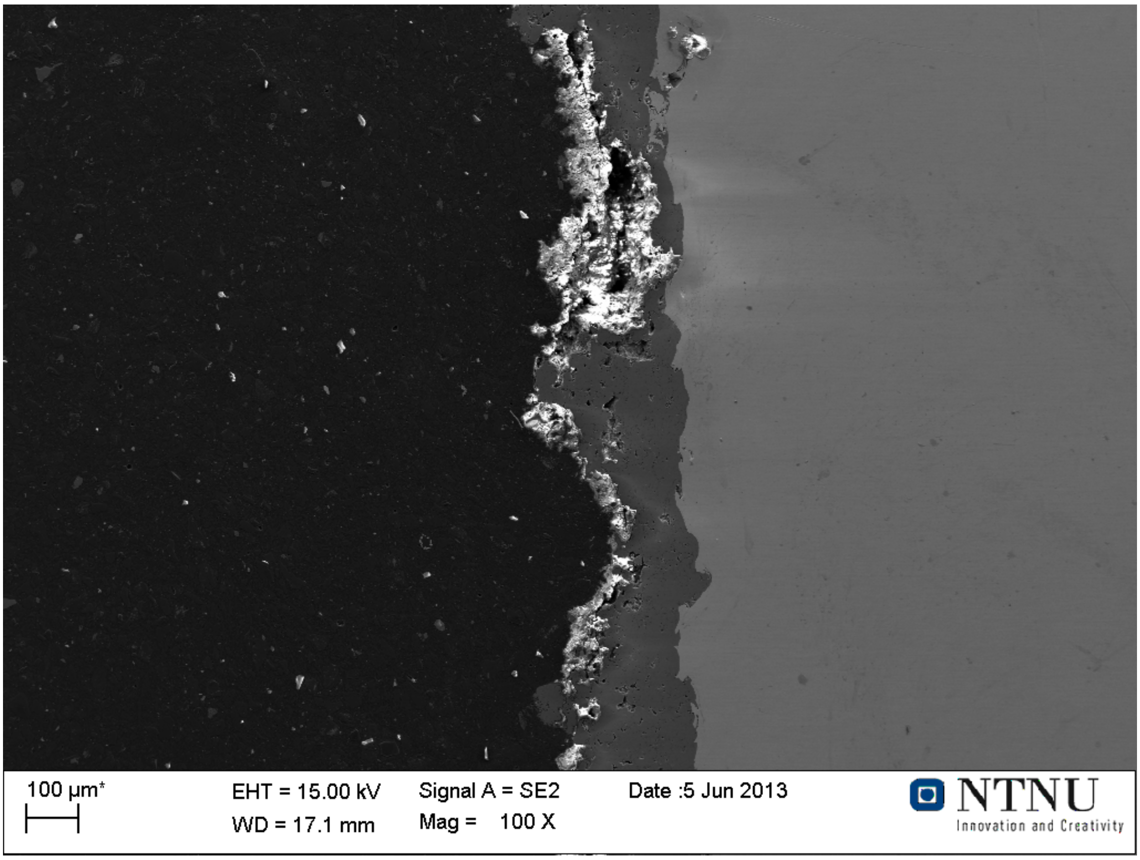


Figure 12 Image approximately from the 190°C-tempered area showing damaged coating.