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Corrosion Inhibition of Carbon Steel under Two Phase Flow (Water-Petroleum) Simulated by Turbulently Agitated System

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Abstract

The corrosion of carbon steel in single phase (water with 0.1N NaCl) and two immiscible phases (kerosene-water) using turbulently agitated system is investigated. The experiments are carried out for Reynolds number (Re) range of 38000 to 95000 corresponding to rotational velocities from 600 to 1400 rpm using circular disk turbine agitator at 40 °C. In two-phase system test runs are carried out in aqueous phase (water) concentrations of 1% vol., 5 % vol., 8% vol., and 16% vol. mixed with kerosene at various Re. The effect of Reynolds number (Re), percent of dispersed phase, dispersed drops diameter, and number of drops per unit volume on the corrosion rate is investigated and discussed. Test runs are carried out using two types of inhibitors: sodium nitrite of concentrations 20, 40, and 60 ppm and sodium hexapolyphosphate of concentrations 485, 970, and 1940 ppm in a solution containing 8 % vol. aqueous phase (water) mixed with kerosene (continuous phase) at 40 °C for the whole range of Re. It was found that increasing Re increases the corrosion rate and the presence of water enhances the corrosion rate by increasing the solution electrical conductivity. For two phase solution containing 8% vol. and 16% vol. of water the corrosion rate was higher than single phase (100 % vol. water). The main parameters that play the major role in determining the corrosion rate in two phase were concentration of oxygen, solution electrical conductivity, and the interfacial area between the two phases (dispersed and continuous). Sodium nitrite and sodium hexapolyphosphate were found to be efficient inhibitors in two phase solution for the investigated range of Re.

Keywords: corrosion, two-phase, kerosene, water, turbulent, carbon steel.

Introduction

The mixing of immiscible liquid phases is among the most important chemical engineering operation, yet quantitative information on the mixing process is rather lacking. Most available information is applicable only to specialized equipment or to particular liquid system. In mixing two immiscible fluids in a stirred system energy is transferred to the fluid by the stirrer and the energy serves to suspend the dispersed phase to create turbulence in the fluid. If the intensity of the turbulence is uniform throughout the tank the suspended droplets would be subdivided until they were of size that was no longer affected by the turbulence. In the usual case the intensity of the turbulence is not uniform throughout the tank and regions of varying intensity exist. In region of lower intensity colliding droplets may coalesce, the larger droplets thus formed on passing to regions of higher intensity will again be sheared and broken up. The end state of this sequence of dispersion is a dynamic equilibrium where distribution of droplet size is established throughout the tank. Agitation systems give good similarity for emulsion type that occurs in the equipment under actual production in oil and gas deposit. Metal surface comes in contact with emulsion of oil in water or water in oil types. The first type is normally encountered in wells with high water content. Also in oil refineries these two types of emulsion are encountered. Because of considerable experimental difficulties involved, it is only recently that the corrosion of metals in emulsion systems has begun to be studied and the mechanism of this process remains unclear for along time. Crude oil must undergo refining before it can be used as product. Once oil is pumped from the ground, it travels through pipelines to tank batteries. A typical tank battery contains a separator to separate oil, gas, and water [1].

For oil and gas pipeline applications, diffusion (or mass transfer) controlled corrosion models needs to predict corrosion rates not only in single-phase flow conditions but, more importantly, in multiphase flow conditions. It is well known that the flow variations along pipelines, such as flow regime, water wetting, and liquid flow velocity, have significant effects on the corrosion process in multiphase flow conditions. However, all of the current corrosion models have no virtual capability to compute the effects of multiphase flow [2].

Many experimental studies were carried out to investigate the corrosion of metals under two or multiphase flow conditions [3, 4, 5, 2, 6, 7]. Wang et al [5] proposed the following correlation to predict mass transfer coefficient for gas-liquid two phase flow at superficial gas velocity of 4.8 m/s:

$$Sh=0.544Re^{0.61}Sc^{0.33} \tag{1}$$

Wang and Nesic [2] proposed the following correlation for mass transfer coefficient in stratified two phase flow:

$$Sh=0.64Re^{0.59}Sc^{0.33} \tag{2}$$

Ashassi et. al. [22] studied the inhibition effects on carbon steel in solutions containing different amines in petroleum- water corrosive mixtures containing acetic acid and NaCl using cyclic polarization (CP) at 25 °C. Hassanzadeh et. al. [8] compared graphically the results of Ashassi et. al. [22] of corrosion inhibition behavior of the above mentioned amine compounds. Their results showed that the graphical method provides a good interpretation of corrosion inhibition behavior.

The present study aims to determine the corrosion rate of carbon steel under two phase flow of water- petroleum for various values of velocity (or Reynolds number) at different water- petroleum fractions. Furthermore it is aimed to investigate the effect of droplet size on corrosion rate for a wide range of dispersed phase fraction. Also the work aims to study the effect of inhibitors at different concentrations on corrosion rate using different rotational velocities in two phase mixture.

Agitation and mixing of liquids

Many processing operations depend for their success on the effective agitation and mixing of fluids. The key to effective mixing for liquids is to create multiple flow patterns in the fluid being mixed. This motion is imparted to a fluid "pocket" as it contacts the blade on the rotating agitator. The momentum of this pocket will keep it in motion until it either contacts the wall of the vessel, or runs into another moving pocket. The nature of the liquids and suspensions themselves affect fluid flow and mixing properties as well. Specific properties of concern are the fluid densities, viscosities, temperatures, pressures, and volatility. These properties have been related in a dimensionless formula called the Reynolds impeller number defined here [9, 10]:

$$Re = \frac{\rho \times D_a^2 \times N_I}{\mu} \tag{3}$$

Basic relation exists between hold up (ψ) (the volume fraction of dispersed phase in the system), the interfacial area per unite volume (a), and the bubble or drop diameter (D_P). If the total volume of dispersion is taken as unity, the volume of dispersed phase, by definition, is ψ. Let the number of drops or bubbles in this volume be n. Then if all the drops or bubbles were spheres of diameter (D_P), the total volume would be given by [9, 11]:

$$\Psi = \frac{\pi n D_P^3}{6} \tag{4}$$

The total area of drops or bubbles in this volume would be

$$a = \pi n D_P^2 \tag{5}$$

Dividing equation (4) by equation (5) and rearranging give

$$a = \frac{6\Psi}{D_P} \tag{6}$$

The interfacial area per unit volume of dispersion is proportional to the hold up and inversely proportional to the drop size. Usually large area is desired to give high rate of mass transfer or reaction.

To account for a distribution of drops size, an equivalent average diameter (D_S) is used based on the total volume and total area of dispersed phase. The diameter (D_S) is the volume surface mean diameter (Sauter mean diameter), and it can be calculated from the following equation if the drop size distribution is known:

$$D_S = \frac{\sum_{i=1}^{n} n_i \times D^3{}_P}{\sum_{i=1}^{n} n_i \times D^2{}_P} \tag{7}$$

If the interfacial area and holdup can be measured independently, the average drop size can be determined by using:

$$D_S = \frac{6\Psi}{a} \tag{8}$$

Various types of equipment can be used to disperse liquid, say kerosene in water (an immiscible liquid). A stride tank: liquid-liquid dispersions have a high interfacial area, but they are not stable, since the drops will settle or rise and coalesce in the absence of agitation. Stable emulsions of very small droplets can be formed in colloid mills or other high shear device [12].

An important dimensionless group is the Weber number (We), denoted by which for stirred tank is the ratio of the flow kinetic energy at the impeller tip speed to surface tension stress based on impeller diameter (D_a) [12].

$$We = \frac{\rho_C {N_I}^2 D_a}{\sigma} \qquad (9)$$

One of the several proposed correlations for the dispersion of the liquid with stander six blade turbines is [10]:

$$\frac{D_s}{D_a} = 0.058(1+5.4\Psi)We^{-0.6} \qquad (10)$$

Experimental Work

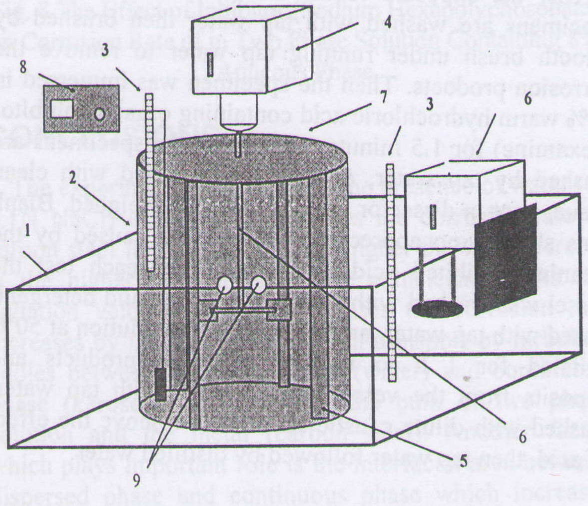
Experimental work was carried out to study the corrosion and inhibition of carbon steel under two phase (water-kerosene) flow conditions for Re = 4000 to 95000 at 40 °C ∓ 0.5 °C and various kerosene/water ratios using weight loss method. Re is based on the impller diameter. The volume percent of aqueous phase (0.1N NaCl solution) are 1%vol, 5%vol, 8%vol, 16%vol. The dynamic system for performing the experimental work is illustrated in Fig.1. The agitation system is composed of cylindrical perspex vessel especially designed to perform the experimental work. The dimensions of the vessel obtained from design equations [10] are shown in Fig. 3. The vessel is of four equally spaced vertical baffles made of perspex each of 2 cm width, a prespex 6-blade disc impeller 8 cm in diameter with blade length of 2 cm, blade width 1.6 cm, as shown in Figs. 2 and 3. It is located 8 cm from the tank bottom. Thermometers are used to measure temperature and pH of solution is monitored by pH meter.

At start of the run the vessel is filled with 12.2 liters of test solution of prefixed volume percentages to height equal to its diameter and covered with flat perspex sheet. In single phase experiments the solution is water of 0.1N NaCl and in two phase the solution is composed of kerosene (continuous phase) and water with 0.1N NaCl (dispersed phase) at various percents. The electrolyte was stirred using a glass rod in order to obtain a homogenous solution, and then the stainless steel heater and controller in the bath is set to the required temperature 40±0.5 °C inside the agitation system for one hour to achieve thermal equilibrium before starting the experimental run.

Prior to use the carbon steel specimens (of analysis shown in Table 1) are abraded in a sequence of emery papers grades: 120, 200, 320, 400, and 600, washed with tap water followed by distilled water, dried with clean tissue, immersed in annular methanol for 5 minutes, rinsed with clean acetone and dried with clean tissue. The specimens then stored in vacuum desiccator over high activity silica gel for 2 h. Then they are weighed by sensitive digital balance with accuracy to 4th decimal and directly exposed to the corrosion environment for 5 h. Sodium nitrite and sodium hexapolyphosphate are used as corrosion inhibitors. The specimens are fixed in the wall of agitation vessel tightly enough and Teflon is used to avoid the leakage of the test solution. They are fixed at a distance 16 cm from the bottom of agitation vessel and 2 cm apart. In each test two specimens are used and each test is carried out twice.

Table 1: Analysis of Specimen.

Component	*wt%*
C	0.0755
Si	0.1507
Mn	0.416
P	0.0013
Cr	0.017
Mo	0.043
Cu	0.059
V	0.0478
Fe	Balance



1	Water bath.	6	Shaft with CD-6 blade turbine.
2	Agitation cylinder.	7	Perspex cover.
3	Thermometer.	8	PH meter.
4	Agitation motor.	9	Location two specimens.
5	Baffles.	10	Heater and controller

Fig. 1 Diagrammatic Arrangement of Mixing System

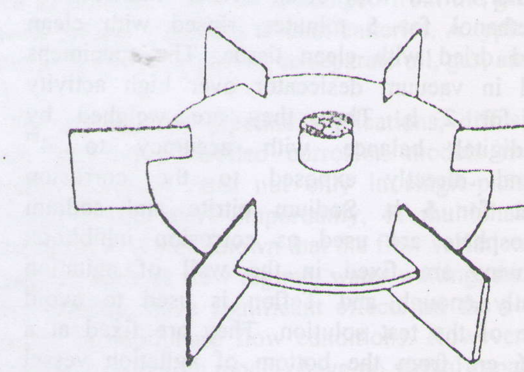


Fig. 2 Circular Disk Turbine (Six- blades)

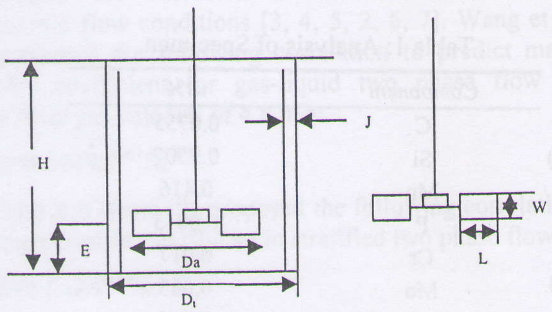


Fig 3 Dimensions of Tank and Disk Turbine (Six- Blades Turbine)

After the exposure to the corrosion environment the specimens are washed with tap water then brushed by smooth brush under running tap water to remove the corrosion products. Then the specimen was immersed in 20% warm hydrochloric acid containing organic inhibitor (hexamine) for 1.5 minutes. After that the specimens are washed by tap water, distilled water, dried with clean tissue, kept in dissector for 2 h, and then weighed. Blank tests showed no appreciable weight loss caused by the cleaning inhibited acidic solution. After each test the vessel was washed with tap water using liquid detergent, rinsed with tap water, and with 15% HCl solution at 50°C agitated for 1 h to remove corrosion products and deposits from the vessel wall, washed with tap water, washed with dilute caustic solution to remove the effect of acid, then tap water followed by distilled water.

Results and Discussion

The experimental results of corrosion rates under single and two phase flow conditions in presence and absence of corrosion inhibitors are shown in Figs. 4 to 8. The physical properties of kerosene (continuous phase) are taken from Nelson [13].

Since corrosion of iron in aerated solutions is controlled by the rate of diffusion of oxygen to the surface [14, 15, 16, 17, 19] therefore factors affecting the rate of diffusion will affect the rate of corrosion or mass transport between the specimen and the bulk of the solution.

Fig. 4 shows the variation of corrosion rates (expressed in gram per square meter per day) with Re. It is clear that increasing solution Re (or velocity) increases the corrosion rate in single phase and two phase for all aqueous phase (water with 0.1N NaCl) concentrations. This is due to the increased oxygen transport to the surface [16, 19, 18]. Also the figure reveals that as the volume percent of water (aqueous phase) increases the corrosion rate increases. Also at low water percents, namely 1% and 5%, the corrosion rate is lower than that in single aqueous phase (100% of water with 0.1N NaCl) indicating that the presence of kerosene (continuous phase) debase the corrosion rate. This is ascribed to the fact that the electrical conductivity of kerosene is low despite its oxygen content is higher than that of water (NaCl solution). At higher aqueous phase percents, namely 8% and 16%, the corrosion rate is higher than the single phase. This increase is attributed to the fact that the presence of aqueous phase in relatively high percents leads to increase the electrical conductivity of two phase solution and since the two phase solution is higher in O_2 concentration than single phase therefore the corrosion rate will be higher.

Fig. 5 shows the variation of mean Sauter diameter (calculated by Eq. (10)) of drop with Weber number. The figure indicates that as We increases the Sauter diameter of dispersed phase (water) decreases due to the increase in turbulence and in the shear forces causing the drops to subdivide into smaller drops. Also Fig. 5 indicates that as the percent of dispersed phase increases the drop Sauter diameter increases. The increase in number of drops per cm^3 with We (Fig. 6) leads to increase the interfacial area for mass transfer of O_2 from continuous phase (of high O_2 concentration) to dispersed phase (of lower O_2 concentration) and therefore more O_2 arriving to the metal surface enhancing the corrosion rate. Hence the higher the number of drops (calculated from Eq. (4)) is the higher the corrosion rate. Accordingly, increasing the solution velocity (or Re) leads to increase the corrosion rate via two ways. First, by increasing the O_2 transport by turbulent eddies between phases and from phases to metal. Second, by increasing the interfacial area between phases by subdividing the dispersed phase to further drops. In a stirred tank the average drop size depends on a balance between breakup of large drops in regions of high shears and drop coalescence in regions of lower shear. Shear stress at the drop surface tends to deform the drop, and deformation is resisted by the interfacial tension and the viscosity of the dispersed phase [12].

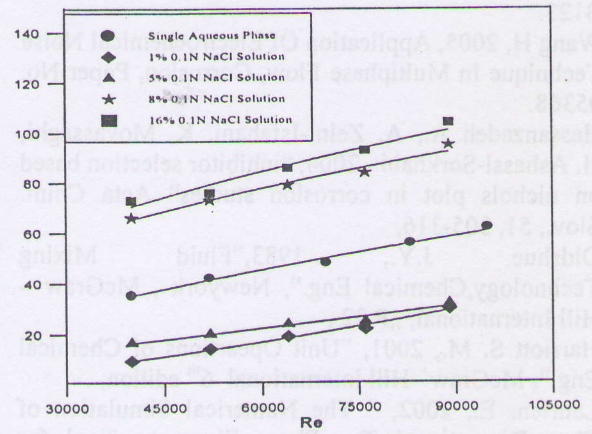


Fig.4 Variation of Corrosion Rate with Re at Various Aqueous Phase Percents

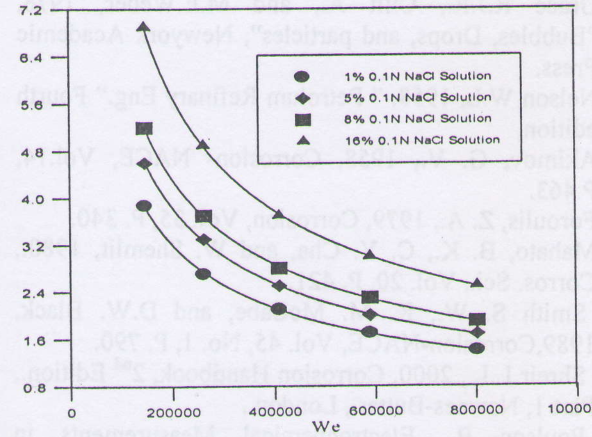


Fig. 5 Variation of the Drop Mean Sauter Diameter with We at Various Aqueous Phase Percents

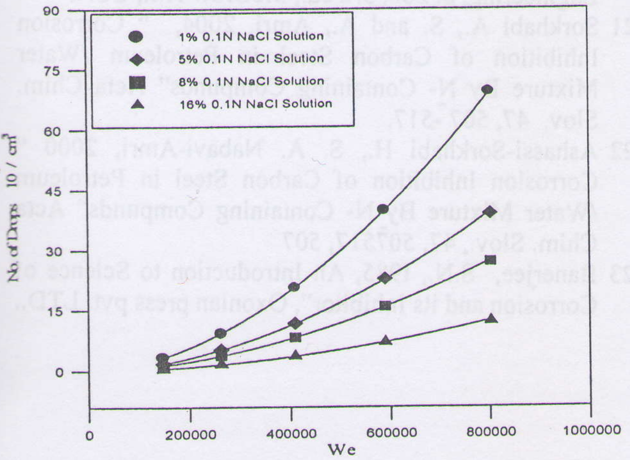


Fig. 6 The Effect of We on the Number of Dispersed Phase Drops at Various Aqueous Phase Percents

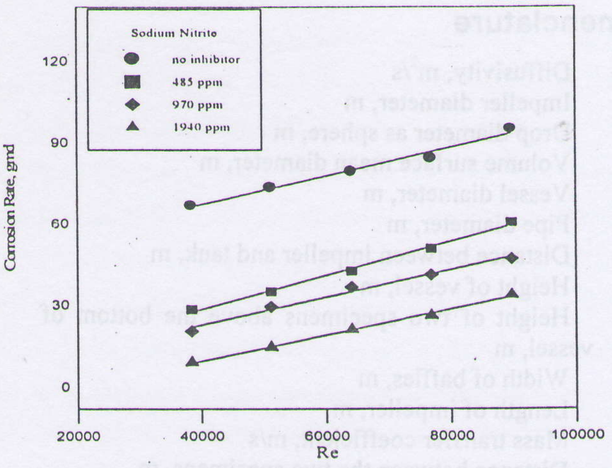


Fig.7 Effect of Inhibitor (Sodium Nitrite) on Corrosion rate of in Two Phase Solution Containing 8% Aqueous Phase

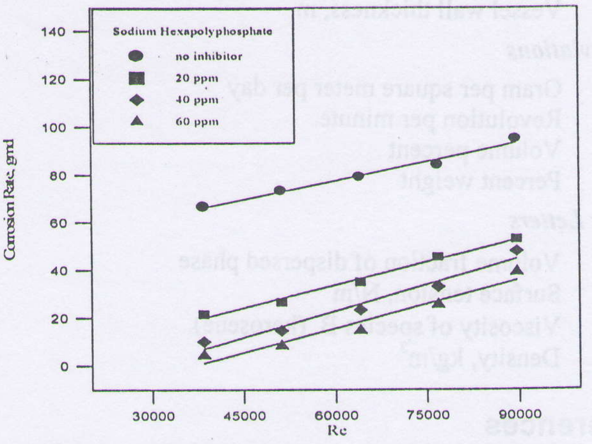


Fig. 8 The Effect of Inhibitor (Sodium Hexapolyphosphate) on Corrosion Rate of in Two Phase Solution Containing 8% Aqueous Phase

CONCLUSIONS

The experiments revealed that the presence of water (of 0.1N NaCl) in kerosene enhances the corrosion rate of carbon steel in kerosene and the higher the water percent is the higher the corrosion rate enhancement. As the agitation velocity (or Re) increases the corrosion rate increases by increasing the oxygen transport by turbulent eddies between dispersed phase (water) and continuous phase (kerosene) and between the bulk of two phase solution and the metal (carbon steel). Another factor which plays important role is the interfacial area between dispersed phase and continuous phase which increases with the increase in the number of drops resulting from increased shear forces due to high agitation velocity. Also the experiments showed that the sodium nitrite and sodium hexapolyphosphate give good corrosion inhibition action in two phase solution for the whole investigated range of Re.

Nomenclature

D	Diffusivity, m^2/s
D_a	Impeller diameter, m
D_p	Drop diameter as sphere, m
D_s	Volume surface mean diameter, m
D_t	Vessel diameter, m
d	Pipe diameter, m
E	Distance between impeller and tank, m
H	Height of vessel, m
h	Height of two specimens above the bottom of vessel, m
J	Width of baffles, m
L	Length of impeller, m
k	Mass transfer coefficient, m/s
M	Distance between the two specimens, m
N_I	Rotational speed of the impeller, rps
n	Number of drops
Re	Reynolds number
T	Vessel wall thickness, m

Abbreviations

gmd	Gram per square meter per day
rpm	Revolution per minute
%vol	Volume percent
%wt	Percent weight

Greek Letters

Ψ	Volume fraction of dispersed phase
σ	Surface tension, N/m
μ_B	Viscosity of species B (kerosene).
ρ	Density, kg/m^3

References

1. 1 Jaske C.E and J.A. Beavers, "Predicting the Failures and Remaining Life of Gas Pipelines Subject to Stress Corrosion Cracking," Proceedings of 1998 International Gas Research Conference, pp. 281-290.
2. Wang S. and S.Nesic, 2003, On Coupling CO_2 Corrosion And Multiphase Flow Models, Corrosion 03631, paper Np. 03631.
3. Langsholt, M, M. Nordsveen, K.Lunde, S. Nesic, and J.Enerhaug, 1997, "Wall Shear Stress And Mass Transfer Rates- Important Parameters In CO_2 Corrosion", BHR Group.
4. Wang H. ,W.P. Jepson ,J.Cai ,T.Hong ,M.Gopal and H.D.Dewald, 2000, Effect Of Bubbles On Mass Transfer In Multiphase Flow, Corrosion, Paper No. 00050
5. Wang H, T. Hong, J.Y.Cai, W.P.Jepson, and Ch.Bosch, 2002, Enhanced Mass Transfer And Wall Shear Stress In Multiphase Slug Flow, Corrosion, Paper No. 02501.
6. Wang H., H. D. Dewald, and W.P.Jepson, 2004, Mass-Transfer Enhancement In Large- Diameter Pipeline Under Water/Gas Stationary Slug Flow, Journal of the Electrochemical Society, 151(3) B114-B123.
7. Wang H, 2005, Application Of Electrochemical Noise Technique In Multiphase Flow, Corrosion, Paper No. 05368.
8. Hassanzadeh A., A. Zeini-Isfahani, K. Movassaghi, H. Ashassi-Sorkhabi:, 2004, "inhibitor selection based on nichols plot in corrosion studies" Acta Chim. Slov., 51, 305-316,
9. Oldshue J.Y., 1983,"Fluid Mixing Technology,Chemical Eng.", Newyork , McGraw – Hill International, ,,P.32 .
10. Harriott S. M., 2001, "Unit Opeartions of Chemical Eng.", McGraw –Hill international 6th edition, .
11. Laurien. E., 2002, " The Numerical Simulation of Three-Dimentional Two-Phase Flows as Tool for Light- Water Reactor Design and Safety Analysis"; Proc. of the Annual Meeting of Nuclear Technology, INFORUN Vrlagsgesllschaft, Bonn, 45-50.
12. Grace R.J.R., Clift A., and M.E.Weber, 1978, "Bubbles, Drops, and particles", Newyork Academic Press.
13. Nelson W.L, 1958, " Petrolum Refinary Eng." Fourth edition,
14. Akimov, G. V., 1958, Corrosion- NACE, Vol.14, P.463.
15. Foroulis, Z. A., 1979, Corrosion, Vol. 35, P. 340.
16. Mahato, B. K., C. Y. Cha, and W. Shemlit, 1980., Corros. Sci., Vol. 20, P. 421.
17. Smith S. W., K. M. McCabe, and D.W. Black, 1989,Corrosion-NACE, Vol. 45, No. 1, P. 790.
18. Shreir L.L., 2000, Corrosion Handbook, 2nd Edition., Part 1, Newnes-Butter., London..
19. Poulson B., Electrochemical Measurements in Flowing Solutions ,Corrosion Science, Vol, 23, No. 1,P. 391,1983.
20. Fontana, M.G, and Greene, 1987, Corrosion Engineering, p. 282, 3rd ed., McGraw-Hill, USA.
21. Sorkhabi A., S. and A., Amri, 2004, " Corrosion Inhibition of Carbon Steel in Petroleum /Water Mixture By N- Containing Compunds" Acta Chim. Slov. 47, 507-517.
22. Ashassi-Sorkhabi H., S. A. Nabavi-Amri, 2000 " Corrosion Inhibition of Carbon Steel in Petroleum /Water Mixture By N- Containing Compounds" Acta Chim. Slov., 47, 507̃517, 507
23. Banerjee, S.N., 1985, An Introduction to Science of Corrosion and its Inhibitor", Oxonian press pvt. LTD..