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Sektion 6 a

Heat distribution – pipe properties

Thermal conductivity of polyurethane foam - best performance

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Thermal conductivity of polyurethane foam Best performance

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Introduction

Polyurethane (PU) foam has been used for pre-insulated district heating pipes for many years. Originally CFC-11 (Freon 11) was used as a blowing agent for this type of foam. Due to the very low thermal conductivity of CFC-11 the insulating properties of the foam became excellent. After the ban of CFC-11 in the 1990's there has been a very hard competition to find alternative blowing agents and upgraded material properties to achieve an insulation capacity in the same magnitude as earlier.

The development work has up till today resulted in a PU-foams with smaller cells and lower densities than earlier and with cyclopentane in combination with carbon dioxide as blowing agent. The vapour pressure of cyclopentane is 34 kPa at 20°C and the amount of cyclopentane in gas phase will therefore be limited at room temperature. When the foam is produced the cell gas pressure needs to be at least just over atmospheric level (100kPa). Consequently the cell gas mixture will often be saturated with cyclopentane (about 34 % by volume at 20°C) but the main gaseous compound will be carbon dioxide, originating from the chemical reaction between isocyanate and water. In some cases isopentane, that has a lower vapour pressure than cyclopentane, is also added.

The thermal conductivity of an insulating foam depends on the conductivity of the cell gas mixture, the conductivity of the solid polymer and the radiation between cells. The radiation of heat has been reduced by making the cells smaller and the conduction of heat in the solid polymer has been reduced by decreasing the foam density. However, conduction in the cell gas mixture stands for the main part of the thermal conductivity of a foam. About 65-80% of the insulation capacity of a foam is due to the cell gas mixture while cell size and density stands for the rest.

A number of requirements have been put on the PU-foam used for district heating pipes. One of the top priorities is the thermal conductivity and it is therefore important that the accuracy of the conductivity measurements is high. The requirements for determination of the thermal conductivity of pre-insulated pipes are stated in EN253:2003. However the test procedure is quite complicated and the spread in results are some times too high. In the European standardization work, CEN/TC107, two Round Robin projects have been conducted in order to minimize the deviation between laboratories both regarding test procedure and equipment. At this moment no test procedure is described for flexible pipes.

There is struggle to reduce the thermal conductivity to a minimum. How far can we go? In this project we have studied the thermal conductivity of six different PU-foams for pre-insulated as well as for flexible pipes. The foams are of the "latest generation" and manufactured by three different raw material producers.

Experimental

All relevant material properties concerning thermal conductivity were determined. Cell size and cell structure were determined by scanning electron microscopy (SEM), cell gas content by cell gas analysis by gas chromatography [1] and thermal conductivity by measurements in a Heat Flow Apparatus [2].

SEM photos of the six different PU-foams are shown in Figure 1.

Foams with normal cellular structure, cell size 0,25-0,30 mm



Standard foam for DH-pipes (Type A)



Standard foam for DH-pipes (Type B)

Foams with microcellular structure, cell size 0,10-0,20 mm



Semi-flexible foam (Type C)



Semi-flexible foam (Type E)



Microcellular rigid foam (Type D)



Semi-flexible foam (Type F)

Figure 1. SEM photos of the six different PU-foams. Type A and B are foams designed for traditionally (non-continuous) made pre-insulated district heating pipes and type C-F are microcellular foams for rigid and flexible pipes.

Calculations

The thermal conductivity of PU foam is due to three modes of heat transfer, conduction in the cell gas mixture, conduction in the solid polymer and radiation between the cell walls.

 $\lambda_{total} = \lambda_{gas} + \lambda_{solid} + \lambda_{radiation}$

The thermal conductivity due to conduction in the cell gas mixture has been calculated using Wassiljewa's equation [3].

$$\lambda_{gas} = \sum_{i=1}^{n} \frac{y_i \cdot \lambda_i}{\sum_{j=1}^{n} y_j \cdot A_{ij}} \qquad \text{where} \quad A_{ij} = \frac{\varepsilon \left[1 + \left(\frac{\lambda_{iri}}{\lambda_{irj}}\right)^{\frac{1}{2}} \cdot \left(\frac{M_i}{M_j}\right)^{\frac{1}{4}}\right]^2}{\left[8\left(1 + \frac{M_i}{M_j}\right)\right]^{\frac{1}{2}}} \qquad (Eq. 1)$$

Input data:

Gas	$\lambda_{10} (W \cdot m^{-1} \cdot K^{-1})$	$\lambda_{50} (W \cdot m^{-1} \cdot K^{-1})$	Molecular weight
Air [4]	0,0250	0,0282	30
Carbon dioxide [4]	0,0157	0,0184	44
Cyclopentane [5]	0,0127	0,0155	70

The conduction of heat in the solid PU structure is a combination of the heat flow in the cell walls and the struts. The thermal conductivity (λ_{PU}) of the solid PU polymer from crushed foam samples is reported to be 0,26 W·m⁻¹·K⁻¹ [6] and the fraction of solids in the struts (f_s) has been reported to 0,8 [7]. The thermal conductivity [7] can be described by

$$\lambda_{conduction} = \lambda_{PU} \cdot \frac{1}{3} \cdot f_s \cdot (1 - \delta) + \lambda_{PU} \cdot \frac{2}{3} \cdot (1 - f_s) \cdot (1 - \delta) \qquad \text{where} \quad \delta = 1 - \frac{\rho_f}{\rho_s} \quad (\text{Eq. 2})$$

The radiation between the cell walls has been calculated by the Rossland equation with the extinction coefficient of the cell wall material $K_w = 60000 \text{ m}^{-1}$ suggested by Glicksman [7].

$$\lambda_{radiation} = \frac{16 \cdot \sigma \cdot T^3}{3 \cdot K} \qquad \text{where} \quad K = 4,10 \cdot \frac{\sqrt{\frac{f_s \cdot \rho_f}{\rho_s}}}{d} + \left[\frac{(1-f_s) \cdot \rho_f}{\rho_s}\right] \cdot K_w \qquad (\text{Eq. 3})$$

Symbols:

Κ	Extinction coefficient	m^{-1}
М	Molecular weight	kg·kmole ⁻¹
Т	Temperature	Κ
d	Cell diameter	m
$\mathbf{f}_{\mathbf{s}}$	Fraction of solid in strut $f_s=0.8$	-
y _i	Molar fraction of gas	-
δ	Volume fraction of voids or cell interiors	-
λ	Thermal conductivity	$W \cdot m^{-1} \cdot K^{-1}$
$ ho_{f}$	Density of PU foam	kg·m ⁻³
ρ_s	Density of PU polymer	kg·m ⁻³
σ	Stephan Boltzman constant = $5,7 \cdot 10^{-8}$	$W \cdot m^{-2} \cdot K^{-4}$

The results from the calculation model can be compared with measurements of the total thermal conductivity using the heat flow apparatus. The input parameters used in the calculations are taken from the determination of cell gas content, cell size measurements by SEM and density measurements. The influence of the foam density on the thermal conductivity of a microcellular cyclopentane blown foam (cell size = 0,15mm) is shown in Figure 2.



Figure 2. Calculated contributions of radiation, conduction in cell gas mixture and PU matrix to the thermal conductivity of a cyclopentane blown PU-foam with a cell size of 0,15 mm which corresponds to a microcellular foam.

Results

	Foam	Density kg·m ⁻³	Cell size*	$\begin{array}{c} \lambda_{10} \\ W {\cdot} m^{\text{-1}} {\cdot} K^{\text{-1}} \\ {}_{x10^{\text{-3}}} \end{array}$	$\begin{array}{c} \lambda_{40} \\ W {\cdot} m^{\text{-1}} {\cdot} K^{\text{-1}} \\ {}_{x10^{\text{-3}}} \end{array}$
А	Rigid foam	64	0,26-0,31	22,16	-
В	Rigid foam	55	0,29-0,31	22,10	25,51
С	Microcellular Rigid	68	0,15-0,25	21,32	24,43
D	Microcellular Semi-flexible	66	0,12-0,15	20,24	-
Е	Microcellular Semi-flexible	72	0,10-0,15	21,85	25,18
F	Microcellular Semi-flexible	57	0,18-0,22	21,06	24,59
B C D E F	Rigid foam Microcellular Rigid Microcellular Semi-flexible Microcellular Semi-flexible Microcellular Semi-flexible	55 68 66 72 57	0,29-0,31 0,15-0,25 0,12-0,15 0,10-0,15 0,18-0,22	22,10 21,32 20,24 21,85 21,06	25,51 24,43 - 25,18 24,59

Table 1. Measurements of thermal conductivity.

* measured in two perpendicular directions

Foam	Total Pressure ^Φ kPa	Oxygen Vol-%	Nitrogen Vol-%	Carbon dioxide Vol-%	Cyclo- pentane Vol-%	Iso- pentane Vol-%	Water vapor Vol-%	Others Vol-%
А	117	1,6	0,9	61	34	-	1,0	0,8
В	126	0,2	0,8	65	32	2	0,4	0,5
С	105	0,3	1,1	44	35	16	1,6	1,5
D	87	1,5	1,5	61	32	-	1,0	3,1
Е	98	0,5	1,9	61	35	-	0,6	0,9
F	104	0,2	0,9	67	30	1	0,7	0,5
x								

Table 2. Measurements of cell gas content.

 $^{\Phi}$ at temperature of analysis = 24°C



Figure 3. The influence of temperature on the thermal conductivity is represented by a straight line in the temperature range 10 - 40°C. The relationship is based on measurements on 5 foam samples. The thermal conductivity can be written: $\lambda(T)=0,02064 + 11,28 \cdot 10^{-5} \cdot T \quad (W \cdot m^{-1} \cdot K^{-1})$

As the thermal conductivity strongly depends on the temperature it is important to establish this relation. For most PU-samples the thermal conductivities have been determined at various temperatures (Figure 3). Due to variation in density, cell size and structure and cell gas content there is a difference in thermal conductivity between the PU-samples. However, the dependency of temperature on the thermal conductivity seems to be the same for all foams within the temperature range 10-40°C.

Discussion

Comparison of the different foams

The foaming conditions when producing the PU-boards (A-F) were very good and it is not likely that a pipe producer, at present, would manufacture foams with substantially superior insulating properties. The thermal conductivities presented represent the lowest thermal conductivities available today.

For the foams studied, representing best available foam today, the thermal conductivity for "standard foams" for pre-insulated pipes was 22,1-22,2 mW·m⁻¹·K⁻¹ at 10°C and 25,9-26,3 mW·m⁻¹·K⁻¹ at 50°C (density range 55-64 kg·m⁻³). For the "microcellular" foams the corresponding figures were 20,2-21,9 mW·m⁻¹·K⁻¹ at 10°C and 24,6-25,4 mW·m⁻¹·K⁻¹ at 50°C (density range 57-72 kg·m⁻³).



Figure 4. Comparison between measured (Heat Flow Meter Apparatus - ISO 8301) and calculated thermal conductivity of six different PU-foams (A-F).

When comparing calculated and measured values a difference up to 3% can be observed. This spread may be due to the absence of knowledge about how foam morphology influences radiation and conduction in the solid PU-material and lack of knowledge on the true values of the blowing agent thermal conductivities.

Different values of the thermal conductivity of gases have been given in literature. An overview of the thermal conductivities of some blowing agents is given in [8]. For cyclopentane conductivities in the range 11,3 - 12,4 mW·m⁻¹·K⁻¹ has been given. Thus, the choice of value of the thermal conductivity will influence the calculations. Another

important factor is how the interactions between different gasses, e.g. cyclopentane and carbon dioxide, should be calculated. Different models give different results.

It is noticed that the difference between "standard foam" and "microcellular foam" is not very large. The cell size of the microcellular foam is approximately half of the "standard foam" and the thermal conductivity is about 1-2 mW·m⁻¹·K⁻¹ lower.

The differences in density $(55-72 \text{ kg} \cdot \text{m}^{-3})$ between the tested foam samples make the comparison of the thermal conductivity more difficult. Therefore a re-calculation of the thermal conductivity to a normalized density of 60 kg·m⁻³ has been made for all foams. This re-calculation results in minor changes and the results are presented in figure 5.



Figure 5. Thermal conductivity at 10° C and 50° C of the different foam samples as a result of a re-calculation to a foam density of $60 \text{ kg} \cdot \text{m}^{-3}$.

The thermal conductivity of foam of a "normalized" density (60 kg·m⁻³, cell size 0,3 mm) is for a standard foam for district heating pipes 26,3-26,8 mW·m⁻¹·K⁻¹ at 50°C and for a microcellular foam 24,2-25,8 mW·m⁻¹·K⁻¹ at 50°C.

How far can the thermal conductivity be reduced?

Small cell size, low foam density, low thermal conductivity of the solid PU-material and a cell gas mixture with a high percentage of cyclopentane shoud be the best option. The reduction of density of the foam will decrease conduction in the solid PU-structure but increase radiation due to thinner cell walls.

Today a mixture of isopentane, cyclopentane and carbon dioxide is used for some foams. According to [8] the conductivity of isopentane is in the range $13,4 - 14,8 \text{ mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ and thermal conductivity of carbon dioxide is 15,7 [4]. Thus, the presence of isopentane will probably lower the conductivity of the new gas mixture in comparison to the mixture cyclopentane/carbon dioxide. The use of isopentane is also expected to contribute to a better a long term thermal performance of a foam since isopentane will diffuse much slower than carbon dioxide.

The cell gas mixtures of the studied PU-boards were almost the same (except foam C with 16 vol-% isopentane), 30-35 vol-% of cyclopentane, 61-67 vol-% of carbon dioxide and 3-4 vol-% of air. The thermal conductivity of the corresponding mixtures is 0,0180-0,0184 W·m⁻¹·K⁻¹ at 50°C.

If the different contributions (radiation + conduction in solid = 0,004, conduction in cell gas = 0,018) to the thermal conductivity are summarized a value of 0,022 W·m⁻¹·K⁻¹may be reached. A foam with this insulating capacity must have a very small cell size (<0,1 mm) and a low density (< 50 kg·m⁻³). The best foam in this study has a thermal conductivity of 0,024 W·m⁻¹·K⁻¹ at 50°C.

If a substantially lower thermal conductivity should be reached, another blowing agent than cyclopentane must be used.



Figure 6. Calculated contributions of radiation and conduction in the solid polymer. In the density range 45-60 kg/m³ and cell size range 0,075-0,15 mm which corresponds to microcellular foam, the contribution to the thermal conductivity is estimated to be 4-6 $\cdot 10^{-3}$ W·m⁻¹·K⁻¹. Thermal conductivity of the solid PU-material has been chosen to 0,22 W·m⁻¹·K⁻¹ [9].

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