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Isocyanates formation from thermal degradation of polyurethane foam during welding of district heating pipes

Svetsning i fjärrvärmerör. Bildning av isocyanater genom termiskt sönderfall av polyuretanskum

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Master’s Thesis

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ABSTRACT

Polyurethane insulation foam, which is used as insulation on district heating steel and copper pipes, is made from polymerisation of polyol and diisocyanates monomers. Installation of new district heating pipes or replacement of old pipes involves masses of welding activities. Welding processes of pre-insulated district heating pipes can cause exposure of polyurethane insulation to high heat generated during the welding process. Temperatures of more than 150 °C can lead to thermal degradation of polyurethane insulation and isocyanates formation. Exposure of isocyanates to welders can cause allergy, irritation of eyes, nose, throat, skin, and lung problems, and isocyanate asthma. In this thesis project welding processes of varying nominal sizes of district heating pipes, varying welding method and consequential formation of isocyanates have been studied. This project has found that selection of welding method plays a key role in the formation of isocyanates. It was identified that although the oxy-fuel welding method is considered as easy method for welding, there is a generation of high heat. This since oxy-fuel welding warm up the district heating pipes to high temperatures, which lead to thermal exposure of polyurethane insulation and ultimate formation of hazardous isocyanates. Other aspect such as varying nominal sizes of the pipes and varying length of insulation-free ends effect the exposure of polyurethane insulation to high heat and eventual formation of isocyanates. This study found that small nominal sizes of district heating pipes DN20, DN25, DN32, DN50, DN65, DN80 of insulation-free ends from 20 to 22 cm, welded by oxy-fuel welding, have a low risk to generate critical high heat 150 °C. But if the length of the insulation-free ends is reduced to 16 cm it can lead to thermal degradation of polyurethane insulation and isocyanates formation. For air samples of isocyanates collected during welding of nominal pipe sizes DN100, DN150, DN200 having insulation-free ends 22-20 cm welded by oxy-fuel welding, the analysis showed notable types of monoisocyanates MIC, PHI, ICA and diisocyanates 4.4´-MDI. The concentration of the detected monoisocyanates ICA and diisocyanates 4.4´-MDI in some samples were higher than the acceptable short-term exposure limit STEL (µg / m^3) determined by AFS 2018:1. The presence of large fractions of isocyanates in samples collected from surroundings of high-temperature-exposed polyurethane insulation showed high risks of isocyanates exposure to welders.

Key words: *Polyurethane; Isocyanates; District Heating Pipes; Oxy-fuel Welding; Manual Metal Arc Welding.*

SAMMANFATTNING

Polyuretanisolering, som används som isoleringsmaterial på fjärrvärmestål och kopparrör, är gjord av polyol- och diisocyanatmonomerer polymerisation. Vid installation av nya fjärrvärmerör eller utbyte av gamla, krävs mycket svetsning. Svetsning av förisolerade fjärrvärmerör kan exponera polyuretanisolering för hög värme som genereras under svetsningsprocessen. En temperatur över 150 °C kan leda till termisk nedbrytning av polyuretanisolering och bildning av isocyanater. Svetsares exponering av isocyanater kan orsaka allergi, irritation av ögon, näsa, svalg, hud och lungproblem och isocyanat-astma hos svetsare. I detta examensarbete har svetsning av varierande nominella storlekar av fjärrvärmerör, varierande svetsmetoder och därav följande bildning av isocyanater studerats. Resultatet visade att val av svetsmetod spelar en nyckelroll i bildandet av isocyanater. Oxy-fuel-svetsningen värmer upp fjärrvärmerören till hög temperatur vilket leder till uppvärmning av polyuretanisoleringen och slutligen bildning av farliga isocyanater. Andra aspekter som varierande storlekar på fjärrvärmerören och varierande isoleringsfria ändar påverkar också uppvärmningen av polyuretanisolering. Denna studie vasade att små nominella storlekar av fjärrvärmerör, DN20, DN25, DN32, DN50, DN65, DN80 med isoleringsfria ändar 20 till 22 cm svetsade med oxy-fuel svetsning har en relativt låg risk att generera en kritiskt hög temperatur (150 °C), men om längden på de isoleringsfria ändarna minskas till 16 cm kan det leda till termisk nedbrytning av polyuretanisolering och bildning av isocyanater. Luftprover för isocyanater insamlade under svetsning av rörstorlekarna DN100, DN150, DN200 med isoleringsfria ändar 22–20 cm svetsade genom oxy-fuel-svetsning innehåll monoisocyanaterna MIC, PHI, ICA och diisocyanater-4.4´4. MDI. Koncentrationen av detekterade monoisocyanater ICA och diisocyanater 4.4´-MDI i vissa prover låg över korttidsexponeringsgränsvärdet STEL (µg/m3) i AFS 2018:1. De höga förekomsterna av isocyanater i prover som samlats in från omgivningen av exponerad polyuretanisolering och svetsfläckar visar att det finns en hög risk för exponering av isocyanater för svetsare.

Nyckelord: *Polyuretan; Isocyanater; Fjärrvärmerör; Oxy-fuel-svetsning; Manuell metallbågsvetsning.*

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ABBREVIATIONS AND SYMBOLS

BIC Butyl isocyanate

BZ Breathing zone

DN Diameter nominal

DBA Dibutylamine

DHP District heating pipe

EIC Ethyl isocyanate

HDI Hexamethylene diisocyanate

ICA Isocyanic acid

IPDI Isophorone diisocyanate

LC Liquid Chromatography-

MAMA Methylaminomethyl anthracene

MIC Methyl isocyanate

MMA Manual metal Arc

MDI Methylene diphenyl diisocyanate

MS Mass Spectrometry

NDI Naphthalene diisocyanate

PHI Phenyl isocyanate

PU Polyurethane

PIC Propyl isocyanate

S Surrounding area to collect isocyanates arround welding spot

STEL Short term exposure limit

TDI Toluene diisocyanate

2MP 2-methoxyphenyl piperazine

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1 Introduction

1.1 Isocyanates

Polyurethane products containing polyurethane polymers which are used widely include polyurethane foams, thermoplastics elastomers, polyurethane paint, surface coatings, insulation material, packing materials and adhesives. Among these products polyurethane foam synthesized (Figure 1) through polymerisation of diisocyanates monomers and polyol is used as an insulation material extensively due to its good technical properties (Karlsson et al., 2000; Gylestam et al., 2012; Bengtström et al., 2016).

O=C=N-R´-N=C=O + OH-R-OH ⟶ O= C- N - R´ - N – C =O -R- O ----(1)

diisocyanate Polyol Polyurethane

Figure 1- *General structure of isocyanate and reaction of diisocyanate monomers with Polyol to form Polyurethane.*

The ability of isocyanates to undergo polyaddition reactions with polyols to form polyurethane was described by Bayer in 1937 when Toluene diisocyanate (TDI) was reacted with polyol to form polyurethane (Franklin et al., 2000; Henneken et al., 2007).

Grinding, cutting, and welding processes of metals and materials having polyurethane products such as district heating pipes having polyurethane insulation foam thermally degrade polyurethane products. Thermal degradation of polyurethane results in the formation of hazardous isocyanates. The most known form of isocyanates are monoisocyanates such as Methyl isocyanate (MIC), Ethyl isocyanate (EIC), Butyl isocyanate (BIC), Propyl isocyanate (PIC), Phenyl isocyanate (PHI) and Isocyanic acid (ICA), and diisocyanates such as Toluene diisocyanate (TDI), Methylene diphenyl diisocyanate (MDI), Hexamethylene diisocyanate (HDI), Napthlene diisocyanate (NDI), Isophorone diisocyanate (IPDI) in particles and gas form (Tinnerberg et al., 1996; Skarping et al., 1988; Karlsson, 2001). The exposure of welders and workers to monoisocyanates and diisocyanates can cause health problems.

1.1.1 Exposure to isocyanates

Exposure to isocyanates more in the form of aerosol in breathing zone at workplace cause respiratory and other health problems. Exposure to isocyanates can cause irritation, allergy and asthma. Between 5 to 13 % of the workers who are exposed to isocyanates develop isocyanate asthma (Swensson et al., 1957; White et al., 1980; Vandenplas et al., 1993; Franklin et al., 2000; van Kampen et al., 2000 Ott, M.G. et al.,2002; Krone et al., 2005).

1.2 District heating pipes

The delivery of heat by installing district heating pipes network is being used in United States since 1870 and in Europe from the earliest of 20th century. The major growth of district heating system in Europe and in Scandinavia started in 1970s (Woods & Overgaard, 2016). Steel and copper pipes insulated with rigid polyurethane foam are the most used district heating pipes

(Figure 2). Hot water at about 80 - 100 ^{o}C is transported from district heating station to internal space heat exchangers of buildings and houses and at about 40 ^{o}C is transported back to district heating station through buried insulated district heating pipes (Mangs et al., 2006).

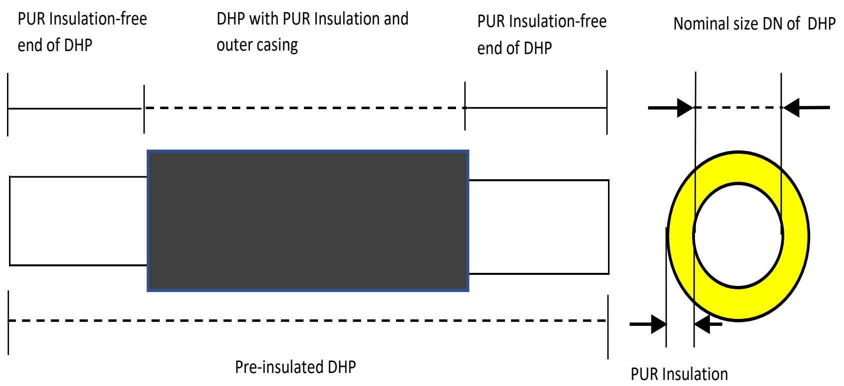


Figure 2. *Schematic diagram of pre-insulated district heating pipe (DHP) applied with polyurethane foam and representation of insulation-free ends of district heating pipes.*

1.2.1 Polyurethane insulation foam on district heating pipes

Application of rigid polyurethane foam as insulation material on district heating pipes is considered an important polymer material due to its versatile technical properties such as low thermal conductivity, less density but strong polymeric material (Huang et al., 2018). These technical properties can sustain rigid polyurethane foam as insulation material of district heating pipes for 25 to 30 years under operational temperature 80 °C to 100 °C of hot water (Mangs et al., 2006). Despite versatile technical properties of polyurethane insulation foam of district heating pipes, the issues of thermal degradation appear when district heating pipes are welded to replace old district heating pipes and/or install new district heating pipes. During welding process of district heating pipes polyurethane insulation foam is affected by high heat from welding process hence thermally degraded. Even though the thermal degradation temperature may vary between different kind of polyurethane foam, studies indicate that thermal degradation may occur at about 150 °C - 200 °C. (Mangs et al., 2006; Zhang et al., 2009).

1.3 Description about workplace

Stockpipe AB was established in 2008 and is a renowned company to install and replace pre-insulated district heating pipes, clean water pipes, hot water plastic pipes in buildings and infrastructure in Stockholm and Sundsvall region. In Stockholm region, the core business area of Stockpipe AB is to install new pre-insulated district heating steel and copper pipes, replace old district heating steel and copper pipes at project sites. Stockpipe AB functions as a contractor of energy companies such as Vattenfall AB, Stockholm Exergi AB and major project management organization and construction companies such as NCC AB, SKANSKA AB etc. Currently there are 50 welders who are working at different project sites according to demand of the project to perform welding tasks during installation and replacement of district heating steel and copper pipes at project sites.

1.3.1 Health and Safety concerns at Stockpipe AB

To fulfil the legal responsibilities Stockpipe AB takes several actions about health and safety of welders and other workers who has risk of exposure to isocyanates. To meet AFS 2011:19 § 37e requirements, mandatory education and training is provided to all welders and workers about use of thermoplastic and allergenic products. The required gears and personal protective equipment to welders are provided. To fulfil the requirement of Swedish Work Environment Act, required risk assessment prior to start installation, replacement, and welding of district heating pipes at project sites are performed. According to AFS 2011:19 § 37f-37g Stockpipe AB arranges for medical examinations and check-ups of welders after every 2 years.

1.3.2 Welding activities at Stockpipe AB

In the majority of welding activities at Stockpipe AB some welding activities are performed by welders at workshop. Preparation before installation, such as welding of metal pieces, welding, and coupling of joints, valves to lines are welded at workshop. The other major welding activities are carried out at project sites. At project sites installation and replacement of pre-insulated district heating pipes are the main activities that require welding tasks of district heating pipes. The concerned key activity of welders involves welding of varying dimensions, sizes and shapes of district heating pipes i.e. nominal pipe size DN20, DN25, DN32, DN40, DN50, DN65, DN80, DN100, DN150, DN200, DN250 of pre-insulated district heating pipes at project sites.

1.4 Welding methods

- Oxy-fuel welding method

Oxy-fuel welding method or gas welding method known due to use of mixture of acetylene and oxygen is a welding method, when mixture of acetylene and oxygen is burnt which generate a heat of about 3200 °C. This high heat melts the metal and joints hence weld the metal joints.

- Manual Metal Arc (MMA) welding method

Manual metal arc (MMA) or also known as arc or stick welding method when electric arc is generated by striking electrode on the metal being welded, the electrode which is melted produce high heat about 6000 - 8000 °C and weld the metal by melted electrode slag.

- Capillary soldering method

Capillary soldering method is also a form of gas welding method which is used to make a joint of copper district heating pipes. An alloy most commonly phosphor copper alloy of lower melting point i.e. 500 - 800 °C than copper is used as a solder. The solder is melted along with copper pipes are heated and the melted solder is filled between the copper pipes joint sleeve.

Oxy-fuel welding is not common in other European Union states except Sweden and Finland. Energy companies who conduct project and provide district heating pipes at project sites recommend Stockpipe AB to use this method to weld different nominal sizes. To weld small nominal pipe sizes DN20, DN25, DN32 of steel district heating pipes oxy-fuel welding is used i.e Oxy-fuel welding is easy and more efficient welding for small nominal district heating pipes as compared to manual metal arc welding. Nominal pipe sizes DN200, DN250 district heating pipes are usually welded by manual metal arc welding by setting up 85 Amp arc current and using 2.5 x 350 mm electrode.

1.4.1 DN- Diameter nominal pipe sizes expression

Pipe sizes expressed as DN in this study are according to internation and European matric method used to describe diameter nominal size of pipes specifically its internal diameter in millimeters. DN pipe sizes numbers are different to nominal pipe sizes used as NPS which are merely the non-matric equivalent in which pipes diameter is expressed in inches.

1.5 Problem description

1.5.1 Cutting and removal of polyurethane insulation from ends of district heating pipes

Pre-insulated district heating pipes of varying dimensions, size, and shapes to be installed or replaced at required project sites are provided by project management organizations and energy companies to Stockpipe AB.

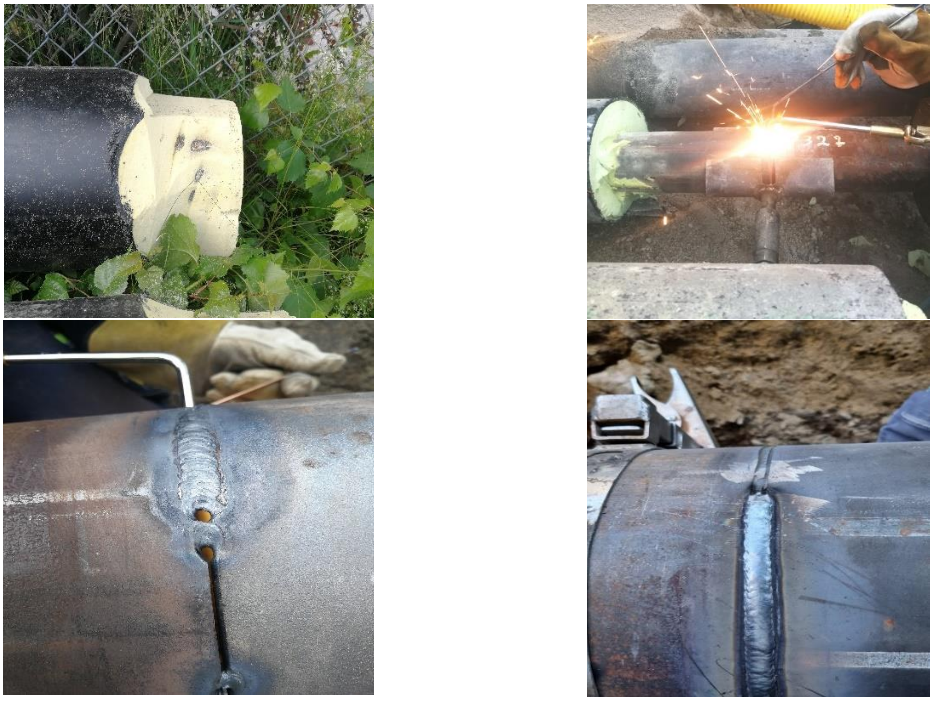


Figure 3. *District heating pipes, polyurethane insulation, welding and risks of formation of isocyanates.*

In some cases, the provided pre-insulated district heating new pipes have insulation-free ends of about 22 cm to 15 cm. Those pipes are installed and welded as they are in the original state. To install required nominal sizes and shapes and length of district heating pipes those are cut with the help of metal cutting saw. After cutting, polyurethane insulation foam is removed in range from 15 to 22 cm from the ends of newly cut pieces of required nominal size of district heating pipes. To remove polyurethane insulation foam from ends cutting saw and axe are used. The newly removed polyurethane insulation-free ends are cleaned with the help of knife, scraper, and sandpaper. Although, efforts are made to make insulation-free ends clean and free from remaining of foam, but still small pieces and particles remain on the newly cut and freshly removed insulation-free ends of district heating pipes (Figure 3).

The problem arises during welding process, high temperature on the ends of district heating pipes thermally expose polyurethane insulation and gases and fumes from the district heating pipes are welded using oxy-fuel and manual metal arc welding the gases and polyurethane insulation foam of district heating pipes.

1.5.2 Assumption of Stockpipe AB about risks of isocyanates

Stockpipe AB assumed that during welding of district heating pipes it is not clear which nominal sizes and length of corresponding insulation-free ends of district heating pipes warm up to high heat that cause thermal degradation of polyurethane insulation and formation of isocyanates. Is it oxy-fuel welding or manual metal arc welding that warmup the ends of district heating pipes to high heat or critical temperature 150 ^{o}C- 200 ^{o}C that cause thermal degradation of polyurethane insulation and formation of isocyanates? Stockpipe AB believed that already existing research about welding of district heating pipes and thermal degradation of polyurethane insulation of district heating pipes and ultimate formation of isocyanates is insufficient. It is insufficient to answer variation in isocyanates formation with respect to varying welding method and varying nominal sizes of district heating pipes.

1.5.3 Concerns of Stockpipe AB linked to current study

To protect welders from health risks of different forms of isocyanates formed during welding and to provide improved working conditions for welders at Stockpipe AB, the main concern is that this master thesis project should help to distinguish nominal sizes and corresponding insulation-free ends length of district heating pipes, and to distinguish welding methods used to weld varying nominal size district heating pipes. It is also focused that this thesis project should help not only Stockpipe AB but also other partners e.g., Stockholm Exergi, Vattenfall AB. It is also focused that this research work should contribute to already existing research related to this specific subject, it should lay down a path for further research of this specific subject in detail.

1.5.4 Initiation of current study

In this thesis project, formation of monoisocyanates and diisocyanates due to exposure of polyurethane insulation foam to critical high temperature 150 ^{o}C - 200 ^{o}C leading to thermal degradation of polyurethane during welding by oxy-fuel and manual metal arc welding of district heating pipes is studied.

This thesis project work instigated forward by considering research work published in report FOU 2002:77 and research made by Karlsson et al., 2002 as a basis. The number of dimensions of district heating pipes selected in this thesis work are more as compared to selected in previous research performed under Swedish district heating pipes association and Karlsson et al., 2002. The strategy to measure temperature and take air samples followed the concept of previous research but instruments and samplers used in this thesis project were different.

1.6 Scope and objectives

The objective of this study was to minimize the exposure of isocyanates to welders working at Stockpipe AB. The objective was to study varying nominal size of district heating pipes having varying length of insulation-free ends between 15 cm to 25 cm. The objective was to study comparative welding method which generate heat at insulation-free ends of district heating pipes and cause thermal degradation. Other objective was that the results of measurements should help to take corrective measures to improve welding methods, associated welding practices and routines involved in welding process.

1.6.1 Aim

The main aim of this project was;

- To study which nominal size and insulation-free ends of district heating pipes can reach high temperatures which can lead to thermal degradation of polyurethane insulation foam and formation of isocyanates.

- To study how different methods such as gas welding and manual metal arc welding can affect the temperature close to polyurethane insulation foam during welding of district heating pipes.

1.6.2 Research questions

- To what extent changes in nominal sizes of district heating pipe affect the formation of isocyanates?

- To what extent variation of welding methods to weld district heating pipes effect on thermal degradation of polyurethane insulation and isocyanates formation?

1.7 Limitations

- In this thesis work, collected samples are analysed to determine monoisocyanates such as, MIC, EIC, PIC, PHI, ICA and diisocyanates such as, 1.6-HDI, 2.4-TDI, 2.6-TDI, IPDI, 4.4—MDI, 2.4—MDI. Sampling and analysis for determination of aminoisocyanates, amines and other hydrocarbons are not performed in this thesis work.

- After completing welding of district heating pipes, the joints are insulated by filling polyurethane foam on site. On-site filling of polyurethane foam is performed by third party. Isocyanates exposure risks associated with on-site filling of polyurethane foam are not included in this study.

- On-site filling of polyurethane foam to the joints and spaces after welding of district heating pipes, the risks related to isocyanates during these activites are assessed and analysed separately. The results of that assessment are not included in this study.

2 Background

2.1 Thermal degradation of polyurethane and isocyanates measuring methods

Rigid polyurethanes foam is being used as an insulation material in district heating pipes for more than 80 years (Mangs et al., 2006; Woods & Overgaard, 2016). Isocyanates formation due to thermal degradation of polyurethane has been the subject of numerous research in the past. Different forms of polyurethane have been studied with different aspects. Effect of change in temperature on thermal degradation, decomposition and pyrolysis has been the topic of these research Streicher et al., 1994; Karlsson et al., 2000; Zhang et al., 2009; Gylestam et al., 2012; Bengtström et al., 2016. In multiple studies the types of isocyanates and hydrocarbons, amount of isocyanates and hydrocarbons formed during thermal processing of polyurethane containing thermoplastic and polymers are studied (Kääriä et al., 2001; Karlsson et al., 2001).

To investigate thermal degradation of polyurethanes Woolley, 1972 studied degradation of ester and ether-based polyurethane. It was found by his research that polyurethane degrade at low temperature 200 °C - 300 °C. Lattimer et al., 1998 have studied that thermal degradation products are detected by mass spectrometry at temperature range 250 ºC to 325 ºC. By this research it was found that first degradation of MDI based polyurethane dissociation or depolymerisation and formation of isocyanates takes place, secondly the cyclic oligomers are formed.

In 2000, exposure of isocyanates due to mechanical and chemical process such as grinding, cutting, and welding in car repair workshop was studied by Karlsson et. al.,2000. Another study about different form of isocyanates, aminoisocyanates and amines formation due to thermal degradation of polyurethane foam during welding of polyurethane pre-insulated district heating pipe was performed by Karlsson et. al., 2001.

In 2001 Font et al., have studied the thermal decomposition of polyurethane product “adhesive” by performing thermogravimetric analysis in inert atmosphere. The formation of hydrocarbons and phenyl isocyanate at varying temperature were studied. A study about fire performance of MDI based polyurethane has been performed by Spirckel et al., 2002, in this study it was found that the thermal degradation of MDI based polyurethanes at temperature 220 ºC to 230 ºC, the low molecular weight isocyanates are detected by gas chromatography analysis. Along with this, the thermogravimetry analysis showed that the dissociation of polyurethane starts at temperature 150 ºC to 220 ºC.

Herrera et al., 2002 studied thermal degradation of MDI based polyurethane product “elastomer”. In this work the thermal degradation of MDI bases elastomer formed highest thermal degradation products at temperature range 280 ºC to 485 ºC.

Låstbom et al., 2003 have studied thermal degradation of both MDI and TDI based polyurethane foam at 300 ºC. It is found that thermal degradation of MDI based polyurethane foam release methylene diisocyanates, methyl isocyanates, phenyl isocyanates. The study about thermal degradation of HDI based car paint and coating at oxidative and inert condition at a gradually increased temperature up to 800 ºC in a furnace was performed by Boutin et al.,

2004. ICA, MIC, EIC, PIC and BIC were the main form of detected isocyanates which showed high concentration at 473 ^{o}C detected by pyrolysis hypernated with mass spectrometry.

Sennbro et al.,2004 made a survey study of isocyanate exposure in 13 Swedish industries which were involving either handling of polyurethane or diisocyanates or both. In these industries formation of polyurethane and processing of polyurethane caused exposure of workers to isocyanates 2.4-Toluene diisocyanates, 2.6-Toluene diisocyanates, Isophorone diisocyanates, 4.4´- methylene diisocyanates, 1.5-nepthalene diisocyanates and phenyl isocyanate. According to this study, 8 hour time weighted average sampling of airborne isocyanates using 1-(2-methoxyphenyl) piperazine (2MP) (using one glass fibre filter impregnated with 2MP) , FINMP method or also known as modified 2MP method (using 2 glass fibre filters impregnated with 2MP reagent), and DBA sampling method (where filters connected in series with impinger flask containing DBA reagent) found that workers are exposed to isocyanates of concentration range 0.004 ppb- 5.2 ppb. Personal exposure to isocyanate were higher in the industries which involved process of continuous foaming of polyurethane as compared to the processes which involve exposure of polyurethane to heat.

As isocyanates during thermal degradation of polyurethane is found in gas and particle phase (Gylestam et al., 2012; Karlsson et al., 2000). In past, to collect isocyanates particle and gas formed from thermal degradation of polyurethane, the impinger flask containing reagents followed by filters has been used as sampler by Spanne et al., 1996; Karlsson, 2000; Blomqvist et al., 2003; Boutin et al., 2004.

In previous research, for sampling of air born isocyanate researchers have used derivatising reagents in impinger flask such as Tinnerberg et. al., 1998 has used 9-N-Methylaminomethyl anthracene (MAMA) derivative reagent to determine Toluene diisocyanate in air. Henriks-Eckerman et al., 2000 have used dibutyleamine (DBA) and 1-(2-methoxyphenyl) piperazine derivative to determine airborne methyl isocyanate (MI). Dibutyleamine (DBA) derivative reagent has been used for air sampling of isocyanates by researchers Spanne et al., 1996; Karlsson, 2000; Blomqvist et al., 2003; Boutin et al., 2004.

To collect isocyanates particle several researchers have used active filter impregnated with 2MP solvent (1-(2-methoxyphenyl) piperazine) as an advanced form of sampler.

Previous research of topic "Exposure to isocyanates at welding of district heating pipes”, published as report FOU 2002: 77 by Swedish district pipes association, researchers Gunnar Bergström, Lisa Lindqvist and Stefan Nilsson made a series of measurements to investigate the effect of welding methods, district heating pipe dimensions, and effect of change in length of insulation-free ends of district heating pipes on isocyanate exposure. In that research the district heating pipes dimensions DN25, DN250, DN500, and 42 mm diameter copper district heating pipes were welded by oxy-fuel and MMA welding method. The temperature corresponding with district heating pipe dimensions and welding methods were measured by attaching thermocouple type K in the interface between steel pipes and polyurethane foam. To sample air born isocyanates, DBA method using impinger flask was used. To analyse the sample liquid chromatography-mass spectrometry was used.

2.2 Health effects

Effects of isocyanates on health has been studied in past (Vandenplas et al., 1993; Dhara et al., 2002; Blomqvist et al. 2003; Krone & Klingner, 2005; Henneken et al., 2007). The first adverse health effect of isocyanate exposure was reported soon after the industrial use of isocyanates (Franklin et al., 2000; Henneken et al,2007). There has been challenges to measure isocyanate exposure and health effects caused by exposure to isocyanate. In past, underreporting of exposure of isocyanates, minimum information about health risks of isocyanates, few isocyanates exposure measurements practices and inappropriate method for analysis has been considered as challenges.

In Sweden, the highest number of cases related to occupational health problems caused by exposure of monoisocyanates and diisocyanate reported to Swedish work environment authority were observed in 2000 (Swedish work environment authority factsheet about isocyanates number 4/2008).According to Swedish work environment authority fact sheet number 4/2008 about occupational injuries, on the base of available data of year 1997 to 2007 state that reported occupational cases in 1997 were above 43 cases where isocyanates has been considered as a cause. The number of reported cases continued to grow, in 2000 the number of reported cases caused by isocyanates exposure were the highest i.e. 105 reported cases. From the data of factsheet number 4/2008, from 2004 to 2007 the reported occupational diseases where isocyanates were seen as a possible cause of diseases, the respiratory problems account for 66 %, skin problems account for 7 %. Similarly, according to the data from 2004 to 2007, the occupational group who deal with isocyanates and report occupational diseases caused by isocyanates are mainly machine operators in the plastic industry, welders, metal sheet workers, and casters.

2.3 Technical standards and regulations

Technical instructions followed by Swedish standard and regulations about welding and joining, insulations, and installations of district heating pipes are issued by Swedish district heating pipes association (Svensk Fjärrvärme AB). In technical regulation D:211- Installation instructions (D:211 Läggningsanvisningar) Swedish district heating pipes association have specified installation instructions, European and Swedish standards for design of pipes, fitting of pipes and valves, single pipe joints, double pipes joints, and standard system for monitoring. Technical regulation D:21 are based on relevant Swedish standards SS-EN 253, SS-EN 448, SS-EN 488, SS-EN 489, and SS-EN 15698.

To minimise the exposure of isocyanates during welding of pre-insulated district heating pipes, the insulation-free ends of district heating pips should be clean from insulation foam, any grease or oil, and corrosion. In case to use new pre-insulated district heating pips the preference should be given to use the district heating pipes which has already district heating pipes ends without insulation, and that insulation free ends should not be less than 15 cm. The general schematic diagram according to SS-EN 253:2009 for design of district heating pipes is shown in Figure 2.

The European standard SS-EN 253:2019 states that prior to weld district heating pipes the insulation-free ends must have 15 cm, however in Sweden 25 cm is the minimum length as recommended in AFS 2011:19.

2.4 Exposure limits

Time weighted average limit values TWLs (mg/m^3) is the highest acceptable exposure limit value for 8hrs. Short term exposure limit value STEL (mg/m^3) is highest acceptable exposure limit values for 15 minutes reference period. According to Swedish work environment authority provisions AFS 2018:1, reference period for short term exposure STEL (mg/m^3) varies according to substance. Short terms exposure limit STEL (mg/m^3) for isocyanates 5 minutes reference period is applied. The exposure limit values for monoisocyanates and diisocyanates, identification number according to Chemical Abstract Service CAS, the year when certain form of isocyanates were introduced or changed into occupational exposure limit value list, and category of isocyanates are presented in Table 1.

Table 1. AFS 2018:1 Occupational exposure limit values of Monoisocyanates and Diisocyanates

Substances		CAS-NO	Year	Time weighted (8hr) limit (TWL)	Short term (5min) exposure limit (STEL)		Remarks
				mg/m^3	mg/m^3	µg/m^3	
Monoisocyanates	Methyl isocyanate (MIC)	624-83-9	2005	0.024	0.047	47	M
	2.6-Diisopropyl-phenylisocyanate (2.6-DIP)	28178-42-9	2005	0.04	0.08	80	M,S
	Phenylisocyanate (PHI)	103-71-9	1984	0.02	0.05	50	M,S
	Isocyanic acid (ICA)	75-13-8	2004	0.018	0.036	36	M
Diisocyanates	Hexametylendiisocyanate (HDI)	822-06-0	2005	0.02	0.03	30	M,S
	Isophorone diisocyanate (IPDI)	4098-71-9	2005	0.018	0.046	46	M,S
	4,4´-Methylenediphenyl diisocyanate (4,4´-MDI)	101-68-8	2005	0.03	0.05	50	M,S
	Toluene diisocyanate (TDI) 2,4-Toluendiisocyanat (2,4-TDI) 2,6-Toluendiisocyanat (2,6-TDI)	26471-62-5	2005	0.014	0.04	40	C,M,S
	1.5-Naphthalene diisocyanate (1.5-NDI)	3173-72-6	2005	0.017	0.044	44	M,S
	Trimetylhexametylendi isocyanat	28679-16-5	2005	0.017	0.004	4	M,S

Where as;

C = The substance is carcinogenic. There is a cancer risk even with an exposure other than inhalation. For certain carcinogenic substances which do not have limit values, prohibition may apply, or authorization may be required, in accordance with the provisions on chemical hazards in the working environment.

M = Medical supervision may be required for handling of this substance. Please refer to the provisions on occupational medical supervision. For certain substances, medical control is required only when the substance is used as a thermosetting plastic component. Please refer to the provisions on thermosetting plastics.

S = The substance is sensitizing. Sensitizing substances can lead to allergies or other hypersensitivity. Hypersensitivity problems mainly affect the skin or respiratory organs. Hypersensitivity means that persons react upon contact with substances which do not normally cause problems. Allergies are a subgroup of hypersensitivity; they are caused by reactions within the body's immune system. Particularly low limit values have been set for substances with more pronounced respiratory passage-sensitizing properties.

3 Material and Methods

3.1 General approaches to conduct measurements

To achieve aim and objective of this study, for measurements and experimental work a two steps approach was adopted. It means, at first step, during welding of DN20, DN25, DN32, DN40, DN50, DN65, DN80, DN100, DN150, DN200, DN250 district heating pipes having varying insulation-free ends welded by corresponding oxy-fuel and manual metal arc the temperature measurements according to temperature measurement strategy (Figure 4) were performed. The purpose to measure temperature at first step was that it should be found first which nominal dimensions i.e nominal size, insulation-free ends of district heating pipes have critical high heat i.e. 150 °C -200 °C at temperature measuring spot during welding. At second step, air sampling for isocyanates during welding of DN100, DN150, DN200, DN250 having varying insulation-free ends welded by oxy-fuel and manual metal arc only was performed.

3.1.1 Strategy for temperature measurements

To measure temperature during welding of varying nominal size district heating pipes of varying insulation-free ends which have been cleaned from remaining pieces and particles of polyurethane insulation foam, a temperature measurement spot was marked. The marked spot was 0.5cm close to polyurethane insulation of district heating pipe and 16 cm – 22 cm from welding spot. IR thermometer was placed at a distance less than 1 meter from marked spot for temperature measurement.

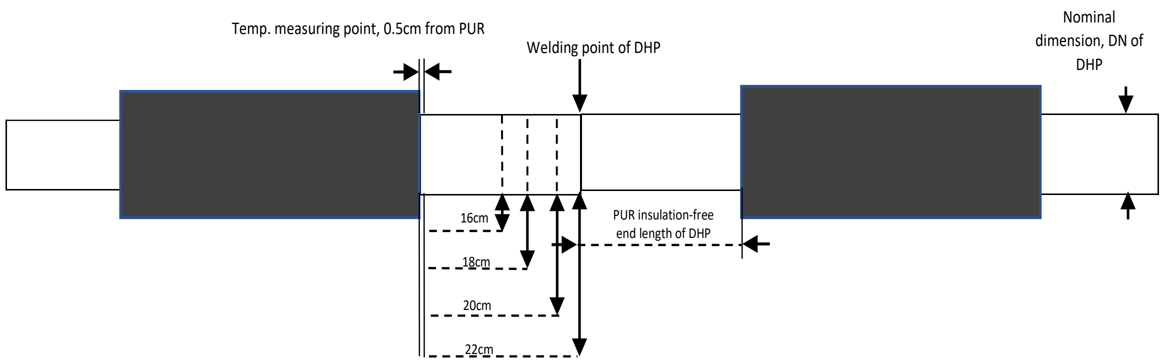


Figure 4. *Schematic diagram of varying nominal size and insulation-free ends length of district heating steel pipe to indicate temperature measurement spot and insulation-free ends length of district heating pipes.*

3.1.2 Strategy for isocyanates air sampling

The strategy to collect maximum detectable types and quantity of isocyanates in air samples, three sampling units (i.e. sampling unit consist of ASSET ® EZ4-NCO dry sampler connected with SKC Model 220-1000TC air sampling pump) were used. Two sampling units were assigned to be used in breathing zone (i.e. BZ1, Breathing Zone 1 where air sampling pump was attached to welder and dry sampler was passing over right shoulder and clipped in breathing zone; BZ2, Breathing Zone 2 where air sampling pump was attached to left side of welder and dry sampler was passing over left shoulder and clipped in breathing zone). Third sampling unit was assigned to collect isocyanates from surrounding (i.e. S, Surrounding where dry sampler and air sampling pump was positioned in such way that collected fumes and gases which were emitting from polyurethane insulation and welding spot during welding).

3.1.3 Temperature measurement instruments

Temperature measurements were performed by using calibrated IR thermometer Marelco 42.1303 (Temperature measurement range -32 ^{o}C to +600 ^{o}C) (Appendix 2), IR thermometer Testo 830-T4 (Temperature measurement range -30 °C to + 400 °C) (Appendix 3) and IR camera Flir C3 (Appendix 4). To analyse the results of temperature measurements steps IR Marelco 42.1303 was used as reference temperature measuring instrument, while to observe the precision of the instruments IR Testo 830-T4 and IR camera Flir C3 were used as complementary parallel temperature measurement instruments.

3.1.4 Isocyanates sampling instruments

Dry sampler ASSET® EZ4-NCO

To collect and derivatise isocyanates during sampling process a dry sampler ASSET ® EZ4-NCO as described by ISO17334:1 was used (Figure 5 & Appendix 6). Dry sampler EZ4-NCO consist of polypropylene tube and multipore filter which are in series. Denuder section is loaded with reagent di-n-butyl amine (DBA) as derivatization reagent. During sampling the reagent is released continuously to the filter. This process enables the availability of regent on the filter for efficient derivatisation of collected isocyanate particles. Vapour and gas phase of isocyanate are collected in denuder section while particle on filter.

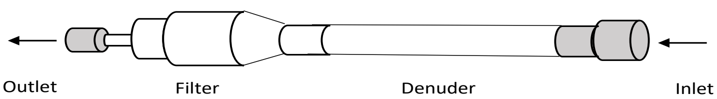


Figure 5. *Schematic diagram of ASSET EZ4-NCO Dry sampler*

Air sampling Pumps SKC Model 220-1000TC

Air sampling pumps SKC Model 220-1000TC SKC USA (Appendix 5) were used to perform air sampling during welding of district heating pipes.

In this project following Visits at workplace, Survey, Temperature measurement method, Air sampling and analysis method are used.

3.2 Visits at workplace

To observe welding practices of welders and as a ground for planning measurements several visits at project sites and workshop of Stockpipe AB were made. During the visits general routines, working hours and activities of welders were noticed. It was also noticed which welding methods and which nominal sizes of district heating pipes are used. Process of removing of polyurethane from ends of district heating pipes was also noticed.

3.3 Survey

Survey method was used to collect qualitative and general information from welders. A questionnaire was distributed to all welders who were employed by Stockpipe AB. The questions through this survey questionnaire were asked to both types of welders i.e. those who weld using manual metal arc and Oxy-fuel welding respectively. The survey questionnaire is shown in Appendix 1.

3.4 Temperature measurements

3.4.1. Varying diameter nominal pipe size and insulation-free ends

Measurement of temperature during welding of DN20, DN25, DN32, DN40, DN50, DN65, DN80, DN100, DN150, DN200 DN250 district heating steel pipe of insulation-free ends 16 cm to 22 cm welded by Oxy-fuel and manual metal arc MMA welding were performed in workshop of Stockpipe AB and at different project sites. Temperature at temperature measurement spot 0.5 cm close to polyurethane insulation on insulation-free ends were recorded individually. The summarised temperature measurement methodology is presented in Table 2.

Table.2 Temperature measurement method during welding of varying nominal district heating steel and copper pipes with varying insulation-free ends length welded by oxy-fuel and MMA welding.

Welding method		Oxy-fuel welding				Manual metal arc				soldering	Temp. measurement time (min)		Welding activity place	
Insulation-free ends		16cm	18cm	20cm	22cm	16cm	18cm	20cm	22cm	22cm	Oxy-fuel	MMA	Workshop	Sites
Nominal sizes	DN20			☒							8		☒	
	DN25				☒						7		☒	
	DN32								☒		9		☒	
	DN40			☒							11		☒	
	DN50				☒						10		☒	
	DN65				☒						12			☒
	DN80								☒		15		☒	
	DN100			☒							18			☒
	DN150				☒						20			☒
	DN200	☒	☒	☒	☒	☒	☒	☒	☒		13,12,13,13	19,18,14,22	☒	
	DN250					☒	☒	☒	☒			34,35,31,29	☒	
	54mm									☒	8			☒

3.5 Isocyanates air sampling and analysis

3.5.1 Air sampling

Air sampling units to collect isocyanates were set-up according to sampling strategy. Air sampling pumps were started right at the time when welder started welding activity. The air flow rate of sampling pumps was adjusted 0.5 l/min, the initial air flow rate was noted at the start of sampling. The air flow rate of all three air sampling pumps were noted and stopped the pumps when welder completed task. The time of sampling was noted, the airborne isocyanate sampling time was same as it was the welding time of required nominal sized of district heating pipes. After sampling the dry samplers were detached from air sampling pumps and inlet and outlet ends were closed with plugs. After sampling the dry samplers were packed and shipped to laboratory for analysis of isocyanates in air samples where these samples were analysed by LC-MS technique.

3.5.2 Samples analysis

Airborne isocyanates collected during welding of varying dimensions of selected district heating pipes were analysed by EHS Analytics laboratory in Staffanstorp. To determine the isocyanates in air samples the n-dibutylamine (DBA) derivatised isocyanates were extracted and analysed through LC-MS liquid chromatography-mass spectrometry technology. The analysis of derivatised isocyanate detected forms of isocyanates by LC-MS with detection limits (MIC)=0.005 µg, Ethyl isocyanate (EIC)= 0.005 µg, Propyl isocyanate (PIC)= 0.02 µg, Phenyl isocyanate (PHI)= 0.005 µg, Isophorone diisocyanate (IPDI)= 0.003 µg, 1.6-HDI= 0.003 µg, 2.4-TDI = 0.003 µg, 2.6-TDI = 0.003 µg, 4.4´-MDI = 0.003 µg and Isocyanic acid (ICA)=0.300 µg per sample.

4 Results

4.1 Result of Visits

On visits it was found that 50 welders currently working 40 hours per week at Stockpipe AB. About half of them are experts in oxy-fuel welding and other half are experts in manual metal arc welding. Few of them can use both welding methods. It was found that before starting installation and replacement of district heating pipes at project sites welders perform partial welding activities in workshop of Stockpipe AB. Those activities include cutting and welding of metal pieces used to make frames and supports to be used in installation and replacement of district heating pipes, welding and coupling of valves to the lines and pipes. To protect welders and workers from hazardous fumes and gases produced beside welding and metal cutting activities in workshop facility flexible fumes extractor arms for capturing of gases, smoke and fumes are installed over each welding stations.

After preparation in workshop welders transport ready-made material to project sites accompanying welding devices, tools, and necessary equipment. District heating pipes which are provided by energy companies and project management organizations are also transported to project sites according to the requirement.

To make insulation-free ends of average length 15 cm to 22 cm welders remove polyurethane insulation foam from the ends of district heating pipes. Removing of polyurethane insulation foam from the ends of district heating pipes itself seems a tough task which involve cutting of outer casing of district heating pipes with the help of cutting saw and then removing of polyurethane foam. It found that in most of the cases the removing of polyurethane foam is not removed evenly. Small leftover pieces and particles of polyurethane foam on the surface of ends of district heating pipes remain sticking. In some cases, before starting welding welders try to clean remaining by using knife, sandpaper, or scraper from ends, but this was not always practiced. It was noticed that welders perform welding activities for 4 to5 hours on average in one working day.

On visits it was noticed that to perform welding tasks welders adopt body posture which are not ergonomically appropriate. Welders lay down and bend unevenly on ground in a closed space of excavated ditch. It was also noticed that welders seldom use personal protective gears to protect themselves from gases, fumes and smoke produced during welding activities.

4.2 Result of Survey

The relevant information obtained after survey method were as follow; 21 welders who responded to the survey questionnaire, 25 % of them had been working as welders from 1 to 10 years at previous workplaces and Stockpipe AB. The welders who have been working as welders since 10 to 30 years at the time of survey were 45 % and those who were working since 40 to 50 years were25 %. 80 % of welders responding have information and awareness about isocyanates and health risks related to isocyanates resulting from welding activities, 3 welders have named Asthma, allergy and cancer as a health problem caused by isocyanates. 20 % of welders responding do not have information and awareness about isocyanates and health risks caused by isocyanates. Survey questionnaire have found that welders have access to personal protective gears to protect themselves from isocyanates and other hazards during welding activities.

The preference to remove polyurethane insulation from the ends of district heating pipes was answered by respondent welders that they prefer to remove 20-25 cm. 15 cm is not preferred always except when it is needed. For cleaning of insulation-free ends after removing polyurethane insulation foam from the ends of district heating pipes 50 % of welders responding mentioned that they "always" clean the ends to remove polyurethane foam pieces and particles, 40 % answered that they clean "sometime", 10 % responded that they "never" clean the ends prior to start welding.

It was also found that all welders spend varying time to weld varying dimensions of district heating pipes, e.g. to weld DN50 by MMA welding method if one welder take 19 minutes but other one take 13 minute to weld same nominal size of district heating pipes.

4.3 Results of temperature measurement method

The temperature measured by using marelco 42.1303 IR thermometer according to temperature measurement strategy along nominal size of district heating pipes and corresponding welding method is shown in Table 3 in detail. In this table highlighted temperature measurements indicate that DN100 of insulation-free ends 20 cm, DN150 of insulation-free ends 22 cm and DN 200 of insulation-free ends 16 cm and 18 cm welded by using oxy-fuel welding has high temperature and can result in isocyanates formation and exposure of welders to isocyanates when welding these dimensions. Temperature measured in case of capillary soldering of 54 mm copper district heating pipe is presented in Table 4. Welding time (min) and Temperature (^{o}C) relationship of varying nominal size and varying insulation-free ends district heating steel and copper pipe welded by oxy-fuel, Manual metal arc and copper pipe welded by capillary soldering to note critical temperature 150 ^{o}C are presented in Figure 5, 6, 7, 8, 9, 10 and 11.

Table 3 Temperature (ºC), Time (min) measured during welding of varying nominal size and varying length of insulation-free ends of DHP welded by corresponding Oxy-fuel and MMA welding method.

Size	DN20	DN25	DN32	DN40	DN50	DN65	DN80	DN100	DN150	DN200	DN200	DN200	DN200	DN200	DN200	DN200	DN200	DN250	DN250	DN250	DN250
Method	Oxy-fuel	Oxy-fuel	MMA	Oxy-fuel	Oxy-fuel	Oxy-fuel	MMA	Oxy-fuel	Oxy-fuel	Oxy-fuel	Oxy-fuel	Oxy-fuel	Oxy-fuel	MMA	MMA	MMA	MMA	MMA	MMA	MMA	MMA
Time (min)	20 cm ⊠	22 cm ⊠	22 cm ⊠	20 cm ⊠	22 cm ⊠	22 cm ⊠	22 cm ⊠	20 cm ⊠	22 cm ⊠	16 cm ⊠	18 cm ⊠	20 cm ⊠	22 cm ⊠	16 cm ⊠	18 cm ⊠	20 cm ⊠	22 cm ⊠	16 cm ⊠	18 cm ⊠	20 cm ⊠	22 cm ⊠
	Temperature (ºC) measured by marelco 42.1303 IR thermometer																				
0	19	19	25	19	17	26	21	19	21	36	29	35	23	17	15	28	16	17	18	18	13
1	22	21	27	29	19	38	22	33		51	46	45	42	19	18	32	18	18	19	19	15
2	26	22	28	40	28	46	23	45	25	64	49	48	48	23	20	34	20	19	20	20	18
3	31	23	30	44	36	63	24	57		84	69	55	62	28	23	38	21	21	21	22	20
4	39	26	31	56	45	76	26	80	30	91	74	68	71	34	37	40	23	24	22	24	21
5	48	27	34	64	53	84	28	95		105	82	75	76	38	47	42	26	26	23	25	22
6	50	29	37	74	67	93	30	102	44	119	90	92	92	44	60	44	28	29	24	26	23
7	55	29	39	89	79	104	31	124		125	101	104	94	48	66	46	30	32	26	27	26
8	68		41	95	98	109	33	130	65	133	113	114	101	50	74	51	32	35	27	28	27
9	65		40	108	106	127	35	144		144	126	122	106	53	88	52	34	40	29	30	28
10				136	117	131	39	163	95	158	132	133	113	57	91	56	35	42	30	32	29
11				141	110	140	46	174		167	147	139	118	60	92	63	41	44	32	33	30
12				139		132	49	184	116	169	158	142	123	64	94	69	44	46	33	34	31
13							51	193		172	164	144	136	68	95	72	48	48	34	36	32
14							53	201	139	169	163		135	70	96	74	53	52	36	37	34
15							56	206						74	93	77	58	55	38	38	35
16							55	211	151					78		77	61	57	40	39	37
17								209						80		79	64	63	42	40	39
18									161					85		82	67	64	45	42	42
19														90		80	71	65	48	43	44
20									186					94			70	67	50	44	50
21														98				69	52	45	52
22									193					102				75	54	47	54
23														98				78	57	51	55
24									201									81	60	53	60
25																		85	62	55	61
26									209									87	63	58	63
27																		92	65	60	64
28									191									93	67	61	65
29																		93	70	62	66
30																		90	73	63	67
31																			76	64	68
32																			74	67	69
33																				68	69
34																				71	69

* Highlighted values illustrate temperature measurement values described as critical temperature i.e. >150 °C that may cause thermal degradation of polyurethane insulation during welding of respective size of district heating pipes.

Table 4. Temperature (°C) and Time (min) measured during capillary soldering of 54 mm copper district heating pipe.

Size	54 mm copper district heating pipe
Method	Capillary soldering method
Time (min)	Insulation free-ends length 22 cm
	Temperature (°C) measured by Testo 830 -T4
0	17
1	30
2	48
3	70
4	90
5	70
6	87
7	92
8	104
9	92

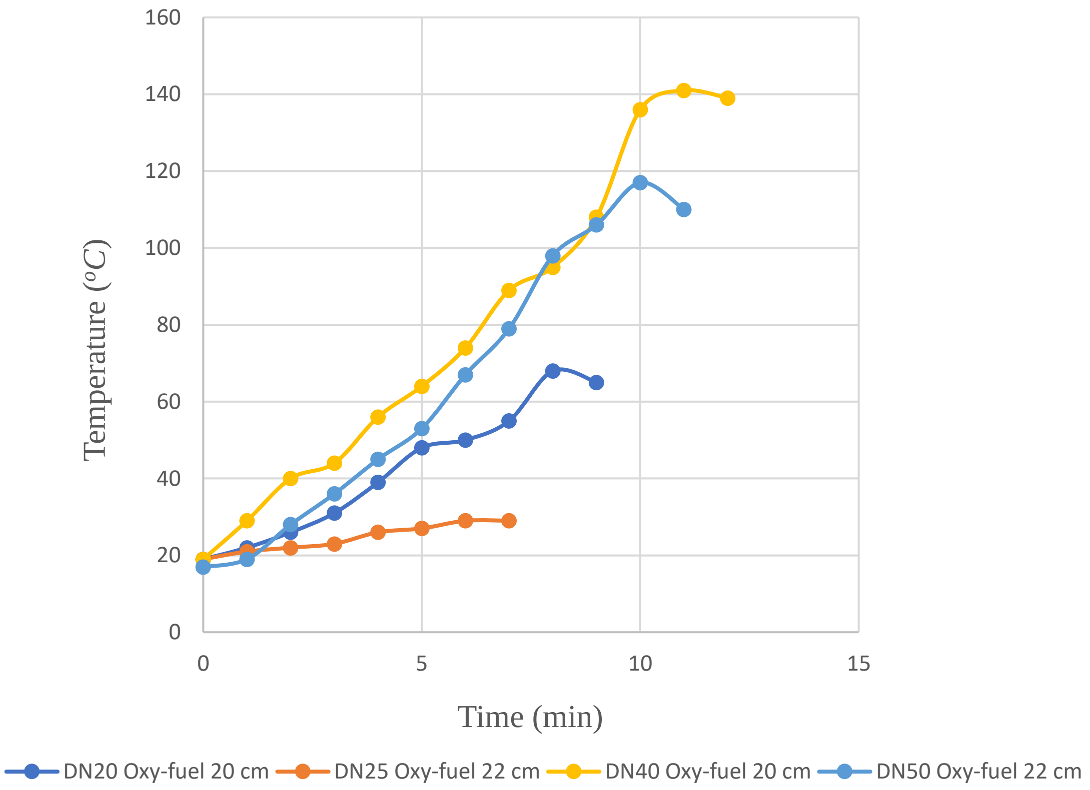


Figure 6. *Welding time (min) and Temperature (°C) relationship representing critical temperature 150 °C measured during welding of varying nominal size DN20, DN25, DN40, DN50 having varying length of insulation-free ends welded by Oxy-fuel welding.*

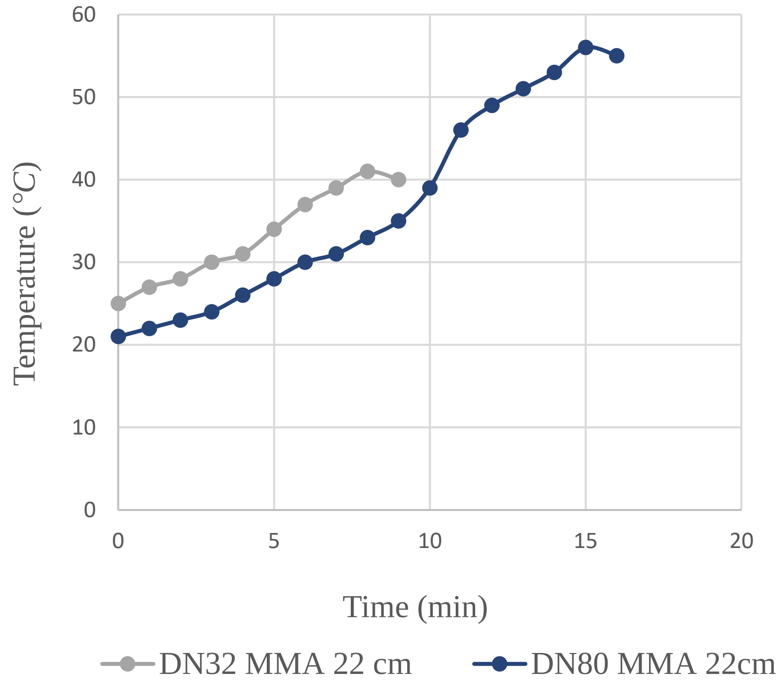


Figure 7. *Welding time (min) and Temperature (°C) relationship representing critical temperature 150 °C measured during welding of nominal size DN32, DN80 of varying insulation-free ends district heating steel pipe welded by MMA.*

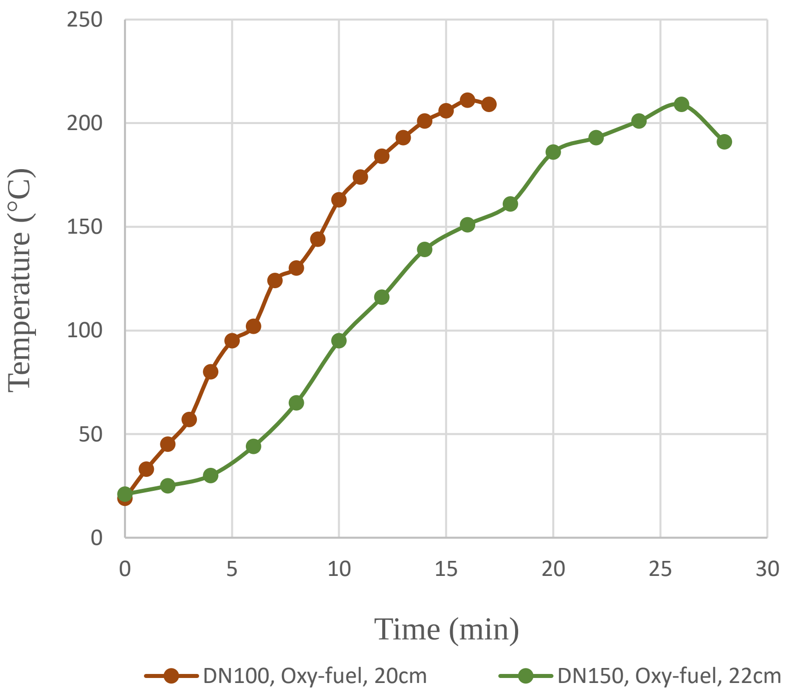


Figure 8. *Welding time (min) and Temperature (°C) relationship representing critical temperature 150 °C measured during welding of nominal size DN100 having 20 cm, DN150 having 22 cm insulation-free ends district heating steel pipe welded by oxy-fuel welding.*

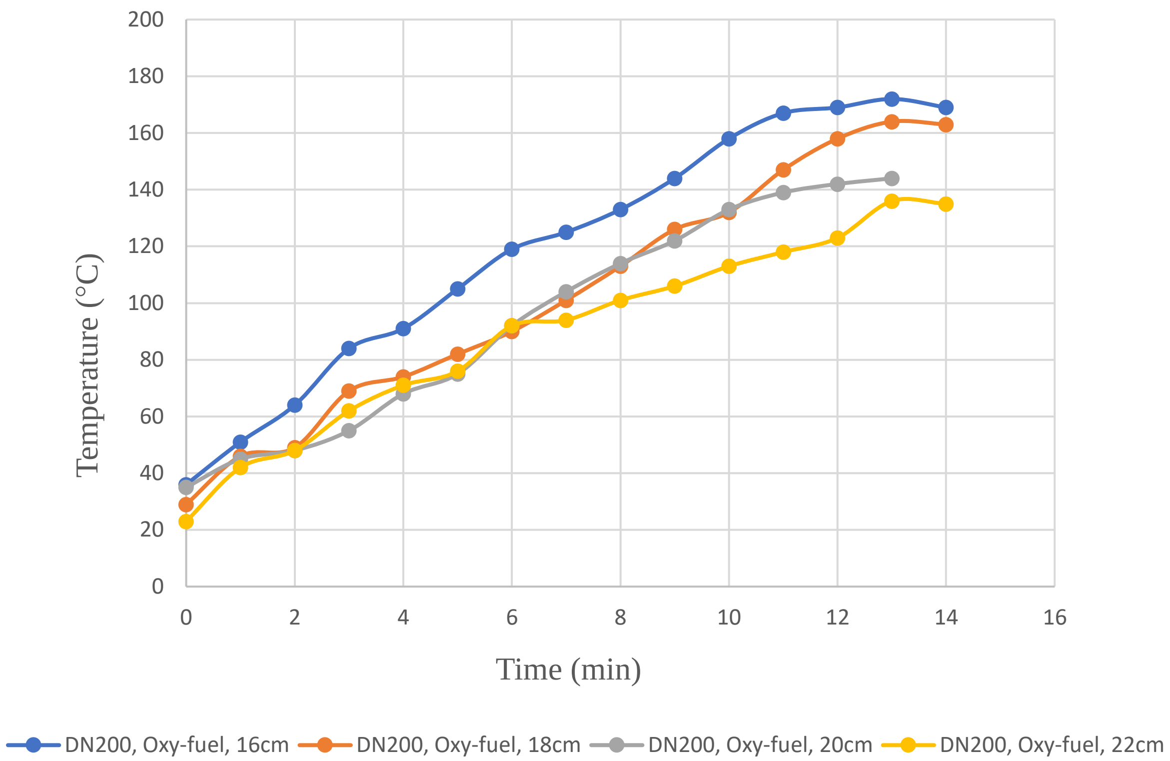


Figure 9. *Welding time (min) and Temperature (°C) relationship representing critical temperature 150 °C measured during welding of nominal size DN200 having varying insulation-free ends district heating steel pipe welded by oxy-fuel welding.*

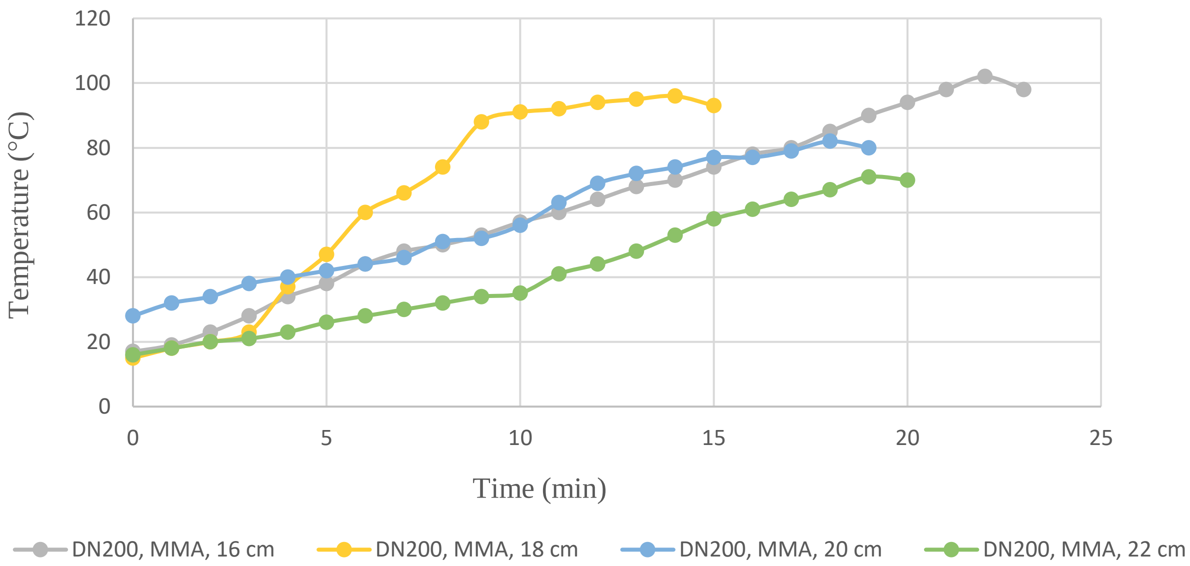


Figure 10. *Welding time (min) and Temperature (°C) relationship representing critical temperature 150 °C measured during welding of nominal size DN200 having varying insulation-free ends district heating steel pipe welded by MMA welding.*

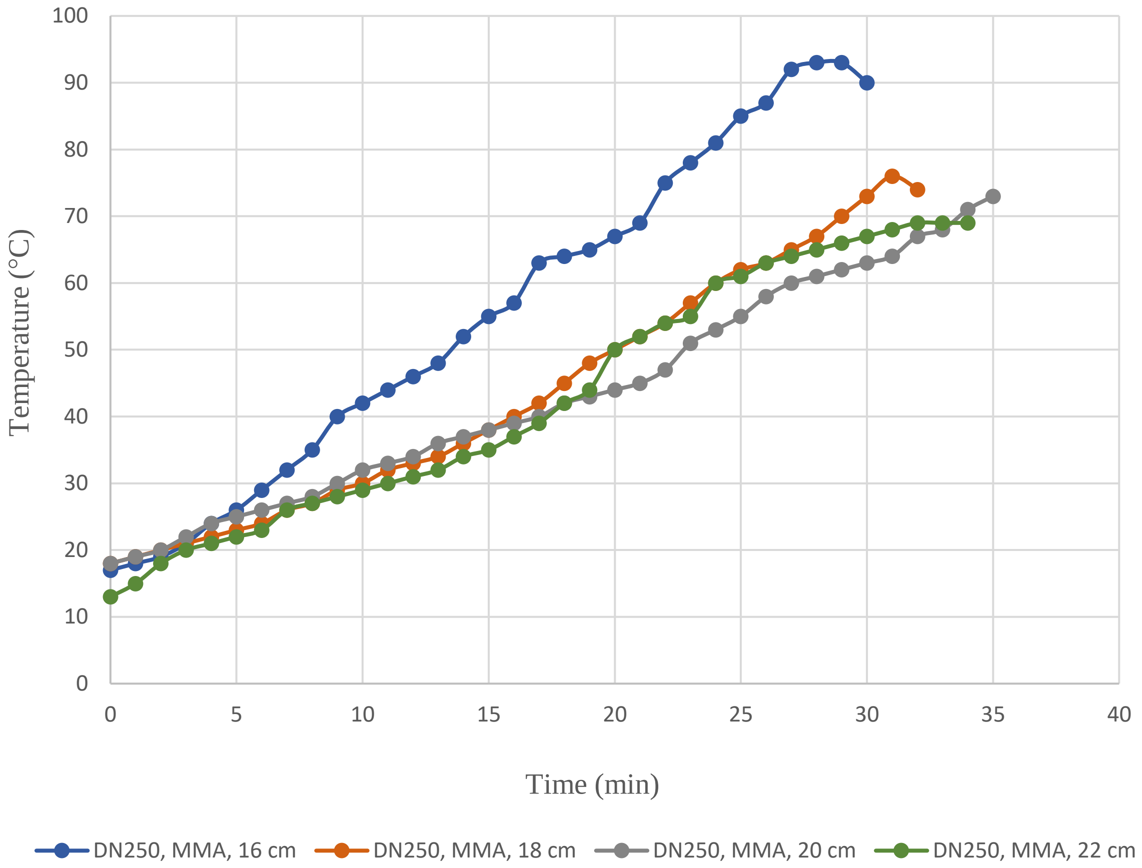


Figure 11. *Welding time (min) and Temperature (°C) relationship representing critical temperature 150 °C measured during welding of nominal size DN250 of varying insulation-free ends district heating steel pipes welded by MMA welding.*

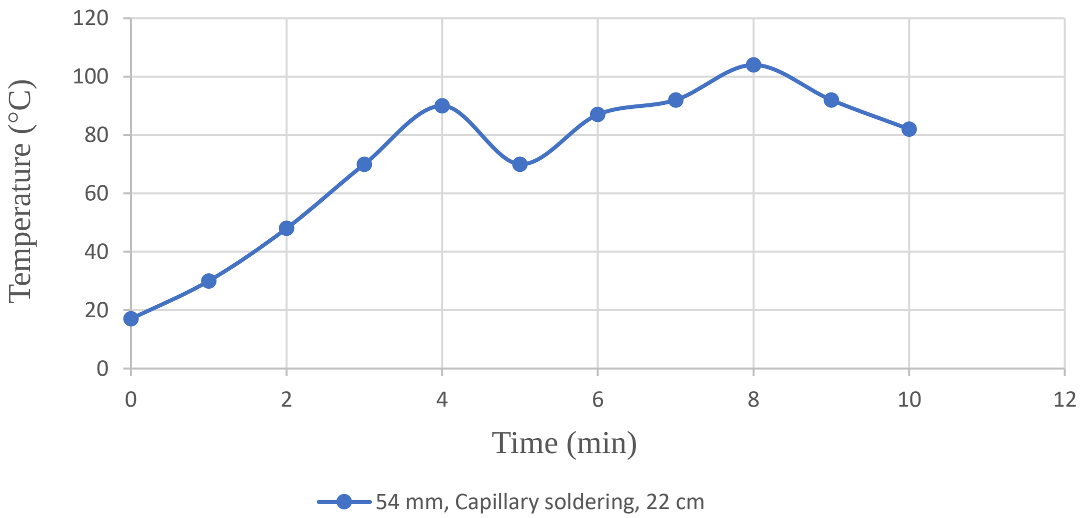


Figure 12. *welding time (min) and Temperature (°C) relationship representing changes in temperature measured during welding of district pipe 54 mm diameter having insulation-free ends length 22 cm welded by Capillary soldering method.*

4.4 Results of isocyanates samples analysis

The analysis of samples collected in the course of welding of nominal size DN100 district heating steel pipe with insulation-free ends length 22 cm welded by oxy-fuel welding method, nominal size D150 of 22 cm insulation-free ends length welded by using oxy-fuel welding method, DN200 of insulation-free ends length 16 cm, 18 cm, 20 cm,22 cm welded by using oxy-fuel and manual metal arc welding method the concentration of monoisocyanates and diisocyanates detected by LC-MS in individual samples collected from breathing zone (BZ1,BZ2) of welder and from surrounding (S) of exposed polyurethane is presented in detail in Table 5. Highlighted concentration of monoisocyanates and diisocyanates in Table 5 represent the concentration of isocyanates found in corresponding samples and are higher than acceptable short term exposure limit STEL (µg/m^3).

Table 5. Analysis results of Isocyanates in air samples collected during welding of varying nominal sizes of district heating steel pipes.

Nominal dimension	Welding method		Length of PUR-free end of DHP	Sampling time (min)	Flow rate (l/min)	Sampling position	Monoisocyanates conc. (µg/m^3)					Diisocyanates conc. (µg/m^3)					MDI Oligomers (µg/m^3)		
	Gas	MMA					MIC	EIC	PIC	PHI	ICA	1.6-HDI	2.4-TDI	2.6-TDI	IPDI	4.4´-MDI	3-RING-MDI	4-RING-MDI	2.4´-MDI
DN100	☒	☐	22	13	0.5	BZ1	0.8	-	-	3.9	-	-	-	-	-	100	×	×	×
						BZ2	-	-	-	-	-	-	-	-	-	10	×	×	×
						S	7.2	-	-	40	220	-	-	-	-	1200	×	×	×
	☒	☐	22	13+14 =27[a]	0.5	BZ1	-	-	-	-	-	-	-	-	-	-	×	×	×
						BZ2	-	-	-	-	-	-	-	-	-	-	×	×	×
						S	-	-	-	-	-	-	-	-	-	0.4	×	×	×
DN100 (Trial sampling results)	☒	☐	22	23	0.515	BZ1	-	-	-	-	-	-	-	-	-	0.6	-	-	-
					0.520	BZ2	-	-	-	-	-	-	-	-	-	1.7	-	-	-
					0.540	S1	-	-	-	2.9	33.5	-	-	-	-	24.3	3.4	0.5	-
			22	25	0.52	BZ1	-	-	-	-	-	-	-	-	-	0.4	-	-	-
					0.52	BZ2	-	-	-	-	-	-	-	-	-	1.4	0.3	-	-
					0.52	S1	-	-	-	0.8	-	-	-	-	-	7.5	1.6	-	-
					0.52	S2	-	-	-	-	-	-	-	-	-	3.5	0.2	-	-
DN1 50	☒	☐	22	18	0.5	BZ1	-	-	-	0.7	-	-	-	-	-	8.4	×	×	×
						BZ2	-	-	-	-	-	-	-	-	-	5.0	×	×	×
						S	0.7	-	-	6.7	47	-	-	-	-	320	×	×	×
DN200	☒	☐	16	13	0.5	BZ1	-	-	-	-	-	-	-	-	-	0.5	-	-	-
						BZ2	-	-	-	-	-	-	-	-	-	0.6	-	-	-
						S	-	-	-	-	-	-	-	-	-	0.6	-	-	-
	☒	☐	18	13	0.5	BZ1	-	-	-	-	-	-	-	-	-	0.5	-	-	-
						BZ2	-	-	-	-	-	-	-	-	-	-	-	-	-
						S	-	-	-	1.2	55	-	-	-	-	6.3	-	-	1.0
	☒	☐	20	12	0.5	BZ1	-	-	-	-	-	-	-	-	-	-	-	-	-
						BZ2	-	-	-	-	-	-	-	-	-	-	-	-	-
						S	-	-	-	-	-	-	-	-	-	0.7	-	-	-
	☒	☐	22	13	0.5	BZ1	-	-	-	-	-	-	-	-	-	-	-	-	-
						BZ2	-	-	-	-	-	-	-	-	-	0.5	-	-	-
						S	-	-	-	1.5	-	-	-	-	-	7.6	-	-	1.1
DN200	☐	☒	16	22	0.5	BZ1	-	-	-	-	-	-	0.3	-	-	0.5	-	-	-
						BZ2	-	-	-	-	-	-	-	-	-	0.4	-	-	-
						S	-	-	-	-	-	-	-	-	-	1.1	-	-	-
	☐	☒	18	14	0.5	BZ1	-	-	-	-	-	-	-	-	-	0.6	-	-	-
						BZ2	-	-	-	-	-	-	-	-	-	0.6	-	-	-
						S	1.8	-	-	1.2	61	-	-	-	-	1.7	-	-	-
	☐	☒	20	18	0.5	BZ1	-	-	-	-	-	-	-	-	-	0.4	-	-	-
						BZ2	-	-	-	-	-	-	-	-	-	0.5	-	-	-
						S	-	-	-	2.0	-	-	-	-	-	5.2	1.5	-	0.9
	☐	☒	22	19	0.5	BZ1	-	-	-	-	-					0.6	-	-	-
						S	-	-	-	-	-					-	-	-	-

* Highlighted values illustrate concentration of monoisocyanates, diisocyanates detected in respective samples are higher than acceptable STEL (µg / m^3) for short-term exposure limit determined by AFS 2018:1

5 Discussion

5.1 General discussion

In this thesis project extent of formation of thermal degradation products monoisocyanates and diisocyanates by varying welding methods and varying ends length of particular diameter nominal sizes of district heating pipes have found that welding of pre-insulated district heating pipes either by using oxy-fuel or manual metal arc welding involve risks and hazards in terms of hazardous isocyanates which can potentially harm the health of welders and other workers at place where welding activities are carried out. Direct association of small length of polyurethane insulation-free ends and availability of polyurethane to be expose to high heat and ultimate formation of isocyanates is noticed prominently in case of oxy-fuel welding. Since oxy-fuel welding of district heating pipe warm up the district heating pipes to high temperature which lead to thermal exposure of insulation and ultimate formation of hazardous isocyanates. Manual metal arc and capillary soldering generate less heat.

The remaining of small pieces and particles on the ends of district heating pipes, uneven removal of polyurethane insulation foam, and unspecific length of insulation-free ends of district heating pipes can increase the risk of exposure of isocyanates to welders and workers in surrounding at workplace. During welding either by using oxy-fuel or manual metal arc welding, the high heat, i.e. critical temperature 150 ^{o}C - 200 ^{o}C, generated from welding spot can expose remainings, pieces and particles of polyurethane insulation foam present on the insulation free-ends. Furthermore, during welding unremoved polyurethane insulation foam available after length 15 - 22 cm under outer casing of district heating pipes can be exposed to that high heat. Despite that fact cleaning of polyurethane insulation foam pieces and particles from freshly removed insulation-free ends of district heating pipes is always suggested. Presence of polyurethane pieces and particles and other impurities such grease, oil at any spot on the ends of district heating pipes can result in formation of isocyanates. In this study normal practices to clean the ends of district heating pipes before starting welding were adopted, there is needed to investigate to what extent remainings of polyurethane insualtion effect the formation of isocyanates.

Welding time can be considered an aspect which can affect the formation of isocyanates. The large gap between joints can increase welding time and can lead to generate high heat which is considered as primary cause of isocyanate formation. In this study assessments of formation of isocyanates are not judged on time basis but this can be considered an important basis to evaluate the formation of isocyanate.

Formation of isocyanates as a result from thermal degradation of polyurethane insulation in the process of welding of district heating steel pipes has been judged not to be a problem when welding small dimensions DN20, DN25, DN32, DN40, DN50, DN65 and DN80 and 54 mm copper pipes.

Hence, only nominal sizes DN100 having insulation-free ends 22 cm, DN150 having insulation-free ends length 22 cm welded by using oxy-fuel welding, and DN200 of insulation-free ends length 16cm, 18 cm, 20 cm, 22 cm welded by using oxy-fuel welding have been considered for airborne isocyanate sampling and further analysis for isocyanates. LC-MS analysis of each samples detected the concentration of isocyanates. Among identified isocyanates ICA, MIC, EIC, BIC, PIC, 1.6-HDI, 2.4-TDI, 2.6-TDI, IPDI, 4.4´-MDI, 2. 4´MDI, analysis of air samples for isocyanates showed that most prominent form of identified isocyanates are MIC, PHI, ICA and 4.4´-MDI. DN250 district heating steel pipe of insulation-free ends 18 cm, 18 cm, 20 cm, 22 cm welded by manual metal arc welding and temperature measurement noted amide these welding were not significantly high temperature measured at measurement spot, hence airborne isocyanate sampling was not performed.

5.2 Methodological consideration

The intention of investigation through this thesis project is ascertained owing to qualitative and quantitative methodology. Visits at workplace and survey to gather information about welder's tasks, activities and welding related practices intensified and formulated the ground for measurement methods. Experimental piece of work intended to measure temperature, air sampling and analysis of isocyanates amassed information. Accompanied temperature measurement and isocyanate air sampling strategies emulated to get feasible information. The temperature measurement strategy strengthened point of view of suppression of cost for samples analysis. As it was avoided to collect huge number of air samples for isocyanates across all corresponding welding of nominal sizes of varying insulation-free ends of district heating pipes i.e., only identified nominal sizes were welded and air sampling and isocyanates analysis was performed. Temperature measurement strategy may help in the stage of correctness and minimization of isocyanates risks.

5.3 Results description

5.3.1 Visits and Survey results

4-5 hours welding activities in a working day appear as where welder have risk to be exposed by hazardous gases. Additionally, welding activities in closed spaces where welders lay down and bend the body which are considered ergonomically not suitable posture can have consequences. Welding of district heating pipes after laying and bending expose welder̓s breathing zone notably to potential isocyanates risk. Findings about habits of seldom cleaning of ends of district heating pipes after removing polyurethane insulation and infrequent use of personal protective gears add up the risks of isocyanates exposure to welders. 20 % of welders responding survey who do not have information and awareness about isocyanates and health risks caused by isocyanates can be impacted by isocyanates exposure risk due to lack of information and awareness about isocyanates.

5.3.2. Temperature Measurement results

In this thesis project, formation of isocyanates as a result from thermal degradation of polyurethane insulation in the process of welding of district heating steel pipes has been judged not to be a problem when welding small dimensions DN20, DN25, DN32, DN40, DN50, DN65 and DN80 and 54 mm copper pipes.

Although, it was found that small dimension DN20, DN25, DN32, DN40, DN50, DN65, DN80 of insulation-free ends length 20 cm to 22 cm welded either by oxy-fuel welding or manual metal arc welding are not to be a problem of thermal degradation and isocyanate formation.

But welding of these small dimensions of insulation-free ends less than20 cm can have risk of thermal degradation of polyurethane insulation and isocyanates formation.

Nominal sizes DN100, DN150 of insulation-free ends 20 cm to 22 cm and DN200 of insulation-free ends 16cm to 20cm welded by oxy-fuel welding have shown high heat i.e. more than 150 ^{o}C at temperature measurement spot. It is known that application of heat above 150 ^{o}C - 200 ^{o}C to polyurethane foam results in thermal degradation of polyurethane foam, hence, welding of DN100, DN150 having insulation-free ends 20 cm to 22 cm and DN200 having insulation-free ends 16 cm to 20 cm welded using oxy-fuel welding has high chances of formation of isocyanates due to potential exposure of polyurethane insulation foam to high heat.

The variation in length of insulation-free ends of district heating pipes has proven that welding of district heating pipes having 16 cm insulation-free ends have high heat close to polyurethane insulation of district heating pipes which can be exposed to high heat as compared to 22 cm or 25 cm. It means welding of district heating pipes of short insulation-free ends have high chances of thermal degradation of polyurethane insulation foam and formation of isocyanates during the process of welding of district heating pipes.

The relationship between welding time (min) and change in temperature (^{o}C) with respect to varying nominal sizes, insulation-free ends and corresponding welding method showed that (Figure 6, 7, 8, 9, 10 11 and 12) temperature at temperature measurement spot increase parabolically with respect to time. It was also noticed that oxy-fuel welding generates high heat i.e critical temperature 150 ^{o}C- 200 ^{o}C as compared to manual metal arc welding. This was seen in case of welding of DN100, DN150, DN200 district heating steel pipes having insulation-free ends 20 cm-22 cm.

Welding of DN250 having varying insulation-free ends 16 cm, 18 cm, 20 cm, 22 cm using manual arc welding the temperature measured at temperature measurement spot was not more than critical temperature i.e. 150 ^{o}C.

Effects of welding time has shown slight differences in temperature at temperature measurement spot. It was seen when a welder who welded DN 200 of insulation-free ends 16cm using manual metal arc welding took 22 minutes. Temperature measured at temperature measurement spot was 102 ^{o}C. While second welder welded same dimension of district heating pipe with identical welding method took 14 minutes. The temperature in second case was measured 96 ^{o}C.

5.3.3 Air sampling and analysis of isocyanates result

The connection between thermal degradation of polyurethane due to critical high temperature i.e. 150 ^{o}C and formation of isocyanates is judged by the analysis of air samples for isocyanates collected during welding of DN100, DN150, DN200 by oxy-fuel welding. The obtained analysis results of air samples of isocyanates prove that MIC, PHI, ICA and 4.4΄-MDI are prominently formed during these welding processes. Although, concentration of isocyanates varies in sample to samples, i.e. concentration of identified isocyanates in samples collected from surrounding is found more e.g. 4.4΄-MDI =1200 µg/m^3 in sample S, as compared to samples which are collected from breathing zone (BZ1, BZ2) e.g. 4.4´-MDI = 100 µg/m^3, 10 µg/m^3 in sample BZ1, BZ2 during welding of DN100 having insulation-free ends 22cm welded by oxy-fuel welding. Similarly, concentration of PHI= 40 µg/m^3 in sample S is more but concentration of PHI = 3.9 µg/m^3 in sample BZ1, and concentration of ICA=220 µg/m^3 in sample S but ICA was not found in air samples collected from breathing zone BZ1, BZ2. The clear difference in concentration of isocyanates is found in samples S, BZ1, BZ2 which were collected during welding of DN150 having insulation-free ends 22 cm and DN200 having insulation-free ends 16 cm - 22 cm. The varying concentration of isocyanates in both type of samples is due to that; during sampling in surrounding of exposed polyurethane the sampler was positioned in such way that collected fumes directly emitting from the sources i.e. polyurethane insulation foam and from welding spot. While movement of welders to avoid fumes and gases during welding collected less airborne isocyanate in samples of breathing zones.

The measurement of isocyanates formed through thermal degradation of polyurethane has large variabilities. There is no direct evidence that identical type of isocyanates were found in all analysed samples. It is proved by noticing the analysis results of all air samples, e.g. in some samples prominent types of MIC, PHI, ICA and 4.4´-MDI are found but in other samples the type of prominent isocyanates vary. Difference in concentration of isocyanates with respect to change in nominal sizes of district heating pipe is also noticed. Although, no direct relationship is found, concentration of isocyanates varies notably. But, according to the analysis results of samples collected in case of welding of DN100 show that the concentration of diisocyanate 4.4´-MDI (µg/m^3) in sample BZ1 (100 µg/m^3) and S (1200 µg/m^3), concentration of monoisocyanate PHI in sample S1 (2.9 µg/m^3) , concentration of ICA (33.5 µg/m^3) in sample S1 are more as compared to the concentration of diisocyanate 4.4´-MDI (8.4 µg/m^3) , (5.0 µg/m^3), (320 µg/m^3) present in BZ1, BZ2 and S respectively collected during welding of DN150 district heating pipe. Similarly, concentration of ICA=220 µg/m^3 in sample S, and 33.5 µg/m^3 in sample S1 of second set of samples collected during welding of DN100 are apparently higher than ICA, 47 µg/m^3 in sample collected during welding of DN150, and ICA= 55 µg / m^3 in sample S collected during welding of DN200 having insulation-free end 18 cm.

The variation in welding methods to weld district heating pipes and its effect on thermal degradation of polyurethane insulation and isocyanates formation is found in case of welding of DN250 having insulation-free ends 16 cm, 18 cm,20cm, 22 cm using oxy-fuel and manual metal arc welding. Air sample for isocyanate analysis found that PHI, ICA and 4.4´-MDI present in both type of samples. Although the difference in concentration of isocyanates do not appear to be affected by changes in welding method but temperature measurements can strengthen the point of view that oxy-fuel welding generate high heat as compared to manual metal arc welding hence oxy-fuel welding can thermally degrade polyurethane insulation and form isocyanates.

5.4 Conclusion

The presence of monoisocyanate ICA in samples collected either during oxy-fuel welding or manual metal arc welding processes indicated that concentration (µg/m^3) and presence of ICA were not dependent on the welding method and specific nominal size of district heating pipes.

ICA can be formed from welding processes and varying concentration of ICA (µg/m^3) can be detected in most of isocyanate air samples as commented in previous research.

The presence of diisocyanate 4.4´-MDI in samples either collected from breathing zone or from surrounding validated the obvious reason as rigid polyurethane foam used on district heating pipes as an insulation material are synthesized using MDI based isocyanates. Thermal degradation of MDI based polyurethane formed 4.4´-MDI.

It was found that oxy-fuel welding generated high heat that heated up insulation-free ends of district heating pipes fast. Fast conduction of heat from welding spot toward insulation of district heating pipe resulted temperature higher than 150 ^oC during welding of varying insulation-free ends and varying nominal sizes of district heating pipes. Temperature measured during welding of manual metal arc was not high enough as it was measured in case of oxy-fuel welding. The adopted strategy to measure temperature as represented in Figure 4 found that during welding of DN100 having insulation-free ends 20 cm, DN150 insulation-free ends 22 cm and DN200 having insulation-free ends 16 cm welded by oxy-fuel welding generated enough high heat that can form isocyanates through thermal degradation of polyurethane insulation. The evidence was that the analysis results of samples collected during welding of those nominal sizes of district heating pipes had hazardous types of monoisocyanates such as, MIC, PHI, ICA and diisocyanates such 4.4´-MDI.

It was found that the concentration of detected monoisocyanates and diisocyanates in some samples were higher than acceptable STEL (µg / m^3) for short-term exposure limit determined by AFS 2018:1. Concentrations of detected monoisocyanates and diisocyanates which were higher than acceptable short-term exposure limit were found only in few samples which were collected from breathing zone of welder. But significance concentration of monoisocyanates ICA, MIC and diisocyanates, 4.4´-MDI were found in samples which were collected from surrounding of exposed polyurethane insulation and welding spot.

Presence of high concentration of isocyanates in surrounding of welding spot and surrounding of exposed polyurethane insulation project that there exists high risk of isocyanates to welders, welders have a risk to be exposed to those isocyanates.

Higher concentration of isocyanates in samples collected from the surroundings of polyurethane exposed to high heat and welding spots as compared to samples collected from breathing zone of welders presumed that welder´s working positions varried a lot during the process of welding.

5.5 Recommendations for the future

- In case to use strategies adopted in this study in future research it is recommended to use comparative temperature measurement instruments.
- Heat generated from saw cutting need to be considered for measurement.
- It is recommended to comprehensively evaluate the risks of isocyanate formation from the remains of insulation on ends of district heating pipes.

5.6 Recommendations for welders at Stockpipe AB

- In case to use oxy-fuel as welding method, it is recommended to investigate small nominal sizes DN65 and DN80 of insulation-free ends of least recommended length i.e. 15 cm/16 cm. These small nominal sizes with least insulation free-ends length have a low likelihood of formation of thermal degradation products.
- In case to remove polyurethane insulation from ends of DN100, DN150 and DN200 and then to weld using oxy-fuel welding method, it is recommended that insulation-free ends length should not be less than 18 cm. There is high chance of formation of isocyanates above the acceptable limit values.
- Higher welding time has high chance of formation of isocyanates, it is recommended to reduce welding time.
- Large gap increases welding time and generate high heat and risk of formation and exposure of isocyanates, it is recommended to reduce gap and welding time.
- It is recommended to use several heat elimination or heat minimization techniques prior to weld DN100, DN150 and DN200 using oxy-fuel welding method.
- To increase awareness about risks of isocyanates, importance of cleaning of insulation-free ends before starting welding process, training or education to welders should be reviewed.
- Inspection and cleaning of flexible fume extractor installed over welding station in workshop is recommended.
- Prevent isocyanates from spreading to tools, surfaces, and clothing by having good order and well-thought-out cleaning routines.
- It is recommended to use proper personal protective equipment during welding jobs.
- Do not eat or smoke during welding.

5.7 Follow-up

To improve knowledge of welders about health risks associated with isocyanates and to have improved welding practices and working conditions of welders during welding at welding project sites and at workshop a short course training has been conducted at Stockpipe AB.

To avoid formation of isocyanates by taking possible measures during welding of DN100, DN150 and DN200 during oxy-fuel welding a separate assessments have been performed. It has been found that prior starting welding the application of cooling paste/thermal paste and making a muffle with the help of clothing towel on the ends of district heating pipes show significant results. Use of thermal paste or clothing towel reduce high heat at temperature measuring spot. The results of that assessment are not included in this thesis project.

6 References

Bergström, G., Lindqvist, L., Nilsson, S., (2002). Isocyanatexponering vid svetsning av fjärrvärmerör "Exposure to isocyanates at welding of district heating pipes". report FOU 2002: 77. Svenska Fjärrvärmeföreningens Service AB "Swedish district pipes association".

Bengtström, Linda, Mariëlle Salden, and Anna A. Stec. "The role of isocyanates in fire toxicity." *Fire Science Reviews* 5.1 (2016): 1-23.

Blomqvist, P., Hertzberg, T., Dalene, M., & Skarping, G. (2003). Isocyanates, aminoisocyanates and amines from fires—a screening of common materials found in buildings. *Fire and materials*, *27*(6), 275-294.

Boutin, M., Lesage, J., Ostiguy, C., Pauluhn, J., & Bertrand, M. J. (2004). Identification of the isocyanates generated during the thermal degradation of a polyurethane car paint. *Journal of Analytical and Applied Pyrolysis*, *71*(2), 791-802.

Chambers, John, and Colin B. Reese. "The thermal decomposition of some polyurethane foams." *British Polymer Journal* 8.2 (1976): 48-53.

Dhara, V. R., & Dhara, R. (2002). The Union Carbide disaster in Bhopal: a review of health effects. *Archives of Environmental Health: An International Journal*, *57*(5), 391-404.

Franklin, Phillip J., et al. "Too hot to handle: an unusual exposure of HDI in specialty painters." *American journal of industrial medicine* 37.4 (2000): 431-437.

Font, R., Fullana, A., Caballero, J. A., Candela, J., & García, A. (2001). Pyrolysis study of polyurethane. *Journal of Analytical and Applied Pyrolysis*, *58*, 63-77.

Garrido, María A., et al. "Isocyanate emissions from pyrolysis of mattresses containing polyurethane foam." *Chemosphere* 168 (2017): 667-675.

Gylestam, Daniel. *Isocyanates-methodology for gas and particle generation, sampling and detection*. Diss. Department of Analytical Chemistry, Stockholm University, 2012.

Henriks-Eckerman, M. L., Välimaa, J., & Rosenberg, C. (2000). Determination of airborne methyl isocyanate as dibutylamine or 1-(2-methoxyphenyl) piperazine derivatives by liquid and gas chromatography. *Analyst*, *125*(11), 1949-1954.

Herrera, M., Matuschek, G., & Kettrup, A. (2002). Thermal degradation of thermoplastic polyurethane elastomers (TPU) based on MDI. *Polymer degradation and stability*, *78*(2), 323-331.

Henneken, H., Vogel, M., & Karst, U. (2007). Determination of airborne isocyanates. *Analytical and bioanalytical chemistry*, *387*(1), 219-236.

Huang, X. Y., Cornelis, F., Peng, X. P., Xie, J. L., Qi, J. Q., Jiang, Y. Z., . & Nie, S. X. (2018). Thermal stability analysis of polyurethane foams made from microwave liquefaction bio-polyols with and without solid residue. *BioResources*, *13*(2), 3346-3361.

Karlsson, Daniel, et al. "Determination of isocyanates, aminoisocyanates and amines in air formed during the thermal degradation of polyurethane." *Journal of Environmental Monitoring* 4.2 (2002): 216-222.

Karlsson, D., Spanne, M., Dalene, M., Skarping, G. 2000. Airborne thermal degradation products of polyurethane coatings in car repair shops. Journal of Environmental Monitoring 2, 462-469.

Karlsson, D., Dalene, M., Skarping, G., Marand, A., 2001. Determination of Isocyanic Acid in air. Journal of Environmental Monitoring 3, 432-436.

Krone, C. A., & Klingner, T. D. (2005). Isocyanates, polyurethane and childhood asthma. *Pediatric allergy and immunology*, *16*(5), 368-379.

Kääriä, Katja, et al. "Exposure to 2, 4-and 2, 6-toluene diisocyanate (TDI) during production of flexible foam: determination of airborne TDI and urinary 2, 4-and 2, 6-toluenediamine (TDA)." *Analyst* 126.7 (2001): 1025-1031.

Lattimer, R. P., Polce, M. J., & Wesdemiotis, C. (1998). MALDI-MS analysis of pyrolysis products from a segmented polyurethane. *Journal of Analytical and Applied Pyrolysis*, *48*(1), 1-15.

Liu, Xiu, Jianwei Hao, and Sabyasachi Gaan. "Recent studies on the decomposition and strategies of smoke and toxicity suppression for polyurethane based materials." *RSC advances* 6.78 (2016): 74742-74756.

Låstbom, L., Colmsjö, A., Johansson, R., Karlsson, D., Melin, J., Nordqvist, Y., & Skarping, G. (2003). Effects of thermal degradation products from polyurethane foams based on toluene diisocyanate and diphenylmethane diisocyanate on isolated, perfused lung of guinea pig. *Scandinavian journal of work, environment & health*, 152-158.

Liu, Xiu, Jianwei Hao, and Sabyasachi Gaan. "Recent studies on the decomposition and strategies of smoke and toxicity suppression for polyurethane based materials." *RSC advances* 6.78 (2016): 74742-74756.

Mattsson, Christian, Christian H. Lindh, and Håkan Tinnerberg. "Underestimation of toluene diisocyanate concentration using long-term sampling with 1-(2-methoxyphenyl) piperazine impregnated filters." *International journal of hygiene and environmental health* 211.3-4 (2008): 458-462.

McKenna, Sean Thomas, and Terence Richard Hull. "The fire toxicity of polyurethane foams." *Fire Science Reviews* 5.1 (2016): 1-27.

Mangs, S., Ramnäs, O. J., Persson, C., Jarfelt, U., & Fröling, M. (2006). PET and PUR foam insulated District Heating Pipes–Study: Environmental Comparison. *Euroheat & Power*, *3*(1), 26-31.

Marand, Åsa, et al. "Determination of technical grade isocyanates used in the production of polyurethane plastics." *Journal of environmental monitoring* 6.7 (2004): 606-614.

Nilsson, N. H., Jeppesen, C. N., & Clausen, A. J. (2013). Survey of certain isocyanates (MDI and TDI), part of the LOUS-review.

Ott, M. Gerald. "Occupational asthma, lung function decrement, and toluene diisocyanate (TDI) exposure: a critical review of exposure-response relationships." *Applied occupational and environmental hygiene* 17.12 (2002): 891-901.

Rosenberg, Christina, et al. "Biological monitoring of aromatic diisocyanates in workers exposed to thermal degradation products of polyurethanes." *Journal of Environmental Monitoring* 4.5 (2002): 711-716.

Rosenberg, C., 1984. Direct determination of isocyanates and amines as degradation products in the industrial production of Polyurethane coated wire. The Analyst 109, 859-866.

Spirckel, M., Regnier, N., Mortaigne, B., Youssef, B., & Bunel, C. (2002). Thermal degradation and fire performance of newphosphonate polyurethanes. *Polymer Degradation and Stability*, *78*(2), 211-218.

SS-EN 253:2019 Swedish Standard, District heating pipes - Bonded single pipe systems for directly buried hot water networks - Factory made pipe assembly of steel service pipe, polyurethane thermal insulation, and a casing of polyethylene.

Swensson A, Holmquist CE, Lundgren KD. Injury to the respiratory tract by isocyanates used in making lacquers. British Journal of Industrial Medicine. 1955 Jan;12(1):50-53. DOI: 10.1136/oem.12.1.50. PMID: 14351646; PMCID: PMC1037600.

Shufen, Li, et al. "Studies on the thermal behavior of polyurethanes." *Polymer-Plastics Technology and Engineering* 45.1 (2006): 95-108.

Spanne, M., Tinnerberg, H., Dalene, M., & Skarping, G. (1996). Determination of complex mixtures of airborne isocyanates and amines. Part 1. Liquid chromatography with ultraviolet detection of monomeric and polymeric isocyanates as their dibutylamine derivatives. *Analyst*, *121*(8), 1095-1099.

Sennbro, C. J., Lindh, C. H., Oestin, A., Welinder, H., Jönsson, B. A., & Tinnerberg, H. (2004). A survey of airborne isocyanate exposure in 13 Swedish polyurethane industries. *Annals of Occupational Hygiene*, *48*(5), 405-414.Streicher, R. P., E. R. Kennedy, and C. D. Lorberau. "Strategies for the simultaneous collection of vapours and aerosols with emphasis on isocyanate sampling." *Analyst* 119.1 (1994): 89-97.

Tinnerberg, Håkan, and Christian Mattsson. "Usage of air monitoring and biomarkers of isocyanate exposure to assess the effect of a control intervention." *Annals of occupational hygiene* 52.3 (2008): 187-194.

Tinnerberg, H., Karlsson, D., Dalene, M., & Skarping, G. (1997). Determination of toluene diisocyanate in air using di-n-butylamine and 9-N-methyl-aminomethyl-anthracene as derivatization reagents. *Journal of liquid chromatography & related technologies*, *20*(14), 2207-2219.

Vandenplas, O., Cartier, A., Lesage, J., Cloutier, Y., Perreault, G., Grammer, L. C., ... & Malo, J. L. (1993). Prepolymers of hexamethylene diisocyanate as a cause of occupational asthma. *Journal of Allergy and Clinical Immunology*, *91*(4), 850-861.White, W.G., Sugden, E., Morris, M.J. and Zapata, E., 1980. Isocyanate-induced asthma in a car factory. *The Lancet*, *315*(8171), pp.756-760.

Woods, P., & Overgaard, J. (2016). Historical development of district heating and characteristics of a modern district heating system. In *Advanced District Heating and Cooling (DHC) Systems* (pp. 3-15). Woodhead Publishing.

Woolley, W. D. (1972). Nitrogen-containing products from the thermal decomposition of flexible polyurethane foams. *British Polymer Journal*, *4*(1), 27-43.

Zhang, Y., Xia, Z., Huang, H., & Chen, H. (2009). Thermal degradation of polyurethane based on IPDI. *Journal of Analytical and Applied Pyrolysis*, *84*(1), 89-94.

Appendix

Appendix 1

Questionnaire to conduct a general introductory survey to collect general information, observations, and opinion of welders working at Stockpipe AB.	
Ethical consideration disclaimer and aim: To whom who are working as welders at Stockpipe AB, it is requested to you to help in collection of general data/statistics/information by answering following general questions. The main aim of these questions is to know your general opinions, observations, your normal practices during welding work at Stockpipe AB. Collected information will only be used to supplement ongoing in-house research work about isocyanates.	
1-Are you a stick welder (Arc or MMA) or Gas (Oxy-fuel) welder or both?	Stick welder☐ Gas welder ☐ Both ☐
2-Do you have required qualification to work as a welder?	Yes ☐ No ☐
3-How long have you been working as a welder?	……………………… Years at Stockpipe AB ………………………Years at previous (if any)
4-How many hours per day (or per week) you work at Stockpipe AB	----------------hrs/day -----------------hrs/week
5-On average, how many hours per day (or per week) you specifically perform welding activity?	--------------hrs/day ------------hrs/week
6- What are the other activities (exclude welding activity) you perform during working day? (e.g. to prepare to start welding)?	- - - -
7-On average, how many hours per day (or per week) other activities take time?	---------------------hrs/day
8-Do you have access to personal protective gears to be used during welding work?	Yes☐ No ☐
9- If yes (if you have access to PP gears), do you use them during welding works?	Yes ☐ No☐ Sometime☐
10-Which type of personal protective gears you have (in your access) or you use?	- - -
11- Do you have any knowledge (info/have you heard) about Isocyanates?	Yes ☐ No ☐
12- Are you aware about any health risks of Isocyanates? If yes, can you name anyone?	Yes ☐ No ☐ -------------
13-Have you attended any training to work in a work environment which may have isocyanates risks?	Yes ☐ No ☐
14- In case you have to remove polyurethane (PUR) insulation foam from the ends of DHP before starting welding, in normal practice how much length you remove/peel off?	22 cm ☐ 20 cm ☐ 18 cm ☐ 16 cm ☐ Or-----------------cm
15-In above case i.e. if you remove PUR from the ends of DHP and in general how often you clean foam particles or other impurities (scaling, rust, oil etc) from the surface of DHP ends before welding?	Always ☐ Sometime ☐ Never ☐
16- In case to weld following dimension of DHP, according to your observations how much time it take to weld these dimensions of DHP by using comparative welding method?	DN Gas weld Stick weld 20 ----- min --------min 25 ------ min --------min 32 ------min --------min 40 ------min -------min 50 ------min ------ min 65 -------min -------min DN Gas weld Stick weld 80 -------min -------min 100 -------min -------min 150 -------min -------min 200 -------min -------min 250 -------min ------min

Appendix 2

IR TERMOMETER, -32°C- +600°C

M1303 är en IR-termometer för beröringsfri mätning på ytor där vanlig temperaturmätning är besvärligt t.ex. på objekt som är svåra att komma åt, spänningsförande objekt eller föremål som rör sig. Med bakgrundbelyst display och laserpekare kan man använda termometern i svagt belysta miljöer. Med snabb uppdateringshastighet (250ms) och automatiskt MAX-, MIN-, MED- och DIFF-Hold kan man "skanna" mätytor och få direkt information temperaturvariationer - tidseffektivt. Ringlaser med mittpunkt visar mätområdet.

Optiken är 12:1 vilken ger mätytan 1 dm på avståndet 1,2m. Med justerbar eller med fem förinställda ε - emissivitetskonstanter, kan termometern kalibreras för noggrann mätning oavsett material som skall mätas. Den knivskarpa EBTN-skärmen i färg erbjuder tydlig avläsning i både skarpt ljus och mörker.Möjlighet finns att sätta alarmgränser för Min- och Max-temperaturer som ger varning med både ljud och ljus. 3-färgs LED.

Levereras med väska och svensk bruksanvisning.

Artikelnr: 42.1303

E-nr: 4207533

Tillverkare: Marelco

marelco

Specifikationer

Mätområde	-32°C till 600°C (-26,5°F till 1112°F)
Mått	161,5 x 90 x 48 mm
Vikt	204 g
Batteri	1 st 9V 6LR61. > 8 timmar (alkaliskt batteri)
Upplösning	0,1°C (0,1°F)
Temp.koefficent	Mätomr.spec. gäller i intervallet 23 °C - 25 °C. Temp ≤ 0°C, addera +1°C
Arbetstemperatur	0°C till +50°C, <90% (ej kondenserande)
Mätprincip	Infraröd strålningsdetektering
Responstid	≤250ms (95% av avläst värde)
Spektral respons	8 m till 14 m
Synfält (Optik)	12:1
Sikte ringlaser markör	<1mW (class2) 630-670nm

Appendix 3

testo

testo 830-T4

Instruction manual

en

1. General Information

Please read this document through carefully and familiarise yourself with the operation of the product before putting it to use. Keep this documentation to hand so that you can refer to it when necessary.

2. Product Description

Accessories

Name	Item no.
Water-tight immersion/penetration probe, -60 to +400°C/ -76 to +752°F	0602 1293
Quick-reaction surface probe, -60 to +300°C/ -76 to +572°F	0602 0393
Robust air probe, -60 to +400°C/ -76 to +752°F	0602 1793
Leather protection sleeve	0516 8302
Emissivity adhesive tape ε=0.95	0554 0051

3. Safety Information

Avoid electrical hazards:

- Contact measurement: Do not measure on or near live parts. Infrared measurement: Please adhere to the required safe distance when measuring on live parts.

Preserving product safety/warranty claims:

- Operate the instrument properly and according to its intended purpose and within the parameters specified. Do not use force.
- Do not expose to electromagnetic radiation (e.g. microwaves, induction heating systems), static charge, heat or extreme fluctuations in temperature.
- Do not store together with solvents (e.g. acetone).
- Open the instrument only when this is expressly described in the documentation for maintenance purposes.

Ensure correct disposal:

- Dispose of defective rechargeable batteries and spent batteries at the collection points provided.
- Send the instrument directly to us at the end of its life cycle. We will ensure that it is disposed of in an environmentally friendly manner.

4. Intended Use

testo 830 is a compact infrared thermometer for the non-contact measurement of surface temperatures. A contact measurement can additionally be made with a connected probe.

Not suitable for diagnostic measurements in the medical sector!

5. Technical Data

Feature	testo 830-T4
Parameter	°C/°F
Infrared measurement range	-30 to +400°C/-22 to +752°F
Infrared resolution	0.1°C/0.1°F
Infrared accuracy (at 23°C/73°F) +/- 1 digit	±1.0°C/1.8°F or 1.0% of reading (+0.1 to +400°C/+32 to +752°F)[1]; ±1.5°C/2.7°F or 1.5% of reading (-20 to 0°C/-4 to +32°F)[1]; ±2.0°C/3.6°F or 2.0% of reading (-30 to -20°C/-22 to -4°F)[1]
Emissivity	0.2 to 1.0 adjustable
Infrared measurement rate	0.5s
Temp. sensor	Thermocouple Type K (attachable)
Measurement range of temp sensor	-50 to +500°C/-58 to +932°F
Resolution of temp. sensor	0.1°C/0.1°F
Accuracy of temp. sensor (±1 digit)	±0.5°C/0.9°F+0.5% of reading at rated temperature 22°C/72°F
Measuring rate of temp. sensor	0.5s
Optics (90% value)	30:1 (regarding the distance of 1,0 m to measuring object typically)[2]
Operating temperature	-20 to +50°C/-4 to +122°F
Transport/Storage temperature	-40 to +70°C/-40 to +158°F
Power supply	9V block battery
Battery life	15 h
Housing	ABS
Dimensions (LxHxB)	190 x 75 x 38mm/7.5 x 3.0 x 1.5in
CE guideline	2004/108/EEC
Warranty	2 years
Laser	
Laser type	2 x laser
Power	< 1 mW
Wavelength	645 to 660 nm
Class	2
Standard	DIN NE 60825-1:2001-11

[1] the larger value applies
[2] +Opening diameter of the sensor (16mm/0.6in)

6. Initial Operation

- Insert battery: See 9.1 Changing the battery.

Appendix 4

Appendix 5

Appendix 6

Supelco ASSET™EZ4 Dry Samplers for Isocyanates

Two ASSET EZ4 Samplers Available Providing Ultimate Sensitivity for Vapor Phase and Particulate Isocyanates

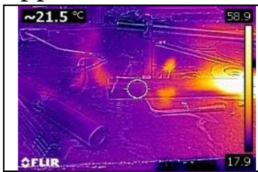
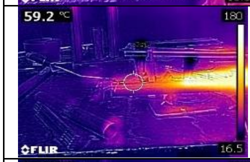
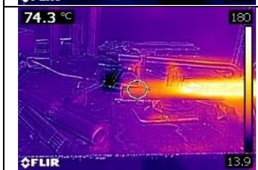
The ASSET EZ4 dry samplers for isocyanates are the easy-to-use dry samplers offering the ultimate sensitivity for collection & measurement of vapor phase and aerosol isocyanates. The *ASSET EZ4-NCO* Dry Sampler collects the full range of isocyanate monomers and oligomers; while the *ASSET EZ-ICA* sampler is designed to collect isocyanic acid (ICA) and methyl isocyanate (MIC) at low levels.

Key Features and Benefits

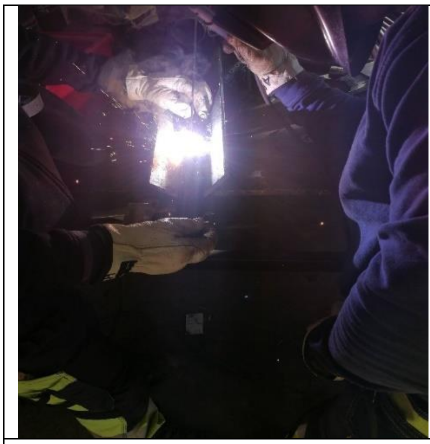
- Ability to achieve reliable, low detection limits
- Only device to measure vapor phase and aerosol isocyanates
- No interferences, no field extraction
- 2 yr. shelf life

	ASSET EZ4-NCO Dry Sampler	ASSET EZ4-ICA Dry Sampler
Sampling Flowrate	From 20 mL/min – 850 mL/min	From 20 mL/min – 200 mL/min
Sampling Time	From 5 minutes up to 12 hrs.	From 5 minutes up to 4 hrs.
Storage	Ambient (before & after sampling)	Refrigeration (before sampling); Ambient (after sampling)
Stability	4 weeks after sampling	2 weeks after sampling

Appendix 7

	Temperature measured at Time interval 1min, Temperatuer measured by FlirC3= 21.5 °C Marelco 42.1303 IR =22 °C
	Temperature measured at Time interval 2min, Temperatuer measured by FlirC3= 26.2 °C Marelco 42.1303 IR=26 °C
	Temperature measured at Time interval 3min, Temperatuer measured by FlirC3= 32.0 °C Marelco 42.1303 IR=31 °C
	Temperature measured at Time interval 4min, Temperatuer measured by FlirC3=39.9 °C Marelco 42.1303 IR= 39 °C
	Temperature measured at Time interval 5min, Temperatuer measured by FlirC3=48.2 °C Marelco 42.1303 IR= 48 °C
	Temperature measured at Time interval 6min, Temperatuer measured by FlirC3= 59.2.2 °C Marelco 42.1303 IR= 50 °C
	Temperature measured at Time interval 7min, Temperatuer measured by FlirC3= 62.7 °C Marelco 42.1303 IR = 55 °C
	Temperature measured at Time interval 8min, (Welding completed at this time interval), Temperatuer measured by FlirC3= 74.3 °C Marelco 42.1303 IR= 68 °C
	Temperature measured at Time interval 9min, Temperatuer measured by FlirC3=66.2 °C Marelco 42.1303 IR= 65 °C
Temperature measurement and images taken during welding of DN20 of insulation-free ends length 20cm welded by oxy-fuel welding method	

General presentation of welding activity of welding DN25 of insulation-free ends length 22 cm welded by manual metal arc in Stockpipe AB workshop.

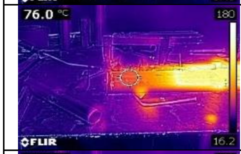
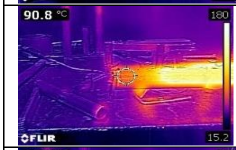


General presentation of welding activity of DN32 of insulation-free ends length 22 cm welded by MMA welding method in Stockpipe AB workshop.

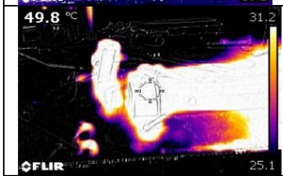
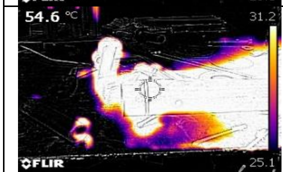
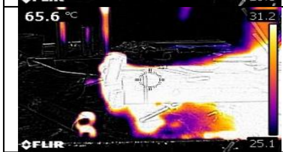
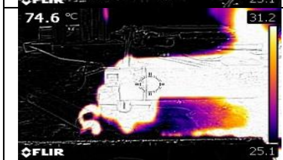
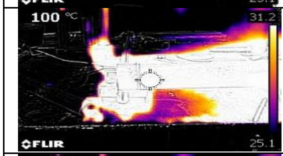
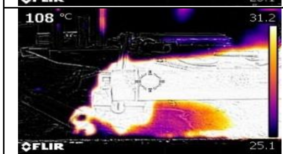
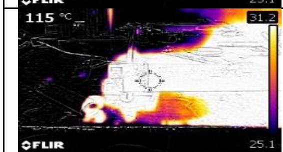
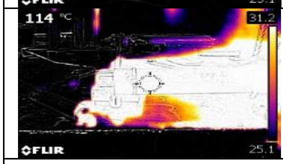
Temperature measured at Time interval 8min,
Temperature measured by
FlirC3= 42.5 ºC
Marelco 42.1303 IR= 41 ºC

*Welding completed at this time interval

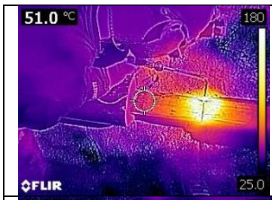
Temperature measurement and images taken by FLIR C3 IR during welding of DN32 of insulation-free ends length 22 cm welded by manual metal Arc method

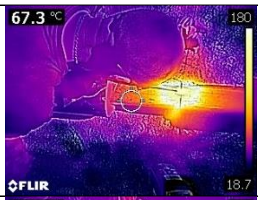
	Temperature measured at Time interval 1min, Temeperature measured by FlirC3= 26.5 °C Marelco 42.1303 IR=29 °C
	Temperature measured at Time interval 2min, Temeperature measured by FlirC3= 43.2 °C Marelco 42.1303 IR=40 °C
	Temperature measured at Time interval 3min, Temeperature measured by FlirC3=44.8 °C Marelco 42.1303 IR=44 °C
	Temperature measured at Time interval 4min, Temeperature measured by FlirC3=52 °C Marelco 42.1303 IR=56 °C
	Temperature measured at Time interval 5min, Temeperature measured by FlirC3=71.2 °C Marelco 42.1303 IR= 64 °C
	Temperature measured at Time interval 6min, Temeperature measured by FlirC3=76.0 °C Marelco 42.1303 IR= 74 °C
	Temperature measured at Time interval 7min, Temeperature measured by FlirC3=86.1 °C Marelco 42.1303 IR= 89 °C
	Temperature measured at Time interval 8min, Temeperature measured by FlirC3=90.8 °C Marelco 42.1303 IR= 95 °C
	Temperature measured at Time interval 9min, Temeperature measured by FlirC3= 103 °C Marelco 42.1303 IR= 108 °C
	Temperature measured at Time interval 10min, Temeperature measured by FlirC3=134 °C Marelco 42.1303 IR=136 °C
	Temperature measured at Time interval 11min, Temeperature measured by FlirC3= 155 °C Marelco 42.1303 IR= 141 °C
	Temperature measured at Time interval 12min, Temeperature measured by FlirC3=152 °C Marelco 42.1303 IR= 139 °C

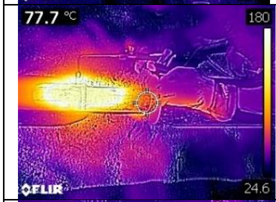
Temperature measurement and images taken by FLIR C3 IR during welding of DN40 of insulation-free ends length 20 cm welded by oxy-fuel welding method.

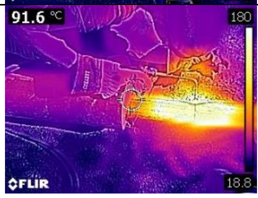
	Temperature measured at Time interval 1min, Temperature measured by FlirC3=18.6 ºC Marelco 42.1303 IR= 18.5 ºC
	Temperature measured at Time interval 2min, Temperature measured by FlirC3=26.8 ºC Marelco 42.1303 IR=28 ºC
	Temperature measured at Time interval 3min, Temperature measured by FlirC3= 34.4 ºC Marelco 42.1303 IR=36 ºC
	Temperature measured at Time interval 4min, Temperature measured by FlirC3 =49.8 ºC Marelco 42.1303 IR= 45 ºC
	Temperature measured at Time interval 5min, Temperature measured by FlirC3=54.6 ºC Marelco 42.1303 IR= 53 ºC
	Temperature measured at Time interval 6min, Temperature measured by FlirC3= 65.6 ºC Marelco 42.1303 IR= 67 ºC
	Temperature measured at Time interval 7min, Temperature measured by FlirC3= 74.6 ºC Marelco 42.1303 IR= 79 ºC
	Temperature measured at Time interval 8min, Temperature measured by FlirC3= 100 ºC Marelco 42.1303 IR= 98 ºC
	Temperature measured at Time interval 9min, FlirC3 =108 ºC Marelco 42.1303 IR =106 ºC
	Temperature measured at Time interval 10min (Welding completed at this time interval),Temperature measured by FlirC3=115 ºC Marelco 42.1303 IR= 117º C
	Temperature measured at Time interval 11min, Temperature measured by FlirC3=114 ºC Marelco 42.1303 IR =110 ºC

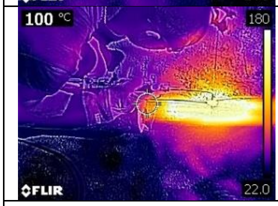
Temperature measurement and images taken by FLIR C3 IR during welding of DN50 of insulation-free ends length 22 cm welded by oxy-fuel welding method.



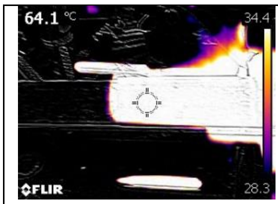






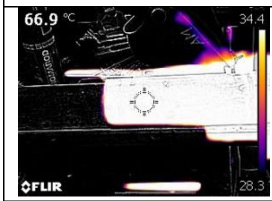


Images taken by FLIR C3 IR thermal camera to measure the temperature during welding of DN65 of insulation-free ends length 22 cm pre-insulated steel district heating steel pipe.



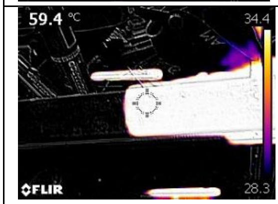
Temperature measured at Time interval 14min
Tmeperature measured by
FlirC3 =64.1 °C
Marelco 42.1303 IR=53 °C

*These images were taken at almost the end of welding process



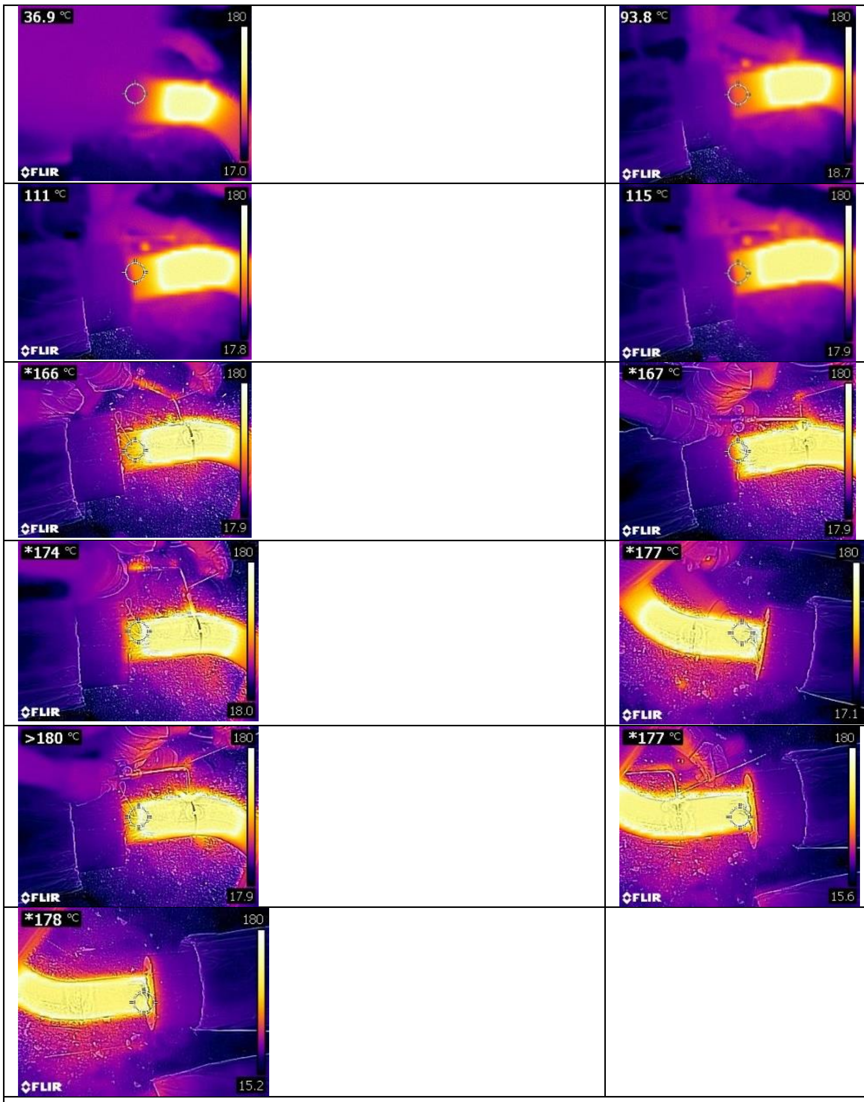
Temperature measured at Time interval 15min,
Temperature measured by
FlirC3 = 66.9 °C
Marelco 42.1303 IR, 56 °C

*Welding completed at this time interval



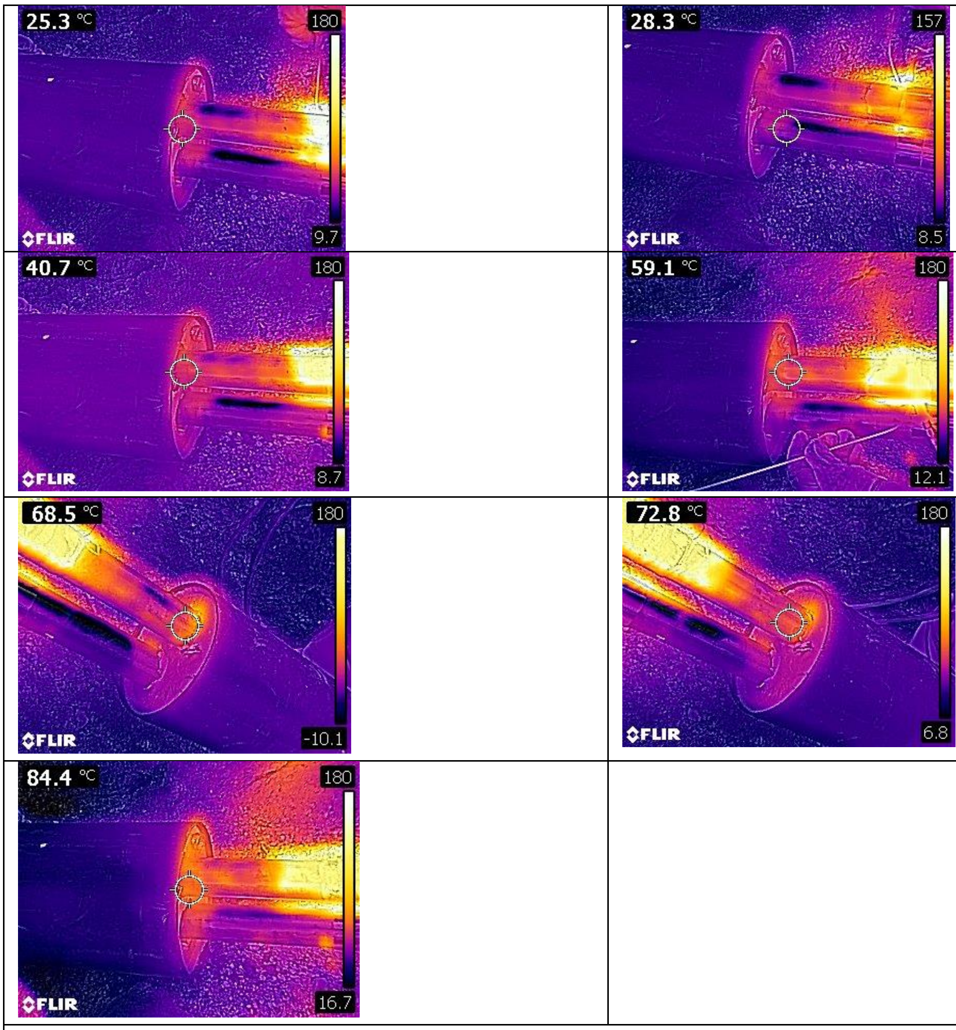
Temperature measured at Time interval
Time=16min
FlirC3, Temper 66.9 °C
Marelco 42.1303 IR, 56 °C

Temperature measurement and images taken by FLIR C3 IR during welding of DN80 of insulation-free ends length 22 cm welded by manual metal arc welding method.



Temperature measurement and images taken by FLIR C3 IR during welding of DN100 of insulation-free ends length 20 cm welded by oxy-fuel welding method.

General presentation of DN150 of insulation-free ends length 22 cm welded by Oxy-fuel welding method at project site.



Temperature measurement and images taken by FLIR C3 IR during welding of 54mm nominal size of insulation-free ends length 22 cm copper district heating pipeswelded by capillary soldering method.