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# INHIBITION OF DIFFUSION CONTROLLED CORROSION IN EQUIPMENT HANDLING PULP SLURRY

**Olfat A. Fadali [1], Mamdouh M. Nassar[1], Ebrahim H. Mahmoud[1]**
**Omnia H. Abdelraheem[2], Sara K.Mohamed[1]**

*[1]Chemical Engineering Department, Faculty of Engineering, Minia University, El-Minia, Egypt*
*[2]Basic Engineering Sciences Department, Faculty of Engineering, Beni-Suef University, Egypt*

## ABSTRACT:

Corrosion of the wall of an agitated vessel containing pulp-fiber suspensions was studied using an accelerated test which involves the diffusion controlled dissolution of copper in acidified dichromate. Variables studied were pulp slurry flow rates, slurry concentrations and pulp fiber size. Three different pulp sizes were studied, namely: fiber-pulp slurry, fine-pulp slurry and the whole-pulp slurry. The rate of mass transfer controlled corrosion of copper was found to increase with increasing slurry flow rate and decreased by increasing pulp slurry concentrations. Fines in pulp slurry were found to play a major role in decreasing the rate of diffusion controlled corrosion due to its ability to damp small scale eddies at the wall of the agitated vessel in a manner similar to drag reducing polymers in pipes. Percentage inhibition efficiency using fine- pulp slurry ranged from 40% to 76%, while for the whole-pulp slurry the value ranged from 28% to 47%, when pulp slurry concentration ranged from 0.1% to 0.4%.

**Keywords:** *Pulp slurry transportation, Drag reduction, Diffusion controlled corrosion.*

## 1. INTRODUCTION:

The flow of pulp-fiber suspension occurs in most of the operations encountered in pulp and paper manufacture. The hydrodynamic properties of the pulp fiber suspension are different from that of water (Newaz-zaki,et.al 1999). Pulp-fiber suspension even at low concentration interact and entangle to form three dimensional coherent network and produce a plug flow of coherent network occupy the center of the pipe (Vaseleski and Metzner, 1974). The main part of the shear occurred in the boundary layer which exist at the pipe wall (Steenberg, etal 1960). Several mechanisms have been given based on study the transport properties and turbulence on the behavior of pulp suspension flow (Huhtanen and Karvinen, 2005; Steenberg et al, steenberg et.al, 1960; Robertson and Mason, 1957 and Higgins and Wahern, 1982). At low flow rate, the layer between the plug and the pipe wall is thin and the frictional resistance is greater than that of water alone but at higher flow rates, fibers pulled out from the plug pulp-fiber network and modify eddy formation and dissipated near the wall and thus damp turbulence. At very high flow rates the fiber suspensions friction factor values drops to levels near, or even below these of water (Vaseleski and Metzener, 1974).At this end, fiber suspension, according to Hoyt (1972) exhibit very appreciable drag reducing effect.

Flow of pulp slurry can affect the rate of steel pipelines corrosion in many ways, to explain the mechanism by which pulp slurry can affect the rate of corrosion, the

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mechanism of corrosion should be reviewed first (Fontana ,1987). Steel corrosion takes place through the formation of a galvanic cell between its more noble phase $Fe_3C$ (cementite) and its less noble phase Fe (ferrite)

Fe / electrolyte / $Fe_3C$

Cell reactions:

Anode (Fe): $Fe = Fe^{++} + 2e$

Cathode ($Fe_3C$): $2H^+ + 2e = H_2$ (pH 4)

Or

$\frac{1}{2} O_2 + H_2O + 2e = 2OH^-$ (pH 4- 10)

Side reaction: $Fe^{++} + 2\,OH^- = Fe(OH)_2$

$Fe(OH)_2$ undergoes oxidation with dissolved oxygen to give a porous oxide film on the steel surface. The porous oxide film allows further corrosion to take place (Schmitt and Bakalli, 2008).

In industry the pH ranges mostly from 4-10, accordingly dissolved oxygen reduction takes place as a cathodic reaction. Previous studies (Fontana, 1987) have revealed that the rate of steel corrosion in the pH range 4-10 is controlled by the rate of dissolved oxygen diffusion from the solution bulk to the corroding surface.

Pulp slurry can decrease the rate of steel corrosion by either decreasing the diffusivity of dissolved oxygen or by damping the small scale eddies which accelerate the rate of mass transfer of dissolved oxygen to the corroding surface under turbulent flow conditions. In view of the slowness of steel corrosion by dissolved oxygen an accelerated test was used in the present work which simulates natural corrosion, namely the diffusion controlled dissolution of copper in acidified $K_2Cr_2O_7$ ( Fontana,1987 and Sedahmed et. al, 2004 ). The system has been used widely to study diffusion controlled corrosion (Sedahmed et.al, 2004, Greggory and Riddiford, 1960 and Abdel-Aziz, 2013).

The aim of this study is to investigate the effect of pulp-fiber components (fiber-pulp slurries, fines-pulp slurries and whole- pulp slurries) on the rate of corrosion in agitated vessel using the diffusion controlled dissolution of copper in acidified dichromate technique. Although the present results were obtained using an agitated vessel, the results can be extended to pipelines carrying pulp slurries under turbulent flow at least quantitatively. Agitated vessels are used in paper industry to mix different ingredients e.g. bleaching agents, sizing material, etc. with the pulp slurry.

## 2. EXPERIMENTAL WORK

### 2.1. Apparatus

The experimental unit used in the present work is shown in fig .1. The unit consisted mainly of cylindrical glass vessel of 11.8 cm diameter and 14.7 cm height, with a sheet of copper lining the inside wall of the glass vessel. The solution (9 cm height) was stirred with an agitator which consisted of stainless steel shaft fitted with $45^o$ pitched of turbine 5 cm diameter. The shaft and turbine were coated with epoxy resin. The shaft was driven by a 0.5 horse power variable speed motor. Impeller rotational speed was controlled by means of a variac and was measured by an optical tachometer. Rotational speed ranged from 50 to 400 r.p.m.

### 2.2. Materials

Copper dissolution in acidified dichromate is known to be diffusion controlled reaction (Greggory and Riddiford, 1960). This technique is simple, therefore it widely used to study liquid-solid mass transfer under different hydrodynamic conditions (Patil and Shama, 1983 and Gruber and Melin, 2003). The solution used in this study consists of acidified potassium dichromate with the following composition : (0.003M $K_2Cr_2O_7$ + 0.5M $H_2SO_4$) , and bleached bagasse pulp slurry was added at different concentrations ( 0.1% , 0.2% , 0.3% and 0.4% ) .

The used pulp slurry was obtained from Misr Edfu Pulp Writing and Printing Paper Company (MEPPCO). The pulp produced from cooking of bagasse by alkaline process (Kraft pulping) and bleached by three stages (oxygen, chlorine dioxide and peroxide).

Fiber pulp classification was carried out by Baur Mc-Mett classifier using 100-mesh screen. The pulp retained above 100-mesh screen was considered fiber-pulp slurry and that passed the 100- mesh screen was considered as fine- pulp slurry, therefore, three types of pulp slurries were used namely; fine- pulp slurry, fiber- pulp slurry and whole-pulp slurry.

Microscopic examination for bagasse components was carried out using Optical Microscope, Amscope 40X-2000X.

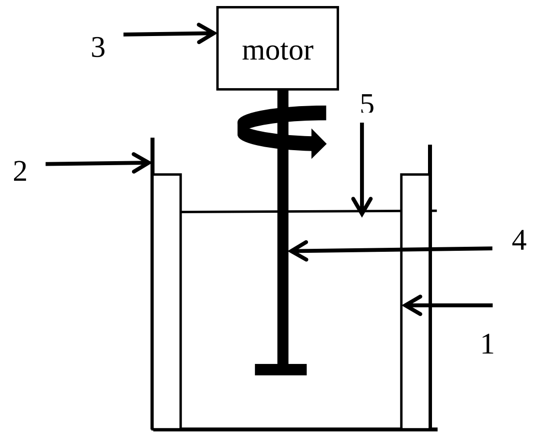


**Fig.1.** Schematic diagram of the experimental setup.

1: copper cylindrical sheet. 2- 1L glass container. 3- variable speed digital motor. 4: 45 $^o$ pitched turbine impeller. 5- solution level.

### 2.3. Procedure

The experiment was carried out at room temperature (24$^o$ C). The rate of copper dissolution in acidified dichromate solution was followed by withdrawing 5 $cm^3$ samples at 3 minutes intervals for dichromate analysis. Dichromate was analyzed by using a UV- visible Spectrophotometer (Shimadzu Model: 1601 UV) at 352 nm wave length .

## 3. RESULTS AND DISCUSSIONS

### 3.1. Pulp structure

Bagasse pulp is made from bagasse (bagasse is the solid residue that remain after extraction of sugar from sugarcane). According to Rydholm (1967) and Nassar(1975) bagasse is composed of different cellulosic materials such as fiber, vessel cells and pith cells all are intermixed, therefore bagasse pulp is composed of fibers and fines (fines in bagasse pulp is mainly small parts from broken pith cells).

Figure (2-4) shows micrograph of bagasse. Figure (2) shows the mixture of all cellulosic materials, on top left hand of the picture there is a vessel cell, the long dark stiff lines are fibers and all other small parts dispersed in the graph are parts from broken pith cells. Figure (3-4) show pith cells in different orientation, it can be noticed how they are very thin, therefore easily broken down to small parts during pulping and is considered as fines. According to Nassar, (1975) and Rydholm, (1967) bagasse consists of 65% fiber fraction ( fiber and vessel ) and 35% pith cell, after depith 20-18% of pith remain in bagasse (Nassar, 1975, and Misr Edfo Company, 2018).

At this end, bagasse pulp is considered as a mixture of fibers and fines .According to Ronald, (1969) pulp slurries passes 100-mesh screen are considered fines and that retained on the 100-mesh is fiber fraction. In this study it was found that 22.1% of fines passed 100 mesh screen and 77.9% retained on 100 mesh and considered as fiber fraction (fibers in pulp slurries are flexible and easily entangled and can form coherent structure).

Three types of pulps are used, fine- pulp slurry passed 100 mesh, fiber-pulp slurry retained in100- mesh and whole- pulp slurry without screening. According to Huhtanen and Karvinen (2005), during flow of pulp slurry in pipe, fibers are interact, form coherent network and occupy the center of the pipe as plug flow. As flow rate increased, fines and very short fibers are detached and gathered near the wall, accordingly the three types of pulp slurries will affect differently the rate of mass transfer of dissolved oxygen and consequently the rate of corrosion.

**Fig.2.** Mixture of all materials (fiber, vessel and pith ) (40 X)

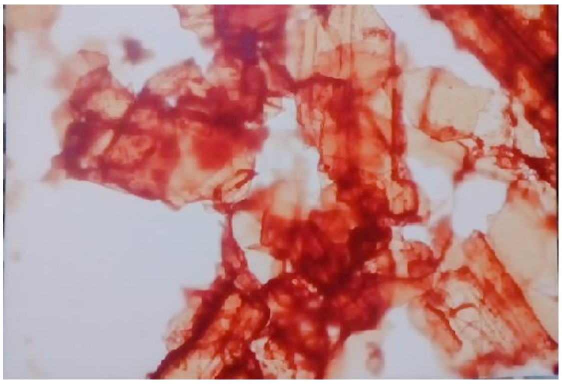

**Fig.3.** Longitudinal pith cells (2000 X)

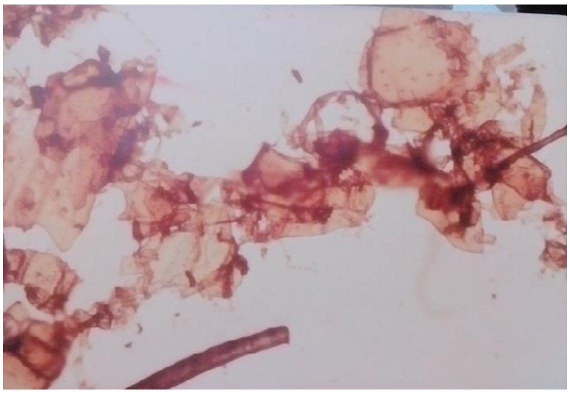

**Fig.4.** Broken pith cells (2000 X)

### 3.2. Effect of pulp flow rate on rate of diffusion controlled of copper corrosion

For a batch reactor, where a diffusion controlled reaction takes place, the concentration- time relation is described by the differential equation (Walsh, 1993):

$$\frac{dC}{dt} = -\frac{KAC}{V} \quad (1)$$

Upon integration

$$V\ ln\frac{Co}{C} = \mathrm{K.A.t} \quad (2)$$

Where V is volume of the solution, $cm^3$, K is a mass transfer coefficient, cm/s, $C_o$ and C are the initial concentration and concentration after time (t, min) in ppm A is an area of copper vessel wall, $cm^2$, respectively.

Figures (5-7) show a typical $lnC_o/C$ vs. time plot for the obtained results at different agitation speed for 0.4% concentration of fiber, fine and whole pulp slurries. The present data fit equation 2 quite well the same results were observed for other pulp concentrations (0.1, 0.2, and 0.3%). The mass transfer coefficient (K) was obtained from the slope of ln $C_o/C$ vs. time lines, for copper dissolution in acidified dichromate solution in presence of different types of pulp slurries. It can be observed that the rate of copper dissolution increases with increase stirring this confirms that copper dissolution is diffusion controlled. The data were correlated for the three types of the studied pulps in terms of K and angular velocity (ω) rev. $s^{-1}$.

Figures (8-10) the data fit the following equations: For whole- pulp slurry

$$K \propto \omega^{0.65} \quad (3)$$

For the fiber-pulp slurry

$$K \propto \omega^{0.63} \quad (4)$$

For the fine –pulp slurry

$$K \propto \omega^{0.48} \quad (5)$$

**Table 1:** K values at different concentration for the three types of pulp Suspension, r. p.m. = 400 and Ko=0.0055 $cms^{-1}$

| Conc. % of pulp | whole-pulp slurry | Fiber-pulp slurry | Fine – pulp slurry |
|---|---|---|---|
| | K, cm/s | | |
| 0.1 | 0.00396 | 0.00368 | 0.0033 |
| 0.2 | 0.0033 | 0.00309 | 0.0027 |
| 0.3 | 0.0029 | 0.00224 | 0.0019 |
| 0.4 | 0.00294 | 0.00194 | 0.0013 |

The exponent in equations 3-5 are in the range of 0.65 to 0.48 which is consistent with the hydrodynamic boundary layer theory. The theory assumed that K increases with increase ω as a result of the decrease in the diffusion layer thickness (Incropera & Dewitt, 2005). Moreover, the lower value of K in equation 5, for the fine-pulp slurry can be attributed to that, at higher stirring rates short fiber and fines are pulled out from the fiber-pulp network. This result in increased viscosity in the boundary layer near the copper pipe wall and decrease the mass transfer. Also presence of fines may form a layer that can retard diffusion of the acidified dichromate to reach copper-wall and decrease corrosion of copper. Exponent of 0.65 in equation (3) for the whole pulp is higher than that given by Amin,et.al (2014) for rice straw pulp (exponent 0.51), this may be attributed to the shorter fiber length of rice straw (1.5mm, Rydholm 1967) compared to bagasse (1.7mm, Nassar, 1975). The K values for whole -pulp (Equation 3) is higher than that for fine-pulp fraction (Equation 5), this may be attributed to the fact that, amount of fines incorporated within fibers network are little. In the same time long fibers are entangled together form coherent structure thus firmly entrapped fines and the very short fibers, in consequent little amount of fines will be pulled out to the boundary layer. Under such conditions diffusion of acidified dichromate will be high and K values will be high. On contrary the amount of fines in the fine-pulp slurry (Equation 5) are already high. During pulp flow much fines will be separated from the bulk and suspended in the boundary layer damp the small scale turbulence which prevail in the hydrodynamic boundary layer at the vessel wall and reduce K in a manner similar to drag reducing polymers (Hoyt, 1972 and Newaz et.al., 1999).

### 3.3. Effect of pulp concentrations on rate of diffusion controlled copper corrosion

Figures (8-10) depict that, for a given stirring rate, K decreases with increase pulp concentration; this can be attributed to the following:

1- On increasing pulp slurry concentration, the network strength of the fiber structure increased, form flat plug, and entrapped much of the cellulosic materials of small dimensions (fines). The physical and hydrodynamic nature of the system is changed depending on how much of cellulosic fine material pulled out to be concentered in the hydrodynamic boundary layer. Presence of fine and very short fiber in the boundary layer will obstruct the diffusion of the depolarizer i.e. decrease its diffusivity (D) with a consequent decrease in K ($K= D/\delta$).

2- The small dimension cellulosic materials ( fine and short fibers) exist in the boundary layer act as drag reducer and damp the small eddies in the hydrodynamic boundary layer, this leads to increasing the diffusion layer thickness ($\delta$) across which the chromium ions diffuses to the copper-wall with a subsequent decrease in the corrosion rate.

From the data in table 1, it can be seen that fines suspended in the hydrodynamic boundary layer have considerable effect on corrosion rate of copper, due to its ability to damp the small scale eddies which prevail in the hydrodynamic boundary layer at the vessel wall. In this regard the fine-pulp act as drag reducing polymer (Hoyt, 1972).

### 3.4. Inhibition efficiency of fine-pulp slurry

Figure (11) shows the effect of fines on percentage of inhibition efficiency (% IE) for the three pulp slurries.

% I E is calculated by the following equation:

$$\% IE= (K_o - K)*100 / K_o \qquad (6)$$

Where $K_o$ and K are mass transfer coefficient of blank (without pulp) and in presence of pulp respectively. The high values of % I E of fine fraction suggested the high inhibition effect of fines on rate of copper dissolution, probably due to not only the higher percentage of fines in the boundary layer but also due to nature of fines (pith).Pith has higher hemicellulose (33.2 % of hemicellulos in pith and 30.7 % in fiber, Nassar, 1975.) hemicellulose swell easily in aqueous medium and increase viscosity in consequent minimize the number of the generated small eddies during pulp flow and increase the thickness of hydrodynamic boundary layer and finally decrease K and decrease corrosion rate of copper.

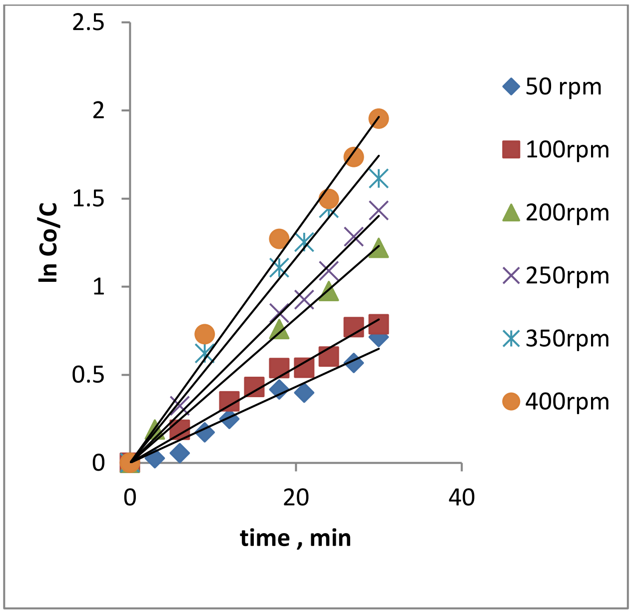


**Fig.5.** ln Co/C vs. time for 0.4% fiber- pulp consistency at different rpm.

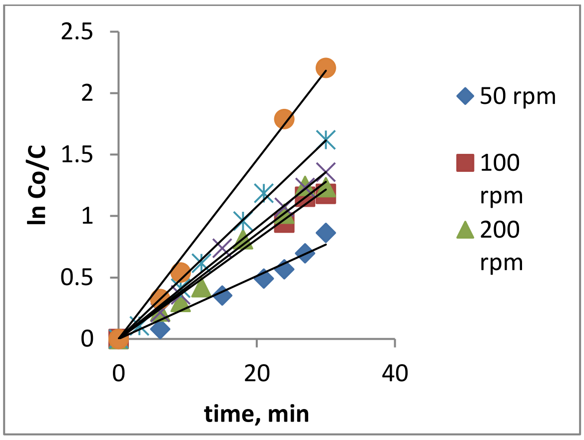


**Fig.6.** lnCo/C vs. time for 0.4% fine- pulp consistency at different rpm

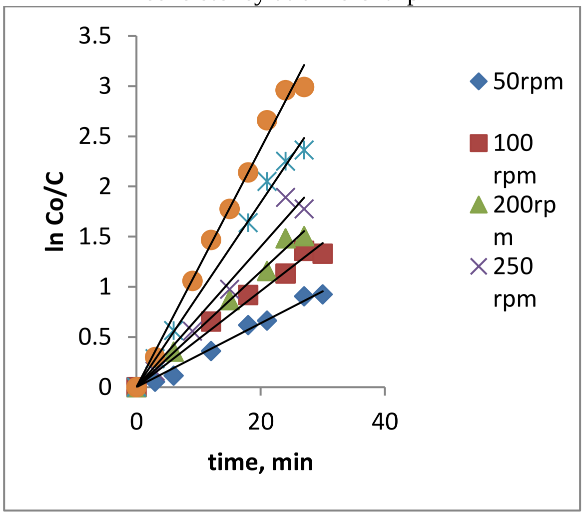


**Fig.7.** lnCo/C vs. time for 0.4% whole-pulp consistency at different rpm

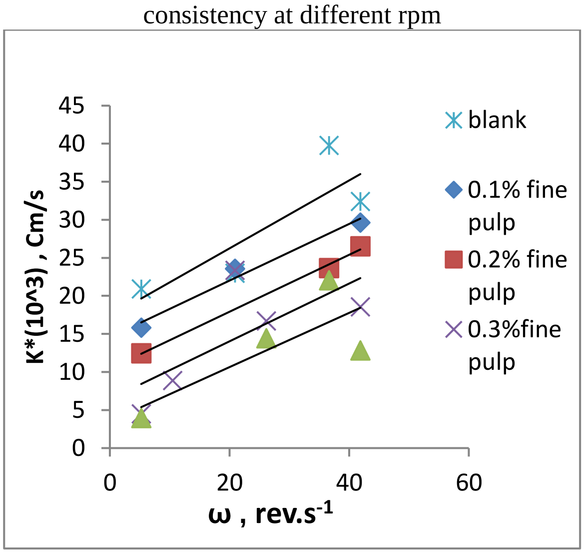


**Fig.8.** effect of impeller rotational speed on mass transfer coefficient at different whole- pulp consistency

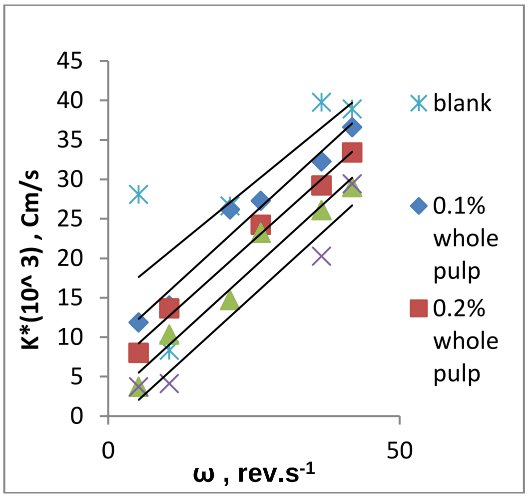


**Fig.9.** effect of impeller rotational speed on mass transfer coefficient at different fine- pulp consistency

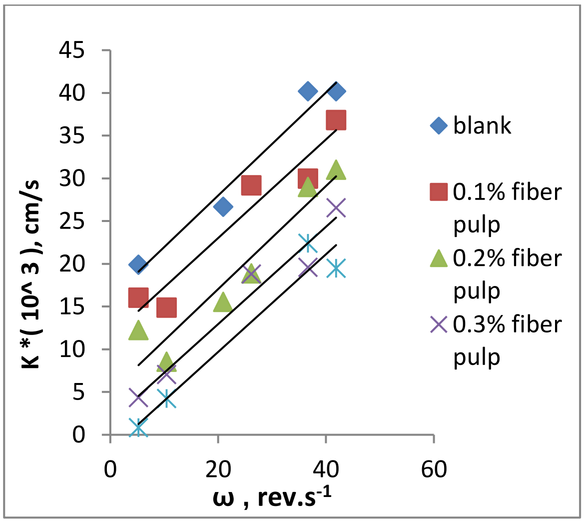


**Fig.10.** effect of impeller rotational speed on mass transfer coefficient at different fiber- pulp **consistency**

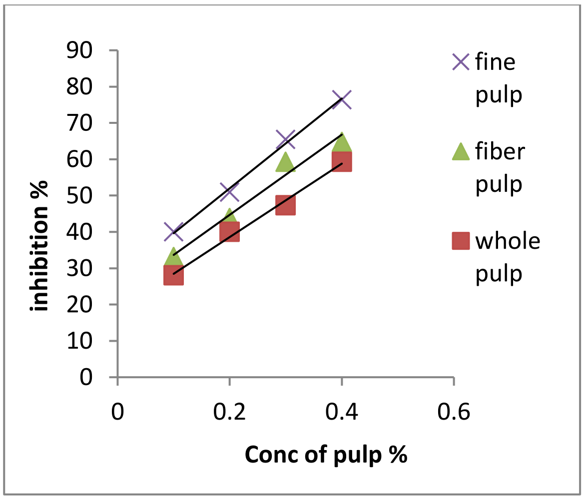


**Fig.11.** Relation between inhibition % vs. Conc. % for different pulp slurry consistency at 400 rpm

## 5. CONCLUSIONS:

- The diffusion controlled corrosion of agitated vessel wall was found to decrease in the presence of pulp slurry. The corrosion inhibition efficiency of pulp slurry is a function of pulp slurry types, pulp slurry concentration and agitation speed. The rate of diffusion controlled copper corrosion in acidified dichromate, increased by increasing agitation and decreased by increasing pulp slurry concentration. The percentage of inhibition efficiency ranged from 40% to 76% depending on the operating condition, fine-pulp is more effective than whole pulp.
- Fine-pulp slurry was found to cause the highest reduction of mass transfer coefficient, while whole-pulp slurry gives the least reduction of the mass transfer coefficient, this is attributed to the presence of fine in the boundary layer which damp turbulence, thus increasing the hydrodynamic boundary layer thickness with a consequent decrease in the rate of depolarizer diffusion and copper corrosion.
- In view of the significant effect of fines-pulp in inhibiting diffusion controlled corrosion in a manner similar to drag reducing polymer, the use of fines-pulp in practice is recommended to inhibit corrosion and reduce mechanical power consumption in equipment operating under turbulent flow such as pipelines, agitated vessels and heat exchangers. Using fine-pulp as a drag reducer would have the advantages that, unlike drag reducing polymer and surfactants, it is mechanically nondegradable and nonpolluting because it can be separated by filtration.

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**الملخص:**

تمت دراسة تآكل جدار الوعاء المحتوي على معلقات من ألياف اللب باستخدام اختبار سريع يتضمن تحلل النحاس و انتشاره في ثنائي كرومات الحمض. كانت المتغيرات التي تمت دراستها هي معدلات تدفق الياف اللبّ ، وتركيزات الالياف وحجم ألياف اللب. تمت دراسة ثلاثة أحجام مختلفة من اللب ، وهي:لبعجينة الألياف ، لب عجينة الورق ولب عجينة الورق بالكامل. وجد أن معدل تآكل النحاس المتحكم في الانتشاريزداد بزيادة معدل تدفق الالياف وانخفض بزيادة تركيز الياف اللب. تم العثور على الجرامات الموجودة في الياف عجينة الورق لتلعب دورًا رئيسيًا في تقليل معدل التآكل الذي يتم التحكم فيه بواسطة الانتشار نظرًا لقدرته على تقليل الدوامات الصغيرة الحجم على جدار الوعاء بطريقة تشبه سحب البوليمرات المخففة في الأنابيب. تراوحت كفاءة تثبيط النسبة المئوية باستخدام الياف اللب الدقيق من 40 ٪ إلى 76 ٪ ، في حين تراوحت قيمة الالياف كامل اللب من 28 ٪ إلى 47 ٪ ، عندما تراوح تركيز الياف اللب من 0.1 ٪ إلى 0.4 ٪.