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MASS TRANSFER STUDY IN “AUTOCIRCULATION” REACTOR FOR H_2S REMOVAL OF ACID GAS STREAMS

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Abstract

In this paper, oxygen mass transfer in an Airlift reactor for single step H_2S removal from acid gas streams has been studied experimentally.

Oxygen and nitrogen were used as gas phase. Water, chelated iron solution (500ppm) and a slurry solution 0.08%(wt%) sulfur per 100 ml of solution of chelated iron) were used as liquid phase. Experiments were carried out in a 60 liters internal loop airlift reactor. Results show that mass transfer coefficient (K_La) for three different types of liquid phase are almost equal. Adding of nitrogen accompanied with oxygen causes an increase in mass transfer coefficient, decreasing saturation concentration (C*) and consequently decreasing mass transfer flux. Finally, new correlations expressing variation of mass transfer coefficient in terms of air and nitrogen superficial velocities were presented. There is a good agreement between this work and similar experimental works.

Key words: *Airlift reactor; chelated iron solution; mass transfer coefficient; mass transfer flux; H_2S removal.*

1. Introduction

The liquid redox technology for single step H_2S removal and converting it to elemental sulfur was firmly established method since the 1920 ’s. The most widely used method is the “iron redox” process or the “chelated-iron” process. This process was done in a reactor named “Autocirculation”. The unique feature of the Autocirculation reactor is that no pumps are required to circulate solution between absorber and oxidizer. In this reactor absorption and regeneration are carried out in a single vessel according to the following equations respectively.

Oxidation reaction: $H_2S + 2Fe^{3+} \rightarrow 2Fe^{2+} + S^0 + 2H^+$

Regneration reaction: $O_2(g) \rightarrow O_2(eq.)$

$O_2(eq.) + 4Fe^{2+} + 2H_2O \rightarrow 4Fe^{3+} + 4OH^-$

In this paper, oxygen mass transfer from gas phase (air) in presence of nitrogen to the liquid phase for regeneration of chelated iron has been investigated. The transfer of oxygen from the gas phase to the liquid phase must take place along certain pathway that some resistance can exist (Moo-young and Blanck, 1981)[8]. Not at all the resistances are significant. Thus, in practice Air lift reactor operates at such levels of turbulence in the fluids that convective transport dominates in the body of the liquid and hence the associated resistance can be ignored. So, the resistances to transfer in each phase is localized in the thin films close to the interface, this eliminates all the transport resistances except those around the gas-liquid interface. So the oxygen transfer problem is thereby reduced to that of gas-liquid interfacial mass transfer. The catalyst solution is water base mainly. So the oxygen transfer phenomena was handled in water. At least in another step the mass transfer phenomena in presence of chelate iron and sulfur solution of iron-chelated (Cs=0.08 wt% sulfur/100 ml solution) were studied.

First of all the volumetric mass transfer coefficient (K_La) in presence of O_2 was studied, then the effect of nitrogen investigated.

All the experimental data were analyzed and correlated as K_La versus superficial gas velocity as the equation expressed by other researcher [1,4].

All these correlations were used to develop a computer model prepared. Also the correlations that show the effect of the nitrogen in mass transfer coefficient were presented.

2. Experiment

The experimental apparatus for study of the volumetric mass transfer coefficient was an internal loop Airlift reactor constructed of glass material with internal diameter and height of down comer equal to 17.5 and 180 cm respectively. The diameter and height of draught to be were 14.5 and 190 cm, respectively. This makes the ratio of the cross section area of the riser to the down comer equal to 0.375. The superficial gas velocity was in the rang of 0.04-0.25 cm/sec. Distilled water, chelated iron with 500 ppm and slurry solution (0.08 wt% sulfur/100 ml solution) was applied as the fluid. Figure (1) is experimental set up.

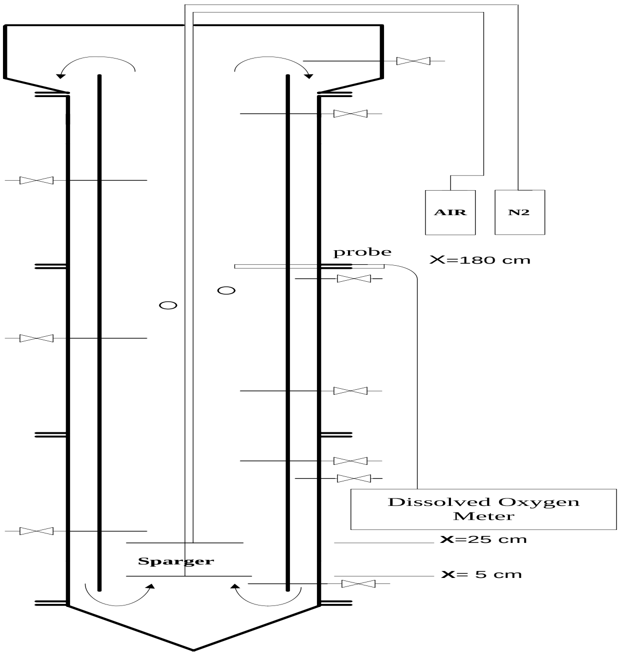

Figure 1. Experimental set up

The hydrostatic pressure difference due to gas sparging in riser causes a circulating motion between riser and down comer.

Nitrogen or air sparger was located 5cm above the bottom of riser respectively. Oxygen electrode was located 180cm above the bottom of riser. Temperature and pressure were considered fixed ($T=26\pm1^0C$&P=1 atm.) during the test and superficial gas velocity were fixed in rang of 0.25-0.4 cm/sec.

The air was supplied by a compressor and nitrogen by gas cylinder connected to system. Before testing the oxygen meter was calibrated.

In this experiment the volumetric coefficient of liquid-phase mass transfer (K_La) was determined. Prior to an experiment for K_La determination, the liquid in the column was sparged with a sufficient amount of nitrogen from a cylinder until the concentration of dissolved oxygen in the liquid become negligible. Then air supply to the column was started. The dissolved oxygen concentration(C) increased with time t. Data acquisition was done in the first 10 min [1,3].

From an oxygen balance:

$$dC/dt = K_L a(C^* - C) \qquad (1)$$

Where C^* is the value of concentration in equilibrium with the average oxygen partial pressure in the air and can be obtained from the oxygen meter, when it reaches a steady state. Upon integration of equation (1) we have

$$Ln(C^* - C) = -K_L a.t + Cons\tan t \qquad (2)$$

With considering boundary condition and initial condition $\{t = 0 \quad \rightarrow \quad C_L = C_{L0}$

$$\{t = t \quad \rightarrow \quad C_L = C_L$$

Following equations is derived:

$$Ln\left(\frac{C^* - C_{LO}}{C^* - C_L}\right) = K_L a.t \qquad (3)$$

If a fractional approach to equilibrium (E) is defined as the ratio of the mass transfer at any instant (ie: C_L=C_{L0}) to the maximum possible transfer (ie: C^*- C_{L0}), we have

$$E = \frac{C_L - C_{L0}}{C^* - C_{L0}} \qquad (4)$$

Figure (2) is very smooth dissolved oxygen time profiles were obtained from data analyzing. Then equation above may be written in terms of (E) as:

$$\mathrm{Ln}\,(1 - \mathrm{E}) = -\mathrm{K_L a.t} \qquad (5)$$

The coefficient, K_La, could be calculated as the slope a semi log plot of $(Ln\frac{1}{1-E})$

Vs. time. This plot is shown in Figure(3).

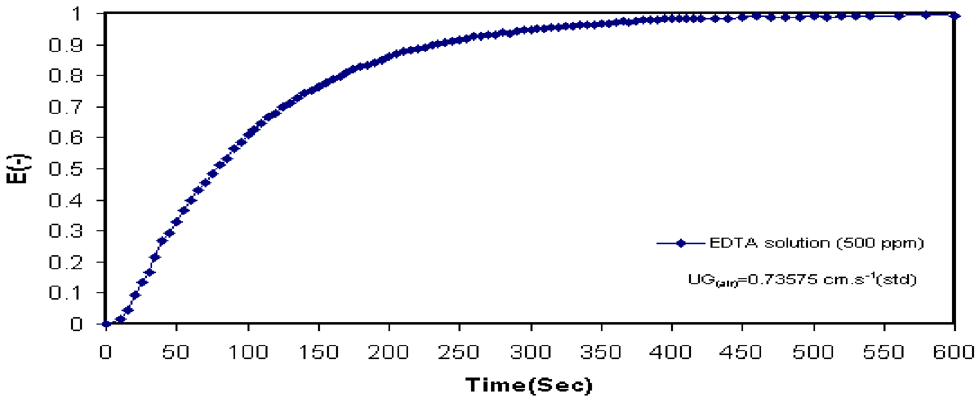

Figure 2. A typical E vs time profile for Air-EDTA

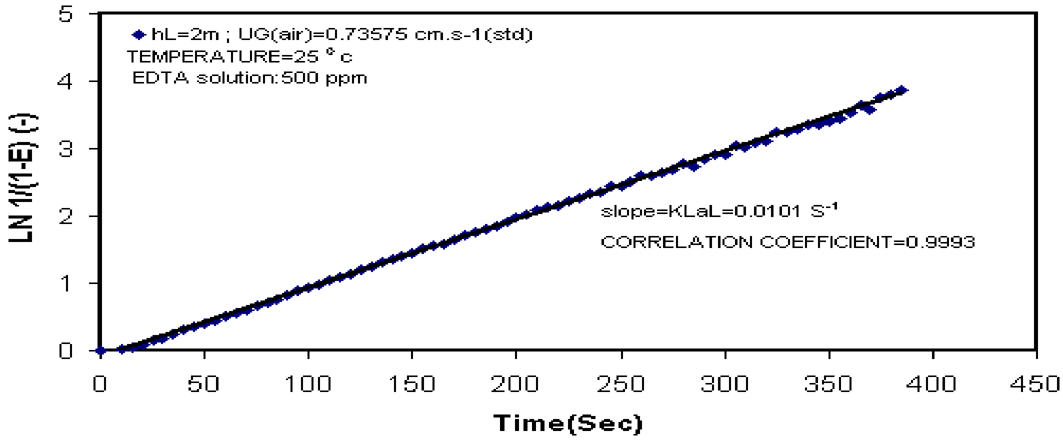

Figure 3. A typical 1/(1-E) vs. time

This figures is similar to graph that were obtained by another researcher.

This method of evaluating K_La was based on three assumptions.

1) The liquid phase was perfectly mixed [2].

2) The driving potential for mass transfer was uniform through out the column [3].

3) Response of the oxygen electrode to a change of the dissolved oxygen concentration was sufficiently fast.

The mass transfer coefficient is affected by reactor geometry and physical properties of fluids. So it is necessary to know these properties [6]. Relevant physical properties at temperature 26 ± 1^0C and atmospheric pressure of the liquids used are listed in Table (1).

Table (1). Properties of liquids used (30^0C & 1 atm)

Liquid Phase	**DL* 10^5 (cm^2/s)**	**ρ (g/cm^3)**	**TDS (r/lit)**	**Conductivity (ms/cm)**	**Salinity**
Distilled Water	2.6	0.925	0.07	0.13	0.1
EDTASolution 500 ppm	0.16	1.03	4.58	9.17	6
EDTA Solution Slurry 0.08(wt%) Sulfur/100 ml solution	0.17	1.11	4.46	8.94	6

Bases for correlation

In this study, the dependency of KLa vs. superficial gas velocity was obtained using experimental correlations considering the reactor geometry and physical properties. These experimental correlation are similar to that expressed in other references [1,7].

These main correlations for these parameters are compiled in Table (2). The correlations were obtained in this research given in Table (3). It is necessary to mention that in this case only air was sparged to system.

Table (2). Other Works Correlations

Reactor Type Reference	**Correlation**	**Parameter Range**
External Loops Draught - tube Internal loops (annulus sparged) Bubble column ***Bello et al.1985***[7]	$K_La=0.79[1+A_d/A_r]^{-2}\ UG_{(air)}^{\ 0.8+0.1}$	Air- water or aqueous salt solution 0.15($kmol.m^{-3}$) Nacl, H_d=1.8 m, D_r=0.152m UG =(0.0137,0.086), $m.s^{-1}$ (Bubble flow) A_d/A_r=0.11 to 0.069 (External Loops) A_d/A_r= 0.13, 0.35 and 0.56 (Internal loops) Bubble Column, A_d/A_r=
External Loops ***Chisti et al 1986***[1]	$K_La=[1+A_d/A_r]^{-1}(0.349-0.102\ C_s)\ UG_{(air)}^{0.837+0.062}$	Air- Slurry Solution at above conditions

Table (3). Suggested Correlations In This Study with sparged Air

Reactor Type	**Equation**	**Range–Parameter**
Internal Loops	$K_La=0.1107[1+A_d/A_r]^{-2}UG_{(air)}^{0.8979}$	Air- water, D_c or D_r = 0.145 m, H_d=2 m UG= 0.04 to 0.25, $cm.s^{-1}$ (Bubble flow) A_d/A_r= 0.37455 (Internal Loop)
Internal Loops	$K_La=0.5641[1+A_d/A_r]^{-2}UG_{(air)}^{0.6239}$	Air-EDTA Solution(500 ppm) at above Condition
Internal Loops	$K_La=[1+A_d/A_r]^{-1}(0.5584-6.519C_s)UG_{(air)}^{0.5514}$	Air-Solution Slurry 0.08(wt%) Sulfur/100 solution at above condition

In comparison Table (2), (3) it is recognized that in case of distilled water as fluid, we have a good agreement with another investigators. A difference in coefficient of these equations is related to different reactor geometry. It should be mentioned that in these experiments we had fixed A_d/A_r.

In comparison with another equations was obtained by another investigator, different solution, oxygen solubility and reactor geometry are caused a difference in coefficient and power of equations.

3. Results and Discussion

In this section the effect of fluid and sparging of air with and without nitrogen is compared. It is shown that oxygen solubility in iron chelate is lower than distilled water.

As it shown in Figure (4) the variation of oxygen concentration versus time in iron chelate solution is under the distilled water, and also the equilibrium concentration in iron chelate is lower than distilled water. Sparging of air in presence of nitrogen were caused the variation of concentration become larger and the equilibrium concentration lowered. It is shown in Figure (5).

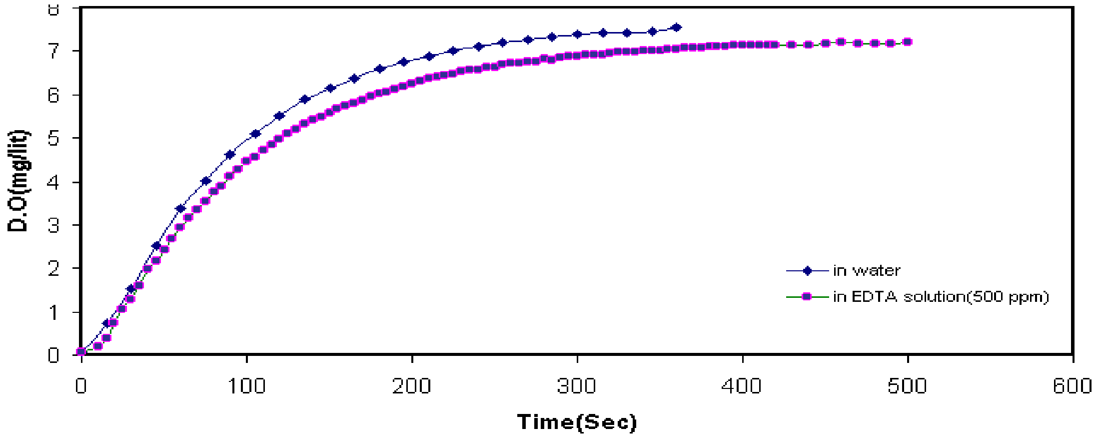

Figure 4. Effect Of Liquid Type on Dissolved Oxygen for EDTA solution

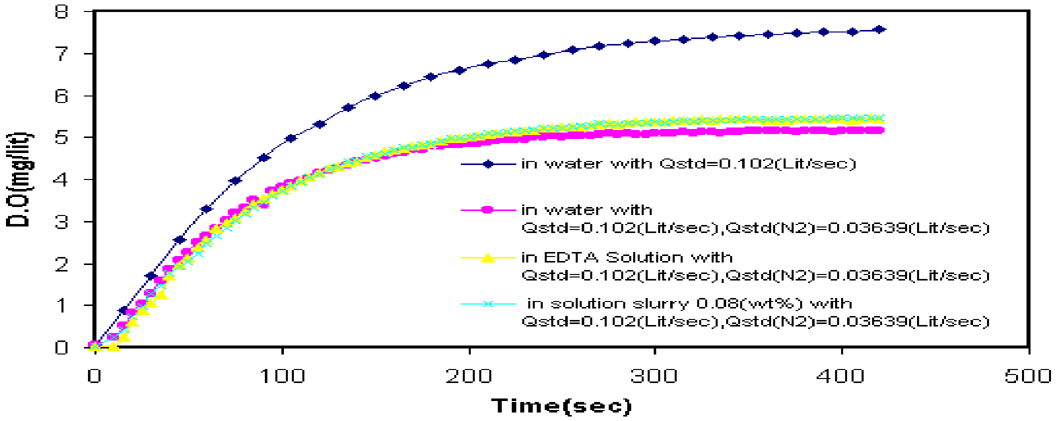

Figure 5. Effect of Nitrogen on Dissolved Oxygen for water, EDTA and slurry solution

This matter is related to lowering mole percent of oxygen in gas mixture and striping effect of nitrogen.

The volumetric mass transfer coefficient versus superficial gas velocity (air) for three kinds of fluid is shown in Figure (6). As it mentioned before the variation of fluid viscosity and physical properties of fluid result different (K_La).

Because of lower concentration of iron chelate and solid in solution this difference in K_La obviously is not sensed. This graph is similar to graph that are given by another investigators [1].

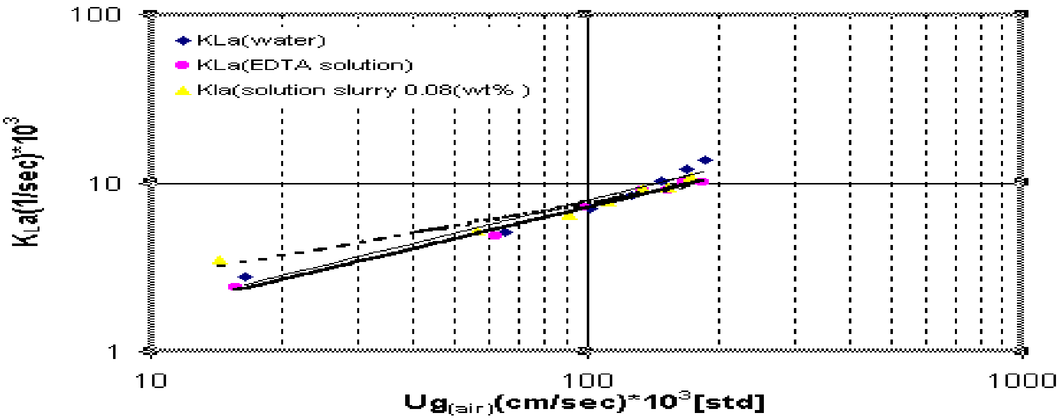

Figure 6. MTC vs. riser superficial gas velocity. Comparison of the oxygen MTC in water, EDTA solution (500ppm) and EDTA slurry solution 0.08(wt%)

3.1 Nitrogen effect

K_La was increased when nitrogen injected to the system because of the turbulence effect and increasing the liquid circulation. This matter was observed in any fluid. Figure (7) is shown this fact in case of iron chelate solution (500 ppm). Also in case off distilled water and slurry solution is obtained same as figure. As it pointed before, nitrogen injection to the system caused the equilibrium concentration decreased. Consequently the Volumetric mass flux (N_A) decreased according to equation (6).

$$N_A = K_L a(C^* \text{-} C) \qquad (6)$$

The variation of mass transfer flux versus superficial gas velocity (Ug) with and without nitrogen for iron chelate solution is compared in Figure (7).

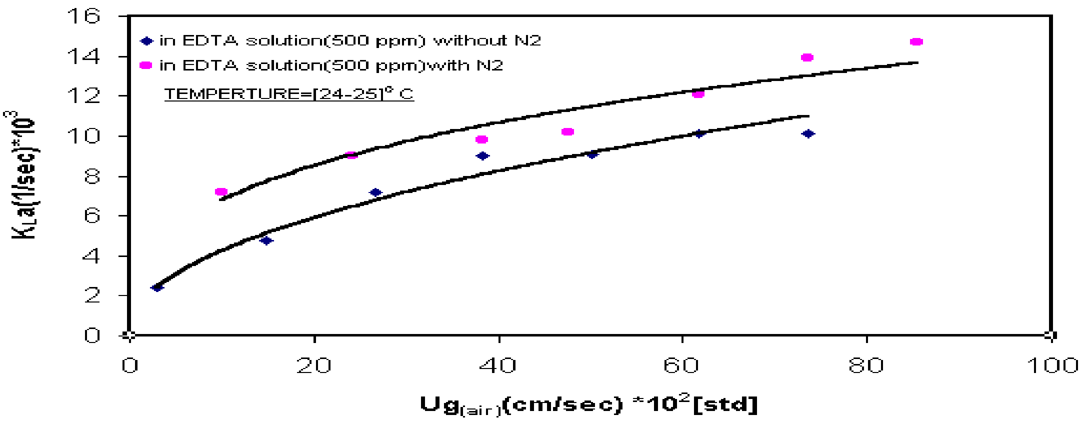

Figure 7. Effect of Nitrogen on Kla

According to Figure (8) the variation curve of volumetric mass flux versus superficial gas velocity, in presence of nitrogen is below the case of without nitrogen.

As it pointed out before, the nitrogen injection causes the K_La increase and the equilibrium concentration decreases. But the volumetric mass transfer flux is sensitive to variation of equilibrium concentration so it decreases.

In this research developing an equation that relates the mass transfer coefficient versus superficial gas velocity of N_2 and air for the computer program simulation is necessary so the software "Table curve" in three dimensions is used for developing this correlation. This correlation is presented in Table (4).

Table (4). New Correlations (Effect of nitrogen) for water, EDTA solution and slurry

Reactor Type	Equation	Parameter Range
Intenal Loops	$K_La=0.6118[1+A_d/A_r]^{-2} UG_{(N2)}^{0.8819} UG_{(air)}^{0.6767}$	Air, N2 - Water, D_c or D_r=0.145 m, H_d=2 m $UG_{(air)}$ = 0.04 to 0.25, cm.s $^{-1}$ $UG_{(N2)}$ = 0.04 to 0.25, cm.s $^{-1}$ (Bubble flow) (Internal Loop) A_d/A_r=0.37455
Internal Loops	$K_La=0.18454 [1+A_d/A_r]^{-2} UG_{(N2)}^{0.506} UG_{(air)}^{0.49267}$	Air, N_2 – EDTA Solution (500 ppm) at above condition
Internal Loops	$K_La=[1+A_d/A_r]^{-1}(0.58127-5.379 C_s) UG_{(N2)}^{0.4252} UG_{(air)}^{0.5873}$	Air , N_2 – EDTA Solution Slurry 0.08(wt%) Sulfur/ 100 ml solution

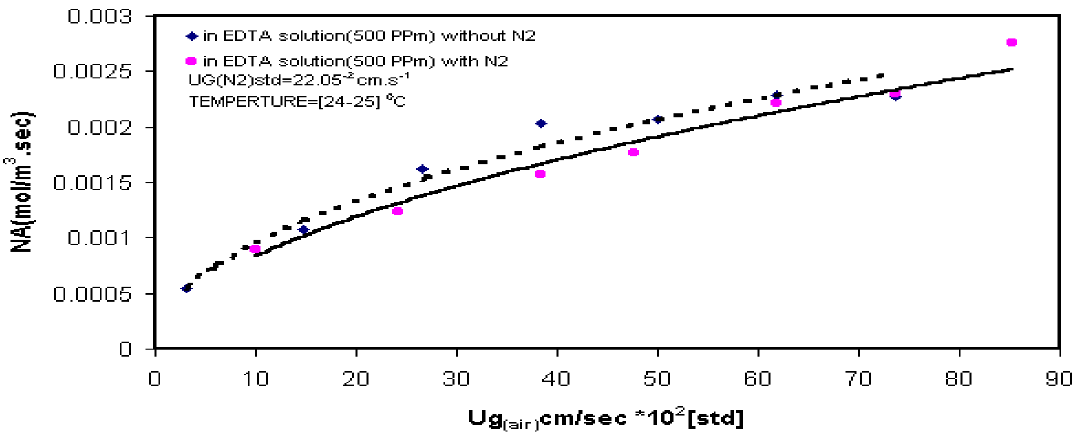

Figure 8. Effect of Nitrogen on Mass Transfer Flux; NA

4. Conclusion

Oxygen solubility decreases with changing typical fluid from distilled water to iron-chelate solution and K_La increases but volumetric mass flux (N_A) decreases with nitrogen injection to system. At least some experimental correlation that mass transfer coefficient relates to superficial gas velocity of nitrogen and air are presented.

In this study we want to correlate the mass transfer coefficient as parameters of the reactor for H_2S removal from acid gas streams, same as superficial gas velocity, concentration of slurry solution and handling effect of existence two sparger. Finally these experimental new correlations are employed in soft ware computer.

Nomenclature

A_d - Area section downcomer, cm^2
A_r Area section riser, cm^2
a- Specific gas –liquid interfacial area based on clear liquid volume, cm^3/cm^2, or cm^{-1}
C- Dissolved oxygen concentration, mg/l
C* - Steady state (or saturation) dissolved oxygen concentration, mg/l
c- Constant
C_{L0}- C at intial condition, mg/l
D- Column diameter, cm
DL- Liquid phase diffusivity,$cm^2.s^{-1}$
E - Fractial approach to equilibrium
K_La - Volumetric mass transfer coefficient, s^{-1}
N_A- Mass flux, $mol.m^{-3}.s^{-1}$
Ppm - Part per million
T-Temperature, ^0C
t - Time, sec
TDS - Total dissolved salt, gr/litUG= Superficial gas velocity based on riser, $cm.s^{-1}$

Greek letters

ρ= Liquid density, $g.cm^{-3}$

5. References

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