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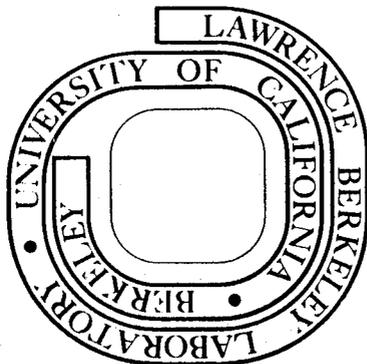
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Minimum Concentration Attainable in a
Porous Flow-Through Electrode Reactor

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Abstract

The minimum concentration attainable in a porous flow-through reactor is estimated by applying the thermodynamics of electrochemical cells with a knowledge of the maximum reactor operating potential. This predicted concentration is the equilibrium wall concentration at the back of the reactor and is qualitatively compared to the experimentally measured minimum average bulk values observed by various authors for the deposition of copper, silver, lead, and mercury, and for the oxidation of ferrous ions. It is suggested that a knowledge of the current versus reactor operating potential will elucidate lower limits observed for any metal system. In particular, the case of antimony removal is discussed.

1. Introduction

The removal of heavy metals from industrial wastes by porous flow-through electrode reactors is promising, though not yet proved to be technologically and economically feasible. Encouraging results have been obtained in studies [1,2,3] on the removal of various metals and in comparisons [4,5] to other electrochemical reactors.

On the other hand, there are results which are less encouraging. In the removal of lead ions the authors [6] have had difficulty in reducing the effluent concentration below 0.5 mg/l. In the work of Kuhn and Houghton [7], the concentration of antimony was reduced from 100 mg/l in the feed to a dilute product concentration not lower than 5 mg/l. This apparent limit was explained as being the equilibrium concentration at which deposition and dissolution of antimony occurs at the same rate.

The purpose of this paper is to suggest a criterion by which one may estimate the minimum attainable dilute product concentration given the maximum operating potential, or given a desired dilute product concentration the minimum value of the operating potential at which this dilute product concentration can be achieved, thus providing a basis for design and operation.

In the design of electrochemical reactors, it is desirable to avoid side reactions. Such reactions occur if

the potential variation in the solution exceeds a certain limit. Since a characteristic of porous flow-through electrode reactors is the non-uniform ohmic potential drop, the potential may not be set arbitrarily high. The maximum operating potential is that potential which may be maintained in the reactor at which an appreciable side reaction does not occur. This can be determined experimentally by measuring the current versus the potential of the cathode or anode current collector relative to a given reference electrode placed in the effluent stream (VOP). This value VOP_{max} may then be used to predict the lower limit of removal of the reactant ion in a porous flow-through electrode reactor.

2. Analysis

To calculate the minimum attainable concentration in a porous flow-through electrode reactor, using the values of VOP_{max} , one can construct mentally an electrochemical cell which consists of the working electrode and the given reference electrode. An expression for the open-circuit cell potential U may then be derived using thermodynamics if the following assumptions are made:

- 1) The reactor has been run sufficiently long that metal deposition of the reactant has occurred.
- 2) Equilibrium exists between the reacting species and the deposited metal.

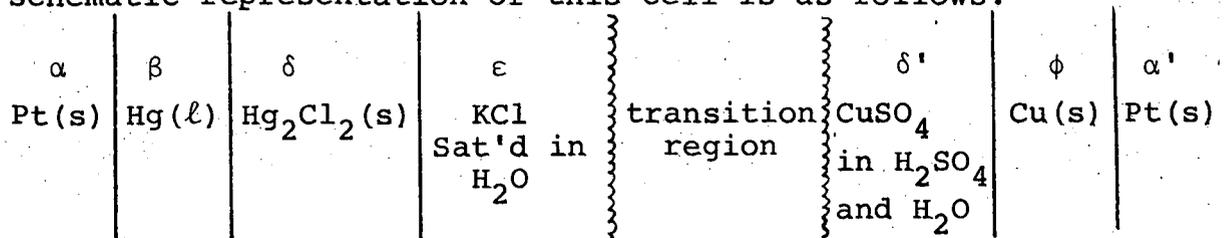
3) The molecular and ionic forms of the reacting species are known.

The value of VOP_{\max} is then substituted for U , and the equilibrium wall concentration for a particular reacting species is obtained. The total equilibrium wall concentration is simply the sum of all the reacting species which are in equilibrium with the deposited metal. This calculated value will be lower than the actual effluent concentration because of a lack of equilibrium at the downstream end of the reactor due to a nonzero reaction rate and electrode kinetic and mass-transfer limitations.

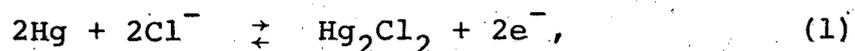
The following examples will help to clarify the method.

2.1 Copper Deposition from Sulfate Solutions

Bennion and Newman [1] have obtained the current-potential behavior of a porous carbon reactor used in the removal of copper from sulfate solutions. From their data, a value of VOP_{\max} equal to -0.25 V may be chosen. A schematic representation of this cell is as follows:



where the reaction at the left electrode is



and one possible reaction at the right electrode is



An expression for the open-circuit cell potential U may be derived using the thermodynamics of electrochemical cells, for example, see Newman [8a]. For this cell, the open-circuit cell potential was found to be

$$\begin{aligned} FU = FU^\theta + \frac{1}{2} RT \ln \frac{c_{\text{Cu}^{2+}} c_{\text{Cl}^-, \text{sat}}^2}{\rho_o^3} + \frac{1}{2} RT \ln f_{\text{Cu}^{2+}, \text{Cl}^-} \\ + F(\Phi^\delta - \Phi^{\delta'}), \end{aligned} \quad (3)$$

where

$$FU^\theta = \mu_{\text{Hg}}^o - \frac{1}{2} \mu_{\text{Cu}}^o - \frac{1}{2} \mu_{\text{Hg}_2\text{Cl}_2}^o + \frac{1}{2} RT \ln \lambda_{\text{Cu}^{2+}, \text{Cl}^-}^\theta. \quad (4)$$

Thus, the value of the standard cell potential for this cell at 25°C is

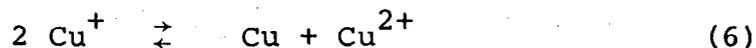
$$U^\theta = 0.337 \text{ V} - 0.2676 \text{ V} = 0.0694 \text{ V}.$$

Omission of the activity coefficient and liquid junction potential terms (the fourth and fifth terms) in equation (3) will result in a satisfactory estimate of the equilibrium copper concentration. With these considerations equation (3) may be re-arranged to yield an expression for the equilibrium cupric concentration as follows:

$$c_{\text{Cu}^{2+}} = \frac{\rho_0^3}{c_{\text{Cl}^-, \text{sat}}^2} \exp\left(\frac{2F}{RT} \Delta V_k\right) = 9.07 \times 10^{-13} \text{ mole/l} \quad (5)$$

where U has been set equal to VOP_{max} , $\Delta V_k = VOP_{\text{max}} - U^\theta$, and $c_{\text{Cl}^-, \text{sat}} = 4.17 \text{ moles/l}$.

As was mentioned previously, the deposition of copper from cupric ions is not the only equilibrium electrode process. Cuprous ions are also in equilibrium with both the deposited copper and the cupric ions. The equilibrium cuprous concentration can be calculated as was done earlier for the cupric ions. However, cuprous ions disproportionate according to



The equilibrium constant for this reaction is [8b]

$$\frac{c_{\text{Cu}^+}^2 f_{\text{Cu}^+}^2}{c_{\text{Cu}^{2+}} f_{\text{Cu}^{2+}} \rho_0} = \frac{1}{1.67 \times 10^6} \frac{\text{mole}}{\text{Kg}} \quad (7)$$

With neglect of activity coefficients the equilibrium cuprous concentration is found to be:

$$\begin{aligned} c_{\text{Cu}^+} &= \left(c_{\text{Cu}^{2+}} \rho_0 / 1.67 \times 10^6 \frac{\text{Kg}}{\text{mole}} \right)^{1/2} \\ &= 7.359 \times 10^{-10} \frac{\text{moles}}{\text{l}} \end{aligned} \quad (8)$$

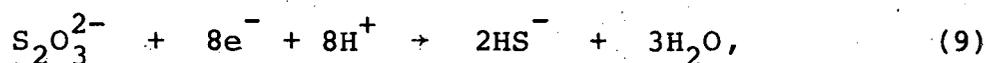
Therefore the total equilibrium copper concentration is

$$(c_{\text{Cu}})_{\text{total}} = c_{\text{Cu}^{2+}} + c_{\text{Cu}^+} = 7.37 \times 10^{-10} \text{ moles/l}$$

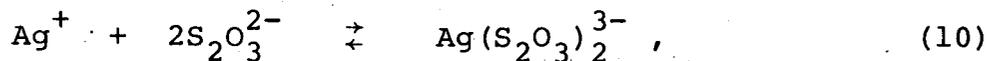
or $4.68 \times 10^{-5} \text{ mg/l}$.

2.2 Silver Deposition From Photographic Fixing Solutions

Van Zee and Newman [2] have obtained the current-potential behavior of a porous carbon reactor used for removing silver from photographic fixing solutions. From their data, a value of $VOP_{\text{max}} = -0.46 \text{ V}$ was chosen due to appreciable side reaction, thought to be



which occurs at a significant rate for more extreme values of VOP. Silver ions in solutions containing thiosulfate form a very stable complex [9]:

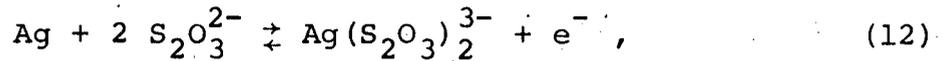


which has a value of the stability constant β_2 of approximately [9]:

$$\beta_2 = \frac{f_{\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}} c_{\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}} \rho_0^2}{f_{\text{Ag}^+} c_{\text{Ag}^+} \left(f_{\text{S}_2\text{O}_3^{3-}} c_{\text{S}_2\text{O}_3^{3-}} \right)^2}$$

$$= \frac{\lambda^\theta_{\text{Ag}^+} \left(\lambda^\theta_{\text{S}_2\text{O}_3^{2-}} \right)^2}{\lambda^\theta_{\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}}} = 1.7 \times 10^{13} \left(\frac{\text{Kg}}{\text{mole}} \right)^2 \quad (11)$$

Therefore, it will be necessary to consider the deposition of silver from the silver-thiosulfate complex:



which has an expression for the standard electrode potential

$$\begin{aligned} F U_{\text{Ag}/\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}}^\theta &= \frac{1}{2} \mu_{\text{H}_2}^* - \mu_{\text{Ag}}^\circ - 2 RT \ln \lambda_{\text{S}_2\text{O}_3^{2-}}^\theta \\ &+ RT \ln \lambda_{\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}}^\theta / \lambda_{\text{H}^+}^\theta . \end{aligned} \quad (13)$$

The value for $U_{\text{Ag}/\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}}^\theta$ may be calculated from the value of the stability constant of the species $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ and the standard electrode potential of the non-complexed silver deposition reaction:



The expression for the standard electrode potential is

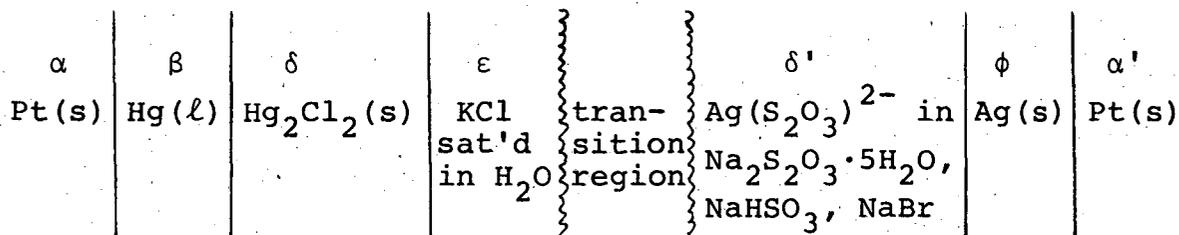
$$F U_{\text{Ag}/\text{Ag}^+}^\theta = \frac{1}{2} \mu_{\text{H}_2}^* - \mu_{\text{Ag}}^\circ + RT \ln \lambda_{\text{Ag}^+}^\theta / \lambda_{\text{H}^+}^\theta \quad (15)$$

where $U_{\text{Ag}/\text{Ag}^+}^\theta = 0.7991 \text{ V}$. Equations (13) and (15) lead to

$$\begin{aligned} U_{\text{Ag}/\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}}^\theta &= U_{\text{Ag}/\text{Ag}^+}^\theta - \frac{RT}{F} \ln \beta_2 \\ &= 0.0164 \text{ V} , \end{aligned} \quad (16)$$

which indicates that silver will be much more difficult to plate in the presence of thiosulfate ions due to hydrogen evolution.

A schematic of the electrochemical cell which consists of a silver-silver thiosulfate electrode and the calomel reference electrode is as follows:



An expression for the equilibrium $\text{Ag(S}_2\text{O}_3\text{)}^{2-}$ concentration as a function of VOP may be derived as was done previously for the copper system. This expression with neglect of activity coefficients and the liquid junction potential is

$$c_{\text{Ag(S}_2\text{O}_3\text{)}_2^{3-}} = \frac{c_{\text{S}_2\text{O}_3^{2-}}^2}{c_{\text{Cl}^-,\text{sat}}} \exp\left(\frac{F}{RT} \Delta V_k\right), \quad (17)$$

where $\Delta V_k = \text{VOP} - U_{\text{Ag/Ag(S}_2\text{O}_3\text{)}_2^{3-}}^\theta + U_{\text{cal}}^\theta$. For $c_{\text{S}_2\text{O}_3^{2-}} = 1.737 \text{ moles/l}$ and $\text{VOP}_{\text{max}} = -0.46 \text{ V}$, the value of the equilibrium silver concentration is $2.14 \times 10^{-4} \text{ moles/l}$ or 23 mg/l of silver.

2.3 Mercury Removal from Brine Solutions

This example combines aspects of the previous two examples, i.e., multiple electrode reaction equilibria and complexing. Mercuric ions Hg^{2+} form very stable chloride complexes with stability constants of the form

$$\beta_\epsilon = \frac{f_{\text{HgCl}_\epsilon}^f c_{\text{HgCl}_\epsilon}^{2-\epsilon} c_{\text{HgCl}_\epsilon}^{2-\epsilon}}{f_{\text{Hg}^{2+}}^f c_{\text{Hg}^{2+}} \left(f_{\text{Cl}^-}^c c_{\text{Cl}^-} \right)^\epsilon} = \frac{a_{\text{Hg}^{2+}}^\theta \left(a_{\text{Cl}^-}^\theta \right)^\epsilon}{a_{\text{HgCl}_\epsilon}^\theta} \quad (18)$$

which have values: $\ln \beta_1 = 12.2$, $\ln \beta_2 = 29.4$, $\ln \beta_3 = 32.0$, and $\ln \beta_4 = 34.3$ [10]. The mercurous dimer Hg_2^{++} does not complex appreciably in chloride solutions [11].

Table 1 lists the expressions and values for the standard electrode potentials of mercury. The standard electrode potentials involving the complexed species were calculated using the above stability constant data. For example, entries 6 and 8 were calculated from entries 2 and 1, respectively, using the value of β_4 as follows:

$$U_{\text{Hg}/\text{HgCl}_4}^\theta = U_{\text{Hg}/\text{Hg}^{2+}}^\theta - \frac{RT}{2F} \ln \beta_4 \quad (19)$$

$$U_{\text{Hg}_2^{++}/\text{HgCl}_4}^\theta = U_{\text{Hg}_2^{++}/\text{Hg}^{2+}}^\theta - \frac{RT}{F} \ln \beta_4 \quad (20)$$

Expressions for the equilibrium mercuric chloride complex concentrations as a function of VOP may be derived as was

done in previous examples:

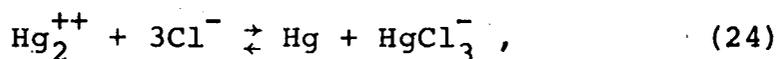
$$c_{\text{HgCl}_2} = \frac{c_{\text{Cl}^-}^2}{c_{\text{Cl}^-, \text{sat}}^2} \exp \left(\frac{2F}{RT} \Delta V_k \right), \quad (21)$$

$$c_{\text{HgCl}_3^-} = \frac{c_{\text{Cl}^-}^3}{c_{\text{Cl}^-, \text{sat}}^2} \exp \left(\frac{2F}{RT} \Delta V_k \right), \quad (22)$$

$$c_{\text{HgCl}_4^{2-}} = \frac{c_{\text{Cl}^-}^4}{\rho_o c_{\text{Cl}^-, \text{sat}}^2} \exp \left(\frac{2F}{RT} \Delta V_k \right), \quad (23)$$

where ΔV_k refers to the electrode reaction involving the appropriate mercuric complex (activity coefficient corrections and the liquid junction potential were neglected).

The expressions for the species HgCl^+ and Hg^{2+} are not given since their contribution to the equilibrium mercury concentration is negligible in comparison with the highly complexed species. The equilibrium concentration of the mercurous dimer may be related to the mercuric chloride complex concentrations by the appropriate disproportionation reaction. For example, consider the reaction



with the result

$$c_{\text{Hg}_2^{++}} = \frac{\rho_o^3 c_{\text{HgCl}_2^-}}{c_{\text{Cl}^-}^3} \exp \left[\frac{2F}{RT} \left(U_{\text{Hg}_2^{++}/\text{HgCl}_3^-}^\theta - U_{\text{Hg}/\text{HgCl}_3^-}^\theta \right) \right]. \quad (25)$$

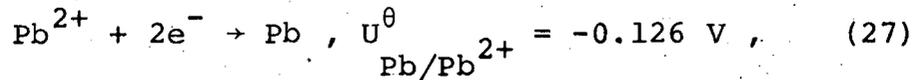
From entries 5 and 7 of Table 1,

$$c_{\text{Hg}_2^{++}} = \frac{\rho_o^3 c_{\text{HgCl}_3^-}}{c_{\text{Cl}^-}^3} (2.08 \times 10^{-12}) \text{ mole/l}, \quad (26)$$

and may therefore be neglected from further consideration. Preliminary data on this system have been obtained by the authors [12] in a porous carbon reactor. For a feed concentration of 4.12 mg/l of mercury, a value of $VOP_{\text{max}} = -0.46 \text{ V}$ was found, with $c_{\text{Cl}^-} = 4.35 \text{ moles/l}$ in the brine. Substituting these values into equations (21) through (23) yields a total mercuric concentration of $1.36 \times 10^{-14} \text{ mg/l}$, the complex HgCl_4^{2-} predominating. Under these conditions equation (25) or (26) yields the estimate of the mercurous dimer as $1.52 \times 10^{-27} \text{ mg/l}$.

2.4 Lead Removal from Lead-Sulfate Solutions

A preliminary study has been made on this system by the authors [6]. An expression for the equilibrium lead ion concentration may be obtained by considering the working electrode reaction to be



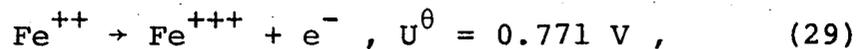
with the result

$$c_{\text{Pb}^{2+}} = \frac{\rho_o^3}{c_{\text{Cl}^{-}, \text{sat}}^2} \exp\left(\frac{2F}{RT} \Delta V_k\right). \quad (28)$$

For a feed concentration of lead of 4.32 mg/l a maximum operating potential VOP_{max} was found to be -0.56 V. Substituting this value into equation (28) yields an equilibrium lead ion concentration of $c_{\text{Pb}^{2+}} = 1.35 \times 10^{-7}$ mole/l or 0.028 mg/l of lead.

2.5 Oxidation of Ferrous Ion

Adams, Hollandsworth, and Bennion [13] have studied ferrous oxidation on a porous carbon electrode from a dilute stream containing 1.43 g/l of H_2SO_4 . On an inert carbon electrode, only the following redox reaction need be considered:



where the equilibrium ferrous composition may be estimated from

$$c_{\text{Fe}^{++}} = \frac{c_{\text{Fe}^{+++}} c_{\text{Cl}^{-}, \text{sat}}}{\rho_o} \exp\left(\frac{-F}{RT} \Delta V_k\right) \quad (30)$$

if the ferric composition is known. If the reactor is long enough, the reaction (equation (29)) will have gone to complete conversion except for the equilibrium composition exiting at a particular value of the operating potential. Thus, for a feed composition of 705 mg/l ferrous ion and a maximum value of the operating potential of $VOP_{\max} = 0.7 \text{ V}$, the equilibrium ferrous concentration may be estimated to be $c_{\text{Fe}^{++}} = 1.4 \text{ mg/l}$.

2.6 Experimental Minimum Concentration

The minimum wall concentration calculated in sections 2.1 to 2.5 must be compared with the minimum bulk average concentration leaving the reactor because the equilibrium wall concentration is not easily measured. Table 2 lists the measured minimum bulk concentration obtained by various authors in porous flow-through electrode reactors. Also, shown are the predicted minimum wall concentrations for these systems which were calculated in sections 2.1 to 2.5 for the experimental values listed in the table.

The experimental bulk concentration will approach the predicted wall concentration values if the reaction is carried to a greater degree of completion. This may be achieved by reducing the flowrate, while holding VOP constant, making the electrode thicker, or adding additional reactors operating with equal values of VOP.

The discrepancies which exist between the predicted minimum wall concentration and the experimental bulk values may be explained as follows. For copper removal, the reactor was designed to operate with a mass-transfer limitation to remove copper from 667 mg/l to 1 mg/l, and not to remove all the copper. For mercury removal, the experimental minimum bulk concentration of less than 5×10^{-3} mg/l reported in Table 2 is due to the limitations of the analytical technique used for detecting mercury. For the operating potential reported, samples obtained from the dilute product stream of the reactor contained no detectable mercury. For ferrous oxidation only, the predicted minimum wall concentrations is greater than the observed bulk value. Adams et al. report that the current measured for this system is greater than that based on the feed composition ($i = nF v c_f$) at current efficiencies approaching 100 percent. One explanation presented by these authors is the oxidation of ferrous species by oxygen, a reaction which is catalyzed on a graphite surface. For silver, the agreement is good; it should be noted that effluent values as low as 0.8 mg/l were achieved at VOP values as extreme as -0.55 V, but with a considerable loss of current efficiency due to side reactions.

3. The Removal of Antimony

As mentioned earlier, Kuhn and Houghton [7] have reported an apparent limit in the removal of antimony from aqueous solutions using a porous flow-through electrode reactor. Application of the criterion suggested in previous sections using the data of Kuhn and Houghton [7] is not possible since their study was one of transient response and no steady-state current-potential data were provided. However, qualitative information about their experiments allows a thermodynamic analysis to be undertaken which indicates that a minimum exists in the antimony concentration as a function of VOP.

3.1 Analysis

The chemistry of antimony in aqueous solutions is quite complex, and many molecular and ionic species are possible. Kuhn and Houghton [7] report that in their experiments the oxidation state of the dissolved antimony species was plus three. Table 3 lists the standard electrode potentials of various antimony species which are known to exist in the plus three oxidation state (values of which have been calculated from thermodynamic data [14] or found tabulated in the literature [15]). Stability data indicate that Sb(OH) , and SbO^+ are the most probable species and that Sb^{+++} rarely exists except under extremely acidic conditions [11]. Expressions for the equilibrium wall concentration as a function of VOP for each of the antimony species may

be derived as before and are also given in Table 3.

3.2 Results

Figure 1 depicts the dependence on VOP of the equilibrium wall concentration of the various antimony species found in Table 3, where the concentration of hydrogen ion has been set to 1 mole/l. The solid line represents the total equilibrium antimony concentration if all of these species are present in solution.

The minimum exhibited by the total antimony concentration is due to the evolution of stibine (SbH_3) in a minus three valence state at high cathodic potentials (negative values of VOP). This supposition is supported qualitatively by the data of Kuhn and Houghton [7], who report stibine evolution and low current efficiencies. The low current efficiencies are due to cell operation at too high cathodic potentials where both the evolution of stibine and hydrogen are appreciable. However, quantitatively the estimated equilibrium wall concentration (shown in Figure 1) lies thirteen orders of magnitude below the reported bulk value. As discussed earlier, the bulk value will exceed equilibrium value somewhat because of electrode-kinetic and mass-transfer limitations; however, a large discrepancy does exist. This may be explained by considering the range of potential at which the predicted equilibrium wall concentration is less than or equal to the measured bulk value (5 mg/l). Calculations (using the expressions

found in Table 3) indicate that this range of potential is $-0.655 \leq \text{VOP} \leq -0.130 \text{ V}$. Since Kuhn and Houghton [7] operated their cell galvanostatically, their cell potential could vary over a wide range. To resolve the question of the practical lower limit attainable for antimony removal, careful, controlled-potential, steady-state experiments will be required.

4. General Considerations

As discussed earlier, the bulk concentration of the reactant species will approach the equilibrium wall concentration predicted by thermodynamics if the reactor is made thicker or additional reactors are placed in series. This may be seen quantitatively by considering the analysis presented by Bennion and Newman [1] for a reactor operating at the limiting current.

For reactions carried to a high degree of completion the maximum allowable potential variation across a reactor was found to be

$$|\Delta\phi|_{\text{max}} = \frac{nF v^2 c_f}{a k_m \kappa} \quad (31)$$

This equation shows that the ohmic potential drop across a reactor is directly proportional to the feed concentration. In the copper recovery process of Bennion and Newman [1]

a value of the operating potential VOP may be chosen to be -0.25 V (the potential at the fluid outlet). If their reactor were operating at the design specification, $|\Delta\phi|_{\max} = 0.2 \text{ V}$, the driving force at the front of the reactor would be -0.45 V. The data indicate that the magnitude of this value does not produce appreciable side reactions -- thus if this driving force could be maintained throughout the depth of the reactor the effluent concentration will ultimately be reduced. With this in mind, the ultimate value of VOP is then -0.45 V. Equations (5) and (8) then yield an estimate of the lowest attainable equilibrium wall concentration for copper of $1.94 \times 10^{-8} \text{ mg/l}$.

To achieve this in practice consider reactors placed in series: if for example the concentration in the first reactor has been reduced by 99 percent, then the total current density in the second reactor ($i = nF v c_f$) will be smaller resulting in a reduction in the ohmic potential drop (see equation 31), and the electrode potential can be maintained closer to -0.45 V throughout the second reactor.

This also applies to short reactors where the reaction rate is non-zero at the back of the reactor resulting in an appreciable surface overpotential, thereby producing a wall concentration higher than the equilibrium value. Increasing the reactor thickness will also decrease the wall concentration toward the equilibrium value if the counterelectrode and current collector are placed upstream

(or if the matrix conductivity is high) [16].

5. Conclusions

A criterion has been suggested for determining the minimum concentration attainable in a porous flow-through electrode reactor. This may be done by measuring the current-potential behavior of the working electrode relative to a given reference electrode placed in the dilute product stream. Thermodynamics may then be applied, and the equilibrium wall concentration of the reactant species can be estimated. Comparison of this concentration with the experimentally observed bulk concentration suggests that the procedure is essentially correct, although the effluent concentration will be higher than that calculated if the reactor thickness is small and mass-transfer and electrode-kinetic limitations still exist at the fluid outlet.

Measurement of the reactor operating potential in this manner should help to clarify lower limits observed in flow-through electrochemical reactors. It should also aid in the design of reactor systems, since information on the allowable potential variation across the reactor is provided.

Acknowledgment

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Notation

a	specific interfacial area, cm^{-1}
a_i^θ	$= \lambda_i^\theta / \rho_o$ property expressing the secondary reference state, liter/mole
c_i	molar concentration of species i , mole/liter
$c_{\text{Cl}^-, \text{sat}}$	concentration of chloride ion in a saturated calomel reference electrode compartment
f_i	molar activity coefficient of species i
$f_{i,n}$	$= f_i / f_n^{z_i/z_n}$ molar activity coefficient of species i referred to the ionic species n
F	Faraday's constant, 96, 487 C/equiv.
k_m	coefficient of mass transfer between flowing solution and electrode surface, cm/s
n	number of electrons involved in electrode reaction
R	universal gas constant, 8.3143 J/mole-deg
T	absolute temperature, deg K
U	open-circuit cell potential, V
U_k^θ	standard electrode potential for electrode reaction k , V
VOP	potential of the cathode current collector relative to a given reference electrode placed in the dilute product stream, V
$(\text{VOP})_{\text{max}}$	maximum value of VOP at which appreciable side reaction does not occur, V

$$\Delta V_k \quad \text{VOP} - U_k^\theta + U_{\text{cal}}^\theta$$

Greek Letters

β_ϵ overall stability constant, where ϵ denotes the number of ligand in the complex, (liter/mole) ^{ϵ} or (kg/mole) ^{ϵ}

κ effective conductivity of solution, mho/cm

λ_i absolute activity of species i

λ_i^θ property expressing secondary reference state, kg/mole

$\lambda_{i,n}^\theta = \lambda_i^\theta / \lambda_n^\theta z_i^{z_n}$ property expressing secondary reference state of species i referred to ionic species n

μ_i electrochemical potential of species i , J/mole

ρ_0 density of pure solvent, g/cm⁻³

Φ quasi-electrostatic potential, V

$|\Delta\Phi|_{\text{max}}$ maximum allowable ohmic drop across a porous flow-through electrode reactor operating at the limiting current, V

Superscripts

o pure state

θ secondary reference state at infinite dilution

$*$ ideal-gas secondary reference state

Subscripts

f feed

sat saturated

cal calomel

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Table 1. Standard electrode potentials of mercury referred to the hydrogen electrode. Aqueous solutions at 25°C.

Reaction	FU^θ	U^θ , volt
1) $\text{Hg}_2^{++} \rightarrow 2\text{Hg}^{2+} + 2e^-$	$\frac{1}{2} \mu_{\text{H}_2}^* - \frac{1}{2} RT \ln \lambda_{\text{Hg}_2^{++}}^\theta + RT \ln \lambda_{\text{Hg}^{2+}}^\theta / \lambda_{\text{H}^+}^\theta$	0.920
2) $\text{Hg} \rightarrow \text{Hg}^{2+} + 2e^-$	$\frac{1}{2} \mu_{\text{H}_2}^* - \frac{1}{2} \mu_{\text{Hg}}^\circ + \frac{1}{2} RT \ln \lambda_{\text{Hg}^{2+}}^\theta / \left(\lambda_{\text{H}^+}^\theta\right)^2$	0.8545
3) $2\text{Hg} \rightarrow \text{Hg}_2^{++} + 2e^-$	$\frac{1}{2} \mu_{\text{H}_2}^* - \mu_{\text{Hg}}^\circ + \frac{1}{2} RT \ln \lambda_{\text{Hg}_2^{++}}^\theta / \left(\lambda_{\text{H}^+}^\theta\right)^2$	0.789
4) $\text{Hg} + 2\text{Cl}^- \rightarrow \text{HgCl}_2 + 2e^-$	$\frac{1}{2} \mu_{\text{H}_2}^* - \frac{1}{2} \mu_{\text{Hg}}^\circ - RT \ln \lambda_{\text{Cl}^-}^\theta + \frac{1}{2} RT \ln \lambda_{\text{HgCl}_2}^\theta / \left(\lambda_{\text{H}^+}^\theta\right)^2$	0.4768
5) $\text{Hg} + 3\text{Cl}^- \rightarrow \text{HgCl}_3^- + 2e^-$	$\frac{1}{2} \mu_{\text{H}_2}^* - \frac{1}{2} \mu_{\text{Hg}}^\circ - \frac{3}{2} RT \ln \lambda_{\text{Cl}^-}^\theta + \frac{1}{2} RT \ln \lambda_{\text{HgCl}_3^-}^\theta / \left(\lambda_{\text{H}^+}^\theta\right)^2$	0.4434
6) $\text{Hg} + 4\text{Cl}^- \rightarrow \text{HgCl}_4^{2-} + 2e^-$	$\frac{1}{2} \mu_{\text{H}_2}^* - \frac{1}{2} \mu_{\text{Hg}}^\circ - 2RT \ln \lambda_{\text{Cl}^-}^\theta + \frac{1}{2} RT \ln \lambda_{\text{HgCl}_4^{2-}}^\theta / \left(\lambda_{\text{H}^+}^\theta\right)^2$	0.4138
7) $\text{Hg}_2^{2+} + 6\text{Cl}^- \rightarrow 2\text{HgCl}_3^- + 2e^-$	$\frac{1}{2} \mu_{\text{H}_2}^* - \frac{1}{2} RT \ln \lambda_{\text{Hg}_2^{2+}}^\theta \left(\lambda_{\text{H}^+}^\theta\right)^2 - RT \ln \left(\lambda_{\text{Cl}^-}^\theta\right)^3 / \lambda_{\text{HgCl}_3^-}^\theta$	0.09787
8) $\text{Hg}_2^{2+} + 8\text{Cl}^- \rightarrow 2\text{HgCl}_4^{2-} + 2e^-$	$\frac{1}{2} \mu_{\text{H}_2}^* - \frac{1}{2} RT \ln \lambda_{\text{Hg}_2^{2+}}^\theta \left(\lambda_{\text{H}^+}^\theta\right)^2 - RT \ln \left(\lambda_{\text{Cl}^-}^\theta\right)^4 / \lambda_{\text{HgCl}_4^{2-}}^\theta$	0.03852

Table 2. Experimental minimum bulk concentration and predicted minimum wall concentration for various systems.

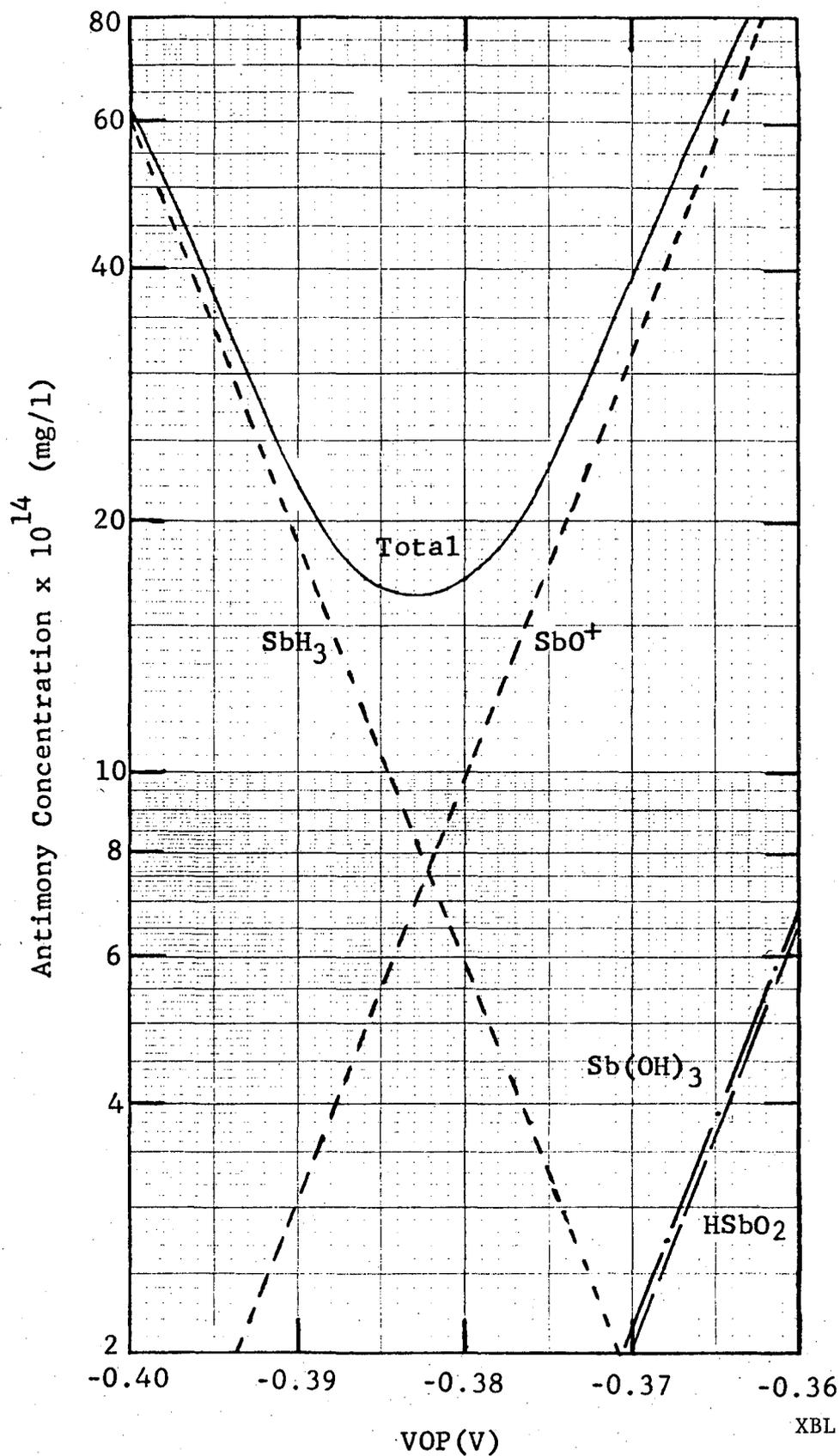
System	Feed Concentration mg/l	Observed Effluent Concentration mg/l	Electrode Potential V	Calculated Wall Concentration mg/l
copper	667	0.06	-0.25	4.7×10^{-5}
silver	1000	42	-0.46	23
lead	4.32	0.55	-0.56	0.028
mercury	4.12	<0.005	-0.46	1.36×10^{-14}
antimony	100	5	-0.3828*	1.62×10^{-13}
ferrous oxidation	705	1	0.7	1.4

* Potential at which the calculated antimony wall concentration exhibits a minimum (see Figure 1).

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Table 3. Standard electrode potentials of antimony referred to the hydrogen electrode. Aqueous solutions at 25°C. Equilibrium wall concentration of antimony as a function of VOP.

Reaction	U^θ , volt	Concentration, mole/l
1) $\text{SbH}_3 \rightarrow \text{Sb} + 3\text{H}^+ + 3\text{e}^-$	-0.5104	$c_{\text{SbH}_3} = \frac{\left(\frac{c_{\text{H}^+} c_{\text{Cl}^-, \text{sat}}}{\rho_o}\right)^3}{\rho_o^5} \exp\left(-\frac{3F}{RT} \Delta V_k\right)$
2) $2\text{Sb} + 3\text{H}_2\text{O} \rightarrow \text{Sb}_2\text{O}_3 + 6\text{H}^+ + 3\text{e}^-$	0.1445	$c_{\text{Sb}_2\text{O}_3} = \frac{\rho_o^{13}}{\left(\frac{c_{\text{H}^+} c_{\text{Cl}^-, \text{sat}}}{\rho_o}\right)^3} \exp\left(\frac{6F}{RT} \Delta V_k\right)$
3) $\text{Sb} + \text{H}_2\text{O} \rightarrow \text{SbO}^+ + 2\text{H}^+ + 3\text{e}^-$	0.2075	$c_{\text{SbO}^+} = \frac{\rho_o^6}{c_{\text{H}^+}^2 c_{\text{Cl}^-, \text{sat}}^3} \exp\left(\frac{3F}{RT} \Delta V_k\right)$
4) $\text{Sb} + 3\text{H}_2\text{O} \rightarrow \text{Sb(OH)}_3 + 3\text{H}^+ + 3\text{e}^-$	0.2307	$c_{\text{Sb(OH)}_3} = \frac{\rho_o^7}{\left(\frac{c_{\text{H}^+} c_{\text{Cl}^-, \text{sat}}}{\rho_o}\right)^3} \exp\left(\frac{3F}{RT} \Delta V_k\right)$
5) $\text{Sb} + 2\text{H}_2\text{O} \rightarrow \text{HSbO}_2 + 3\text{H}^+ + 3\text{e}^-$	0.2309	$c_{\text{HSbO}_2} = \frac{\rho_o^7}{\left(\frac{c_{\text{H}^+} c_{\text{Cl}^-, \text{sat}}}{\rho_o}\right)^3} \exp\left(\frac{3F}{RT} \Delta V_k\right)$
6) $\text{Sb} + 2\text{H}_2\text{O} \rightarrow \text{SbO}_2^- + 4\text{H}^+ + 3\text{e}^-$	0.4633	$c_{\text{SbO}_2^-} = \frac{\rho_o^8}{c_{\text{H}^+}^4 c_{\text{Cl}^-, \text{sat}}^3} \exp\left(\frac{3F}{RT} \Delta V_k\right)$



XBL 766-8365

Figure 1. Equilibrium antimony concentration as a function of electrode potential relative to a saturated calomel electrode.

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