# ELECTROCHEMICAL STUDIES ON THE INHIBITION OF THE CORROSION OF IRON AND STEEL IN METAL-HYDROGEN SULPHIDE-WATER TERNARY SYSTEMS. I

## Investigation of the applicability of passivator-type inhibitors

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The application of corrosion inhibitors in the petroleum industry is frequently necessary due to the corrosive nature of the water and gases associated with the hydrocarbons. The electrochemical corrosion in sour wells is caused primarily by the presence of $H_2S$ and is accelerated by $CO_2$, organic acids, haloid ions and oxygen. The $H_2S$ is produced mainly by sulphate-reducing microorganisms. The aim of this paper is to evaluate, on the basis of laboratory experiments, the applicability of chromates as passivator-type corrosion inhibitors in aqueous systems containing $H_2S$. Experimental results obtained by intermittent galvanostatic polarization suggest that, since in the presence of $H_2S$ passivity is impossible, chromates should be added in concentrations high enough to oxidize $H_2S$ and iron sulphides completely.

## *Interpretation of the inhibiting effect of chromates on the basis of potential/pH equilibrium diagrams*

The applicability of different types of corrosion inhibitors depends mainly on the products of the interaction of the metal, of the corroding medium and of the inhibitor and also on the driving force of the corrosion reaction. The role of the above factors can be analysed theoretically on the basis of potential/pH equilibrium diagrams as shown by POURBAIX [1] for iron and several oxidizing agents. The problem of inhibition by oxidants can be analysed in a similar manner for systems containing $H_2S$ and metal sulphides. Calculations necessary for the construction of the potential/pH diagram of the Fe—S—$H_2O$ ternary systems are based on the general formulae developed by POURBAIX et al. [2, 3]. All standard free energy values used for the calculation were obtained from LATIMER [4]. Equations are written in the direction of reduction. Potentials throughout are given in volt, on normal hydrogen scale. Diagrams are calculated for 25 C°. Domains of the thermodynamic stability of iron sulphides are based on the following equations:

1. $Fe^{2+} + 2e^- = Fe$
$$\varepsilon = -0,441 - 0,0295 \log a_{Fe^{++}}$$
2. $FeS + 2 H^+ + 2e^- = Fe + H_2S$
$$\varepsilon = -0,334 - 0,0591 \, pH - 0,0295 \log a_{H_2S}$$
3. $FeS + H^+ + 2e^- = Fe + HS^-$
$$\varepsilon = -0,564 - 0,0295 \, pH - 0,0295 \log a_{HS^-}$$

4.  $FeS + 2e^- = Fe + S^{2-}$

$\varepsilon = -0{,}970 - 0{,}0295 \log a_{S^{2-}}$

5.  $Fe^{2+} + H_2S = FeS + 2\,H^+$

$\log K = -3{,}7$

$\log a_{Fe^{2+}} = 3{,}7 - 2\,pH - \log a_{H_2S}$

6.  $FeS_2 + 2\,H^+ + 2e^- = FeS + H_2S$

$\varepsilon = -0{,}187 - 0{,}0591\,pH - 0{,}0295 \log a_{H_2S}$

7.  $FeS_2 + 2e^- + H^+ = FeS + HS^-$

$\varepsilon = -0{,}423 - 0{,}0295\,pH - 0{,}0295 \log a_{HS^-}$

8.  $FeS_2 + 2e^- = FeS + S^{2-}$

$\varepsilon = -0{,}837 - 0{,}0295 \log a_{S^{2-}}$

9.  $Fe_2O_3 + 4\,SO_4^{2-} + 38\,H^+ + 30e^- = 2\,FeS_2 + 19\,H_2O$

$\varepsilon = 0{,}390 - 0{,}0748\,pH + 0{,}0078 \log a_{SO_4^{2-}}$

10. $Fe^{2+} + 2\,H_2S = FeS_2 + 4\,H^+ + 2e^-$

$\varepsilon = -0{,}140 - 0{,}118\,pH - 0{,}0295 \log a_{Fe^{++}}$

The potential/pH equilibrium diagram shown on Fig. 1 was constructed considering unit activities for $H_2S$, $HS^-$ and $S^{2-}$. From the above equations it follows that parallel with the decrease in the hydrogen sulphide content the domain of thermodynamic stability of iron sulphides gradually diminishes. More detailed diagrams for iron sulphides have been given by BOUET and BRENET [5]. Simple potential/pH equilibrium diagrams for FeS and other metal sulphides can be found in a paper of HORVÁTH and NOVÁK [6].
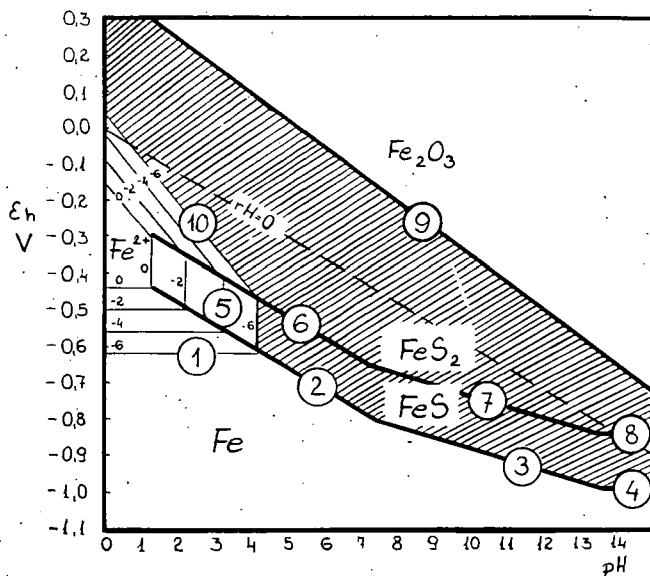


Fig. 1. Potential/pH equilibrium diagram of the Fe—S—H₂O ternary system. Hatched area represents the stability domain of FeS and FeS₂

Encircled numbers in Fig. 1 refer to the equations given above. Concerning the driving force of the corrosion reaction it can be established, that if the cathodic reaction consists in the evolution of hydrogen, the driving force is the difference between the equilibrium potentials of the $Fe/FeS/H_2S$ and $H^+/H_2$ electrodes.

Considering the potential/pH equilibrium diagram of the $Fe-H_2O$ binary system, POURBAIX [1] concluded that in aqueous solutions containing no activators (e. g. chlorides), passivation of iron is theoretically possible by an oxidizing inhibitor which has a more positive oxidation-reduction potential than the Flade potential of iron. The inhibiting efficiency of an oxidant depends also on the products of its reduction. Superimposing the equilibrium diagrams of the $Fe-H_2O$ and $Cr-H_2O$ binary systems (Fig. 2) it can be established that chromates and dichromates may
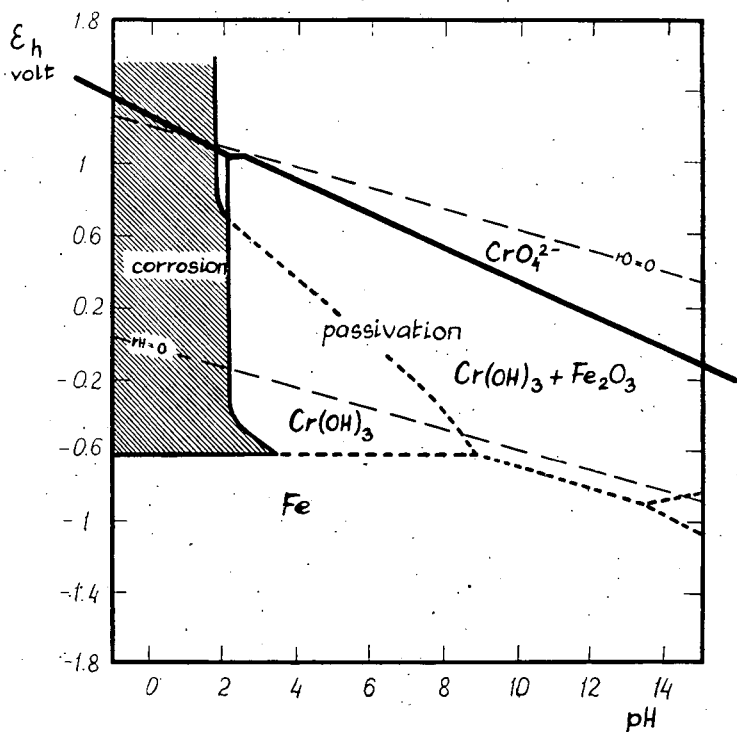


Fig. 2. Theoretical domains of corrosion, immunity and passivation of iron in the presence of $10^{-2}$ mol/l chromate inhibitor (according to Pourbaix)

be reduced by the parallel oxidation of iron to some hydrated oxide of trivalent chromium. The presence of chromium in the passivating film has been detected by radioactive tracer method by HACKERMAN [7] and BRASHER [8]. Fig. 2, constructed by POURBAIX [1] indicates the theoretical possibilities of the passivation of iron by chromates. The heavy line represents oxidation-reduction potentials below which the reduction of hexavalent chromium ($H_2CrO_4$, $HCrO_4^-$, $Cr_2O_7^{2-}$ and $CrO_4^{2-}$ in

solutions of 0,01 M/1) is possible, producing ions or compounds of trivalent chromium ($Cr^{3+}$, $CrO_2^-$, $Cr(OH)_3$). The unhatched area in Fig. 2 represents the theoretical domains of immunity and passivity of iron in the presence of chromates.

Theoretical kinetic considerations and the dependence of the electrode potential of the passive metal on the protective nature of the passivating film are shown in Fig. 3. The heavy continuous curve represents the typical passivation charac-
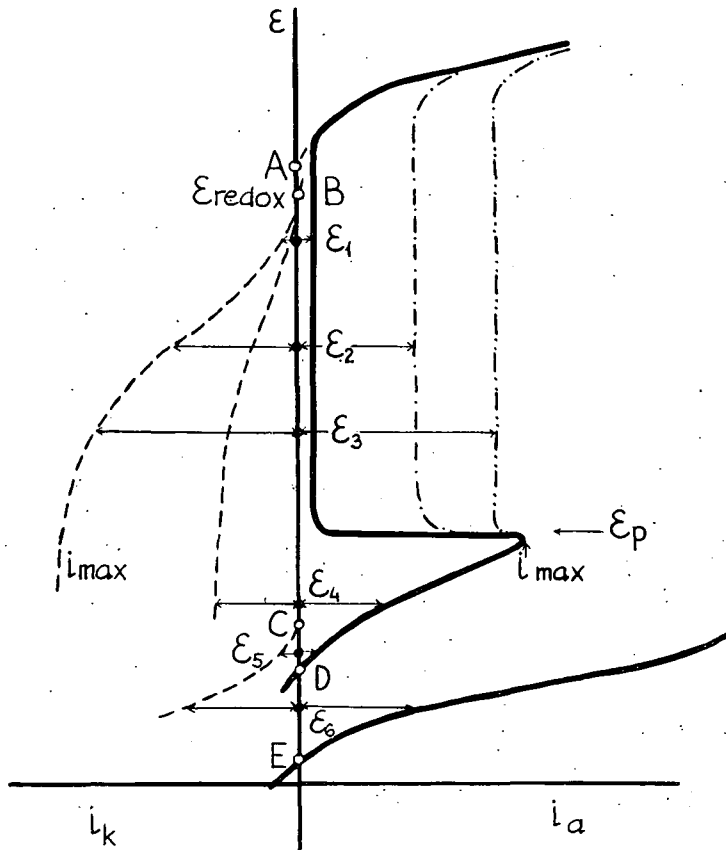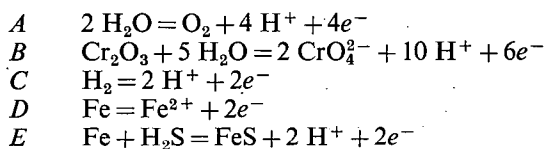


Fig. 3. Schematic diagram of the electrode potential — current density relationships favourable for passivation and active dissolution of iron in the presence of an oxidizing inhibitor and hydrogen sulphide, respectively

teristics of iron in aqueous solutions. Detailed kinetic interpretation has been given by VETTER [9]. If the passivating film provides an effective barrier against the anodic dissolution of the metal, i. e. $i_a$ is very low, the potential of the passive metal is nearly equal to the oxidation-reduction potential of the oxidant ($\varepsilon_1 \cong \varepsilon_{redox}$). Since under steady-state conditions $i_a = i_k$, at this potential the rate of cathodic reduction of the oxidizing agent is also very low. As the protective value of the passivating film decreses, the potential of the passive metal shifts to less positive values ($\varepsilon_2$ and $\varepsilon_3$) parallel

with the increase of $i_a$ and $i_k$. If the reduction rate of the oxidizing agent is lower than $i_{max}$, the maximal current density necessary to reach $\varepsilon_p$, passivation of iron cannot take place, on the contrary, the dissolution rate of the metal is considerably higher, than in the absence of the oxidant. The corresponding corrosion potentials in Fig. 3 are $\varepsilon_4$ and $\varepsilon_5$, respectively. In the presence of $H_2S$ the primary corrosion product is FeS. This corrosion product, especially in acidic and neutral media, cannot provide a barrier against anodic dissolution, on the contrary, $HS^-$ ions stimulate corrosion, probably by a mechanism described by JOFA et al. [10]. Corrosion potential in the presence of $H_2S$ is represented by $\varepsilon_6$. Along the potential axis of Fig. 3 we have indicated the points A, B, C, D, E which, deduced from the equilibrium potential/pH diagram relative to the Fe—$H_2O$, Cr—$H_2O$ binary systems [3] and the Fe—S—$H_2O$ ternary system [11], respectively, represent the circumstances of equilibrium of the following electrochemical reactions:

$A$    $2 H_2O = O_2 + 4 H^+ + 4e^-$

$B$    $Cr_2O_3 + 5 H_2O = 2 CrO_4^{2-} + 10 H^+ + 6e^-$

$C$    $H_2 = 2 H^+ + 2e^-$

$D$    $Fe = Fe^{2+} + 2e^-$

$E$    $Fe + H_2S = FeS + 2 H^+ + 2e^-$

### Experimental results and discussion

Experiments have been carried out by stationary galvanostatic and intermittent galvanostatic polarization. Experimental technique has been discussed previously [12]. Theoretical bases of the method of intermittent galvanostatic polarization have been described by LANGE, NAGEL et al. [13, 14]. In our experiments the stock solution contained 5% $Na_2SO_4$ to which $K_2CrO_4$ was added in different quantities. Saturation with $H_2S$ was carried out by bubbling $H_2S$ gas through the solution, previously deareated with nitrogene. Electrodes were made of electrolytic iron. Cylindrical surface area was about 2 $cm^2$. Prior to the experiments electrode surfaces were polished with different grades of emery paper, degreased with acetone and etched at room temperature in a solution containing 20% $HNO_3$ and 5% HF.

Characteristic polarization diagrams obtained under different experimental conditions are shown in Figs. 4., 5., 6. and 7.

Curves of Fig. 4 were obtained by stationary galvanostatic polarization. Curve 1 shows that in the case of anodic polarization the electrode potential-current density relationships are characteristic to the normal dissolution kinetics of the metal up to $i_{max}$, the critical current density necessary for passivation. Corrosion potential corresponding to curves 1 and 1′ in Fig. 4 is representative for $\varepsilon_4$ on the schematic diagram of Fig. 3. At higher current densities equal or higher than $i_{max}$ the potential of the specimen shifts rapidly towards the transpassive region. This represents the case when the concentration of the inhibitor is insufficient. It is seen, that if $i_{corr} < < i_{max}$, passivation can not take place spontaneously. To achieve passivity the electrode should be polarized by a current density equal or higher than $i_{max}$, i. e. anodic protection should be applied (see anodic curve 1 in Fig. 4). If $i_{corr} > i_{max}$ passivation takes place spontaneously. Corrosion potentials for curves 2, 2′ and 3, 3′ correspond to $\varepsilon_5$ and $\varepsilon_6$ in Fig. 3.

Changes in inhibitor efficiency with time were investigated by intermittent galvanostatic polarization. Fig. 5 was obtained under similar conditions as curves 1, 1′ in Fig. 4. Prior to anodic polarization the electrode was treated cathodically for five minutes. Electrode potentials obtained during anodic polarization (upper
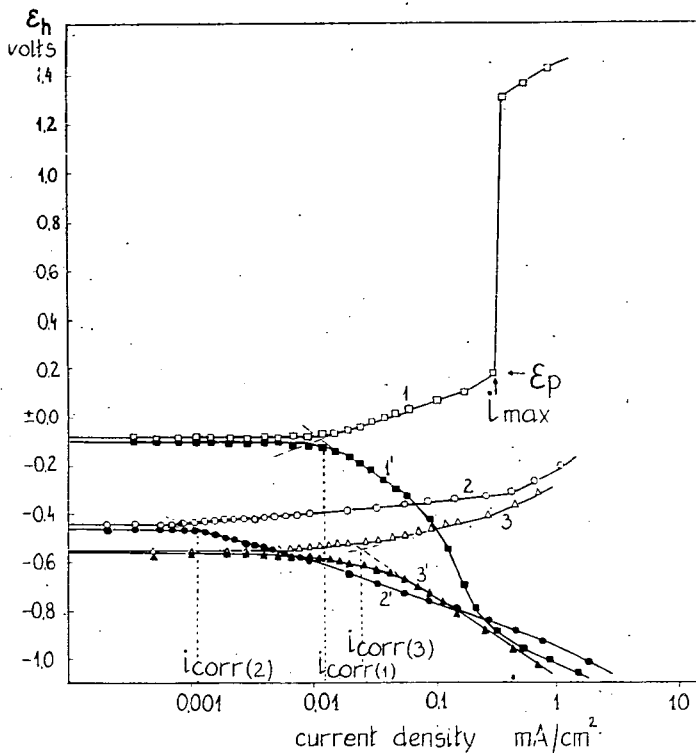


*Fig. 4.* Anodic and cathodic polarization curves obtained in the presence
and absence of $CrO_4^{2-}$ and $H_2S$.
1 □,1′ ■ — 5% $Na_2SO_4$—$10^{-3}$:mol/l $K_2CrO_4$
2 ○,2′ ● 5% $Na_2SO_4$ soln. deareated with $N_2$ gas
3 △,3′ ▲ 5% $Na_2SO_4$ soln. deareated with $N_2$ gas, saturated with $H_2S$

boundary of the hatched area in Fig. 5) suggest that 1 mA/cm² current density is higher than $i_{max}$ and is satisfactory for anodic protection in the case of insufficient inhibitor concentration. The potential stop obtained during the currentfree period can be identified with the $Fe_3O_4 \rightarrow Fe_2O_3$ transformation in the Pourbaix- diagaram of the Fe—$H_2O$ binary system. Also it corresponds to the corrosion potential of iron in the presence of $CrO_4^{2-}$ (intersection point of the extrapolation of Tafel lines for curves 1, 1′ in Fig. 4) the concentration of which is insufficient for spontaneous passivation of iron.

If the concentration of the oxidizing agent is sufficient for spontaneous passi-vation, *i. e.* $i_{corr} > i_{max}$, in the case of anodic polarization started after cathodic treatment the electrode potential shifts rapidly towards the highly positive potential
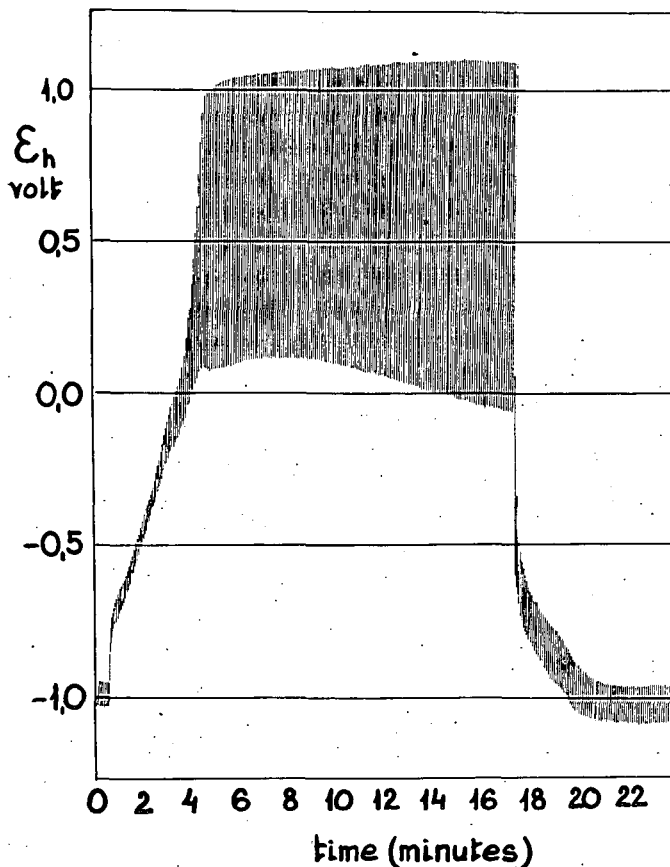
*Fig. 5.* Potential-time diagram obtained by intermittent galvanos-
tatic polarization for iron in 5% Na$_2$SO$_4$ soln. in the presence of
10$^{-3}$ mol/l K$_2$CrO$_4$. Current density 1 mA/cm$^2$

region characteristic of transpassivity and even in the currentfree periods it does
not fall back to the corrosion potential. This case is represented by Fig. 6.

Fig. 7 shows the decomposition of the passivating oxide or oxygen film in the
presence of H$_2$S. In the initial period of the experiment the solution was saturated
with H$_2$S. Simultaneously with the start of anodic polarization 1,0 N K$_2$CrO$_4$ solution
was added until H$_2$S was completely oxidized to sulphate and the electrode became
passive. During this period the polarization potential of the electrode shifted rapidly
towards the positive potential region. Considering equations 1—10 it should be
assumed, that parallel with the decrease in the activity of hydrogen sulphide and
its dissociation products sulphide layers are also eliminated by oxidation. Without
the complete oxidation of surface sulphide layers passivation of the metal would
not take place due to the defect structure of FeS and FeS$_2$. In the second period
of the experiment the solution was saturated with hydrogen sulphide again, des-
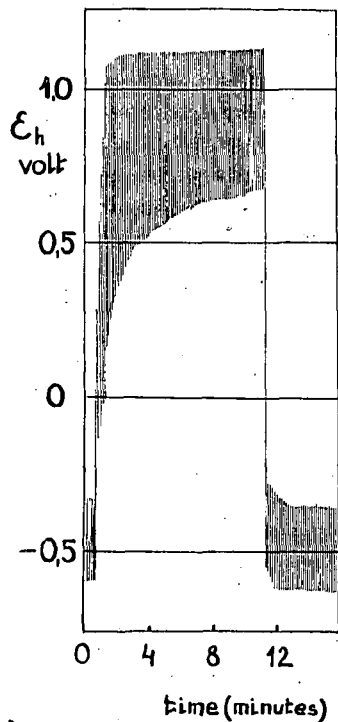
Fig. 6. Potential-time diagram for iron obtained by intermittent galvanostatic polarization, in 5% $Na_2SO_4$ soln+$10^{-2}$ mol/l $K_2CrO_4$. Current density 1 mA/cm²
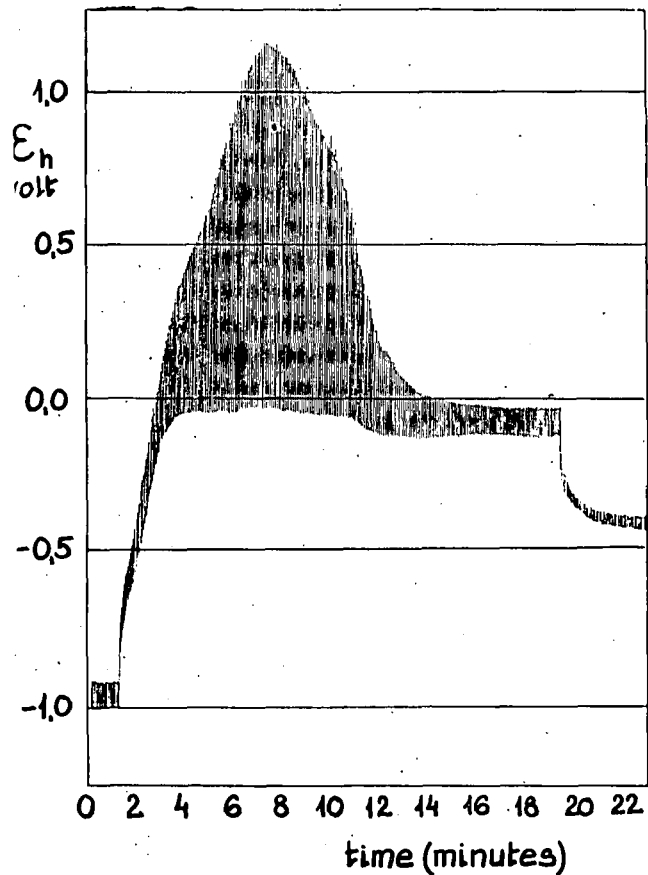
Fig. 7. Potential-time diagram for iron in 5% $Na_2SO_4$ soln. treated with $CrO_4^{2-}$ inhibitor and saturated with $H_2S$. Current density 1 mA/cm²

troying passivity due to the formation of surface iron sulphides, the free energy of formation of the latter being more negative, than that of oxides [4]. For this reason the overvoltage of the anodic reaction decreases to low values, giving rise to rapid metal dissolution again. In. Fig. 7 this effect is represented by the negative shift of polarization potentials after the positive maximum. During the final period of the experiment the potential arrest obtained during anodic polarization can be identified with the $FeS_2/Fe_2O_3$ equilibrium in Fig. 1. The possible relationship between the shift of electrode potentials towards the negative direction and the increase in the rate of anodic dissolution is shown in Fig. 3 by points corresponding to $\varepsilon_1$, $\varepsilon_2$ and $\varepsilon_3$. The latter experiment was carried out to approach the conditions of inhibitor treatment encountered in practice.

## Conclusions

Experimental results suggest that intermittent galvanostatic polarization is a useful method for the evaluation of inhibitor efficiency, especially if efficiency changes with time.

Concerning the effectivity of chromate in aqueous media containing hydrogen sulphide, it can be established that it can be effective by oxidizing hydrogen sulphide and metal sulphides and then by passivating the metal. For permanent protection, however, the required concentration can be high depending on the quantity of hydrogen sulphide in the solution. This is in good agreement with the practical observations of BREGMAN [15] in the petroleum industry in the course of primary production and secondary recovery. Considering these disadvantages it can be concluded that in aqueous media containing hydrogen sulphide the application of other inhibitor-types — e. g. organic amines of the cationic type — taking advantage of the presence of hydrogen sulphide, would be more economical.

In subsequent papers the problems outlined above will be discussed on the basis of experimental results obtained by galvanostatic and potentiostatic methods.

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# ЭЛЕКТРОХИМИЧЕСКОЕ ИЗУЧЕНИЕ ИНГИБИЦИИ КОРРОЗИИ ЖЕЛЕЗА И СТАЛИ В ТЕРНИРНЫХ СИСТЕМАХ МЕТАЛЛА-СЕРЫ-ВОДЫ

## I. О применении ингибиторов пассиваторного типа

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В нефтяной промышленности коррозионные ингибиторы часто приобретают широкое использование в силу коррозионной натуры воды и газов сопровождающих углеводороды. В кислых колодцах коррозия электрохимического характера получается прежде всего вследствие присутствия $H_2S$ и коррозия ускоряется под влиянием $CO_2$, органических кислот, галоидных ионов и кислорода. Сернистый водород часто образуется сульфат-редуцирующими микроорганизмами. Цель этой работы — на основе лабораторных данных оценивать возможности применения хроматов как коррозионных ингибиторов пассиваторного типа в водистых системах содержащих сероводород. Экспериментальные данные приобретены прерывной гальваностатичной поляризацией указывают что так как в присутствии $H_2S$ пассивность невозможна, хроматы должны быть применены в концентрациях способных полностью окислять $H_2S$ и металлические сульфиды.