STUDY OF THE ELECTROCHEMICAL BEHAVIOUR OF A CARBON STEEL IN A REAL AND TREATED GEOTHERMAL ENVIRONMENT

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Key words: carbon steel. corrosion, inhibitor, geothermal environment, hydrogen sulfide, electrochemical techniques

ABSTRACT

The geothermal installations exploiting the Dogger aquifer in the Paris Basin encounter operational difficulties in the form of corrosion of carbon steel well casings, scaling and clogging, due essentially to the corrosivity of the fluids In ordcr to optimize anticorrosion treatment in geothermal wells. various corrosion inhibitors were tested on site Using electrochemical techniques (monitnring of open circuit potential as a function of time, mcasurcmcnt of corrosion rates from Tafel plots, polarisation resistance and electrochemical impedance], different corrosion inhibitors were selected. characterized and compared according to their efficiency in reducing the carbon steel corrosion rate in a real geothermal environment

1. INTRODUCTION

French "low enthalpy" geothermal energy is primarily used for the heating of housing units and the production of *hot* water. The water of the Dogger aquifer, exploited at the present time by around 40 geothermal doublets in the Paris region *is* highly mineralized and contains dissolvcd gases. including hydrogen sulfide (H_2S) and carbon dioxide (CO_2). The main physico-chemical characteristics of the fluids are temperatures ranging from 47 to 85 °C, pH between 6 1 and 6.5, total dissolved salts (TDS) between 6 and 35 g/l much of which is Cl-, [H_2S. HS^-] from 5 tn 100 mg/l, [SO_4^{2-}] from 300 to 1200 mg/l, [CO_2/HCO_3^-] from 250 to 600 mg/l and no oxygen undcr normal conditions These characteristics make it one of the inost corrosive natural fluids for carbon steel (Ellis. 1981)

Some authors havc shown that at such high concentrations the H_2S forms non-protective deposits (Ikeda *et al.*, 1985) and activates corrosion of carbon steel Actually, their action is such that it increases the number of active dissolution centres and activates the reduction process by favouring the discharge of hydrogen (Pound *et al.*, 1980 and 1985). High concentrations of CO_2 in the geothcrmal environment buffer the mcdium and participate actively to the corrosion. Indeed. at the temperature and pH of the fluid, the CO_2, mainly in dissolved Corn. produces very soluble corrosion products such as iron hydrogenocarbonate $Fe(HCO_3)_2$, and less soluble and more protecting products such as iron carbonate $FeCO_3$. Nevertheless. since the distribution of the latter *is* not homogeneous, pitting has been observed in sites near iron carbonate (Ikeda *et al.*, 1985, Crolet, 1988). Morcovcr, Cl^- increase the risk of corrosion by pitting and favour the dissolution of protective layers. Various theories and mechanisms have heen suggested to explain the effect of these ions on the protective layers of the substrates (Lin *et al.*, 1981 and 1984; Pou *et al.*, 1984. Sato 1982; Pickering and Frankenthal, 1972) The analysis of polished sections by X-ray images (EDS) of the scale from various depths in gcothcrmal wells shows that the chloride ion content in these deposits increases as we move from the scale-solution interrace towards the scale-metal interface (Amalhay *et al.*, 1994a). I his confirms the preponderant role of Cl^- in the activation of corrosion. These deposits have two distinct layers. The first, inside, layer is formed essentially of iron salts such as FeO(OH,Cl), ($FeCl_2$, $4H_2O$), $Fe_2(OH)_3Cl$, of iron carbonate ($FeCO_3$) and of iron sulfide (Fe_xS_y) in small quantities. 'I'he second, outside. layer is madc up predominantly (80%) of iron sulfide (Amalhay *et al.*, 1994a) This iron sulfide is for the must part madc up of mackinawite. 'I'hc other phases of iron sulfide such as pyrite, marcasite, greigite and pyrrhotite are all present but in small proportions I'he scale. because of the fact that its standard potential is greater than that of metal, can even contribute to an increasc in corrosion kinetics Some authors (e g., Khodes, 1976) have shown that iron sulfides are cathodic sites facilitating the discharge of hydrogen as indicated above

In order to improve operating conditions of geothermal exploitation in the Paris region. most of the doublets have been treated by corrosion inhibitor sincc 1989 Most of the corrosion inhibitors currently being ured for the treatment of wells are quaternary ammonium salts which havc proved their effectiveness in the field of petroleum. The objcctive of this study is to compare the effectiveness of thcsc products and other molecules or formulas nor yet on the market and to better understand the mechanisms controlling the inhibition of corrosion of carbon steel in geothcrmat fluids We also attempt to determine the optimal concentration of inhibitor It must be sufficiently effective at economically feasiblc concentrations and there must he no nsk under certain conditions of favouring localised corrosion. Finally. it would be of interest to evaluate the adsorption-desorption kinetics of inhibitors in order to determine how long the inhibitor remains effective after treatment has ceased

2. MATERIALS AND MFI'HODS

The study consists in determining. by electrochemical measurements, the corrosion rate of a carbon steel identical to that of casings in a real geothermal environment as a function of immersion time and tensioactive compound concentration. The on site experiments have the advantage of using an aqueous medium which it is almost impossible to duplicate in the laboratory Corrosimetric experiments were done on stationary and rotating samples in static reactors of a small volume *so* that initial conditions could bc casily reproduced for shon experimental times. I'he temperature in the cells was 65 °C The pH was that of real geothermal fluid. 6.4 Six organic inhibitors were tested at concentrations of 0, 2 5 and 5 mg/l The products tested are:

- Solamine 129R. Norusr 491, Aquaprox MIX' 1300. formulations of surfactants already used for the treatment of geothermal wells or for combatting boiler scaling (Aquaprox)
- Fatty Amine, Soluble Amine. Cyclic Amine are svnthetic industrial molecules or formulations of surfactants the naturc of which are industrial secrets These are not yet commercialised and are still the object of research concerning their effectiveness in inhibiting corrosion and crystal growth

The geothermal fluid was collected at the production wellhead and sent through insulated pipes to measurement cells upstream from which a flowrate regulator enabled us tu maintain a flowrate of 30 l/h. The inhibitor was injected directly into the two electrochemical cells [onecontaining a stationary sample. rhe other a rotating sample) by means of two clectric pumps of the HPLC type.

The measurement of corrosion rate and the assessment of the inhibitive action nf the formulas tested were done with stationary and transitory electrochemical methods.

The electrochemical behaviour of the material (API K55 type carbon steel) in the geothermal medium was studied with linear potential sweep voltammetry The plotting of cathodic and anodic polarisation curves is done in the potentiodynamic mode with a sweep rate of 0 1 mV s^{-1} in order to ensure quasi-stationary conditions To measure polarisation resistance, the sweep covers only 20 mV around the open circuit corrosion potential, usually at the same sweep rate and in the Same direction

Before each polarisation test, the *open* circuit potential (E_{corr}) was monitored. It enables us to detect whether the surface becomes noble by the formation of passive films and helps us to determine stationary conditions, needed before any electrochemical measuring can he done, The determination of the polarisation resistance, Rp. equal to the reciprocical of the slope ofthe current vs. potential at the vicinity of the E_{corr}, gives the corrosion rate. This technique *is* based on the same theoretical hypotheses as the Tafel law but the fact that it applies to low overpotentials, anodic and cathodic, enabled Stern and Geary (1957)to simplify its mathematical formalism and to linearly Link the current taken by the metal to the potential imposed and, consequently. to link Rp to the corrosion current (I_{corr}) according to the following equation.

$$I_{corr} = \frac{1}{2303.(b_a + b_c)Rp}$$

where b_a and b_c are the anodic and cathodic Tafel slopes, respectively.

The application of the Tafel law assumes a pure transfer regime that will be shown below. Knowing the density of the corrosion current. the corrosion rate is determined using the Faraday's formula. The effectiveness of the inhibitor is determined using the values of comosion rate in the presence and absence of inhibitor.

We therefore used non-stationary electrochemical methods based on the analysis of the response of the metal-solution interface during the application of an external disruption of low amplitude Electrochemical impedance measurements were carried out in the frequency range of 10^5 to 10^{-3} Hz. The measurement was dnne in the open circuit of steel with a disruption of 5 mV peak to peak for frequencies higher than 1 Hz with 8 measures taken per decade, and 10 mV peak to peak for frequencies lower than 1 Hz, with 2 integration cycles. The measurement of electrochemical impedance is done alternately with the other electrochemical methods, allowing enough time for the stabilisation of the samples.

The material studied is an API K55 type carbon steel supplied bv Valourec Industries (Montbard, France). The average composition by weight per cent of the steel samples is. C: 0.42% (±0.04); Mn- 1 08% (±0.001); Mo: 0.014% (±0.01); Si: 0.34% (±0.04); Ni: 0.092% (±0 005); Cr- 0.100% (±0.005); P:0.01%; S: 0.004% The casings of geothermal wells exploiting the Dogger aquifer of the Paris Basin *are* made of this material

The corrosive environment is a natural geothermal fluid corning directly from the production wellhead of Melun l'Almont site. This site was chosen because it is also one of the few Dogger sites that have not yet been treated, and because the fluid there is generally representative of the sites to the south of Pans (TDS- 12 7 g/l; surface pH= 6.4; production temperature- 72°C; concentrations (mg/l): $[Na^+]$= 4250. $[Ca^{2+}]$=580, [Cl']= *7200,* $[SO_4^{2-}]$- 680. alkalinity $[HCO_3^-]$- 317.0, $[SiO_2]$= 42.5; dissolved gas (GLR=14.9%), mainly CO_2= 17.6%, CH_4- 53.3%, N_2- 19.7%. The production flow rate varies over the year between 25 m^3/h (in a thermosiphon) and 150 m^3/h. The bubble pint pressure is around 7 bars. Dissolved sulfide content is 15 mg'l in S^{2-} equivalent.

Depending on the tests to be carried out. we chose one of two types of working electrodes. either cylindrical (diameter of the haw- @ 7 cm, height= 0 31 cm) with an exposed cylindrical rurface area of 2 0 cm^2, or disk-shaped (diameter=1 133 cm; thickness= 1 5 mm). with an exposed surface area (flat and circular) of 1 0 cm^2 Before the experiments the working electrode is polished with sandpaper (320. 600 and 1200 grade). cleaned with acetone or alcohol and deionised water in an ultrasonic bath and then dried in pulsed warm air The working electrodes can be stationary or rotating. Concerning the last. it is attached to a turning device (EG&G PARC, RDE 616) whose rotating speed can be varied from 0 to 9,994 rpm. The electrodes are held in place with a metallic rod which is protected against corrosion by a hollow PTFE cylinder.

We chose as a reference a KCl saturated calomel electrode (SUE) At 25°C, the difference in potential with a normal hydrogen electrode (NHE) IF 0.2415 V In tests in geothermal fluid. the electrode potentials arc measured in relation tu an Ag/AgCl electrodc whose ptential is 0.2223 V/NHE (volts with respect to the NHE electrode) Thcse reference electrodes were connected to the aggressive solutions through a salt bridge All of the potentials are hereafter reported with respect to the KCl saturated calomel electrodc and their unit is given as V/SCE

In order to minimise the effects of polarisation. we use a large platinum iridium electrode (Pt 90%; Ir 10%) as a counter electrode It is made up of a cylindrical grid, 55 mm in diameter and 65 mm high surrounding the working and reference electrodes. Some tests are carried out with a counter electrode built out of the same material but having the shapc of a concave plate (2x4 cm^2) which does not surround the electrodes but is placed near them

For the electrochemical studics, the cells are *two* 500 ml cylindrical "Pyrex" reactors in which the fluid is at atmospheric pressure. Conical holes in its cover permit the attachment of electrodes (temperature, pH and Eh, measurement prohcs. reference, counter and working electrodes) and the inhibitor injection system

The electrochemical corrosion techniques were carried out using an EG&G PARC Model 352 system The impedance measurements were performed using an EG&G PARC Model 398. The set up includes:

- an EG&G PARC potentiostat-galvanostat (model 273A),
- an EG&G I'ARC loch-in amplifier, model 5210,
- two electrochemical cells
- two HPLC type pumps (SHIMADZU model LC-6A and KNAUER model L64) for the injection of corrosion inhibitor into the two cells
- a BROOKS 8500 flowrate regulator

The piloting of these instruments and the gathering and processing of data are done with a Cheer Personal Computer

3. RESULTS AND DISCUSSION

Because of the absence of dissolved oxygen in the medium. the half redox reactions are the oxidation of iron into ferrous ions at the anode and the reduction of H' ions into H_2 at the cathode

3.1. Behaviour of the carbon *steel* at the open circuit potential

Anodic behaviour

the oxidation reaction of iron into ferrous ions is $Fe \rightarrow Fe^{2+} + 2e^-$ The thermodynamic potential of oxidation of iron into ferrous ion. assimilating the activity of Fe^{2-} ions to their concentrations is

$$E_{Fe^{2+}/Fe} = E^\circ_{Fe^{+2}/Fe} + (RT/2F) \ln [Fe^{2+}]$$

$E^\circ_{Fe^{2+}/Fe}$ = -0.681 V/SCE (Besson, 1984), standard potential of the Fe^{2+}/Fe couple

R is the constant of perfect gases (R = 8 32 J K^{-1} mol^{-1})
T is the absolute temperature of the electrolyte
I is the Faraday constant (F 96450 C)
$[Fe^{2+}]$ is the concentration of Fe^{2+} ions in solution

At the temperature used in our experiments (65 °C or 338 K), the potential *of* the anodic reaction of iron dissolution is

$$E_{Fe^{2+}/Fe} = -0.681 + 0.03357 \log[Fe^{2+}]$$

Cathodic behaviour

The reduction of H^+ ions into H_2 is $H^+ + e^- \rightarrow 1/2\ H_2$
By assimilating the activity of the H^+ ions lo their concentration, the thermodynamic potential of reduction of H^+ ions to the cathode is given by the following equation

$$E_{H^+/H_2} = E^\circ_{H^+/H_2} + RT/F \ln [H^+] - RT/F \ln pH_2^{1/2}$$

Knowing that $E^\circ_{H^+/H_2}$ = -0.2415 V/SCE. the thermodynamic reduction potential of H^+ ions at the temperature uf the electrolyte (65°C) is:

$$E_{H^+/H_2} = -0.2415 - 0.03357 \log ([H^+]^2/pH_2)$$

Open circuit potential, Ecorr

This is determined by the following equation

$$E_{corr} = E_{H^+/H_2} = E_{Fe^{2+}/Fe}$$

$$E_{corr} = -0.4395 + 0.03357 \log([H^+]^2/([Fe^{2+}].pH_2))$$

The open circuit potential therefore depends on the Fe^{2+} concentration, the pH and the H_2 partial pressure in the metal;solution interface.

Furthermore, the Fe^{2+} concentration is controlled by the FeS solubility product defined by the equation $K_s(FeS) = [Fe^{2-}][S^{2-}]$

At the anodic sites the Fe^{2+} ions dissolve and later precipitate as FeS when the K_s is reached. The S^{2-} concentration is controlled by the H_2S acidity constants defined by the following equations:

$$K_{a1}(H_2S) = ([HS^-][H^+])/[H_2S] \quad (1)$$

$$K_{a2}(HS^-) = ([H^+][S^{2-}])/[HS^-] \quad (2)$$

If we multiply (1) and (2), we obtain the following relationship:

$$[H^+]^2[S^{2-}]/[H_2S] = K_{a1}(H_2S) \cdot K_{a2}(HS^-), \text{ thus}$$

$$E_{corr} = -0.4395 + 0.03357 \log(K_{a2HS^-} K_{a1H2S} [H_2S])/(K_{sFeS} \cdot pH_2)$$

The E_{corr} depends therefore on the H_2S concentration and the H_2 pressure Nevertheless, the layer of deposit formed on the surface of the steel contains species such as iron hydroxy-chloride which can influence the redox processes and therefore the corrosion potential

3.2. Behaviour of the carbon steel during linear potential sweep voltametry io the absence of inhibitor

Anodic behaviour: Anodic polarisation curves clearly show the absence of any passivation domain (Fig 1) This behaviour is justified by the fact that the K55 steel is a soft steel. Furthermore, for both the stationary electrode and the rotating electrode, the anodic polarisation curves show a linear domain beyond +50 mV compared to the corrosion potential. This is characteristic of a pure charge transfer regime The anodic Tafel slope. ba, slope of the rectilinear part of the anodic polarisation curves, varies depending on the electrode rotating speed. It has an average value of 75 mV/decade at 0 rpin and 60 mV/decade at 1000 rpm after 4 h and 3 5 h of immersion respectively This difference can be explained by the fact that the iron dissolution kinetics are more rapid in the case of the rotating electrode and are therefore controlled by the electrode rotating speed

Cathodic behaviour The cathodic polarisation curves do not show any diflusion plateau (Fig. 1) The reduction reaction is therefore controlled by the charge transfer and is not limited by the input of matter The cathodic Tafel slope, bc, slope of the linear part of the cathodic polarisation line. varies almost not at all as a function of the electrode rotating speed. It has an average value of 200 mV/decade at 0 rpm and 190 mV/decade at 1000 rpm for a similar immersion lime of 4 h and 3.5 hours. respectively Furthermore, the high bc d u e s compared to ba values show that the reduction reaction is the main control of the corrosion process in the absence of inhibitor

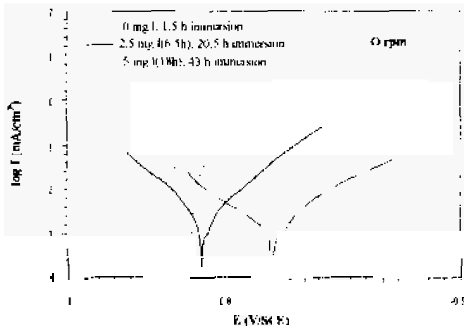

Fig.1 Polarisation cuncs for carbon steel with different concentrations of Solamine at 0 rpm

Behaviour of carbon steel during the first fifteen hours of immersion without treatment At 1000 rpm, the corrosion rate decreases rapidly from an initial value of 0.625 to 0.470 mm/y after 3 h of immersion without treatment. It levels out and stabilises at 0.425 mm/y between 6 and 8 h of immersion then decreases rapidly to 0.075 mm/y after 15 h of immersion (Fig 2) At 0 rpm, after an increase of 0.050 mmiy during the first hour of immersion, the corrosion rate decreases rapidly from 0.530 to 0.375 mm/y between the first and the fifth hour of immersion then decreases slowly to 0.300 mm/y after 15 h of immersion. This decrease in the corrosion rate during the first 15 h of immersion might he due to the formation of a protective deposit such as amorphous irun sulfide whose relatively dense structure and low porosity would contribute to ensure a better protection of the metal. Moreover, during the first tiftcen hours of immersion, the open circuit potential of hoth samples is relatively stable at -830 mV/SCE and -815 mV/SCE for the stationary and rotating samples. respectively In the case of the rotating electrode, the shift of the corrosion ptential towards more noble potentials can be explained by an increase in the kinetics of the reduction reaction occurring at the surface of the scale Indeed, the hydrodynamic regime created by the rotating electrode might contribute to the formation of a laycr of iron sulfide more homogeneous than in the case of a stationary elcctrode, facilitating the discharge of the hydrogen This phenomenon could explain the higher corrosion rates observed in the case of the rotating electrode during the first 10 h of immersion

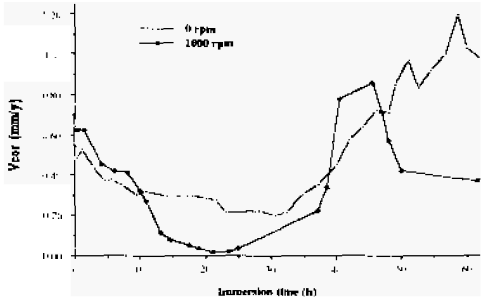

Fig. 2. Corrosion ratc as a function ot the elcctrode rotating speed dunng the first sixty five hours of immersion without trcatment

Behaviour of carbon steel between lifteen and sixty-five hours of immersion without treatment: At 1000 rpm, the corrosion rate of steel betwccn 22 and 45 h of immersion increases 12-fold. evolving very rapidly from 0.070 to 0.85 mm/y (Fig 2) The corrosion rate of the stationary sample alm rises sharply from 0.2 to 1.2 mm/y betwcen 30 and 70 h of immersion (Fig 2) This phenomenon can be explained by a crystallisation of the amorphous iron sulfide which causes an increase in the porosity of the scale and therefore an increase in the corrosion rate Moreover, this crystallisation seems to hc kinetically activated by the electrode rotating speed. Indeed. the moderate decrease in the corrosion rate at 1000 rpm after 45 h of immersion (Fig 2) is probably due to the fact that the crystals formed are larger and more protective This is also corroborated by the fact that at 0 rpm the increase in the corrosion ratc after 30 h of immersion is progressive and a s i p of slow crystallisation kinetics. The deposition

of a great quantity of amorphous FeS after the high corrosion rate can also explain this decrease in corrosion rate.

3.3. Behaviour of carbon steel when corrosion inhibitors are added

Addition of 2.5 mg/l after the first phase of immersion without treatment

The effectiveness of the various inhibitors was evaluated over a period of 10 h of treatment with 2.5 mg/l of inhibitor after a first phase of immersion without treatment This enabled us to evaluate the action of the inhibitors in the presence of scale and simulate real conditions encountered in geothermal doublets which have been operating for several years.

Stationary sample

After adding 2.5 mg/l, the six inhibitors decrease significantly the corrosion rate. notably batty Amine and Soluble Amine for which the effectiveness is, respectively, 87 5 and 92% after two hours of treatment (Table 1) Aquaprox and Solamine are 79 and 64 5% effective for similar treatment and immersion times These differences in corrosion rate two hours after the beginning of treatment are caused by different adsorption kinetics. the most rapid being those of Soluble Amine and Fatty Amine. Norust and Cyclic Aininc, on the other hand. have much slower adsorption kinetics Their effectiveness after *two* hours of treatment is only 46.9 and 25%, respectively. Ten hours after the start of treatment. the difference between inhibitors is less marked They are all nearly or more than 90% effective except Norust which *is* only 23 6% effective, a value lower than its effectiveness after two hours of treatment (Table 1)

In presence of the six inhibitors the open circuit potential becomes more noble during treatment with 2 5 mg/l of inhibitor This shift of potential ranges from +145 mV (for Norust) to +112 mV (for Soluble Amine) after 10 h ofrreatment (Tahlc 1).

The analysis of the impedance diagram shows the absence of coating action of the inhibitors during this first phase of treatment with 2.5 mg/l of inhibitor for around 10 h 'Ihe electrochemical impedance measurements revealed the effect of inhibitor on the decrease in the corrosion rate Indeed. in all cases. the addition of 2 5 mg/l of inhibitor caused a decrease in the capacity of the double layer and an increase in the diameter of the capacitive loop This diameter is simply the polarisation resistance identical to that determined by polarising the sample at +/-20 mV on either side of E_{corr} The results of the two methods are similar. Therefore, for Cyclic Amine, the polarisation resistance method gives Kp values of 218 and 340 ohm.cm^2, respectively, at 0 iind 2 5 mg/l (1 5 h nf treatment) while electrochemical impedance gives values of 206 and 320 ohm.cm^2 for the same immersion time and treatment conditions (Fig 3)

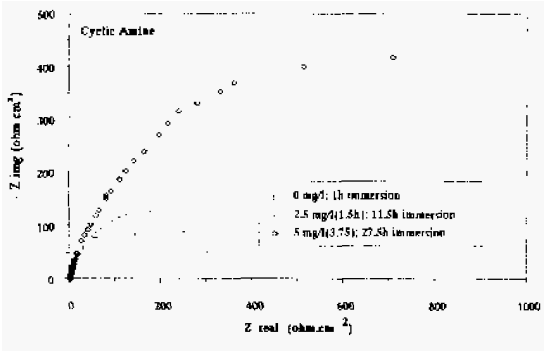

Fig 3 Electrochemical impedance diagram for a stationary sample as a function of time and Cyclic Amine concentration at 0 rpm

Fatty Amine and Soluble Amine increase ba and decrease bc and reduce the corrosion current whilc shifting the corrosion potential towards cathodic values They act as mixed inhibitors Solamine, which docs nut modify ba and decreases bc is a cathodic inhibitur, causing a shift in the corrosion potential towards more noble values (Fig 1) The three other inhibitors, which cause a decrease in bc and ba make the potential more noble but, like Solamine. their action decreases two hours after their injection because their adsorption kinetics *at* anodic sites seems to be slower The inhibiting effect of Norust at 2 5 mg/l is less than 50% and docs noi increase with the length of treatment

Rotating sample

Corrosion tests run on rotating samples (1000 rpm) art compared to stationary tests under the same treatment and immersion time conditions–2 5 mg'l of inhibitor added for 10 h after an immersion phase of 10 to 15 h without treatment

The decrease in the corrusion rate is very significant right from the start of treatment. The corrosion rate is indeed lowcr than 0.067 mm/y after two hours of treatment for all the inhihitors except Fatty Amine *and* Solamine On the average. the inhibiturs are 89% effective after two hours of treatment, except for Aquaprox which is only 44% effective (Tahlc 1) This behaviour during the first hours after injection is different from what was observed in the case of the stationary electrode and shows the influence of the hydrodynamic regime created by the rotating electrode on the adsorption kinetics of inhibitors

Thus. for Cyclic Amine and Norust. passing from 0 to 1000 rpm increases the effectiveness 4-fold and 2-fold, respectively The increase in ha ohscrved when we pass from 0 io 1000 rpm suggests that the increased effectiveness of these two inhibitors at 1000 rpm is due to an activation of the adsorption kinetics at the anodic srtes

The effectiveness of Soluble Amine after 10 h of treatment is half what it had becn after two hours of treatment Aquaprox and Cyclic Aininc behave in a similar manner. although with a more moderate decrease of around 30% in their inhibiting effectiveness The inhibiting power of Fatty Aininc, which was ineffective after two hours of treatment. increases with the length of treatment. I his is not the case for Solamine which remains ineffective after two hours ut' treatment Norust was very effective. tts level of inhibition remained at around 80% (Table 1).

As for the stationary sample. the six inhibitors make the metal more noble, the greatest effect being that of Solamine (+265 mV) Fatty Amine shifts the potential only by +90 mV and the four nther inhibitors by an average of +230 mV (Table 1) The increase in corrosion potential is therefore clearly marked for the rotating sainple. The average shift caused by the Inhibitors is +210 mV, while it was around +72 mV for stationary samples.

The electrochemical impedance diagrams obtained for the rotating electrode are similar to those of the stationary sample Nevertheless the values for polarisation resistance at 1000 rpm arc higher Therefore, liir Cyclic Arninc, the polarisation resistance is 4276 ohm cm^2 after almost 4 h of treatment with 2 5 mg/l ai 1000 rpm while it is 320 ohm.cm^2 after 1 5 h of treatment with 2.5 mg/l at 0 rpm. This is in agreement with observations mentioned above

In the case of the rotating electrode, all of the inhibitors increase the anodic Tafel slope and decrease the cathodic Tafel slope They are mixed inhibitors (anodic and cathodic) which make the metal more noble Cyclic Amine. Norust. Soluble Amine adsorb most rapidly Aquaprox has a low adsorption rate which even diminishes with time. The effectiveness of Solamine and Fatty Amine is mediocre or even nil under such conditions of immersion and hydrodynamic regime Electrochemical impedance measurements did not reveal any coating action with 2 5 mg/l and for around 10 h of treatment

The effect of adding an additional 2.5 mg/l of inhibitor after the initial treatment with 2.5 mg/l

The effect of adding 5 mg/l of inhibitor was studied for around 10 hours after the end of the first phase of treatment with 2 5 mg/l of inhihitor.

Stationary sample

The evolution of the corrosion rate when the quantity was increased from 2 5 to 5 mg/l varied depending on the **naturc** of the inhibitor. The adding of 5 mg/l **increases** the effectiveness of Norust **4-fold** (Table 1). For **Fatty Amine. Aquaprox** and Solamine. the adding of an additional 2 5 mg/l has no effect. Nevertheless, the increase in the diameter of the capacitive **loop** (in the impedance diagrams) resulting from the **addition** of 2 5 mg/l attests to the increase in effectiveness of the inhibitor at this concentration **(Fig** 3)

3.5. The effect of stopping treatment

While **there** was no increase in the corrosion rate 6 h **aftcr** treatment **with** 5 mg'l of Solamine was stopped. 16 hours after trcatmcnt was stopped the effcctivcncss **of** Solamine was only 68%, down frnm 98% when treatment was stopped. This means **ihat** 30% of **the** inhibitor had been desorbed **With** Cyclic Amine, *6* h after treatment **was** stopped, the corrosion rate was unchanged hut was twice as great 16 **hours** after treatment had stopped Soluble Amine does not desorb 8 h **after** the end of trcatmcnt because no variation in the corrosion

Table 1. Comparison of the effectiveness (Einh) and corrosion potential (Ecorr) Variation for the different inhibitors with various concentrations and immersion times (Timrs) at 0 and 1000 rpm. NM: Not measured or not measurable.

		without treatment	2 hours of treatment with 2.5 mg/l			without treatment	10 hours of treatment with 5 mg/l				without treatment	10 hours of treatment with 2 5 mg/l		
Name of inhibitor	Timrs h	Vcorr mm/y	Vcorr mm/y	Einh %	Timrs h	Vcorr mm/y	Vcorr mm/y	Einh %	Ecorr variation mV	Timrs h	Vcorr mm/y	Vcorr mm/y	Einh %	Ecorr variation mV
at 0rpm														
Fatty Amine	12 00	0.32	0 04	87 5	20	0.275	0 015	94 5	60	30.00	0.24	0 026	89.2	60
Soluble Amine	15 00	0.31	0.025	92.0	23	0.21	0.015	92 9	112	NM	NM	NM	NM	NM
Aquaprox	17.25	0.31	0 065	79 0	25 25	0 21	0 02	90.5	53	35.5	0 308	0.038	87 7	111
Solamine	16.00	0 31	0 11	64 5	24	0 21	0.016	92	69	34 00	0 438	0 02	95 4	34
Norust	11.5	0 32	0 17	46 9	19.5	0 275	0 21	23 6	45	39 5	0 185	0 013	93	95
Cyclic Amine	12.00	0.32	0.24	25 0	20	0 275	0 03	89	92	30 00	NM	NM	NM	30
at 1000 rpm														
Fatty Amine	10.75	0 175	0.19	NM	18.75	0 03	0.02	33 3	90	32.00	0.143	0 008	94.4	37 5
Soluble Amine	9 00	0 36	0.04	88 9	17	0 05	0.03	40.0	240	28.00	0.085	0.038	55.3	112 5
Aquaprox	12.00	0 12	0 067	44 2	20	0.03	0.02	33.3	230	31.00	0.125	0.02	84 0	47
Solamine	17.75	0 05	0 1	NM	25.75	0.065	0.1	NM	265	41.00	0 5	0 038	92 4	62 5
Norust	8.00	0 4	0.065	83.8	16	0.063	0 012	81 0	230	NM	NM	NM	NM	NM
Cyclic Amine	6.00	0 42	0 025	94.0	14	0 08	0.025	68 8	205	46 00	NM	0 022	NM	45

Rotating sample

Increasing ttic inhihitor to 5 mg/l increases the effectiveness of Fatty Amine 3-fold and that of Aquaprox 2 **5-fold** (Table 1) There IF a spectacular rise in the effectiveness with **Solamine** and **a** inorc modcratc increase with Soluble Aminc for uhich the effectiveness is only 55% after 28 h of treatment. It therefore **seems** that Soluble Aminc **has** a restrained **action** on the inhibition of iron sulfide crystal growth for which we hare hypothesiscd a crystallisation after 22 h of immersion at 1000 rpm (see paragraph *3 2)*.

3.1. The effect of immersion time on the effectiveness of the inhibitor

We compared the behaviour of inhibitors at immersion times for which there was an increase in the corrosion ratc between 22 and 45 hours for the rotating sample and between 30 **and** 70 hours for the stationary sample (see paragraph 3 2.). Nevertheless, because of the **lack** of data beyond 35 hours of immersion without treatment at 1000 rptn we had tu **limit** our study to the hehaviour at 0 rpm. For Soluble **Aininc at** 0 rpm, we noted a decrease in effectiveness with 2 5 mg/l after 30 **hours** of immersion Therefore, at 20 hours of immersion and compared with the case without treatment, it reduces the corrosion ratc from 0 27 to 0 **015** mm/y, **in** other words **an** effectiveness of 94% while at 40 hours of immersion its effectiveness is only 71% (Fig 41 For **Aquaprox.** no **decrease** in effectiveness was observed Indeed, **after** 30 hours of immersion, this inhihitor is 87.5% effcctivc while it is 87.9% effective aftcr 40 hours

No increase **in** the corrosion rate **is** measured after 30 hours of immersion **at** 0 **rpm for** Solamine and Norust Likewise, the effectiveness **of Cyclic Arninc passes** from XI to 88% **at** similar immersion times These four inhibitors therefore have a very positive behaviour concerning the inhibition of crystal growth. On the othcr hand. Fatty Amine shows a slight decrease in effectiveness frotn 92 5 to 82.2% between 30 and **44 hours** of immersion These results confirm the **effectiveness of** 2.5 mg'l of Soluble Amine in the presence of crystallised iron sulfide and show that Cyclic Amine. Solamine, Aquaprox and Norust have a good behaviour at 2 5 mg/l **in** the presence of crystal growth of scale. The inhibiting action **of** Fatty Amine is slightly affcctcd by the presence of crystallised **dcposits**

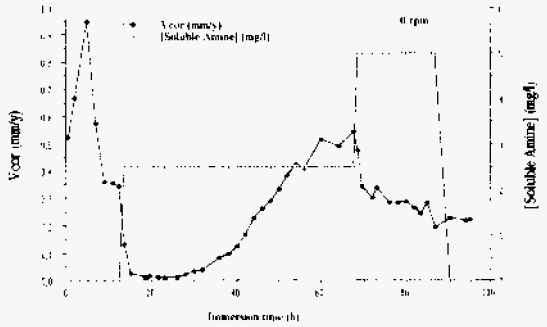

Fig. 4. Corrosion ratc as **a** function of Soluble Aminc cnnccntration and immersion titnc at 0 rptn

rate is observed The effcctivcncss of Fatty Aminc decreased from 87% when treatment was stopped to 84% 5 **hours** later proving that this inhibitor is almost not desorbed On the othcr hand. 10 hours after the end of trcatmcnt. the effcctivcncss is only 46%, or about 40% of **the** inhibitor **is dernrbed.** We **have** no data concerning the effectiveness of Aquaprox and Norust aftcr the stopping **of** treatment

4. CONCLUSION

Work carricd out on **sitc** cnablcd us to study the effect **of** real geothermal fluid and the adding of **various inhibitors** on **the** corrosion **of** carbon steel We were able to ensure a **constant** fluid temperature. pressure and physico-chemistry during the total **duration of'the** tests

In ***the*** real fluid, as in **the** partially reconstituted **fluid.** scale plays **a preponderant role** in the evolution of **the** corrosion, especially iti **the** case of **the** real **tluid. where the** study of **the** cathodic slopes of the Tafel lines, **shows that** the cathodic reaction probably occur? entirely on the **scalc** and controls the kinetics **of** the corrosion **reactions** Without treatment, the large decrease in the corrosion rate of steel which was **seen during** the first 20 hours of immersion is **due to** the formation of amorphous iron sulfide **which** temporarily protects the **metal**

In the case of the rotating electrode, it was also shown that the hydrodynamic regime thus created has a direct influence on the homogeneity of the scale. Indeed, the rotation of the electrode ensures a better distribution of the iron sulfidc, facilitating the discharge of the hydrogen. This phenomenon explains the higher corrosion rates observed at 1000 rpm during the first hours of immersion. Amorphous iron sulfide crystallisation was also shown after 22 and 30 hours of immersion at 1000 and 0 rpm, respectively. For these immersion times, we noted a large rise in the corrosion ratc, the kinetics of which would be controlled by the electrode rotating speed. Analyses of scale sampled at various periods of immersion will be used to study these phcnoincna.

At 0 rpm, the injcction of 2 5 mg/l of inhibitor after a phase of immersion without treatment of 10 to 15 hours showed very rapid adsorption kinetics for Fatty Amine and Soluble Amine for which the inhibition rate was around 90% two hours after injcction. While the effect of Ayuaprox, Solamine and Cyclic Amine on the dccrcase of the corrosion ratc right from the onset of treatment is less evident. they arc nevertheless 90% effective afler 10 hours of treatment. On the other hand, Norust has the slowest adsorption kinetics with a mediocre inhibition ratc which does not increase with the lcngth of treatment The injection of 5 mg/l does noi significantly incrcasc the effectiveness of the inhihitors except in the case of Norust for which it increases 4-fold after 10 hours of treatmcnt.

The differences seen in the action of inhibitors on the evolution of anodic and cathodic Tafel slopes between the stationary and rotating electrode clearly show that the behaviour of the inhihitor on the redox reaction kinetics is controlled by the electrode rotating speed. As a result, there are large differences in the inhibition action The effectiveness of Norust increases 2-fold whcn we pass frum 0 to 1000 rpm for similar treatment and immersion lime On the other hand, the inhibiting action of Solamine, Fatty Amine and Aquaprox is considerably rcducccd at 1000 rpm

At 0 rpin. an increase in the immersion time also caused a significant decreased in the effectiveness of Soluble Aminc injected at 2.5 mg/l in the presence of crystalline iron sulfide scalc On the other hand, Cyclic Amine, Solamine, Aquaprox and Norust seem tu effectively inhibit crystal growth The effectiveness of Fatty Amine is slightly affected by the presence of crystallised scalc

The stopping of treatment revealed relatively similar desorption kinetics for Solamine, Cyclic Amine, Soluble Aminc and Faity Aininc On the average, 6 hours after the end of treatmeni, nu increasc in the corrosion rate was observed The desorption rate of Fatty Amine seems slower though bccause the corrosion rate 8 hours after the end of the injection is Identical to what was observed at the onset of the end of treatment

The 6 inhibiturs tested all seem to decrease the value ofthe cathodic Tafel slope, decreasing the cathodic overtension and limiting the process of reduction and therefore of corrosion. They seem to act by blocking the cathodic sites thus causing an inhibition of *the* discharge of hydrogen at the iron sulfide On the other hand, thcir action on the oxidation reaction is controlled by the electrode rotating speed the effect ofwhich Seems preponderant on the hehaviour of the inhibitor at the anodic sites.

The results of the analysis of impedance diagrams are concordant with those of polarisation methods. The electrochemical impedance curves on the Nyquist plane show that corrosion under these conditions is controlled by the charge transfer. The diagrams show only one capacitive loop whose diameter is the samc as the polarisation resistance calculated using polarisation techniques. This ulso shows that the scale formed does not form a physical barrier to the mass transfer between the solution and the metal, capable of modifying the global corrosion kinetics The coating action of the inhihitors was not observed at concentrations of 2.5 and 5 mg/l under conditions of immersion time and length of treatment of our experiments.

ACKNOWLEDGMENTS: This is the BRGM contribution N°95006 This work was carried out in the framework of the Commission of European Communities contract N°JOU2-CT92-0108, and received financial support from a BRGM rcsearch project (S08)

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