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Laboratory evaluation of rubber linings used in flue gas desulphurization plants by the gravimetric method and impedance spectroscopy

Special cells made of austenitic steel were employed to carry out accelerated tests of lining materials in the autoclave at elevated temperature and at a pressure gradient along the sample's thickness. The tests were carried out on three kinds of rubber linings: prevulcanized soft two-ply lining based on bromobutyl rubber, selfvulcanizing two-ply lining based on bromobutyl rubber and prevulcanized lining based on chlorobutyl rubber. Distilled water, 1% aqueous solution of HCl and aqueous solution containing 50 g/dm^3 of sulphuric acid and 26 g/dm^3 of sodium bisulphate (IV) were used as the working medium in the tests. The temperature of the working medium in the autoclave was kept at 110±2 °C and the sample exposure time amounted to 48 hours. The change in the mass of the samples after the proper time of exposure in the autoclave was determined by the gravimetric method. A measuring system made up of an Agilent 4294A high-frequency impedance analyzer and a low-frequency impedance analyzer with a Keithley 428 current/voltage transducer was used to perform measurements in a frequency range from 0.1 mHz to 10 MHz at activation with an voltage amplitude of 1 V$_{RMS}$. The impedance measurement results show that despite the severe corrosive conditions in the autoclave and the gain in the mass of the samples, the tested coating materials did not undergo significant degradation during their exposure and keep good dielectric and protective properties.

1   Introduction

The materials used for construction of flue gas desulphurization (FGD) plants, including rubber linings, should remain in failure-free service for at least ten–twenty

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years. As the materials wear out as a result of chemical action, high temperature, thermal shock and abrasion, it is necessary to repair or replace them, which entails downtimes, resulting in considerable financial losses [1,2]. From the economic and environmental points of view it is vital to select proper materials for the particular components working in different aggressive environments [3]. For several reasons this task is quite difficult. First of all, novel materials are the subject of ongoing research in many industrial and academic research laboratories and their verification in the real service conditions takes a long time. Before sufficient knowledge about the behaviour of a novel material in FGD plant is gained, new novel materials appear on the market. Therefore it becomes necessary to employ methods enabling one to determine material resistance in a relatively short time. The best solution is to use accelerated testing methods in which samples of the tested material are subjected to the action of an environment much more aggressive than the real one. On the other hand, this approach is more likely to lead to false conclusions. Another difficulty is posed by the variation of FGD operating conditions over time as a result of, e.g., an attempt to recover more heat whereby the temperature of the exhaust gases changes. Legal regulations, e.g., the necessity to burn biomass, may have serious consequences for FGD operation and so for the behaviour of the materials. This means that the material previously resistant enough may turn out to be unreliable.

The organic linings, including rubber linings, working in FGD plants are most degraded as a result of water vapour penetrating into the material where it undergoes condensation, causing an increase in the material's volume and its separation from the base [4]. Therefore in an accelerated test, such conditions should be created in which water vapour penetration will proceed much faster than in the real conditions. It is also important that conditions in the test chamber most closely simulate the ones prevailing in FGD systems. Accelerated corrosion tests were carried out in a system in which differential pressure was produced on both sides of the samples. The differential pressure constituted the driving force for water vapour and other volatile matter penetration into the tested material.

2 Methodology and scope of research

2.1 Test cell

Cells made of austenitic steel (Figs. 1 and 2), for the accelerated testing of coating materials in an autoclave at elevated temperature and at a pressure gradient along the sample's thickness, were designed and built. Thanks to the use of the

autoclave the penetration of water vapour (and other gaseous components of the solution) into the tested material and so the degradation of the latter can be speeded up.
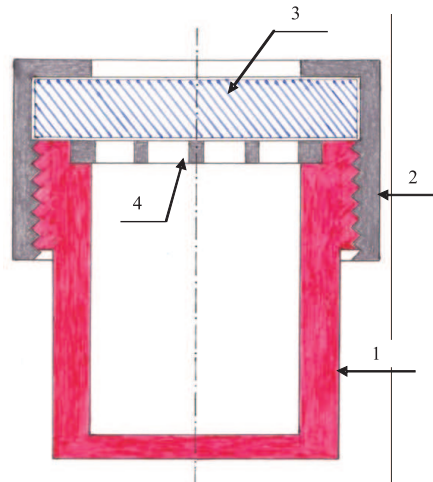

Figure 1. Scheme of cell for testing coating materials and linings in pressure gradient conditions: 1 – steel cylinder, 2 – sealing ring fixing tested sample, 3 – tested sample, 4 – steel screen supporting sample.

Figure 2. Cells for testing of rubber linings in autoclave.

Three kinds of rubber linings: prevulcanized soft two-ply lining based on bromobutyl rubber (denoted as sample A), two-ply self-vulcanizing lining based on bromobutyl rubber (denoted as sample B) and prevulcanized lining based on chlorobutyl rubber (denoted as sample C) were subjected to the tests. A 4 mm thick and 40 mm in diameter rubber sample would be formed, placed in the upper

part of the cell (Fig. 1) and pressed against the steel cylinder (1) by means of the sealing ring (2). Samples would be placed on a Teflon stand in the upper part of the autoclave, above the working liquid level. Each time three cells, each containing a different sample, would be placed inside the autoclave. There was distilled water or an electrolyte solution, imitating in the autoclave operating conditions for FGD plant. The temperature of the working medium in the autoclave was kept at 110 ± 2 °C and the time of exposure of the samples amounted to 48 hours. Distilled water, 1% aqueous solution of hydrochloric acid (solution I) and aqueous solution containing 50 g/dm^3 of sulphuric acid and 26 g/dm^3 of sodium bisulphate(IV) (solution II) were used as the working medium in the tests. In the case of solution I, there was gaseous HCl besides water vapour in the autoclave, whereas in the case of solution II, besides water vapour, gaseous SO_2 liberated in the reaction of sulphuric acid with sodium bisulphate (IV) was present.

2.2   Electrochemical impedance spectroscopy investigations

Electrochemical impedance spectroscopy (EIS) measurements consist in activating the electrode with a low-amplitude sinusoidal voltage signal in a wide frequency range and analyzing the system response. Usually three-electrode system comprising the tested electrode, auxiliary platinum electrode and reference calomel electrode is used for this purpose. Besides the electrochemical vessel, testing set consisted of potentiostat, sinusoidal oscillator, response analyzer, controlling and recording unit and test chamber.

The tested rubber materials are characterized by very high impedance, amounting to above 100 GΩ for a few millimetres thick rubber linings. Therefore the traditional systems for impedance investigations are inadequate in this case [5]. A solution was found in the form of a new method in which the measuring system consists of a function generator and a current amplifier and is additionally equipped with an appropriate attachment for measuring dielectric materials [6]. The method was developed in the Micro- and Nanostructures Metrology Unit at the Faculty of Microsystems and Photonics at Wrocław University of Technology. The tested sample would be placed directly between two covers without the use of electrolyte solutions.

A measuring system made up of an Agilent 4294A high-frequency impedance analyzer and a low-frequency impedance analyzer incorporating Keithley 428 current/voltage transducer was used in the tests. Measurements were performed in a frequency range from 0.1 mHz to 10 MHz at activation with an AC voltage amplitude of 1 V_{RMS}. A special grip (Fig. 3) was constructed to make repeatable measurements of the poorly conductive flexible samples possible. Its top

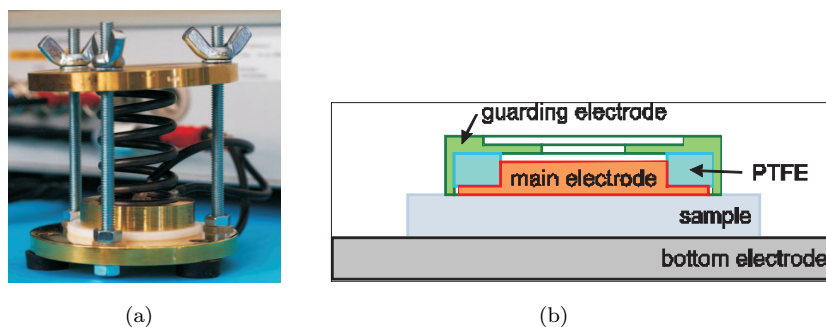(a)   (b)

Figure 3. Custom-built fixture: photograph with PTFE (polytetrafluoroethylene) sample (a), and section view of the electrodes (b).

electrode consists of the main and guarding electrodes. Such solution eliminates the influence of parasitic capacitance and fringe field on the measurement result and minimizes the surface leakage current [7]. The force with which the top electrode squeezed the sample was controlled by the compression of the spring and it was equal to 100 N for each sample despite of its thickness. Measurements were started in one hour after placing the sample in the fixture to allow the elastic sample to achieve good and stable contact with the fixture.

3   Results and discussion

After the samples were taken out from the autoclave the change in their mass was determined and their appearance was visually evaluated. Then the impedance investigations were carried out.

3.1   Gravimetric measurements

Table 1 shows the results of testing the rubber linings at a temperature of 110 $^{\circ}$C in the autoclave containing the working medium in form of: distilled water, solution I (1% aqueous solution of HCl) or solution II (aqueous solution containing 50 g/dm^3 of sulphuric acid and 26 g/dm^3 of sodium bisulphate (IV)), for 48 h.

Presented indicated that the largest gain in mass for all the samples occurred when the autoclave contained solution II from which gaseous SO$_2$ was liberated. Much smaller gains in mass were recorded for solution I when gaseous HCl was liberated. The smallest gains in mass were recorded when the autoclave contained distilled water. The gain in mass of the tested rubber linings is due mainly to water absorption [3].

Table 1. Results of gravimetric analysis of rubber linings after 48 h of exposure at temperature of 110 °C in autoclave.

Medium in autoclave	Gain in sample mass, mg		
	Sample A	Sample B	Sample C
Distilled water	20	21	23
Solution I	41	26	28
Solution II	46	43	75

3.2   Impedance measurements

Impedance spectra were analysed using equivalent circuit modelling. Depending on the material one of two models were used.

Models contain the Constant Phase Elements (CPE), which admittance at given radial frequency ω is evaluated as:

$$Y_{CPE} = Q(j\omega)^n \,, \tag{1}$$

where Y_{CPE} is the admittance of the CPE, Q and n are the parameters of the CPE.

First equivalent circuit (Fig. 4a) was used for spectra with non-Debye loss peak in the middle of frequency range [8] while the second one (Fig. 4b) is common model for dielectric with additional conduction mechanism or low frequency dispersion (LFD) [9].

Figure 4. Electric equivalent circuits used in the analysis. CPE, CPE$_1$, CPE$_2$ – Constant Phase Elements, R$_1$ – resistance.

Fitting was done by nonlinear complex least squares method using Scribner ZView software. Results of fitting was presented graphically in Figs. 5, 6 and 7 while the values of the equivalent circuit parameters were included in Tabs. 2, 3 and 4 for samples A, B and C, respectively.

The impedance measurements indicate that the low-frequency impedance module for sample A is much larger than for samples B and C, which means that from among the three tested rubbers one can expect rubber A to have the
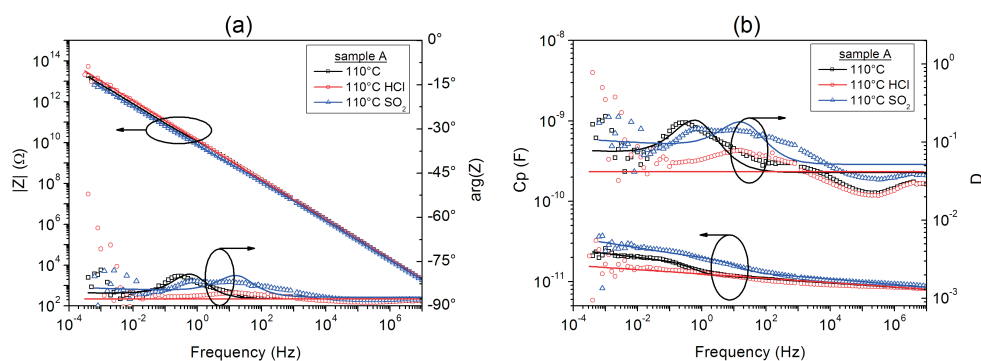
Figure 5. Measured (dots) and fitted (lines) impedance spectra of sample A: modulus and argument of impedance (a), parallel capacitance C_p and loss factor D (b).

Table 2. Parameters of the equivalent circuit (Fig. 4a) for sample A. Q_{CPE}, n_{CPE} – parameters of CPE, R_1 – resistance, Q_{CPE1}, n_{CPE1} – parameters of CPE_1.

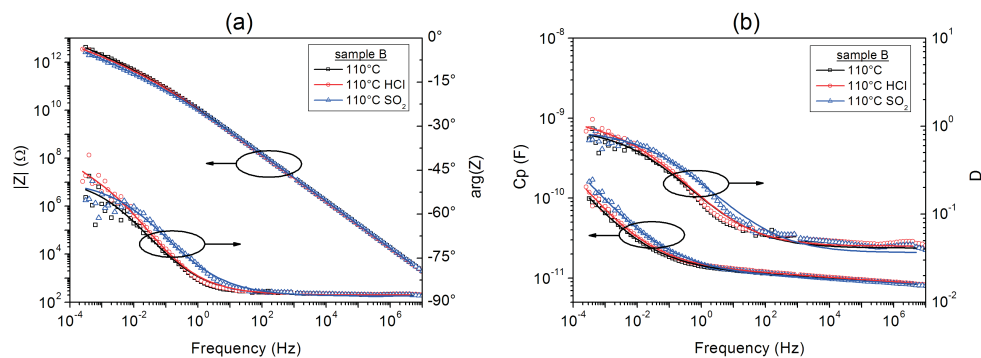| Ageing conditions	Q_{CPE} $[Ss^n]$	n_{CPE} $[-]$	R_1 $[\Omega]$	Q_{CPE1} $[Ss^n]$	n_{CPE1} $[-]$
110 °C + H_2O	1.29×10^{-11}	0.973	6.24×10^{10}	4.99×10^{-12}	0.911
110 °C + HCl	1.31×10^{-11}	0.973	–	–	–
110 °C + SO_2	1.55×10^{-11}	0.967	2.26×10^{9}	6.98×10^{-12}	0.884

Figure 6. Measured (dots) and fitted (lines) impedance spectra of sample B: modulus and argument of impedance (a), parallel capacitance C_p and loss factor D (b).

best protective properties. The impedance spectra for sample A significantly differ from the ones for samples B and C. Regardless of the medium in the autoclave, the sample A spectra show a capacitive character in the whole frequency range

Table 3. Parameters of the equivalent circuit (Fig. 4b) for sample B. Q_{CPE1}, n_{CPE1} – parameters of CPE$_1$, Q_{CPE2}, n_{CPE2} – parameters of CPE$_2$, R_1 – resistance.

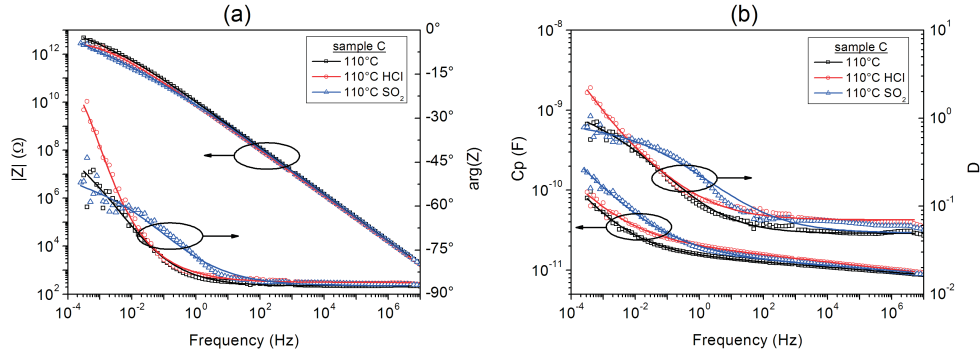| Ageing conditions	Q_{CPE1} [Ss^n]	n_{CPE1} [–]	Q_{CPE2} [Ss^n]	n_{CPE2} [–]	R_1 [Ω]
110 °C + H_2O	1.31×10^{-11}	0.974	5.98×10^{-12}	0.524	–
110 °C + HCl	1.39×10^{-11}	0.972	6.22×10^{-12}	0.5	4.58×10^{12}
110 °C + SO_2	1.22×10^{-11}	0.956	1.05×10^{-11}	0.539	–

Figure 7. Measured (dots) and fitted (lines) impedance spectra of sample C: modulus and argument of impedance (a), parallel capacitance C_p and loss factor D (b).

Table 4. Parameters of the equivalent circuit (Fig. 4b) for sample C. Q_{CPE1}, n_{CPE1} - parameters of CPE$_1$, Q_{CPE2}, n_{CPE2} – parameters of CPE$_2$, R_1 – resistance.

Ageing conditions	Q_{CPE1} [Ss^n]	n_{CPE1} [–]	Q_{CPE2} [Ss^n]	n_{CPE2} [–]	R_1 [Ω]
110 °C + H_2O	1.54×10^{-11}	0.968	3.76×10^{-12}	0.5	5.12×10^{12}
110 °C + HCl	2.07×10^{-11}	0.955	4.56×10^{-12}	0.534	3.93×10^{12}
110 °C + SO_2	1.62×10^{-11}	0.968	1.31×10^{-11}	0.572	8.71×10^{13}

(10^{-4}–10^7 Hz), whereas the spectra of samples B and C show a resistive character in the low-frequency range (10^{-4}–10^{-2} Hz).

Another parameter which clearly distinguishes sample A from samples B and C is the loss factor (D), which for the latter samples increases as the frequency is decreased, (Figs. 6(b) and 7(b)) whereas for sample A (Fig. 5(b)) it shows maxima in the particular frequency ranges (there is some analogy to water which transmits visible radiation, but attenuates infrared and ultraviolet light).

4 Conclusions

Special cells for accelerated testing of rubber lining materials in an autoclave at elevated temperature and at a pressure gradient along the sample's thickness, were designed and built. In these conditions penetration of water vapour and other gaseous components of the solution into the tested material can be speeded up. The largest gain in mass for all tested samples occurred when the autoclave contained solution from which water vapour and gaseous SO_2 was liberated.

The impedance measurements show that low-frequency impedance module for prevulcanized soft bromobutyl rubber is larger than for other tested samples, which may indicate the best protective properties.

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Laboratoryjna ocena wykładzin gumowych używanych w instalacjach odsiarczania spalin, metodą grawimetryczną i spektroskopii impedancyjnej

S t r e s z c z e n i e

Zastosowano specjalne komórki ze stali austenitycznej, umożliwiające przeprowadzenie przyspieszonych badań materiałów powłokowych w autoklawie w warunkach podwyższonej temperatury i gradientu ciśnienia na grubości próbki. Badania wykonano dla trzech rodzajów wykładzin gumowych: wstępnie wulkanizowanej miękkiej wykładziny dwuwarstwowej na bazie kauczuku bromobutylowego, dwuwarstwowej samowulkanizującej się wykładziny na bazie kauczuku bromobutylowego i wstępnie wulkanizowanej wykładziny na bazie kauczuku chlorobutylowego). W badaniach jako medium robocze stosowano wodę destylowaną, 1% roztwór wodny kwasu solnego oraz roztwór wodny zawierający 50 g/dm^3 kwasu siarkowego i 26 g/dm^3 wodorosiarczanu(IV) sodu. Temperaturę medium roboczego w autoklawie utrzymywano w zakresie 110 $\pm$2 °C, a czas ekspozycji próbek wynosił 48 godz. Metodą grawimetryczną oznaczano zmianę masy próbek po odpowiednim czasie ekspozycji próbek w autoklawie, a wykorzystując system pomiarowy zestawiony z wysokoczęstotliwościowego analizatora impedancji Agilent 4294A oraz niskoczęstotliwościowego analizatora impedancji z przetwornikiem prąd-napięcie Keithley 428 wykonywano pomiary w zakresie częstotliwości od 0,1 mHz do 10 MHz przy pobudzeniu o amplitudzie napięcia przemiennego 1 V$_{RMS}$. Otrzymane wyniki badań impedancyjnych pozwalają stwierdzić, że badane materiały powłokowe, pomimo ostrych warunków korozyjnych w autoklawie i zwiększenia masy próbek, nie uległy znaczącej destrukcji podczas ekspozycji i zachowały dobre właściwości dielektryczne i ochronne.