THERMODYNAMICS OF AIRBURN OF CARBON ANODES IN ALUMINIUM REDUCTION CELLS

1. Background

For about 100 years, aluminium has been produced predominantly by the Hall-Héroult process. Alumina (Al_2O_3) dissolved in a bath of molten salt (cryolite) is electrolytically reduced to aluminium. The cathode consists of the carbon lining of the bottom of the bath, and the pool of molten aluminium previously discharged. The anode is a block of carbon suspended in the bath (see diagram).
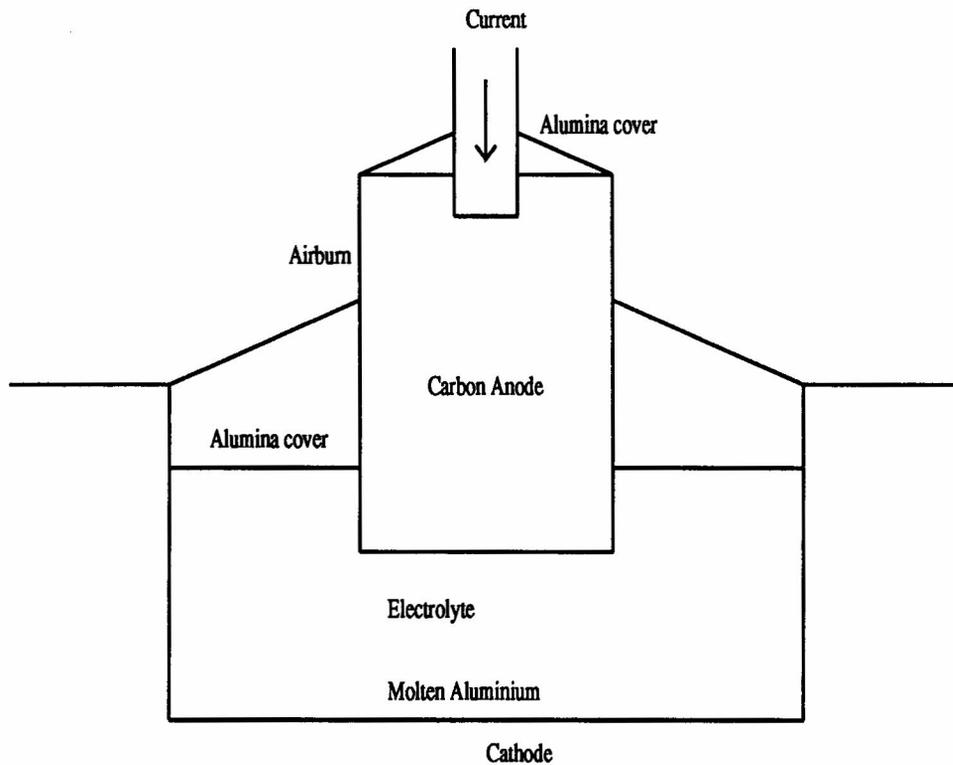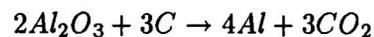

Figure 1: Diagram of the cell configuration.

The product at the anode is carbon dioxide, with the carbon taken from the anode. The overall reaction is:

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$$

36

The rate of consumption of the anode carbon is comparable to the rate of aluminium production, and the anode blocks must be continually lowered to maintain a constant anode to cathode distance, which determines the electrical resistance of the cell.

The loss of carbon in the electrolysis is inevitable, but in addition a significant amount is wasted in unwanted reactions with CO_2 (in the bath) and O_2 (above the electrolyte, where the carbon at temperatures of 500-800$^{\circ}C$ is exposed to the air). The latter reaction, termed 'airburn', was the topic considered at the MISG.

Anodes are normally covered with a layer of alumina powder to reduce air access and hence airburn. At some smelters, anodes are also sprayed with aluminium. Nevertheless, airburn typically causes around 10% of total anode carbon consumption. The carbon loss and the above protective measures add millions of dollars to the annual operating costs of the smelters.
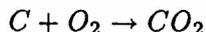
Quite a good general description of an electrolysis cell, with emphasis on events in the electrolyte, is given by Ai [1]. A reasonably complete attempt at modelling it is described by Boero [2], but without the treatment of the air movements given below.

2. Airburn

Most airburn occurs on the upper part of the sides of the anodes (see diagram) as this area is often uncovered, especially early in the life of the anode. The rate of airburn [2] depends on the surface temperature, oxygen access and the intrinsic reactivity of the carbon. The surface temperature is very variable, typically ranging from 500° C to 800° C depending on position, anode age and depth of cover. Airburn of exposed surfaces commences at around 450° C and increases rapidly with temperature, reaching a maximum rate at around 650-700° C when the rate of gas diffusion in the boundary layers becomes limiting.

3. The kinetic and diffusion regimes

The airburn reaction between carbon and oxygen:

$$C + O_2 \rightarrow CO_2$$

occurs at a rate approximately proportional to the concentration (partial pressure) of oxygen at the surface ($[O_2]_s$)[3,4]:

$$\frac{dC}{dt} = -k_1[O_2]_s$$

The rate constant k_1 increases rapidly with temperature, and is in fact a much investigated instance of the Arrhenius behaviour

$$k_1 \sim e^{-\frac{E}{RT}}, \quad E = \text{activation energy}, \quad R = \text{gas constant}$$

The actual reaction rate does not increase as fast, because the surface concentration $[O_2]_s$ diminishes. The temperature range in which the diminution is relatively small is called the 'kinetic regime' ([3,4]), and the range of higher temperatures where $[O_2]_s$ is much smaller than its atmospheric value is called the 'diffusion regime', since it is now the ability of the oxygen to diffuse through the other gases near the surface that determines the reaction rate. Note that each carbon atom lost escapes as part of a molecule of carbon dioxide, and this CO_2 flux is equal to the influx of O_2.

In the case of a first-order reaction, there is a neat relationship between diffusion and kinetics [3,4]. If the diffusive flux density F of O_2 is proportional to the concentration difference:

$$F = k_2([O_2]_\infty - [O_2]_s) = k_1[O_2]_s$$

then expressing in terms of the known atmospheric concentration:

$$F = \frac{k_1 k_2}{k_1 + k_2}[O_2]_\infty$$

This is in effect an Ohm's law for two resistances in series, with the k's playing the role of conductances.

Figure 2 shows the two regimes; the axes are chosen so that the Arrhenius kinetics appear as a straight line. Note that the intermediate temperature range is quite narrow. As far as we can tell from the data, once the anode has reached thermal equilibrium, it is well in the diffusion regime, and although for perhaps the first few hours it may be cooler than that, the airburn is then much slower. So the study group concentrated on the diffusion regime.

4. The boundary layer

The motion of the hot gases near the surface cannot be ignored; in fact the temperature gradients are very steep, since the bulk of the air in the pot is not very much hotter than ambient (perhaps 60°C). In this context of buoyant flow with diffusion, there are two important dimensionless numbers[5]. The Rayleigh number Ra is

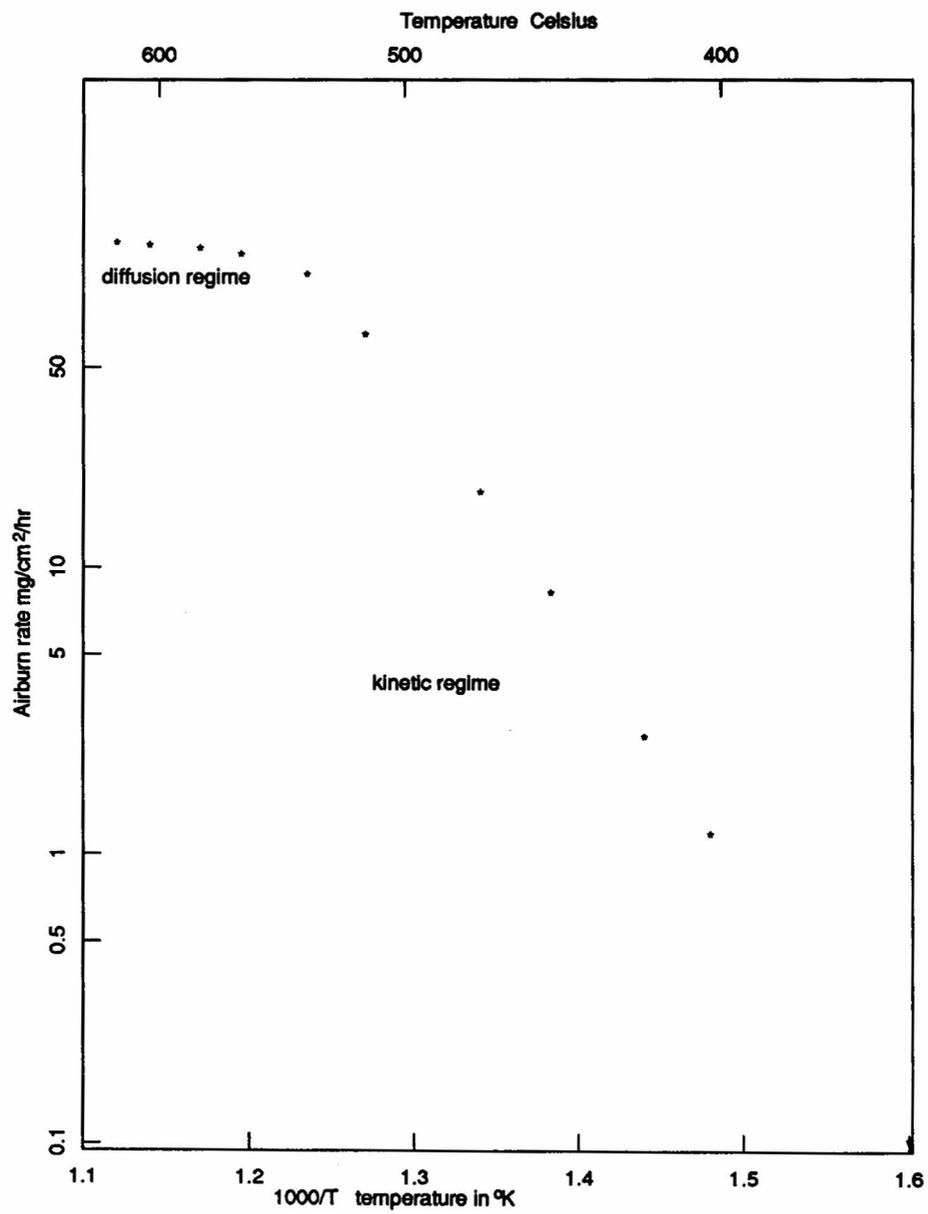$$Ra = \frac{gL^3(T_s - T_\infty)}{\nu k T_\infty}$$

Figure 2: Combustion kinetics of Bell Bay anode carbon.

where g = acceleration due to gravity, L is a representative length, the T's are absolute temperatures, and ν, k are the respective diffusivities of momentum (kinematic viscosity) and heat. For a near-ideal gas, ν and k are approximately equal. The Rayleigh number measures the importance of buoyancy compared with the various diffusivities. Its importance here is twofold:

- Natural convection with a Rayleigh number of more than about 10^8 is usually turbulent. Here the Rayleigh number is about 2×10^6, and the flow is therefore almost certainly laminar.

- There are well-established relations between the transfer coefficients (like k_2 above) and the Rayleigh number, for certain flows.

The heat transfer coefficients h are usually introduced via the dimensionless Nusselt number Nu:
$$Nu = hL/k$$
which is effectively the ratio of convective losses to conductive losses. We took as our model the flow induced by a vertical heated surface. This somewhat imperfectly represents the conditions at both ends of the surface; the error at the top, where the model fails to account for the freedom of the gas to move over the block, is probably not important, but the error at the bottom, where instead of air drawn in freely from below there is a horizontal surface and also a fixed flux of carbon dioxide, may be important - this is discussed later.

In this model, with laminar flow the relation [5] is

$$Nu = 0.5Ra^{1/4}.$$

There is a corresponding relation for turbulent flow, and an empirical relation covering the transition region (see [5]), but the above relation proved quite sufficient for our needs.

5. Properties of air

It is necessary to use some properties of air at high temperature, and these are only available at certain temperatures, so an idea of temperature dependence is useful. In addition, it is desirable to follow through to find the temperature dependence of the result.

The gas properties which are needed are ρ, the density, D, the molecular diffusivity (of oxygen in air), ν, the kinematic viscosity, and α, the thermal

diffusivity. The last three are in almost constant ratio; in particular ν/α is the Prandtl number, and is virtually constant at 0.70.

The gas theory for low densities [6] works almost perfectly at these temperatures, and predicts $D/\nu = 1.184$. It also predicts that each of D, ν and α vary approximately as $T^{3/2}$, while ρ varies as T^{-1}. Consequently the products of D, ν and α with ρ vary rather more slowly, as $T^{1/2}$, approximately, and so it is preferable to deal with them where possible. The following table shows how nearly true this approximation is:

Temperature $(^\circ K)$	$\rho \, D \, T^{-1/2} \, kg \, m^{-1} \, s^{-1} \, (^\circ K)^{-1/2} \times 10^{-6}$
300	1.30
600	1.52
800	1.59
1000	1.65

The conductivity $(D\rho)$ of oxygen in air, using formulae from the molecular theory of gases, with constants given in [6].

Approximations used hereafter will be:

$$\rho = 353/T \ kg \ m^{-3}$$

$$D = 4.53 \times 10^{-9} T^{1.5} \ m^2 \ s^{-1}$$

$$\nu = 3.83 \times 10^{-9} T^{1.5} \ m^2 \ s^{-1}$$

$$\alpha = 5.47 \times 10^{-9} T^{1.5} \ m^2 \ s^{-1}$$

$$D\rho = 1.6 \times 10^{-6} T^{.5} kg \ m^{-1} \ s^{-1}$$

In the boundary layer theory below, these quantities are generally evaluated at the mean temperature $T_f = (T_s + T_\infty)/2$. It is convenient to normalise this:

$$\theta = T_f/T_\infty$$

6. Calculation of convection and boundary layer resistance

The dimensionless numbers were calculated thus, using mks units:

$$Ra = \frac{gL^3(T_s - T_\infty)}{\nu k T_\infty}$$

$$\approx \frac{10}{3.83 \times 5.47 \times 10^{-18} \times 350^3} \times L^3 \times \frac{2\theta - 2}{\theta^3}$$

41

assuming $T_\infty = 350°K$

$$\approx 1.1 \times 10^7 \times \frac{2\theta - 2}{\theta^3}$$

$$\approx 2.8 \times 10^6 \text{ with } \theta = 2, \text{ i.e. } T_s = 1050°K$$

$$Nu = 0.5 \times Ra^{1/4}$$

$$\approx 162 L^{3/4} (\frac{2(\theta - 1)}{\theta^3})^{1/4}$$

$$\approx 29(\frac{2(\theta - 1)}{\theta^3})^{1/4}$$

$$\approx 20$$

The average oxygen flux density

$$F = Nu[O_2]_\infty D/L$$

The oxygen concentration $[O_2]_\infty = 0.2$ kgm^{-3} at $350°K$, so

$$F \approx 0.00115 \times (\frac{\theta - 1}{\theta})^{.25} \times \theta \times L^{-.25} \ kg \ m^{-2} \ s^{-1}$$

Note that in this formula, D is calculated at average temperature, while the density is calculated at the external temperature. This is necessary because the Nusselt number gives a transfer coefficient for the boundary layer, so the external density is the one to use.

The Bell Bay anodes are about .81 m long by .53 m wide; the perimeter is about 2.68 m, so the exposed area is 2.68 L m^2; the mass flux of carbon is, from the stoichiometry, 12/32 that of oxygen, and so, expressed as loss of carbon per day:

$$\text{Flux of } C = 0.00115 \times \frac{12}{32} \times 86000 \times 2.68 \times L^{3/4} \times (\theta^3(\theta - 1))^{1/4}$$

$$\approx 30 \text{ kg/day}$$

when L=0.1 m, anode temp = $1050°K$.

Here is a table of predicted fluxes at various anode temperatures.

Temperature of anode $°C$	Temperature of anode $°K$	Daily loss kg of carbon
500	773	22.33
550	823	23.73
600	873	25.09
650	923	26.45
700	973	27.81
750	1023	29.15
800	1073	30.47

42

The observation that the result varies with $L^{3/4}$ allows the total airburn to be calculated, assuming that L diminishes to zero at a uniform rate. The total loss is just 4/7 of what it would have been had it continued at the initial rate. In general, had the variation been as L^n, the fraction would have been $1/(1+n)$. So if the total duration of exposure of the carbon is 1 week, the airburn will be about 116 kg of carbon.

This loss is rather higher than that usually observed, but 10 cm of initial exposure is also rather high. Correction for a deviation angle ψ of the oxidising face from the vertical has surprisingly little effect on the Nusselt number, varying it by about $(\cos \psi)^{1/4}$. More significant is the effect on the exposed surface area, which increases by about $(\cos \psi)^{-1}$.

7. Spatial variation of burn rate

The relation between the Rayleigh number and Nusselt number which was used in the previous section derives from a similarity solution of the Navier-Stokes equation [7]. Further examination of this solution shows that the thermal conductance of the gas layer actually varies as $x^{-1/4}$, where x is a height variable, normalised to vary between 0 and 1. In terms of this, the flux density of oxygen is

$$F = 0.5D\phi\rho cx^{-1/4},$$

where D and ϕ are the diffusivity and volume fraction of oxygen in air, and

$$c = \left(\frac{g\Delta T}{4\nu^2 T_\infty}\right)^{1/4}.$$

Some concern was expressed about the apparent singularity at x=0. It was argued, though, that this was not significant because:

1. The singularity is integrable, and will cause no numerical difficulty in (say) a finite element model, provided that an appropriate quadrature formula is used.

2. The singularity reflects the incorrect assumption that the gas is free to rise vertically from below at x=0; in fact, of course, there is a stagnation point, so the flux would be finite. That means that the flux is locally overestimated, but because of the smallness of the negative power, the overestimate is small.

3. The flux quoted above is derived on the assumption that it is determined by the resistance of the boundary layer. In most places this is the largest

resistance, so the formula is effective. However when x approaches zero, the other limits to oxygen flow, particularly the finite kinetic rate of oxidation, become important, and ensure that the flux density remains bounded.

A widespread view was that in practice correcting the integrated flux formula would be more trouble than it is worth. The simplest version of that formula is: if Fl is the total flux of carbon (or oxygen, or heat), then the flux leaving between points x_1 and x_2, $x_1 < x_2$ is

$$(x_2^{3/4} - x_1^{3/4})Fl.$$

8. The final profile

The model can predict the shape of the anode as it emerges from the pot. It has been established that the overall burn rate is proportional to $L^{3/4}$, where L is the diminishing height exposed, and locally proportional to $x^{-1/4}$. If the initial exposed height is h_1, and we consider a point at fixed height above this, then the non-dimensional height x is $(h + L - h_1)/L$. So the rate of loss of carbon at height h is :

$$K(\frac{h + L - h_1}{L})^{-1/4}L^{3/4}$$

where K is a constant. Integrating this until the exposed height is $h_1 - h$, so that the carbon at height h is covered, we have that the total carbon loss at that height is :

$$loss(h) = K \int_{h_1-h}^{h_1} \frac{LdL}{(h + L - h_1)^{1/4}} = K(\frac{4h}{7} + \frac{16h_1}{21})h^{3/4},$$

assuming that L diminishes at a uniform rate. The constant K can be found in terms of the total loss by integrating with respect to h. The total volume G of carbon lost is:

$$G = \int_0^{h_1} loss(h)dh = K\frac{16 \times 65h_1^{11/4}}{77 \times 21}$$

so, substituting for K,

$$loss(h) = \frac{77}{260}Gh^{3/4}(3h + 4h_1)h_1^{-11/4}.$$

This corresponds to the shape of the carbon profile, and indicates that the width of the stub should be maximum at the bottom, receding at a rate increasing rather slowly with height, as shown in Figure 3.
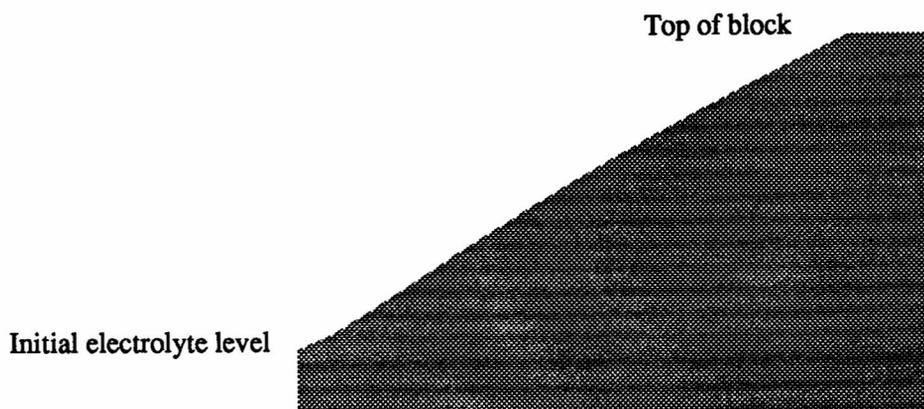
Top of block

Initial electrolyte level

Figure 3:   The airburn-eroded final shape of the anode stub.

9. Some warnings concerning the model

Here is a list of some assumptions made in the model which certainly will not be exactly true:

1. The wall is semi-infinite and vertical; there are no other obstructions to gas flow. The difficulties with this assumption have been mentioned. At the top, the assumption of more heated wall above probably exaggerates the gas flux; this is partly countered by the other discrepancy, that gas is free to flow over the top of the block, instead of being confined by the imaginary extension of the wall. At the bottom, access of air is restricted by the horizontal electrolyte surface, and further there is hot carbon dioxide bubbling up. The flux of CO_2 may be estimated from the rate of electrolytic consumption of the anode, which is about 0.2 gm s^{-1} ; it is about .4 litre per metre of circumference per second, very roughly equivalent to a velocity of 0.5 cm s^{-1} over a 10 cm wide band.

2. There is no gas recirculation; this probably affects mainly the temperature of the gas entering the boundary layer. This assumption is probably sound, because of the forced withdrawal of exhaust gases; it is worth mentioning, though, because there are also useable models of circulating flow which could be invoked if they seem more appropriate.

3. The wall temperature is uniform - in fact we had difficulty in getting information on the temperature distribution over the wall. An alternative assumption would have been that the heat flux is uniform. A complication is that airburn affects the temperature.

4. The gas entering the boundary layer is air at approximately ambient temperature - in fact there is CO_2 bubbling up from below, and the temperature distribution in the gas phase is even more uncertain than in the anode.

The reasonableness of these assumptions we can only leave to the judgment of readers, noting that there is not much data to support anything fancier.

10. The effect of a cover on the horizontal upper surface

Potentially, the losses by airburn from the upper surface are probably greater than those from the sides, since the top is exposed for a longer time. The free convection problem is also treated in [5, Sec B.1.c]; the relation between Nusselt and Rayleigh number is similar to that for the vertical plate:

$$Nu \approx 0.42 Ra^{1/4}.$$

The length used in the Rayleigh number is area/perimeter, or about .15 m; so by comparison with the vertical wall, we can expect a Nusselt number of about 23, and a mass transfer coefficient of about 0.01 $m\ s^{-1}$, which in the worst case could produce airburn at about 40 kg/day. The top can, however, be fairly easily covered with a non-oxidising material to shield the carbon from the air. The material used is often alumina.

As mentioned above, the pathway followed by the oxygen may normally be seen as the passage through two resistances in series, where at high temperatures the air layer is most significant. The interpolation of an inert layer simply places a third resistance in series, and the study group considerations showed that even a layer of a few millimetres was enough to outweigh all other resistances, except perhaps at very low temperature.

No data was available on the gas diffusivity of the alumina; however because of the presumed lack of interaction between the solid and gas phase, it is possible to make some reasonable estimates. We assumed that the gas occupied 10% of the volume of the powder layer, and that there was a tortuosity factor of 2 (to allow for the extra distance a molecule would have to travel around the particles). In that case, the conductance of a layer d mm thick would be

conductance of air × fraction of volume occupied by air / tortuosity

46

$$= 10^{-4}/10/2/(d * 10^{-3}) = 0.005/d \ m \ s^{-1}$$

which may be compared with the transfer coefficient (also a conductance) of the top air layer of $0.01 \ ms^{-1}$. To get an upper bound to the carbon loss, we multiply by the ratio of molecular weights, 12/32, and the mass per m^3 of oxygen $(.4/5$ at about $1000^{\circ} K)$, and the number of seconds in a day:

$$12/32 \times 0.005/d \times .4/5 \times 86400 \approx 13/d \ kg \ m^{-2} day^{-1}$$

Note that even though the prediction is that a quite thin cover would greatly reduce burn rate, this is based on the assumption that the cover is uniform. No doubt in practice several centimetres of material would be required to ensure that all the surface was reasonably covered.

11. Conclusion

Although the modelling of the air motion is rather approximate, it should be realistic, and in any case the degree of approximation is appropriate given the information available. The assumption that airburn is limited by oxygen access gives good quantitative predictions of the rate. Airburn from the top can be effectively prevented by a cover of a few centimetres of inert material.

12. Literature

We had available a considerable body of information on the kinetics of oxidation of carbon, some specifically in the context of this problem. There is [2] a survey article by J. F. Rey Boero, on anode burning, and an investigation of the kinetics in the relevant temperature range by Gregg and Tyson [8]. The latter authors reported difficulty in getting reproducible results, and their results are for pure oxygen at 7.6 cm Hg pressure (.1 atm, or about 1/2 normal partial pressure).

There is an analysis by Amundson [9] of the mass transport considerations, and a discussion of this by Rosencrans [10]. There is also a longer examination by Adomeit, Hocks and Henriksen [11-12], with emphasis on higher temperature combustion. Some of this work, like that of Mulcahy and Smith[4], is primarily directed at the rather different problem of improving coal combustion. There has been considerable study of the effect of the carbon structure, including the porosity; the paper of Masters and McEnaney is representative [13].

Acknowledgements

References

1. D.K. Ai "The hydrodynamics of the Hall-Héroult cell" Light Metals, 1985 pp 593-605.

2. J. F. Rey Boero. "A mathematical model of anode burning and factors affecting it." Light Metals, 1983, 867-885.

3. D. A. Frank-Kamenetskii "Diffusion and Heat Transfer in Chemical Kinetics", Plenum Press, N.Y. 1969.

4. M.F.R.Mulcahy and I.W.Smith, "Kinetics of combustion of pulverised fuel: A review of theory and experiment", Rev. Pure and Appl. Chem. **19**, 81-108 1969.

5. W.M. Rohsenow, J.P. Hartnett, and E.N. Ganic, "Handbook of Heat Transfer Fundamentals", 2nd Ed, McGraw-Hill, N.Y. 1985.

6. R. Bird, R. Stewart, and E. Lightfoot. "Transport Phenomena"

7. Schlichting, H. "Boundary Layer Theory" 7th Ed, McGraw-Hill, N.Y. 1979.

8. S.J. Gregg and R.F.S. Tyson,"The kinetics of oxidation of carbon and graphite by oxygen at 500°-600°", Carbon **3**, 39-42 1965.

9. N. Amundson, "Char Combustion", in Partial Differential Equations and Dynamical Systems, ed. W.E.Fitzgibbon III, Pitman 1984

10. S.I. Rosencrans, "On Amundson's model of the unsteady combustion of a slab of carbon", Quart Appl Maths, **45**, 795-807 1987.

11. G. Adomeit, W. Hocks and K. Henriksen,"Combustion of a carbon surface in a stagnation point flow field", Combustion and Flame **59**,273-288 1985.

12. G. Adomeit, W. Hocks and K. Henriksen,"Combustion of a carbon surface in a stagnation point flow field II: Ignition and Quench Phenomena", Combustion and Flame **71**,169-177 1988.

13. K.J. Masters and B. McEnaney, "The development of structure and microporosity in cellulose carbon", Carbon, **22**, 595-601, 1984.