

## Process aspects in aluminium reduction cells with wettable cathodes

This paper deals with process modifications that may result from the use of  $TiB_2$  and other similar materials as a substitute for carbon cathodes in aluminium reduction cells\*). These materials, often referred to as RHM (refractory hard metals), are wettable by liquid aluminium and thus the metal layer in the cell can be reduced to a thin liquid film. The anode-cathode distance (ACD) can therefore be reduced significantly with a great potential for energy saving. The assumption that this potential could be effectively realised without radical changes in the electrolytic cell has increased the interest in wettable cathodes. These have been recognised as one of the most promising prospects in aluminium smelting<sup>1) to 3)</sup>.

However, although the conceptual basis of the process would remain unchanged, the new cathodes would involve significant modifications in the electrolytic apparatus and in the process itself. Moreover, there are complex problems with the supply and costs of appropriate materials as well as the insufficiently developed related technologies. Thus, in evaluating the actual possibilities of RHM cells, the three following correlated aspects should be considered: Cell design and engineering, process modifications, materials.

Billehaug and Øye<sup>4) 5)</sup> have reviewed the literature and patents on prospective materials and cell designs. Recently, Dorward<sup>6)</sup>, from Kaiser, presented extensive experimental results on process modifications in various RHM cells. While in a previous review we made an overall analysis of the three aspects referred to above<sup>7) 8)</sup>, in this paper we will mainly concentrate on some process aspects with a brief reference to cell design and engineering. A further consideration of the materials question will shortly be published elsewhere<sup>9)</sup>.

### Cell design and engineering

Most of the solutions proposed are reviewed in refs. 4) and 5). We will consider here just the De Varda cell, developed in Italy by Montecatini (a parent company of Alluminio Italia SpA) and a cell developed by Kaiser within a project sponsored by the U.S. Department of Energy.

#### The De Varda cell

The cell is shown schematically in fig. 1<sup>10) 11)</sup>. Its potential advantages (relatively low amperages, high productivity, low energy consumption) stimulated a major development effort during the 1960 s. Early in the 1970 s the project was considered impracticable due to technological reasons mainly associated with the lack of appropriate materials at acceptable costs.

The lining material should be a good insulator in order to reduce current losses through non-interelectrode paths as much as possible. Since carbon is not suitable for electrodes, RHM and other appropriate materials should be

used for cathodes and inert anodes. Recent progress in the field of materials suggests that the difficulties previously mentioned could be overcome.

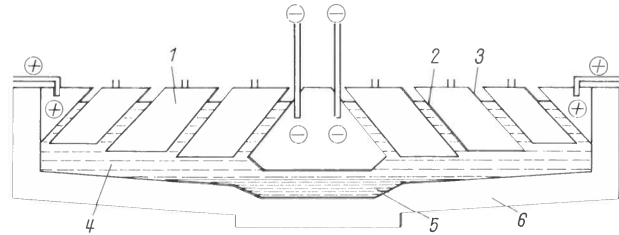


Fig. 1: Schematic transverse section of De Varda cell<sup>10) 11)</sup>; 1 bipolar electrode, 2 anodic surface, 3 cathodic surface, 4 bath, 5 liquid aluminium, 6 insulating lining

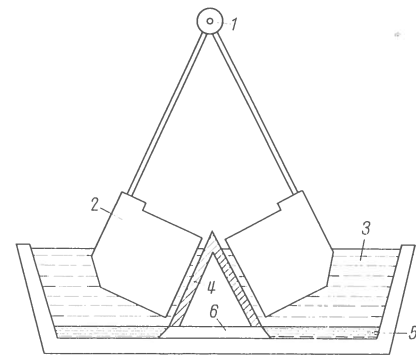


Fig. 2: Schematic transverse section of Kaiser RHM cell<sup>12) 13)</sup>; 1 anode support, 2 anode, 3 bath, 4 RHM cathode assembly, 5 liquid aluminium, 6 cathode support

#### The Kaiser-U.S. department of energy project

For more than two decades Kaiser Aluminium and Chemical Corporation devoted a significant effort to the development of RHM cathodes. More recently, a project has been set up with the sponsorship of the U.S. Department of Energy (DE) for the development of a 40 kA cell with  $TiB_2$  cathodes. Data relevant to the project have been obtained from a 15 kA cell, a sketch of which is shown in fig. 2<sup>12) 13)</sup>. The cathode is made of  $TiB_2$  as either plates or rods and its external faces are the active surfaces. The anodes hang from a support that allows them to rotate in order to adjust the ACD. The same geometry is kept for the design of the 40 kA cell. Accurate tests of components and materials were carried out before the effective construction of the cell<sup>14) to 17)</sup>. According to the technical progress report of April 19th 1983 (the most recent seen by the authors), the cell was put in operation in October 1982 and operated for one week to provide energy consumption and other process data<sup>18)</sup>. It seems clear that extensive research is necessary before a complete assessment is possible. Whatever the outcome, the Kaiser experience constitutes a point of reference for any other research in the same field.

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## Process modifications

Whatever the design of a RHM cell, it should operate with a small ACD, a thin film of metal on the cathode, a new electrode geometry and without any significant electromagnetic agitation. These conditions are different from those of a conventional industrial cell and therefore the whole situation should be entirely re-assessed. Unfortunately the information on process modifications in RHM cells currently available is insufficient. The scarcity and high costs of appropriate materials limit the number and the size of experiments. In this context, the Kaiser experience referred to above assumes a great importance: results obtained with various cells during a period of about 20 years have recently been published by Dorward<sup>6)</sup> and many features of the DE sponsored project are publicly known. In previous papers some possible process modifications in RHM cells were examined in the light of laboratory information<sup>7) 8)</sup>. In this paragraph these modifications are discussed in the light of Dorward's and other results from Kaiser. Relevant modifications may be expected in relation to the following aspects: Current efficiency and sodium separation, decomposition voltage of alumina, alumina dissolution, gas evolution and electrode geometry.

### Current efficiency

Any variation in an aluminium electrolysis system that accentuates anode-cathode interaction tends to produce negative effects on current efficiency. Thus at small ACD the losses in current efficiency could balance out the beneficial effects of a lower voltage drop in the electrolytic bath. In industrial cells ACD is kept relatively high in order to reduce the negative effects of electromagnetic agitation of the melt on current efficiency. However, even in laboratory cells, where this kind of agitation is practically non-existent but all other conditions are similar to those of the industrial operation (current density, electrode geometry, bath composition and temperature) a significant decrease in current efficiency has been observed at an ACD of less than 3 cm<sup>19)</sup>. Such an effect may be a serious limitation of the RHM cells.

The relatively low current efficiency in aluminium electrolysis results from the overlapping of various correlated phenomena and the observed effects are difficult to interpret<sup>20)</sup>. We will focus here in two kinds of efficiency losses: chemical and electrochemical.

Chemical losses are mainly associated with the well known "metal fog" which forms near the cathode surface by dissolution of the metal in the bath and then diffuses towards the anodes where re-oxidation, mainly by CO<sub>2</sub>, occurs. These processes are accentuated by high temperatures and, in industrial cells, by electromagnetic agitation. Chemical losses also depend upon the composition of the bath and the current density (current efficiency increases when current density increases).

The electrochemical losses are primarily associated with the separation of sodium from the cryolitic electrolyte. Although the difference between the reversible standard potentials for the discharge of aluminium and sodium donors is favourable to aluminium separation, the discharge of sodium ions can actually occur due to a concentration polarisation effect<sup>21)</sup> (this originates in the limit layer of the electrolyte at the cathode surface where the concentrations of aluminium and sodium donors are respectively lower and higher than in the bulk). In industrial cells under normal operational conditions, the electrochemical losses are not relevant since the concentration of aluminium donors is suffi-

ciently high and the electromagnetic agitation homogenises the melt.

Thus the agitation has two opposite effects on current efficiency: negative (accentuating chemical losses) and positive (reducing electrochemical losses). The decrease of current efficiency at short ACD has already been pointed out. The negative effects of high temperatures and high cryolitic ratios (high NaF content) are also well known in both laboratory and industrial cells. An outline explanation of all these features can be found in the above losses description. However the Kaiser experiments suggest that current efficiency at short ACD is not a major problem. In fact in the 15 kA cell with TiB<sub>2</sub> cathodes, a sketch of which is shown in fig. 2, a current efficiency of 85% has been observed with an ACD of 1.9 cm<sup>12) 13)</sup>. The bath temperature was low (about 850°C), but this choice seems to derive from operational reasons to avoid crust formation – which is necessary in order not to obstruct anode movements –, to reduce corrosion in some components) rather than the need to increase current efficiency. Dorward<sup>6)</sup> reports a current efficiency of 87 to 88% for a cell of 10 kA nominal capacity operating at 970°C and cryolitic ratio of 1.35 to 1.5 by weight with an ACD of 1.9 cm. The TiB<sub>2</sub> cathodes were slightly sloped. The high value of the current efficiency in such unfavourable conditions (high temperature and high cryolitic ratio) is noteworthy even considering the value of the current density (1.6 A/cm<sup>2</sup>) and it is difficult to explain in terms of the chemical and electrochemical effects referred to above. Although the electrode geometry is not very different from the conventional (5° sloped to horizontal), changes in the distribution of mass transfer and electrode processes and therefore in the gas-fog interactions cannot be excluded.

Further research seems necessary in order to establish the actual relevance of different processes that may affect current efficiency and correlated phenomena. For example, the concentration polarisation, besides favouring losses in current efficiency would add an overvoltage that may be significant. Moreover, sodium effects on the cathode material should be evaluated. If the losses in current efficiency prove to be significant the technical and economic feasibility of radical changes in the bath composition and/or in the electrode geometry should also be evaluated.

### Decomposition voltage of alumina

The advantages of operating cells at relatively low temperatures are widely recognised. In RHM cells low temperature operation may be necessary in order to keep adequate current efficiency and for appropriate thermal balance conditions without a significant increase in current density. Nevertheless the fact that the alumina decomposition voltage increases when the temperature of the electrolyte decreases, must be taken into account. The Kaiser-DE experiments indicate that such an effect can be considerable. In fact, it has been reported that the total decomposition voltage (reversible + overvoltage) increases from 1.7 V at 980°C to 2.1 V at 800°C, i.e., 400 mV at a rate of about 2.5 mV/°C. This is considerably higher than that of the reversible decomposition voltage evaluated at about 0.6 mV/°C<sup>14) 22) 23)</sup>. The large increase observed may be associated with an electrode overvoltage (anode and/or cathode) the nature of which remains unexplained. The total decomposition voltage seems to be dependent on the bath composition. The values referred to above were obtained using a bath consisting of an equimolar mixture of lithium and sodium cryolites. The voltage increase observed in similar conditions with potassium cryolites is 50 to 100 mV less. If low

temperature operation were unavoidable, the bath composition would be one of the few variables with which to play.

#### Alumina dissolution

Dissolution of alumina is highly endothermic. About 700 kcal/kg (alumina) are required to increase the ordinary Bayer alumina concentration in the bath at 950 °C from 1.5 to 7% by mass (alumina at room temperature). This amount of heat is roughly equal to the heat freed by the solidification of 5.5 kg of cryolite<sup>24</sup>). Alumina dissolution will certainly be more effective when the amount of heat available in the bath is great and when agitation of the melt occurs. Moreover, agitation produces a homogenisation of the alumina concentration in the bath, including the anode-cathode gap, which in industrial cells is relatively large. The situation is less favourable in RHM cells with a short ACD (therefore less heat available) and little agitation of the melt. Normal diffusion deriving from concentration gradients does not seem to be sufficient for a satisfactory homogenisation in acceptable periods of time<sup>25</sup>). Thus, significant amounts of alumina can remain undissolved while the electrolyte in the anode-cathode gap will remain depleted.

The effects deriving from a poor alumina dissolution ought to be investigated in order to establish their actual relevance and to explore alternatives to counteract them (e.g. changes in the bath composition, particle size and  $\gamma/\alpha$  ratio of alumina, appropriate alumina feeding system with mechanical vibration).

#### Electrode geometries and gas bubble effects

Although electrode geometry can have a great influence on electrolytic processes, the horizontal position of the electrodes, with their flat anode surface facing downwards, has always been standard in the design of aluminium reduction cells. The possibility of using wettable cathodes could change this practice since they must have a sloped position. Therefore, electrode geometries become another variable to be optimised in cell design.

The structure and geometrical arrangement of the electrodes primarily affect the development of the gaseous products of the electrolysis. The configuration of the gaseous mass affects the oxidation rate of the metal fog (and thus the current efficiency) and the active volume of the bath (and thus the voltage drop in the bath). Both kinds of effect are greater at small ACD. In molten salts the gas evolution is difficult to observe directly. Thus experimental studies are limited to the observation of some effects that can only be interpreted in terms of hypothesis or models that are not easy to verify. On the other hand, the possibilities of modifications in the structure or in the geometrical arrangement of the electrodes are in practice very limited. The situation is certainly more favourable with aqueous solutions. Thus, laboratory studies or industrial operations mainly in the chlorine and caustic production may help in the interpretation of some of the processes of interest for aluminium reduction.

The effect of the gas configuration on the voltage drop has been studied in detailed laboratory experiments using both electrochemical measurements and ultrafast cinematographic techniques<sup>26</sup>) to <sup>33</sup>). Thus an overvoltage associated with the reduction of the active volume of the bath by the gas near the anode surface has been measured under different conditions. With an anode geometry favourable to the elimination of the gas (vertical, highly sloped, or upward-facing horizontal anodes) an overvoltage which rapidly tends to a stationary value was observed. Instead, with downwards-

facing horizontal anodes the anode overvoltage is higher and tends to oscillate with frequency and amplitude increasing with the current density. The oscillations are clearly associated with the growth and release of the gas bubbles from the anode. All conditions being equal, the overvoltage is significantly reduced when mechanical vibrations are introduced to the anode. Although this reduction of the overvoltage has been observed with each of the anode geometries, it is more pronounced with downward-facing horizontal anodes. The experiments show that anode geometry has a considerable influence also on anode effect. This occurs at higher values of the current density when the geometry is more favourable to gas elimination. Thus the smallest values of current density for the anode effect were observed with concave hemispheric and downwards-facing flat anodes. On the other hand, with vertical flat and convex hemispheric anodes, values of the current density for anode effect are considerably higher.

These experiments prove the great relevance of the gas evolution phenomena and the possibility (at least in principle) of controlling these by modifying the electrode geometry. Useful lessons can also be learnt from the industrial production of chlorine and caustic by electrolysis of sodium chloride solutions<sup>34</sup>) to <sup>42</sup>).

The electrolytic cells used in the chlorine-alkali industry are, essentially, of two different types: mercury and diaphragm. Until recent times the anodes were made of graphite for both types of cell. In the mercury type the electrodes are almost horizontal and the cathode is formed of a mercury layer gliding over a slightly sloping steel plate. In diaphragm cells the electrodes are vertical and separated by an asbestos diaphragm. Gas bubble effects have traditionally constituted a major limitation to the energy efficiency with both types of cell. During the last decade, the industry widely adopted dimensionally stable anodes (DSA) consisting, essentially, of a titanium grid-like structure coated with ruthenium oxide. The use of DSA resulted in a significant improvement of energy efficiency mainly due to both the electrocatalytic effect of ruthenium oxide and the elimination of a large fraction of the gas content in the anode-cathode gap. Thus, for example, in the most advanced mercury cells, the ACD is about 2.5 to 3 mm and a typical value of the overvoltage associated with gas bubbles is 100 mV with a current density of about 1 A/cm<sup>2</sup> and a gas bubble layer of 1 mm depth. In contrast, with old grooved and bored graphite anodes the bubble layer reached a few millimetres with an associated overvoltage of about 700 mV at a current density of 0.5 A/cm<sup>2</sup>. Also in diaphragm cells the performance has been greatly improved by DSA of complex shapes that facilitate gas elimination through appropriate cavities and ducts.

In his experiments with TiB<sub>2</sub> pilot aluminium cells, Dorward observed effects that can be attributed to gas bubbles<sup>6</sup>). These effects are consistent with a model in which a bubble layer of 1 cm depth at the anode surface produces a voltage drop of 0.2 to 0.35 V. These values amount to 10 to 15% of the total bath voltage drop in a typical cell and they may be expected to increase with larger anodes. The Kaiser-DE experiments with the 40 kA cell having almost vertical cathodes show that the bath voltage drop does not decrease as expected at small ACD and the energy consumption actually realised is higher than expected. Contributions to the observed overvoltage other than gas bubbles cannot be excluded. In particular, the concentration polarisation may be relevant. However, the laboratory experiments referred to above, the chlorine-alkali industry experience and the Kaiser results all lead to the conclusion that gas bubble effects are

relevant. An appropriate consideration of such effects therefore seems crucial to the prospects of RHM cells. If more extensive results with the 40 kA Kaiser cell confirm the large overvoltage at small ACD, many concepts in the cell design—particularly in the electrodes—should be revised. However, technical alternatives may be very complex. Industrial experience with chlorine-alkali cells may offer useful hints but successful innovations in this field are certainly not easy to transfer to aluminium technology. Some attempts to facilitate gas elimination have been made with inert anodes<sup>43,44</sup>). The use of this kind of anode may be necessary to take full advantage of wettable cathodes. However, anode shapes or appropriate devices which permit efficient gas elimination may present materials and engineering problems, satisfactory solutions to which are at present difficult to foresee<sup>9</sup>).

As regards the effects of electrode geometry on current efficiency, the Kaiser results seem to suggest that the geometry does not significantly affect current efficiency. High values of this have been observed with both slightly sloped and near vertical electrodes. Although further research on this matter is necessary, effects of geometry on current efficiency may be expected to be less relevant than the gas bubble overvoltage.

### Conclusions

Some process effects, if not appropriately considered, may neutralise to a large extent the advantages of wettable cathodes. Most of these effects are present in conventional aluminium electrolysis but may become critical at short ACD and poor agitation of the melt. The most serious limitation seems to be due to gas bubbles which produce an overvoltage that becomes larger when the ACD decreases.

Gas bubble effects are well known with aqueous solutions and particularly in the chlorine-alkali industry which may offer some hints. However, the particular conditions of aluminium electrolysis make it difficult to adopt similar solutions. In any case, the conception of an electrolytic reactor substantially different from conventional reduction cells seems necessary and the retrofitting of existing plants may be difficult.

It may be preferable that wettable cathodes and related modifications be evaluated in comparison with entirely different alternative processes. None of these seem to offer sufficient advantages at present to justify a significant substitution of Hall-Héroult based technologies in the foreseeable future. Thus, changes related to new electrodes, even radical, still remain attractive and further efforts to make them into a successful innovation appear, for the time being, sufficiently justified.

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