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Removal of Copper from Wastewater by Cementation Utilizing Iron Beads Packed Bed

By

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Abstract

By cementation process, the removal of copper from wastewater was investigated experimentally. Apparatus was utilized the packed bed of iron spheres. Analysis was made based on the film theory with first irreversible reaction at the packing surface. Findings are that many deep pits are produced in the surface of beads by cementation, and the effective interficial area is about 2.3 times of perfect smooth surface of packed beads. J factor of mass transfer can be presented by $J_D=2.6Re_p^{-0.5}$.

Introduction

Cementation is widely used in the mining industry, where dissolved noble metal is recovered from solution by exchange with less noble metal. Recently, cementation has received attention in the treatment of wastewater issuing from metal finishing and hydrometalluagy, as a means for removal of toxic metals[11] and studies have been made on the kinetics of reactions [1,3,4,7–9,12,17]. Richard and Fuerstenau[13] have been attempted to clarify the mechanism of copper cementation by iron.

Extent of copper removal by cemntation was investigated experimentally by an iron spheres packed bed as a model of scrap iron packed tower. Few investigations[16] have been undertaken for the cementation with packed bed system. Analysis was made based on the film theory with first order irreversible reaction[13] ($Fe + Cu^{2+} \rightarrow Fe^{2+} + Cu$) at the packing surfaces.

Experimental

The column was made of Pylex glass packed with iron spheres, and was 2.56cm in I.D. and 8.0~50.0cm in length. Four different sizes of iron particles (d_p=0.446, 0.200, 0.156 and 0.080 cm) were utilized to examine the effect of particle size. When copper sulfate solution as a simulated wastewater (25ppm and 100ppm as concentration of copper ion) was flowing through the iron spheres packed bed, removal of copper ion was measured. The concentraion of copper ion was determined by Atomic-absorption spectrophotometer. The solution was in the range of pH between 3.8 and 4.6 and its temperature was regulated at 30°C. The interstitial linear velocity was changed at the range of 0.1 to 1.5cm/sec, therefore, the Reynolds number, based on the particle diameter, ranged from 1.0 to 50.

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Analysis

Based on film theory[15], Cu^{2+} balance gives Eqs. (1) and (2).

$$u_i \frac{dC}{dZ} = K_L \cdot a(C_s - C), \tag{1}$$

$$K_L \cdot a(C_s - C) = K_C \cdot C_s, \tag{2}$$

where C and C_s are Cu^{2+} concentrations of bulk flow and of the stagnant film. k_L and k_C are mass transfer coefficient and kinetic constant. a is the effective interficial area (per bed volume). a is $(6/d_p)(1-\epsilon)$ for sphere, having ragular surface. u_i is interstitial linear velocity. The cementation reaction of Cu^{2+} + Fe is kown to approximated by irreversible first order reaction[13]. With the boundary conditions of $C^{out}=(C)_{Z=Lz}$ and $C^{in}=(C)_{Z=0}$, one gets the conversion, $f=C^{out}/C^{in}$ as Eq. (3).

$$f = C^{out}/C^{in} = \exp\left(-K_L \cdot a \times \frac{L_z}{u_i} \times \frac{K_c}{K_L \cdot a + K_c}\right) \tag{3}$$

For Cu^{2+} + Fe system, the conversion is kown to be controlled mainly by mass transfer, since the reaction at the iron surface is very fast[13] ($K_C >> K_L$).

Equation (3) can be written simply as Eq. (4) by this information.

$$f = \exp\left(-K_L \cdot a \times \frac{L_z}{u_i}\right) \tag{4}$$

By Eq. (4), mass transfer coefficient k_L can be calculated from experimental a, L_z, u_i and $f=C^{out}/C^{in}$.

Results and Discussion

The calculated mass transfer coefficient was plotted as J_D factor $(k_L \times S_c^{2/3}/u_i)$ against Re_p number $(d_p \times u_i/\nu)$ in Fig. 1.

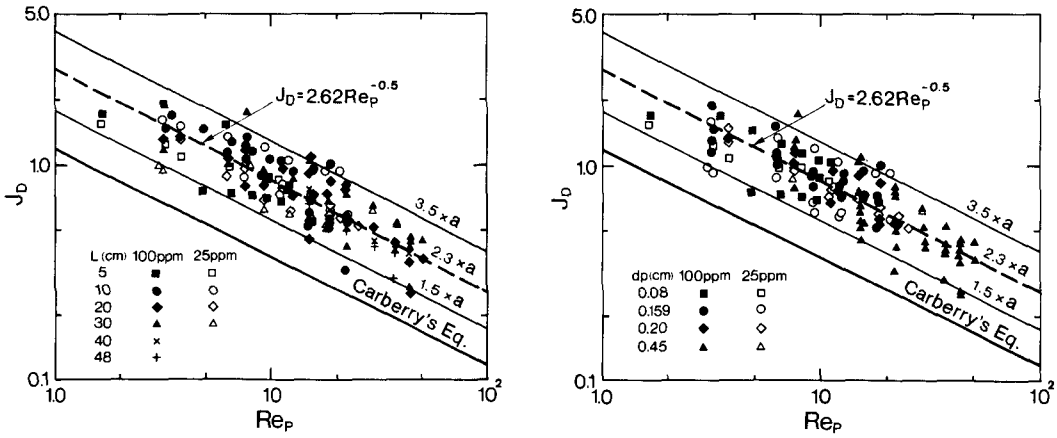

Fig. 1 Plots of J_D against Re_p

Carberry's equation[2] is also shown with the solid line in the figure. The experimental value of J_D factor is larger than that of Carberry's equation. This tendency may explained as follows. The iron spheres used have smooth surfaces and so, as the effective interficial area of packed bed, a was assumed to equal $(1-\epsilon)\times 6/d_p$ in the analysis. However, in a cementation system, the surface of sphere becomes uneven immediately after dissolution of iron and cementation of copper to iron spheres are initiated.

Figure 2 shows photograph taken by a microscope (magnification, ×600). Initial copper ion concentration was 100ppm. Surface of an iron sphere used (2.0mm in diameter) in a cementation experiments is shown. The deep irregular pits are clearly visible. The surface of iron sphere becomes pitted. Some cement product adhered to the iron sphere in patches.

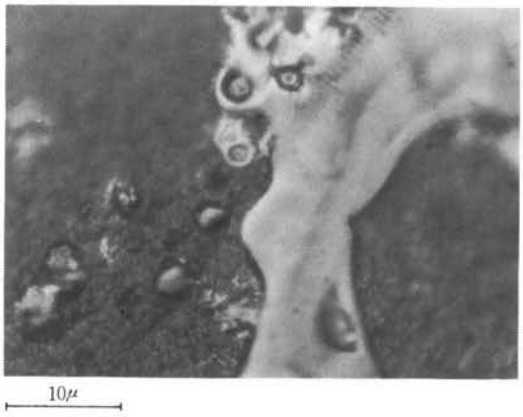

Fig. 2 Surface of an iron sphere used in a cementation

The effective interficial area seems to increase. The dotted line indicates Cabbery's equation for the case when the effective interficial area is increased by 2.3 times of regular surface area. The experimental cementation data show good agreement with the dotted line. This agreement indicates that the pits may increase the effective interficial area of iron sphere surface. However, though the pits become deeper with longer cementation time, the effective interficial area remains from 1.5 to 3.5 times of a perfectly smooth surface area of sphere. For the case when a is raised by the factor of 2.3, J_D can be presented as Eq. (5).

$$J_D = 2.6\, Re_p^{-0.5} \tag{5}$$

Increase in diffusivity owing to electric field in the mass transfer film may be negligible, since Fe^{2+} and Cu^{2+} have almost the same diffusivity[5,6]. The bed length varied from 5.0cm to 50cm. The experimental J_D factor was influenced by the bed length. The experiment at two different initial concentrations (25ppm and 100ppm) was also attempted. The value of J_D factor was not evidently affected by change of the initial concentration.

The experimental data have scattering in some degree, the scattering may be explained as follows. Bed length L_z may affect J_D factor in the cementation over Carberry's model. Irregurality of the sphere surface may change for the axial direction of the bed length, accompanied with the proceeding of the cementation reaction. The decrease in pH during cementation, side reactions concerning H^+ are reported[11, 13, 16], may also be related.

Conclustion

From the preceding experiment and discussion, following conclusions can be drawn concerning copper cementation by iron. Many deep pits are produced in the surface of spheres by

cementation, and the effective interficial area is about 2.3 times of packed beads, where surfaces have perfectly smooth. For the Cu-Fe cementation system, J_D can be presented by Eq.(5). Equation (5) is very useful for the design of packed bed in order to remove copper ion from wastewater by the cementation process.

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Nomenclature

a	= effective interficial area	[cm^2/cm^3]
C	= concentration of copper ion in bulk flow	[$meq./cm^3$]
C_S	= concentration of copper ion at the stagnent film	[$meq./cm^3$]
D	= diffusivity of copper ion	[cm^2/sec]
d_p	= diameter of packed bead	[cm]
f	= conversion	[–]
J_D	= J factor of mass transfer	[–]
k_C	= kinetic constant	[l/sec]
k_L	= mass transfer coefficient	[cm/sec]
L_z	= bed length	[cm]
Re_p	= Reynolds number ($=d_p u_i/\nu$)	[–]
S_c	= Schmidt number ($=\nu/D$)	[–]
u_i	= interstitial linear velocity	[cm/sec]
z	= distance of axial direction	[cm]
ϵ	= void fraction	[–]
ν	= kinematic viscosity	[cm^2/sec]

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