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APPLICATION OF NUMERICAL MODELING TO STUDY OF DISPERSION OF BHT IN POLIETHYLENE PIPES

ZASTOSOWANIE MODELOWANIA NUMERYCZNEGO DO BADANIA TRANSPORTU BHT W PRZEWODACH POLIETYLENOWYCH

Abstract: PE-HD water pipes are exposed to adverse environmental conditions, both during production and their subsequent use in the construction industry. Organic compounds migrating into water may lead to deterioration of water quality, especially its taste and odor. Commonly used antioxidant BHT and its products of degradation are leaching into water as a result of degradation of the pipes material. This paper presents the results of laboratory tests considering changes of BHT concentration in the water circulating in the PE-HD pipe of 30 m length as well as our numerical studies. Numerical calculations were performed using the commercial software Fluent, Ansys Inc., based on the computational fluid dynamics (CFD). The analyses of water samples confirmed the migration of the tested antioxidant from the pipe material into water. The results of numerical analysis showed the good agreement with the measured values.

Keywords: antioxidants migration, BHT, PE-HD pipes, numerical modeling

Introduction

Polyethylene is nowadays the material which application to the construction of new and renovation of old networks and water supply systems [1]. Water pipes made of PE-HD are exposed to the adverse environmental conditions, both at the production and their later use in construction. Polyethylene pipes exposure to UV radiation, high temperature, mechanical stress, oxidative compounds used for water disinfection may lead to damage and degradation of pipes material and release of organic compounds form the material of water pipes [2, 3].

In order to improve the mechanical and physical properties and to extend the life of pipes made of PE-HD, the organic and inorganic compounds such as: stabilizers, dyes, fillers are added to the material at the stage of production [3-7]. Stabilizers are substances designed to improve polymer resistance to aging in time of its processing as well as during the use of material. Among stabilizers the following can be distinguished: thermal stabilizers, light stabilizers, antioxidants and biological stabilizers [8]. Antioxidants are used in the production of almost all commercial polymers in the amount of up to 2% [9].

Researches in numerous scientific reports show that organic compounds migrating into the water can cause changes of its organoleptic properties, deterioration of taste and smell [5, 7, 10-12]. Compounds responsible for the deterioration of the organoleptic properties of water include BHT antioxidant (4-methyl-2,6-di-tert-butyphenol), or products of its degradation as well as alkylobenzenes, ketones or esters [13]. Researches performer by *eg* Mikami et al [14], Matsuo et al [15], Fernandez-Alvarez et al [16] shown that BHT released into water is degraded as a result of oxidation reaction and the following compounds may

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be formed: BHT-COOH (3,5-di-tert-butyl-4-hydroxybenzoic acid), BHT-OH (2,6-di-tert-butyl-4-(hydroxymethyl)phenol), BHT-CHO (3,5-di-tert-butyl-4-hydroxybenzaldehyde), BHT-Q (2,6-di-tert-butylcyclohexa-2,5-diene-1,4-dione).

BHT is a fat-soluble antioxidant which found wide application in the polymer, fuel, food and pharmaceutical industry [17]. According to the Directive 67/548/EWG on the classification of dangerous chemicals, BHT is a flammable, toxic and irritant compound. This compound is considered as safe to use if the amount of the antioxidant in food does not exceed 0.02% of the total fats and oils [17]. BHT is also used to improve the stability of pharmaceuticals, fat-soluble vitamins and cosmetics [18]. Addition of BHT to plastics prevents polymer decomposition during its processing, and extends life of the finished products [19].

Modeling of water quality in distribution networks is now becoming a very useful tool supporting designing process and network management. Computational Fluid Dynamics methods (CFD) allow to calculate dispersion of contaminants in water pipes at different flow conditions, having regard to chemical reactions in the water and on the walls of pipes [12, 20]. CFD is now being used with great success in many areas of science and technology, including the modeling of hydraulic parameters in water supply systems, as well as in the sewer systems [21, 22]. One of the most popular commercial CFD software with wide range of computing capabilities is Fluent, Ansys Inc. [23, 24]. The literature contains many examples of use of Fluent software in a variety of fluid flow simulation calculations [23-25].

Mathematical description of water movement in water pipes applied in Fluent model is based on the laws of mass and momentum conservation and the Navier-Stokes equation. These equations are solved with the proper set of computational simplifications, boundary conditions and initial data. [23, 26]. Qualitative calculations including transport, mixing and disintegration of chemical compounds in the water, reacting or not with other components of the mixture, are usually based on the equation of mass conservation for a given component of the mixture [27].

This paper presents the laboratory tests of BHT concentration changes in the water circulating in the loop with a length of 30 m, made of new PE-HD pipes, and numerical investigations reflecting the laboratory experiment. Numerical calculations were performed using the commercial software Fluent, Ansys Inc., on the computational fluid dynamics (CFD). Numerical calculations were used for quantitative evaluation of the analyzed antioxidant in the water having contact with the PE-HD pipes.

Materials and methods

Measuring installation

Laboratory measurements of changes in the concentration of BHT in the water were carried out on a specially prepared laboratory installation (Fig. 1). It was built with new PE-HD 80 pipes, PN 12.5, with a diameter of 32x3.0 mm produced in Poland in accordance with PN-EN 12201-2:2011 purchased directly from the manufacturer. Pipeline length was 30 m, inner surface of pipes was equal to 2.45 m^2, and the volume of water in the analyzed system - 15.9 m^3.
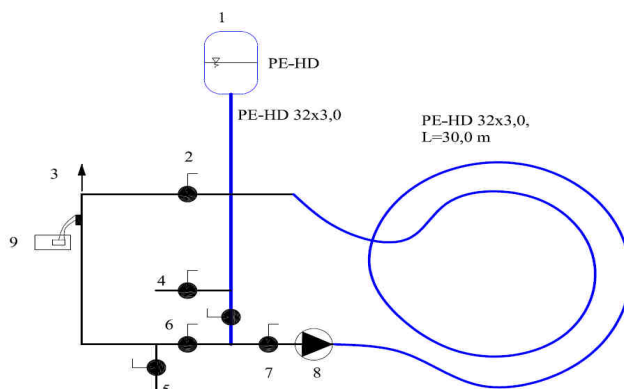
Fig. 1. Scheme of the measuring installation: 1 - water tank to fill up installation, 2, 6, 7 - stop valve, 3 - deaerator, 4, 5 - drain valve, 8 - centrifugal pump, 9 - PortaFlow 300 ultrasonic flowmeter

Before testing, measuring installation was rinsed with the deionized water prepared with Milli-Q (Millipore, Molsheim, Germany) providing at least 3-fold exchange of water in the system. Then, the system was filed with test water. Basic parameters of deionized water used for rinsing and then for filling the system were as follows: TOC ≤ 0.5 ppb, resistivity 18.2 MΩm. Setting of water flow in the system equal to 0.6 m/s (Re = 13650) was maintained with the help of WILO MVIe 203-1/16/E/3-2/B centrifugal pump. Water samples were collected into testing glass vials with a capacity of 40 ml in accordance with the schedule of research, and then they were subjected to the analyses by gas chromatography Trace Ultra Thermo coupled with Polaris Q (GC-MS) mass spectrometer. Prepared samples were subjected to stationary phase extraction using a blue SPME fiber. Gas chromatography working conditions were as follows: analytical column RTx5 (Dioxin) 60 m × 0.25 mm df = 0.15 μm by Restek, as a carrier gas He (99.9996%) was used flowing with intensity of 1.2 cm^3/min. Working conditions of Polaris Q-Thermo mass detector were as follows: ion source temperature - 250ºC, transfer line temperature - 275ºC. Results of the analysis were retention spectra (area under peak of characteristic ion - base peak - 205) and mass spectra confirming the presence of the analyzed compound.

Results of laboratory measurements

Results of laboratory measurements of water samples, carried on GC-MS are shown in Table 1.

Table 1

BHT concentration in the water from the measuring stand

Sample No	A	B	C	D	E	F	G	H	I	J
Time [hr]	0	2	4	6	11	24	48	72	100	147
BHT concentration [μg·dm^{-3}]	20.8	19.8	41.1	49.5	60.9	93.9	115.3	138.4	177.6	194.2
Water temperature [ºC]	21.6	22.2	22.4	22.9	23.5	22.3	22.5	23.0	24.1	25.0

Detectability limit for water samples marked by GC-MS was 2.7 ng·dm^{-3}, while quantification limit (*QL*) was 8.1 ng·dm^{-3}.

For the first 40 hours of measurements (samples from A to G, samples marking in accordance with Table 1), counting from the start of the experiment, the fastest BHT growth in the water was observed.

The revealed results of measurements of the BHT concentration in the water indicate that after about 70 hours, counting from the start of the stand, in the samples relatively small increase of antioxidant content has been observed. During the duration of measurement, 10-fold concentration increase was observed, from 20.8 μg·dm^{-3} (in the first hour of measurement, *t* = 0) to 201.8 μg·dm^{-3} (in the last hour of measurement *t* = 147 h). Obtained results of BHT concentration in water are comparable with the values obtained by Widomski et al [25] for BHT migrating from PE-HD 100 pipes.

CFD modeling

Numerical modeling of selected antioxidant (BHT) propagation in the analyzed water, moving with constant mean velocity, was performed using the finite element method in a commercial program Fluent 6.3 which is the part of Ansys 14.0 computational package, Ansys Inc. Computational domain range reflecting the capacity of water filling measuring installation consisted of 149783 finite elements and 179090 junctions. While creating geometric model reflecting measuring installation, necessary assumptions and simplifications were accomplished. The model does not include centrifugal pump - water movement with constant rate in the model was obtained by giving a constant flow rate to selected, small control volume [25].

In numerical research, in order to determine BHT concentration in the water the following assumptions were made: simulation time according to the duration of the laboratory measurements; numerical calculations were carried out on the basis of the law of conservation of mass, momentum and energy, as well as in relation to viscous, dual-equation model of turbulence *k-ε* [28]; the assumed value of the diffusion coefficient of BHT from the material surface into the water equal 7.15E-16 m^2·s^{-1} [29]; time step length - 60 s; boundary condition of contaminants transport: variable in time, reflecting concentration value of BHT in the boundary layer, described as the mass fraction of the analyzed antioxidant.

Table 2

Input data to simulation calculations

Average flow rate	Water temperature	Water viscosity coefficient	BHT molar mass	Coefficient of BHT diffusion from the material into the water	Boundary condition Dirichlet, mass fraction	Time
[m·s^{-1}]	[K]	[Pa·s]	[g·mol^{-1}]	[m^2·s^{-1}]	[-]	[hr]
0.63	288	0.001308	220.35	7.15E-16	9.15E-07	*t* = 0 - *t* = 24
					2.37E-07	*t* = 25 - *t* = 147

Changes of BHT concentration caused by water sampling for chemical analyses, and the addition of ultrapure water in order to fill the capacity of measuring stand was not included in the calculation, due to its negligible values. The model does not take into

account the chemical reaction of antioxidant degradation in the water. Input data assumed for the calculation is presented in Table 2.

Results and discussion

The calculation results of BHT transport in water included three-dimensional distribution of mass fraction of the analyzed antioxidant inside the polyethylene pipe. The results of numerical calculations of BHT concentration changes in water are presented in Table 3.

Table 3

Results of numerical calculations of BHT concentration changes in water

Time	[hr]	0	2	4	6	11	24	48	72
BHTconcentration	[µg·dm^{-3}]	0	71.5	76.6	77.7	79.1	82.2	109.0	134.0

The BHT mass fraction distribution in water for the flow rate $v = 0.63$ m·s^{-1} indicates that the concentration increases during the time duration of experiment. During the simulation calculations, the increase of mass fraction value has been observed from $7.15 \cdot 10^{-8}$ (in the 2nd hour) to $1.85 \cdot 10^{-7}$, which corresponds to the following concentrations: from $c = 71.5$ µg·dm^{-3} to $c = 185.0$ µg·dm^{-3}.

Figure 2 shows BHT concentration changes in time for the measured and calculated values obtained in the experiment.
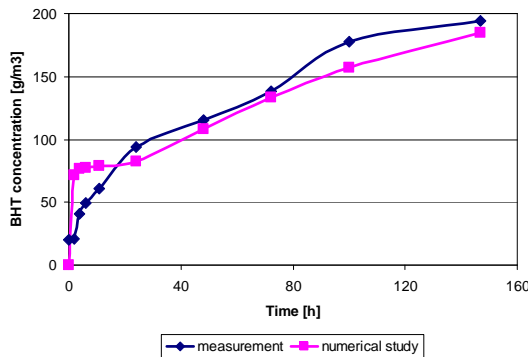

Fig. 2. BHT concentration change in time obtained for the measured and calculated values

Increase of BHT content in water observed during numerical calculations, is consistent with the measured values. In both cases, more than 2.5-fold increase of BHT in the water has been observed.

Average values of the BHT concentration in water obtained by numerical calculations, show quite good agreement with the measured values. Correlation coefficient $R = 0.92343$ and determination coefficient $R^2 = 0.83436871$ were determined in Statistica 7.1 for $p = 0.05$.

Conclusions

The conducted laboratory measurements and numerical calculations show an increase of BHT concentration in water. During laboratory research, in 147th hour, counting form the start of our experiment almost 10-fold increase of BHT in the water (from $c_0 = 19.8$ µg·dm^{-3} to $c_{147} = 194.2$ µg·dm^{-3}). The range of obtained calculation value were $c_2 = 71.5$ µg·dm^{-3} to $c_{147} = 185.0$ µg·dm^{-3}. Numerical calculations of BHT spreading in the water conducted by finite elements method allowed to obtain the results characterized by the considerable compliance with the values of laboratory measurements. The calculated final BHT content was lower that the measured value by 4.7%. Values of the coefficients of: correlation $R = 0.92346$ and determination $R^2 = 0.83436871$ confirmed that a good agreement with compared sets has been achieved. Calculated values of mean square error RMSE = 0.024644861 and Nash-Sutcliff's coefficient $E = 0.761738$ reveal good prognostic ability and efficiency of the model. However, to obtain such a good agreement of the results, it was necessary to introduce the two values of boundary condition for mass transport ($t = 0$-24 h - $9.15 \cdot 10^{-7}$, $t = 25$-147 h - $2.37 \cdot 10^{-7}$). It may be caused by omitting the chemical reaction of BHT decomposition in the water with oxygen in the numerical model. The presented measurements and numerical calculations shown the necessity to conduct further research with regard to chemical models of the analyzed contaminant mass transport, as well as to examine and describe the kinetics of the reaction of BHT decomposition in the flowing water and further including the received results into the developed numerical model.

Acknowledgement

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ZASTOSOWANIE MODELOWANIA NUMERYCZNEGO DO BADANIA TRANSPORTU BHT W PRZEWODACH POLIETYLENOWYCH

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Abstrakt: Przewody wodociągowe wykonane z PE-HD narażone są na wpływ niekorzystnych warunków zewnętrznych zarówno na etapie produkcji, jak i ich późniejszego wykorzystania w budownictwie. Związki organiczne migrujące do wody mogą powodować zmianę jej właściwości organoleptycznych, pogorszenie smaku i zapachu. W wyniku degradacji materiału przewodów do wody wymywany jest m.in. powszechnie stosowany przeciwutleniacz BHT lub produkty jego degradacji. W pracy przedstawiono wyniki badań laboratoryjnych zmian stężenia BHT w wodzie krążącej w przewodach z PEHD oraz badań numerycznych. Obliczenia numeryczne wykonano z wykorzystaniem komercyjnego programu Fluent, Ansy Inc., bazującego na obliczeniowej dynamice płynów (CFD). Analiza próbek wody potwierdziła migrację przeciwutleniacza z materiału rury do wody. Wyniki analiz numerycznych dały dobrą zgodność z wartościami pomierzonymi.

Słowa kluczowe: migracja przeciwutleniaczy, BHT, rury PEHD, modelowanie numeryczne