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EFFECT OF IONIC STRENGTH ON ELECTRO-CORROSION IN CHLORIDE AND CHLORIDE-SULFATE ENVIRONMENTS

Lyubomyr Poberezhny

Ivano-Frankivsk National Technical University of Oil and Gas,
Ivano-Frankivsk, Ukraine

Summary*. Corrosion tests in 12 model environments simulating the composition of soil electrolytes at different levels of current density has been made. For the best comparative analysis, the ionic strength of the electrolyte has been proposed to be used as the characteristic indicator. The inversion of the corrosion rate under the action of an alternating current is found, which exhibits an inhibitory effect in the environment containing sulfate ions. It is shown, that with the decrease of the pH level, the intensification of hydrogen release is observed and the danger of hydrogen embrittlement of steel is increasing.*

Key words*: AC corrosion, soil electrolytes, ionic strength, distribution gas pipelines, hydrogen embrittlement of steel.*

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Statement of the problem. Buried pipelines are the important elements of the oil and gas pipeline complex of Ukraine and are of special attention in the life of modern society being the guarantee of its power independence. Providing of the continuous operation of the pipelines transport taking into account all characteristics of its operation (coating, covering, monitoring of the cathode stations operation and the pipelines structural health monitoring) are the foremost tasks in order to prevent accidents and damages, which result in the pipe integrity. The break in the continuous supply of natural gas for the industrial facilities contributes to the decrease of the country economic growth, as well as the living standard and welfare of the population of the country. Taking into account the specific role of our country as the biggest power resources transiter to the EU it must be noticed, that the stable and effective operation of the Ukraine fuel and power complex is the guarantee of our power safety and EU safety in particular.

The most portion of accidents (80%) at the pipelines are caused by different types of corrosion: general corrosion, crevice corrosion under the coating being scaled, spot corrosion, corrosion cracking under stress, etc. Having resulted from the corrosion the decrease of the pipeline cross-section occurs, which contributes to the ecological risk of further operation of such metal structures, which makes the problem of their residual life-time estimation of special attention.

Steel pipelines for the oil and gas transporting often cross the highways or are located parallelly to the AC power transmission lines. They are nearby the electric railway lines, which are supplied by AC. Besides, in the urban areas the most metal pipelines are located near the AC power source and the pipelines are used as the gas pipe earth. It causes the creation of the EPC on the buried pipelines and appearance of the alternative voltage difference between the pipe metal and the earth. Mutual investigations presented in the collected articles CIGRE confirm the sufficient effect of the alternative current on the pipeline corrosion, but the general theory of the metal electro-chemical corrosion specifies the electro-corrosion, which is in the ground under the action of DC and notes unsufficient effect of AC on the soil corrosion. DC of 1A damages 9kgs of metal during 1 hour, 11 kgs of zinc and copper, 34 kgs of lead, 3kgs of aluminium, the stray current radius being dozens of kilometers increasing the danger of a such

Corresponding author: Lyubomyr Poberezhny; e-mail: lubomyrpoberezhny@gmail.com corrosion. The portion of damages caused by AC is 1% of those caused by the DC.

Analysis of the available results of investigation. It was assumed in 1927 in the technical journal of the engineering institute of Canada, that the major cause of the AC corrosion is the current density. This assumption was not paid special attention to and any investigations, which would associate the initiation of the through corrosions on the pipelines with the effect of AC were not carried out. Reports on the corrosion anomalies on the gas pipelines started to be registered in Europe in early 80-s of the last century. In 1986 in Germany there were revealed corrosion damages caused by the AC of 162/3 and 50hz [1]. In 1987 similar situation was in Switzerland [2]. Then similar cases were in the USA, Canada and France, here, as it was reported, the rate of the pipeline wall drain caused by the AC corrosion being high enough and equals 0,8 – 1,47mm/per year correspondingly.

It was noted in all these publications, that the pipelines being in operation were under the cathode protection and the values of the cathode protection met the required criteria. The most probably, some previous cases of the corrosion could be treated as those caused by AC, but because of the lack of data and unsufficient information on this type of corrosion they were not paid attention to. One of the reasons, why this type of corrosion was not associated with the AC effect, is that the cathode protection was thought to cover totally the AC effect.

It is known, that every type of the corrosion can be identified according to the special corrosion products, corrosion damage of the surface and the consequences of their effect. AC corrosion characteristics were not available at that time. The needed information, which would associate the effect consequences with AC, have been accumulated during sufficient laboratory and field investigations. The damages caused by AC action [6] can be specified as follows:

- creation of the rigid ground and corrosion products dome of the cluster-shape;
- AC corrosion results in the creation of the corrosion spots with round edges;
- corrosion spots sizes are as a rule bigger than those of the coating defects sizes.

Such anomalies were revealed on the pipeline constructed in 1992 in Los Angeles. The corrosion products dome was revealed on the pipeline, the corrosion losses being 20%. Similar anomalies were found on the other area of the pipeline, but the corrosion losses were sufficiently greater, than those at the previous one and equaled 50%. In 1993 there were revealed 31 corrosion damages of the protection coating of the gas pipeline in France as the result of the flow detection. The pipeline of the 100mm diameter and 6km length had an area of the parallel broaching with the 3km power transmission line of 400kw. The depth of the corrosion damage was from 0,1 till 0,8mm [7].

Similar damages were found as the result of the planned pitting of the protection coating on the buried pipelines in Huston.

The pittings showed, that the electro-corrosion rate is dangerously high – the metal loss of the pipe wall thickness during 4 years was 30% [8, 9].

Although the data on the corrosion losses caused by AC has been accumulated for the last 40 years, the International standards NACE do not take into account the danger of the AC effect on the buried pipelines and quit the possibility of the sufficient corrosion damages initiation, specifying the application of the passive and active protection, which prevents the AC corrosion effect [10].

Statement of the task. The chosen for the experimental investigations model environments (ME) (Table 1) differ in their component composition and the electrolytes concentration. To compare better the environment effect and the electrolytes classification according to the corrosion activity there is a need to introduce the unflying criterion for all environments. The ionic strength of the solution is known to be this criterion, which takes into account the concentration of all ions available in the solution and is found due to the formula:

$$\mu = \frac{1}{2}\sum_i Z_i^2 \cdot C_i \,, \qquad (1)$$

where μ – ionic strength; Z_i – ion charge; C_i – its concentration.

The ionic strength has the concentration dimension. Due to the formula (1) the value of the ionic strength for the ME1-12 (Table 1) has been calculated.

Table 1. Chemical composition of the model environments with the calculated value of the ionic strength

Model environ-ment(ME)	Concentration, mol/l				Ionic strength, mol/l
	NaCl	Na_2SO_4	HCl	H_2SO_4	
1	0,01	–	–	–	0,01
2	0,05	–	–	–	0,05
3	0,1	–	–	–	0,1
4	0,005	0,005	–	–	0,02
5	0,025	0,025	–	–	0,1
6	0,05	0,05	–	–	0,2
7	0,01	–	0,00001	–	0,01001
8	0,05	–	0,0001	–	0,0501
9	0,1	–	0,001	–	0,101
10	0,005	0,005	–	0,000005	0,020005
11	0,025	0,025	–	0,00005	0,10005
12	0,05	0,05	–	0,0005	0,2005

Besides, the ionic strength specifies the environment conductivity. At greater values of the ionic strength the rate of the current in the electrolytes is greater too and vice versa. That is why the estimation of the results obtained for the control specimens and the specimens under the different AC density will make possible to estimate the effect of the environment and the AC effect at equal values of the ionic strength, as the environment with different component composition can possess equal values of the ionic strength. As it is seen from the Table 1 among the neutral chloride and chloride-sulfate environments equal values of the ionic strength are those for ME3 and ME5. The greatest value is for ME6, which makes possible to predict the greatest corrosion rate just in this environment. But according to the diagram built according to the results of experiments at different values of the current density in the neutral environments the sufficient increase of the corrosion rate is noticed in the ME1-3.

Results of investigations. The neutral chloride-sulfate electrolytes ME4-6 are specified by the monotoneous growth of the corrosion rate (Fig. 1). Sufficient increase of the absolute corrosion rate is noticed in the chloride electrolytes, when the current density increases, and the electrolytes concentration increases due to the increase of the ionic strength. More sufficient is the intensification of the corrosion under transition from the current density 10 – 15 A/m^2 and from 15 – 20 A/m^2 and great bend on the boundary of the environments ME2 – ME3. At the current density 5 A/m^2 the obtained experimental dependence looks like that for the control specimens, that is, the monontoneous increase tending to sufficient growth, when the chloride concentration increases, which results in the environment ionic strength.

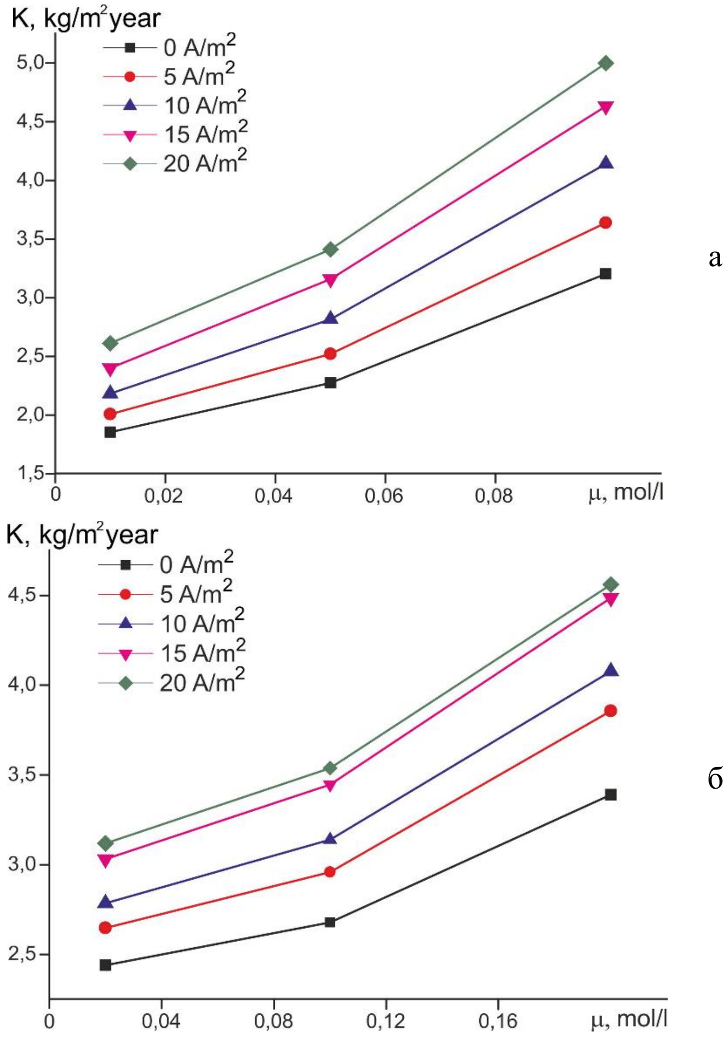
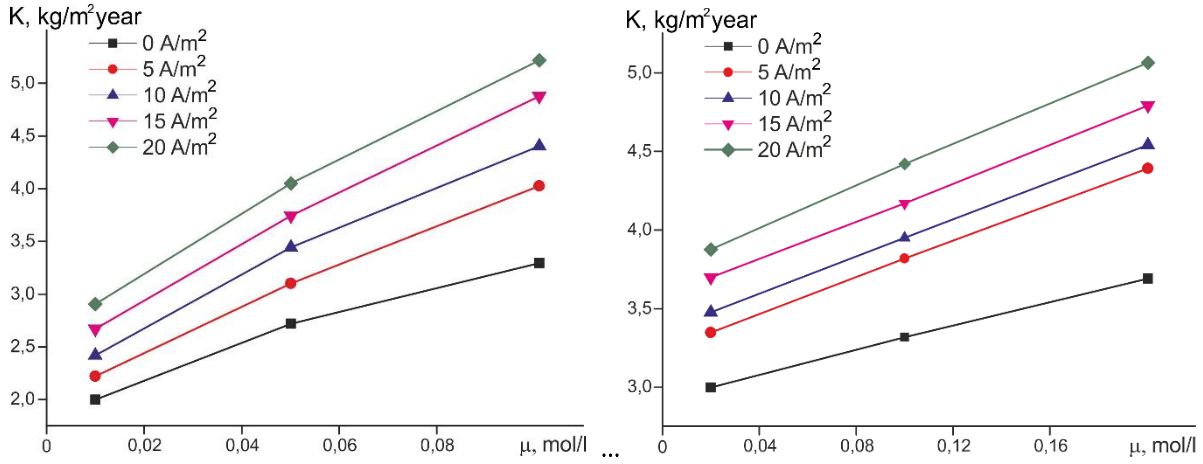


Figure 1. Dependence of the absolute rate of corrosion in neutral chloride (a) and chloride-sulfate electrolytes (b) on the value of current density and ionic strength

On the contrary to the neutral chloride environment in the neutral chloride-sulfate environments the monotoneous growth of the absolute corrosion rate is noticed without bends and visible areas to the intensive growth. As it is seen from Fig. 1 at all current densities during the transition from ME4-ME5 the values of the absolute rate obtained as the result of the experiment are sufficiently greater as compared with those similar for the neutral chloride environments. But when the current density increases further, the intensification of the corrosion processes does not take place. On the contrary, their damping can be predicted. Although the ionic strength in these environments is of the greater values, but the composition of the ground electrolyte is of greater effect here. The sulfite ions are of sufficiently greater sizes in comparison with the chloride ions, which is the cause of the change of the corrosion nature mechanism and creation of the corrosion products.

Investigation of the corrosion degradation in the acidified chloride environments (Fig. 2) showed sufficient increase of the corrosion rate, when the concentration of chloride ions and the current density increase. Sufficient transition is seen from the control specimen to the specimens subjected to the AC effect. Although the ionic strength of the acidified chloride electrolytes is equal to those of the ionic strength of the neutral chloride electrolytes (Table 1), the intensity of the corrosion processes is greater than those in the neutral chloride environments (Fig. 2). It can be concluded, that at the equal values of the ionic strength the component composition of the environment must be taken into account as well as the effect of other corrosion factors, the AC in particular.



(a) (b)

Figure 2. Dependence of the absolute rate of corrosion in acidified chloride (a) and chloride-sulfate electrolytes (b) on the value of current density and ionic strength

Investigation of the Steel 3 in the acidified chloride-sulfate environments showed the monotonous corrosion growth, when the ionic strength and the AC density for ME10-12 increase, as well as the intensive monotonous corrosion rate increases for ME7-9. Intensification of the corrosion processes is the characteristic for all values of the current density, when the ionic strength of the electrolytes increases. In general, the graphic dependencies obtained for the acidified chloride and chloride-sulfate environments (Fig. 2) are similar to those of the neutral chloride and chloride-sulfate environments (Fig. 1). The greater values of the corrosion rate are available for the lower concentration of the electrolytes in all acidified chloride-sulfate environments as well, the further decrease being in the areas of the ionic strength growth. But, if compared with ME4-6 (Fig. 1), unsufficient rate growth is noticed in ME10-12. Such difference can be caused by the presence of the hydrogen ions in ME10-12, which possess high mobility and intensify the corrosion processes at the initial stages and their damping, because of the corrosion products accumulation on the surface being corroded.

Similarly, as for the neutral environments the curves inclination angle in the acidified environments for the acidified chloride environments is different from that the inclination angle in the acidified chloride-sulfate environments, which is caused by the different mechanism of the corrosion damages development on the metal surface.

Generalized diagram of the dependence of the pipeline wall drain rate in the 12 model environments under AC effect in general does not present generalized estimation of the physical-chemical system effect on the corrosion processes procedure. For example, according to the diagram (Fig. 3) very interesting fact can be noticed, which is not the characteristic of the ground corrosion, when such electrolytes are available. The most dangerous in such conditions are neutral chloride-sulfate and acidified chloride-sulfate electrolytes. Only when the concentration ratio of chlorides to sulfates is 1:5, the corrosion processes inhibitation takes place [11]. This dependence is true for the control specimens and the results inversion is noticed under the mutual effect of the environment and AC, which has been identified for the first time. That is, the most dangerous from the corrosion point of view are the neutral and the acidified chloride environments, the danger of the seal failure caused by the through corrosion in the ground containing sulfates under the AC effect being the smaller.

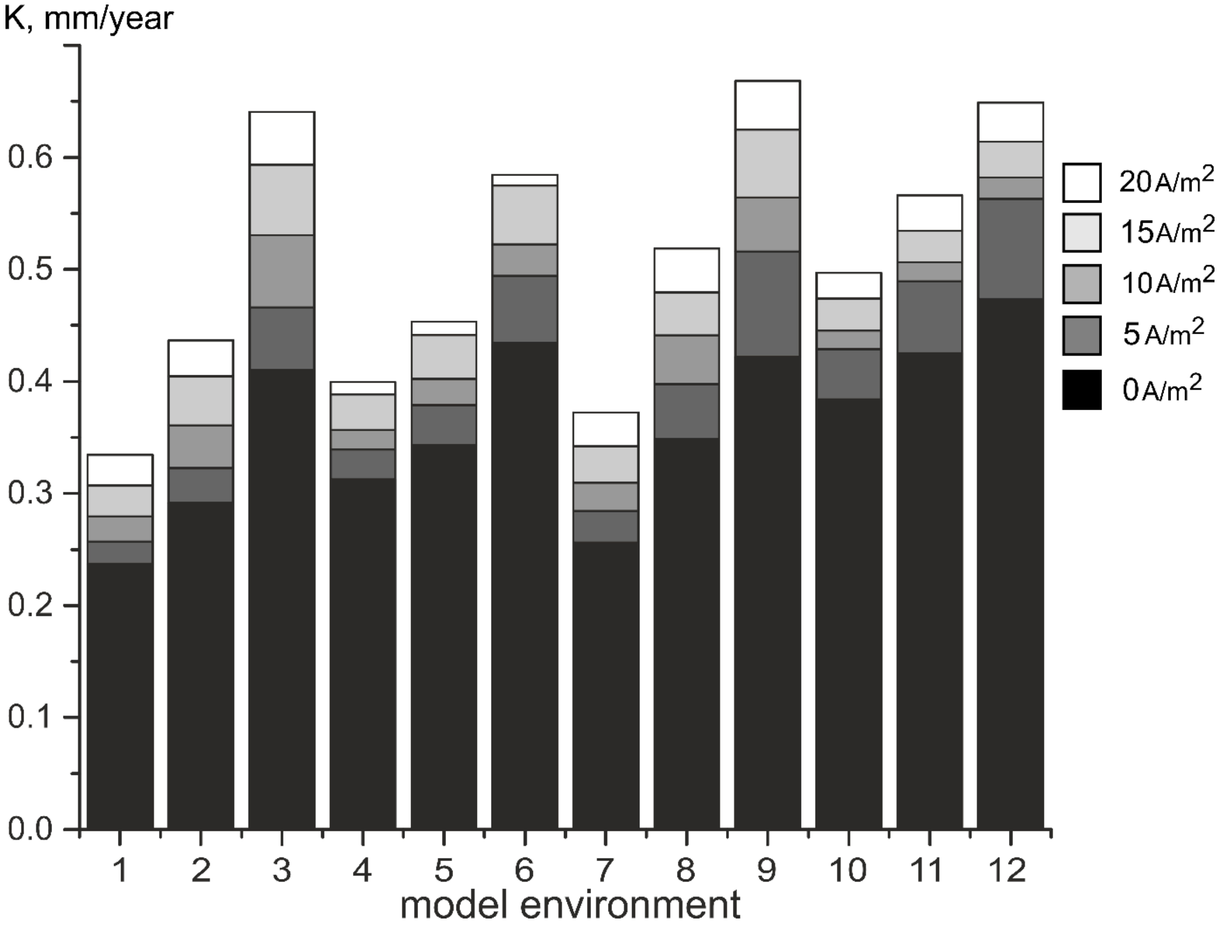


Figure 3. Dependence of the pipeline wall thickness rate in 12 model environments in the range of current density 5, 10, 15 20 A/m^2

Conclusions. Corrosion tests in 12 model environments simulating the soil electrolyte composition at different levels of the current density have been carried out. The ionic strength of the electrolyte was proposed to be the characteristic indicator for the better comparative analysis.

It was proved, that at the current density 5 A/m^2 the corrosion rate growth in the neutral and acidified soil electrolytes is greater in 5% for both tested steels, which confirms the need to specify the standard regulations.

The corrosion rate inversion has been identified under the AC effect, which is inhibiting in the environment containing the sulfate ions.

It is shown, that when the pH level decreases, the intensification of the hydrogen release is observed and the danger of the hydrogen embrittlement of steel arises.

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ВПЛИВ ІОННОЇ СИЛИ НА ЕЛЕКТРОКОРОЗІЮ В ХЛОРИДНИХ ТА ХЛОРИДНО-СУЛЬФАТНИХ СЕРЕДОВИЩАХ

Любомир Побережний

Івано-Франківський національний технічний університет нафти і газу,
Івано-Франківськ, Україна

Резюме. *Проведено корозійні випробовування у 12 модельних середовищах, що імітують склад ґрунтових електролітів за різних рівнів густини струму. Для кращого порівняльного аналізу запропоновано в якості характеристичного показника використовувати іонну силу електроліту. Виявлено інверсію швидкості корозії при дії змінного струму, який виявляє інгібуючу дію у середовищах, що містять сульфат-іони. Показано, що зі зменшенням рівня рН спостерігається інтенсифікація виділення водню та зростає небезпека водневого окрихчення сталі.*

Ключові слова: *електрокорозія, ґрунтові електроліти, іонна сила, розподільчі газопроводи, водневе окрихчення сталі.*

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