

TECHNICAL PROPOSAL

for the delivery of monitoring system of corrosion status
of carbon steel equipment in the department of gas purification from CO₂

1. INTRODUCTION

Currently, the control (monitoring) of corrosion condition and control of corrosion speed of devices and pipelines in contact with aggressive environment, get the same value in order of importance as the control and regulation of the basic parameters of technological processes.

The active form of corrosion control provides for anticorrosive and technological measures that reduce the corrosion rate to acceptable values on the basis of received information.

With the help of corrosion control systems can be efficiently solved the problems of control and corrosion protection of industrial equipment in sulfuric acid, phosphoric acid, hydrochloric acid, chloride, ammonia environments, as well as the circulating water, fertilizer solutions and solutions of gas purification from CO₂.

It was found that in aggregates of ammonia synthesis gas cleaning environment from CO₂ are highly corrosive in relation to the carbon steel.

To reduce the corrosion rate of the equipment in hot Benfield solutions is used as an inhibitor of vanadium pentoxide. However, the inhibitory (critical) concentration of V⁺⁵- ions depends on several conditions - both process (temperature, CO₂, etc.) and corrosion (steel surface condition, its potential).

Currently, control of the content of the inhibitor and corrosion of equipment in the Benfield solution carry on the results of laboratory analyzes of vanadium ions and iron ions.

The main disadvantages of a laboratory method for the determination of vanadium ions and iron are the frequency analysis (once daily), as well as its complexity and subjectivity.

The disadvantage of determining the corrosion rate by the corrosion-electrochemical methods in the laboratory is the complexity of modeling the conditions of the industrial apparatus (pressure up to 28 atm and temperatures above 100 °C, surface irrigation, the saturation of CO₂, etc.).

Research has shown that the most effective way to determine and maintain the passive state of equipment is control of corrosion state by the potential.

There is a clear dependence between the rate of corrosion of carbon steel in Benfield solutions and the value of the corrosion potential. Therefore, the surface potential of the equipment reflects its state of corrosion most objectively.

The sharp increase of the rate of corrosion of equipment is the result of a violation of the passive state. At the same time to reduce the rate of corrosion of equipment to acceptable values you need an increased concentration of pentavalent vanadium, and to maintain a passive state concentration of V^{+5} - ions can be reduced in several times.

2. TECHNICAL PART

Has been developed and successfully operated the system of control of corrosion state of process of equipment made of carbon steel in the department of gas purification from CO_2 .

The system is based on the method of controlling of corrosion state of the equipment by the potential, that based on the dependence between the rate of corrosion of passivating metal and the value of the potential of its surface.

Electrochemical method of determining the concentration of inhibitor in the stream of technological solution based on the dependence between the cathodic and anodic current and the concentration of penta-and tetravalent vanadium, respectively.

Purpose of the system:

The system is designed for monitoring the corrosion of the equipment of gas purification from the CO_2 in the potential and the control of the content of five-and tetravalent vanadium in Benfield solution.

The system provides:

- continuous monitoring of the corrosion of the equipment and signaling the possible violation of the passive state;
- continuous monitoring of the dynamic changes in the concentration of five and tetravalent vanadium in the stream of the Benfield solution directly.

The system includes sensors that are installed in areas most exposed to corrosion damage, spark protection barriers, potentiostatic devices and industrial machines, spaced on the CPU.

In addition to the existing analytical control methods of corrosion rate of equipment and content of the inhibitor in the Benfield solution the proposed system will:

- reduce the probability of emergency stopping of the ammonia unit due to corrosion damage by effective control of corrosion of the equipment;
- determine the moment of the displacement of the potential in the zone of the active dissolution and take prompt measures to preserve the passive state of the metal surface by continuous measurement of corrosion potential of equipment under operating conditions; reduce the corrosion rate of technological equipment in the department of gas purification from CO_2 to the normative values;
- take action on the regeneration of the inhibitor by the continuous determination of the concentration of five- and tetravalent vanadium is directly in the stream of technological solution;
- significantly reduce the use of corrosion inhibitor for its greater efficiency by simultaneous monitoring of corrosion status of equipment and determine the concentration of the inhibitor.

Using a computer allows you to visualize information about the corrosion status of the equipment, save and view the history of the process of inhibitor protection.

Durable and reliable operation of monitoring system of corrosion status of equipment and electrochemical parameters of technological solutions on a number of chemical companies allowed to reduce the corrosive destruction of equipment and control of composition of the technological environments.

Monitoring system of corrosion status of carbon steel equipment in the department of gas purification from CO_2 was launched in the shop ammonia-3 at JSC "Grodno Azot" in 2003, and has successfully operated for 3 years.

Technical characteristics of the system :

- number of control points of corrosion state of equipment, pcs.- under 18;
- number of control points of concentration of the inhibitor, pcs. – 2;

- measuring range of potential of the equipment ± 1000 mV;
- measuring range of the concentration of pentavalent vanadium to 1.0%;
- measuring range of the concentration of tetravalent vanadium to 0.5%.

For example, for the department of gas purification from CO₂ of the TEC machine system includes:

- sensors of the corrosion state and concentration of the inhibitor - 12 pcs. (including reserves);
- potentiostatic device (potentiostat) - 3 pcs. (including reserve);
- spark protection unit - 3 units (including reserve);
- industrial PC - 1 pcs.;
- the software.

Engineering services includes:

- inspection of the department of gas purification from CO₂, identification and alignment of control points. Delivery of documentation on the input sensor units. Alignment of technical requirements;
- corrosion- electrochemical studies of carbon steel in model environments in laboratory conditions, definition of protective potentials and concentrations of the inhibitor, determination of their values, depending on various factors;
- the development and delivery of user guide;
- complete the system with the equipment;
- supervision of installation of the sensors;
- installation and commissioning of the system;
- training of service personnel;
- carrying out warranty tests, delivery of the system into service.

The proposed system can be introduced during 4 months.

Continuous monitoring of corrosion state will significantly reduce the use of expensive inhibitor and increase the reliability of the equipment.

Attachment 1

CALCULATION

estimated economic effect of the introduction of the system,
obtained by preventing corrosion damage of equipment

1. The probability of stopping of the unit because of corrosion damage of the equipment - once in 20 years.

2. Minimal losses from stopping and launching of the unit.

$$1500\text{t/day} \times 1100 \text{ m}^3/\text{t} = 1650000 \text{ m}^3/\text{day}$$

$$1650000 \text{ m}^3/\text{day} \times 3 \text{ days} = 4950000 \text{ m}^3$$

$$4950000 \text{ m}^3/1000 \times 300 \text{ USD} = 1\,485\,000 \text{ USD}$$

where 1500t/day- productivity of the unit of ammonia;

1100 m³/t- gas consumption;

3 days- duration of stopping and starting;

300 USD- value of 1000 m³ of natural gas at 1.12.11 r.

3. Calculation of losses for 1 year are:

$$1\,485\,000 / 20 \times 8,0 = 594\,000 \text{ UAH}$$

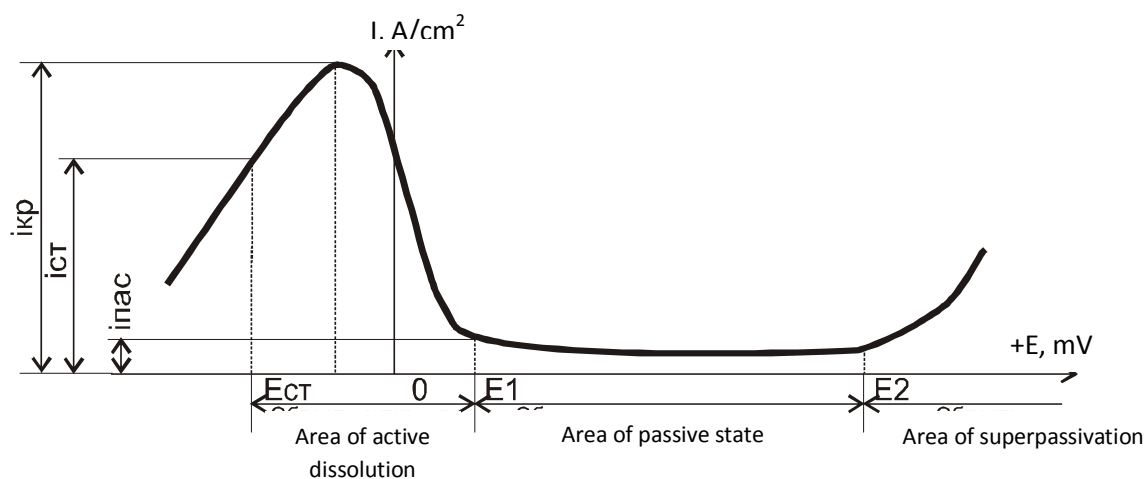


Fig.1

E_{cm}, i_{cm} - stationary potential and dissolution current

E_1, E_2 - lower and upper limits of the passive area

i_{nac} - current of passive state

E_{kp}, I_{kp} - critical potentials and critical current

Protection of metals from corrosion by inhibitors of oxidative type (for example, NO_3^- -ions) is based on the phenomenon of passivation of metals.

The possibility of passivation of metals depends on the nature of the anodic polarization curve, that has the form (fig. 1).

On the polarization curve is shown the dependence between the current (corrosion rate) and the potential established on the metal surface.

Stationary potential (E_{CT}) is setting spontaneously in the absence of the inhibitor on the metal surface, which corresponds to a high rate of corrosion. When move the potential in the area of the passive state (E_1 - E_2), the corrosion rate decreases sharply, which can be seen by the value the polarizing current (i_{nac}). So, the problem of inhibitor protection of metals from corrosion consists in moving the potential of the protected surface in the passive area and in the lasting maintenance of it in this area.

The method of inhibitor protection includes the displacement and maintaining of potential of the protected surface of the metal in the passive area by creating and maintaining required concentration of inhibitor.

When creating sufficient concentration of the inhibitor the potential of the protected metal surface moves from the area of active dissolution in the passive

area and the corrosion rate decreases. However, during the transition of the potential from the stationary in the passive area there is an increase current at the anodic polarization curve (fig. 1), which corresponds to the critical value of the potential E_{kp} . Therefore, during the implementation of inhibitor protection the concentration of inhibitor need to be enough to overcome the critical potential. After passivation of the metal surface to maintain a passive state is required considerably less amount of inhibitor.

With a considerable decrease of the concentration of inhibitor the potential spontaneously returns to stationary value, i.e. takes place the activation of surface of equipment and its enhanced corrosion.

For each particular case (the nature of the aggressive environment and protected metal, temperature, etc.) the type of the polarization curve is different. Therefore, for the control of the corrosion state of equipment and for inhibitor protection in laboratory conditions is necessary to shoot the polarization curve, determine boundaries of the area of active dissolution and passive area. Optimal value of the protective potential is determined according to corrosion data.

The principle of control of the corrosion state of the equipment by potential based on the dependence of the corrosion rate of passivating metal on the value of potential of its surface.

Figure 1 shows a general view and description of a typical anodic polarization curve for the passivated metal. Figure 2 shows the real anodic polarization curves of carbon steel in the 25% K_2CO_3 . As can be seen from the figure, the higher the temperature, the greater the value of the critical density of passivation current (i_{kp}) and, consequently, the concentration of the inhibitor should be greater to put the carbon steel in the passive state. For the temperature 100°C inhibitory concentration about 0,4% V_2O_5 .

If the concentration of V_2O_5 is not enough to overcome i_{kp} , then, as an inhibitor of oxidative type, V_2O_5 will shift the stationary potential of corrosion ($E_{стат.}$) to more positive values of potential (the potential is in the area of active dissolution) and increase the corrosion rate of steel.

On the other hand, if carbon steel is already passive ($E < - 300mV$) then you can maintain a passive state by the concentration of V_2O_5 much smaller than for overcoming i_{kp} .

Figure 3 shows the dependence of the rate of corrosion of carbon steel on the value of the potential. Displacement of the potential of the $E_{стат.}$ to more positive values - up to E_{kp} . significantly increases the rate of corrosion (such a danger occurs when the inhibitor concentrations are insufficient to transfer steel from active to passive state). At the potentials of the passive area ($<300mV$) corrosion

rate of steel is about $0,01 \div 0,05 \text{ g/m}^2\text{hour}$. Maintenance of capacity in this area will provide a low corrosion rate of carbon steel.

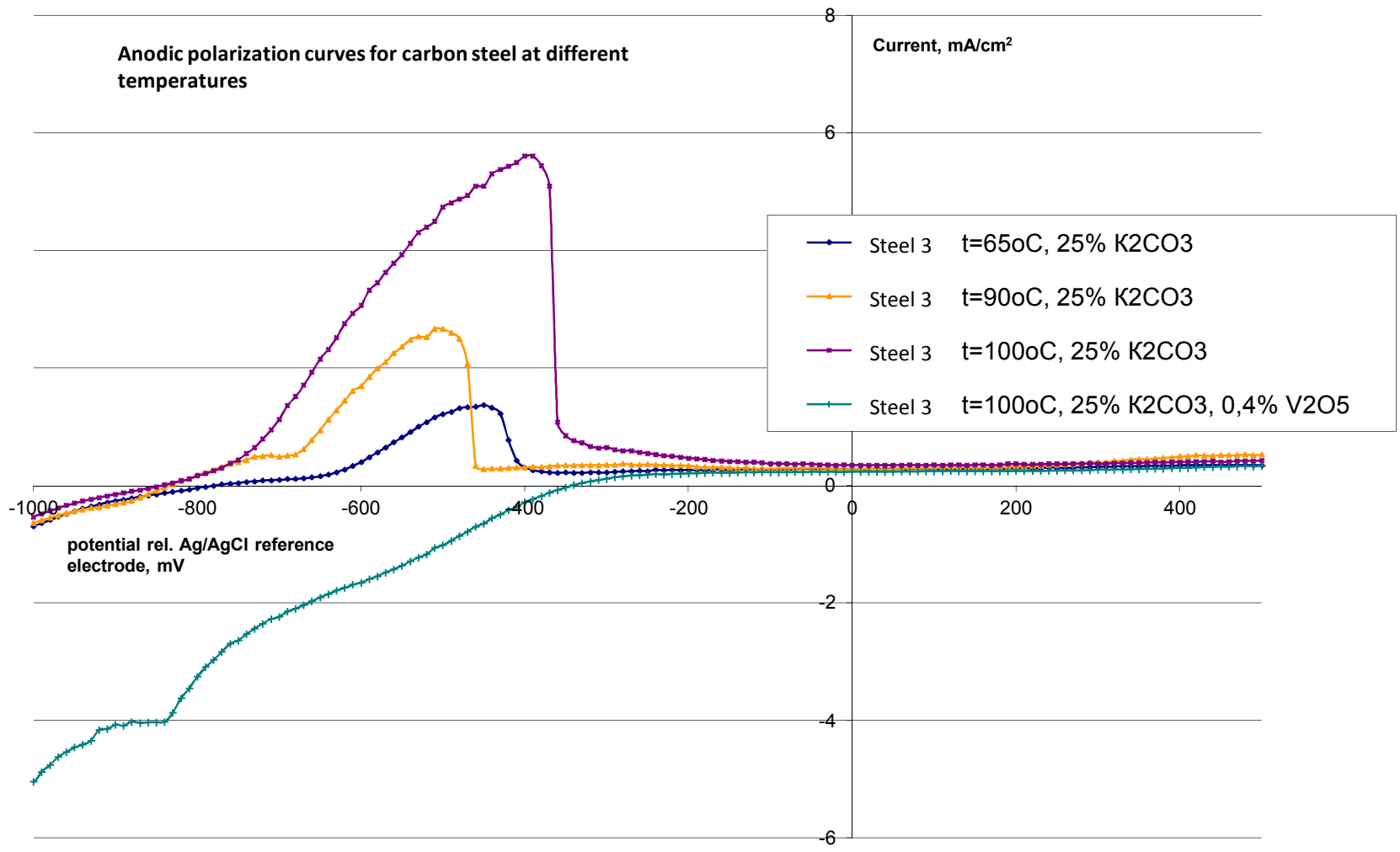


Fig. 2

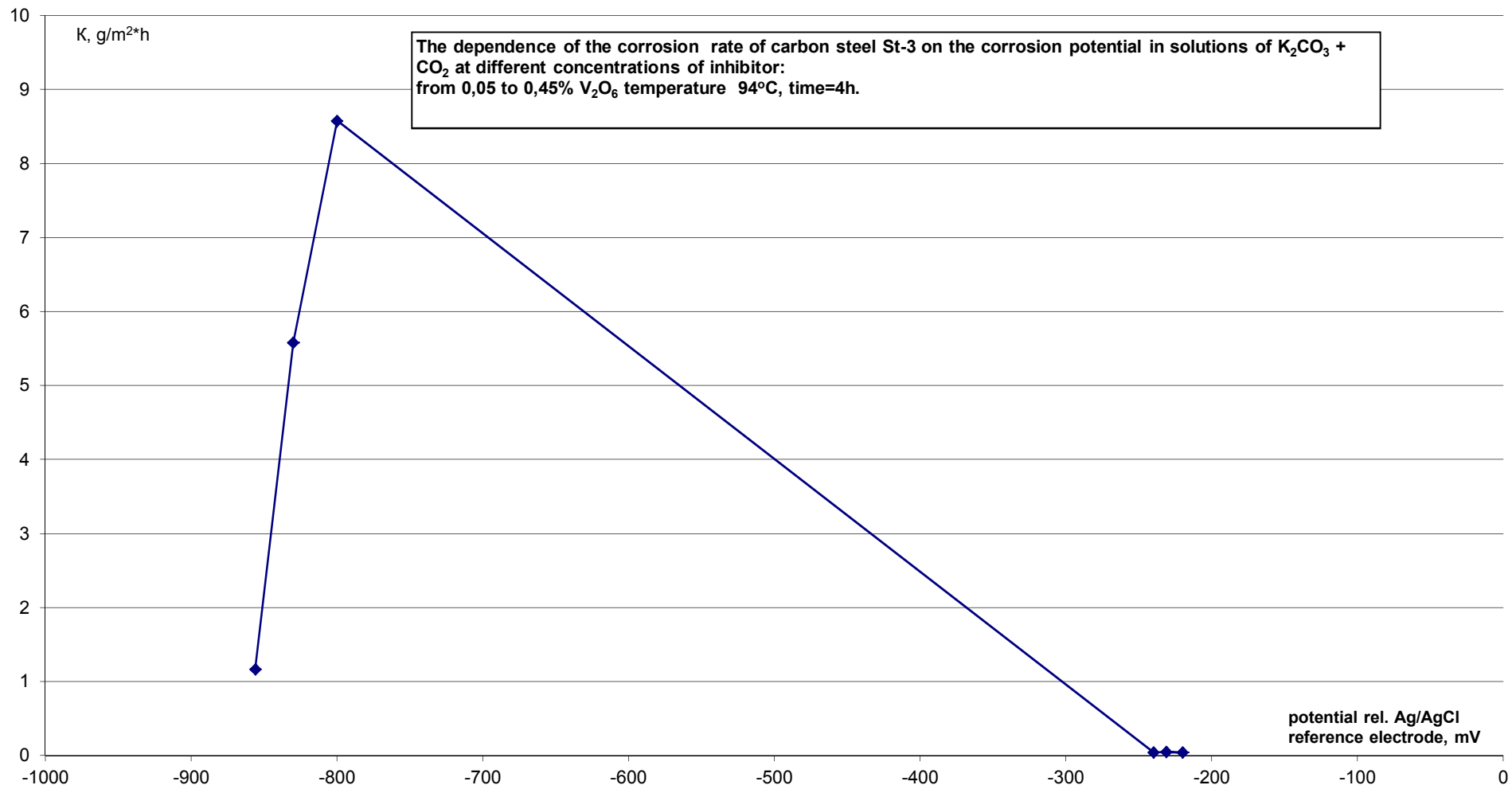


Fig. 3

Attachment 2

Principle of determination of V^{+5} and V^{+4} ions based on the dependence of the cathodic and anodic current on the indicator polarizable electrode on the value of the concentration of these ions. Figure 4 shows the voltammetric curves taken on the indicator electrode. On the the anode branch of the curve takes place oxidation of V^{+4} ions, and on the cathode branch - the repair of the V^{+5} ions (the higher the concentration of these ions, the greater the value of the anode and cathode current, respectively). Therefore, the increase and decrease of the cathode and the anode current would indicate a change in the concentration of V^{+5} (cathode current) and V^{+4} (anode current) in the solution.

Figure 5 shows the dependence of potential value of carbon steel in time with changing the concentration of the inhibitor, as well as measured values of oxidation and reduction currents, connected with the concentrations of V^{+4} and V^{+5} in model poor Benfield solution.

The stationary potential of corrosion of carbon steel in the studied conditions $E_{\text{кор.}}$ is equal to -840mV in the absence of inhibitor. Increasing the concentration of inhibitor to 0.1% moves the potential up to -790mV and in the future with increasing concentration of V_2O_5 to 0.32% potential of carbon steel is still in the area of potentials of active dissolution. When reaching a concentration above 0,4% V_2O_5 potential of carbon steel moves to the passive area.

So, the system records the change of concentration V^{+5} and V^{+4} and the corrosion state of carbon steel.

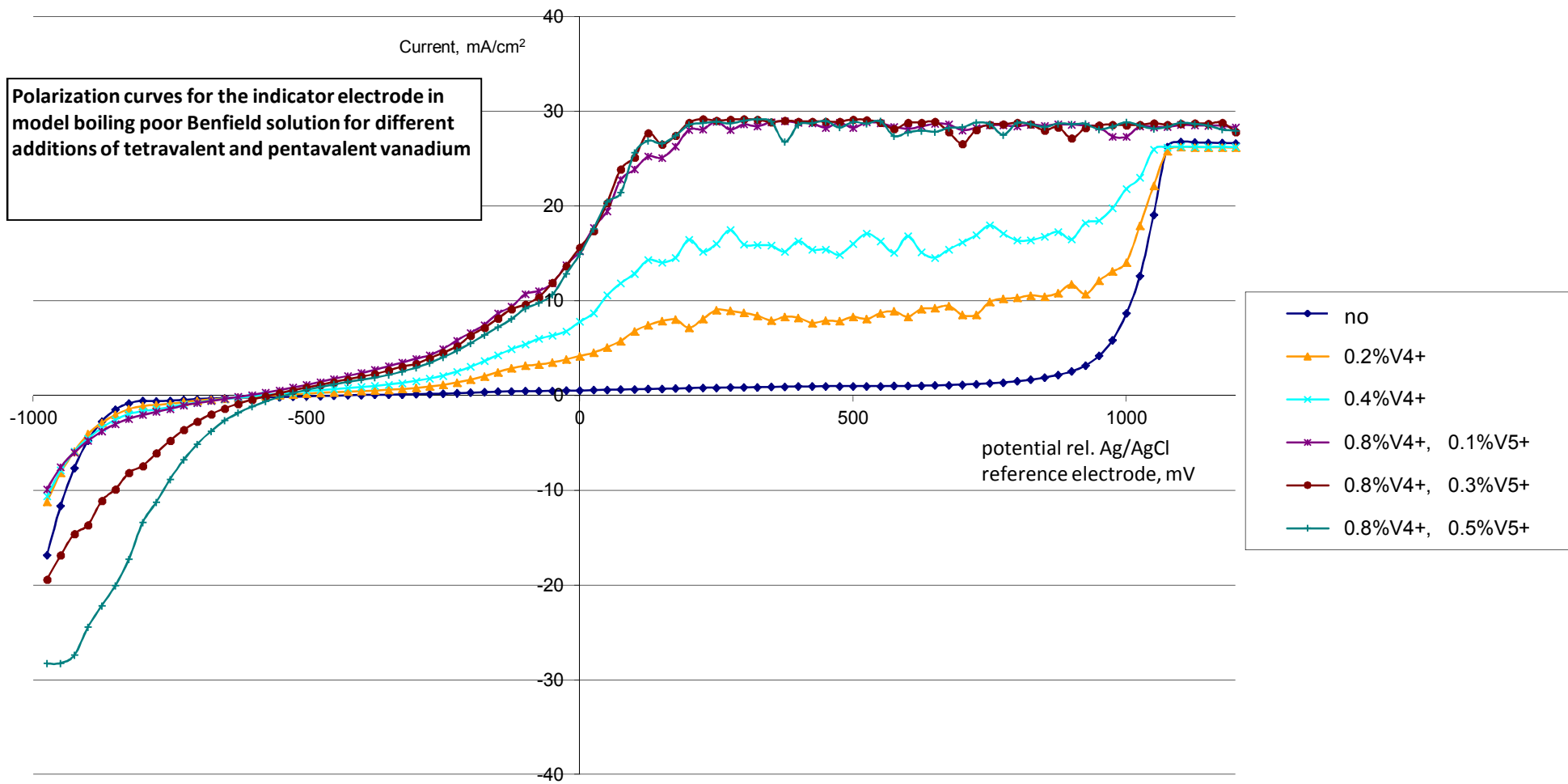


Fig. 4

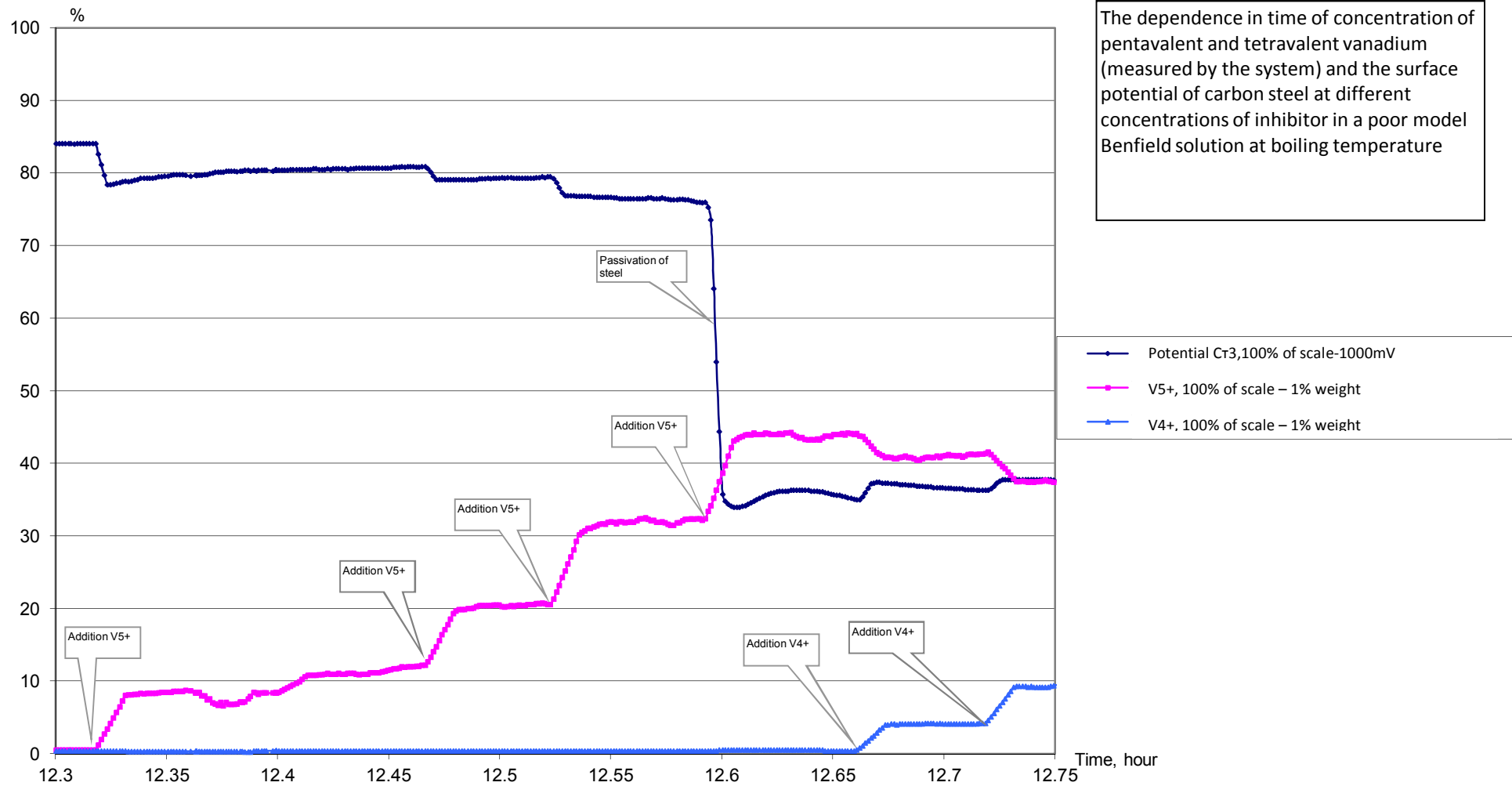


Fig. 5

