BUBBLE FORMATION AND MOVEMENT IN ALUMINIUM REDUCTION CELLS

1. Introduction

The Hall-Héroult process has been used in the production of aluminium for the last century (see Ai (1985), Evans *et al.* (1981), Moreau (1988)). This process involves the electrolytic reduction of alumina (Al_2O_3) dissolved in molten cryolite, a sodium aluminium fluoride salt. The aluminium which is produced forms a pad of molten metal on which the electrolyte floats. The aluminium is periodically tapped to maintain a constant level.

The surface of the molten aluminium pad acts as the working face of the cathode. The anode consists of a set of carbon blocks (see Figure 1) partially immersed in the electrolyte so that the bottom or working face of each of these electrodes is about 4-5 cm above the surface of the aluminium pad.

The primary cell reaction is given by

$$2Al_2O_3(dissolved) + 3C\ (solid) \rightarrow Al\ (liquid) + 3CO_2(gas) \qquad (1)$$

with molten aluminium produced at the cathode and the carbon dioxide gas formed at the anode face. As a result of the above reaction, the carbon anodes are consumed. During operation, the anodes are continually lowered to maintain a constant anode cathode distance (acd), and eventually replaced.

The carbon dioxide gas produced on the underside of each anode forms bubbles that move away toward the edge of the anode. When bubbles come into contact with each other, they can coalesce. This bubble layer underneath the approximately horizontal anode surface is about 1 cm thick. When the bubbles reach the edge of the anode, they rise rapidly because of their buoyancy, and escape up the side of the anode.

The overall voltage drop due to resistance in the cell is about 2 to 2.5 volts; the electrochemical potential is about 1.7 volts. The current density in the electrolyte is typically between 0.75 and 1.1 amps cm^{-2} (Ai (1985), Evans *et al.* (1981)). The resistivity of the electrolyte is much greater than the other materials in the current path, so the current flow between the anode and the surface of the aluminium pad is essentially vertical and uniform. The power dissipated produces the heat which maintains the cell temperature at its operating level of 900^o to 1000^{o}C. This level is critical, for it is not much above the melting point of the electrolyte, but must be low enough to maintain the frozen crusts around the edge of the pot needed to protect the walls from corrosion.

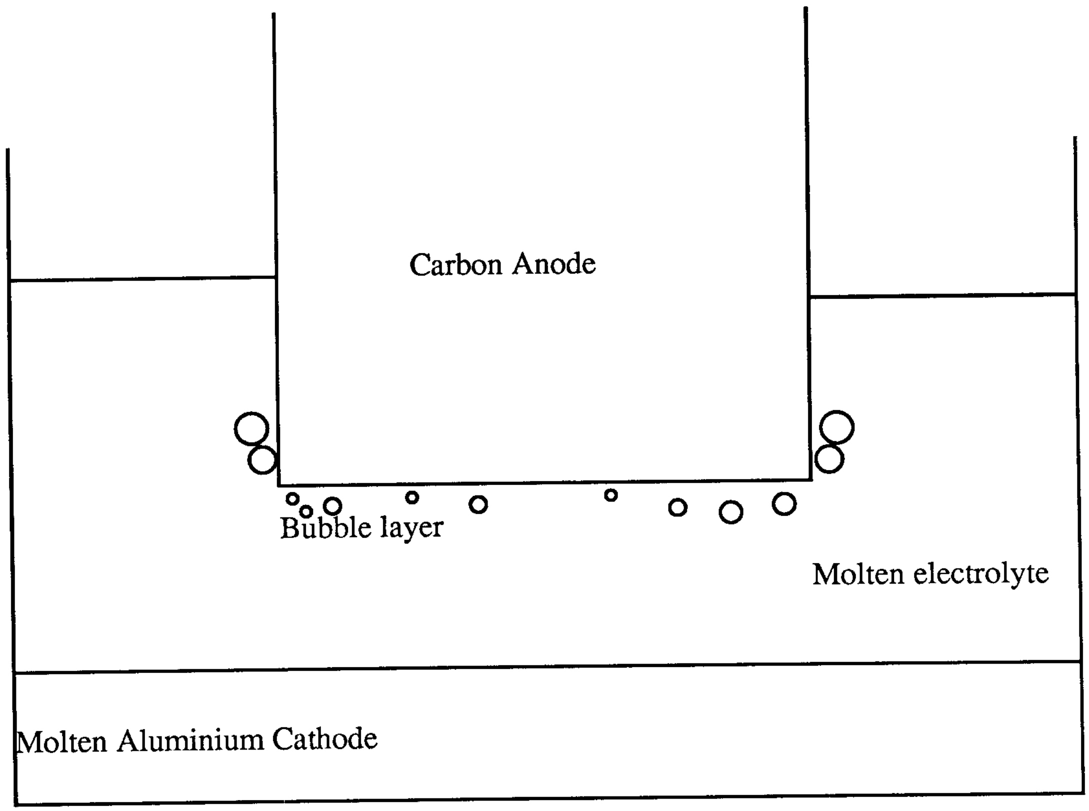

Figure 1: Diagram of one anode block within pot.

There are substantial magnetohydrodynamic effects which keep the aluminium in motion, and cause instabilities in the metal-electrolyte interface (Muller & Solberg, Sneyd (1985)). In the electrolyte, there are some mhd effects, but they are less important. The main cause of motion in the electrolyte is the movement of the carbon dioxide bubbles produced at the anode surface. The effect of this motion on the electrolyte circulation and the aluminium surface was considered by the MISG. A number of useful references to the theory of bubbly flows with buoyancy were found: these were Brown & Kranic (1968), Couët & Strumolo (1987), Durst *et al.* (1986), Fortin *et al.* (1984), Harper (1972), Johanson *et al.*, and Klidonas & Whalley (1985).

2. Bubble motions.

Among the important effects produced by the bubbles liberated at the anode are the following:

1. The non-conductivity of the bubbles raises the current density, and so increases the resistive losses. The waste of energy is undesirable, and the extra heating may cause melting of the protective coating of frozen electrolyte on the cell walls.
2. The tendency of the moving bubbles to drag liquid with them creates a velocity gradient between the electrodes. This has a stirring effect which assists heat transfer, and creates pressure gradients which may affect the shape of the aluminium pad, and hence the acd.
3. The velocity gradient may aggravate instabilities on the interface between the aluminium and the electrolyte.

There are at least three kinds of force which could propel the bubbles towards the outside of the anode block:

- magnetic field effects produced either in the electrolyte or within the molten cathode,
- convective effects due to the large release of heat between the electrodes, and
- buoyancy effects.

The study group considered each of these.

3. Magnetohydrodynamic effects.

Four different kinds of effect were considered, each with a characteristic scale.

1. *Effects on the scale of the whole cell.* These certainly are present, and produce eddies in the aluminium with velocities of several cm s^{-1}. A common pattern is sketched in Figure 2. The magnetic fields responsible are produced predominantly by conductors external to the cell, particularly the current supply bars. Consideration of these eddies was not pursued, because the bubble motions being investigated are outwards in all directions under each anode; the bubbles are observed to emerge on all sides. Currents on this large scale could only carry the bubbles in one direction. Nevertheless, these large-scale effects must cause any centrifugal motion of the bubbles to be considerably biased.

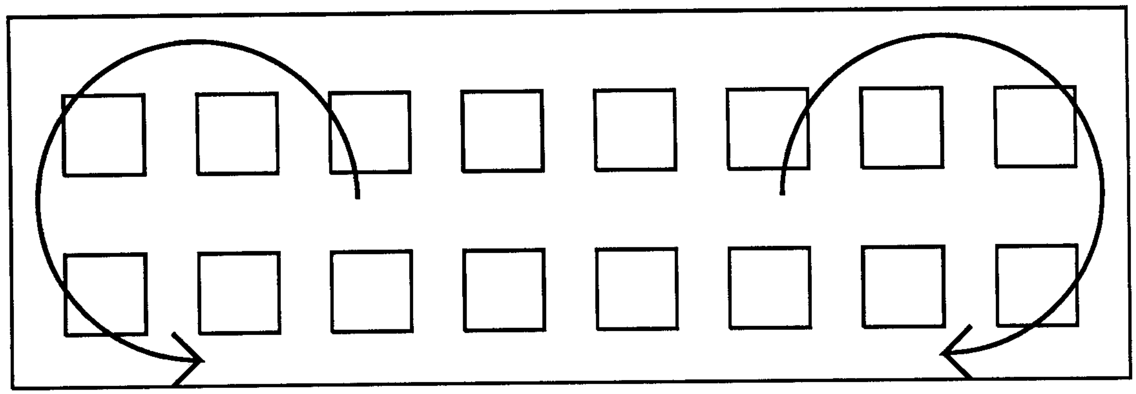

Figure 2: Typical large scale magnetically induced circulation pattern in the electrolyte.

2. *Effects on the scale of the anode blocks.* These could certainly affect centrifugal bubble motions, and might be expected because of the gradations in the current density **J** at the anode periphery. However the predominant magnetic field **B**, which as mentioned above is produced by external horizontal conductors, is vertical, and so is approximately parallel to **B**. So the body force, which is their cross-product, is small.

3. *Waves on the cathode surface.* These are well-known, and are monitored during operation because if they are too large there can be shorting between electrodes, and other ill-effects. Moreau shows that there are two modes with predicted wavelengths of 20 cm and 150 cm. The longer waves are responsible for the main observed fluctuation in cell voltage, which has a period of about 40 s. Again the waves travel on the scale of the whole cell, and so would not have a specifically centrifugal effect in each electrode gap. As a result of monitoring, and consequent adjustment of the acd, the amplitude is kept to a few mm. As long as that control is obtained, the effect on bubble motion should be small.

4. *MHD forces in the immediate bubble neighborhood.* The bubble itself distorts both the current density and the magnetic field lines in its neighborhood. The results of this were briefly examined, and appear to produce rotation in contrary directions above and below, rather than direct linear acceleration. However our analysis was far from complete, and it remains an interesting problem, whose investigation we commend to the mathematical community.

4. Thermal considerations

It is necessary to jump ahead here and note that both observation and buoyancy considerations suggest bubble and fluid motions of the order of 0.1 m s^{-1}. The question arises: is this sufficient to dissipate the heat generated, or would large temperature gradients be expected, producing convective cells?

The following calculations satisfied us that the mass flow of electrolyte would remove the heat without much difficulty, although a plausible alternative mechanism of removal by conduction to the aluminium is quite inadequate.

About 20Kw of heat is dissipated beneath each anode block. If removed by convection within the cryolite, the area through which it escapes (around the anode perimeter) is about 0.08 m^2, giving a flux density of 25×10^4 watts m^{-2}.

The specific heat of cryolite is 1.66×10^3 joule/kgm/^{o}K, or 3.5×10^6 joule $m^{-3}/^o$K. So the product of the velocity V and the temperature difference ΔT is

$$V\Delta T = 25 \times 10^4 / 3.5 \times 10^6 \qquad (2)$$
$$\sim 8 \times 10^{-2}\ {}^o\mathrm{Kms}^{-1}. \qquad (3)$$

With anticipated velocities of about 0.1 m s^{-1}, a temperature difference of $< 1^o$K would provide sufficient heat flow. In that case, extra convective motions would be negligible.

Because the cryolite layer is thin and the aluminium is moving, and in any case a good conductor, we wondered whether conduction to the aluminium layer might even more efficiently dispose of the heat. This proved to be not so; a temperature gradient of 10^5 ^{o}K m^{-1} would be required to remove all the heat in this way.

5. Modelling a buoyancy-driven bubble layer.

After a short time, the bottom surface of the anode acquires a small but significant slope, rising towards the outside by about 2^o. The persistent occurrence of this slope in itself suggests that the buoyant rise of bubbles along it may be important; on that hypothesis the slope would be produced when the initially sluggish disposal of the bubbles produced a congregation in the centre, which, being thus partly protected, is worn away more slowly than the exterior. The following consequences of a flow driven by this buoyant effect were deduced.

The rate of CO_2 production is equivalent to that of a uniform flow at about 1 mm s^{-1} emerging from the anode surface. The observed variation of the ohmic resistance between the electrodes is proportional to the acd but with an offset of about 10 mm, and this is often taken to be the thickness of the bubble layer. If so, we still have no real idea of the void ratio λ in that layer, but assigning to it values over quite a wide range allows some inferences. The mean bubble speed at a distance x metres from the anode centre is $x/(10\lambda)$ m s^{-1}, giving a maximum of $.05/\lambda$ m s^{-1} at the outer edge.

Now there is a well-established semi-empirical formula, due to Davies and Taylor, for the speed of rise (V) in still fluid of a large bubble whose upper surface has a radius of curvature a metres, *viz.*

$$V^2 = \frac{4}{9}ga, \text{ where } g = 9.8\text{ms}^{-1} \tag{4}$$

Adapting it in a simple-minded way for bubbles constrained beneath a slope α,:

$$V^2 = \frac{4}{9}ga\sin\alpha \tag{5}$$

and taking (as a guess) $a = 2.25 \times 10^{-3}$ m, $\alpha = 1/30$, then $V \sim 1.7\times 10^{-2}$ m s^{-1}.

V must be interpreted as the speed of the bubble relative to the liquid, and it is quite small when compared to the absolute bubble speed. So to a first approximation, the liquid is driven at the bubble speed $x/10\lambda$ m s^{-1}.

This can be checked roughly against the viscosity ($\nu = 10^{-6}$ms^{-1}). Assuming an effective shear layer width of Δy m, the shearing force per unit area is $\rho g \sin\alpha$, where $\rho =$ density of cryolite, giving $\nu = \lambda^2 \Delta y/15$. If that implied a thickness greater than the bubble layer, there would be a difficulty, but even for a quite small void ratio of 0.1, the thickness is little more than 1 mm.

A new study by Couët & Strumolo (1987) of large two-dimensional bubbles has reached us since the MISG. In a horizontal duct, bubbles grow until they reach half the duct height h and move out at a speed $V = 0.5\sqrt{gh}$, and the velocity is close to this for a duct inclined at a few degrees to the horizontal. This value of V (about 0.35 m/s in our case if h = 5 cm) would be an upper bound for practical bubbles, which might be broken up by the flow, whose speed is comparable to V. More experimental work is needed, to see the actual shapes and sizes of bubbles under rigid lids (but see Couët & Strumolo). Results on air in water would be useful, as in Fortin *et al.* (1984), and much cheaper to make and easier to observe than carbon dioxide in cryolite.

Conclusion

The buoyant rise of bubbles is important in determining fluid velocities in the space between anode and cathode in a Hall-Heroult cell. It is possible that mhd forces are as significant; this question was left unanswered. The bubble- induced motion is sufficient to account for heat dissipation, and the stirring helps to maintain the supply of electrolyte.

References

D.K. Ai, "The hydrodynamics of the Hall-Héroult cell", *Light Metals* (1985), 593 - 605.

F. C. Brown & W. L. Kranic, " A model for the prediction of velocity and void fraction profiles in two-phase flows", *A.I.Ch.E. Journal* 14 (1968), 750 - 758.

B. Couët & G.S. Strumolo, " The effects of surface tension and tube inclination on a two-dimensional bubble", *J. Fluid Mech.* 184 (1987), 1-14.

F. Durst, B. Schonung, K. Selanger & M. Winter, "Bubble-driven liquid flows", 170 (1986), 53 - 82.

J.W. Evans, Y. Zundelevich & D. Sharma, "A mathematical model for prediction of currents, magnetic fields, melt velocities, melt topography and current efficiency in Hall-Héroult cells", *Metal Transactions B* 12B (1981), 353 - 360.

S. Fortin, M. Gerhardt, & A.J.Gesing "Physical modelling of bubble behaviour and gas release from aluminium reduction cell anodes", *Light Metals* (1984), 721 - 741.

J.F. Harper, "The motion of bubbles and drops through liquids", *Adv. Appl. Mech.* 12 (1972), 59.

S.T. Johansen, F. Boysan & W.H. Ayers, "Mathematical modelling of bubble driven flows in metallurgical processes" *Applied Scientific Research* 44, 197 - 207.

G. Klidonas & P.B. Whalley, " A comparison between void fraction correlations for high pressure single component gas-liquid flows", *Proc. 2nd Int. Conf on Multi-Phase Flow* (London, 1985), 109 - 117.

R.J. Moreau, " On the hydrodynamics of Aluminium reduction cells", (to appear).

T.B. Muller & K.O. Solberg, "Numerical calculation of mass convection patterns in an Aluminium reduction cell", unknown *Journal*, 151 - 158.

A.D. Sneyd, "Stability of fluid layers carrying a normal electric current", *J. Fluid Mech.* 156 (1985), 223 - 236.