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Feasibility of Recovering High Valency Metal Cyanide Complexes with a Fluidized Bed of Resin

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ABSTRACT

A commercially available strong base ion-exchange resin IRA 958 was used to recover polyvalent metal cyanide complexes in a fluidized-bed application. A method for modeling the expansion of a fluidized bed of resin is proposed. The method takes into account the difficulties associated with the hydrodynamic characteristics of a macroporous resin of this nature.

INTRODUCTION

The recovery of metal cyanides from the effluent of mineral processing plants has been of interest to engineers for many years. Cyanide, which has been used for the leaching of gold for most of this century, has the preference to combine with many transition metals, forming mono-, di-, and polyvalent metal cyanide complexes. Although cyanide is poisonous to all life forms, its natural attenuation in the environment is well understood and normally follows a predictable mechanism. Free cyanide is rapidly destroyed in the presence of ultraviolet light, while weak complexes, e.g., $Zn(CN)_4^{2-}$ and $Cd(CN)_3^-$, tend to destruct relatively quickly. Moderately strong to strong complexes, such as $Cu(CN)_4^{3-}$, $Co(CN)_6^{4-}$, $Ni(CN)_4^{2-}$, and $Fe(CN)_6^{4-}$, which form readily under suitable conditions and are found in great abundance in the effluent of mineral processing plants, can exist in the environment for up to 5 years. Smith and Mudder (1) published the average concentrations of transition metals in the effluent of mineral processing plants throughout the world, and from their data it is clear that *copper* and *iron* are responsible for the holdup of free cyanide. This conclusion is reached when cyanide holdup is defined on the basis of the product of their (copper, iron) average global concentrations in the effluent, and the stoichiometric number of cyanide molecules which will attach when an excess of free cyanide is present.

As the pH of any cyanide-bearing mineral slurry has to be elevated to prevent the formation of HCN, only strong-base resins can be considered for the removal of metal cyanides. Research carried out in recent years (2) has shown that it is possible to selectively adsorb metal cyanides onto strong-base resins on the basis of polyatomic valency. The triethyl-ammonium functional group has a greater affinity for the mono- and divalent metal cyanides, while the trimethyl-ammonium functional group tends to adsorb the polyvalent metal cyanides more readily. As iron and copper form polyvalent metal cyanides in the presence of an excess of free cyanide, it is clear that only a resin with the trimethyl-ammonium functional group should be considered.

The poor desorption performance of metal cyanides from strong-base resins has been an obstacle to the commercial use of the ion-exchange route for cyanide retrieval. However, it was evident from initial tests that IRA958 strong-base resin, which has an acrylic matrix and a macroreticular pore structure, is able to adsorb and desorb these polyvalent metal cyanides fairly easily. IRA958 currently sees application in sugar refining plants, where its chief function is the adsorption of large organic molecules (de-ashing) similar in size and nature to metal cyanide complexes.

Attempting adsorption in a fluidized bed has the advantages of improved kinetics and a semicontinuous process operation (e.g., Streat–Cloete column) (3). Being able to predict the expansion of a fluidized bed of resin is essential for the purposes of designing a receptacle to hold the resin and for determining the ion-exchange duty that can be expected from such a fluidized bed. Despite a profusion of literature on the modeling of the expansion of a fluidized bed of particles, two characteristics of a fluidized bed of *resin* are not clearly addressed. The reticular nature of the resin bead would imply that the resin bead should primarily display an apparent density under fluidizing conditions, which would be impossible to measure using standard gravimetric means, and secondly would result in difficulty with the determination of the free wet-settled voidage. Both of these values are essential for the application of the *Serial model* (4) and for predict-ing the bed expansion of any fluidized particles, which have the tendency to display particulate or smooth fluidization.

ADSORPTION

The cyanide complexes of nickel, iron, copper, and cobalt were adsorbed separately onto IRA958 in batch stirred tank reactors and in the presence of excess cyanide. The transition metal concentrations used were similar to the average concentrations found in the effluent of mineral processing plants throughout the world, and the amount of resin used was sufficient to adsorb approximately 66% of the metal cyanides present. The metal cyanides of iron and nickel were manufactured by the dissolution of their cyanide salts, while the solutions of cobalt and copper cyanide complexes were the result of the dissolution of their potassium salts in the presence of excess cyanide.

The adsorption process was repeated in the presence of 1000 ppm sulfate. Sulfate, like the metal cyanides complexes, is a polyatomic anion, and according to data published by Smith and Mudder (1), is present in high concentrations in mineral processing effluent. It is clear from Fig. 1 that all the polyvalent metal cyanides are readily and quickly adsorbed.

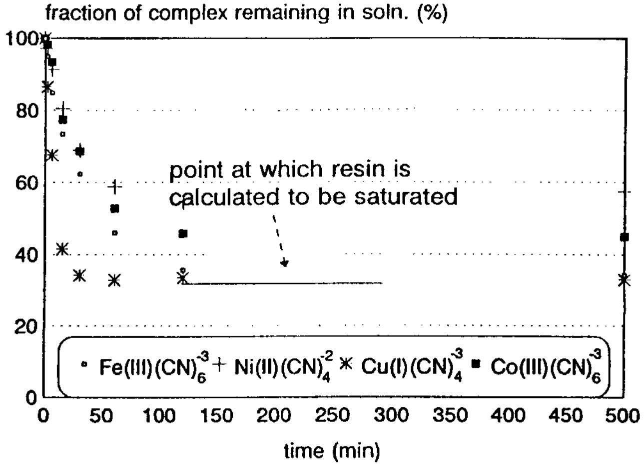

FIG. 1 Adsorption profiles of metal cyanides onto IRA 958. Initial concentration of Fe = 108.1 ppm, Ni = 91.52 ppm, Co = 138.4 ppm, Cu = 385.1 ppm; volume of wet-settled resin = 2 mL; volume of reactor = 1.5 L.

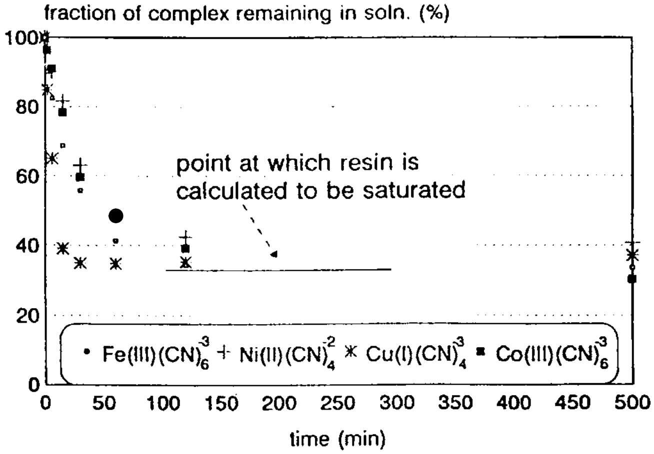

FIG. 2 Adsorption profiles of metal cyanides onto IRA 958 in the presence of 1000 ppm sulfate. Initial concentration of Fe = 105.8 ppm, Ni = 96.59 ppm, Co = 134.4 ppm, Cu = 375.6 ppm; volume of wet-settled resin = 2 mL; volume of reactor = 1.5 L.

The observation can also be made that the divalent nickel cyanide complex is not adsorbed quite as easily, which is in line with the previously stated affinity characteristics of the trimethyl-ammonium group. From Fig. 2 it is apparent that the addition of 1000 ppm sulfate only marginally affects the adsorption process, hence one may conclude that despite the presence of large amounts of sulfate in solution, IRA958 could still be used to adsorb metal cyanides.

DESORPTION

The loaded resins were regenerated separately in the same stirred tank reactors used for the adsorption process. Unlike other general purpose strong-base resins, i.e., IRA420, and IRA900, most of the metal cyanide complexes were readily and rapidly removed from IRA958. Figure 3 shows the desorption of the nickel, copper, cobalt, and iron cyanide complexes, with analytical grade 2 M sodium chloride solution used as an eluant. It is significant that this level of regeneration is achieved after only a single batch contact with the eluant. The regeneration exercise was repeated (Fig. 4). However, on this occasion a 2 M brine solution was used. Once again, most cyanide complexes were rapidly and readily removed, verifying that in normal industrial operation IRA958 could be safely and cheaply regenerated.

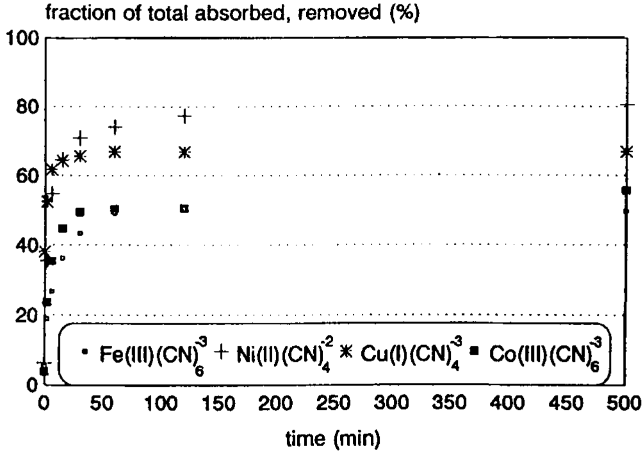

FIG. 3 Desorption profiles of metal cyanides from IRA 958 using NaCl (analytical grade). Loading of resin: Fe = 0.001 mole, Ni = 0.0008 mole, Co = 0.001 mole, Cu = 0.001 mole; volume of wet-settled resin = 5 mL; volume of reactor = 1.5 L.

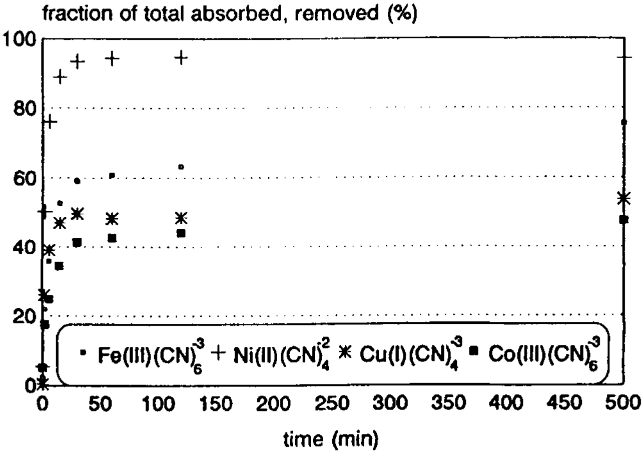

FIG. 4 Desorption profiles of metal cyanides from IRA 958 using brine. Loading of resin: Fe = 0.00128 mole, Ni = 0.0008 mole, Co = 0.0008 mole, Cu = 0.0009 mole; volume of wet-settled resin = 4.5 mL; volume of reactor = 1.5 L.

FLUIDIZATION CHARACTERISTICS

The Levenspiel criterion (5) for determining fluidization stability suggests that resin beads fluidized by an aqueous medium will tend to exhibit particulate or smooth fluidization. The design and construction of a fluidized-bed reactor would require optimization, or at least determination, of the constraints of the linear fluidization velocity. A flow would have to be established at a velocity not exceeding the terminal velocity of the smallest resin bead in the least dense state, and not less than the minimum fluidization velocity of the largest bead.

The *Serial Model*

The *Serial model* describes the relationship between the expansion of a multi-species fluidized-bed and the linear liquid velocity, given the physical properties of the solid particles and the fluidization medium. It assumes that the overall expansion of a heterogenous particulately fluidized-bed of particles is simply the sum of the individual expansions that each species would display, if fluidized separately, by the same parameters.

Equation (1) is based on Richardson and Zaki's approach (6) and describes the expansion characteristics of a mono-species, homogeneously fluidized-bed, and from which the expansion component for a given linear liquid velocity may be calculated by Eq. (2).

$$u/u_t = e^n \tag{1}$$

where u = empty tube linear fluid velocity ($e = 1$) [m/s]
u_t = particle terminal velocity [m/s]
e = voidage
n = an empirical parameter which is function of particle Galileo number

$$EF = \frac{1 - e}{1 - e_{fws}} \tag{2}$$

where EF = expansion component (1 = no expansion; 2 = 100% expansion)
e_{fws} = free wet settled voidage

If the theory on which the *Serial model* is based is applied to resin, the overall bed expansion component should be equal to the sum of the individual expansion components advanced by the various resin size fractions, thus:

$$EF_t = \left[\sum_{i=dp_s}^{i=dp_l} V_i(EF_i - 1)\right] + 1 \tag{3}$$

where V_i = the volume fraction of the ith particle size
dp_l = the largest particle size
dp_s = the smallest particle size
EF_t = total bed expansion
EF_i = the expansion component of the ith resin size

The terminal velocity and n value for the individual resin sizes, both of which are required by Eq. (1), can be calculated from the following published empirical relationships (6, 7):

$$\mathrm{Ga} = 18\mathrm{Re}_t + 2.7\mathrm{Re}_t^{1.687} \qquad (3.6 < \mathrm{Ga} < 10^5) \tag{4}$$

$$n = \left[5.5 + 23\frac{d}{d_t}\right]\mathrm{Ga}^{-0.075} \qquad (21 < \mathrm{Ga} < 2.4 \times 10^4) \tag{5}$$

$$\mathrm{Ga} = \frac{d^3 g(\rho_s - \rho)\rho}{\mu^2} \tag{6}$$

$$\mathrm{Re}_t = \frac{\rho d v_t}{\mu} \tag{7}$$

where Re_t = particle Reynolds number at terminal velocity
ρ_s = apparent density of resin [kg/m^3]
ρ = density of fluidizing fluid [kg/m^3]
d = diameter of bead [m]
d_t = diameter of containing vessel [m]
μ = viscosity of fluidizing fluid [kg/ms]
v_t = terminal velocity of bead [m/s]
g = gravitational acceleration [m/s^2]
Ga = Galileo number

With the exception of *resin density* and *free wet-settled voidage*, all of the parameters listed are easily measurable. As the resin has a macroreticular structure (sponge) where the liquid phase is continuous throughout the pores of the individual beads, it is impossible to use a gravimetric approach to determine the true wet density of the resin or the voidage of the settled bed. To overcome this problem, a technique was used which comprised of fitting the *Serial model* to expansion versus linear velocity data by searching for the free wet-settled voidage and apparent resin density for an optimal sum of squares. The method of Hook and Jeeves was used to locate the best fit parameters.

Other data required by the *Serial model* are the particle size distribution, measured by multiple screen analysis, while the density and viscosity of the fluidizing medium can be calculated from liquid temperature. Figure 5 is the logic diagram of that section of the algorithm which covers the iterative check utilized by the Hook Jeeves routine to determine best direction for parameter improvement.

Fluidization Testwork

IRA958 resin was fluidized in a 40-mm diameter column of about 1000 mm in length, the bottom of which was closed off by a sintered glass of about 17–40 μm in diameter. For loading and fluidizing purposes, a solution of $Fe(III)(CN)_6^{3-}$ was pumped by a peristaltic pump from a 1-L reservoir to the bottom of the column, and then returned from the top of the column back to the reservoir in a closed circuit. To acquire raw expansion versus flow-rate data at a specific loading, a measured amount of $Fe(III)(CN)_6^{3-}$ was added to the reservoir and the solution allowed to circulate through the resin bed for 20 hours to ensure that all the metal cyanide is adsorbed by the resin. With the liquid and solid phases in dynamic equilibrium, accurate expansion versus linear vertical liquid velocity data could be acquired.

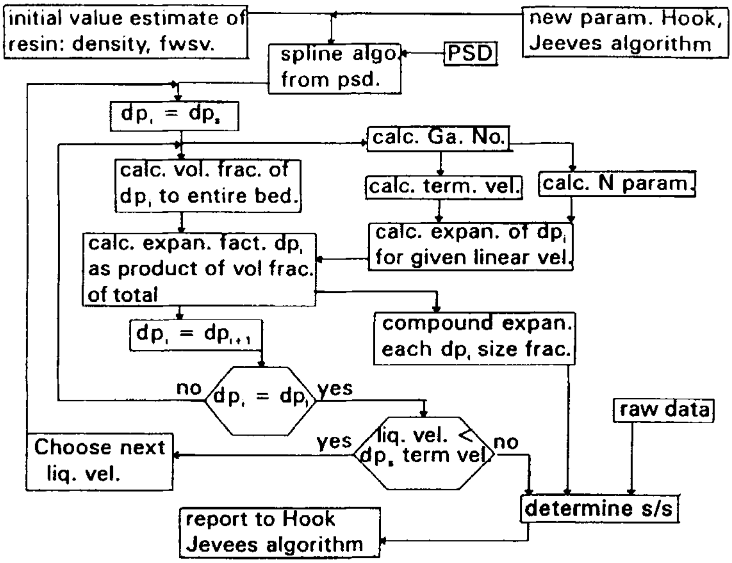

FIG. 5 Logic diagram.

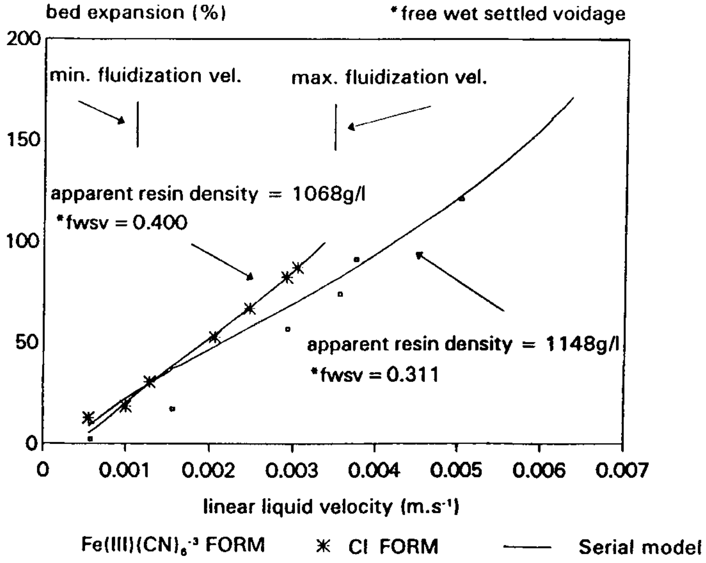

FIG. 6 Expansion versus liquid velocity.

The Fe(III)(CN)$_6^{3-}$ metal cyanide ion was chosen as the loading ion, primarily because of its abundance in the effluent and secondly because of the ease with which its presence can be determined on the basis of solution color. Furthermore, it has a higher mass per equivalent than Cu (CN)$_4^{3-}$, the other most abundant metal cyanide, which means that during loading the expected larger density change would result in greater variations to the fluidization characteristics of the resin. Figure 6 presents the results of the expansion behavior of IRA958 in the Cl$^-$ and Fe(III) (CN)$_6^{3-}$ forms, including the fitted *Serial model.* As can be predicted, there is a large difference in the curves, mainly as a result of altered density and free wet-settled voidage.

CONCLUSION

It is clear from the study presented in this paper that if the ion-exchange route for the removal and/or recovery of metal cyanide ions is to be pursued, the use of Amberlite IRA-958 resin may well be a feasible alternative. It is envisaged that a mineral plant effluent, after undergoing semiclarification (e.g., bank of hydrocyclones), might be contacted with IRA-958 resin in a semicontinuous fluidized-bed application before disposal on the slimes dam or tailing pond.

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