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Correspondence

The effect of anodic bubble formation on cathodic mass transfer under natural convection conditions

Comment

We welcome the contribution of Mohanta and Fahidy [1] on the study of mass transfer enhancement by anodically generated gas bubbles. However, we disagree with two conclusions drawn in their paper:
(1) that the effect of anode generated gas bubbles on the mass transfer at the cathode has not been studied before, and
(2) that the effect is modest, 20% or less.

We have been studying the enhancement of mass transfer (MT) at the cathode due to the oxygen produced at the anode for several years and have published our results in four papers [2–5]. The enhancement of MT, which we have observed on the upper portion of the cathode due to this effect, led us to improve the cell design by increasing current density in this area [5, 6]. The improved cell design is successfully used in the INCO copper electrowinning tankhouse in Copper Cliff, Ontario [7].

Our quantitative studies of the MT enhancement by anodic gas show that the effect is quite substantial. E.g. Fig. 2 in [3] shows the mass transfer profile in a model copper electrowinning cell 1 m high, 0·5 m wide with 2·6 cm spacing between the surfaces of a cathode and Pb/Sb anode. The cell was operated at 250 A m^{-2} and 40° C using electrolyte containing 60 g l^{-1} Cu and 150 g l^{-1} H_2SO_4. It can be seen that the mass transfer coefficient (k) of the silver tracer ion was approximately constant at $\sim 50 \times 10^{-5}$ cm s^{-1} over the bottom 40 cm. It could visually be observed that the upward moving 'wedge' of anodic oxygen did not get close enough to the cathode to affect the 'pure' natural convection in this area. Above this point, however, the turbulence associated with the 'wedge' of rising oxygen bubbles approached the cathode surface and began to increase the local values of k gradually from $\sim 50 \times 10^{-5}$ cm s^{-1} to $\sim 150 \times 10^{-5}$ cm s^{-1} near the electrolyte surface. As could be expected, the region of enhanced MT was absent when anode bubbles were restrained near the anode by a diaphragm and the value of k was $\sim 50 \times 10^{-5}$ cm s^{-1} over the whole cathode height.

To compare our results with the correlation proposed by Mohanta and Fahidy [6] one has to use an average k for the whole cathode i.e. $\sim 55 \times 10^{-5}$ cm s^{-1} for the 'pure' natural convection case with about 85×10^{-5} cm s^{-1} in the electrowinning test without a diaphragm. Thus, the average value of k for Ag^+ ion was enhanced by $> 50\%$ due to the O_2 produced on the anode. It is not difficult to see that k for the copper ion will be enhanced nearly proportionally although the absolute values will be $\sim$ 15% lower due to the relation between mass transfer and diffusion coefficients of different ions in the same electrolyte.

Using now the Mohanta and Fahidy correlation [6] to predict the enhancement

$$(Sh) = (Sh_B) + 3{\cdot}09(Re_g)^{0{\cdot}77}(Sc)^{0{\cdot}25}(h/b)^{0{\cdot}336}$$

we calculate for our case:

$$\begin{aligned}
\gamma &= 1{\cdot}14 \times 10^{-2}\ \mathrm{cm^2\,s^{-1}}\\
D_{Ag^+} &= 0{\cdot}95 \times 10^{-5}\ \mathrm{cm^2\,s^{-1}}\\
(Sc) &= 1200\\
(Re_g) &= 24\\
(Sh_B) &= 5790\\
h/b &= 38\\
(Sh) &= 5790 + 3{\cdot}09(11{\cdot}6 \times 5{\cdot}88 \times 3{\cdot}39)\\
&= 5790 + 714 = 6500
\end{aligned}$$

E.g. [6] thus predicts enhancement of (Sh) (or of k_{Ag}) by only 12% while our experimental results suggest 4 x greater enhancement. A similar discrepancy is also found when comparing measured and predicted MT enhancement for other tests performed in our laboratory. The discrepancy is far beyond the error expected due to the use of two different methods for measuring the mass transfer parameter.

It is our opinion, that correlation [6] is only valid within or near the range of conditions used in the study and doesn't permit extrapolation to the range of conditions prevailing in commercial cells [$h \sim 100$ cm, h/b 20–50, $(Sc) \sim 1000$ and (Re_g) 10–30]. It may also be pointed out that in practical electrowinning operations, the minimum local value of the MT coefficient is more critical than its average value, since local roughness and shorts will develop when higher current density is used than can be tolerated by the area of the cathode with the poorest MT.

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V. A. ETTEL
A. S. GENDRON
INCO Metals Company,
J. Roy Gordon Research Laboratory,
Mississauga, Ontario
and Copper Refinery,
Copper Cliff, Ontario

Reply

Although we did refer to the work by Ettel *et al.* ([5] in our paper) the last sentence should have been phrased to indicate that our Equation 5 is apparently the first such relationship proposed in this specific area of study and we regret the misleading tone of that sentence.

The large apparent discrepancy between mass transport rates of copper ions estimated indirectly via the Ag-tracer technique and our Equation 5 is due to the difference in the mechanism of the current flow pertaining to the different magnitudes of it. In the experiments of Gendron and Ettel (e.g. [1]) the cathode current density (250 A m^{-2}) was significantly lower than the pertinent limiting current density which, using conventional natural convection theory and other authors' experimental data [2, 3], would be at least 457 A m^{-2} at room temperature, and certainly higher at about 40° C. Gendron and Ettel worked in the region of electric charge transfer control, or in the Tafel region, which is also manifested by the uniformity of their local mass transfer coefficients (of the Ag ions); in the mass transfer control regime these coefficients should follow the usual $-1/4$ exponential dependence on the distance measured from the bottom of the cathode. On the other hand, our measurements are strictly related to the mass transport controlled region and as such, our Equation 5 cannot be employed at the experimental conditions used in the works cited by Ettel.

Asada *et al.* [4] have shown very clearly the effect of the cathode potential on mass transfer coefficients (e.g. Fig. 1), underlining the caution needed in comparing data taken in regimes of different control mechanisms (compare, for example, lines 1 and 7 in Fig. 1 [4]). It follows that the value of $(Sh_B) = 5790$ obtained from $k = 55 \times 10^{-5}$ cm s^{-1} in Ettel's computation does *not* represent the value of the Sherwood number at limiting conditions.

We appreciate this opportunity to point out that in our view the results by Ettel and his co-workers, and ours are complementary rather than contradictory in the light of the danger in trying to extrapolate data obtained in a specific mechanism-controlled regime to others.

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T. Z. FAHIDY
Department of Chemical Engineering
University of Waterloo,
Canada
S. MOHANTA
HSA Reactors
44 Fasken Drive, Rexdale,
Ontario, Canada

Further comment

It is true, that copper was plated in our experiments at only about 1/2 of the limiting current of Cu^{2+} ions as it is common in the industrial practice to produce smooth and pure deposits. The co-deposition of Ag^+ tracer ions into the Cu deposit under the same conditions takes place, however, at the limiting current of Ag^+ ions (i.e. pure mass transfer control) as has been proven by rotating disc experiments [1, 2].

The independence of the local mass transfer coefficients of height, which we observed in the absence of stirring by anodic bubbles, is not too surprising for the following reason. The $1^{-0\cdot25}$ dependence of the limiting current on anode height is only valid for natural convection with a laminar boundary layer, whereas under the 'real electrowinning' conditions used by us, the boundary layer flow is turbulent. For these conditions Fouad and Ibl [3] found that with tall electrodes ($> 0\cdot5$ m) the limiting current density tends to become independent of height.

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V. A. ETTEL
A. S. GENDRON
Inco Metals Company,
J. Roy Gordon Research Laboratory,
Mississauga, Ontario
and Copper Refinery,
Copper Cliff,
Ontario