

# Intensification of the rate of heavy metal removal from industrial effluents by cementation on a reciprocating array of vertical parallel plates

A.H. Elshazly

Chemical Eng. Dept., Faculty of Eng., Alexandria University, Alexandria, Egypt  
Elshazly\_a@yahoo.com.

The rate of  $\text{Cu}^{++}$  removal from synthetic waste solution by cementation on an array of oscillating parallel vertical plates of zinc was studied under different conditions of frequency and amplitude of vibration (vibration intensity), initial copper ion concentration, separation between zinc plates, and temperature. The activation energy of the reaction was found to be 20 kcal/gmole which shows that the reaction is under mixed control conditions. Under the present range of conditions it was found that pulsation increased the rate of cementation by a factor ranging from 2.75 to 4.8 compared to the value without pulsation. The data were correlated by the following overall mass transfer correlation  $Sh = 5.2 \cdot Sc^{0.33} Re^{0.6} (B/L)^{-0.75}$  في البحث تم دراسة معدل التخلص من أيونات النحاس الموجودة في مخلف صناعي مخلق باستخدام تقنية السمطة على أسطح مجموعة من الألواح المصنوعة من الزنك و الموضوعة في شكل رأسي متوازية وواقعة تحت تأثير حركة ترددية وذلك تحت ظروف مختلفة من السعة و التردد أو (شدة السرعة الترددية)، التركيز الابتدائي لأيونات النحاس في المحلول ، المسافات البينية بين ألواح الزنك و درجة الحرارة. أيضا تم حساب طاقة التنشيط بالنسبة للتفاعل ووجد انها حوالي ٢٠ كيلو سعر/جرام مول مما يوضح ان التفاعل محكوم بخطوتى الانتشار و التفاعل الكيميائي . أيضا أتضح من النتائج ان استخدام الحركة الترددية أدى الى زيادة معدل انتقال المادة و السمطة بمعامل يتراوح بين ٢,٧٥ الى ٤,٨ مقارنة بحالة عدم استخدام الحركة الترددية. كذلك تم استنتاج معادلة عامة لانتقال المادة خلال هذه العملية عن طريق استخدام التحليل الابعدي والتي اتخذت الصورة التالية:

$$Sh = 5.2 Sc^{0.33} Re^{0.6} (B/L)^{-0.75}$$

**Keywords:** Waste water, Cementation, Copper recovery, Mass transfer, Pulsation

## 1. Introduction

The adoption of hydrometallurgical processes which make use of chemical reactions in aqueous phase at room or moderate temperatures for the winning or extraction of metals from metallurgical wastes or other industrial waste solutions have been steadily increasing in the recent years. Conventional methods of recovery of metals from purified leach liquors, include, electro-winning from aqueous solutions, gaseous reduction by hydrogen, chemical precipitation of metal compounds and cementation,. In cementation a less noble metal is used to displace a more noble metal from its metal ions. Because of its importance in the recovery of metal values from metallurgical wastes and low-grade ores, considerable work has been done to understand the fundamentals of cementation which is applicable not only for recovery of metallic values from leach liquors

of any concentration but also has been extensively used for purification of leach liquors prior to recovery by other methods [1]. Waste solutions containing  $\text{Cu}^{++}$  (toxic) are produced in industrial processes such as pickling of copper and its alloys, electroplating rinsing solutions, engraving, printed circuit etching solutions, etc.

Since copper cementation on less noble metals is a diffusion controlled process[1], different authors have used different methods to enhance the rate of mass transfer and the rate of cementation such as rotating disc [2,3], rotating cylinders [4], agitated vessels [5], gas sparging [6], fixed and fluidized beds [7]. The objective of the present work is to study the effect of pulsation on the rate of removal and or recovery of cupric ions from industrial waste solutions by cementation using pulsated array of zinc sheets (vertical parallel plates). Little work has been done on the effect of vibration on cementation .The

kinetic behavior of the cementation of Ag from an industrial waste solution of  $\text{Ag}(\text{CN})_2^-$  with granulated spherical zinc in vibrating reactor was investigated by Ornelas et al. [8], they reported that vibration leads to a considerable increase in the rate of cementation. Ashari et al. [9,10] who studied the effect of vibration on the rate of cementation of copper on scrap iron and on the purification of zinc electrolyte from more noble metals with granular zinc found that both reaction time and consumption of the reducing agent were diminished. The rate of copper recovery from industrial waste solution by cementation on reciprocating horizontal perforated zinc disc was investigated by Mubarak et al. [11], it was found that disc pulsation increased the rate of cementation by a factor which ranged from 2.8 to 5.5 compared to cementation on stagnant disc.

Podesta et al. [12], who studied the effect of vibration on the rate of liquid solid mass transfer at a vibrating disc found that, for a given velocity vibrating discs produce higher rates of mass transfer than rotating discs i.e vibrating motion is more effective in enhancing solid liquid mass transfer than rotary motion.

## 2. Experimental technique

Fig. 1 shows the experimental setup used in the present study, it consisted of the vibrating system and the reactor which consisted of an array of three parallel vertical plates (F), each plate had 3cm width and 6 cm height. The three plates were fixed to a horizontal insulated stainless steel wire by welding each plate at its top to the stainless steel wire. The horizontal stainless steel holder was welded to a vertical insulated stainless steel stem (E). The parallel plate array was placed in a plastic container containing 6 liter  $\text{CuSO}_4$  solution. Stainless steel parts and welded parts were isolated by epoxy resin. The upper end of the stem was connected to the vibrator (D) through a teflon sleeve. Vertical oscillation was induced to the plates by means of mechanical vibrator connected to the upper end of the stem. The mechanical vibrator (D) consisted of disc rotated by means of a variable speed electrical motor (A). The rotating motion of the disc was transferred

into a reciprocating motion by means of a crank shaft connected to the disc at a distance from its center. The frequency of vibration was measured by means of a portable digital tachometer and changed by means a set of pulleys and gear box (C) connected to the electrical motor (A). Amplitude was adjusted by adjusting the distance between the rotating disc center and the point of its connection with the crank shaft. The rate of cementation of copper on pulsated zinc sheets was followed by measuring the change in concentration of cupric ions with time. Before each run six liters of fresh copper sulphate solution were placed in the column, in the mean time solution was subjected to oscillation at the required vibration intensity, samples of the solution (5ml) were withdrawn at regular time intervals, the intervals ranged from 2 minutes to 3 minutes at high and low vibration intensities respectively. The samples were analysed by iodometry [13]. The mass transfer coefficient was calculated from the concentration time data as shown in fig. 2, four different concentrations of copper sulphate solution were used in the present work 0.01, 0.05, 0.10, 0.15 M, all solutions were prepared using A.R. chemicals and distilled water. Experiments were carried out at temperatures ranging from 25 to 40°C. A digital portable pH meter was used to fix the pH of the solution at 4.4.

## 3. Results and discussion

The present study was conducted in a simple batch reactor where the rate of reaction is given by [14,15].

$$V_s \frac{dC}{dt} = -KAC,$$

which upon integration yields:

$$V_s \int_{C_0}^C \frac{dC}{C} = -KA \int_0^t dt$$

$$V_s \ln \left[ \frac{C_0}{C} \right] = KA t .$$

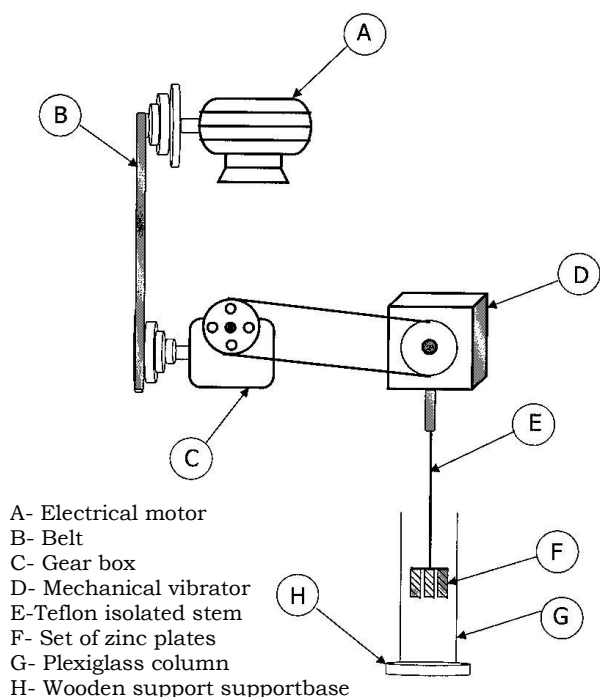


Fig. 1. Experimental apparatus.

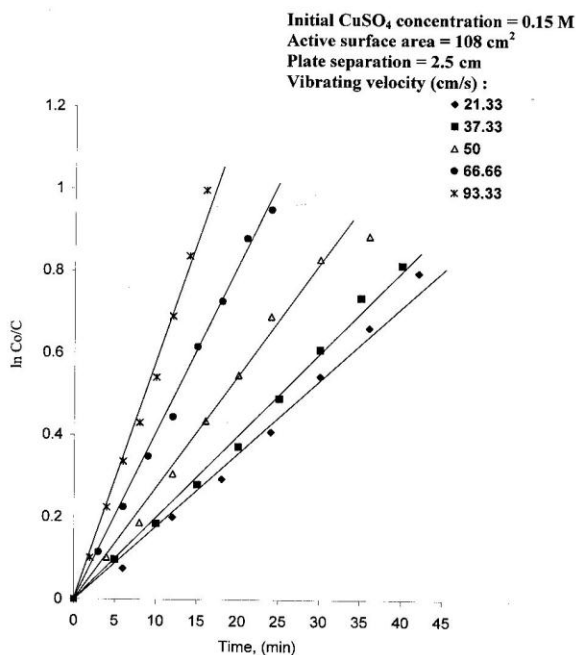


Fig. 2.  $\ln C_0/C$  vs. time at different vibrating intensities.

where,  $V_s$  is the solution volume in the reactor;  $C_0$  &  $C$  are initial  $\text{CuSO}_4$  concentration and concentration at any time  $t$ ;  $A$  is the

active surface area of the zinc sheets and  $t$  is the time of reaction. The mass transfer coefficient of the cementation reaction was obtained under different conditions by plotting

$\ln C_0/C$  vs. time as shown in fig. 2, the slope of the resulting straight line gives  $(KA / V_s)$  from which the mass transfer coefficient can be calculated.

Fig. 3 shows that by increasing the frequency and amplitude of oscillation or vibration intensity  $V_i$  ( $V_i=4A_m f$ ), the value of the mass transfer coefficient and cementation rate increases. This may be attributed to the fact that plates oscillation gives rise to oscillatory flow [16,17], which reduces the thickness of the hydrodynamic boundary layer and the diffusion layer at the surface of zinc sheets. The increase in the rate of cementation with vibration can be also explained by the stretched film effect [18], this effect attributes the enhanced transfer coefficient resulting from the vibration of solid surfaces at high frequencies and small amplitude to the formation of a film of the diffusing species. The area of this film corresponds to the total area swept out during each period and is thus larger than the active area of the solid liquid interface. Also it has to be mentioned that visually observed copper deposits on zinc plates were in the form of powder especially at higher vibration intensities; it is probable that the surface roughness resulting from powder formation induces the generation of turbulent eddies which contribute to enhancing the rate of cementation. Fig. 4 shows that by increasing the initial copper sulphate concentration, at a given vibrating intensity, the mass transfer coefficient increases. At first sight this result seems surprising in view of the decrease in the diffusivity of  $\text{Cu}^{++}$  with increasing  $\text{Cu}^{++}$  concentration [19] which should lead to a decrease in the mass transfer coefficient with increasing  $\text{Cu}^{++}$  concentration. It seems that the increase in the mass transfer coefficient with increasing  $\text{Cu}^{++}$  concentration arises as a result of the formation of rough deposits on the oscillating plate surface at high  $\text{Cu}^{++}$  concentrations [20]. As mentioned above, Surface roughness enhances the rate of mass transfer through promoting turbulence generation at the oscillating plates [21]. In addition, according to the electrochemical

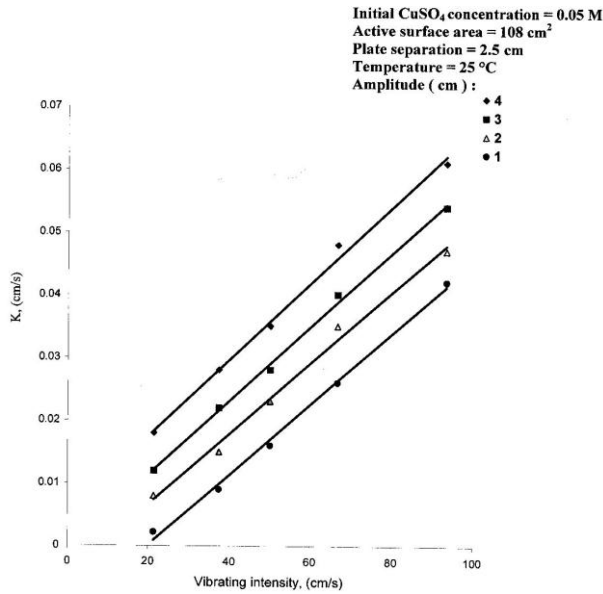


Fig. 3. Mass transfer coefficient vs. vibrating intensity at different amplitudes.

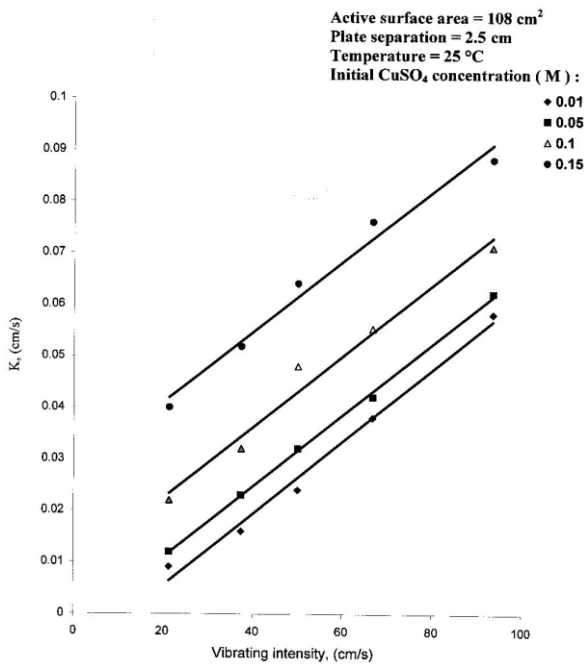


Fig. 4. Mass transfer coefficient vs. vibrating intensity at different initial CuSO<sub>4</sub> concentrations.

theory of cementation which postulates that cementation takes place through the galvanic cell: Zn/ electrolyte/ Cu, increasing the cathode area via copper powder formation would

decrease polarization and consequently would increase the rate of cementation.

Fig. 5 shows the relation between the mass transfer coefficient and the vibrating intensity at different zinc plates separation which ranged from 1 - 2.5 cm, it is seen that the mass transfer coefficient increases with decreasing plates separation. The fact that the mass transfer coefficient increases with decreasing sheets separation may be ascribed to the decrease in cross sectional area (free area) between sheets ( $S=W*B$ ), this causes the solution velocity of the induced secondary flow resulting from plate oscillation inside these free regions to increase with a consequent decrease in the thickness of the hydrodynamic boundary layer and the diffusion layer in the vertical direction. This increases the rate of mass transfer and the cementation rate.

Fig. 6 shows the relation between the mass transfer coefficient and the vibrating intensity at different temperatures ranging from 25 - 40 °C. It is clear that the increase in temperature at a given vibration velocity increases the value of the mass transfer coefficient. This may be attributed to the increase in the value of the diffusion coefficient according to Stokes-Einstein equation:

$$D\mu/T = \text{constant}$$

Where;  $D$  is the diffusion coefficient;  $\mu$  is the solution viscosity; and  $T$  is the absolute temperature. The increase in  $D$  increases the mass transfer coefficient ( $K=D/\delta$ ). Where;  $\delta$  is the thickness of the hydrodynamic boundary layer. Fig. 7 shows that the data fits Arrhenius equation [22]:

$$K = A_0 e^{-E/RT}$$

The activation energy of the reaction was found to be 20 Kcal/gmol, which shows that the reaction is under mixed control conditions.

Dimensional analysis was used to correlate the present data, the mass transfer coefficient can be related to other variables by the functional equation:

$$Sh = a Sc^a Re_v^\beta (B/L)^\gamma$$

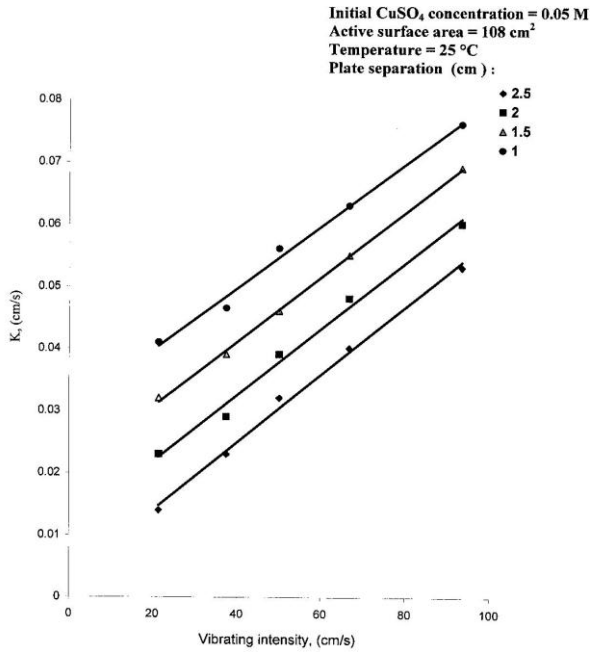


Fig. 5. Mass transfer coefficient vs. vibrating intensity at different plates separation.

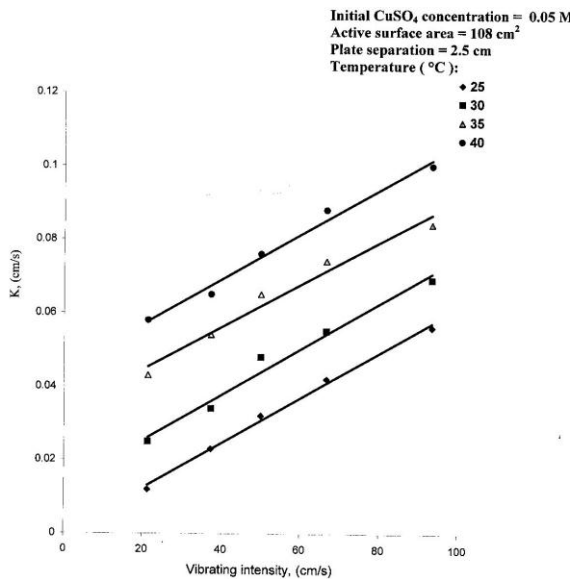


Fig. 6. Mass transfer coefficient vs. vibrating intensity at different temperatures.

According to previous theoretical and experimental studies of mass transfer [23, 24] the value of  $\alpha$  was fixed at 0.33, figs. 8 and 9 show that the value of  $\beta$  and  $\gamma$  are 0.6 and -0.75 respectively; fig. 10 shows that the present data fit the equation:

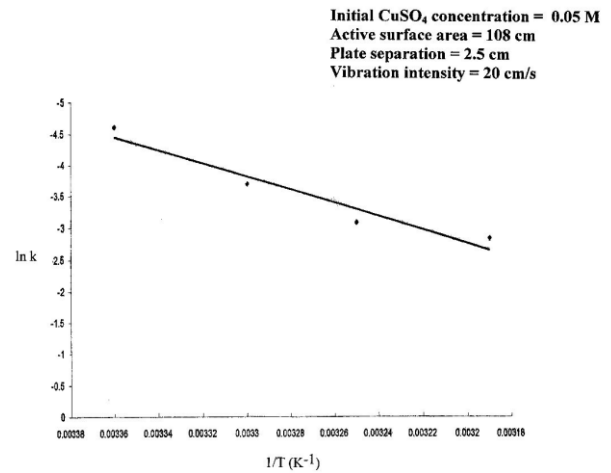


Fig. 7.  $\ln k$  Vs  $1/T$ .

$$Sh = 5.2 * Re_v^{0.6} Sc^{0.33} (B/L)^{-0.75},$$

with an average deviation of  $\pm 15\%$ . The above correlation is valid for the following conditions:

$$0.16 < B/L < 0.4, 14342 < Re_v < 33620 \text{ and } 1327 < Sc < 1401.$$

The length of the pulsated zinc sheet was used as a characteristic length in calculating  $Re_v$  and  $Sh$  numbers.

Comparison between the mass transfer behavior of pulsating vertical array of parallel plate obtained in this research and pulsating horizontal perforated disc obtained by Mubarak et al. [11] is shown in fig. 11, which indicates that the rate of mass transfer has been increased by higher values using horizontal perforated zinc disc this may be attributed to the higher turbulence generated by using perforated discs, however the simple geometry of array of parallel plates and the ease with which the product (copper powder) can be collected make it more attractive in building cementation reactors.

#### 4. Conclusions

The present study has revealed that surface oscillation is a powerful tool for enhancing the rate of cementation of metals

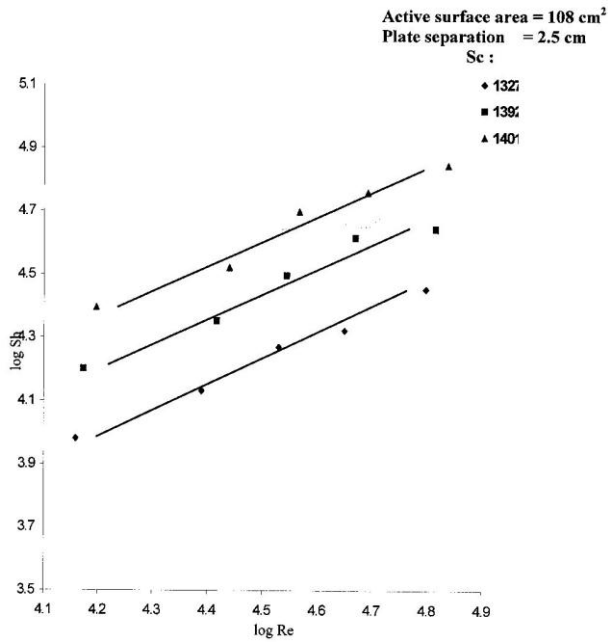


Fig. 8.  $\log Sh$  vs.  $\log Re$  at different  $Sc$ .

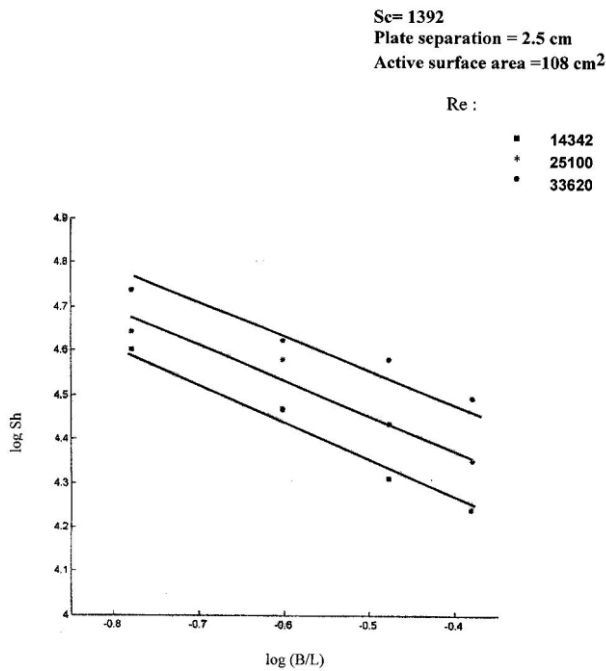


Fig. 9.  $\log Sh$  vs.  $\log (B/L)$  at different  $Re$ .

on an array of vertical parallel plate reactor. The rate of cementation increase with increasing vibration intensity, initial concentration of  $Cu^{++}$  and temperature, the rate of cementation

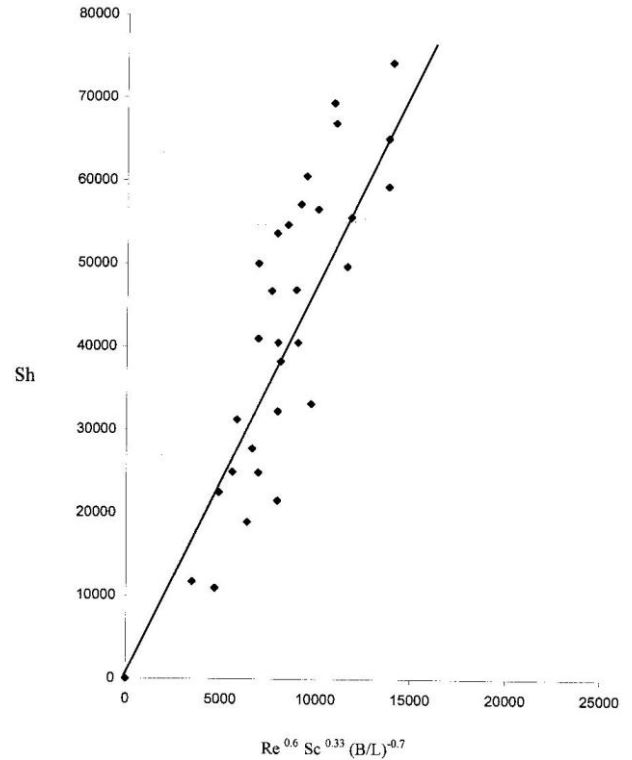


Fig. 10. Overall mass transfer correlation for cementation of copper at vibrating set of zinc plates in a batch reactor.

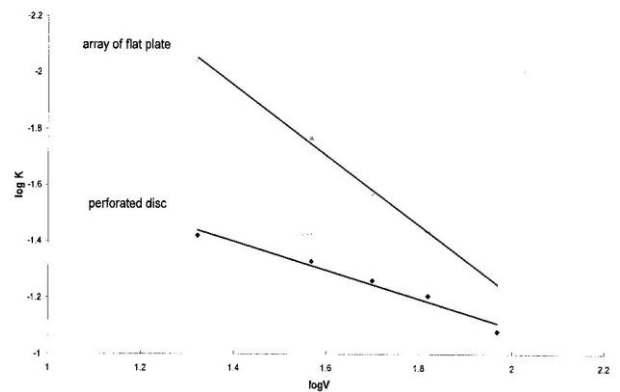


Fig. 11. Comparison between the mass transfer behavior of a pulsating vertical array of parallel plates and pulsating horizontal perforated disk.

increased also with decreasing plate separation in the array. The present results suggest the use of oscillating parallel plate array in the design of industrial high space-time yield cementation reactor. The present dimensionless mass transfer correlation can be used in the design and operation of the suggested reactor.

**List of symbols**

$A$	is the active surface area of the oscillating zinc sheets,
$A_m$	is the amplitude of oscillation,
$A_o$	is the constant in Arrhenius equation,
$B$	is the plate separation,
$C_o, C$	is the initial $CuSO_4$ concentration and concentration at any time,
$D$	is the solution diffusivity,
$E$	is the activation energy,
$f$	is the frequency of oscillation,
$K$	is the mass transfer coefficient,
$L$	is the length of zinc sheet,
$R$	is the gas constant,
$t$	is the time,
$T$	is the absolute temperature,
$V_i$	is the vibration velocity (Intensity). ( $V_i = 4A_m f$ ),
$V_s$	is the solution volume,
$W$	is the width of zinc sheet,
$Re_v$	is the Vibrational Reynolds number ( $\rho V_i L / \mu$ ),
$Sc$	is the Schmidt number ( $\mu / \rho D$ )
$Sh$	is the Sherwood number ( $KL / D$ ),
$\rho$	is the solution density,
$\mu$	is the solution viscosity, and
$\delta$	is the diffusion layer thickness.

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