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Corrosive synergic effects of acetic acid and atmospheric pollutants on lead and zinc

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The aim of this paper was to evaluate the possibility of presence of the synergic corrosive effect between acetic acid and chosen air pollutants such as: Cl_2, SO_2, NaCl, H_2S, NH_3, NO_x. The metals chosen for following experiments were lead and zinc as they are known to be sensitive to volatile organic compounds. Acetic acid occurs often at indoor environment, where other pollutants may be present. The idea was to describe the influence of other pollutants on increasing the corrosion aggressivity of atmosphere contaminated by acetic acid. Synergic effect was found on lead for following pollutants: sulphur dioxide, chlorine, ammonia and nitrogen oxides. And on zinc the found pollutants are: sodium chloride, sulphur dioxide, chlorine, hydrogen sulphide and nitrogen oxides.

INTRODUCTION

This project is focused on observing corrosion rates of metals in environments containing acetic acid and other inorganic pollutants to find out any possible synergic effects between them and acetic acid. The acetic acid is a major corrosive pollutant in indoor environment, especially in archives, it is emitted from wood, released from glues, adhesives, or some plastic tools. Emission of acetic acid from wood consists of the hydrolysis of acetyl group in the hemicellulose. The rate of the emission of acetic acid is higher at high relative humidity and higher temperatures. Hard wood types show higher emission rates than the soft woods [1],[2]. There are tends to prevent the indoor metallic parts from corrosion attack, especially lead which is sensitive to the acetic acid presence. Therefore, it is desirable to be informed about the possible existence of synergic effect between the acetic acid and other pollutants such as Cl_2, SO_2, NaCl, H_2S, NH_3, NO_x, which may be present indoor. These pollutants may occur from human activity (plants, incinerators, traffic, etc) – mainly outdoor, or may be released by degradation of organic compounds (such as wood, plastics, paints or oils) or can be present due to the cleaning products used [3],[4]. The aggressivity of an environment is increased by the presence of volatile organic compounds, such as formic acid or acetic acid (AA). Lead and zinc are sensitive to the presence of acetic acid in atmosphere. Lead sensitivity begins when the concentration of acetic acid is higher than 0.43 mg m^{-3} at 54% RH [5],[6].

Corrosion rate of lead in atmospheric conditions without the presence of acetic acid is very slow due to the formation of oxide-based protective films on the surface. In case of presence the acetic acid, the protective films are disrupted or dissolved, which leads to a higher corrosion rate of lead. The mechanism depends on relative humidity, electrolyte on the metal surface is necessary to dissolve the organic acids vapours. When acetic acid is dissolved in the electrolyte, the acetate salts are formed on the Pb surface instead of protective film [2],[3],[7],[8].

The corrosion rate of zinc in atmospheric conditions depends on a level of pollution. Under non-polluted conditions zinc corrodes very slowly because of the protective hydroxides layer formation. The atmospheric corrosion process on Zn surface in the presence of the acetic acid is initiated by acetate (CH_3COO^-) or by proton (H^+). For promotion of these reaction the continuous aqueous film is needed. Acetate-initiated process leads to formation $Zn_5(OH)_8(CH_3COO)_2 \cdot H_2O$ and proton-induced process leads to formation of ZnO [5],[9].

The pollutants chosen for the experiments were: Cl_2, SO_2, NaCl, H_2S, NH_3, NO_x. These pollutants represent most common contaminants. The typical outdoor pollutants were represented by SO_2, NO_x and NaCl. Hydrogen sulphide (H_2S) is typical indoor contaminant as a product of the anaerobic degradation of organic sulphur compounds. Chlorine has been involved in the study as a representative of emission from chlorine based sanitizes that might be used indoors. Ammonium (NH_3) originate mostly in anthropogenic sources but also from natural sources like sea water. Agriculture is the major emitter NH_3. Thus, ammonia is present both indoors and outdoors.

In the case of zinc corrosion, the SO_2 is the most aggressive pollutant, at 75 % RH. Nitrogen monooxide doesn't affect the zinc significantly, because of formation thin basic hydrated zinc nitrates [10]. The effect of SO_2 and SO_2 + NO_2 in humid atmosphere (90 % RH) was

studied on lead and zinc coupons. It showed remarkable synergistic effect on lead concerning the deposition rate of SO_2, because the presence of NO_2 increased the deposition of SO_2 on lead surface. On the contrary on the zinc, the deposition of SO_2 wasn´t increased by NO_2 [11]. Zinc corrosion induced by NaCl leads to heavy pitting, in case of presence CO_2 in the atmosphere, the level of pitting is lover [12].

Synergic effects between organic compounds and pollutants were studied on lead. The synergy effect wasn´t found between formaldehyde and CO_2. Formaldehyde is an important indoor pollutant towards Pb surface [4].

Synergic effects were also studied on other metallic materials. The influence of H_2S, SO_2 and NO_2 was studied on silvered glass and aluminium in the study on reflector materials for solar cells. Their experiments showed the synergy effect between H_2S and NO_2 and between H_2S and SO_2 [13]. Other study focused on aluminium corrosion in environment polluted by Cl^- and SO_2 showed synergic effect between them only when one of the pollutant wasn´t at significantly higher level than the other [14].

Resistometric sensors have been used to evaluate the corrosion rate of lead and zinc. Schematic picture of a resistometric sensor is on the Fig. 1. The principle of the resistometric method as a corrosion monitoring consists in measuring the electrical resistance. When the metal corrodes, the thickness of the metal track is getting lower, and therefore the resistance higher. There are two parts of the sensor – the measuring part and the reference part. The measuring part is in contact with the environment, and the reference part is masked and is not in the contact with the environment, the main role of the reference part is to compensate the temperatures changes. This method provide real-time monitoring of the corrosion depth [8],[15].

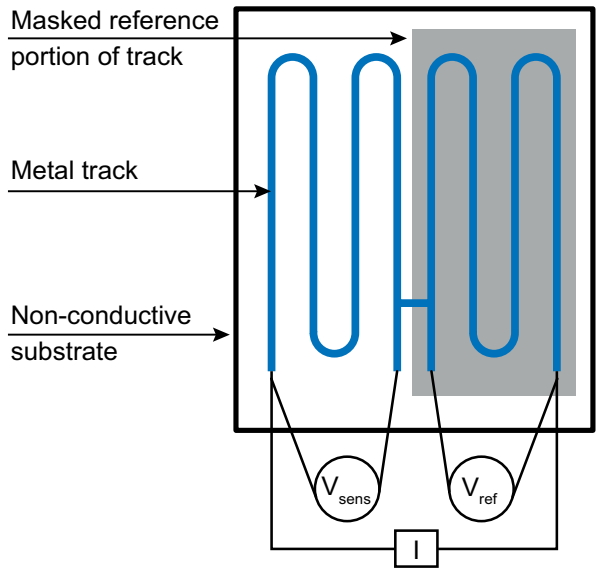

Fig. 1. Schematic image of the resistometric sensor [8]

The possibility of the existence of the synergic effect between acetic acid and some pollutant consist in higher corrosion rate in environment containing AA and a pollutant, than the linear combination of the corrosion rates in environment containing only acetic acid and only a pollutant. This phenomenon has been investigated using resistometric sensors and corrosion coupons with the aim to identify prospective combination of AA and a pollutant with synergic corrosive effect towards lead that would be studied later in more details.

EXPERIMENTAL PART

The experiments consisted of exposing the resistometric sensors and corrosion coupons in different gaseous conditions. Firstly, the sensors and coupons were produced and prepared. All the metals are involved in ISO 11844-1 standard as materials for determination of corrosion rate for classification of low corrosivity of indoor atmospheres. The electrical resistance sensors and corrosion coupons were produced from lead and zinc, the metals mostly sensitive to organic volatile acids. The following experiments were set up to describe the possibility of presence of the synergic corrosive effect between acetic acid and selected pollutants. The typical outdoor pollutants were represented by SO_2, NO_x and NaCl and indoor pollutants represented by H_2S, Cl_2 and NH_3, which is common for both – indoor and outdoor. The sources of pollutants were following. Chlorine was taken from vapours of detergent (SAVO) containing NaClO (4.7 %), the vapours from closed vessel were taken to the cell using a micro syringe. The sources of the H_2S and SO_2 were the pressure vessels, the pollutant was collected from flowing gas in the hose by micro syringe. The source of NaCl was saturated solution of NaCl in methanol, this solution was applied by spraying. The reaction of iron and nitric acid was a source of NO_x, gaseous products have been collected with syringe from closed beaker. NH_3 vapours were collected by micro syringe from a closed vessel with liquid NH_3.

Preparation of sensors and coupons

AirCorr type electrical resistance sensors [15] were used for recording corrosion depth of lead and zinc in time. The original thickness of the lead and zinc track was 25 μm and 50 μm, respectively. The sensors were connected with ACD-03 Metricorr logger by a 10-wire cable fixed to contact pads of the sensor by soldering. The reference part of it was covered by the two-component epoxide resin (UHU plus). The image of the sensor is on the Fig. 1. The sensors right before exposure were pickled in 1 % HCl solution for 30 s, rinsed with distilled water and then dried with ethanol.

The corrosion coupons have been produced from thick metal sheet (1 mm). Compositions of all metals meets the conditions of the standard ISO 11844-2. The size of the coupons was 50×20 mm. Firstly, all the coupons have been marked with number and then Zn coupons have been grinded manually with the SiC paper P320 (320 grains/cm^2) and Pb coupons have been grinded using abrasive wool 3M Scotch-Brite CF-HP. The coupons were rinsed and degreased and ultrasonicated in acetone for 15 minutes. Clean coupons were immersed in 1 % HCl solution for 30 s and weighted with Sartorius analytical balance.

Exposure of resistometric sensors

The exposure of resistometric sensors were conducted to reveal corrosion response of the materials to changing conditions in terms of the presence of acetic acid and the pollutant. In the first part of the experiment, the sensors (Pb and Zn) were exposed in the cells containing only pollutant.

In the second part, the sensors were exposed in the cells containing acetic acid (0.01 mol/l) and after certain time the pollutant was added to this environment.

The aim of this paper was to compare corrosion rates of metals at different environments (only pollutant, only acetic acid vapours and their mixture). The comparison led to evaluation of the presence of any synergy effect.

Corrosion response to presence of pollutants

The sensors exposures have been conducted in closed boxes (volume 1.8 l) in the environment with 100 % relative humidity (a beaker containing 100 ml of distilled H_2O). The experiment was started by placing new sensors (Pb and Zn) into the box with distilled water in a beaker, after 3 days the pollutant was added using the micro syringe (500 µl of gaseous pollutant) or the spraying applicator (1 spray for NaCl). The duration of the experiment was 10 days. The aim of the study was not to determine the corrosion rate as a function of the amount of pollutant in the test atmosphere, but to investigate the existence of a synergistic effect between the pollutant and acetic acid.

Corrosion response to pollutant and acetic acid mixture

The resistometric sensors (Pb and Zn) and a beaker with acetic acid solution (100 ml, c = 0.01 mol/l) were put into a box. The volume of the closed box was 4,5 l in this case but the ratio of amount of pollutant and volume of the box was kept similar, app. 0.25 ml/l. Three different pollutants were tested in this experiment (NO_x, H_2S, NH_3), sampling was conducted in the same way as in case of coupons exposure. The timeline of the experiment is shown in the Tab. 1, the duration of the experiment was 10 days.

Exposure of coupons

Prepared coupons (Pb and Zn) have been exposed in closed boxes in environments containing combinations of pollutants and acetic acid (c = 0.01 mol/l). The list of components in the exposure cells are written in the Tab. 2. The volume of the cells was 1,8 l. The pollutants chosen for this experiment were: Cl_2, H_2S, NaCl, NH_3, NO_x and SO_2. Micro syringe with 500 µl volume was used for sampling all the pollutants.

Tab. 2. List of components in exposure cells

Cell number	Component	Cell number	Component
1	Acetic acid (AA)	8	NH_3
2	Cl_2	9	NH_3 + AA
3	Cl_2 + AA	10	NaCl
4	H_2S	11	NaCl + AA
5	H_2S + AA	12	NO_x
6	SO_2	13	NO_x + AA
7	SO_2 + AA		

Data evaluation

Evaluation the coupons results

The coupons were weighted after exposure. According to the ČSN ISO 8407, they were pickled in the pickling solution in 4-5 cycles. Each pickling cycle consisted of pickling for a certain time, rinsing, drying, and weighing. The pickling solutions and pickling times for each metal can be found in the Tab. 3. The dependence of mass on the number of pickling cycles is shown on the Fig. 2. Point A represents the mass just before first pickling. Between the points A and B, the corrosion products are removed, between the point B and C, all the corrosion products are removed, and the mass loss is represented only by metal dissolution. The point D represents the mass of the metal free of corrosion products. This weight was obtained from the pickling curve and used for calculations of corrosion rate.

Tab. 1. Timeline of the exposure of sensors in environment with acetic acid and pollutant

Start of the experiment	After 1 day	3 days later	3 days later	after 10 days
+ beaker with distilled water	+ source of acetic acid vapours (0.01 mol/l)	first pollutant addition	second pollutant addition	end of the experiment

Tab. 3. Pickling conditions

Material	Pickling solution	Pickling time	Temperature
Cu	54 ml H_2SO_4 filled to the volume 1 l with distilled water	5 min	laboratory
Fe	500 ml/l HCl and 3.5 g/l hexamethylenetetramine	10 min	laboratory
Pb	1.5 kg/l ammonium acetate	5 min	laboratory
Zn	100 g/l ammonium acetate	2 min	70 °C

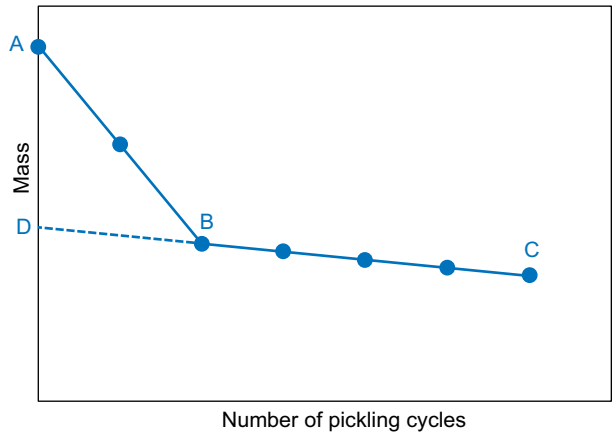

Fig. 2. Evaluation of coupons – pickling of coupons in pickling solution. A = mass after exposure, B = mass of the coupons without corrosion products, C = mass after last pickling, D = mass of the metal without any corrosion products after exposure

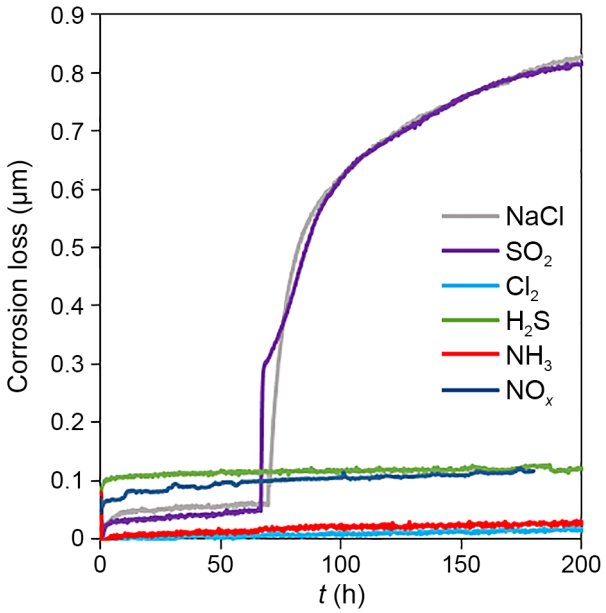

Fig. 3. Zinc sensors response to a pollutant introduction at 72 hours of exposure

Evaluation of the data from sensors

The data from data logging systems (Metricor ACD-03 and Agilent 34970A) were processed and from the measured resistances were calculated the corrosion losses. The corrosion depth of electrical resistance sensors was calculated in accordance with the equation 1.

$$\Delta h = h_0 \cdot \left(1 - \frac{R_{ref}}{R_{sens}} \cdot \frac{R_{sens,0}}{R_{ref,0}}\right) \quad (1)$$

where Δh – thickness change, h_0 – initial thickness, R_{ref} – resistance of the reference part, R_{sens} – resistance of the sensing part, $R_{ref,0}$ and $R_{sens,0}$ – initial resistances of reference and sensing part.

RESULTS

Exposure of resistometric sensors in the presence of pollutant

The lead and zinc resistometric sensors were exposed in the cells to the environment of chosen pollutant. The pollutant was added at the 72nd hour of exposure. The results are shown on the Fig. 3 and 4. In the case of zinc sensor, no corrosion response was obtained after introduction of hydrogen sulphide and nitrogen oxides

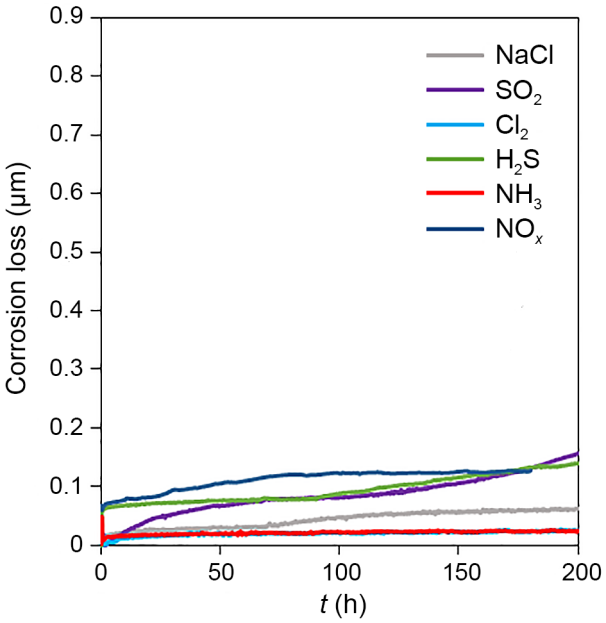

Fig. 4. Lead sensors response to a pollutant introduction at 72 hours of exposure

to humid air. Chlorine and ammonium induced only short-time and slight increase of corrosion rate. NaCl and SO_2 performed as the most aggressive pollutants for zinc sensors showing immediate and rapid corrosion loss after insertion of the pollutant. NaCl and SO_2 induced observable response of the Pb sensor as well but at much weaker extent. Among the other pollutants, only H_2S increased corrosion rate of lead.

Tab. 4. Corrosion rates for 12 h period after pollutant addition and for whole time after its addition

List of pollutant	Corrosion rates 12 h after pollutant (µm·h^{-1})		Corrosion rates after pollutant (µm·h^{-1})	
	Pb	Zn	Pb	Zn
NaCl	$4.0 \cdot 10^{-4}$	$3.3 \cdot 10^{-2}$	$3.3 \cdot 10^{-4}$	$4.5 \cdot 10^{-3}$
SO_2	$2.0 \cdot 10^{-4}$	$1.3 \cdot 10^{-2}$	$7.0 \cdot 10^{-4}$	$4.4 \cdot 10^{-3}$
Cl_2	$4.0 \cdot 10^{-5}$	$1.2 \cdot 10^{-4}$	$1.3 \cdot 10^{-5}$	$8.3 \cdot 10^{-5}$
H_2S	$8.0 \cdot 10^{-4}$	$8.0 \cdot 10^{-5}$	$8.7 \cdot 10^{-4}$	$6.9 \cdot 10^{-4}$
NH_3	$8.3 \cdot 10^{-5}$	$2.0 \cdot 10^{-4}$	$1.3 \cdot 10^{-5}$	$1.9 \cdot 10^{-4}$
NO_x	$7.0 \cdot 10^{-4}$	$1.0 \cdot 10^{-4}$	$6.9 \cdot 10^{-4}$	$6.5 \cdot 10^{-4}$

Corrosion rates of sensors are sum up in the Tab. 4, it describes the corrosion rates in 12 h intervals after adding the pollutant, and corrosion rates of sensors since pollutant addition until the end of exposure.

Universal parameter for comparison of the zinc and lead response to the presence of a pollutant in humid air could be the ratio of corrosion rates 12 hours after pollutant addition and 12 hours before. These ratios are shown in the Tab. 5. It says that if the ratio is high, the addition of pollutant rapidly increased the corrosion rate, for example NaCl or SO_2 for Zn. Low ratio means that the pollutant is not aggressive, or it acts nonaggressively under given circumstances for the metal, such as SO_2, Cl_2, NH_3, NO_x for Pb and Cl_2, H_2S, NH_3, NO_x for Zn. It is clear from the ratios that chlorides and sulphur dioxide are much more corrosive to zinc compared to lead while hydrogen sulphide accelerates corrosion of lead significantly but not in the case of zinc.

Tab. 5. Ratio of corrosion rates 12 hour after and 12 h before pollutant addition

List of pollutant	Ratio – (corrosion rate after) / (corrosion rate before pollutant)	
	Pb	Zn
NaCl	**4.0**	**326**
SO_2	0.4	**63**
Cl_2	0.4	0.6
H_2S	**8.9**	0.4
NH_3	0.8	0.4
NO_x	0.9	0.2

Exposure of resistometric sensors in the presence of acetic acid and pollutant

The resistometric sensors have been used to detect changes in corrosion rate after changing of conditions in exposures cells. Firstly, the sensors were exposed to elevated humidity free of corrosion stimulators, then the source of acetic acid vapours was inserted without changing the relative humidity, and later, a pollutant was introduced without removing the source of acetic acid. Thus, the pollutant and acetic acid acted at the same time. The results of that screening are shown below.

Acetic acid and Cl_2

Lead and zinc sensors were put in the exposure box to study the behaviour of these metals in environment containing acetic acid vapou rs and chlorine at high RH (100 %). The data provided by the resistometric sensors are plotted in the Fig. 5.

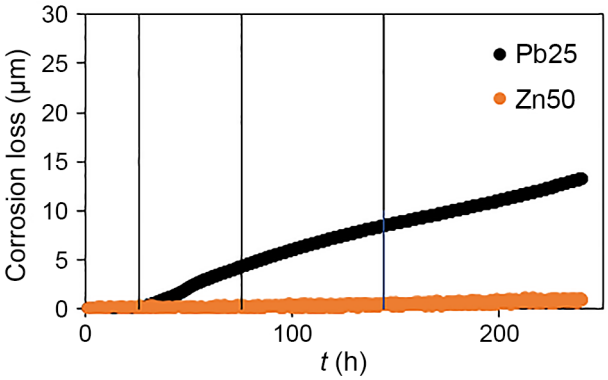

Fig. 5. Exposure of lead and zinc sensors in the environment containing acetic acid and Cl_2 (timeline: 0-24 h: 100 % RH, 24 h: + AA (0.01 mol/l), 70 h: + 1 ml Cl_2, 144 h: + 5 ml Cl_2)

Negligible corrosion loss in pure humid air of both lead and zinc was followed with elevated corrosion rate after insertion of the source of acetic acid (0.01 M acetic acid solution). The additions of chlorine did not result in an increase of corrosion rate, since chlorine does not act aggressively to lead, as shown above. The Zn sensors did not react at any changes in environment and their corrosion rate was slightly zero. Tab. 7 presents the corrosion rate of short intervals (12 hours) before and after changing the conditions.

Tab. 8 presents the corrosion rates of each period. The highest corrosion rate of Pb was in the environment with acetic acid.

Tab. 9 shows ratios of corrosion rates after and before condition change (humid air → AA, AA → AA + + chlorine). The ratios confirm what was written above,

the addition of acetic acid leads to rapid increase of corrosion rate and chlorine addition doesn´t increase the corrosion rate of lead nor zinc in combination with acetic acid.

Tab. 6. Corrosion rate (μm·h^{-1}) when conditions are changed (12 h interval)

Corrosion rate (μm·h^{-1}) / material	Before acetic acid	After acetic acid	Before Cl_2	After Cl_2
Pb	$3.5 \cdot 10^{-4}$	$7.3 \cdot 10^{-2}$	$1.7 \cdot 10^{-1}$	$6.7 \cdot 10^{-2}$
Zn	$6.3 \cdot 10^{-4}$	$3.2 \cdot 10^{-3}$	$2.0 \cdot 10^{-3}$	$6.9 \cdot 10^{-4}$

Tab. 7. Corrosion rate (μm·h^{-1}) of sensors at different time sections

Material/environment	Corrosion rate (μm·h^{-1})	
	Pb	Zn
Humid air	0.0004	0.0006
Acetic acid	0.105	0.001
First Cl_2 addition	0.055	0.002
Second Cl_2 addition	0.051	0.003

Tab. 8. Corrosion rate ratio (12 h after / 12 h before condition change)

	Change from humid air to AA	Change from AA to AA + Cl_2
Pb	208.6	0.4
Zn	5.1	0.3

Acetic acid and H_2S

Lead and zinc sensors were put to the exposure cell to evaluate the synergy effect between acetic acid and H_2S. The sensors responses on changes in condition are plotted on Fig. 6.

Corrosion loss of both materials in humid air was very low. The corrosion rates before and after changes are sum up in the Tab. 9. Tab. 10 describes the overall corrosion rates during segment. The lead sensor showed the increase of the corrosion rate after the addition of acetic acid vapours as well as in other exposures. The zinc sensor didn´t show any important increase of corrosion rate after the acetic acid addition. The corrosion rate of lead sensor after H_2S addition remained on the same level as in the only acetic acid vapours environment but after delay the corrosion rate was reduced. The delay may have been caused by non-sufficient ventilation, so it took longer time for pollutant to reach the sensor surface. Approximately after 30 hours since the H_2S addition, the corrosion rate started to slow down, which may be a consequence of some leakage of the box. Zinc sensor corrosion rate increased after hydrogen sulphide.

Tab. 9. Corrosion rates of sensors at 12 h intervals before and after condition change

Corrosion rate (μm·h^{-1}) / material	Before acetic acid	After acetic acid	Before H_2S	After H_2S
Pb	$3.1 \cdot 10^{-3}$	$6.1 \cdot 10^{-2}$	$6.6 \cdot 10^{-2}$	$6.8 \cdot 10^{-2}$
Zn	$1.4 \cdot 10^{-3}$	$5.2 \cdot 10^{-3}$	$3.9 \cdot 10^{-4}$	$2.8 \cdot 10^{-3}$

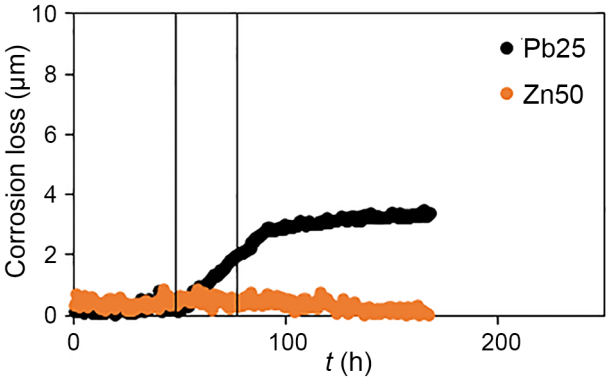

Fig. 6. Exposure of Pb and Zn sensor in environment containing acetic acid and H_2S (timeline: 0-48 h: 100 % RH, 48 h: + AA (0.01 mol/l), 77 h: + H_2S

Tab. 10. Corrosion rate (μm·h^{-1}) of sensors at different time sections

Material / environment	Corrosion rate (μm·h^{-1})	
	Pb	Zn
Humid air	0.003	0.001
Acetic acid	0.064	0.001
H_2S addition	0.015	0.002

Tab. 11 shows the ratio of corrosion rates of 12 hours long segments after and 12 hours before change of the conditions. It illustrates what is written above, that the lead corrosion rate increased after acetic acid addition. From the previous experiment it is known, that H_2S is aggressive to lead and not to zinc. In combination with acetic acid the corrosion rate of lead is not increased. And the corrosion rate of zinc is increased 7 times after hydrogen sulphide introduction into the cell.

Tab. 11. Corrosion rate ratio (12 h after / 12 h before condition change)

	Change from humid air to AA	Change from AA to AA + H_2S
Pb	19.7	1.0
Zn	3.7	7.2

Acetic acid and SO_2

To study synergy effect of acetic acid and SO_2 on lead and zinc were used resistometric sensors. The results are plotted in Fig. 7. The corrosion rate of lead sensor increased after the acetic acid addition and accelerated after first SO_2 addition. Zn sensor didn´t measure any markable changes in thickness until the second addition of SO_2. The corrosion rates of both sensors are shown in Tab. 12 and 13. Tab. 12 describes corrosion rates of 12 hours long intervals before and after change of conditions in exposure box. Tab. 13 shows overall corrosion rates per each period.

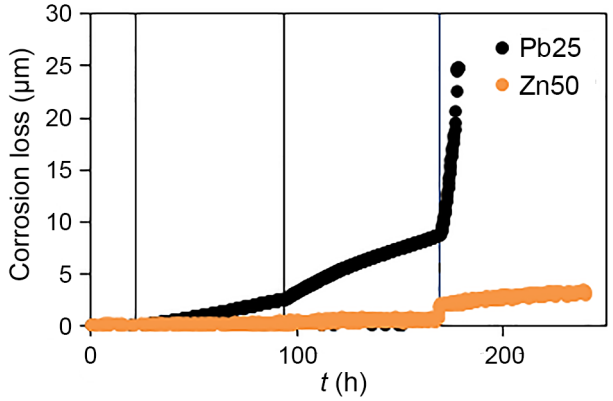

Fig. 7. Exposure of lead and zinc sensors in environment containing acetic acid and SO_2 (timeline: 0-24 h: 100 % RH, 24 h: + acetic acid (0.01 mol/l); 93 h: + 1 ml SO_2; 160 h: + + 5 ml SO_2)

Tab. 12. Corrosion rates of sensors at 12 hours intervals before and after condition change

Corrosion rate (µm·h^{-1}) / material	Before acetic acid	After acetic acid	Before SO_2	After SO_2
Pb	$1.4 \cdot 10^{-3}$	$2.9 \cdot 10^{-2}$	$3.9 \cdot 10^{-2}$	$1.1 \cdot 10^{-1}$
Zn	$3.2 \cdot 10^{-3}$	$7.1 \cdot 10^{-3}$	$7.0 \cdot 10^{-3}$	$9.2 \cdot 10^{-3}$

Tab. 13. Corrosion rate (µm·h^{-1}) of sensors at different time sections

Material/environment	Corrosion rate (µm·h^{-1})	
	Pb	Zn
Humid air	0.001	0.003
Acetic acid	0.041	0.007
First SO_2 addition	0.102	0.009
Second SO_2 addition	2.381	0.017

Ratios of corrosion rates (12 hours after change)/ /(12 hours before change) are shown in the Tab. 14. It describes well the changes of corrosion rates after changes conditions in exposure cell. The higher the ratio is the higher the corrosion rate in new environment is.

Tab. 14. Corrosion rates ratio (after/before change of conditions)

	Change from humid air to AA	Change from AA to AA + SO_2
Pb	20.7	2.8
Zn	2.2	1.3

Rapid increase of corrosion rate of lead after acetic acid addition and also after sulphur dioxide addition is clear from Fig. 7 and from the Tab. 14. Lead corrosion rate increased after each change. Corrosion rate of lead after SO_2 addition is 2.8 times higher than in acetic acid. Sulphur dioxide itself is not aggressive toward lead according to the previous experiment, but combination of acetic acid and sulphur dioxide is very corrosive. The synergic effect between them is evaluated on Fig. 13.

On the contrary zinc sensor corrosion rate didn´t increase much during the exposure. Surprisingly, the corrosion rate did increase only 1.3 times after SO_2 addition, knowing that SO_2 is aggressive to zinc. The combination of acetic acid and sulphur dioxide doesn´t express any synergism mechanism.

Acetic acid and NH_3

Lead and zinc sensors were used to evaluate the possibility of presence of synergy effect between acetic acid and NH_3. The data from sensors are plotted on the Fig. 8. The lead sensor shows an increase of corrosion rate when acetic acid was added. The response of zinc sensor on the changing condition was negligible. The slope of lead sensors right after the NH_3 introduction wasn´t linear, it may be caused by insufficient ventilation, so it took longer time for pollutant to reach the sensor surface. Approximately after 30 hours since the NH_3 addition, the corrosion rate started to slow down, which may be a consequence of some leakage of the box.

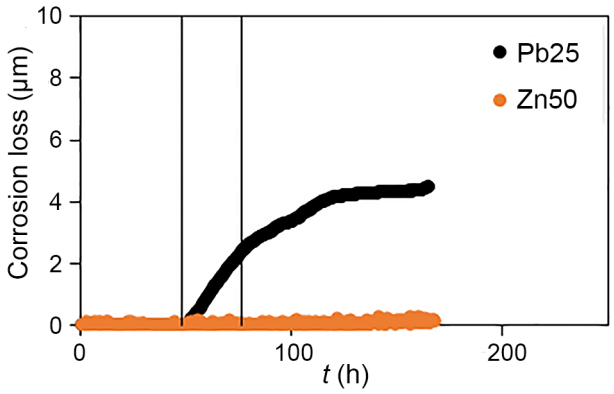

Fig. 8. Exposure of lead and zinc sensors in environment containing acetic acid and NH_3 (0-48 h: 100% RH, 48 h: AA (0.01 mol/l), 76.5 h: + NH_3)

The corrosion rates of sensors are shown in the Tab. 15 and 16, Tab. 15 describes the corrosion rates at 12 hours long intervals around changes of conditions.

Tab. 15. Corrosion rates of sensors at 12 hours intervals before and after changes in conditions

Corrosion rate (µm·h^{-1}) / material	Before acetic acid	After acetic acid	Before NH_3	After NH_3
Pb	$3.9 \cdot 10^{-4}$	$8.2 \cdot 10^{-2}$	$8.4 \cdot 10^{-2}$	$4.9 \cdot 10^{-2}$
Zn	$7.2 \cdot 10^{-4}$	$8.8 \cdot 10^{-4}$	$1.9 \cdot 10^{-4}$	$1.5 \cdot 10^{-3}$

Tab. 16 describes the overall corrosion rates at each segment separately.

Tab. 16. Corrosion rate (µm·h^{-1}) of sensors at different time sections

Material/environment	Corrosion rate (µm·h^{-1})	
	Pb	Zn
Humid air	0.0004	0.0007
Acetic acid (48 h)	0.091	0.0002
NH_3 addition (76.5 h)	0.022	0.002

Tab. 17 shows the ratio of corrosion rates 12 hours after the change / 12 hours before.

Tab. 17. Ratios of corrosion rates

	Change from humid air to AA	Change from AA to AA + NH_3
Pb	210.3	0.6
Zn	1.2	7.9

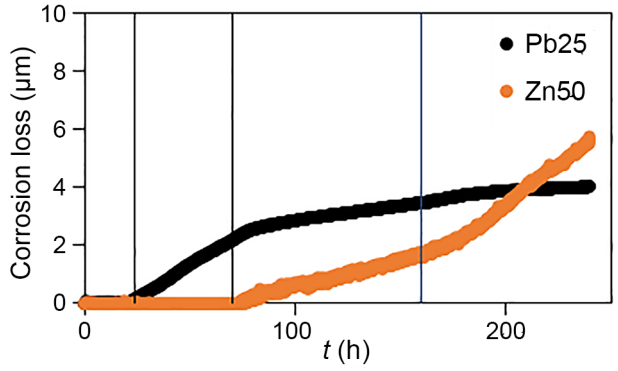

Fig. 9. Exposure of lead and zinc sensors in environment containing acetic acid and NaCl (timeline: 0-24 h: 100% RH; 24-70 h: acetic acid (0.01 mol/l); 70 h AA + NaCl; 160 h AA + + NaCl

Lead performed rapid increase of corrosion in environment containing the acetic acid vapours, addition of ammonia didn´t result in another increase of the corrosion rate. It remained at same level. Ammonia itself didn´t show any corrosion rate increase from the previous experiment. Combination of ammonia and acetic acid doesn't provide any synergic effect on lead corrosion.

Corrosion rate of zinc remained same and very low after the acetic acid introduction, when ammonia was released into the exposure cell, the corrosion rate increased almost 8 times. Nevertheless, the corrosion rate was still close to zero, so it wouldn´t be correct to proclaim this as a synergic effect. Ammonia as a pollutant itself wasn´t aggressive towards zinc, according to the previous experiment above.

Acetic acid and NaCl

Resistometric sensors were used to study the synergy effect between acetic acid and NaCl. The graph based on sensors data is plotted on the Fig. 9. After the acetic acid vapour introduction, the lead started to corrode faster and zinc corrosion rate rested on the same level as before. After first spraying of NaCl the lead corrosion rate slowed down, on the contrary the zinc corrosion rate was increased. The corrosion rates are sum up in the Tab. 18 and 19.

Tab. 18. Corrosion rates of 12 hours interval around change in condition

Corrosion rate (µm·h^{-1}) / material	Before acetic acid	After acetic acid	Before NaCl	After NaCl
Pb	$5.2 \cdot 10^{-4}$	$4.2 \cdot 10^{-2}$	$3.8 \cdot 10^{-2}$	$2.2 \cdot 10^{-2}$
Zn	$2.3 \cdot 10^{-4}$	$5.8 \cdot 10^{-4}$	$1.3 \cdot 10^{-4}$	$2.6 \cdot 10^{-2}$

Tab. 19. Corrosion rate (µm·h^{-1}) of sensors at different time sections

Material/environment	Corrosion rate (µm·h^{-1})	
	Pb	Zn
Humid air	0.0005	0.0002
Acetic acid (24 h)	0.032	0.001
First NaCl addition (70 h)	0.012	0.014
Second NaCl addition (160 h)	0.005	0.030

Tab. 18 describes the corrosion rates at short (12 h long) intervals before and after the change of condition, such as introduction of acetic acid or spraying of NaCl. Tab. 19 shows the overall corrosion rates of sensors during each segment separately.

Tab. 20. Ratio of corrosion rates (12 h after change / 12 h before change)

	Change from humid air to AA	Change from AA to AA + NaCl
Pb	80.8	0.6
Zn	2.5	200.0

Tab. 20 shows the corrosion rates ratios, which describe how the corrosion rate changed during condition change. Change from humid air to acetic acid vapours was same for every exposure cell and showed similar result. Change to conditions containing acetic acid and NaCl didn´t increase the lead corrosion rate in comparison with condition containing only acetic acid. Sodium chloride and acetic acid doesn´t express corrosion synergy effect on lead. The great increase of corrosion rate was observed on the zinc while NaCl was sprayed on the sensor in environment with acetic acid. Previous experiment with only one pollutant showed rapid corrosion rate increase on zinc with sodium chloride. The comparison of zinc corrosion rates in environment with acetic acid, sodium chloride and their combination would describe the possibility of synergy effect.

Acetic acid and NO_x

Lead and zinc sensors were used to study the synergy effect of acetic acid and nitrogen oxides. The data gathered by the sensors are plotted on Fig. 10. After the addition of source of acetic acid into the exposure cell, the lead corrosion rate increased, zinc corrosion rate almost remained on the same level. First addition of nitrogen oxides increased a corrosion rate of Pb sensor, on the other hand it didn´t promoted zinc sensor corrosion.

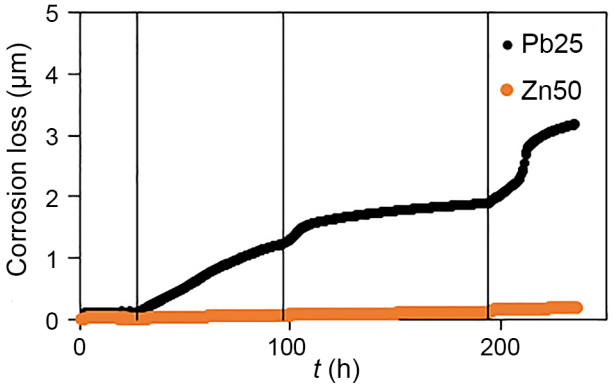

Fig. 10. Exposure of lead and zinc sensors in environment containing acetic acid and NO_x (timeline: 0-27 h: 100% RH; 27 h: acetic acid (0.01 mol/l); 97 h: + 1 ml NO_x; 194 h: AA + 5 ml NO_x)

Tab. 21 and 22 describe the corrosion rates over the exposure. Tab. 21 presents the corrosion rates of 12 hours long interval before and after change of condition. The corrosion rates of sensors at each segment of exposure are shown in the Tab. 22.

Tab. 21. Corrosion rates of 12 hours interval around change in condition

Corrosion rate (µm·h^{-1}) / material	Before acetic acid	After acetic acid	Before NO_x	After NO_x
Pb	$7.7 \cdot 10^{-4}$	$1.6 \cdot 10^{-2}$	$1.0 \cdot 10^{-2}$	$2.9 \cdot 10^{-2}$
Zn	$2.7 \cdot 10^{-4}$	$2.0 \cdot 10^{-3}$	$6.5 \cdot 10^{-4}$	$6.0 \cdot 10^{-4}$

Tab. 22. Corrosion rate (µm/h) of sensors at different time sections

Material/environment	Corrosion rate (µm·h^{-1})	
	Pb	Zn
Humid air	0.0008	0.0003
Acetic acid (27h)	0.017	0.001
First NO_x addition (97 h)	0.031	0.001
Second NO_x addition (194 h)	0.025	0.002

Tab. 23. Ratio of corrosion rates from 12 hours long interval (after / before) change

	Change from humid air to AA	Change from AA to AA + NO_x
Pb	20.8	2.9
Zn	7.4	0.9

The ratios of corrosion rates around the time when conditions were changed (12 hours after / 12 hours before) are shown in Tab. 21. The introduction of acetic acid into the exposure cell resulted in increase of lead and zinc corrosion rate. Nitrogen oxides didn´t affected much corrosion rates of both, the lead was increased by 2.9 times and zinc remained same.

Summary of resistometric sensors

Corrosion rates of both materials in different environments – acetic acid, pollutant and pollutant with acetic acid are summarized on the figures below (Fig. 11-14). The corrosion of metal in acetic acid was determined as 100 %, the other corrosion rates were expressed as percentage relative to the acetic acid corrosion rate. The summary of the all results gained from resistometric sensors is on the Fig. 11-16. It shows the possibility of presence of the synergy effect if the corrosion rate at combined environment (pollutant + acetic acid) is higher than sum up of individual corrosion rates.

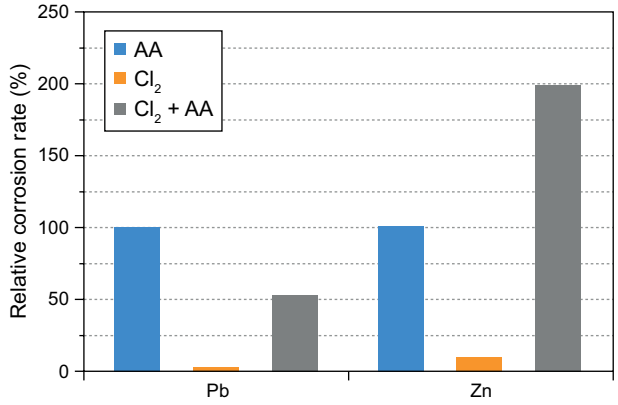

Fig. 11. Corrosion rate of resistometric sensors (Pb and Zn) in environments containing AA, Cl_2 and AA + Cl_2

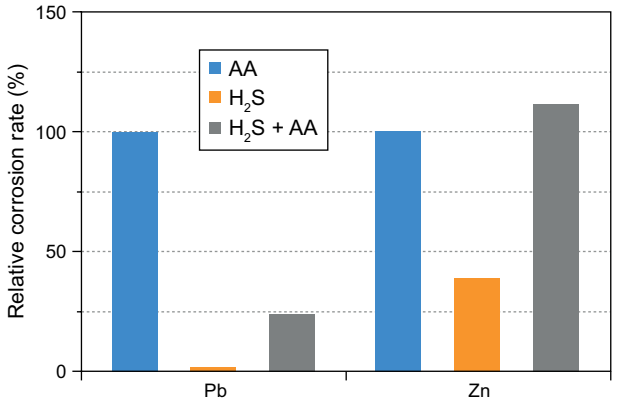

Fig. 12. Corrosion rate of resistometric sensors (Pb and Zn) in environments containing AA, H_2S and AA + H_2S

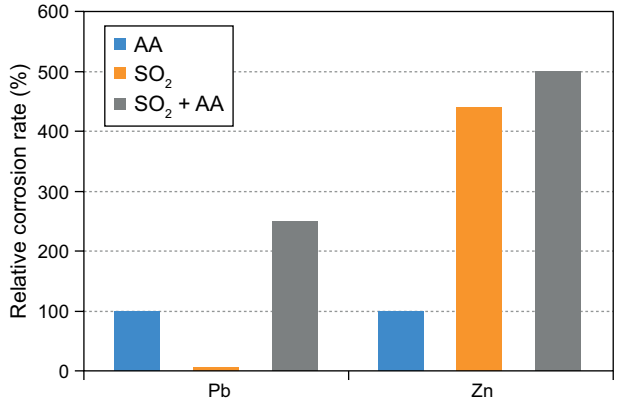

Fig. 13. Corrosion rate of resistometric sensors (Pb and Zn) in environments containing AA, SO_2 and AA + SO_2

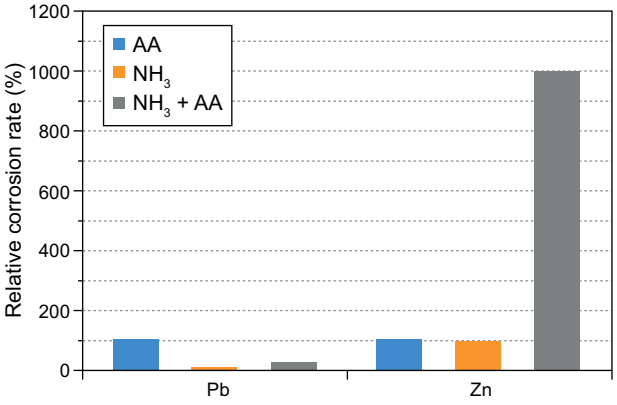

Fig. 14. Corrosion rate of resistometric sensors (Pb and Zn) in environments containing AA, NH_3 and AA + NH_3

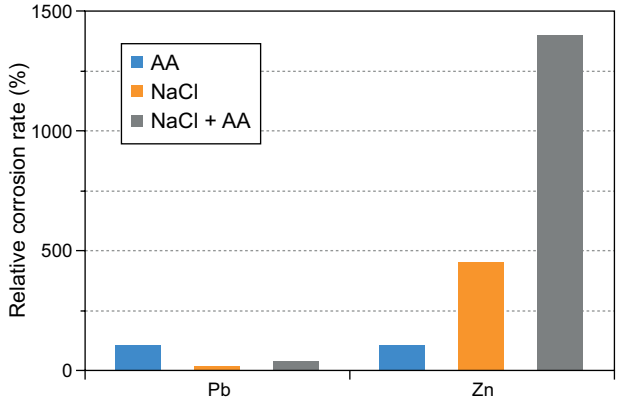

Fig. 15. Corrosion rate of resistometric sensors (Pb and Zn) in environments containing AA, NaCl and AA + NaCl

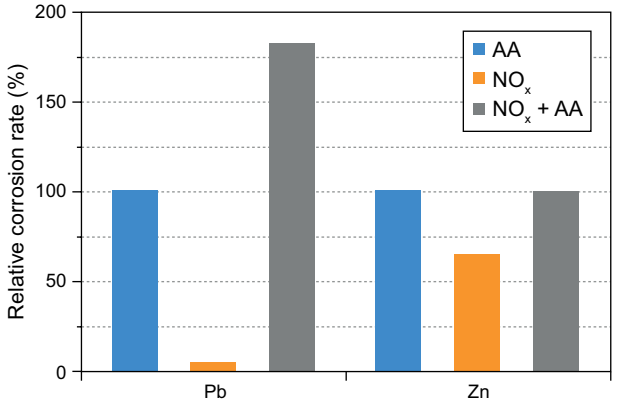

Fig. 16. Corrosion rate of resistometric sensors (Pb and Zn) in environments containing AA, NO_x and AA + NO_x

The synergy effect on lead sensors was observed for combination of acetic acid and sulphur dioxide and also for combination acetic and nitrogen oxides (see Fig. 13 and 16). Other pollutants in combination with acetic acid didn´t show any increase of corrosion rate.

Zinc resistometric sensors revealed synergic effect between acetic acid and following pollutants: sodium chloride, chlorine and ammonia (see Fig. 11, 14 and 15). The sodium chloride was much more aggressive in combination with acetic acid to the zinc resistometric sensor, but the surface of sensor after the exposure was covered with pits, that increased the electrical resistance of zinc track and though give overestimated corrosion rate. It fits well in comparison with corrosion rate obtained from corrosion coupons. The synergy effect between acetic acid and ammonia seems to be very strong, according

to the Fig.14, in fact the corrosion rates were in a range of 10^{-3} µm·h^{-1}. The change from nearly zero corrosion rate to this value was huge but it is still almost negligible corrosion rate.

Exposure of coupons

The corrosion rates of corrosion coupons are summarized in the Tab. 24 and relative corrosion rates are sum up on the Fig. 17-22. The values correspond to mean corrosion rate calculated from the corrosion mass loss at the specific environment. This is different from corrosion rate obtained with electrical resistance probes, in the case of which the changes of corrosion rate after changes in conditions were monitored. Thus, the corrosion rate of the electrical resistance probes was influence by conditions and corrosion before the conditions have changed. The corrosion rate at acetic

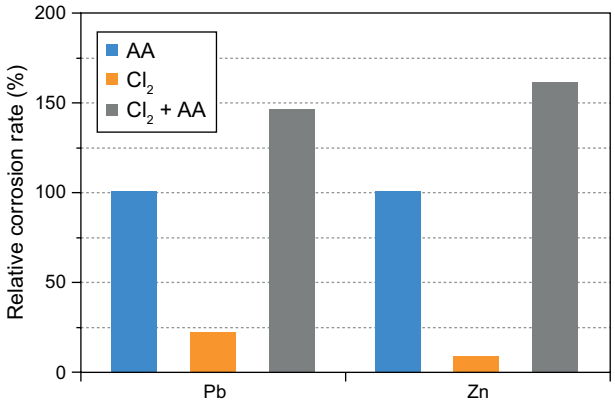

Fig. 17. Result of coupons exposure (Pb and Zn) with combinations acetic acid and pollutant Cl_2

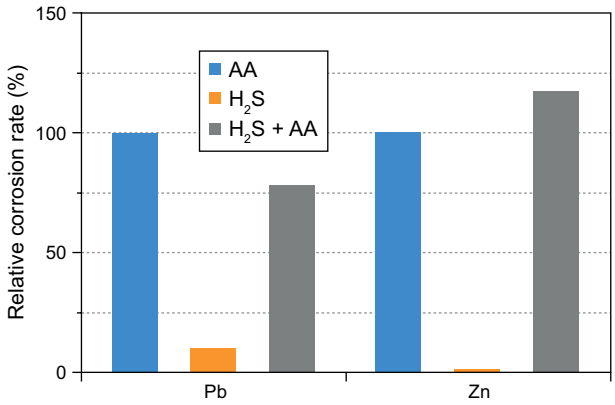

Fig. 18. Result of coupons exposure (Pb and Zn) with combinations acetic acid and pollutant H_2S

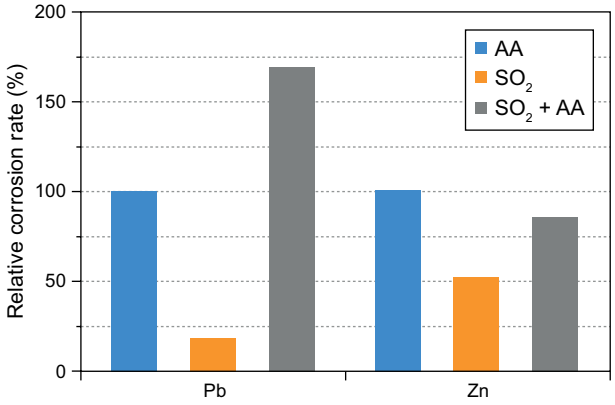

Fig. 19. Result of coupons exposure (Pb and Zn) with combinations acetic acid and pollutant SO_2

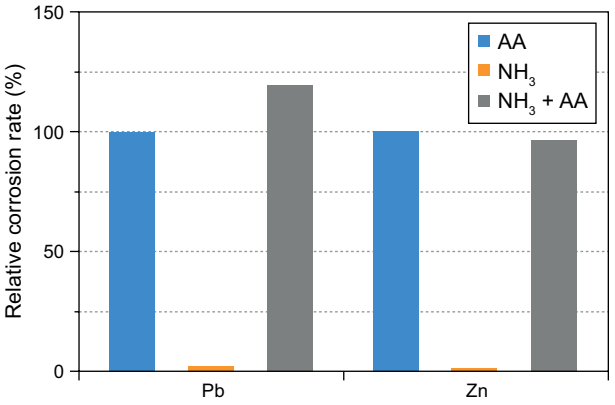

Fig. 20. Result of coupons exposure (Pb and Zn) with combinations acetic acid and pollutant NH_3

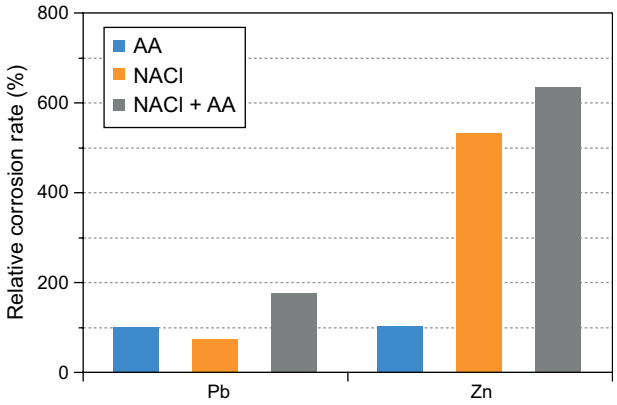

Fig. 21. Result of coupons exposure (Pb and Zn) with combinations acetic acid and pollutant NaCl

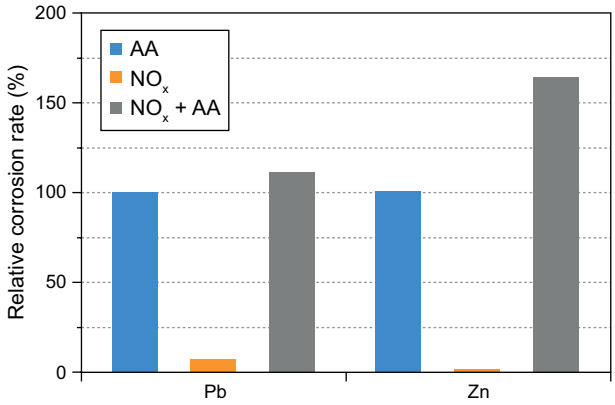

Fig. 22. Result of coupons exposure (Pb and Zn) with combinations acetic acid and pollutant NO_x

acid containing environment was set up as 100 %, the other corrosion rates were related to that number. Lead and zinc corrosion coupons have been exposed to the 3 types of environments: acetic acid, pollutant and acetic acid with pollutant.

The coupons corrosion rates were compared. If the corrosion rate at combined environment (AA + pollutant) was higher than sum up of separate corrosion rates (only AA + only pollutant), there was a possibility of synergy effect presence. It is same as for evaluation of resistometric sensors exposure.

The synergy effect on lead was found for acetic acid in combination with chlorine, ammonia, sulphur dioxide and two possible pollutants nitrogen oxides and sodium chloride. The NO_x and NaCl are suspicious, because the corrosion rate at combined environment were higher by only few percent, thus the synergic effect is likely for these combinations but cannot be pronounced as approved.

The synergy effect on zinc coupons was found between acetic acid and following pollutants: chlorine, hydrogen sulphide and for nitrogen oxides (see Fig. 17, 18 and 22). NaCl seems to be a candidate as a pollutant for synergic effect, but there is same complication as in previous paragraph with NO_x and NaCl.

Tab. 24. Corrosion rates of coupons at different environments

Environment	Corrosion rate ($g \cdot m^{-2} \cdot h^{-1}$)	
	Lead	Zinc
AA 0.01M	$4.08 \cdot 10^{-2}$	$4.37 \cdot 10^{-3}$
Cl_2	$8.96 \cdot 10^{-3}$	$4.17 \cdot 10^{-4}$
Cl_2 + AA	$6.00 \cdot 10^{-2}$	$7.08 \cdot 10^{-3}$
SO_2	$7.29 \cdot 10^{-3}$	$2.33 \cdot 10^{-3}$
SO_2 + AA	$6.92 \cdot 10^{-2}$	$3.75 \cdot 10^{-3}$
NaCl	$2.98 \cdot 10^{-2}$	$2.33 \cdot 10^{-2}$
NaCl + AA	$7.25 \cdot 10^{-2}$	$2.77 \cdot 10^{-2}$
NO_x	$1.93 \cdot 10^{-2}$	$1.04 \cdot 10^{-3}$
NO_x + AA	$2.97 \cdot 10^{-1}$	$1.52 \cdot 10^{0}$
NH_3	$4.32 \cdot 10^{-3}$	$1.00 \cdot 10^{-3}$
NH_3 + AA	$3.19 \cdot 10^{-1}$	$8.87 \cdot 10^{-1}$
H_2S	$2.54 \cdot 10^{-2}$	$1.02 \cdot 10^{-3}$
H_2S + AA	$2.08 \cdot 10^{-1}$	$1.08 \cdot 10^{0}$

Summary

The corrosion rate of resistometric sensors and coupons were compared to evaluate a prospective existence of the corrosion synergy effect of acetic acid and chosen inorganic pollutants. The results of resistometric sensors and corrosion coupons exposure are sum up in the Tab. 25. It shows whether pollutant poses the synergy effect or not according to the used methods. Although the exposure history of the resistometric probes is somewhat different compared to the corrosion coupons, the synergic effect is more likely if the result for the particular combination is confirmed by both the methods. This is the case of lead that is exposed in acetic acid and SO_2 or NO_x containing environment. In the case of zinc, the corrosion synergic effect was confirmed by both the experimental approaches only for atmosphere contaminated with chlorine based detergent vapours.

CONCLUSION

The corrosion synergic effects have been tested on volatile organic compounds sensitive metals: lead and zinc. The synergy effect has been evaluated between acetic acid and inorganic pollutants such as: Cl_2, SO_2, NaCl, H_2S, NH_3 and NO_x. Resistometric sensors and corrosion coupons were used to measure the corrosion rate. Resitometric sensors and corrosion coupons were exposed to the environments containing only acetic acid, only pollutant and their mixture. The corrosion rates were compared to determine whether, there is a possibility of presence of the synergic effect or not.

Synergic effect was found on lead between acetic acid and following pollutants: sulphur dioxide, chlorine, ammonia and nitrogen oxides. For zinc the found pollutants are following: sodium chloride, sulphur dioxide, chlorine, hydrogen sulphide and nitrogen oxides. There was a good match between both methods – sensors and coupons.

Acknowledgments

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Tab. 25. Synergy effect list summary

		NaCl	SO_2	Cl_2	H_2S	NH_3	NO_x
Resistometric method	**Pb**	–	Synergy effect	–	–	–	Synergy effect
	Zn	Synergy effect	–	Synergy effect	–	Synergy effect	–
Corrosion coupons	**Pb**	–	Synergy effect	Synergy effect	–	Synergy effect	Synergy effect likely
	Zn	–	–	Synergy effect	Synergy effect	–	Synergy effect

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