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MILD STEEL CORROSION RESISTANCE IN LIQUID FERTILIZER SOLUTIONS

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ABSTRACT

The paper presents results from the investigations on the corrosion behavior of mild steel (0.17 %C) in water solutions of liquid mineral fertilizer „MAXGROW" at different concentrations (0.2, 0.4, 0.6, 1.0 % vol. and concentrate) and temperatures (20, 40, 60°C).

The corrosion rate and corrosion penetration of the steel have been measured by means of gravimetric and electrochemical methods. The conclusion about corrosion resistance of the steel under different conditions has been made – it possesses high resistance in solutions of liquid mineral fertilizer „MAXGROW". The steel could be recommended as good and comparatively cheap construction material for manufacturing of installations, equipment, tanks and other machinery used for handling and operation with this fertilizer.

Keywords: corrosion, mild steels, liquid fertilizers.

INTRODUCTION

The production of complex liquid fertilizers is currently a stably developing industry [2, 6-9]. Permanent and a very important issue during the production, storage and transportation of the fertilizers is their corrosion activity in relation to the equipment by means of which these operations are realized as well as to the machinery used to apply the fertilizers in the practice.

The assessment of the corrosion losses in the agricultural industry is not an easy problem. There is no information at national level about the causes that have led to destruction of the used equipment. There is no organization to collect and process this information as well as to make it public. Everybody involved in this industry resolves the arising corrosion problems according to his capability, which does not guarantee that the best measures are taken for their prevention. Without being particularly accurate, there are data about the industrially developed countries, that the amortization (including also as a result of corrosion) is between 5 and 10 % of the total value of the produced and delivered agricultural machinery [1,3-5,9].

The corrosion activity of the liquid fertilizers is determined by their chemical composition – they contain anions (NO_3^-, NH_2^-, PO_4^{3-}, Cl^-, SO_4^{2-}, etc.), cations (NH_4^+, Na^+, K^+, Ca^{2+}, etc.), micronutrients (Mo, Cu, Mn, Fe, Zn, B, Mg, etc.), complexing agents (EDTA, etc.), other additives. Besides, the solution concentration and temperature is of essential importance for this activity as well as the nature of the construction materials of the equipment used in the different stages of the production and exploitation of these fertilizers [6-9].

The mild steels occupy basic share in the metallurgical production and their major users are the chemical industry, machine building, power engineering, rural economy and the other branches of the economy of every country. That is due to their good mechanical characteristics, availability, comparatively low price, etc. In this regard, the tests for the behavior of these steels in new and different media will lead to expansion of their use in the practice.

The present paper presents the results obtained during investigation of the corrosion behavior of mild steel (0.17 % C) in water solutions of developed in UCTM – Sofia liquid mineral fertilizer „MAXGROW" at different concentrations and temperatures of the medium.

EXPERIMENTAL

Materials and samples

Specimens of mild steel 3 are used. The chemical composition of the steel is given in Table 1.

The specimens have the shape of a disk with a diameter 26 mm, thickness 1 mm and a working surface area S = 0.001 m^2.

Solutions

For working media there are used water solutions of liquid fertilizer MAXGROW with:

- concentrations: 0.2, 0.4, 0.6, 1.0 % vol. and concentrate.
- temperatures: 20, 40, 60°C (± 2°C).
- duration of experiments: 20°C – 24 hours; 40°C – 8 hours ; 60°C – 2 hours .

The concentration and the temperature of the working media are selected both from exploitation and technological considerations.

The composition of the complex liquid fertilizer MAXGROW is: *nitrogen* (N) 9 %, in amide form; *phosphorus*, as diphosphorus pentaoxide (P_2O_5) 9 %, water soluble; *potassium*, as potassium oxide (K_2O) 9 %, water soluble; *micronutrients*: boron (B) 0.01%, copper (Cu) 0.008 %, iron (Fe) 0.02 %, manganese (Mn) 0.01 %, molybdenum (Mo) 0.001%, zinc (Zn) 0.004 %.

The micronutrients Cu, Fe, Mn and Zn are chelated with EDTA. All micronutrients are water soluble.

Methods of investigation

Gravimetric method. The essence of the method consists in determination of the specimen masses before and after the corrosion test in solutions and calculation of the corrosion rate, K:

$$K = \frac{(m_1 - m_2)}{S.\tau}, \quad g/m^2.h$$

where: m_1 – mass of the specimen before the test, g; m_2 – mass of the specimen after the test, g;
S – specimen area, m^2; τ – test duration, h.

Corrosion penetration. Π, mm/y – gives information about the penetration depth of the corrosion attack in the metal, referred to unit time. By this feature the corrosion resistance of the metal with different density can be characterized and quantitative assessment of common or of local corrosion be made. The following formula is used for determination of the corrosion penetration:

$$\Pi = 8.76\ x10^3 \frac{K}{\rho}, \quad mm/y,$$

Table 1. Chemical composition of the steel.

Chemical composition of the steel, %							
C	Mn	Si	P	S	Cr	Ni	Cu
0.17	0.36	0.016	0.01	0.029	0.06	0.06	0.11

Table 2. Liquid fertilizer characteristics.

Liquid fertilizer concentration,$\%_{mass}$	ρ, g/cm^3	pH	σ, mS/cm
0.2	–	7.70	903 μS/cm
0.4	–	7.61	1532 μS/cm
0.6	–	7.55	2.09 mS/cm
1.0	–	7.50	3.25 mS/cm
concentrate	1.245	7.77	94.1 mS/cm

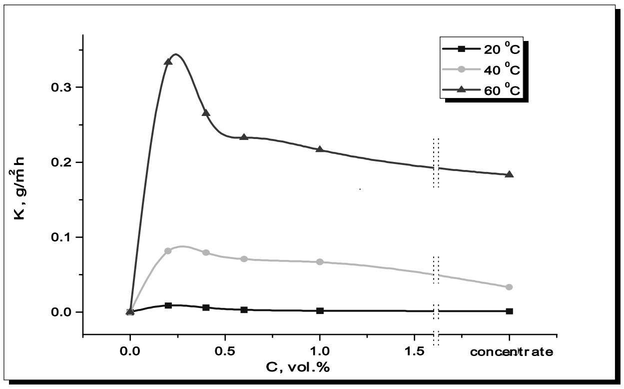

Fig. 1. Effect of the concentration of the liquid fertilizer water solutions on the corrosion rate of steel 3, at different temperatures.

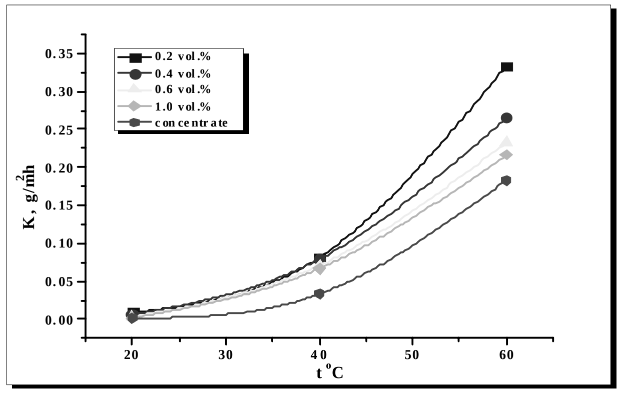

Fig. 2. Temperature effect on the corrosion rate of steel 3 in solutions of different concentration.

where: ρ – metal density, κg/m^3; K – corrosion rate, g/m^{2}h.

Measuring of potentials. During corrosion of metals in electrolyte media non-equilibrium electrode potentials are established – so called corrosion potentials. Although they are not an absolute indicator for the resistance, by their value and their variation with time, important information could be obtained about the character of the corrosion process and the behavior of the metals in exploitation conditions.

Potentiodynamic polarization method. The polarization methods realized by means of potentiostates are convenient for electrochemical and corrosion studies. The potentiodynamic polarization method is characterized by the fact that the potential varies with time at constant speed, according to a preset program. Polarization curves are drawn, which express the potential-current density dependence.

By the taken off polarization curves there could be defined the stationary corrosion potentials, the values of the stationary corrosion currents – a measure for the corrosion rate, etc.

The preparation of the specimens, the equipment for carrying out the investigations and the method of work are described in details earlier [10].

RESULTS AND DISCUSSION

Solution parameters

Table 2 presents the values of the most important indicators that characterize the liquid fertilizer: density, ρ; pH and electric conductivity, σ. From Table 2 it is seen that the concentrate pH values and these of the different concentration solutions are almost equal, a little above 7. The neutral character of the MAXGROW water solutions is extremely significant characteristic that determines complete and harmless absorption of the contained in the fertilizer nutrient substances by the plants. As should be expected, the electric conductivity of the solutions grows with increase of their concentration and is the highest for the concentrate. The densities of the tested solutions are not shown in the Table 2 (except for the concentrate), because virtually they do not differ from that of the water.

Gravimetric studies

By means of the gravimetric studies the change of the specimen masses during their exposure in corrosion media is determined. The corrosion rate K, g/m^{2}h and the corrosion penetration П, mm/y are calculated from the obtained values.

Fig. 1 presents the results of the corrosion rate, K, of the examined steel in dependence of the temperature (20; 40 and 60^{o}C) for different concentrations of the liquid fertilizer water solutions (0.2; 0.4; 0.6; 1.0 $\%_{mass}$; concentrate).

As it is seen from the presented curves, the corrosion rate decreases with the increase of the medium concentration at all solution temperatures and is the lowest for the concentrate. The most probable explanation of the observed dependences may be related to increase of the ion quantity in the medium (phosphate, nitrate, etc., passivating the steel), with increase of the tested solutions concentrations.

The dependences, which express the corrosion rate change by the temperature, at different medium

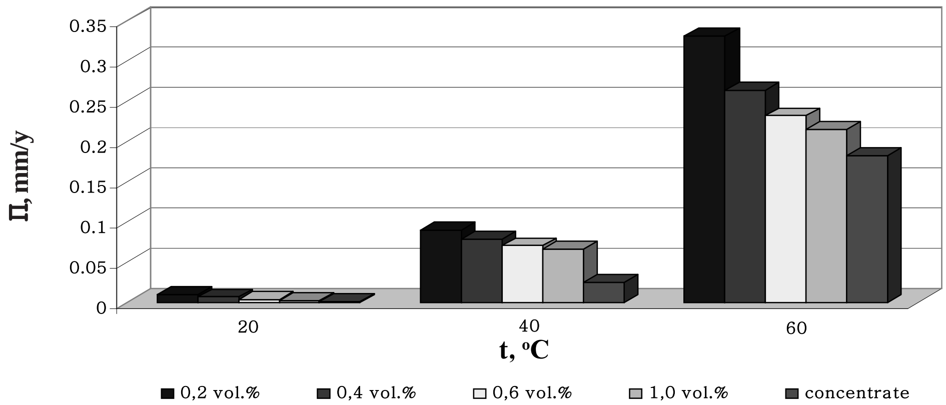

Fig. 3. Corrosion penetration Π, mm/y, at different temperatures and concentrations of solutions.

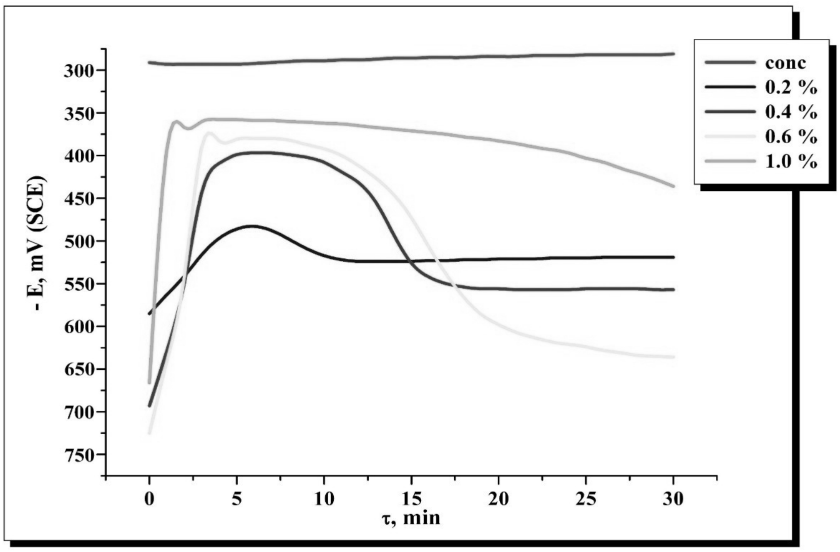

Fig. 4. Potential-time relationships at different concentrations, 20°C.

concentrations, are illustrated in Fig. 2. The curves which describe these dependences have exponential character and show strict sequence of corrosion rate decrease of the examined steel with increase of the solution concentrations. The higher corrosion rates observed at low concentrations, besides the lower content of passivating agents in the solutions, to a certain degree are also because of the greater quantity of oxygen from the air dissolved in them (open system) which well known is a very good depolarizer.

Fig. 3 shows the values of the corrosion penetration, Π, calculated from the experimentally determined corrosion rates of the examined steel and its density, in water solutions of the liquid fertilizer. Conclusion could be made from these results that at 20°C the steel is completely resistant (grade 1), at 40°C – resistant (grade 4-5) and at 60°C – low resistant (grade 6). From the data in the figure it follows further that the steel corrosion resistance grows with increase of the medium concentration at all studied temperatures.

Fig. 4 shows the corrosion potential variation of the examined steel with time in dependence of the solutions concentrations and at temperature 20°C. It follows from the movement of the curves that for all investigated concentrations the potential shifts in positive direction, the speed of this shift increasing with the concentration growth. These results show that difficulties occur in the course of the anodic reaction of metal ionization as a result of the solutions passivating properties. However, at the lower concentrations (0.2-0.6 %) after the initial shift of the potential towards more positive values, later around the tenth minute it becomes

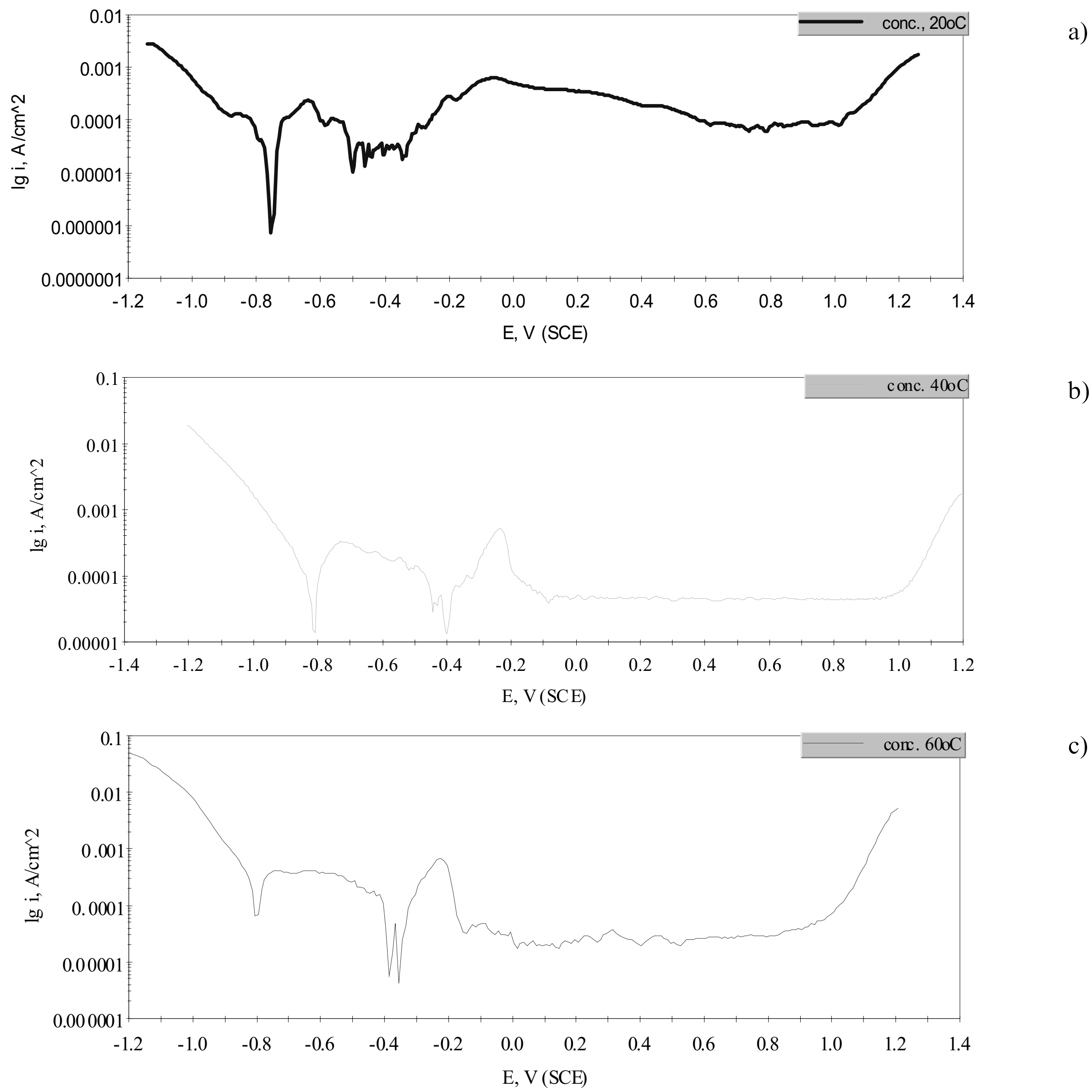

Fig. 5. Polarization potentiodynamic relationships E – lg i, obtained in liquid fertilizer concentrate at different temperatures: a) 20°C; b) 40°C; c) 60°C.

again more negative and after the fifteenth minute reaches a steady-state value. Such a run of the curves could be explained by the insufficient amount of the passivating agents in these concentrations. The corrosion potential obtained in the concentrate solution is the most positive (about -300 mV, SCE) and retains its value almost constant for the time of the measurement. Potentiodynamic polarization relationships of the examined steel in liquid fertilizer concentrate solutions at different temperatures are presented in Fig. 5. These dependences are only used for qualitative characterization of the cathodic and anodic partial reactions of the total corrosion process.

It is seen from the run of the cathode part of the polarization curves that the cathodic reaction speed increases with the temperature raising without change of its mechanism. The anodic part of the curves is characteristic for systems of high tendency to pass in passive state, its stability growing (lower current values in passive state) with increase of the medium temperature. Current fluctuations on the anodic curves in the potential area from -0.5 to -0.3 V, (SCE) are observed for all the three curves which shows that the passive state is not stable in this potential area as a result of the higher effectiveness of the cathodic process.

CONCLUSIONS

The corrosion behavior of mild steel in water solutions of the complex liquid fertilizer MAXGROW has been studied. It is established that this steel possesses high corrosion resistance and could be recommended as a good and comparatively cheap construction material for manufacturing of installations, equipment, tanks and other machinery used for handling and operation with such solutions.

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