# SOME GENERAL CONSIDERATIONS ON RHM CATHODES

B. MAZZA

Moltech/Alcan/De Nora Permelec

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The introduction of new cathodic materials does not modify the conceptual basis of the Hall-Héroult process, but it does 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:

1. cell design and engineering,
2. process modifications,
3. materials.

## 1. Cell design and engineering

I will briefly present a few solutions, which have been tested or at least considered, regarding the use of RHM in electrolysis cell. It should first of all be stated that at present, there is no tested solutions ready to be used in industrial situations. Rather, completely new engineering must be developed in relation to the altered conditions in which the process will have to take place, and to the development of the required materials. At present, the main engineering aim is to design and build apparati which allow conducting the testing that is necessary for evaluating said conditions and developing said materials.

So far, there have been two types of applications proposed for RHM in electrolysis cells:

1. as current conductors, in order to establish a direct contact between the liquid metal deposit and the cathodic busbar;
2. as a cathodic material to be used instead of carbon.

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[*] RHM stands for refractory hard metals.

In the first type of application, the most significant property required is electrical conductivity, while in the second, it is the wettability by liquid aluminum. Of obvious importance in both cases will be the chemical, mechanical and thermal properties which allow the material to be used in operating conditions.

## 1.1. The Alcan - Eltech Systems project

The new cathode tecnology described as "deep pool, non carbon, bottom current exit cathode" (fig. 1) can be considered pertaining to the first type of application of RHM.
The cell geometry is similar to that of the ancient mercury type cells used in the chlorine - alkaly industry, with insulating bottom and current exit collection units. The effect that these conductors have upon the current distribution in the liquid metal must still be accurately evaluated by means of models (increases in the horizontal component of the current would increase the turbulence of the liquid metal).

## 1.2. The Kaiser-U.S. Department of Energy project

For more than two decades Kaiser Aluminum 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 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. 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 allow them to

rotate in order to adjust the ACD.[*] For the design of the 40 kA cell the same geometry is kept.

The Kaiser experience was focused essentially on the study of process modifications.

## 1.3. The De Varda cell (Montecatini project[**])

The cell is schematically shown in fig. 3. Its potential adventages (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 previously-mentioned difficulties could be overcome.

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[*] ACD stands for anode-cathode distance.

[**] Montecatini is a parent company of Aluminia.

## 2. 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 to 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 been published and many features of the DE sponsored project are publicly known.
Relevant process modifications may be expected in relation to the following aspects:

1. current efficiency,
2. decomposition voltage of alumina,
3. anode gas bubble behavior,
4. alumina dissolution,
5. heat balance.

### 2.1. Current efficiency

Any variation in an aluminum 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. However the Kaiser experiments suggest that current efficiency at short ACD is not a major problem. In fact in the 15 kA cell with $TiB_2$ cathodes, a sketch of which has been shown in fig. 2, a current efficiency of 85% has been observed with an ACD of 1.9 cm. The bath temperature was low (about 850°C), but this choice seems to derive from operational reasons (avoids crust formation, which is necessary to do not obstruct anode movements; reduces corrosion in some components) rather than the need to increase current efficiency.

A current efficiency of 87-88% for cell of 10 kA nominal capacity operating at 970°C and cryolitic ratio of 1.35-1.5 by weigh with an ACD of 1.9 cm, is reported too. The $TiB_2$ 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 high value of the current density (1.6 $A/cm^2$). 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 interactions gas-fog can not be excluded.

Further research seems necessary in order to establish the actual relevance of different chemical and electrochemical processes that may affect current efficiency and correlated phenomena.

## 2.2. 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 alumina decomposition voltage increases when the temperature of the electrolyte decreases, must be taken into account. The Kaiser 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. The large increase observed can be associated with an electrode overvoltage (anode and/or cathode) the nature of which remains unexplained.

The total decomposition voltage seem 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 50-100 mV less. If low temperature operation were unavoidable, the bath composition would be one of the few variables with which to play.

### 2.3. Anode gas bubble behavior

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

The structure and geometrical arrangement of the electrodes primarily affect the evolution 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 effects are greater at small ACD.

In the Kaiser experiments with $TiB_2$ pilot aluminum cells, overvoltage effects that can be attributed to gas bubbles were observed and quantified in terms of effective bath resistivity relative to bath resistivity at 5 cm ACD. For example, at an ACD of 1.9 cm the effective bath resistivity was 30-55% higher than at 5 cm ACD. Also the Kaiser 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 due to gas bubble effects. An appropriate consideration of such effects therefore seems crucial to the prospects of RHM cells.

Industrial experience with chlor-alkali cells may offer useful hints but successful innovations in this field are certainly not easy to transfer to aluminum technology. Some attemps to facilitate gas elimination have been made with inert anodes. The use of this kind of anode may be necessary to take full advantages of wettable cathodes.

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.

## 2.4. Alumina dissolution

Dissolution of alumina is highly endothermic, as is well known. 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. 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 vibrations).

## 2.5. Heat balance

It is clear that in a cell in which the ACD is reduced, the liquid aluminum deposit is eliminated and electromagnetic agitation is nullified, there is a great modification in the heat balance with respect to a conventional cell. It is therefore necessary to completely review the cell design and determine the conditions in which the necessary heat is available for operating the cell itself.

From a qualitative point of view if the ACD is reduced to half of the presently achievable values, enough heat will be made available to run the cell, on the condition that the insulation is improved or the current density is increased. The increase in the latter, however, should be rather small, so as not to raise, at the same time, the specific energy consumption. Thus, for a cell with RHM cathodes, the situation must still be evaluated thoroughly.

The design of a new electrolysis cell always begins from the models that have previously been developed and operated. Consequently, there are certain rather well-known parameters that are used in calculations, and the necessary extrapolations of values and situations can be carried out without great difficulties. For cells with RHM cathodes, however, there is no tested model to depart from, and many of parameters are difficult to hypothesize. In this case, the design of the cell must be result of systematic research which includes experiments for every different condition (geometry, insulation, contacts, bath characteristics, etc.) and the development of special calculation models which permit the simulation of various situations.

## 2.6. 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 aluminum 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 become larger when the ACD decreases.

Gas bubble effects are well known with aqueous solutions and particularly in the chlor-alkali industry which may offer some hints. However, the particular conditions of aluminum electrolysis make it difficult to adopt similar solutions. In any case, the conception of an electrolytic reactor substantially different from conventional reduction cells seem 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 foreseable 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.

## 3. Materials

### 3.1. Identification of the most suitable materials and availability

Titanium and zirconium carbides and borides and particularly $TiB_2$, have so far been considered the most suitable materials for substituting cathodic carbon. However, the identification of the most suitable material still remains an open question. In addition to the criteria based upon how well the material meets the necessary requirements, there are other criteria regarding the guaranteed supplies and costs of said materials. The latter also depend upon external factors such as the existence of other fields in which the material can be used, and which would thus contribute to the development of a market for said material. In fact, at the present time, the very limited availability of a suitable material constitutes the major obstacle in the development of RHM cells, and until a solution is found to this problem, pilot scale testing will also be seriously impeded.

Most of the results that have been patented or published contribute to better identifying the properties of the materials as a function of chemical-physical and structural variables, so as to facilitate their sintering (for example, preparation conditions, sintering aids, additives, porosity). So far, these studies do not seem to have contributed to any substantial reduction in the costs of these materials, nor to developing an important market for them. Perhaps the most innovative aspect is represented by the composites made up of a support material (carbon or metal) and a surface coating in RHM. These composites could open up a new path for the use of such materials.

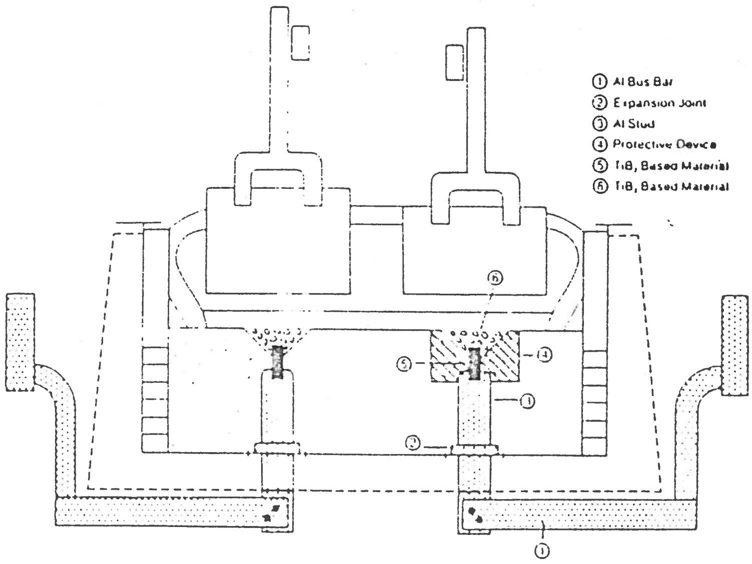
## 3.2. Effective use

The substitution of one material with another presents difficulties (necessarily translated in higher costs) which are associated with the lack of knowledge regarding the overall performance of the new material, as well as the necessary operations for its implementation. In the case in point, carbon has been utilized in electrolysis cells for almost a century, and both its advantages and limitations are well known (for example, its role in the useful life of an industrial cell is judged as being rather good); we know how to work it, how to solder the contacts, how to join one piece to another, etc. Even if a new material were available on the market and even if it met the electrolysis process requirements well, it could not be effectively used without having an equivalent amount of information regarding its overall performance and the necessary operations for its implementation.
A determining factor will be the useful life of the cell. It would seem clear that ceramic material will have a significantly higher cost than the carbon materials presently used. Consequently, the

duration of the cell will represent a significant factor in the balancing out of the price increase, but at the same time, will impose requirements upon the material which will extend well beyond its wettability or electrical conductivity.
As for the operations that are necessary in order to be able to use the materials such as RHM, the following characteristics should be kept in mind: the extreme hardness and brittleness of these materials, their reduced resistance to thermal shock and their oxidability in air. The possibilities of working said materials (cutting, perforating, turning, fitting, soldering) are rather scarce. A particularly important aspect is represented by the electrical contacts where the voltage drops must be minimized and there must be a good seal even at high temperatures. This is one of the aspects that presented considerable difficulties in both the Alcan-Eltech and the Kaiser projects.

## 3.3. Conclusions

In conclusion it seems clear that it will be extremely difficult to develop a RHM cell unless there is a coordinated effort on the part of the aluminum industry and of organizations that are highly qualified in the development of these materials.
Furthermore, since there is no tested model of the new cathode cell, the design of this cell and the development of new materials to be used in it will reciprocally condition one another in the search for a satisfactory solution.

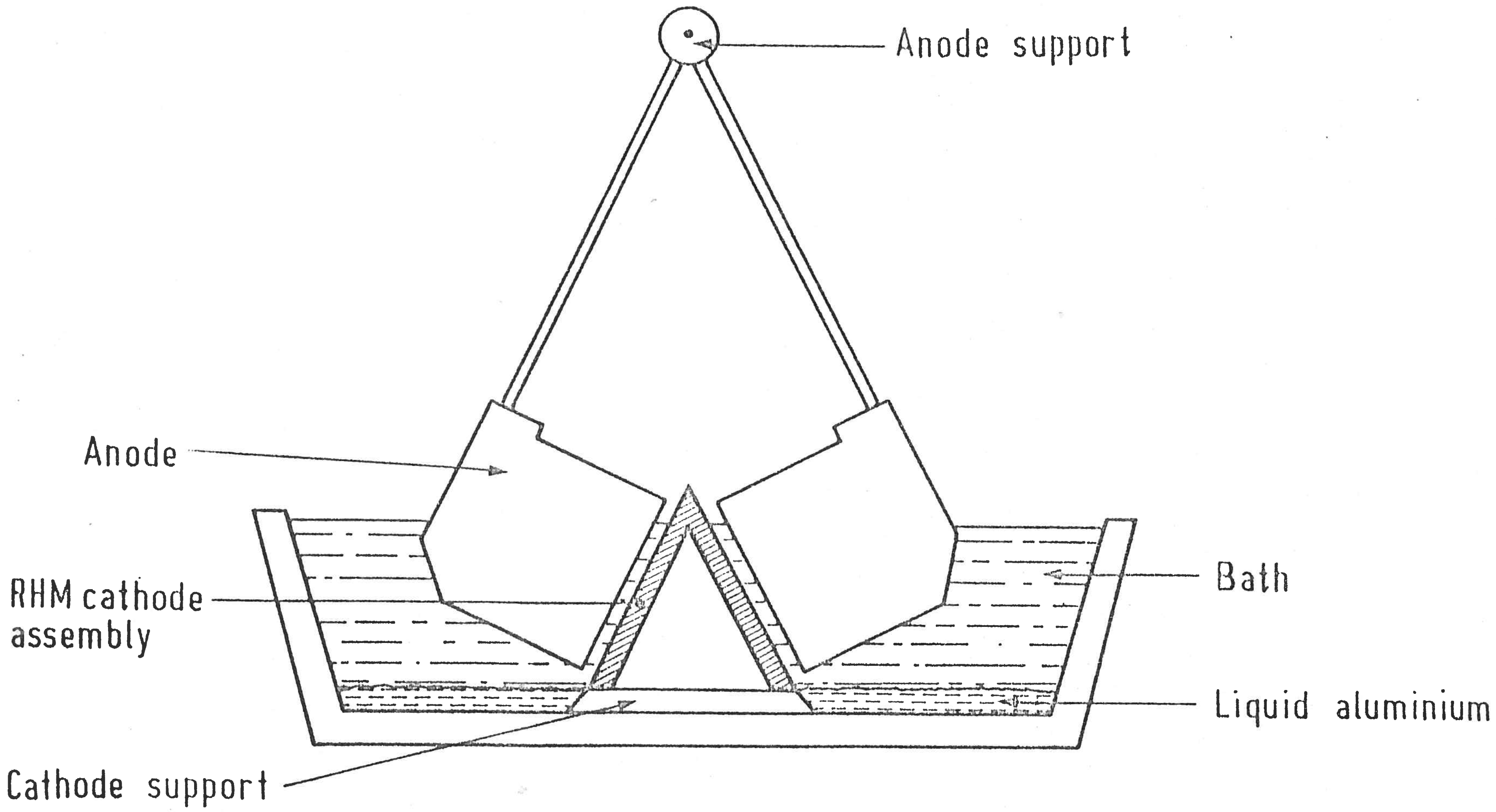


NON CARBON BOTTOM CURRENT EXIT
DEEP POOL CELL DESIGN

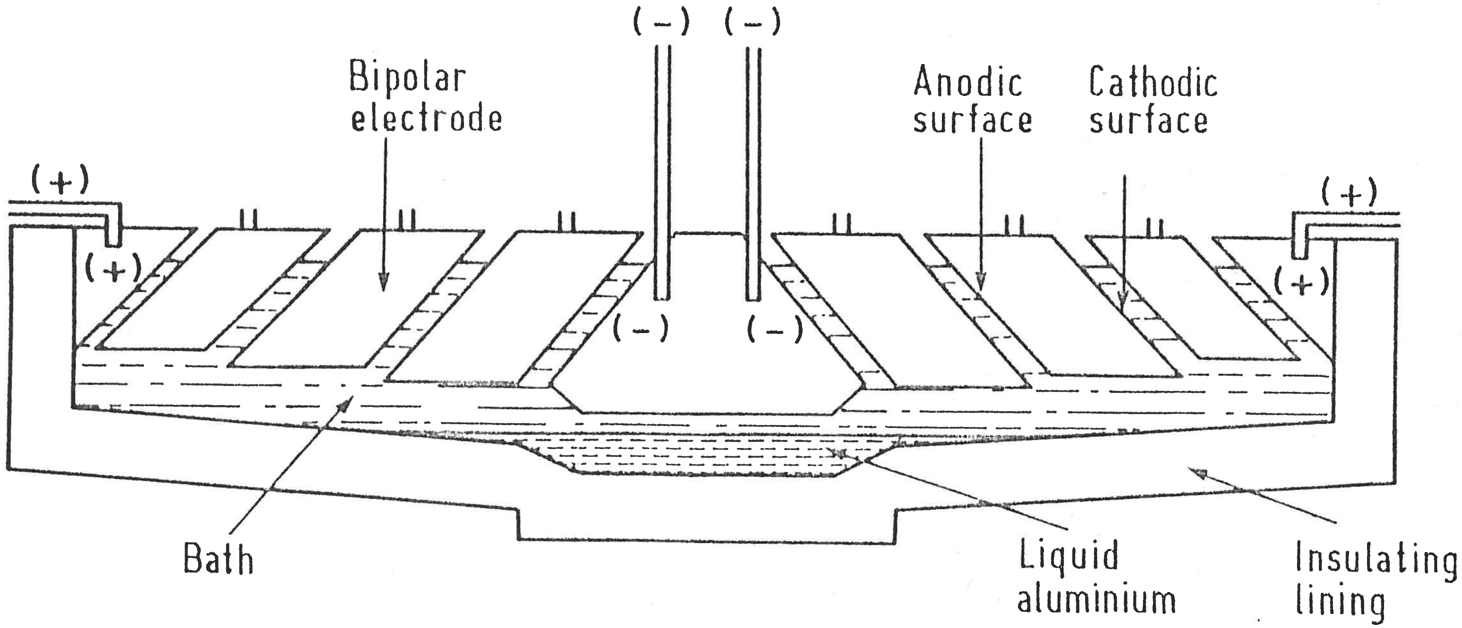
ALCAN-ELTECH SYSTEMS CELL

FIG. 1

FIG. 2



KAISER CELL



DE VARDA CELL

FIG. 3