

INFLUENCE OF ORGANIC OPERATION ENVIRONMENT ON CORROSION PROPERTIES OF METAL STRUCTURE MATERIALS OF VEHICLES

ВПЛИВ ОРГАНІЧНИХ РОБОЧИХ СЕРЕДОВИЩ НА КОРОЗІЙНІ ХАРАКТЕРИСТИКИ МАТЕРІАЛІВ МЕТАЛОКОНСТРУКЦІЙ ТРАНСПОРТНИХ ЗАСОБІВ

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ABSTRACT.

The corrosiveness of cattle manure and mixed manure is considered to be low in relation to standard materials used in agricultural vehicles' metal structures – steels: standard steels (St.3 Steel, St.5 Steel) and quality steels (10 Steel, 15 Steel, 20 Steel, 25 Steel). Local corrosion damages caused by sticking particles (straw, etc.) are found. The corrosion rate of steels groups under investigation for the first day of exposure in filtered manure is found to be in the range of 0.031 to 0.042 mm/year. This rate is 3 to 4 times lower than the rate of corrosion caused by standard test rainwater solution where the further rate reduction up to 0.003 mm/year is caused by inhibitory properties of manure chemical components. In general, the corrosion of steels under study in liquid cattle manure and mixed manure occurs by an electrochemical mechanism. In comparison with distilled water, steady state potentials of the steels under study in these environments assume negative values, and the corrosion currents are to 5 times lower. Tafel constants are higher than in distilled water, which indicates the complexity of both electrode reactions as compared with the standard test environment.

РЕЗЮМЕ

Встановлено, що середовища гноївки великої рогатої худоби і гноївки змішаної мають низьку корозійну активність по відношенню до типових матеріалів металоконструкцій сільськогосподарських транспортних засобів - сталей: звичайної якості (Ст3, Ст5), також якісних сталей (Сталь 10, Сталь 15, Сталь 20, Сталь 25). Виявлено локальні корозійні пошкодження, спричинені налипанням частинок (солома, ін.). Швидкість корозії досліджених груп сталей за першу добу експозиції у відфільтрованих гноївках знаходиться в межах 0,031...0,042 mm/year, що є в 3...4 рази нижчим у порівнянні із модельним розчином дощової води, подальше зниження швидкості до 0,003 mm/year спричинене інгібувальними властивостями хімічних складових гноївок. В цілому, корозія досліджених груп сталей в рідкому гної великої рогатої худоби та змішаному протікає за електрохімічним механізмом. Стаціонарні потенціали досліджуваних сталей у вказаних середовищах в порівнянні з дистильованою водою зміщені в область від'ємних значень, а струми корозії до 5 разів нижчі. Константи Тафеля вищі, ніж у дистильованій воді, що свідчить про утруднення обох електродних реакцій у порівнянні з модельним середовищем.

INTRODUCTION

As a result of joint influence of aggressive environments and mechanical loads of tractor trailers and auger conveyors in agricultural production, about 70% of mechanisms get out of order, 20 to 25% of which are failures caused by operating overload due to the strength loss caused by corrosion damages (Mykhaylovych Y., Pubets' A., 2008; Makarenko M., 2012; Tomashov N.D., Zhuk P.N., Titov V.A., Vedenevaya M.A., 1971; Popovych P.V., Mahlatyuk L.A., Kupovych R.B., 2014; Popovich P.V., Slobodyan Z.B., 2014; Ulig G.G., 1968; GTM 23.2.75.- 82., 1982; Starosvetsky J, Starosvetsky D, Amon R., 2007). Despite the current study of influences of operating aggressive environments on the reduction of the strength and reliability of agricultural vehicles, the problems associated with the corrosion of metal structures caused by organic fertilizers are insufficiently studied (Popovych P.V., Mahlatyuk L.A., Kupovych R.B., 2014; Popovich P.V., Slobodyan Z.B., 2014; Popovych P.V., Lyashuk O.L., et al., 2016).

In particular, in *P. V. Popovych, et al. (2014)*, only two types of steel are studied. It is well known that in the manufacture of metal structures of tractor trailers, the whole range of standard and quality steels is used (*GTM 23.2.75.- 82., 1982; Al-Otaibi M.S., Al-Mayouf A.M., Khan M., Mousa A.A., Al-Mazroa S.A., Alkhathlan H.Z., 2014; Raja P.B., Sethuraman M.G., 2008; Li X., Deng S., Fu H., 2012; Popovich P.V., Slobodyan Z.B., 2014*). Therefore, there is a need to conduct experimental studies for a wider range of metal structure materials of tractor trailers. The reliability of transport machinery, in particular of agricultural trailers and auger conveyors, is ensured by their durability, failure-free operation, and maintainability and performance reliability. For vehicles, fertilizer spreaders, and others, the non-operating time is up to 80% (*Mykhaylovych Y., Pubets' A., 2008*) the performance of trailers is maintained during the storage; the efficiency of storage depends primarily on the quality of cleaning to ensure the removal of organic fertilizers residues and soil as well as on proper preservation of equipment. Even minor deviations from specified storage conditions can cause the corrosive damages. The rate of corrosion of the equipment made of standard and quality steels depends on the environment, time of contact, temperature, state of the metal and protective coatings, etc. The pit corrosion, oxygen concentration corrosion, fretting corrosion, contact corrosion, and corrosive cracking can be traced on some assemblies of tractor trailers (*Makarenko M., 2012*), Fig. 1, Fig. 2. Loss of metal is insignificant, however it most often occurs in significant conjugations of parts' surfaces that limit the reliability and serviceability of vehicles in general. Among organic fertilizers, the most corrosive are peaty composts, less aggressive – lowland and upland peats and cow manure. Thus, water acts as a catalyst of corrosion processes (*Makarenko M., 2012; Popovych P.V., Mahlatyuk L.A., Kupovych R.B., 2014*).

The purpose is to study the influence of exposure time on the corrosion rate of metal structure materials of agricultural vehicles, in particular, standard steel – St.3 Steel, St.5 Steel (DSTU 2651: 2005; DIN 17100) and carbon quality steel – 10 Steel, 15 Steel, 20 Steel, 25 Steel (GOST 1050-88; DIN 17200) as well as their electrochemical properties in cattle manure and mixed manure.



Fig. 1 – Corrosive damage of metal structure material of agricultural trailers



Fig. 2 – Corrosive damage of auger conveyor of agricultural materials

MATERIAL AND METHODS

Corrosion tests were carried out on samples of St.3 Steel, St.5 Steel and 10 Steel, 15 Steel, 20 Steel, 25 Steel under supply conditions. The samples were made in the form of discs with a diameter of 20 mm and with a surface polished to a roughness $R_a = 0.63$. Previously ungreased samples were weighed using a high-accuracy weighing machine to within ± 0.0004 g and stored in a desiccator up to 24 hrs.

As corrosive environments, the organic fertilizers were used: cattle manure and mixed manure in a ratio of 1/2 of cow manure + 1/2 of pig manure (their main content is given in Table 1 and distilled water as standard test condensation and rainwater. Before testing, corrosive environments were filtered using a paper filter to remove dispersed components.

Table 1

Content of major nutrients in fertilizers environments under study									
Components Environment	% mass								
	H ₂ O	N General	N protein	N ammoniac	P ₂ O ₅	K ₂ O	CaO	MgO	SO ₃
Cattle manure	86.7	0.38	-	-	0.12	0.22	0.25	-	-
Mixed manure	75.0	0.50	0.31	0.15	0.25	0.60	0.35	0.15	0.10

Before and after the experimental studies, the pH of solutions was measured using pH-meter I-160M. The rate of corrosion K_m (g/(sm²·hr)) is determined by a gasometrical method after exposure for 1, 7, 12 and 24 days under natural aeration conditions and after the removal of corrosion products (Tomashov N.D., Zhuk P.N., Titov V.A., Vedeneyeva M.A., 1971); calculations were performed using the known dependencies.

The calculations were performed using the following formula

$$K_m = \Delta m / S \cdot \tau, \quad (1)$$

where:

Δm – the sample weight change after exposure to the environment and removal of corrosion products, g;

S – the area of sample, m²;

τ – the exposure time, hr.

The obtained value was converted using the depth index P (mm/year)

$$P = \frac{K_m \cdot k}{\gamma} \cdot 10^{-1}, \quad (2)$$

where: k – the conversion factor of hrs per year;

γ – the iron density 7.86 g/cm³.

The percentage ratio of the degree of steel protection against corrosion Z was defined using the following formula

$$Z = \frac{K_m - K_i}{K_m} \cdot 100\%, \quad (3)$$

where K_m and K_i – the corrosion rates of steel in distilled water and environments.

Polarization studies were conducted using the potentiostat IP-Pro. Samples of steel, pressed in PTFE, were used as the working electrodes; the working surface area is 0.0628 cm². Before each measurement, the sample was grinded by the abrasive paper №0, cleaned with acetone and dried. The comparison electrode is the saturated silver chloride electrode, the auxiliary – the platinum one. The corrosion current and Tafel constants of cathode and anodic reactions were determined from the straight sections of polarization curves.

The current-controlled indexes of corrosion rate were converted to the mass ones using the formula

$$K_i = i \cdot k \cdot A / n \cdot F \quad (4)$$

where: i – the corrosion current, A/cm²;

k – the coefficient ($k = 1$, if the testing time is expressed in seconds, and the area – in cm²);

A – the atomic mass of metal (iron and steel $A = 56$);

n – the valence of metal (iron 2 or 3);

F – the Faraday constant (Ulig G.G., 1968).

RESULTS

The nitrogen-containing compounds (see Table 1), which often have properties of corrosion inhibitors, were revealed during the chemical analysis of cattle and mixed manures. Corrosion tests of exposure studied at various times showed the following corrosion rates of steels in organic fertilizers (see Table 2). The corrosion rate of steel in both groups for the first day is 3 to 4 times lower in comparison with distilled

water, and 8 to 10 times lower than in mineral fertilizer of ammonium phosphate and nitrophosphate when comparing, for example, St.3 Steel and 20 Steel.

Standard steels (St.3 Steel, St.5 Steel) corrode with greater speed than quality structural steels (10 Steel, 15 Steel, 20 Steel, and 25 Steel). The exposure time increases, the corrosion rate significantly decreases. After 24 days, the corrosion rates of steels under study in both environments equalize. Thus, for the first day, the inhibitory effect at the level of 60 to 70% occurs in manures as compared with distilled water. After 24 days, the degree of protection is over 90%. There is no difference between the corrosiveness of liquid cattle and mixed manures. Individual local corrosion damages of steels after exposure in unfiltered original manure is the result of the formation of galvanic couples due to sticking dispersed solid residues of straw, seeds and others on the surface of samples.

After 1 day testing, on the surface of samples only non-systemic single changes in the form of colour variation are found, corresponding to the thickness of the oxide film of the order 460 to 680 Å. After the further testing for 7 to 24 days, the sample surfaces are clean without any visible changes.

Before the corrosion test, pH of cattle manure and mixed manure was pH = 7.45 to 7.50. After exposure of steels in environments during 24 days, pH increased to 8.2.

Corrosion potentials of all steels under study in cattle and mixed manures are defined for 15 to 20 min. They assume more negative values in the standard test rainwater in comparison with distilled water (Fig. 2a, b). The nature of polarization curves on steel samples is the same (Fig. 3a, b). The quality steel cathode curves differ by the area and the value of boundary diffusion currents. In cattle manure the boundary diffusion current is $7 \cdot 10^{-2}$ A/sm² in the range of potentials -630 ... -920 mV; in mixed manure it is $3 \cdot 10^{-2}$ A/sm² in the range of potentials -510... -810 mV. The standard steel cathode curves in both organic fertilizers differ extremely by the range of potentials of boundary diffusion current: -680 ... -1100 mV in cattle manure and -580... -1100 mV in mixed manure. The boundary diffusion current is higher than in quality steels - $9 \cdot 10^{-2}$ A/sm² and $7 \cdot 10^{-2}$ A/sm².

Table 2

Corrosion rate depth index of metal construction materials of tractor trailers in organic fertilizers

Steel	Time Environment	P, mm/year			
		1 day	7 days	12 days	24 days
10 Steel	H ₂ O	0.139	0.080	0.084	0.078
	Liquid manure	0.040	0.007	0.006	0.004
	Mixed manure	0.036	0.004	0.003	0.004
15 Steel	H ₂ O	0.141	0.079	0.081	0.075
	Liquid manure	0.042	0.008	0.005	0.003
	Mixed manure	0.034	0.005	0.003	0.003
20 Steel	H ₂ O	0.13	0.075	0.077	0.071
	Liquid manure	0.038	0.007	0.005	0.003
	Mixed manure	0.032	0.004	0.003	0.003
25 Steel	H ₂ O	0.125	0.072	0.074	0.068
	Liquid manure	0.036	0.007	0.005	0.003
	Mixed manure	0.031	0.004	0.003	0.003
St.3 Steel	H ₂ O	0.117	0.078	0.09	0.088
	Liquid manure	0.040	0.008	0.005	0.003
	Mixed manure	0.035	0.005	0.003	0.003
St.5 Steel	H ₂ O	0.111	0.072	0.083	0.082
	Liquid manure	0.038	0.007	0.004	0.003
	Mixed manure	0.033	0.004	0.003	0.003

Anode curves for steels groups under study have a small area associated with the state of passivity: in liquid manure -480...-530 mV (20 Steel), -480...- 540 mV (St.3 Steel), and in mixed manure -250-320 mV (quality steels), -350...-420 mV (standard steels). The state of passivity is clearly traced in both environments when the potential assumes the values from -250 mV towards less negative ones at high currents of passivation about 10 A/sm².

Corrosion currents of all steels in both types of manure are 4 to 5.57 times lower than in distilled water (Table 3). Instantaneous values of current corrosion rates, listed in (4), satisfactorily correlate with the rates obtained by a gasometrical method for the first day under the condition of iron oxidation 3⁺ (see Table 4). The low corrosiveness of manures under study is additionally confirmed by the analysis of Tafel areas of polarization curves.

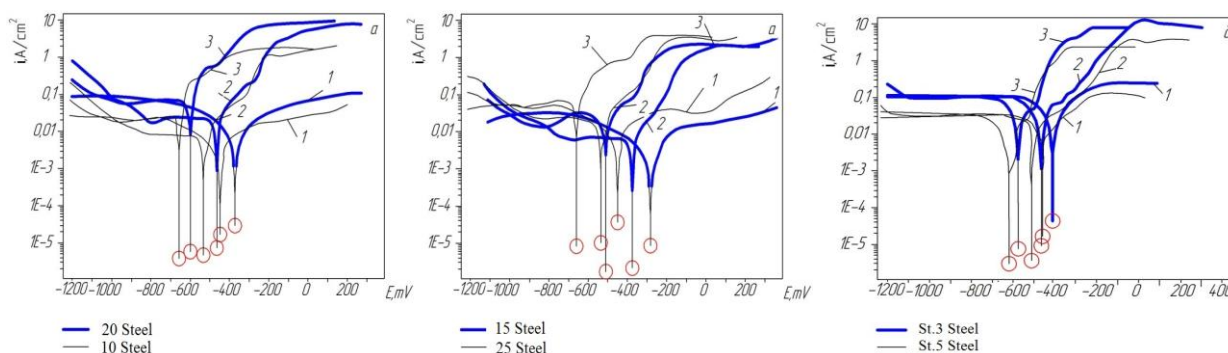


Fig. 3 - Polarization curves a – 10 Steel, 15 Steel, 20 Steel, 25 Steel; b – St.3 Steel, St.5 Steel
 1 – distilled water; 2 – liquid manure; 3 – mixed manure.

Tafel constants of cathode and anodic reactions of these steels groups in environments under study are higher than the corresponding constants in distilled water (see Table 3). This fact ensures a greater over-potential of both electrode reactions compared with electrode reactions in water, resulting in low rates of electrochemical corrosion.

Table 3

Electrochemical properties of metal constructions materials of agricultural vehicles in organic fertilizers

Environment Steel	Cattle manure				Mixed manure				Distilled water			
	$-E_{st}$, mV	$i_{cor} \cdot 10^5$, A/cm ²	b_c , mV	b_a , mV	$-E_{st}$, mV	$i_{cor} \cdot 10^5$, A/m ²	b_c , mV	b_a , mV	$-E_{st}$, mV	$i_{cor} \cdot 10^5$, A/cm ²	b_c , mV	b_a , mV
10 Steel	597	0.8	30.8	28.6	454	0.7	36.1	28.8	392	3.7	22.4	19.8
15 Steel	604	0.7	31.3	29.2	457	0.7	37.2	30.2	380	3.5	23.1	20.2
20 Steel	610	0.7	33.3	30.0	460	0.6	38.5	460	372	3.0	25.0	22.3
25 Steel	617	0.7	34.8	32.1	472	0.5	40.1	33.8	452	3.9	36.2	30
St.3 Steel	590	0.9	30.2	28.1	450	0.8	35.0	27.9	401	4.1	21.3	18.3
St.5 Steel	592	1	30.4	28.4	452	0.9	36.2	30	410	4.3	22.0	19.1

Table 4

Comparing the corrosion rates of metals in organic fertilizers environments derived gravimetrically (K_m , (g/sm²·s)), electrochemically (i_{cor} , A/cm²) and listed from current parameters (K_r , (sm²·s))

Environment Steel	H ₂ O _{distilled}			Cattle manure			Mixed manure		
	$K_m \cdot 10^9$	$i_{cor} \cdot 10^5$	$K_r \cdot 10^9$	$K_m \cdot 10^9$	$i_{cor} \cdot 10^5$	$K_r \cdot 10^9$	$K_m \cdot 10^9$	$i_{cor} \cdot 10^5$	$K_r \cdot 10^9$
10 Steel	3.32	3.70	5.85	0.99	0.70	1.45	0.85	0.70	1.25
15 Steel	3.30	3.50	5.88	1.01	0.8	1.48	0.87	0.70	1.28
20 Steel	3.25	3.00	5.80	0.94	0.70	1.40	0.80	0.60	1.20
25 Steel	3.20	2.80	5.76	0.90	0.80	1.36	0.76	0.50	1.16
St.3 Steel	3.50	4.10	7.80	1.10	0.90	1.70	0.90	0.80	1.50
St.5 Steel	3.42	4.30	7.73	1.03	0.90	1.63	0.84	1.00	1.42

Therefore, cattle and mixed manures are characterised by small corrosive aggressiveness to metal structure materials of agricultural vehicles, standard steels and quality steels. However, concentrators formed as a result of corrosion damages and combined with significant mechanical loads can reduce the equipment durability.

The corrosion in these environments occurs by an electrochemical mechanism at lower rates compared to distilled water, provided natural aeration. The obtained results allow to extend the operating time of agricultural equipment and to optimize its maintenance schedule. In addition, the results of the study of corrosion degradation can be used to create coatings for the metal surface protection.

CONCLUSIONS

1. The corrosion of standard steels and quality steels in cattle and mixed manures is exclusively local in nature. This property is caused by the formation of single galvanic couples as a result of sticking suspended solid particles (straw, etc.).

2. The metal structure materials of tractor trailers under study in both types of manure corrode by an electrochemical mechanism. In comparison with distilled water, steady state potentials of the steels under study in these environments assume negative values, and the corrosion currents are to 4 to 5.37 times lower. Tafel constants are higher than in distilled water, which indicates the complexity of electrode reactions. The values of current rates of corrosion satisfactorily coincide with the values obtained by a gasometrical method.

3. After the removal of suspended particles, the low corrosiveness can be traced in working environments under study in relation to the mentioned steels groups. The corrosion rate of studied metal structures materials of trailers for the first day of exposure is found to be in the range of 0.032 to 0.04 mm/year. This rate is 3 to 4 times lower than the rate of corrosion caused by standard test rainwater solution. The further rate reduction up to 0.003 mm/year is caused by inhibitory properties of manure chemical components.

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