REMOVAL OF SCALE DEPOSITED ON THE INTERNAL SURFACES OF PIPES IN COOLING SYSTEMS

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ABSTRACT

The possibility of using inhibited hydrochloric acid in descaling of water deposits on heat exchanger and cooling system tubes have been investigated. A dynamic flow system was designed for this state. Experiments were carried out using different, temperatures, solution flow rates,times,and different hydrochloric acid concentrations inhibited with Hexamine .
Kinetics of acid – iron oxide scale reaction was studied using hydrochloric acid .The kinetics analysis showed that the acid- FeO scale reaction followes 1st order reaction. It was found that the FeO scale removal was mass transfer controlling process.
Iron- oxide scale removal process was analyzed as mass transfer operation and adequate semi-empirical correlations for scale removal (or mass transfer rate) under different conditions, in a dimensionless form have been obtained. The results of iron- oxide scale removal (or mass transfer rate) are compared with many proposed models particularly those based on the concept of analogy among momentum and mass transfer.
Prandtl- Taylor analogy showed a good agreement with experimental mass transfer results.

الخلاصة

يهدف البحث الى إمكانية استخدام الطرق الكيمياوية في إزالة الترسبات من السطوح الداخلية لأنابيب المبادلات الحرارية وانابيب المياه الحارة والمراجل وأجهزة التبريد.
تم الحصول على نماذج لأنابيب نقل المياه الساخنة من مصفى بيجي (شركة مصافي الشمال) وقد اجري تحليل كامل لهذه الترسبات واعتمادا على هذا التحليل تم اختيار المواد الكيمياوية المناسبة للإزالة.
لقد استعمل حامض الهيدروكلوريك مع الهكسامين كمادة مثبطة للتأكل.
درست حركية تفاعل حامض الهيدروكلوريك مع تكلسات أوكسيد الحديد الموجودة ضمن خليط التكلسات وباستعمال حامض الهيدروكلوريك . وبين التحليل الحركي ان التفاعل هو من الدرجة الأولى نسبة إلى الحامض . وتبين ان تفاعل إزالة تكلسات الحديد مسيطر عليه فيزياويـــا
(أي عملية انتقال الكتلة هي المسيطرة على سرعة التفاعل).
تم تحليل عملية إزالة التكلسات كعملية انتقال كتلة ووضعت علاقات تجريبية وضعية لحساب معدل إزالة التكلسات تحت ظروف مختلفة. وقد تم مقارنة النتائج العملية مع عدة علاقات موضوعية للتعبير عن انتقال الكتلة بين الجدار والمائع وخاصة العلاقات المبينة على التشابه في ميكانيكية الانتقال بـين الكتلـة والزخم

وية إمكانية حساب معدل إزالة التكلسات باستخدام هذه العلاقات. وقد تم اعتماد احد هذه العلاقات للتعبير عن معدل إزالة التكلسات في بداية العملية.

ت علاقة Prandtl Taylor توافقا جيدا مع النتائج العملية لكل قيم درجات الحرارة في بداية عملية إزالة.

KEY WORDS
Scale,Chemical cleaning,Deposit,Hydrochloric acid,Descaling

INTRODUCTION

The deposition of solids occur on industrial equipments surfaces like heat exchanges ,boilers, cooling towers or any surface which water contacts minders along with salts and corrosion products.

Scale deposition in the industrial equipments occurs by any, or all of four mechanisms crystallization-scaling, deposition of particulate matter, corrosion with subsequent transfer of corrosion products, and microbiological growth(Mansfield,G.H.and Terrell(1990).

Various cleaning methods have been used; mechanical, chemical and thermal or a combination of them.Cleaning up by chemicals is probably the most widely adopted procedure(Powell,S.T.(1954)). There is no physical damage to the tube bundle in chemical cleaning although there is a possibility of chemical reaction and corrosion inhibitor. Mineral acids used in chemical cleaning include hydrochloric and (HCl), sulfuric acid,and sulfamic acid (H_2NSO_3H). Other solvents used are organic acids.

Hydrochloric acid is the most commonly used solvent(NACE,T-8A on cleaning,corrosion 15,... and 15,17t(1959)), because this acid is safer, less expensive, can be diluted easily, soluble reaction product. Corrosion caused by the acid cleaning can be prevented or reduced by an inhibitor. Type and amount of the corrosion inhibitor depends on the acid concentration and temperature at which the cleaning solvent is used .

Cleaning solution usually passed in turbulent flow through the system, during acid cleaning process. When turbulent flow occurs in circular tubes, momentum is transferred between layers of fluid, the momentum transfer manfests itself as a frictional resistance and at the wall shear stress, which is equivalent to the time rate of momentum transfer per unit area(Philip J.W.Roberts and Donald R.Webster(2002)).

Mass transfer may occur during turbulent flow. Most of the experimental studies showed that there is a relation exists between mass transfer and skin friction, knowledge of such relationship would allow prediction of the rate of mass transfer from friction loss data.

The work of Osborne Reynold's (Reynolds,O.(1874) in 1874 has led to useful, simple equations relating the friction factor and the mass transfer coefficient by Reynold's analogy(Bennett,C.O.and J.E.Myers,(1982)).

The present investigation of the problem of scale removal is being studied mainly on tubes of heat exchangers obtained from Baiji Refinery using chemical solution (hydrochloric acid).

A special flow system has been designed where parts of these piping were being fixing in exposure to the treatment solution.

Percentages and rates of scale removal were studied as a function of temperature, circulation rate and concentration of an inhibited hydrochloric acid.

Furthermore a mathematical model to describe the solution mechanism was attempted and presented in this investigation.

EXPERIMENTAL WORK

1- Scaled carbon steel pipes from the main hot water lines were used. (10 cm long, 25mm O.D and 20 mm I.D). List of the scale materials was shown in **Table (1).**Hydrochloric acid with concentration of (3-10 wt%) was used.

Table(1) Complete Analysis of Baiji Refinery Scale Deposited on Heat Exchanger Tubes*.

Element Analysis	Wt.%
Iron (FeO)	51.8
CaO	2.2
$CaCO_3$	6.02
Al_2O_3	17.3
$MgCO_3$	7.74
ZnO	2.636
Silical (SiO)	4.12
Chlorine	0.05
SO_4	Traces
L.O.I.(loss on Ignition)	7.214
Total	99.08

* The analysis was carried out in Baji Refinery Laboratories

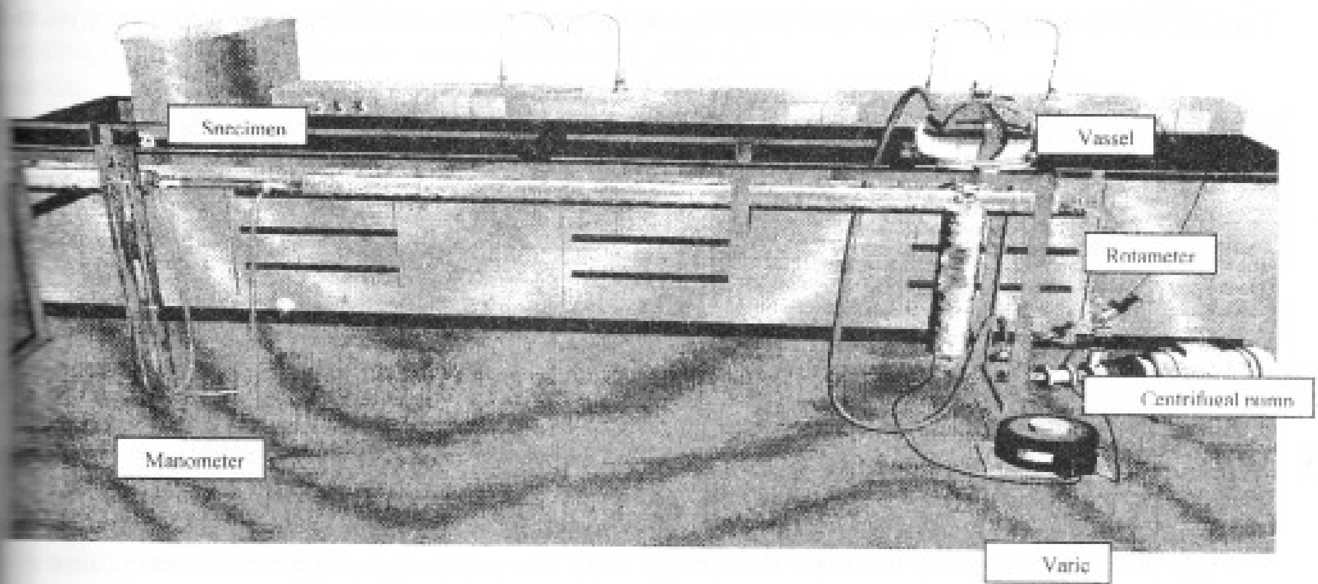
Hexamine was used as corrosion inhibitor with concentration of 0.1 wt%

2- A flow system for the descaling investigation was made of Q.V.F. glass. It consisted of 10 liters round bottom container with four necks, the container was connected from the bottom with the tuping through which hot solution circulated.

A controlled heating tapes were rapped around the insulated Q.V.F. glass tuping for heating the circulating solution.

The circulation of the chemical solution was effected using a centrifugal pump (0.2 KW) and the flow rate was measured using rotameter ranged (0-2000 L/hr).

The solution passed through the scaled metal specimen, and returned to the round bottom container as shown in **Fig.(1).**



Fig(1) Experimental diagram of the system

The pressure drop through the specimen was measured using inverted U-tube manometer. The temperature of the test solution was measured by means of thermometer of the range (0-100 C°).

The concentration of the acid was measured using simple titration method.

The concentration of iron in the acid solution was measured by using Shimadiza UV-160 by determining the absorbance of the ferrous ions.

The amount of scale deposits which has been removed at each run was calculated by weight difference of the scaled tube before and after the tests.

RESULS AND DISCUSSION

Effect of experimental variables on percentage of scale removal:

Figures (2), (3) and (4) show the effect of temperature with the range of (25-70C°), acid concentration of (3-10wt%), solution circulation rate (as Re no.) with the range of (10000-25000) and descaling time of (2-6 hrs) on the scale removal process.

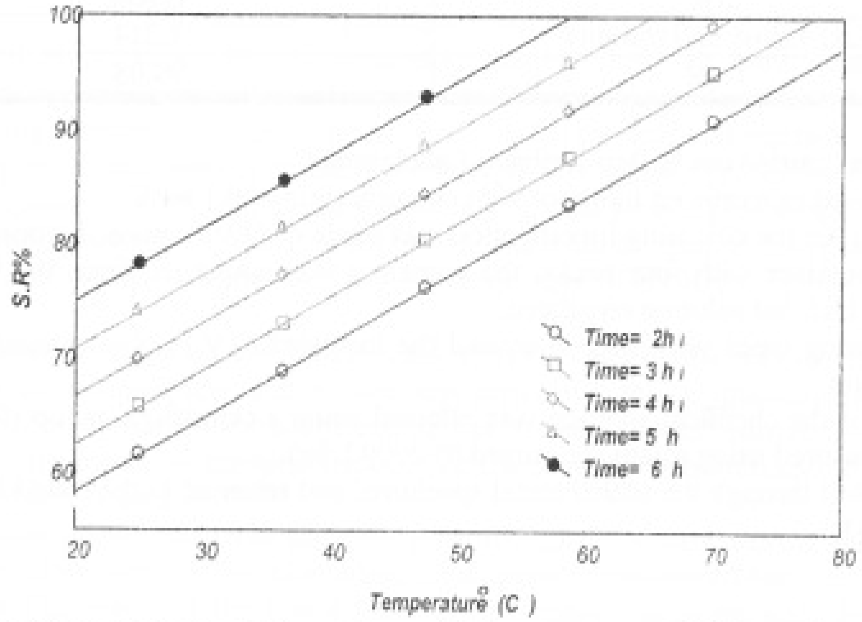
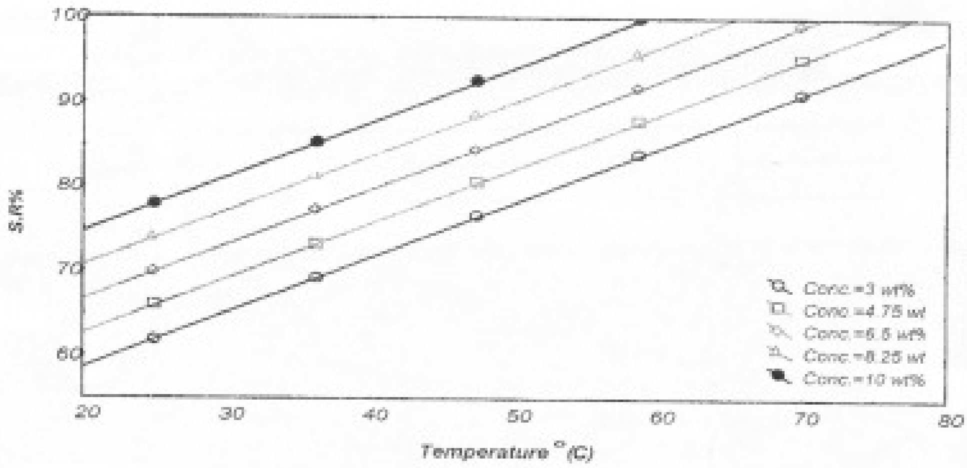


Fig.(2)Variation Of Scale Removal Percentage with Temperature at Different time, Concentration =6.5 wt%, Re=17500



Fig(3)Variation Of Scale Removal Percentage With Temperature at different concentrations ,Time=4hr,Re=17500

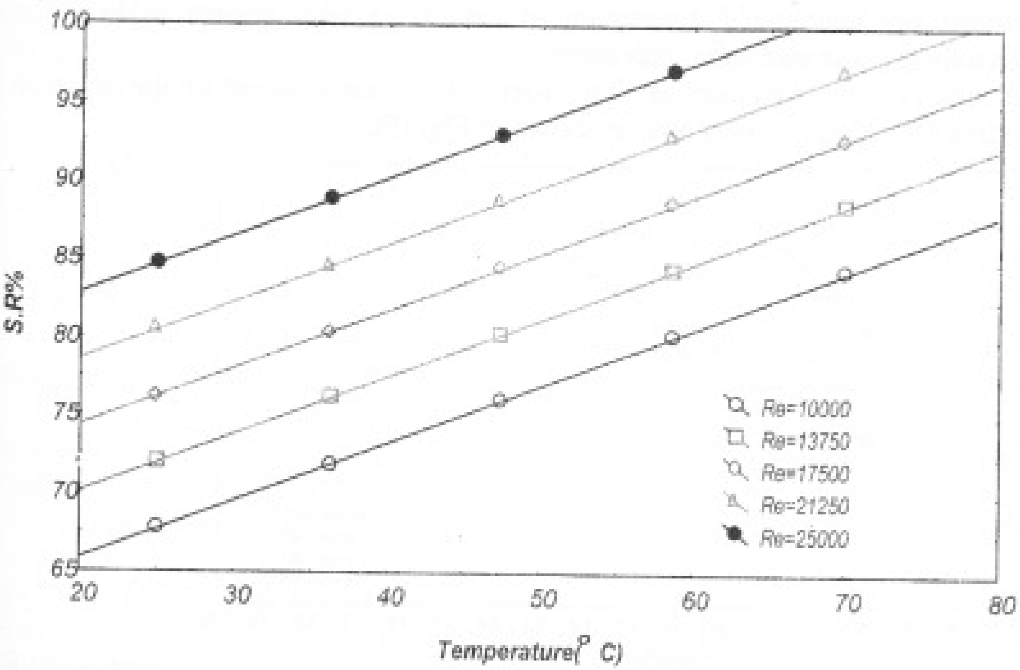


Fig.(4)Variation Of Scale Removal Percentage With Temperature at Different Re ,Time=4hr,Concetration=6.5 wt%

t was shown that the increase of any of the above variables causes to increase the percentage of ale removal.The increasing of percentage of scale removal with increasing the temperature plained by the fact that increasing the temperature cause to increase the reaction rate constant and s its maximum value at the highest temperature. Also increasing the temperature cause to increase e convective mass transfer due to decreasing the solution viscosity and increasing the diffusivity f the solution compounds.

e investigations of Charles and Moor (Charles,M.Loucks(1962) and Moore,R.E.(1972)) agrees th this conclusion.

e increase of acid concentration increases the percentage of scale removal which is due to the rease in concentration gradient between the bulk and the solid solution interface.

reasing the descaling time cause to increase the percentage of scale removal, that is due to the on of the acid to break the bound it. Hence increasing the time of scale exposed to acid solution reasing the percentage of scale removal.

reasing the circulation rate in the cleaning processcause to increase the percentage of scale moval, this behavior can be explained as follows, as the circulation rate increases the laminar b-layer will be very small in thickness as the turbulence is high due to hindrance of fluid at the erogeneous surface of several compounds in the solid phase of the scale, then the chemical ction will also increases as the chemical materials has more chances to touch the particles of the face due to renwal of the chemicals as the boundary laminar sub-layer becomes more thin or will neglected.

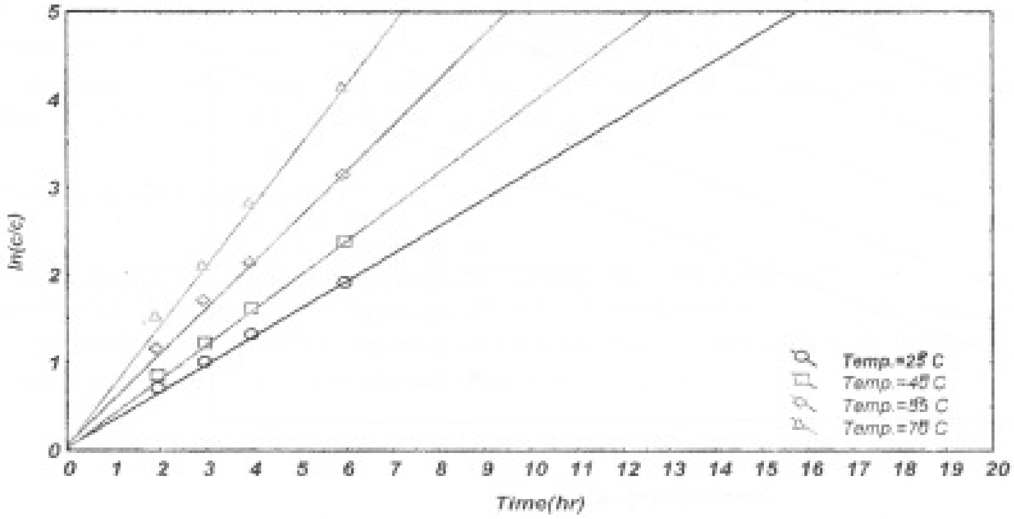
netics of FeO Scale Removal

m the analysis of the scale composition **Table (1)**, it was clear that the most fraction of scale position is (FeO), then the most important reaction is the reaction of FeO scale with rochloric acid, which was studied in this research.

e stoichiometry of the reaction between iron oxide (FeO) and hydrogen ion in solution is esented by the following equation:

$$eO+2H^{+} \longrightarrow Fe^{+2} + H_2O \quad \text{------------(1)}$$

In order to determine the kinetics of dissolution of FeO scale with respect to Fe^{++} ion, the concentration of ferrous ion was measured with time .
The reaction rate order can be assumed as first order . The kinetic order of the reaction was determined by plotting Ln C_{A0}/C_A versus time as shown in **Fig. (5).**



.(FigFig.(5) Rate of Desolution at Re=10000

This figure clearly establishes that the dissolution of iron oxide scale is first order with respect to ferrous ion.
The rate constant is a function of temperature and can be expressed by Arrheniu's equation :

k_r=A exp (–E/RT) (2)

Where :
A : exponential constant.
E : activation energy.
R : gas universal constant.
T : absolute temperature.

According to Arrheniu's equation (2) plot of Ln k_r versus $^1/_T$ as shown in **Fig. (6)** gives the slope equal to –E/R.
Activation energy (E) can be determined from the slope of the line. The value of the activation energy of the desolution process of FeO scale with hydrochloric acid = 15 KJ/mole.

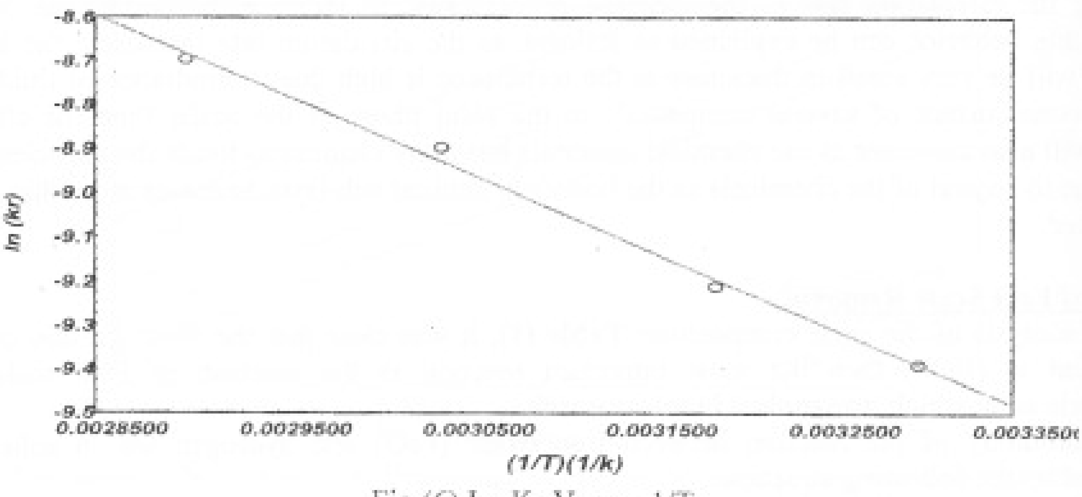


Fig.(6) Ln Kr Versus 1/T

Mass Transfer Results

In the present work mass transfer coefficient was calculated by estimating the mass flux of FeO (Fe^{+2}) ion using the following equation :

$$N_A = \frac{M}{t.A} \qquad (3)$$

$$2N_A = k\Delta C \qquad (4)$$

It is worthy to note that the molar flux of hydrogen equal 2 times that of (Fe^{+2}) ions according to the chemical reaction equation(1).

Where :

k = mass transfer coefficient of hydrogen ion.

ΔC = the bulk concentration of hydrogen ions in the solution

Mass Transfer Limited Model

A complete formulation of the rate equation must take into account both the mass – transfer and chemical reaction rates.

In some instances, one of the rates, mass transfer or reaction, is so much smaller than the other that it becomes the controlling one.

The dominant mechanism can be deflected by observing the effects of certain changes in operating condition experimentally.

The fact that mass transfer rather than a chemical reaction is controlling the rate of reaction indicated by the law activation energy(Schmidt,N.O.(1976))which is in good agreement with the value obtained in this work, (activation energy about 15 KJ/mol for mass transfer controlled process, Tewari and, Campbell(1976).presented that the activation energy is (12-24 KJ/mol). and by the fact that the rate of desolution is increased by increasing the rate of liquid past the scale(Schmidt,N.O.(1976)).

Factors Affecting FeO Descaling And The Mass Transfer Coefficient

Effect of reynolds number and temperature

Figs. (7) and (8) show the variation of mass transfer coefficient and descaling rate with Re at various temperatures respectively. It is clear that (k) and descaling rate increases with increasing Re for all temperature values (25 to 70 °C).

The increase in k with Re can be explained according to the following equation(Bradley,G.W.(1977)and Poulson,B.(1983)).

$$k = \frac{D + \varepsilon_D}{\delta_d} \qquad (5)$$

As Re No. increases the convective mass transport of hydrogen will increase, i.e. mass transfer by eddy diffusion (ε_D) due to the increased turbulence.

Increasing turbulence leads to decrease the thickness of viscous sub-layer and the diffusion layer that represents the main residence to momentum and mass transport respectively(Mahato,B.K.(1980) and Coulson,J.M.(1977)),hence the hydrogen concentration gradient at the surface will be increased leading to increase (k).

Increasing (k) with Re leads consequently to increases (Sh) over the whole range of temperature (or Sc) **Fig.(9)**

The increase in (Sh) with (Re) indicates that increasing Re leads to increase the mass transport by convection (or eddy diffusion) over that by molecular diffusion because Sh is the ratio between the two. The molecular diffusive mass transport (Diffusivity of hydrogen) is independent on Re, it varies only with Sc and temperature.

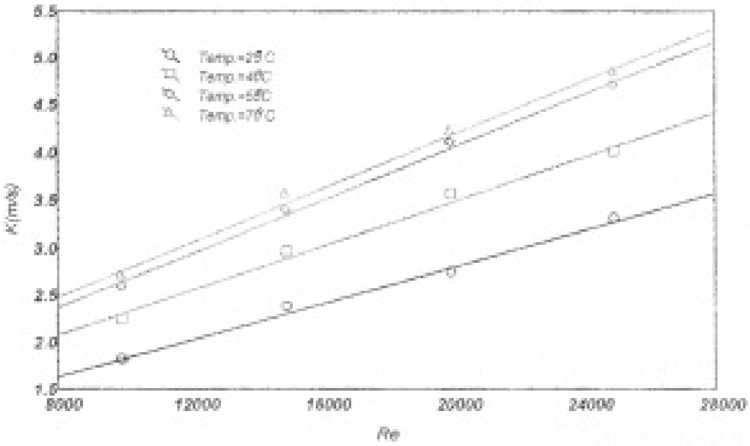


Fig.(7) Variation Of Mass Transfer Coefficient With Re at Various Temperature and t=300sec.

Using statistical analysis the following correlation is obtained for the whole range of Re No. and temperature (Sc) assuming the dependence of Sh on Sc is 1/3 as customarily found(Coulson,J.M.(1977) and Hasan ,B.O.(2003)).

$$Sh = 0.053 \ Re^{0.6208} \ Sc^{1/3} \qquad (7)$$

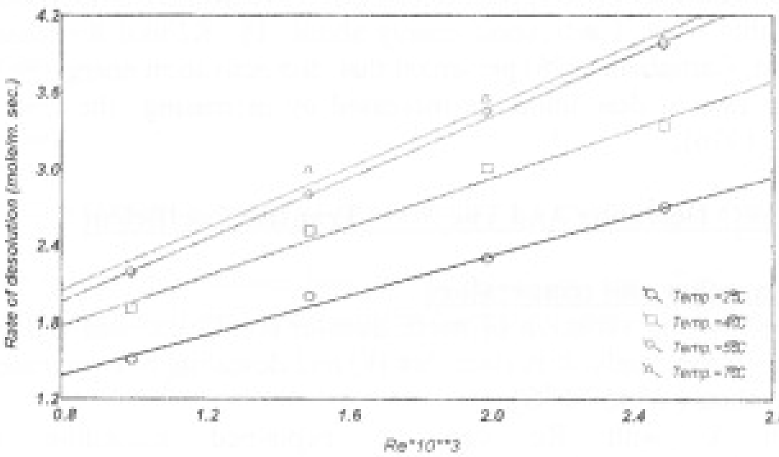


Fig.(8) Variation Of Desolution Rate with Re at time =300 sec.

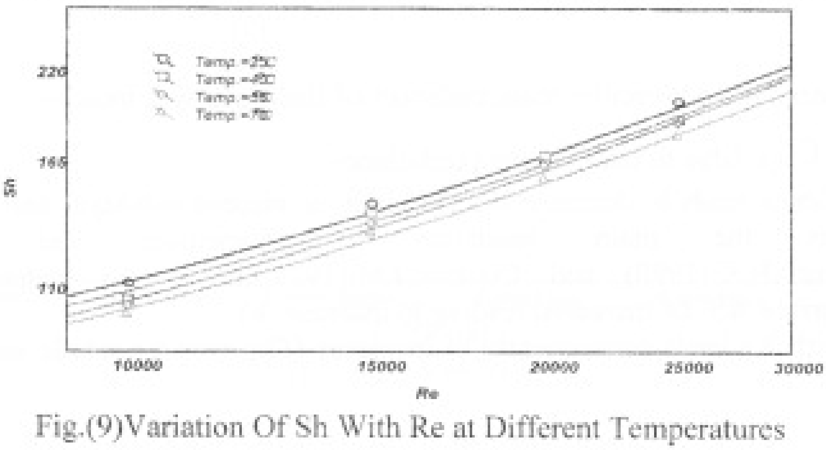


Fig.(9)Variation Of Sh With Re at Different Temperatures

…e effect of increasing temperature on Sh is due to the increase two variables acting in opposing way on the value of Sh. These two variables are the mass transfer coefficient (k)) and the molecular diffusivity(D). Hence, the net effect of temperature on Sh will be determined by the change of the ratio k/D.

Effect of Time

Fig. (10) shows the variation of k or Sh with Re No. at various temperatures and time as a parameter. This figure indicate that at all the temperatures , the time causes a significant decrease in k for all Re range. This can be explained by the decrease of roughness as the time increases due to the scale removal, hence decreasing the mass transfer rate due to decreasing mass transfer area(Knudsen,J.G.(1958),Petulchov,B.S.(1970),Colburn,A.P.(1964),and Kandikar,S.G.,(2001)). Also formation of the chemical reaction product of the scale with the acid influence the mass transfer rate by influencing the hydrogen ion diffusion from the bulk to the scale surface (Brodkey,R.S.(1988).

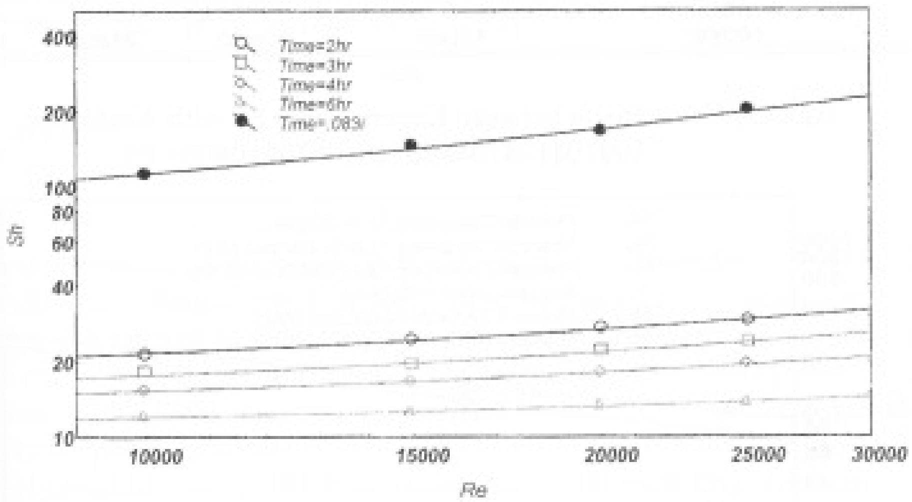


Fig.(10)Variation Of Sh With Re at Different Intervals and Temperature=25 °C

Comparison with The Proposed Model

In this section it is aimed to compare the experimental results of mass transfer with the proposed correlations particularly those which are based on the concept of analogies among momentum and mass transfer.

This comparison serves to investigate how far is the derived correlation deviate from the proposed models.

Making a comparison enable to adapt best correlation that can be employed to estimate scale removal rate through (sh).

The experimental mass transfer results were compared with other correlations presented in the appendix, such as prandtl and Taylor (Eq-1a) and Eq.(1b) and Prandtl–Taylor (Eq.2), Von Karman (Eq.3), Chilton –Colburn (Eq.4) and, Darshnalal (Eq.5).

Graphical comparison is shown in **Fig.(11).** Best agreement found to be with Prandtl-Taylor analogy, Eq.(1a) and Eq.(1b), (with a small difference due to the assumption that the calculated friction factor from the experimental work is equal to the friction factor of Iron-oxide scale) i.e. the scale removal can be well represented by this analogy for the entire range of Re and at the early period of the scale removal process.

Time (or scale removal) affects the capability of analogy correlation to estimate the mass transfer coefficient and mass transfer group (Sh) ,i.e. removing the scale increases the difference between the experimental mass transfer coefficient and that obtained from analogy models .

Fig.(12), shows a comparison between experimental Sh and that obtained from analogies fo (t = 4,6 hr) i.e. when most of the scale removed at all temperatures it is evident that time caus large difference between the mass transfer rate (Sh) during scale removal process that predicted by analogy correlations and experimented results.

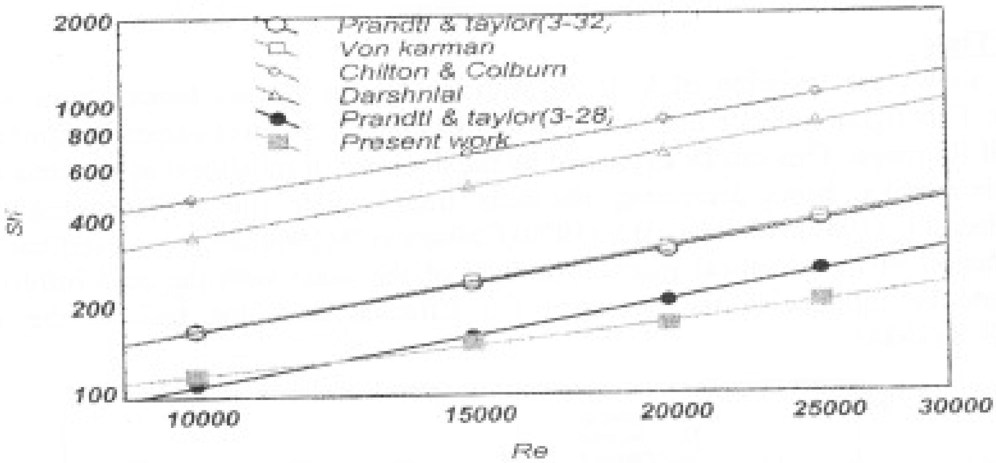


Fig.(11) Comparison between Experimental Sh with Analogies.
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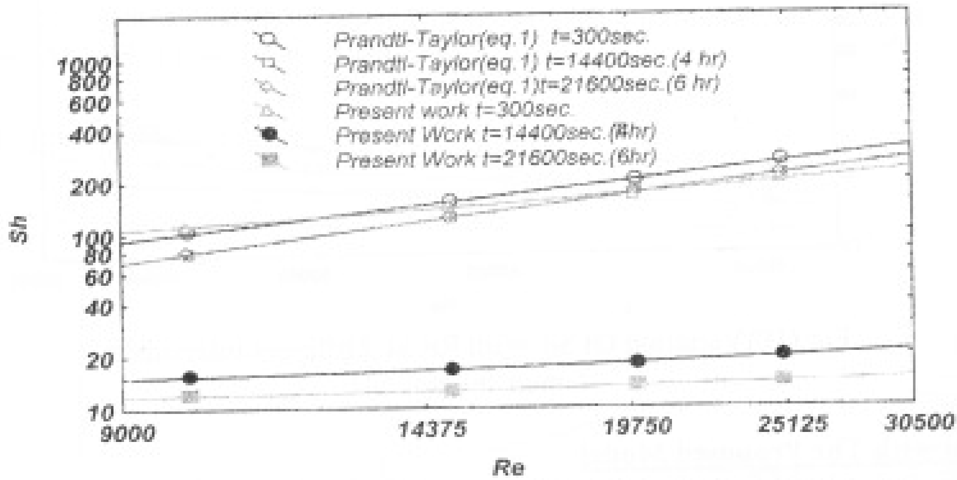

Fig.(12)Comparison of Analogy Models and Experimental Results In Present Work at t=25 ° C

According to above conclusions ,the analogy models can be employed to estimate the mass tra controlled FeO scale removal rate (for the scale type used in this work) at particular Re and Sc determining the friction factor experimentally .

Table(2) lists the values of (Sh) estimated from various analogy models using the friction fa besides experimental values obtained by concentration difference of Fe^{+2} ion for all ranges of Re The chosen analogie are Prandtl and Taylor analogy (Eq.1a) using (Eq.1b) for estimation of (u_x/u_c).

A modification has been done on the correlation to estimated(α) of (Prandtl-Taylor analogy and Eq.1b) to make this analogy can be employed for the descaling process at time (2,4,6) respectively. using statistical analysis the following correlations for (α)values estimation obtained.

$\alpha = 0.00244 Re^{0.516}$ for time 2hr - - - - - - (8a)

$\alpha = 0.0013Re^{0.8}$ for time 4hr - - - - - - (8b)

Table (2) Comparison of experimental Sh No. with analogies t= 300 s and T= 25°C, Sc=378

	Sh No.					
Re .No.	Prandtl Tayler **(Eq.1a)**	Von Karman	Chilton Colburn	Darshnlal	Prandtl Tayler **(Eq.2)**	Present work
10000	104.2	162.18	467.7	346.7	161.18	112.2
15000	152	239.88	660.69	512.8	234.4	144.5
20000	201	309.02	853	660.6	301.9	165.9
25000	255	389.04	1047.12	831.7	380.1	199.5

$\alpha = 0.00294Re^{0.803}$ for time 6hr - - - - - - (8c)

CONCLUSIONS

1- Scale removal by means of inhibited Hydrochloric acid is dependent upon the temperature of reaction, solution circulation rate (as Re) , time of reaction and, acid concentration, it was concluded that the amount of scale removal increases with increasing any factor of them, the condition to obtain high high percentage of scale removal (80-100%) should be ; for Reynolds number values over 17500, reaction temperature over 50°C , acid concentration not below 6.5wt%,and time over four hours.

2- Reaction of Hydrochloric acid with Iron oxide scale is followed first order kinetics model, with activation energy of 15kJ/mole which indicating that the process of Iron-oxide scale desolution is mass transfer controlling process.

3- Correlation for the variation of (Sh) (or mass transfer rate) with Re for the whole range of Re and temperature values

$Sh = 0.0537\ Re^{0.6028}\ Sc^{1/3}$

4-The experimental results for Iron- oxide desolution rates show good agreement with Prandtl – Taylor analogy, (Eq.1) , (using $\alpha = 2\ Re^{-1/8}$) at the early periods of the process, but at the later periods the rate divat from Prandtl –Taylor analogy.

Modification of analogies was obtained, correlations for α values estimation were obtained at different time to make Prandtl –Taylor analogy can be employed for the process.

$\alpha = 0.00244\ Re^{0.516}$ at time = 2hr

$\alpha = 0.0013\ Re^{0.8}$ at time = 4hr

$\alpha = 0.0029\ Re^{0.803}$ at time = 6hr

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APPENDIX

Mass and mor

Prandtl and t

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The frictio
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NOMENCLA
A:Surface area
C:Concentratio
d:Pipe diamete

APPENDIX

Mass and momentum transfer analogy equations

Prandtl and taylor analogy

$$\frac{k}{u_\infty} = \frac{f/2}{1+\left(\frac{u_x|_\delta}{u_\infty}-\right)(Sc-1)} \qquad (1a)$$

$$\alpha = 2Re^{-1/8} \qquad (1b)$$

$$Sh = \frac{(f/2\ )Re.Sc}{1+5\sqrt{\frac{f}{2}}(Sc\ -1)} \qquad (2)$$

-Von- Karman analogy(Brodkey,R.S.(1988)).

$$Sh = \frac{(f/2)Re.Sc}{1+5\sqrt{\frac{f}{2}}\{\ Sc-1+\ln(1+\frac{5}{6}Sc)\ \}} \qquad (3)$$

Chilton – Colburn analogy(Berger,E.B.(1977)).

$$Sh = \frac{f}{2} ReSc^{1/3} \qquad (4)$$

Darshnlal et.al analogy(Darshanlal,T.(1964)).

$$Sh = 0.058\sqrt{\frac{f}{2}}Re\ \ Sc^{0.34} \qquad (5)$$

The friction factor and wall shear stress for rough surface were obtained by measuring the pressure drop across the test section for each value of Re, temperature and time and applying the equations ;

$$f = \frac{d.\Delta\ P}{2\rho u^2 L} \qquad (6)$$

since,

$$\Delta p = \Delta h\rho g \qquad (7)$$

hence,

$$f = \frac{\Delta hdg}{2\ u^{\ 2}\ L} \qquad (8)$$

NOMENCLATURE

A:Surface area of specimen,m^2

C:Concentration,mole/m^3

d:Pipe diameter,m

D:Diffusivity,m/s
f:Friction factor
k:Mass Transfer coefficint,m/s
N_A:Flux of mass transfer,mole/m^2.s
P:Pressure drop,N/m^2
Re:Reynold 's Number
Sc:Schimdt Number
Sh:Sherwood Number
S.R%:Scale removal percentage,wt%
t:Time,h or s
T:Temperature,C°
u:Velocity