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RESEARCH REGARDING FUNCTIONAL PARAMETERS
INFLUENCE ABOUT CORROSION RATE
AT CRUDE OIL PIPES

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Abstract

Crude oil contains formation water, salts and gases as carbon dioxide, which made it an electrolytic medium with an acid pH. Is very important to prevent pipes damage made by corrosion and to avoid crude oil loses.

NORSOK M-506 methodology propose a relation for corrosion rate which depends of many complex parameters such as carbon dioxide fugacity, pH, surface tangent effort, each factor depending of temperature, pressure, fraction of gases and water, oil and water density, pipe area and roughness etc..

In order to predict pipe life time, paper develops an original interactive computer program made to solve the corrosion rate relation proposed in NORSOK M-506. We obtain also new relations between parameters. With the program created we establish that at 60°C we have the maximum corrosion rate and also we analyze the CO₂ partial pressure, pH, pipe area and roughness, water and oil density, total pressure influence about corrosion rate. The results obtained were confirmed by experiments and by industrial practice.

Keywords: *crude oil, carbon dioxide, corrosion rate.*

1. INTRODUCTION

Gas and liquid hydrocarbons became corrosive in the presence of water. Crude oil obtained by deep-well pumping contains 60...70% petroliferous water and important quantity of carbon dioxide. In table 1 is shown for few wells from Vata oil field, some characteristics of formation water.

Table 1. Some characteristics of formation water

Well number	Pump type	pH	CO ₂ free, mg/l	CO ₂ % from gases volume
557 Vata	TB 2 3/8	6,55	147,40	10,75
2408 Vata	2 7/8 RHAC	6,85	132,00	4,39
1078 Vata	2 7/8 RLAM	6,61	325,60	7,47
451 bis	TB 3 1/2	6,96	71,81	6,53

Corrosive effect of CO₂ became stronger with pressure and temperature, because rise the dissolved quantity of CO₂ in water. Formation water aggressivity can be expressed by equation [5]:

$$p_{CO_2} = p \cdot y_{CO_2} \quad (1)$$

were: p_{CO_2} is partial pressure of carbon dioxide, MPa;

p –system total pressure, MPa;
 y_{CO_2} -molar concentration of carbon dioxide, %.

There are the following limits:

$$p_{CO_2} > 0,2 \text{ MPa} \text{ – strong corrosion;}$$

$p_{CO_2} = 0,05 \dots 0,2 \text{ MPa}$ – temperate corrosion;

$p_{CO_2} < 0,05 \text{ MPa}$ –small influence of CO₂ above corrosion.

Corrosion rate of low-alloy steel in CO₂ medium is difficult to evaluate because of the influence of some specific factors met in oil-wells as:

- forming protecting films;
- hydrocarbons presence;
- presence of poly-phase system gas-liquid-solid;
- presence of corrosion inhibitors;
- material type and surface quality;
- friction forces.

From this reasons were developed many semi-empirical models to evaluate corrosion

rate. The influence of many factors was taking into account mostly by lodging some corrective factors.

One of this is SHELL model, [4], which evaluate corrosion rate, as a function of partial pressure of carbon dioxide and temperature. Based on this model in figure 1 is presented SHELL nomogram.

In high temperature zone, results obtained from nomogram are corrected with scale factor. The main SHELL method deficiency is the mindless of medium pH, fluid movement and the influence of friction forces.

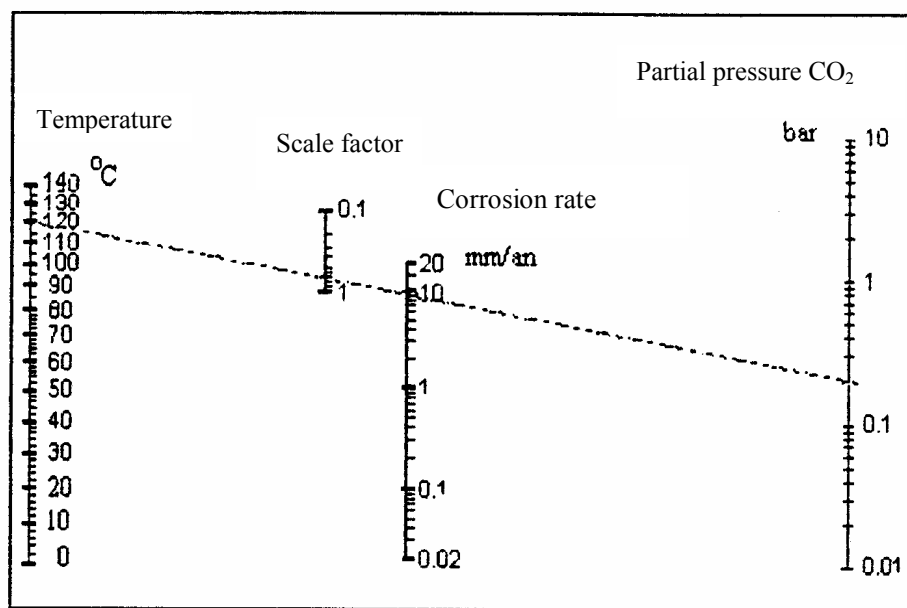


Fig. 1: SHELL nomogram to evaluate corrosion rate

Other modern model is Neuronal Network Model [2]. This model admit to evaluate processes that depends on many factors between we could not establish an analytical connection. To obtain proper results with this method we have to use extended descriptors which assort elementary factors which have causal nexus. For example in the category of extended descriptors we have well-known numbers of Reynolds, Prandtl etc.

To evaluate corrosion rate of low-alloy steel in CO₂ medium the elementary factors as input parameters were:

- temperature, $t=20\ldots 90^{\circ}\text{C}$;
- partial pressure of CO₂, $p_{\text{CO}_2}=0,03\ldots 2,6$ MPa;
- iron density of ionization, $\text{Fe}^{2+}=1\ldots 230\text{ppm}$;
- fluid pH, $\text{pH}=3,5\ldots 7$;

- fluid flow rate, $v=1\ldots 13\text{m/s}$.

Evolved descriptors used to evaluate corrosion rate were [2]:

$$\begin{aligned} e_1 &= \frac{p_{\text{CO}_2}}{t \cdot \text{pH} \cdot \text{HCO}_3^-}; & e_2 &= \frac{\text{Fe}^{2+}}{t \cdot \text{pH} \cdot \text{HCO}_3^-}; \\ e_3 &= \frac{v^{0,4} \cdot \ln(v)}{t \cdot \text{pH} \cdot \text{HCO}_3^-}; & e_4 &= \frac{v^{0,4} \cdot \ln(v)}{p_{\text{CO}_2} \cdot \text{Fe}^{2+}}; \\ e_5 &= \frac{p_{\text{CO}_2}}{\text{pH}}; & e_6 &= \frac{\ln(\text{HCO}_3^-)}{\text{pH}}. \end{aligned} \quad (2)$$

Results obtained with Neuronal Network Model were compared with experimental results. From the figure 2 results, there are a proper correlation between calculated values and experimental values [1].

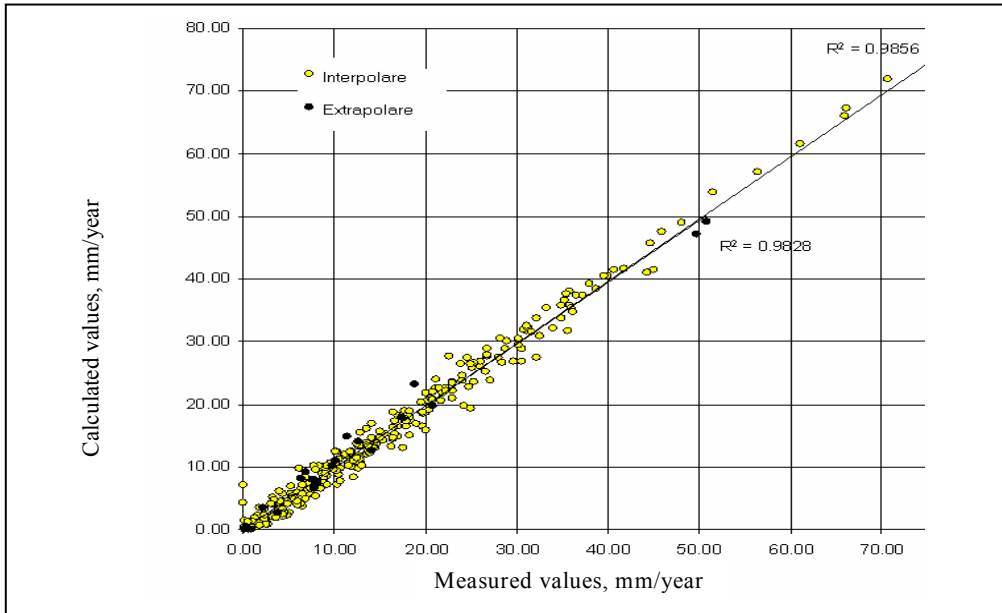


Fig. 2: Comparison between corrosion rate values measured and corrosion rate values calculated with Neuronal Network Model

In figure 3 is presented the correlation between corrosion rate values calculated with SHELL Model and experimental corrosion rate values [1]. From figure 2 and 3 result that

SHELL Model is less sensitive ($R^2=0,72$), than Neuronal Network Model.

However Neuronal Network Model mindless of presence of poly-phase system gas-liquid-solid, surface quality and friction forces.

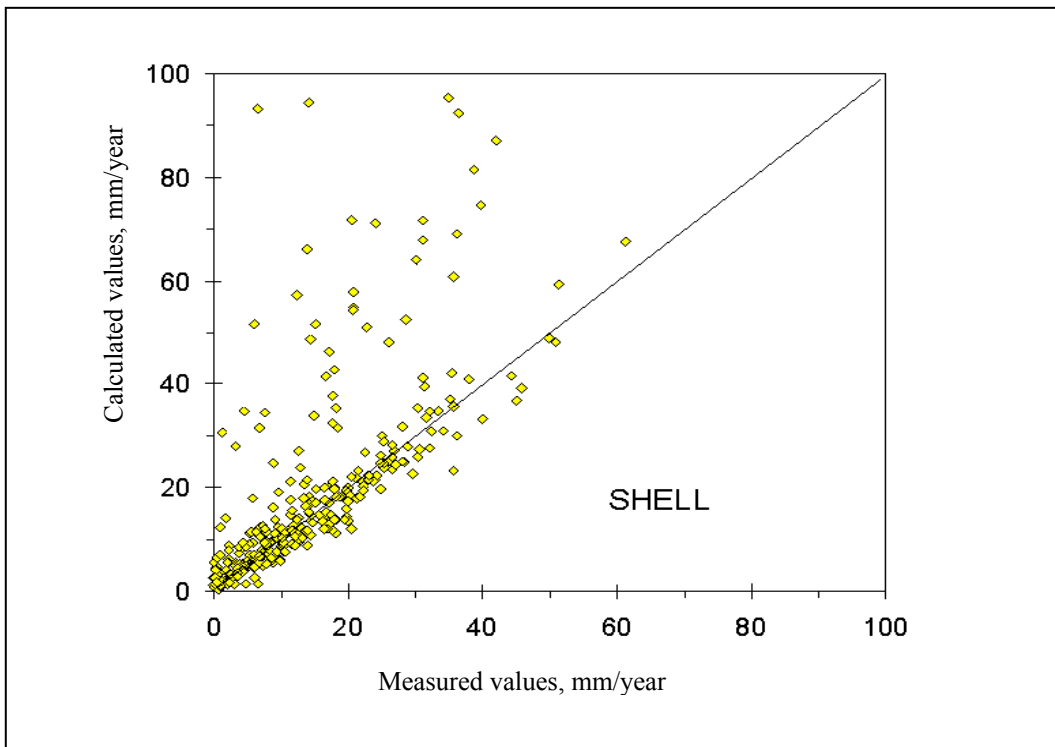


Fig. 3: Comparison between corrosion rate values measured and corrosion rate values calculated with SHELL Model

The newest method to evaluate corrosion rate in petroleum medium with carbon dioxide is proposed by NORSOK M-506 standard [6].

This method depends on partial pressure of carbon dioxide, medium pH, system temperature and tangential stress at liquid-solid interface. Calculus relation for corrosion rate is [6]:

$$v_{cor} = k_t \cdot f_{CO_2} \cdot \phi(pH)_t \cdot \left(\frac{S}{19}\right)^{0,146+0,0324 \cdot \lg(f_{CO_2})} \quad (3)$$

were: K_t is a constant which depends on temperature;

f_{CO_2} - fugacity of carbon dioxide;

$\phi(pH)_t$ - functions of pH and temperature;

S - tangential stress at fluid-solid interface.

Those variables depend of many factors, so we could not solve relation 3 without finding them first.

2. CALCULUS METHODOLOGY

2.1 Establish K_t constant

The values of K_t constant are given in table 2, according to the M-506 standard.

Table 2. K_t constant values

Temperature, °C	Constant K_t
20	4,762
40	8,927
60	10,695
80	9,949
90	6,250
120	7,770
150	5,203

Analyzing dates from table 2 we obtained the following correlation between temperature t and K_t constant:

$$K_t = -0,00307t^2 + 0,393578t - 1,88767, \quad (4)$$

for $20 < t \leq 90^\circ\text{C}$;

For temperatures higher then 90°C , K_t constant with linear switching in, became:

$$K_t = 6,25 + 0,050667(t - 90), \quad (5)$$

for $90 < t \leq 120^\circ\text{C}$;

$$K_t = 7,77 - 0,085567(t - 120), \quad (6)$$

for $120 < t \leq 150^\circ\text{C}$.

2.2 Carbon dioxide fugacity

Fugacity f is a value proportional with partial pressure of a gas which correlates at higher pressure the non-linear behavior:

$$f_{CO_2} = a \cdot p_{CO_2} \quad (7)$$

were: a is fugacity constant, and p_{CO_2} partial pressure of CO_2 .

Fugacity constant depends of total system pressure p and of absolute temperature T :

$$a = 10^{p \cdot (0,0031 - 1,4T)} \quad (8)$$

for $p \leq 25 \text{ MPa}$;

$$a = 10^{(0,775 - 62,5T)} \quad (9)$$

for $p > 25 \text{ MPa}$.

2.3 Establish pH influence

Function $\phi(pH)_t$ can be determinated with relations presented in table 3.

For a medium with $\text{pH}=3,5$, in figure 4 is presented the $\phi(pH)$ function variation versus temperature. We notice that at temperatures between 80°C and 90°C the pH influence is maximal.

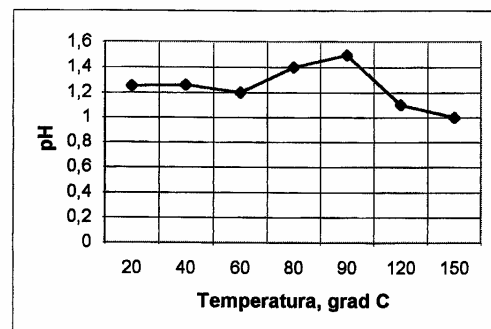


Fig. 4: $\phi(pH)$ function variation versus temperature

Table 3. Calculus relations for function $\phi(\text{pH})_t$

Temp, °C	pH limits	Calculus relations for $\Phi(\text{pH})$
20	$3.5 \leq \text{pH} < 4.6$	$\phi(\text{pH}) = 2.0676 - 0.2309 \cdot \text{pH}$
20	$4.6 \leq \text{pH} \leq 6.5$	$\phi(\text{pH}) = 5.1885 - 1.2353 \cdot \text{pH} + 0.0708 \cdot (\text{pH})^2$
40	$3.5 \leq \text{pH} < 4.6$	$\phi(\text{pH}) = 2.0676 - 0.2309 \cdot \text{pH}$
40	$4.6 \leq \text{pH} \leq 6.5$	$\phi(\text{pH}) = 5.1885 - 1.2353 \cdot \text{pH} + 0.0708 \cdot (\text{pH})^2$
60	$3.5 \leq \text{pH} < 4.6$	$\phi(\text{pH}) = 1.836 - 0.1818 \cdot \text{pH}$
60	$4.6 \leq \text{pH} \leq 6.5$	$\phi(\text{pH}) = 15.444 - 6.1291 \cdot \text{pH} + 0.8204 \cdot (\text{pH})^2 - 0.0371 \cdot (\text{pH})^3$
80	$3.5 \leq \text{pH} < 4.6$	$\phi(\text{pH}) = 2.6727 - 0.3636 \cdot \text{pH}$
80	$4.6 \leq \text{pH} \leq 6.5$	$\phi(\text{pH}) = 331.68 \cdot e^{(-1.2618 \cdot \text{pH})}$
90	$3.5 \leq \text{pH} < 4.57$	$\phi(\text{pH}) = 3.1355 - 0.4673 \cdot \text{pH}$
90	$4.57 \leq \text{pH} < 5.62$	$\phi(\text{pH}) = 21254 \cdot e^{(-2.1811 \cdot \text{pH})}$
90	$5.62 \leq \text{pH} \leq 6.5$	$\phi(\text{pH}) = 0.4014 - 0.0538 \cdot \text{pH}$
120	$3.5 \leq \text{pH} < 4.3$	$\phi(\text{pH}) = 1.5375 - 0.125 \cdot \text{pH}$
120	$4.3 \leq \text{pH} < 5.0$	$\phi(\text{pH}) = 5.9757 - 1.157 \cdot \text{pH}$
120	$5.0 \leq \text{pH} \leq 6.5$	$\phi(\text{pH}) = 0.546125 - 0.071225 \cdot \text{pH}$
150	$3.5 \leq \text{pH} < 3.8$	$\phi(\text{pH}) = 1.0$
150	$3.8 \leq \text{pH} < 5.0$	$\phi(\text{pH}) = 17.634 - 7.0945 \cdot \text{pH} + 0.715 \cdot \text{pH}^2$
150	$5.0 \leq \text{pH} \leq 6.5$	$\phi(\text{pH}) = 0.037$

2.4 Establish tangential stress at fluid-solid interface

Tangential stress at fluid-solid interface it's a parameter which depends of fluid properties and of quality of metallic surface. In calculus of corrosion rate it was used the average tangential stress in normal section of pipe.

Average tangential stress value at high flow rate ($Re > 2300$) is:

$$S = 0,5 \cdot \rho_m \cdot f \cdot u_m^2 \quad (10)$$

were: S is tangential stress at interface, Pa;
 ρ_m – fluid average density, kg/m^3 ;
 f – friction coefficient;
 u_m – flow rate, m/s.

Fluid average density ρ_m is:

$$\rho_m = \rho_l \cdot \varepsilon + \rho_g \cdot (1 - \varepsilon) \quad (11)$$

were: ρ_l is liquid density, kg/m^3 ;
 ρ_g – gas density at p system pressure;
 ε – liquid fraction mixture, which is:

$$\varepsilon = \frac{Q_l}{Q_l + Q_g} \quad (12)$$

were: Q_l is liquid volumetric flow and Q_g gas volumetric flow.

Liquid is an oil and water mixture and thus, taking account of water fraction from oil ϕ , of water density ρ_a and oil density ρ_p , results:

$$\rho_l = \phi \cdot \rho + \rho \cdot (1 - \varepsilon) \quad (13)$$

Gas density depends on total pressure p , specific-gravity relative at air γ_{rg} , factor of gas non-ideality Z and temperature T :

$$\gamma = \frac{627,1047 \cdot p \cdot \gamma_{rg}}{Z \cdot T} \quad (14)$$

Mixture velocity at the surface u_m is:

$$u_m = u_l + u_g \quad (15)$$

Liquid being incompressible, for a pipe section A results:

$$u_l = Q/A \quad (16)$$

For a gas with a non-ideality factor Z at temperature T , results:

$$u_g = Z \cdot \frac{Q_g}{A} \cdot \frac{T}{T_0} \quad (16)$$

Usually, velocity u_l domain is 0...20m/s, and the domain for velocity u_g is 0...40m/s. Friction coefficient f depends on geometrical factors (surface roughness R_z and pipe diameter D), viscosity μ_m and fluid density ρ_m :

$$f = 0,001375 \cdot \left[1 + \left(20000 \cdot \frac{R_z}{D} + \frac{\mu_m}{\rho_m \cdot \mu_m \cdot D} \cdot 10^6 \right)^{1/3} \right] \quad (17)$$

For fluid viscosity μ_m we use a similar relation with (13):

$$\mu_m = \mu_l \cdot \varepsilon + \mu_g \cdot (1 - \varepsilon) \quad (18)$$

For liquid viscosity calculus under the critical point we use the relation [6]:

$$\mu_l = \mu_p \cdot \left(1 + \frac{\frac{\phi}{K_0}}{1,187 - \frac{\phi}{K_0}} \right)^{2,5}, \text{ Pa}\cdot\text{s} \quad (19)$$

were μ_p is oil viscosity and K_0 is a coefficient depending on maximum relative viscosity μ_{relmax} and corresponds to water contents ϕ_c at critical point:

$$K_0 = \frac{\phi_c}{1,187 \cdot \left[1 - \left(\frac{1}{\mu_{relmax}} \right)^{0,4} \right]} \quad (20)$$

If we do not know all dates we could use $\mu_{relmax} = 7,06$ at a water fraction $\phi = 0,5$. Oil viscosity is 0,011 Pa·s at 60°C, and water viscosity is 0,00046 Pa·s.

For systems above critical point:

$$\mu_l = \mu_a \cdot \left(1 + \frac{\frac{1 - \phi}{K_a}}{1,187 - \frac{1 - \phi}{K_a}} \right)^{2,5}, \text{ Pa}\cdot\text{s} \quad (21)$$

were:

$$K_a = \frac{1 - \phi_c}{1,187 \cdot \left[1 - \left(\frac{R}{\mu_{relmax}} \right)^{0,4} \right]} \quad (22)$$

and $R = \frac{\mu_a}{\mu_p}$. For oil medium viscosity at 60°C,

$$R = 0,42.$$

Water viscosity μ_a depends on temperature t :

$$\mu_a = 1,002 \cdot 10^{-3} \cdot 10^{1,3272 \cdot (20 - t) - \frac{0,001053 \cdot (20 - t)^2}{t + 105}}, \text{ Pa}\cdot\text{s} \quad (3.25)$$

In table 4 is presented the parameters domain for interface stress calculus and usually values for forms when we don't have enough dates, [3].

Table 4. Domains and usually values for the parameters used at calculus of interface stress

Parameter	Units	Domain	Usually value
Roughness, R_z	μm	0...100	50
Non-ideality factor, Z	-	0,8...1,0	0,9
Gas relative specific-gravity, γ_{rg}	-	0,5...1,0	0,8
Oil density, ρ_p	kg/m^3	600...1200	914 or calculus
Water density, ρ_a	kg/m^3	900...1100	1024 or calculus
Gas density, ρ_g	kg/m^3	1...1700	calculus
Water viscosity, μ_a	$\text{Pa}\cdot\text{s}$	0,00017...0,0011	0,00046 or calculus
Oil viscosity, μ_p	$\text{Pa}\cdot\text{s}$	0,0002...0,2	0,00909 or calculus
Gases viscosity, μ_g	$\text{Pa}\cdot\text{s}$	0,00002...0,00006	0,00003 or calculus
Water fraction at critical point, ϕ_c	-	0,3...0,9	0,5
Maximum relative viscosity, μ_{relmax}	-	1...100	7,06 or calculus

3. CALCULUS PROGRAM, INFLUENCE OF PARAMETERS AND CONCLUSIONS

In figure 5 is presented the friendly program interface for input dates and corrosion rate

calculus. Based on NORSOK M-506 standard, the originally soft created by authors was made in programming language Visual Fox, [3].

The input parameters values were kept in memory and at a new test must be changed only the value of the parameters we are interested on.

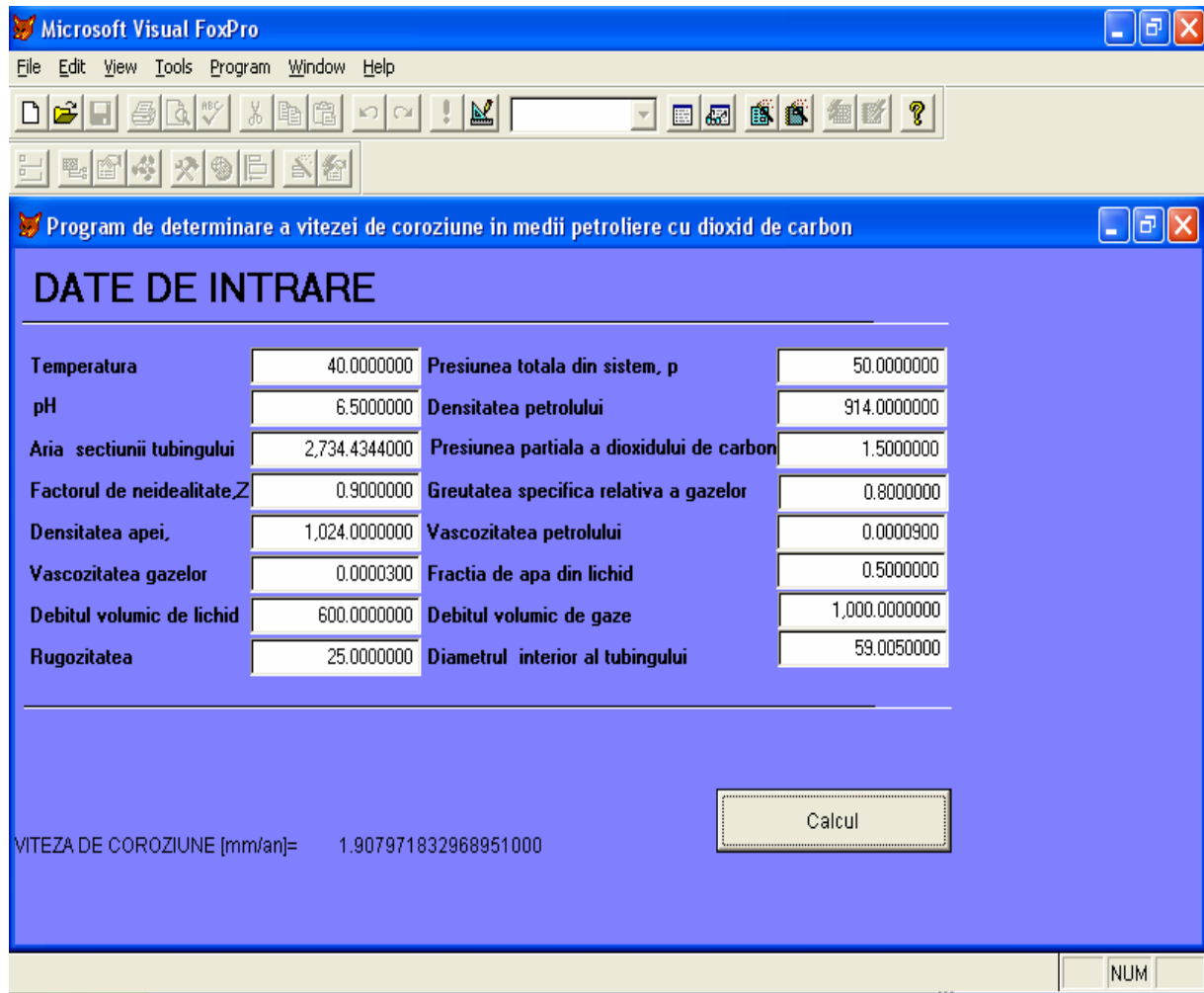


Fig. 5: Simulation window for corrosion rate calculus

To evaluate the influence of involved parameters, with the program created we find corrosion rate for different parameters values. Based on observation that at pH= 3,5 corrosion rate is maximum, with this pH value in figure 6 is presented the influence of temperature for different partial pressure of carbon dioxide. Analyzing the results we notice that at 60°C we have the maximum corrosion rate values. Also the temperature influence is greater at higher partial pressure of carbon dioxide.

This conclusion is confirmed by the results in oil fields.

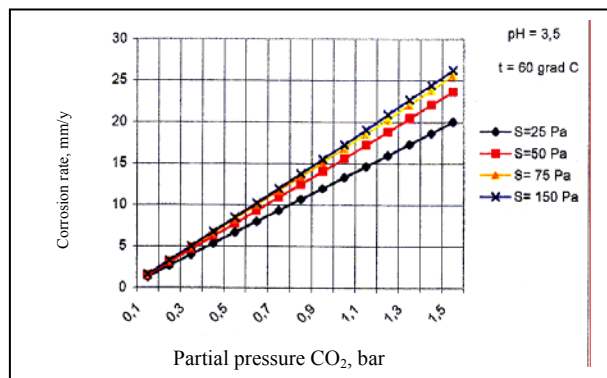


Fig. 6: Corrosion rate versus partial pressure of CO₂ at different temperatures

In figure 7 is presented the influence of tangential interfacial stress above corrosion rate at temperature 60°C.

Analyzing the results we notice that the tangential interfacial stress influence above corrosion rate is smaller. We obtain a limitation of corrosion rate by rising tangential stress. Result that curve corresponding $S=75$ Pa is almost overlying with curve corresponding $S=150$ Pa.

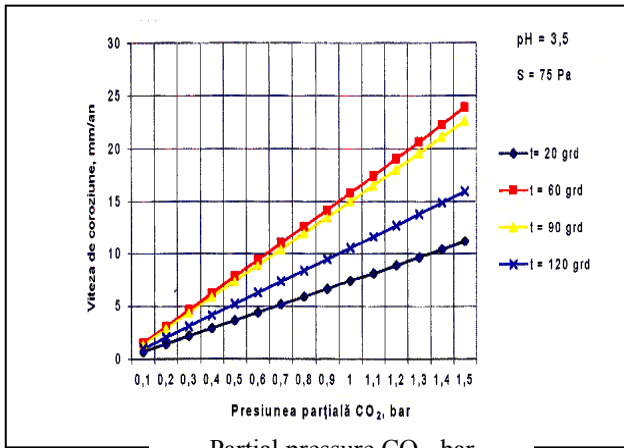


Fig. 7: Corrosion rate versus partial pressure of CO_2 at different tangential stress

To evaluate the flow diameter influence, in Fig. 8 is presented the corrosion rate for a 2 7/8" D tubing with thickness $g=5,11$ mm and 10% oil with gases, different partial pressure of CO_2 and different temperatures at pressure $p=5$ MPa.

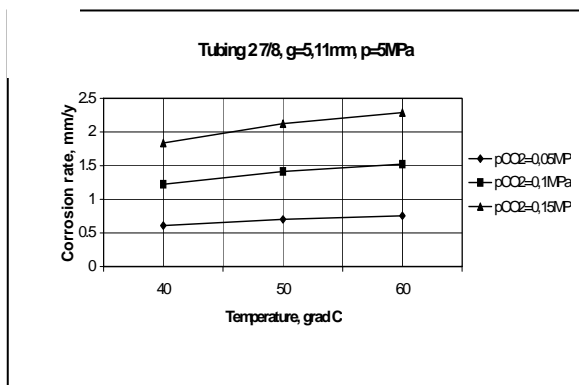


Fig. 8: Corrosion rate versus temperature

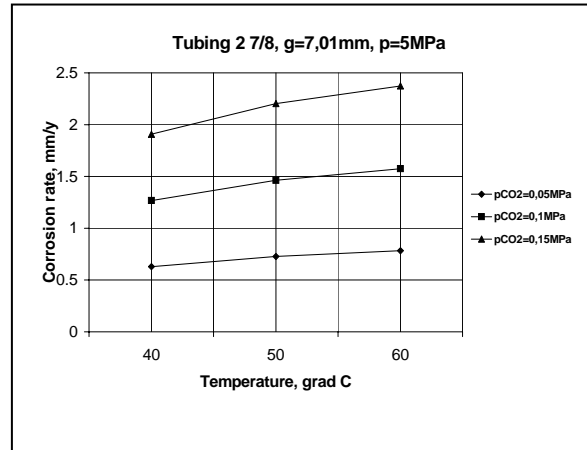


Fig. 9: Corrosion rate versus temperature

We can see that corrosion rate is bigger with a smaller pipe flow section. Also a bigger roughness determines a bigger corrosion rate. The program created assures a fast instrument to evaluate corrosion rate. The measurements made in oil fields above tubing and pipes confirm the results presented.

4. REFERENCES

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