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Influence of oxidation on radiative heat transfer in polyurethane insulation used for district heating pipes

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Abstract

Thermal conductivity of cellular rigid polyurethane foam (PUR) increases by time which leads to higher heat energy losses in district heating pipe networks. The main reason for increased thermal conductivity is diffusion of low conductive gases out of the PUR and diffusion of surrounding air into the PUR. However, oxidation of the PUR occurs during the service-life of the PUR and is accelerated by the higher temperatures close the fluid pipe. The effect that oxidation has on the thermal conductivity is not yet fully understood and existing models for prediction of long-term thermal performance of PUR insulation in district heating applications does not take oxidation processes into account. It is possible that the radiative heat transfer is affected by the oxidation and changes over the service-life of the PUR. In order to investigate the influence of oxidation on thermal conductivity, the *extinction coefficient* was therefore calculated for samples subjected to different levels of ageing. The input data for the calculations were measured by FTIR. The extinction coefficients were then used to calculate the overall thermal conductivity of the PUR with typical gas compositions. Results indicated that the *extinction coefficient* was 22 % higher in the samples exposed to lower temperatures. However, the effect on the overall thermal conductivity of the same samples was an increase of about 1.8 %. Since the comparison was made between two samples subjected to different levels of ageing, the increase in total thermal conductivity should be interpreted as a minimum if considering the total service lifetime of the PUR insulation.

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Keywords: *Extinction coefficient, Polyurethane, District heating, FTIR, Thermal Conductivity, Radative heat ransfer*

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1. Introduction

Heat losses in the Swedish district heating network is estimated to be about 10-15 % of the total heat production. District heating pipes are often insulated by cellular rigid polyurethane insulation, PUR (Figure 1.a), where the operation temperature is between 80-120 °C. This means that the PUR insulation is exposed to high temperatures which leads to accelerated ageing and degradation of insulation performance with higher heat energy losses in the district heating networks as a consequence.

In recent decades the end users, buildings, have become more energy efficient resulting in an increased ratio between heat losses in the district heating network and the energy demand for the end users. Thus, the efficiency of the district heating network becomes essential for energy companies in order to be competitive with other heating systems.

Improving the performance of the PUR insulation used in district heating pipes is not possible without a good understanding of the parameters that influences the thermal performance of the insulation. The heat transport mechanisms involved in PUR insulation are heat radiation between cell walls (both transmission and emission), heat conduction through the cell matrix and heat conduction in the gas enclosed in the cell matrix. A photo of the cells in PUR taken with SEM can be seen in Figure 1.c. Results obtained in previous research projects indicates that the most influential transport mechanism is the heat conduction in the gas phase which represents between 60 % to 80 % of the total thermal conductivity of the PUR foam [1].

In order to improve the insulation properties it is common to use physical blowing agents which produce low conductive gases such as *cyclopentane* (Cp), and *carbon dioxide* in the production of pre-insulated district heating pipes. However, concentrations of the low conductive gases in the surrounding environment are much lower than the gas concentrations in the cells which leads to diffusion of the low conductive gases to surrounding and diffusion of the surrounding gas (e.g. air) into the cells. The thermal conductivity of the air is higher than thermal conductivity of *cyclopentane* and *carbon dioxide* thus, diffusion of gases leads to higher total thermal conductivity. The diffusion process is very slow. However, if given enough time, the cell gases will eventually be replaced by air.

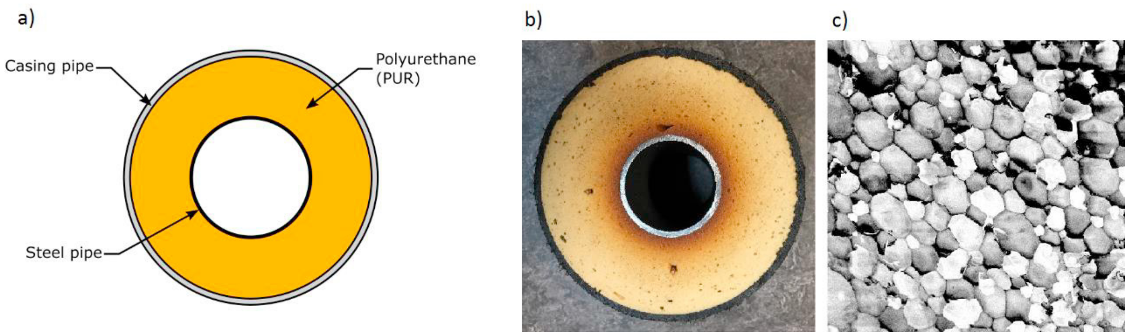

Fig. 1. (a) Structure of a district heating pipe (b) Photo of a cross-section of an aged district heating pipe insulated with PUR (c) Photo of PUR insulation taken with Scanning Electron Microscopy

Generally, long term thermal performance of district heating pipes is determined by estimating the content of the gases in the PUR insulation. In these estimations it is assumed that thermal conductivity of the cell matrix and the contribution of radiative heat transfer are constant.

Over time a discoloration of the PUR foam occurs where the foam typically turns from light yellow to dark brown. It has been shown that the discoloration is a result of oxidation of the PUR cell walls [2]. Here the oxidations process is accelerated by the higher temperatures close to the steel pipe (supply pipe) and clearly visible since the discoloration is more distinct compared to areas closer to the casing pipe, see Figure 1.b.

Estimations of the long term performance of the pre- insulated district heating pipes is vital for economic and environmental reasons. Decisions about the optimal time for renewing an old district heating network relies on accurate estimations on the status of the pipes both thermally and mechanically. It is therefore important to understand the ageing mechanisms in order to make accurate estimations on how the thermal conductivity of PUR insulation changes over time.

Nomenclature

K	Spectral extinction coefficient [m^{-1}]
$\overline{K}_e$	Rosseland's mean extinction coefficient [m^{-1}]
$e_{b\lambda}$	Hemispherical spectral emissive power [W/m^2]
τ	Transmittance [-]
T	Temperature [K]
σ	Stefan-Boltzmann constant ($5.67 \cdot 10^{-8}$) [$W/(m^2K^4)$]
f_s	Strut fraction of polyurethane foam insulation [-]
f_g	Porosity of polyurethane foam insulation [-]
λ	Thermal conductivity [W/mK]
y	Concentration [mol/m^3]
η	Viscosity [Ns/m^2]
M	Molar mass [g/mol]
l_{mf}	Mean free path of photons [m]
A_{ij}	Function of interaction [-]

This project aimed to investigate how oxidation affects the radiative thermal heat transfer as well as the overall thermal conductivity of the polyurethane foam insulation.

The influence of radiative heat transfer on the total heat transfer of the polyurethane was investigated by measuring the extinction coefficient of the cell walls. The coefficient was then used for calculation of the radiative heat transfer by using well established equations for cellular structures. The calculations were performed for samples subjected to different levels of ageing.

2. Calculation of overall heat transfer in polyurethane foam

The overall thermal conductivity of PUR depends on the heat transport mechanisms; radiation, conduction through the matrix and conduction in the gas phase. The contribution from each heat transport mechanism is calculated by utilizing the following equations.

Radiative heat transport is calculated with Rosseland's heat equation for optically thick foams [3, 4]:

$$\lambda_{radiation} = \frac{16\sigma T^3}{3\overline{K}_e} \tag{1}$$

The thermal conductivity through the polyurethane matrix is calculated using the following equation [1]:

$$\lambda_{matrix} = \left[0.48 f_s + 0.66(1-f_s)\right] \cdot (1-f_g) \cdot \lambda_{PUR} \tag{2}$$

For a composition of different gases the thermal conductivity is dependent on the concentration of each gas as well as its individual thermal conductivity. There are a number of methods for determining the overall thermal conductivity, however, in this project Wassiljeva's equations are used which is valid for gases treated as ideal [1]:

$$\lambda_{gas} = f_g \cdot \sum_{i=1}^{n} \frac{y_i \cdot \lambda_i}{\sum_{i=1}^{n} y_i \cdot A_{ij}} \tag{3}$$

Finally the overall conductivity of the polyurethane foam is calculated as follows:

$$\lambda_{total} = \lambda_{matrix} + \lambda_{radiation} + \lambda_{gas} \tag{4}$$

2.1. Extinction coefficient

The *Rosseland's mean extinction coefficient*, $\overline{K}_e$, for an optically thick medium is determined as [5]:

$$\frac{1}{\overline{K}_e} = \frac{\int_0^\infty \frac{1}{K_{e\lambda}} \frac{\partial e_{b\lambda}}{\partial T} d\lambda}{\int_0^\infty \frac{\partial e_{b\lambda}}{\partial T} d\lambda} \tag{5}$$

The extinction coefficient, $K_{e\lambda}$ can be calculated from the measured transmittance, τ, with *Beer's law* [3]*:*

$$\tau = e^{-K x} = e^{-(x/l_{mf})} \tag{6}$$

where x is the sample thickness [m].

3. Experiments

The hemispherical transmittance (τ) was measured for samples subjected to different levels of oxidation. By utilizing Equations 5 and 6 the mean extinction coefficient can be determined.

Perkin Elmer Frontier FTIR system was used and the transmittance for each sample was measured for the wavelengths 2.5 – 25 µm, where the majority of the thermal energy exists for temperatures between 200 and 700 K [5]. All measurements were performed at room temperature.

3.1. Sample preparation

Samples were taken from a CFC-11 blown polyurethane insulation used in a district heating pipe. The pipe had been in service for 32 years and was made by *Ecopipe* in 1983. The fact that temperatures are higher in vicinity of the steel pipe leads to faster ageing processes compared to the outer regions of the insulation. It can be identified by the degree of discoloration where the insulation is darker closer to the steel pipe, see Figure 1.b.

Samples with a diameter of 20 mm were carefully drilled from the PUR close to the steel pipe as wells as close to the casing. Drilled samples were then cut in thin samples using a microtome. The sample thickness were in the range from 0.5 mm to 1.0 mm. The samples were cleaned from dust and stored in closed containers until analyzed with FTIR.

Results and discussion

The measurement results for the light yellow samples are shown in Figure 4. The measured transmission (τ) was used for calculation of extinction coefficient as described in section 2.1. The calculated extinction coefficients for the samples are presented in Figure 5. It is clear that the light yellow samples have a higher extinction coefficient than the dark brown samples. The resulting difference between the mean values of both types of samples shows that the mean extinction coefficient was about 22.0 % higher for the light yellow samples compared to the dark brown samples.

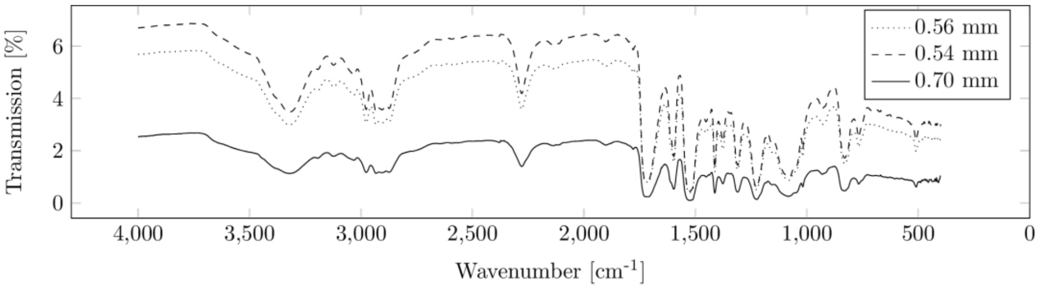

Fig. 4. Results from measurements with FTIR. The graph shows the transmission for three of the samples at the measured wavenumbers.

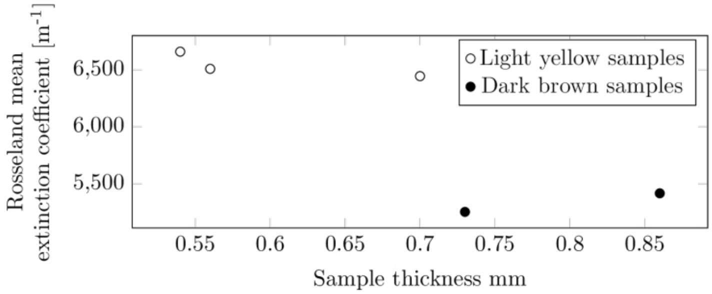

Fig. 5. Rosseland's mean extinction coefficient for measured samples.

The assumption that the samples are optically thick can be validated by relating the extinction coefficients to *free mean path* and compare it with the sample thickness, as in this case the assumption of optically thick samples is valid.

Because of limited access to samples as well as the fact that many of the samples were ruptured during sample preparation there were quite few that qualified for measurements. Ideally, to get more reliable results more measurements needs to be done on the same aged insulation.

3.2. Calculation of the total thermal conductivity

The influence of 22.0% higher extinction coefficient on the total thermal conductivity were estimated by using equation 1-4. In these estimations it was assumed a typical gas phase composition for Cyklopentane blown foam, i.e. (Cp: 60 %, CO_2: 30 %, O_2: 2 %, N_2: 8 %). As a comparison, it is also assumed that after long enough time the gas composition in the PUR will be the same as for the surrounding air. Thus, the total conductivity was also calculated for the case with the same gas composition as in the surrounding air. The estimation results are presented in Table 1.

Table 1. Mean extinction coefficient and overall thermal conductivity for samples of aged light yellow and dark brown foam.

	Light yellow (90 °C)	Dark brown (90 °C)	Light yellow (air filled)	Dark brown (air filled)
$\overline{K}_e$ [1/m]	6574	5388	6574	5388
λ [mW/(m·K)]	28.5	29.0	38.5	39.0

Results presented in Table 1 shows that the extinction coefficient varied significantly between dark and light samples. However, the influence on the total thermal conductivity of the PUR was about 1.8 %. Furthermore, assuming total air filled PUR, the difference in total thermal conductivity between light and dark samples was about 1.3 %. The share of radiative heat transport will be lower for lower temperatures and therefore the average change in the total thermal conductivity in the temperature range 40 °C to 90 °C for the Cyklopentane blown foam was calculated to be about 1.5 %.

Both the light yellow and the dark brown samples went through ageing processes at two temperature levels. This means that the extinction coefficient of the light yellow foam had also increased over time, the increase was just not as much as for the dark brown PUR. It is therefore probable that the total increase in radiative heat transfer for the entire service lifetime of the PUR will be larger than the result presented in Table 1. Thus the change of overall thermal conductivity of 1.8 % should be interpreted as a minimum increase.

3.3. Influence of density

The PUR used in the project had a mean density of 84 kg/m^3 which compared to other PUR can be considered high. In general the higher density the higher extinction coefficient, this means that the results presented in Table 1 can be an overestimation of the extinction coefficient compared to an ordinary PUR.

The density of the PUR also affects the apportionment between the heat transport mechanisms in the PUR. The higher the density the more heat is transferred in the PUR matrix. This means that for PUR with higher density the radiative heat transfer has a smaller effect on the total thermal conductivity compared to PUR with lower density. Thus a PUR with lower density than 84 kg/m^3 an increase in *extinction coefficient* of 22.0 % will probably affect the total thermal conductivity with more than 1.8 %.

3.4. Influence pore size

Since the cell size of the PUR itself is decisive for the radiative heat transfer a cell size analysis was performed where the cell sizes for each sample was determined. The average cell size was found to be about 145 µm without any significant difference between the samples. This means that the difference in radiative heat transfer cannot be explained by differences in cell size.

4. Conclusions

This project investigates the effect of oxidation on the total thermal conductivity of PUR used in district heating pipes. The radiative heat transfer were determined using FTIR on different sections of an aged PUR insulation. Results indicated that the extinction coefficient was about 22.0 % larger in the regions closest to the casing pipe compared to the regions closest to the steel pipe. However, since the radiative heat transport only accounts for a minor part of the total heat transport in the insulation, the difference in total thermal conductance is about 1.8 %.

In order to fully understand how the radiative heat transfer in the PUR insulation changes over time, it is necessary to perform same type of the measurement on a PUR after production and aged PUR. Since the results presented in this study were related to two aged PUR, it is possible that increase in the total thermal conductivity is even higher in comparison between newly produced PUR and aged PUR.

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