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Original Research article

Aluminum in Reaction with Sodium Hydroxide: Summary Action of a Depolarizer and an Inhibitor



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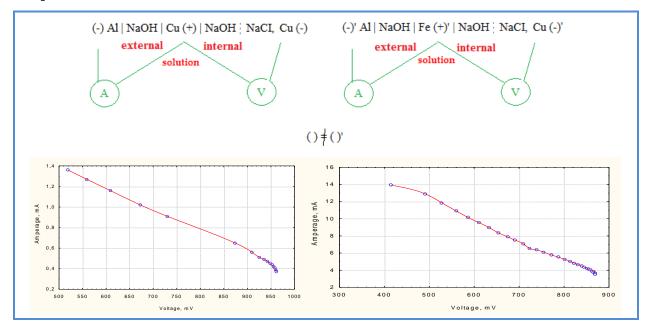
ABSTRACT

An unusual work is that the galvanic cell described is non-standard and has irreversible electrodes. Non-standard are comparative electrodes too. Only 1 electrochemical cell Al | NaOH (it is polarizer, amperage-forming or polarizing agent). By measuring the amperage generated by this electrochemical cell, the dissolution rate of aluminum was investigated. Inhibition of aluminum dissolution was supposed to be achieved for the first time using the "Dorogov antiseptic stimulator of fraction No. 2" or ASD-2F, acceleration by the introduction of a depolarizer (it is depolarizing or amperage-absorbing agent) consisting of steel and copper cores protected from vortex flows caused by anything. The amperage and voltage characteristics "amperage on polarizer + depolarizer-\-voltage on depolarizer" were built. The fastest dissolution occurs when a larger voltage accounts for a larger voltage. A correlation was revealed "the ionic strength of the inhibitor at the N and O atoms of 2nd...5th groups of "organic-part" of ASD-2F I_{Σ2} __5 \ amperage of a galvanic cell for 600 mV", and a correlation was revealed "donor and acceptor strength of molecules of 2nd - 5th groups of "organic-part" of ASD-2F H_{Σ2...5}\ amperage of a galvanic cell for 600 mV». It is very important that each line of each diagram is analyzed individually.

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Graphical Abstract



Introduction

Recently, the interest of researchers from all countries has been causing the behavior of aluminum anode in alkaline solutions, since in alkaline medium, aluminum has a significant electronegative standard potential (-2.35 V) compared with acidic solutions (-1.66 V) [1-3].

Activating ability reaches maximum values at pH 15-16, where the rate of self-dissolution is 150-170 g/(m²/h) [4, 5]. However, it is in such solutions that the aluminum corrosion rate increases significantly and the effectiveness of corrosion inhibitors decreases, and there is also a noticeably negative effect when the potential shifts to the anode side and the general anode amperage flows, while the cathodic process of hydrogen evolution is accelerated [6-8]. The medical ASD-2F (it is inhibitor) was invented in 1948 by A.V. Dorogov, the USSR classified headstock was removed in 1962, however it is still little known, so we decided to dwell on its chemical composition, which was first determined by the authors [9].

The method of chromatography-mass spectrometry gives 121 substances (for 10/X-2013) as part of "organic-part" in ASD-2F. A detailed chemical composition is given in [9] (in Russian). The most important substances in ASD-2F are already divided into groups. The first group of compounds with a total proportion of 18.8% of the mass of organic substances can be composed of 16 amides of lower saturated carboxylic acids. Five further groups of substances can be formed from nitrogen-containing heterocyclic compounds with one or two nitrogen atoms. The total proportion of nitrogen-containing

heterocyclic compounds among organic substances of a different structure is 38.4%. Since 2004, the production of the drug using the technology of the scientist Dorogov has been engaged in the Russian corporation 000 НВЦ «Агроветзащита» [000 NVC "Agro Vet Zashchita"] [9].

The potentiostatic method is used. The distribution pattern of amperage and voltage characteristic was stereotypical. By increasing voltage, the amperage was decreases. The equilibrium position on steel was achieved more slowly (there are more points) than that of copper. In general, a steel depolarizer provided values of lower voltage, but with higher amperage [3]. The inhibitory effect was observed in all cases, which will be proved in various ways below. The following Figures 2-11 are made in STATISTICA 7.0 (pearson's correlation coefficients were also calculated there). The accumulation of data went up to the achievement of 3 identical values of millivolts (mV) and milliamps (mA) (there are a lot of points at the end of curves). Charts were built separately, it was necessary to accurately divide into zones, since in many cases the zones are barely noticeable [10].

Experimental

Preparation in research

Details of structure

Testing galvanic cells

The testing galvanic cells have a structure (with a distance of 9 cm till (-) from (+)). The following describes the device and the composition of the components (Figure 1).

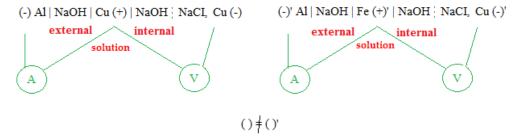


Figure 1. Electrochemical galvanic cells, with help of which the dissolution of aluminum was studied

Structure of polarizing agent Al | NaOH external

A parallelepipedal Al-sample of 15.8 cm² with a polished surface was used, having 4 large faces and 2 small faces. It was hung on a copper wire through a small hole, which, of course, did not come into contact with the sodium hydroxide solution in any cases.

Structure of depolarizing agent both Cu | NaOH external and Fe | NaOH internal

Their structures are the same, with the exception of the metal. The structure is as follows for both: a sample of the corresponding metal (core) of 7.1 cm^2 with a polished surface was used. Electric wire is copperic in case of Cu | NaOH, in the case of Fe | NaOH electric wire is steelic. Around the depolarizer there is an environment: a plastic cylinder with a piston (plastic medical syringe) into which a NaOH solution is sucked. This ensures peace of mind for the adsorption process, in contrast to the conditions in [9] ("quiet adsorption"), and a milliliter scale on it guarantees the reading of the released volume of H_2 -gas during further gas detection. After each experiment, a depolarizing agent of any composition was gently shaken to remove all existing gas bubbles (to accurately account for the volume of H_2 -gas released).

Structure of standard electrode Cu | (0.33%) NaCl

The standard electrode is also selected offbeat in order to broaden the horizons of a reader. Its electrodic potential is unknown, and its value is not needed, since the voltage of galvanic cell is being investigated. Consists of 0.7 mm × 20.0 mm copperic wire, rolled into a globule. For non-mixing of electrolytes both NaCl and NaOH, a semipermeable foam rubber partition is used. 0.33% NaCl changed in the standard electrode after removing each of the cycles "amperage on polarizer + depolarizer-\-voltage depolarizer" even before the appearance of a blue and green color of CuCl₂, the constancy of the electrodic potential was maintained and side electrochemical reactions were excluded.

Measurement of voltage and amperage: voltmeter and ammeter

Measurements were carried out by 2 ANENG Q1 True-RMS digital multimeter counting analog bar graph AC / DC voltage ammeter instruments; one of these devices is used as a millivoltmeter in Figure 1. (it is (V)), the second of these devices is used as a milliammeter in Figure 1. (it is (A)).

Electrochemical solutions

Sodium hydroxide working-basic and sodium hydroxide gas-analyzering

The electrochemical cell contained 120 mL of any liquid. The 0.38 N is used (working-basic NaOH) and 35% gas-analyzering NaOH is used. The latter was required insofar as there was no hope to trace the data on gas evolution inside the depolarization agent due to the low concentration (there were 2 series of experiments: the first detailed, the second special).

Concentrated liquid inhibitor ASD-2F

The formula of "organic part" is $C_{5.53}H_{9.25}N_{1.39}O_{1.07}P_{0.01}$. This research study used a light-yellow liquid with a brown tint, with a specific smell, that mixes well with water. It had a sharp specific smell. The

density was 1.124 g-/-cm³. The "organic part" is represented by organic bases. Judging by the nature of the curves below, only the "organic part" of ASD-2F serves as an inhibitor.

Quantum chemical and correlation methods

ASD-2F is not an individual substance, but a mixture. The molecules of this mixture act synchronously or asynchronously, and their effect on the dissolution of aluminum in an alkaline medium depends on their concentration. Therefore, one organic molecule from each group was selected from the description of the chemical composition (the reader needs to see the introduction). The criterion for choosing an organic molecule was the highest percentage thereof in the "organic part" of ASD-2F. Groups $2^{\rm nd}$ - $5^{\rm th}$ were used (*i.e.*, 4 molecules were taken for quantum chemical calculations in GAMESS2010). The fifth molecule can be called the corrosive medium NaOH (the H_2O solvent was not taken into account, since the side reaction of aluminum with water was most likely strongly suppressed). Quantum-chemical optimization of geometry: 1) MM +, 2) DFT-PBE0 / 4-31G, quantum-chemical calculation of charges on N, O atoms, and HOMO and LUMO energies: DFT-PBE0 / TZV.

The ionic strength I of corrosive environment with ASD-2F was calculated using the assumption first put forward by the author that organic molecules as well as inorganic ions participate in the creation of ionic strength through their charges on heteroatoms. The inorganic ionic compounds gave this work some novelty.

The author also classified the phenomenon "donor and acceptor strength H of corrosive environment with ASD-2F" to similar novelty. An assumption has now been made that a certain soft energy of molecules (that is, a tendency to polarizability and, accordingly, to donation of an electron pair) generated by the energy of HOMO and LUMO and depending on the molar fraction of these molecules in the solution.

When finding the correlation coefficients, the following values were used.

First level array: $_{1mL}I_{\Sigma 2...5}$ $_{\Sigma N}$ -field or $_{\Sigma 0}$ -field + I_{NaOH} and I_{NaOH} and I_{NaOH} and I_{NaOH} .

Formula was $_{n \text{ mL}}I_{\Sigma 2...5} = \frac{1}{2} n \left[\sum (c_i \cdot (\sum z_i^2 0 \text{ or } N)) \right]$ and $I_{NaOH} = \frac{1}{2} \left[c_{i Na+} + c_{i OH-} \right]$.

Second level array: $_{1mL}H_{\Sigma 2...5} + H_{NaOH}$ and $_{2mL}H_{\Sigma 2...5} + H_{NaOH}$ and H_{NaOH} .

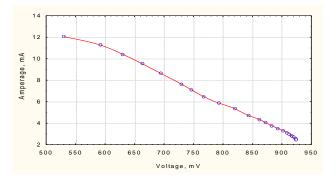
Formula was $_{n \text{ mL}}H_{\Sigma 2 \dots 5} = n\Sigma [N_i \cdot h_i]$ and $H_{NaOH} = N_{NaOH} \cdot h_{NaOH}$.

After that, the correlation "ionic strength of corrosive environment in the N and O atoms of "organic part" of ASD-2F-\-amperage of the galvanic cell at a voltage for 600 mV" and the correlation "donor and acceptor strength of molecules 2nd-5th groups of ASD-2F\amperage of a galvanic cell at a voltage for 600 mV" were directly revealed.

Results and discussion

Depolarizing agent: steel

The curves were not smooth, and the curves can be divided into 3 zones (Figure 2-4) by decreasing the angle with the abscissa axis. The boundaries of the zones cut off certain voltage values on the abscissa axis. Zones hereinafter are generated due to the depolarizing characteristics of the surface. The end of the curves is also analytically important; the beginning of the curves is of less analytical significance.



 $\textbf{Figure 2.} \ \ \textbf{Voltage and amperage characteristic of the aluminum reaction with steel depolarizer and with 0.0 mL of ASD-2F$

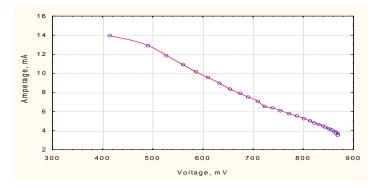


Figure 3. Voltage and amperage characteristic of the aluminum reaction with steel depolarizer and with 1.0 mL of ASD-2F

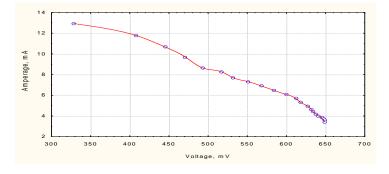


Figure 4. Voltage and amperage characteristic of the aluminum reaction with steel depolarizer and with 2.0 mL of ASD-2F

The zone number	The voltage zone on the depolarizer, mV		
	Without inhibitor	1 mL + steel	2 mL + steel
I	530610	410490	330470
II	610780	490720	470610
III	780923	720870	610650
A for V=600 mV	11.0	9.5	6.0

Table 1. Number interpretation of Figures 2-4

A strong inhibitory effect of "organic part" of ASD-2F is obvious - the values of Table 1. are steadily falling. According to [4, 5, 12], this phenomenon was explained by the adsorption on the depolarizing metal (in particular, on steel) of the components of "organic part" of ASD-2F, comprising 4.8 ... 7.5%.

Depolarizing agent: copper

The methods for describing the zones are different that of the steel depolarizer, since in Table 2. there is no inhibitory effect by analogy with Table 1. Therefore in this case, other mathematical instrument (equation of zones on the curves, consideration on the corresponding graphs of changes in amperage and voltage, and their mathematical relationship) was employed. In the case of using a steel depolarizer, there was no need for zone equations on the curves (Figure 5-7). In the case of using a copper depolarizer the curves are also not uniform. However, when considering their analytical dependencies are much more complicated, since when adding even 1.0 mL of ASD-2F inhibitor, the 2nd zone disappears (therefore, displaying it in Tables 2 and 3. in principle does not make sense). When 2.0 mL of inhibitor was added, many dots appear on the corresponding graph and were dispersed.

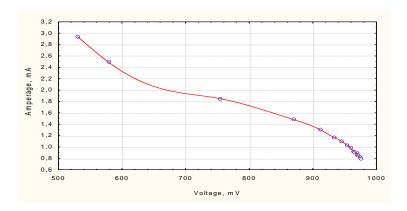


Figure 5. Voltage and amperage characteristic of the aluminum reaction with copper depolarizer and with 0.0 mL of ASD-2F

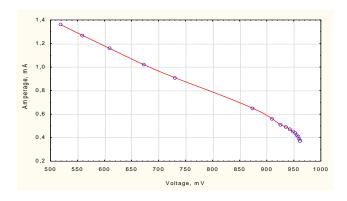


Figure 6. Voltage and amperage characteristic of the aluminum reaction with copper depolarizer and with 1.0 mL of ASD-2F

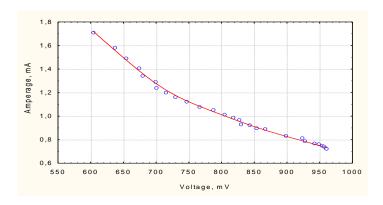


Figure 7. Voltage and amperage characteristic of the aluminum reaction with copper depolarizer and with 2.0 mL of ASD-2F

Table 2. Number interpretation of Figures 5-7

Zone number	Voltage on the depolarizer, mV and other / (ΔΕ/ΔΙ) / ΔΙ / ΔΕ		
	Without inhibitor	1 mL + copper	2 mL + copper
Start of curves	530	520	600
I	<663/144.4/0.90/130	Dissolution	>720/240/0.50/120
II	663885	Dissolution	Dissolution
III	>885/221.8/1.60/355	>885/467.9/0.78/365	Dissolution
End of curves	980	960	960
A for V=600 mV	2.3	1.2	1.7

The author had to select the beginning and end of the curves to avoid cluttering the Table

Table 3. Number interpretation of Figures 5-7 (continued)

Zone	Zone of mathematical equation		
number	Without inhibitor	1 mL + copper	2 mL + copper
I	y = -0.00818x + 7.245	Dissolution	y = -0.00492x + 4.740
II	y = -0.00291x + 4.031	Dissolution	Dissolution
III	y = -0.00758x + 8.194	y = -0.00286x + 3.093	Dissolution

The inhibitory effect in the data of Table 2. can be traced worse, it is good only when considering ΔI (in italics) and the data of Table 3. (coefficient *k* increases and coefficient *b* decreases). Probably, in

| NaOH | Cu (+) | NaOH |

the data of Table 2, even the stimulation of aluminum dissolution can be traced here, which may be due to better outflow of electrons (electron outflow from the depolarizer) due to the chelation of nitrogen-containing organic molecules. Or the outflow of electrons occurs due to the adsorption of negatively charged groups of organic molecules and inorganic anions.

Pearson's correlation coefficients method

The relationship between the structure of the mixture of molecules and the phenomena caused by this mixture can be judged by the data in Table 4.

Ionic strength of the inhibitor by the total charge	Correlation coefficients	
on N and O.	Depolarizer steel	Depolarizer copper
I Σ N-field	-0.97	-0.56
I Σ O-field	-0.96	-0.58
Donor and acceptor strength of molecules 2 5 groups of ASD-2F	-0.97	-0.54
Н		

Table 4. Pearson's correlation coefficients values

Therefore, the more negative the field of total charge on the atoms of "organic part" of ASD-2F used by us, the lower the amperage at the voltage of 600 mV. Also the greater the polarizability of the molecules of "organic part" of ASD-2F, the lower the amperage at the voltage of 600 mV. The relationship is strong (in the case of copper depolarizer, weaker) and favorable for a greater addition of inhibitor.

Hydrogen evolution

Gas evolution is hydrogen evolution, manifested in the place of the green arrow and trapped in a plastic cylinder with divisions with an accuracy of 0.1 mL. For brevity, it was decided to measure gas evolution in without inhibitor ASD-2F and with 1 mL of inhibitor (ASD-2F). The identification of pearson's correlation coefficients was not too necessary, and the author decided to omit their identification, as the available gas volume has many preliminary stages of

evolution, and depends on many conditions. The addition of 1.0 mL of inhibitor ASD-2F causes activation of gas evolution in the case of a steel depolarizer and a slight slowdown in the case of a

copper depolarizer.

The nature of the gas evolution in the depolarization agent also gives the schedule a breakdown into 3 zones (Figure 8-11).

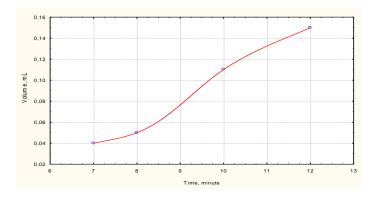


Figure 8. Characterization of hydrogen evolution on a steel depolarizer with 0.0 mL of inhibitor versus time

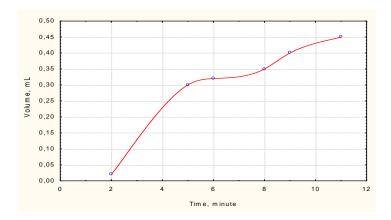


Figure 9. Characterization of hydrogen evolution on a steel depolarizer with 1.0 mL of inhibitor versus time

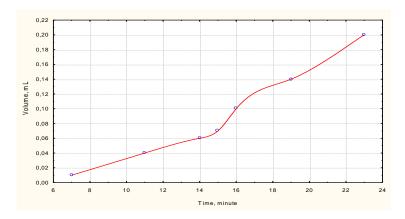


Figure 10. Characterization of hydrogen evolution on a copper depolarizer with 0.0 mL of inhibitor versus time

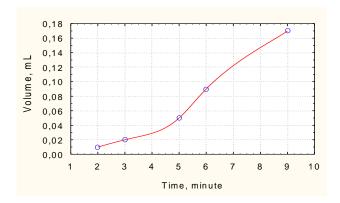


Figure 11. Characterization of hydrogen evolution on a copper depolarizer with 1.0 mL of inhibitor versus time

	Versus time, minutes			
Zone Number	Without inhibitor + steel	1 mL + steel	Without inhibitor + copper	1 mL + copper
I	7.08.5	2.05.2	7.014.5	2.04.3
II	8.510.3	5.27.7	14.519.0	4.36.5
III	10.312.0	7.511.0	19.023.0	6.59.0
$V(H_0)$ for $\tau = 0$ min	0.05	0.25	0.01	0.15

Table 5. Number interpretation of Figure 8-11

Gas formation becomes more intense with increasing concentration. This growth is more striking in the case of a copper depolarizer, which is explained by a large decrease in the hydrogen overvoltage on copper. It can also be assumed that hydrogen was absorbed into the material of a copper depolarizer. In terms of volume, gas generation was more intense on a steel depolarizer.

Conclusions

The inhibitory effect depends on the strength of the adsorption process. This work can be positioned as an aspect of the study of aluminum corrosion in strongly alkaline medium with inhibition (using "organic part" of ASD-2F) and stimulation (using of a depolarizer) of such corrosion. The inhibitor produced the observed action by: 1) reducing the overvoltage of hydrogen on the surface of steel and surface of copper, 2) strong adsorption of positive charges mainly on steel, strong adsorption of negative charges mainly on copper, 3) explains reason No. 2, since a correlation between the polarizability of the mixture of molecules was revealed and its ability to protect aluminum from dissolution.

In this work, the authors do not measure the voltage of a polarizing agent (the metal), since degree of adsorption may decrease due to mixing with hydrogen bubbles, constant updating of the aluminum surface due to the reaction with alkali, due to the side reaction of aluminum with water, the basis of

which sodium hydroxide solutions are prepared. Due to the total presence and action of these phenomena, the true voltage value in Al | NaOH $_{\rm external}$. Therefore, the adsorption acting in all cases of inhibition of electrochemical corrosion [11, 12] was noted as follows: 1) an increase in the voltage of the depolarizing agent and 2) a decrease in the amperage of the polarizing agent, 3) theoretically - for studying the pearson's correlation coefficients. Using of correlation coefficients revealed that there is a direct and very strong relationship between the ionic strength of representatives of groups 2^{nd} - 5^{th} and inhibition of corrosion through a decrease in amperage.

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