TECHNOLOGICAL REVIEW

Mass-transport problems and some design concepts of electrochemical reactors

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Electrochemical cells, designed to operate with reactants at low concentrations, require special provisions to be made for enhancement of mass transport of the reactants to the electrode surface. The different concepts for doing this in industrial or large-scale cells are reviewed. Examples are given of cells and processes in which these ideas have been used. A comprehensive literature survey of the quantitative relationships pertaining to the different configurations is given. The various cell designs are compared on a quantitative basis, using i_{lim}, and some advantages and disadvantages are discussed.

1. Introduction

After nearly a century of industrial electro-chemistry, it is still true to say that all the industrially significant processes are those which do not suffer from a mass-transport problem because the reactant(s) are highly soluble in the electrolyte medium. Looking backwards, one can attribute the failure of at least some formerly practised operations to the enforced low-current densities or low efficiencies. Foremost in this category are those electro-organic processes [23] where the reactants were poorly soluble in the aqueous media used. Indeed, the only viable processes at all, using low-reactant concentrations, appear to have been those based on electrochemical effluent treatment and recovery of metals from dilute solutions, notably silver.

The invention of a 'fluidized bed electrode' a few years ago [28, 72, 100] had important side-effects in that it removed, from the minds of many electrochemists, the pre-conceived idea that an electrochemical cell consisted of two vertical plate electrodes and set them thinking about the role of mass-transport in cells of a larger size than those in normal laboratory use. Of course not all workers required this impetus

to prompt their thoughts in these directions, and apart from those concerned in the design of silver recovery plants, etc., workers such as Ibl, [1] Eisenberg, Tobias or Ross had clearly given much thought to the matter, as their writings show. However Ibl restricted many of his best papers to European journals, while the latter authors wrote largely in the specific contexts of fuel cell technology, ECM or corrosion. The results in both cases were that their message was not as widely appreciated among synthetic or industrial electrochemists as it deserved to have been. More recently Goodridge [97] *et al.* have extensively studied fluidized bed and related electrodes.

Sufficient time has now elapsed to enable the situation to be better appraised. Indeed, it is now true to say that we have a selection of cell designs an order of magnitude better (in terms which will be discussed below) than their predecessors. There is much to be said for the view that reactions hitherto unattractive for the reasons stated above, should now be reassessed in terms of these new reactors, before developing further refinements still. There have been signs in this field of cells being developed for their own sake, rather than to satisfy a required need or

shortcoming in other designs. Then, too, there are indications that cell designs are being 're-discovered' years after their first publication, usually in patents.

It is the aim of this paper to bring together as many different concepts or techniques for the enhancement of mass-transport in electrochemical systems as possible, together with information as to their success on an industrial scale, and particular features of their operation which might render them more or less suitable for a particular application. There have been attempts to do this before [7, 9, 29], but none of these were complete, some were not available in English while others contained various errors of fact or emphasis.

2. Classification and assessment of cell types

Several authors have attempted to define cells in terms of a single parameter; in particular A_s [29] and S_t have been used. The former is 'specific electrode area' that is geometric area per unit volume, the latter is space-time yield. We have decided against both these on the following grounds. Specific area is, it is felt, a valid criterion for genuinely planar electrodes. However, it breaks down not only with true three-dimensional electrodes such as packed beds where (as has been shown) increasing bed thicknesses bring diminished returns, but also with the many cylindrical designs, where the surface area:volume ratio depends on the radius of the cell. Space-time yields are open to similar objections in that they depend on the reaction used to define them, and the concentrations used. They also, give a measure which is very scale-dependent for cylindrical designs. Perhaps the optimum criterion would be a space-time yield figure related to a given dilute solution—say 0·01 M. In the table below, the criterion i_{lim} has been used, where this, too, is normalized to a 0·01 M solution and for a two-electron transfer. Of course, in most cases this is an $i_{lim, avg}$ since it decreases with increased electrode size. Equally useful would be the mass-transfer coefficient.

To make some sweeping, all-embracing, comparison of the 20 cell types listed above would be naïve. Of course all users are seeking maximum current density and efficiency at minimum cell voltage, pumping costs, capital costs, etc., but it is too rarely grasped that simplicity of design and construction or operation, commands a premium which can eclipse the higher performance obtained with more sophisticated designs. One critical step in this ladder is the use of moving or rotating components other than a pump. The second 'break' is the move from cells operating open to atmospheric pressure to those sealed with an internal overpressure which may not be large, but still requires rigorous sealing and gasketing all round.

3. Review of cell designs

3.1. Planar cells

Under this heading we can consider not only those cells with truly planar electrodes, but also those in which the planar surface has been curved into cylindrical shape. In nearly all these cases, the mass-transport properties will largely depend on the texture of the surface. Clearly a roughened surface will have a greater superficial area per geometric unit than its smoother analogue. Under activation control we may state, to the first approximation, that enhancement in activity is directly proportional to the increase in surface area. In the case of diffusion-controlled reactions, and these are the situations treated here, the relationship is less simple and depends largely, as Levich showed [42] on whether the surface asperities are much larger or smaller than the thickness of the diffusion layer. A more recent study of this is due to Ross and Badhwar [30] while many patents in all fields of applied electrochemistry specify shot-blasting, etching or other mechanical or chemical forms of increasing surface roughness creating either a random roughness or a corrugation-type effect. Several papers cited below (in relation to rotating cylinders) explore the differences between rough and smooth surfaces, in one case using coarsely and finely milled surface finishes, and these results can be extrapolated to other cell geometries. Schlichting, too [44], deals with the effect of projections from a surface and its effect on the hydraulic 'smoothness' or otherwise of the surface.

Table 1.

No. in text	Cell description	Mass transport enhancement	Pressurized	i_{lim}* (mA cm^{-2}) (Approx.)	Use/Scale-up (amp)
3.1.1	Widely spaced vertical parallel plates	N.C.	No	1·3 (5 cm high) 0·8 (40 cm high) [4]	1000 + F.S.N.
3.1.2	Widely spaced parallel plates with electrode(s) gassing	A.N.C.	No	variable	1000 + F.S.N.
3.1.3	Horizontal parallel plate, widely spaced	N.C.	No	2·8	1000 + F.S.N.
3.1.4	Parallel plates (vertical), widely spaced, gas-stirred	A.N.C.	No	0·6–1·4 mA	1000 + F.S.N.
3.1.5	Parallel Plates (vertical or horizontal) pumped flow. Spacing 2 cm to 0·02 cm (capillary gap) (including concentric cylinder)	F.C.	Yes	[4] 2·6 ($L = 10$ cm, 25 cm s^{-1}) 8·0 ($L = 10$ cm, 250 cm s^{-1})	1000 + F.S.N.
3.1.7	Parallel plate with integral circulator	F.C.	Yes	as 3.1.5	? P.?`
3.1.8	Serpentine cell (horizontal/ vertical)	F.C./G.F.	Optional	as 3.1.5	1000 + F.S.N.
3.1.9	Parallel plates (vertical or horizontal) packed with inert mesh, netlon, inert beads which may be fluidized	F.C./G.F.	Optional	0·5–0·9 mA	1000 + F.S.N.
3.2	Parallel mesh cells (expanded metal)	F.C./G.F.	Yes	1·0 mA (B)	1000 + L.P.
3.3	Parallel plates—foamed electrolyte	F.C./A.N.C.	Optional	—	? S.P.?
3.4	Wiped cylinder	M.P.C.	Optional	—	? S.P.
3.5	Cylindrical electrode tangential feed	F.C.	Optional	3.6 [16]	50 F.S.
3.6	Rotating disc (horizontal)	M.P.C.	No	2·8 (120 r.p.m.) [4] 8·8 (1200)	1000 + F.S.N.
3.7	Rotating disc (vertical) (half immersed)	M.P.C.	No	—	1000 + L.P.
3.8	Two phase flow (solid/liquid) (gas/liquid)	F.C.	Yes	—	? S.P.
3.9	Rotating cylinder or stirrer in vaned tank	M.P.C.	No	—	1000? L.P. ?
3.10	Rotating (rough/smooth) cylinder, rotating polygon · Archimedean screw impeller	M.P.C.	No	7·0 (150 r.p.m., [4] $\phi = 10$ cm smooth) 38 (2000 r.p.m., $\phi = 2$ cm rough)	100? F.S.N.
3.11	Packed bed ('Restrained bed') packing may be beads of metal or scrap/shavings, metal wool	F.C.	Yes	6 A [31] 115 B 57 C	? ?
3.12	Fluidized bed	F.C.	Yes	Similar to 3.11	2000 L.P.
3.13	Slurry electrode	F.C.	Yes	—	— S.P.?
3.14	Slurry electrode (vortexial feed)	F.C.	Yes	—	50? S.P.
3.15	Vibrating electrode	M.P.C.	No	—	
3.16	Bipolar bed	F.C./G.F.	Optional	—	S.P.

A   mA cm^{-2} on electrode total area basis.
B   mA cm^{-2} on diaphragm area basis.
C   mA cm^{-3} on cathode volume basis.
*i_{lim} is the diffusion limiting current for a solution of 0·01 M. ($n=2$)
Data for bed cells are quoted on the basis of current density per unit electrode volume.
N.C. Natural convection, A.N.C. assisted natural convection, F.C. forced convection, M.P.C. mechanically promoted convection, G.F. gravitational flow often employed.
F.S. = Full scale, N = Now in use, P = Pilot, L.P. = Large pilot, S.P. = Small pilot.
1000+ = Size of units in amperes.

3.1.1. *Widely-spaced parallel plate cells.* Such cells are still used (though not widely) in industry. The reduction of pyridine is probably based on large lead electrodes standing in large vats, one of them enclosed in a porous pot perhaps 40 cm diameter, 130 cm high [23]. Natural convection is the sole means of mass-transport, possibly enhanced by gassing at the electrode surface (see 3.1.2 below) at a later stage in the process. In this process, as, for example, in the older chromic acid regeneration cell, pumps play absolutely no part, and the cell with its electrodes stands until the reaction is deemed to be complete.

Another example using louvred electrodes for Ag recovery in static cells is described in a patent [20]. The general hydrodynamic treatment of such widely spaced parallel plate cells is described both by Ibl [4] and Marchiano [54].

3.1.2. *Widely spaced parallel plates with gas evolution.* The co-evolution of a gas (usually hydrogen) with a second electrode reaction, promotes that reaction, for as the bubbles form and break away, they create an effect on the diffusion layer which can be appreciable. This is a situation of real significance in, for example, the electrolytic manufacture of chlorates. Ibl [4, 141], Venczel [13] and Janssen and Hoogland [12] as well as Fouad *et al.* [18] have all examined this situation and formulated expressions such as $K_L = av^{0.53}$ where v is the volume of gas evolved in cc cm^{-2} min^{-1} and is greater than 0·2; a is some constant and K_L is the mass transfer coefficient. Work by MacMullin *et al.* [41] also treats this type of system while horizontal gassing electrodes are the subject of a paper by Fouad *et al.* [76]. The same author elsewhere describes the combined effects of surface rough-

ness and gassing [79]. See also [135] and Sections 3.1.4, 3.1.8, 3.3.

3.1.3. *Horizontal plates widely spaced.* The authors are not aware of any application of this configuration on a large scale, apart from the mercury cell in the chlorine industry which is, in any case, a pumped cell. It was a suggested layout for inorganic oxidation cells in older German patents, while slightly sloping electrodes have been the subject of patents [43] as recently as the 1950s though it is understood these are not in use. Without some form of pumping, such cells tend to suffer from gas locking at the underside of the upper electrode, even though this be foraminate. Hydro-dynamic relationships have been quoted for this type of cell [4, 50, 53].

3.1.4. *Vertical parallel plates, gas stirred. (Fig. 1.)* Where such plates are reasonably widely spaced, this is a situation that is found not only in many laboratory experiments, but also as normal practice in metal-finishing, where air is injected at the bottom of electroplating vats. In the latter case, electrode gaps of 20–50 cm are normal. A more interesting example is the tightly spaced configuration discussed by Schreiber [57] as used in silver recovery. He does not enthuse over this concept, raising as objections the facts that the air tends to depolarize the (silver) cathode, secondly that the bubbles reduce, by obscuration, the effective electrode area, and thirdly that foaming at the top of the cell causes operating problems [37]. Although this cell design does not seem to have gained widespread acceptance [57, 140] the first of the 'disadvantages' at least does not seem to be serious, except in this particular application and might indeed be a benefit. The concept seems to be the forerunner of the 'foaming' electrode described by Nanis [38]. Ibl has
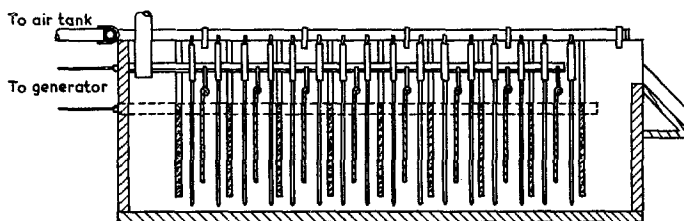

Fig. 1. Parallel plate cell with air sparging (ref. 57). (U.S. Pat. 1866701.)

also examined gas-stirred cells, using concentric cylinders for this [4]. The gas was injected at the bottom through a porous glass frit. In such a system, he obtained i_{lim} values (normalized for 0·01 N) up to 5 mA cm^{-2} using 10 cm high electrodes with 5 mm gaps. Ibl makes the important point that in such cells, the pumping energies (which are mainly those required to force the gas through the frit) are independent of cell height, and thus, as the cell height increases the pumping energy per unit electrode area, can actually decrease. This relation will hold until the electrolyte head becomes significant in relationship to the pressure drop across the frit. An even more effective enhancement of i_{lim} is given when porous electrodes are used, and gas is injected through the pores and here, Ibl quoted [4] i_{lim} values up to 9 mAcm^{-2}, though these were only obtained by injecting 11 cc gas min^{-1} cm^{-2} electrode area. The technological merit of this approach is probably not so attractive since not only are the running costs and capital costs higher, but porous electrodes are prone to blockage, etc. The idea appears to have been taken up again by Drazic and Kadija [45]. Increase in cell voltage due to gas bubbles in the electrolyte is treated by Tobias [77] and a more recent treatment is due to Beck [10, 104], while experiments to determine the thickness of the diffusion layer under gas stirred conditions have been carried out by King [102]. He quotes values of δ (the diffusion layer thickness) of greater than 0·005 cm under these conditions.

The buoyancy forces of bubbles generated in this type of cell may be harnessed to provide an autogenous source of 'pumping' and such cells, known as 'gas-lift cells' are typified in [103] in which Cr(III) is processed in a cell which draws in liquor from below and expels the reacted liquors at the top over a weir. See also Sections 3.1.2, 3.3, 3.8 and [147].

3.1.5. *Parallel plates, pumped flow [152]*. These cells appear to be a standard by which other designs are judged, although it is not easy to think of many applications apart from the cells used in the Monsanto process for adiponitrile. We can here differentiate between those cells which are open-topped and those operating under rather

higher pressure drops. Thus copper refinery cells fall into the former category, and the flow through these is both ill-defined and leisurely, while in the latter class, one might include the capillary gap (Fig. 2) cells of Beck [9] with inter-electrode gap
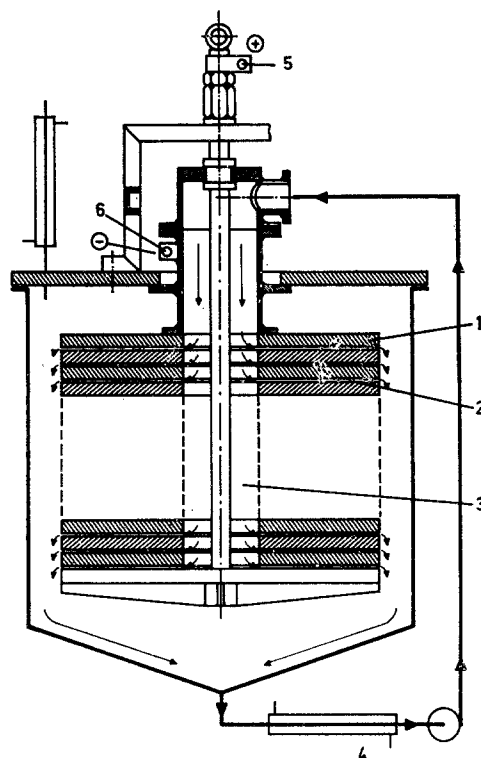

Fig. 2. Capillary gap cell—circular discs, (1) of inert conducting material, (2) capillary gap, (3) centre of stack (4) heat exchanger, (5), (6) current leads.

down to 0·02 cm. The 'performance' of the refinery type cells, for which typical figures are quoted in [33], is much inferior to those in which force-flow regimes operate. Beck's cell, with its very narrow gap, suffers from severe practical drawbacks, mainly the mechanical difficulties of creating and maintaining gaps to such small tolerances. It is really too early to say if its operation at these small gaps is a practicable proposition on the industrial scale. It should be noted too, that the maximum dimensions of the cell in the axis of flow are restricted by the fact that reactant depletion or exhaustions oon occurs. The simple conditions for uniform current density may be formulated where L, the maximum length when exhaustion is complete, is given by:

$$L = \frac{hVMF}{i_{\lim}}$$

where h is cell pitch, V the average velocity in cm s^{-1}, and reactant concentration is M equiv l^{-1}, F is the Faraday. For a 5 mm gap, a solution of 0·01 equiv l^{-1} and a flow rate of 50 cm s^{-1} with $i_{\lim} = 100$ mA cm^{-2}, L is 2·5 m. When one bears in mind that no cell would ever be operated to complete exhaustion and the very much smaller gaps used by Beck, the importance of this type of calculation can be seen [10].

Eisenberg [5] has given an excellent treatment of parallel plate cells, pointing out that the flow is laminar in the majority of practical situations. He quotes work that shows that flow in rectangular channels ranging from 3–165 in their dimensional ratios (width : plate separation) is laminar up to Reynolds numbers 1600–2800 [25]. The treatment of such cells shows the flow to be in two parts. In the first ('entrance effects') the flow is undeveloped. The length of this undeveloped region is given by the expression

$$L_{entr} = 0\cdot04hV/v = 0\cdot04 \, N_{Re}$$

where h is the thickness of electrolyte, V the velocity, v the kinematic viscosity and N_{Re} the Reynolds number based on channel width, following a formula given by Schlichting [44]. The formula

$$i_{\lim (av)} = 0\cdot66nDF \, C_o \, (v/D)^{0\cdot33} \, (V/vl)^{0\cdot5}$$

where l is the downstream distance over which $i_{\lim}$ is arranged, can be used to obtain an integral average for $i_{\lim}$ in the unsmoothed region.

After the flow is fully developed, an expression by Leveque [27] can be used to treat the situation.

$$i_{\lim} = 1\cdot62FC_oV(Vh/v)^{-0\cdot66} \, (v/D)^{-0\cdot66} \, (h/l)^{-0\cdot33}$$

where n is the number of equivalents per mole, F is Faraday's constant, C_o the ionic concentration in the bulk of the electrolyte, V the average linear electrolyte velocity, h the thickness of electrolyte and l the electrode length.

This work has been extended recently by Pickett and Stanmore [2] who also studied the turbulent regions although many of the conclusions, as well as the data of [2], were anticipated in the work of Tobias and Hickmann [81], while

other work along similar lines is understood to be in press from Pickett et al. Marquis et al. [3] demonstrate that the Chilton-Colburn [82, 90, 91] analogy can apply under a range of conditions, while an interesting point made by Beck [9] is that heat dissipation can assume an importance, even becoming limiting. As Ibl points out [4] these relationships have important consequences for scale-up. The $i_{\lim \, avg}$ values decrease as the plate length grows, and the shortcoming can only be made good by increasing the flow rate. However, the effect here is only $V^{0\cdot33}$ and to compound matters, the pumping energy required to create these higher flow rates are themselves based on a logarithmic scale, as the diagram from Eisenberg [5] shows in which, crudely, a tenfold increase in flow rate occurs for an almost thousandfold increase in pumping energy.

In addition to the parallel plate as conceived here, and the integral circulator, Section 3.1.6 below, there are other variants of the theme of industrial importance. Cells based on two concentric tubes are used in electrolysis of sea-water for hypochlorite production where very high flow-rates (10 m s^{-1}) and small gaps are used. Ross and Wragg [46] have examined the hydrodynamics of annular flow and their results are applicable to this type of cell. An interesting design for a 300 A cell was recently published by Eberson et al. [24] using a stainless steel cathode and a graphite anode, while a further variant is the Engelhard cell, which used an outer tube which is electrically split halfway along its length. One half is anodic, the other is made the cathode, while the inner tube, now requiring no electrical connections, is a floating bipole. The makers claim for this configuration, greater ease of electrical connection. Still a further version of the pumped flow parallel plate cell is the Johnson Seacell [143], used for the same purpose as the Engelhard cell for sea-water electrolysis [52]. In this design, a tubular plastic outer casing is filled with pieces of massive Ti which are cylindrical in one axis, and wedge-shaped in the other. The wedge is pierced with a hole. One side of the wedge acts as anode, the other as cathode. The result is that of a 'flight-of-stairs' effect, the wedges being separated by 'O' rings to give the desired anode-cathode gap. The design is of interest in that it neatly packs a bipolar series stack into a plastic tube.

However, it appears to be enormously wasteful of Ti (in essence the outer casing is virtually filled with this material) and also of the space that this metal occupies. One can envisage a development of the idea to eliminate these failings.

3.1.6. Miscellaneous parallel plate cells and related data.

Electrodialysis and ECM (electrochemical machining) are two technologies generating their own mass transfer data. High velocity (2000 cm s^{-1}) cells are described in [105] while several reports [98, 99] deal with flow patterns in electrodialysis cells and the use of turbulence promoters in such cells. A study of a flat plate electrode (laminar flow) located in an intake tube was reported by Iodkazis et al. [106] and in another paper by these authors [107] relating to parallel plate conditions. Other papers of interest relating to parallel plate cells are those of Wranglen [108], Sinkovic [109] and Arvia [110] which contain work relating to concentric cylinders while Newman has treated couette flow [111]. Opposing flows are discussed by Robinson [124].

3.1.7. The parallel plate with integral circulator.

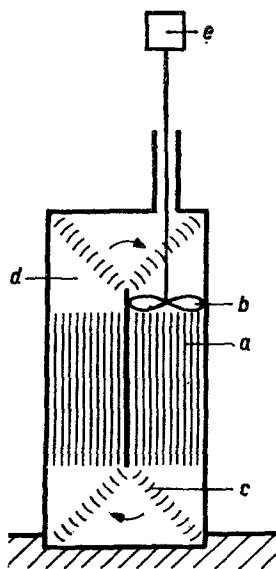(Fig. 3.) This is an idea again derived from Ibl and sets out to eliminate pumping losses outside the system, but essentially it is an elongated parallel plate with successive entry effects [4].

3.1.8. The Serpentine cell.

This type of cell (sometimes known as tortuous path) is again a parallel plate cell coiled up on itself. Usually these types are open to the atmosphere and the convolutions may be horizontal (from left to right and back) or vertical (switchback) but the effect is the same. They are widely used in metal recovery from Ag,Sn,Au plating line wash wastes, when the Lancy recirculatory system is used. A typical example is shown in patent form [26].

3.1.9. Parallel plate cells packed with turbulence promoters.

These can operate both as open and closed-top, and the packing may consist of glass beads, which can be fluidized as suggested by Le Goff et al. [34], or which may be static, or with 'Netlon' plastic mesh or similar material. Cells of 1 m height or more have been constructed by Surfleet et al. [83] for copper recovery. They feature simple planar electrodes resting on lugs to make their electrical contact. They are interleaved with plastic netting of some 3 mm thickness
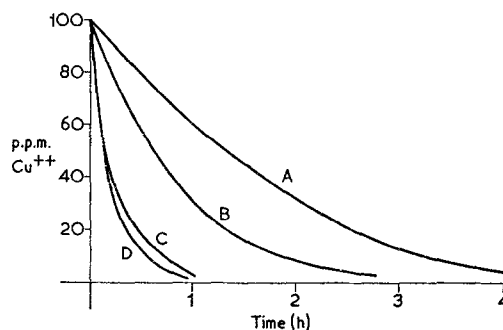

Fig. 3. Parallel plate cell with integral circulation. A = electrodes; B = impeller; C = deflectors; D = change of direction; E = motor.

Fig. 4. Comparison of the performance of different cell designs (removal of Cu^{++} at 100 ppm level). 4l of 1N H$_2$SO$_4$ + 100 ppm Cu^{++} circulated through cell at 277 cm^3 s^{-1}, 2A per 100 cm^2. A—parallel plate cell (as ref. 31); B—cell packed with Netlon; C—cell packed with 2 mm glass beads; D—restrained bed cell, lead bead packing 20 mm bed depth (ref. 31) bead size 2.6 mm.

having windows some 2 cm square. At the 100 p.p.m. Cu level (c.d. = 5 mA cm^{-2}) they operate at 30% current efficiency under a relatively slow flow, though it is worth noting that the smaller scale cells operated at over 50% efficiency, this

discrepancy being attributed to poor manifolding in the large cells. It is clear that manifolding is vital if cell performance is not to fall away on scale-up.

Perhaps the most interesting feature of this type of cell is its facility for operation at substantial overpressures. Although, as usually operated by Surfleet, the flow rate is not such as to induce appreciable overpressure at the cell exit (a weir-type at the top of the cell) the designer has included a flange around the top of the cell tank with facility for securing a cell top. With this in position, flow rates giving rise to considerable pressure drop across the cell may be used, with correspondingly beneficial results. The use of this facility brings out minor difficulties, mainly relating to electrical feed to the cell. Thus use of lugged electrodes on hanger bars becomes less attractive since lugs and hanger become wetted. Nevertheless the idea of a pressure cell in which the components are easily accessible deserves all the attention it can get.

One description of a pressurized parallel plate cell packed with plastic mesh is due to Thyn *et al.* [35] though few results are quoted. In this type of cell too, it is worth noting that the idea is one borrowed from electrodialytic cell design as photographs in [36] clearly show. In this case, however, the plastic mesh is interleaved between sheets of ion-exchange membrane and not, as here, between electrodes. In Fig. 4 is shown the only data known for this type of cell [31], apart from sporadic information such as quoted above. As in other cases, the data from electrodialysis (membrane-to-membrane cells) may be usefully cited, and a study of turbulence promoters in these has been released [99]. A turbulence promoter based on a porous, endless band which passes between the electrodes, has been studied by Ibl and Schalck (referred to in [142]).

3.2. *Mesh electrode with transverse flow (Fig. 5)*

One of the most interesting cells is one in which expanded metal forms at the same time the electrode and the turbulence promoter. This cell is disclosed in a German patent [19] assigned to ICI though whether this has priority is uncertain. Beck certainly refers to the same principle in his lecture of the same year (1966) while his earlier
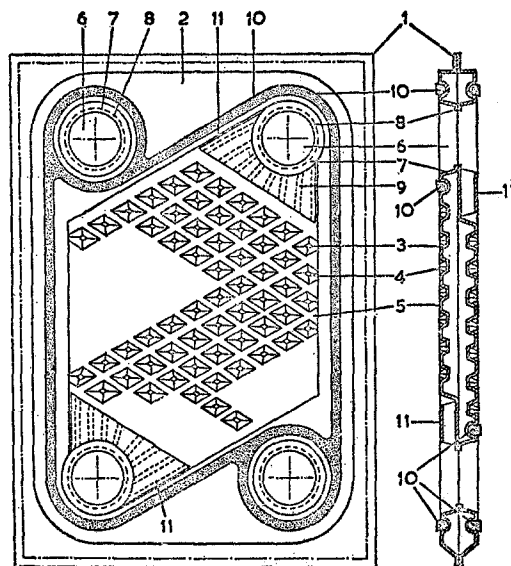

Fig. 5. Mesh electrode cell. Numbers refer to original patent. Large holes are for electrolyte feed and removal. Side and front elevation. (Ger. Pat. 2100214.)

Patents from 1967 [22] refer to the use of 'meshes' of metal as electrodes [150]. In view of the problems—which we shall see—of using true three-dimensional beds on the anodic side—this may be one of the most efficient cell designs now known for use on the anodic side for organic oxidations. Furthermore, in view of the importance of PbO_2 as an electrode material for these reactions, it is worth noting that expanded lead mesh is commercially available, as also is titanium mesh coated with PbO_2 [48]. A further important finding of Beck was that using this type of electrode as a narrow gap cell, separated from the counter electrode by an ion-exchange membrane, solutions of very low conductance could be electrolysed by a mechanism in which ions created at the electrode interface supplied the electrical transport processes. To give some idea of this cell and its performance, it is understood that some 2000A were dissipated in a cell hardly more than 1–2 ft^3 in which some six individual cells were linked. At such current densities heat dissipation becomes important and may in fact become a limiting factor as Beck shows [9].

3.3. *Parallel plates—foamed electrolyte*

This idea, foreshadowed by Garbutt [37] for

enhancing mass transport of a gas to a planar electrode by means of a foaming system, was recently described by Nanis et al. [38] and amounts to a novel approach to gas-consuming electrodes such as those required in fuel cells. The design is clearly cheaper to implement and in so far as air-depolarization (or indeed the use of gases other than air) is always a possibility in process design, the idea may find application. See also Sections 3.1.2, 3.1.4, 3.8.

3.4. The wiped cylinder

This type of cell described in Patent form [39] uses not only a rotating component but also a frictional method and would seem to indicate both high capital and running costs.

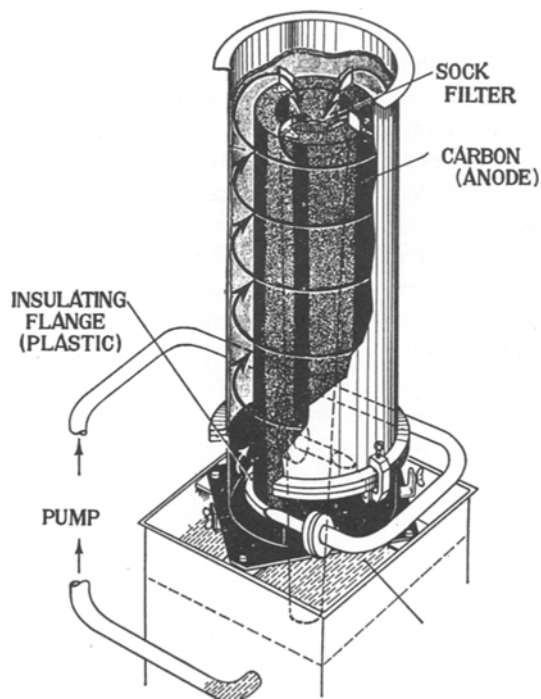## 3.5. Cylindrical electrode with tangential feed (Fig. 6)

Fig. 6. Pumped flow cell with tangential impingement.

This forms the basis of a commercially available silver recovery unit for which little scientific data are available, though it has been discussed in a paper by Cedrone [16] and in a private communication to the authors. A horizontal jet of electrolyte impinges tangentially on a vertical drum at a velocity of some $12 m\ s^{-1}$ (nozzle velocity) through two separate orifices. These nozzles discharge into the annular space between anode and cathode and assisted by vanes, the liquid travels upwards to the top of the cylindrical cathode. Here it is deflected to the centre (where it undergoes filtration) and returns to the sump prior to recirculation. The cathode in the particular unit is some $1 \cdot 1$ m high. The liquid velocity in a horizontal plane is given as $3\ m\ s^{-1}$ (as bottom of cylinder) which has decreased to slightly more than $1\ m\ s^{-1}$ by the time it has spiralled to the top. The difference between these two figures can be accounted for only by assuming that not all the inlet liquor emerges at the top, the balance presumably falling back into the sump. The overall flow rate is $360\ 1\ min^{-1}$ The authors claim that in this type of configuration, high surface velocities are provided without excessive mass flows, and, to illustrate their point, state that if the cell described above were 'unrolled' but keeping dimensions and separations the same, a mass flow of $4500\ 1\ min^{-1}$ would be required in order to provide an average velocity over the surface of $1 m\ s^{-1}$. (This argument appears to overlook the fact that $1 m\ s^{-1}$ is a figure for average velocity in one case, and terminal velocity in another, while also neglecting the pressure-drop effects introduced by vanes and configuration in the first case). Whatever the case, the system is effective and current efficiencies of 90% are achieved at $1 \cdot 5\ g\ l^{-1}\ Ag^+$, that is $1 \cdot 5 \times 10^{-2}$ M at $5 \cdot 8$ A ft. $^{-2}$ ($5 \cdot 8$ mA cm^{-2}). Based on these figures, our normalized i_{lim} is approximately $3 \cdot 6$ mA cm^{-2}. The idea appears to have been revised in [49], [60], and (downward flow, high rate, low pressure) [63].

3.6. Rotating disc (horizontal)

The laboratory application of this is too well known to discuss here. It has also been used as the basis of the Asahi mercury cell for chlorine manufacture [23] where it rotates slowly, spinning the bubbles of chlorine to the periphery, and thus reduces bubble resistance in solution. The cell design has not seemingly been successful

and while all mercury cells suffer from the poor floor space utilization of horizontal electrode cells (tiered mercury cells have been patented but not operated), the combination of this with an assembly of circular cells is guaranteed to give the worst useage of floor space and to maximize busbar length. This situation would be improved by using stacked discs ('Jukebox' cell) rather like Fig. 2 showing the capillary gap cell, except that alternate electrodes would be capable of rotation, or even using the principle of contra-rotation. The assembly thus resembles the colloid-mill apparatus used industrially, and this idea has been advanced by Fleischmann and also by Mitrovic [45] as well as forming the basis of Patents [64] and [65] in the latter of which the discs are eccentrically mounted on the vertical shaft, to promote further turbulence—but again at the expense of electrode gap values.

3.7. *Rotating disc (vertical)*

A 2000 A plant with such an electrode was used in Germany during the war at Gersthofen to extract Na from amalgam in a molten salt process. Badische are understood to have operated a mercury cell in this configuration some years ago [40].

3.8 *Two-phase flow*

The inclusion of 'inert solids' to enhance mass transport is disclosed [6] in a German patent for electrofluorination cells. CaF_2 particles were pumped round with the anhydrous HF electrolyte. One suspects that attrition of the particles must rapidly have occurred, while pump wear was increased. The same is true for [8].

Gases may also be used as one component of a two-phase flow system. Gas-stirred cells as commonly used in the metal finishing industry have been referred to in Section 3.1.4 but in this context, using large electrode gaps with open-topped cells, the action is comparable to paddle-stirring. Gas-injection facilities are built into submarine lead-acid batteries to reduce concentration polarization due to acid consumption. Fig. 1 (from [57]) shows an air-sparged cell with parallel plates, while Ibl [4, 141] describes gas injection both from underneath a cell (through glass sinters) and also through porous electrodes. In all these contexts, however, there is no forced convection of the electrolyte, and none of these systems truly represent two-phase flow. Gosman *et al.* [84] have studied two-phase flow electrochemical cells and apart from the work of Nanis (Section 3.3) the only other system close to this, is the use of gas-sparged [121] electrolytes in secondary zinc-air batteries with recirculating KOH. Jennings *et al.* [85] have studied two-phase flow in a parallel plate reactor while Colquohoun-Lee and Stepanek [89] are currently studying two-phase flow in packed bed reactors using electrochemical probe techniques. In both cases, the enhancement observed appears to result from an increase in N_{Re}, which in turn stems from the decrease in cell cross-sectional area, the remaining space being taken up by the gas phase. In so far as the same benefits appear to be possible by increasing the flowrate of a single phase, the idea is of marginal interest. Special problems arising when air is used were foreshadowed by Schreiber [57] and confirmed by Jennings [85] and stem, in each case, from the oxidizing action of this gas. Of course in certain systems this might be
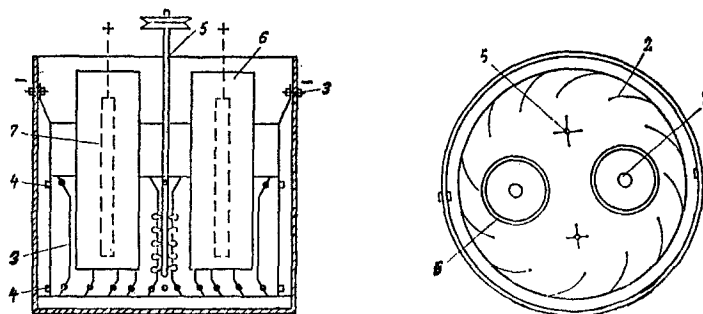

Fig. 7. Stirred tank fitted with vanes.

actually beneficial, while the suggestion has also been made that N_2 could be pumped round as the second phase in an essentially closed loop. That similar work is in progress elsewhere has been indicated by [45, 122, 123], the full contents of [137] which are not available to us at this time. References [10, 104] are also relevant. See also Sections 3.1.4, 3.12.
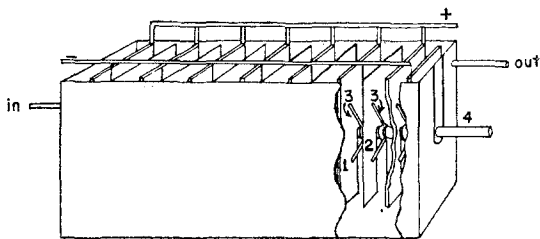

Fig. 8. Paddled-stirred tank. [57]

3.9. *Stirred and vaned tanks (Figs. 7 and 8)*

These appear to have been used for electro-organic reductions on a large scale [7] while silver recovery cells based on the idea are described in [14, 66] (rotating cathode with rotating and fixed vanes) and [67] where liquid is pumped and swirled against fixed vanes (cathodes).

3.10. *Rotating cylinder (Figs. 9–11)*

There is no doubt that such cylinders, especially when their surfaces are roughened, are extremely efficient. However, it is not easy to see a process based on a series of high-speed rotating cylinders each of which must be of limited size. Apparently unpublished data for fairly large cells of this configuration are shown in Fig. 11. As indicated by Ibl [4] such rotating cylinders can have phenomenally high i_{lim} values (up to 19 mA cm^{-2} quoted for 0·01M) and expressions for the hydrodynamics are quoted by him, by Gabe and Robinson [51] and also by Kappesser *et al.* [11] who investigate the effect of both smooth and rough rotating cylinders. No. 3.10 in Table 1 describes a commercially manufactured cell along these lines but incorporating vanes on the cylinder (which can also be [62] a polygon). In the latter case, the 'trailing edge' induces extra turbulence but the inter-electrode gap must be correspondingly enlarged. It is also interesting to note that, in the light of continuing claims for the benefits of electrical pulsed cell operation, such a cell does in fact operate (under mechanical means) in this electrical mode. The 'ARRI' Ag recovery cell uses stationary concentric cylindri-
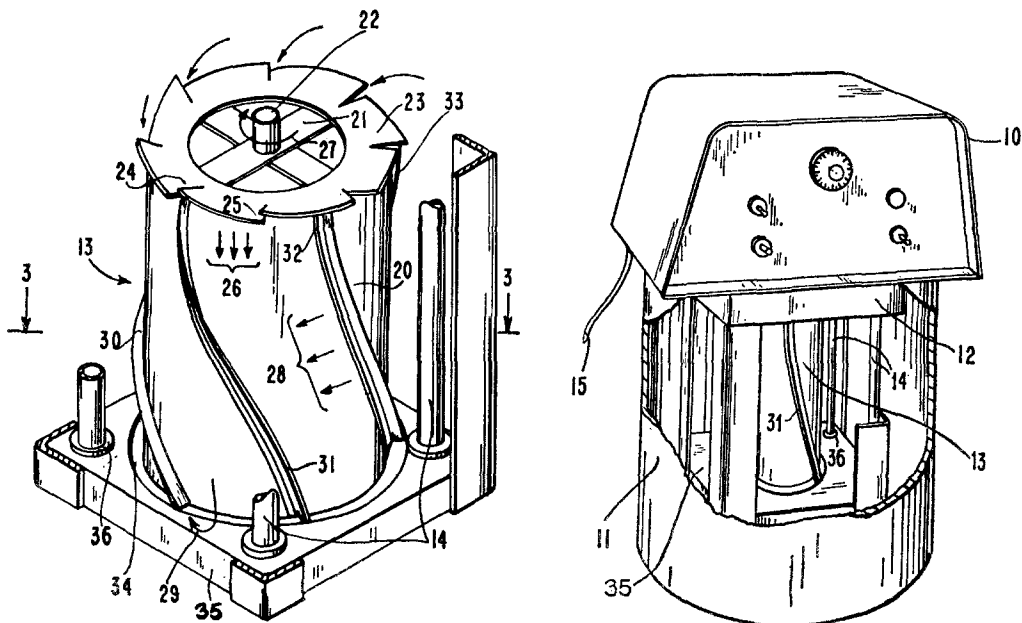

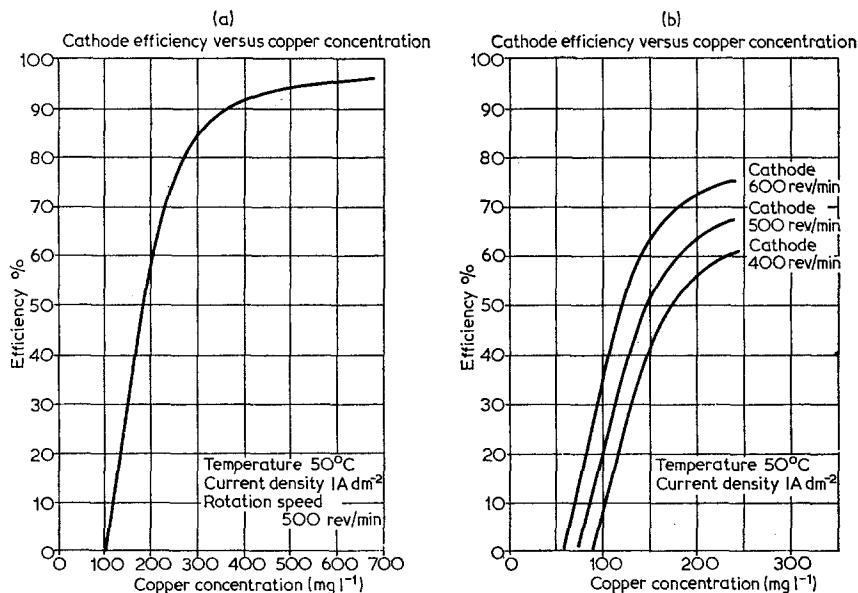Fig. 9. Archimedean screw cell (numbers as in Patent [14].)

Fig. 11. Performance of rotating cylinder cell (Courtesy of R. Pinner, Lancy Laboratories [17].)

cal cathodes with rotating anodic blades on either side of them [57]. An unusual idea [68] is a horizontally rotating cylinder 'wetted' with electrolyte fed from a feeder box, and surrounded by a flexible sheet counter electrode. Gaps down to 0·001 cm are quoted and the system resembles a brake-drum and shoe. It is specially mooted for more viscous liquids. Matic *et al.* [113] have recently reported hydrodynamic data on this system while Gabe has written an exhaustive review on the Rotating Cylinder Electrode (*J. Appl. Electrochem.* **4** (1974) 91). See also [142]

3.11. *Packed bed electrodes*

Here, with the possible exception of No. 3.2. (in Table 1), we come to the first of the so-called 'three-dimensional electrode' cells. Historically, this version is the oldest of this class, though as we shall see, it has been used or suggested in many variants. The normal porous fuel-cell electrode is excluded from this discussion, since it operates in a mode where reaction takes place only to a limited extent *within* the depth of the electrode, being mainly confined to the fine-pore region. However fuel cells were constructed in the 'flow-through' mode, in which liquid electrolyte with or without gases dissolved, flowed through the pores [92–96]

(at rates of up to 10 cc cm^{-2} min^{-1}) to emerge on the far side and this constituted a true three-dimensional electrode system, though few quantitative conclusions were reached, partly because the geometry was ill-defined. Sioda has reported [78, 126–131, 148] a variety of studies relating to electrodes made of stacked gauzes, as well as carbon granules. The flow through these, however, was under gravity or trickle-feed, and the aim was in no way towards technological ends. Bennion too [73] has described the removal of cupric ions at very low concentrations through trickle-flow beds, while Gurevich *et al.* [70] have modelled a fuel-cell 'flow-through' system. Most of the above workers, however, eschewed the use of higher flow rates. Similar work reported in [132–134, 138]

Recently there has been a surge of interest in forced-flow-through packed beds as indicated by [86–88, 151]. Turning to this type of work, Colquhoun-Lee [61] has surveyed the hydrodynamics of packed-bed reactors, and reported, among the various studies, some in which electrochemical methods were used to characterize the flow regimes and mass-transfer characteristics. The actual currents and current densities used in these studies, however, were low and the beds were made of ceramic or similar particles with a net-
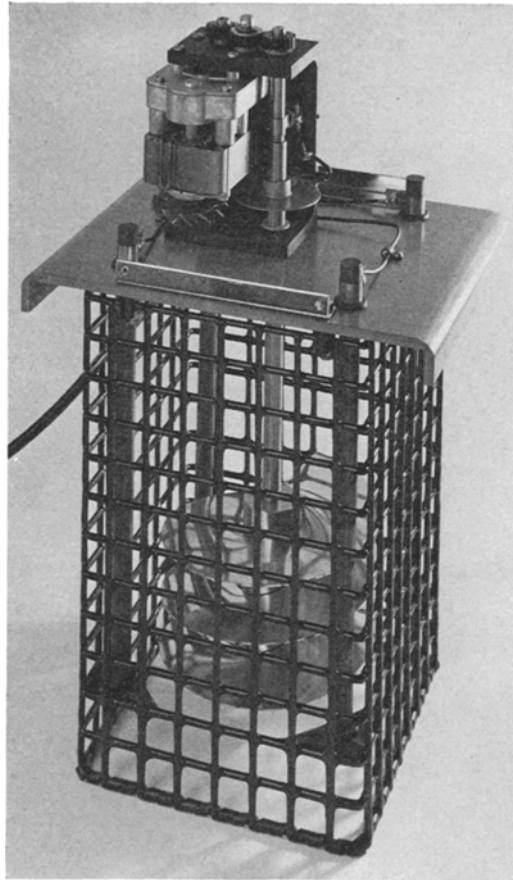
Fig. 10. Auger type cell. (Courtesy Messrs Williamsons Ltd.)

work of electrically connected metal beads interspersed among them. Only in these studies and those mentioned below, were the higher ranges of N_{Re} covered. Houghton et al. [31] have reported [125] in some detail on the removal of Sb^{+++} onto packed beds of lead beads, and describe the effect of flow rate, current density, bead size and other variables in terms of pressure-drop, cell efficiency, etc. The fluidized bed (No. 3.12) which in many ways closely resembles the packed bed, has been operated in the restrained mode, whereby a net prevents the fluidization of the particles under a flow regime that would otherwise promote this. Constructors John Brown (Developments) Ltd. have been active in this field, and [118] and a patent [69] describe such a cell, giving in addition a very interesting graph in which the performance of the same cell under a range of flow rates is compared for both the restrained fluidized and planar sheet modes of operation. At higher flow rates (and consequently degree of bed expansion) the fluidized bed reactor performance falls off markedly in contrast to that of the restrained model.

The cell described by Houghton [31] differs from that apparently in use at Constructors John Brown (Developments) Ltd in that, in the former case, the fluid flow is across the thickness of the bed (along axis of current flow), while in the latter case the flow is along the plane of the bed and at right-angles to the direction of current flow. In so far as the lowest possible pressure-drop across the bed is to be desired (these are shown in [31]) one might envisage larger cells [31] fed from behind, using a separate chamber with perforated front face giving access to the bed proper, with arrangements for exit of the electrolyte made at the bed perimeter or in a similar manner.

Armstrong et al. [21] probably lay claim to first pointing out that as the bed thickness is increased the benefits are decreasingly worthwhile, mainly because of ohmic-drop through the bed. Otherwise the theoretical treatment would seem to be a simple adaptation of the chemical engineering models cited by Colquhoun-Lee et al. Wroblowa has also discussed 'flow-through' electrodes [80]. Eardly et al. [115] have modelled in an ingenious way, as have Lovrecek et al. [116] though in a different way. A porous carbon

electrode to remove trace metals is described in [117, 138].

A number of industrial applications of bed electrodes have been recorded. The NALCO process for the manufacture of tetra-alkyl leads is based [23, 15, 47] on such a bed, while Beck has [144] suggested metal-wool as an electrode packing [149]. Recent patents have suggested porous graphite or carbon as a means of removing mercuric ions from dilute solutions, while [32] is another example. A patent [43] suggested the use of lead scrap as a three-dimensional electrode some 15 years ago. Particle sizes range from 70 to 2500 μm in the various papers cited above and the effect does not appear to be large [125, 118]. Recently, Messrs Koch-Light have introduced the 'Vitromet' range of metallized beads in a number of ranges of metals and sizes, and these should prove valuable both for packed as well as fluidized (No. 3.12) and bipolar (No. 3.16) beds.

3.12. Fluidized beds

So much has already been written of these, e.g. [71, 72, 100, 101, 136] that we are reluctant to do more than summarize the situation. Intrinsically their performance, as has been said, is little better, if at all, than that of packed beds, and can be inferior [69, 118]. However, from an engineering point of view they may be advantageous. For example, in the case of metal deposition, the accretions will be more evenly deposited, and thus eliminate the situation, as in the case of Cu^{++} deposition, for example, where using a packed bed, the whole mass 'freezes' together, thus presenting the most serious operational problems. Not all metals suffer from this as Houghton et al. [125] showed. The second more general advantage is that, during operation, the bed particles may be circulated, exchanged and generally manipulated in a way which is not open to the packed-bed cell operator. Disadvantages of the fluidized bed system are shown when gases' are present or evolved in the reaction, as well as in many cases of anodic reactions where the inter-particulate ohmic resistance due to oxide layers effectively can render the bed inert or partly so [31]. Constructors John Brown (Developments) Ltd., have run beds of 2000 A rating

and clearly see no objections to further scale-up. A further apparent disadvantage of the fluidized bed system is that if bed expansion is to be restricted to (say) 10%, for reasons of inter-particulate conductivity, this precludes the higher flow rates shown to be beneficial in the restrained bed. Two interesting recent studies are those of Jannsen [119] and Heitz [120].

Fig. 12. Slurry electrode in vortex configuration.

3.13. *Slurry electrodes* (*Fig. 13*)

In these systems, which pre-date the fluidized bed, the concept is one of breaking up the electrochemical reaction into two stages. In the first, the conducting particle in the bulk solution comes

into contact with the reactant which may be adsorbed on the particle surface or may, as with a redox reaction, suffer a change in oxidation state following a brief contact with the particle, whose charge state then itself alters. Following this, the particle is swept back into contact with the 'feeder' electrode where it becomes recharged to its pristine level. For slow catalytic reactions, the concept has the additional advantage that the reaction can proceed on the particle surface during the time before its contact with the 'feeder' electrode. The most obvious drawback here is the ease with which such small particles (diam $<100\ \mu m$) can be lost from the system from a quantitative aspect, while a patent [55] shows its industrial application. Two phase + slurry is discussed in [145] and magnetically assisted slurries in [146].
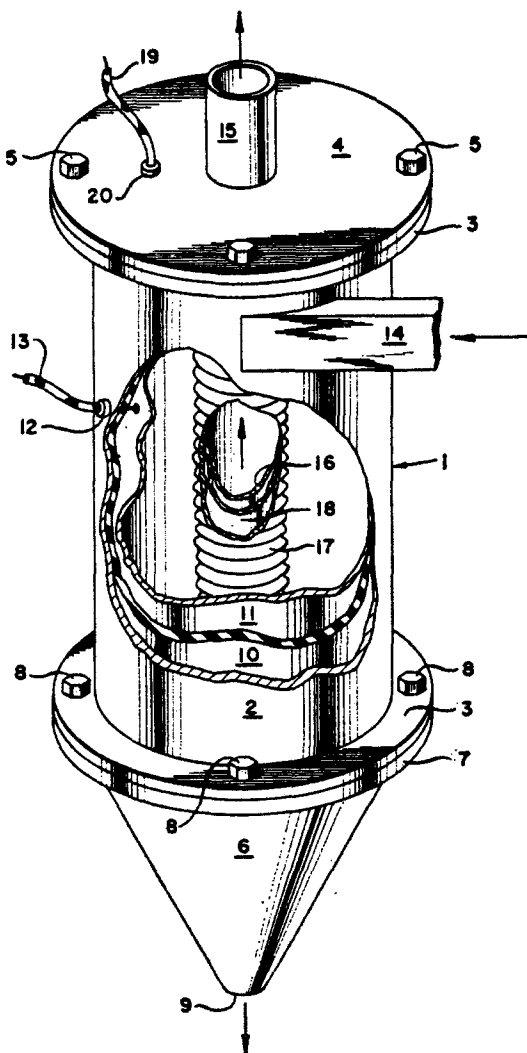
3.14. *Slurry electrode with vortexial feed* (*Fig. 12*)

Here one sees the combination of two ideas, as instanced in No. 3.13 and No. 3.15. The idea is described in patent form [17] and nothing more is known about the work.

3.15. *Vibrating electrodes*

These have been discussed by Beck *et al.* [9] and revived by Mitrovic, Konjovic and Despic [45] while reference to the same idea (as well as oscillating electrodes) is referred to in [65]. Grafov [114] treats this system. Rocking electrodes are also discussed in [36].
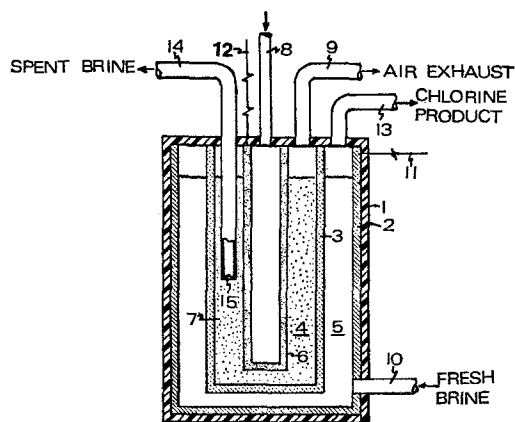

Fig. 13. Slurry electrode (numbers as in Patent [55]).

3.16. Bipolar electrodes

It was realized that, with a poorly conducting electrolyte, the situation might be created where the same conducting solid, be it a metal or a carbonaceous or similar non-metallic solid, could function simultaneously both as anode and cathode. This arises when the resistive-drop through the electrolyte exceeds the sum of the reversible voltage of a complete theoretical cell (for the reaction in question) plus the over-voltages and the resistive-drop through the conducting solid. An early and much publicized application was the 'Resources Control Inc' bed of coke in which $Cu(CN)_2$ was electrolysed to metal and nitrogenous [58, 59, 139] products. In such cells a very high voltage is invariably found. Fleischmann and Tenakoon [74] described a bipolar bed, in which the conducting particles were interspersed with insulating ones. More recently, King [75] has described a 'rod' cell in which a series of parallel horizontal conducting rods are aligned one above the other. Electrolyte is trickled down over these so that only a film exists over them. One sees two situations where the idea has appeal. Firstly, in the processing of very dilute solutions, the mass transport problem is solved as it were, because there are anodic and cathodic sites everywhere. Thus the method proved extremely effective in the destruction of copper cyanides cited above, although the subsequent recovery of the metal proved an invidious task. The second situation of potential value is in 'indirect' electrochemical processing where an inorganic species is electrochemically oxidized, itself oxidizes another compound and is so reduced, then requires re-oxidation. The formation of OBr^- and its oxidation of propylene to propylene oxide is a reaction often mooted for this type of cell.

4. Conclusions

A wide range of concepts for the enhancement of mass transfer in electrochemical processes have been shown. Almost all have analogues in the chemical engineering realms of heat transfer, and there is no doubt that other electrochemical cells based on their counterparts in the chemical engineering technology of heat and mass transfer

will appear in due course. To a certain extent, there has been an effort concentrated on the maximization of i_{lim}, and this may have been misguided. Thus one does not readily foresee the adoption of large-scale cells involving moving parts, not least when these rotate at 2000 r.p.m. Not only are we faced with the inevitable maintenance problems, but there are also the extra capital costs of electric motors, while the problem of feeding in at a moving electrode, and the high DC currents involved, raises their own particular difficulties. Over and above this, the following objection—which has not hitherto been seen—must be raised. A cell with rotating parts must be essentially cylindrical. This being so, it follows that whatever the high i_{lim} possible, (based on a current density figure)—the system is doubly inefficient in its aggregated state. Firstly, because cylinders pack in a wasteful fashion with wasted interstitial space. Unfavourable busbar costs also arise in such a situation; and these should not be underestimated. But more important is the space wasted within the cylinder. In general engineering costs are a function of the volume of the item, and the bulk of this space is wasted.

If, for these reasons, one precludes from possible large-scale use cells with rotating parts, the most natural choice seems to be the parallel plate cell with turbulence promotion, either from inserts of insulating material or by means of electrode geometry or in some other way. The former add almost nothing to cell costs, indeed they are called for in cells of large area fitted with membranes. In such cells one still requires moving parts, as indeed for all systems save those based on natural convection. But because these are pumps and because the problems of mechanical design can be considered and optimized without consideration of electrochemical factors, the authors conclude that 'divide and rule' is the best maxim for the foreseeable future. The table should show how much superior, in terms of mass transfer, the modern cells are to those which are described in the earlier literature. Now, it is firmly believed, is the time to take these cell designs, without striving for even further performance which may well come only at the expense of costly and sophisticated design, such as the use of pulsed

liquid flow or ultrasonics, and to re-assess the many electro-organic processes which once operated or were suggested in the literature. If one cannot be found that can be thus revived, it will be surprising indeed. Work along several fronts at the University of Salford suggests that this is no vain hope.

Acknowledgements

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