

ANOMALOUS EFFECTS ASSOCIATED WITH THE  
ELECTROLYTIC GAS EVOLUTION FROM MOLTEN SALTS

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Summary

High-speed cinematographic techniques have been applied to investigate the anomalous effects associated with the electrolytic gas evolution from molten salts and particularly the anode effect in cryolite-alumina melts.

A general interpretation is proposed considering the hydrodynamic instability conditions described by Helmholtz and Taylor.

Also the manifold experimental aspects of the anode effect in aluminium cells are tentatively arranged in a interpretative schema.

In the field of the electrode processes with gas evolution from fused salts, the so-called "anode effect" is one of the most controversial problems.

Everytime an electrode reaction involves development of gas, whether from melted salts or at the cathode, anomalous effects are met. When the current density is increased, a condition is reached in which the gaseous phase prevents any efficient wetting of the electrode surface by the bath and consequently the normal course of the electrode reaction is hindered.

Depending on the power-supply conditions, an abrupt decrease of the current density ( $i$ ) and/or an increase of the electrode voltage ( $E$ ) are then observed (Fig. 1).

Similar anomalous phenomena occur when the gas development is not of electrochemical source, as in the case of boiling on a heating surface submerged in a pool of initially quiescent liquid.

In the case as well (Fig. 1), by increasing the specific heat flux ( $\phi$ ), a condition is reached in which the heated wall is thermically insulated from the liquid by a continuous vapor film with a consequent decrease of the heat flux itself and/or an increase of the temperature drop ( $\Delta T$ ) from wall to liquid. This is the so-called "burn-out", the noxiousness of which in view of the boiling heat transfer is well known.

In any case, for the above quoted anomalous conditions to occur, the following points appear to be essential:

- i) the exceeding of a critical value in the rate of gas development, i.e. in the volume of gas produced per unit time and area (expressed by  $i$  or  $\phi$ );
- ii) the configuration assumed by the gaseous phase in the range of high values of  $i$  or  $\phi$ .

In addition to the investigations with the usual electrochemical techniques, a systematic research has been performed in our Laboratory utilizing high-speed cinematographic techniques (up to about 5000 frames per second) (1).

In this way the features of the electrodic gas development, both in the critical conditions and in the preceding range, have been observed, in order to characterize the circumstances which influence the formation, growth and detachment of bubbles and their coalescence, till the formation of a gaseous film which insulates the electrode surface from the bath.

Some typical results of this research are collected in a film which is an integrating part of this report; only a brief illustration of it will therefore be given here.

- 1) The first example in the film refers to the chlorine development from molten sodium and potassium chlorides on a flat, vertical graphite anode.

During the test the current is increased with a law which is linear in time, until the anode effect occurs. The actual duration of the test is about one second, while in the film the phenomena appear about two hundred times slower.

Pictures give direct evidence of the close analogy which exists between the electrolytic gas evolution and the boiling of liquids in contact with a heated solid surface.

As a matter of fact, by increasing the current density, three typical regimes in the gas development takes place in a nucleate form, corresponding to nucleate boiling (Fig. 1).

Then the coalescence of bubbles occurs, and the electrical contact between the electrode and the bath can be considered as established through thin liquid bridges (\*).

At higher current density values a transition period intervenes, in which the anode surface is covered by irregular gas blankets in violent motion (Fig. 1). In this period, corresponding to partial film boiling, the gas evacuation becomes more and more difficult.

Lastly the anode effect occurs, corresponding to film boiling. The anode is now practically insulated from the bath by a permanent continuous gaseous film, which is steadily anchored to the contour line of the anode itself (Fig. 1 and 2). Large bubbles are released, which go away with a regular frequency without condensing in the bath. Arc discharges across the gas film are visible on the border, where the film is thinner.

2) The second example concerns the chlorine development from molten sodium and potassium chlorides on a flat, horizontal, downwards-facing graphite anode. These geometrical conditions for the gas development are more similar to the ones we find in aluminium cells.

Gas evacuation is here more difficult and the coalescence of bubbles begins at lower current density values than in the former case. Also the anode effect (Fig. 2) occurs at a much lower critical current density (about half the one found in the former case).

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(\*) Therefore, even before the anode effect occurs, the apparent electrode overvoltage includes a significant contribution due to the presence of the gaseous phase in the anodic layer and on the anode surface. This contribution depends on the circumstances controlling the gas evacuation and therefore on the shape and orientation of the anodes; it is obviously greater on the anodes on which the permanence of the gases is favored (for instance, on horizontal, downwards-facing anodes) (2).

3) The third example refers to the gas development from cryolite-alumina melts on a flat, vertical graphite anode. In this case the investigation with cinematographic techniques has been possible using a suitable electrolysis cell made of boron nitride with small transparent windows of synthetic sapphire.

In spite of the worse quality of the pictures in this case, the features of the phenomena appear to be the same as in the case of chlorine from chloride melts (Fig. 2).

4) The last example concerns the chlorine development from a hydrochloric acid aqueous solution on a horizontal platinum wire. By increasing the current density the typical regimes in the gas development (i.e. development in a nucleate form and anode effect) are met again (Fig. 1), while the transition period prior to the formation of a permanent continuous gaseous film is here practically unexisting. The liquid-gas interface surrounding the filiform electrode during anode effect presents undulating form, with a characteristic wavelength (Fig. 1 and 2).

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What interpretative lines are suggested by these experimental results ?

First of all, an explanation of the anomalies in the electroodic gas development following purely static lines, on the basis, for example, of the values of the equilibrium contact angle, of the changes of the wetting properties with time, etc. does not appear to be acceptable since it would not account for the abrupt occurrence of the anode effect and for its dynamic characteristics (oscillations, etc...).

Of course, all the circumstances which may influence the nucleation of bubbles, their adherence to the electrode surface, their coalescence, etc..., may play a part in deciding the range of current densities in which the transition period and then the anode effect intervene.

In order to explain the occurrence of the anode effect, it appears however necessary to consider the conditions of hydrodynamic instability which are generally deemed to be responsible for the similar aspects of the boiling crisis (3).

With reference e.g. to the geometrical conditions for the gas development shown in Fig. 3, by increasing the current density or the specific heat flux, because of the interaction of bubbles in vertical direction (perpendicular to the solid surface), the gas development in the form of isolated bubbles (that is, in an intermittent form (Fig. 3a)) is replaced by a development in column-wise or continuous form (Fig. 3b).

Now, the stability of this latter configuration depends on the relative velocity between the counterflowing streams of gas and liquid. Above a critical value of the relative velocity, every small disturbance at the separation surface to two adjacent fluid streams will amplify and grow, and thereby distort the flow. Thus a partial gas blanketing may occur and extend over the entire solid surface if the pre-existing gaseous jets were sufficiently close. Lateral interactions as well, in a direction parallel to the solid surface, are thus important.

This hydrodynamic instability which destroys the column-wise configuration, thereby making the gaseous development critical, is known as Helmholtz instability (4).

On the other hand, the stability of a static layer configuration in which the gas (lighter) lies underneath the liquid (Fig. 3c), depends on the wavelength of the disturbances at the interface between the two fluid layers. Taking into account the surface tension effects, it has been shown that, in order to maintain a stable gas layer underneath the liquid layer, the disturbance wavelength must be smaller than a certain critical value, otherwise the interface between the two fluids oscillates until it breaks (Taylor instability (5)).

Well, the critical spacing of the counterflowing gas and liquid streams in the column-wise configuration (i.e. the spacing below which the occurrence of Helmholtz instability yields complete and steady gas blanketing on the solid surface) is just determined by the critical wavelength of Taylor instability.

In conclusion, the hydrodynamic theory postulates that the occurrence of both the burnout and the anomalous effects in the electrolytic gas evolution, arises from Helmholtz-Taylor instability and on the basis of these concepts, it leads us to predict correctly (3,4,5,1) :

- one the one hand, the dependence of the critical current density (of appearance of the anode effect) on the various factors involved : physical-chemical (\*) and geometrical ;

- and on the other hand, the values of the characteristic wavelength of the liquid-gas separation surface in anode effect conditions.

These predictions become quantitative in the case of cylindrical geometry, in which, even in the conditions we experienced (\*\*), the absence of boundary effects admitted by theory can be approximately considered as verified.

Still on the quantitative side we should also take into account the intervention of the nature and the surface condition of the electrode. Since the anomalous condition of anode effect is obtained from the coalescence of the bubbles evolved at the electrode, we can reasonably suppose that the quoted factors act on the amplitude of the transition period.

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(\*) The properties which intervene are : gas and liquid densities, surface tension, acceleration acting on the system (e.g. in conditions of reduced gravity). In particular, according to the theory of hydrodynamic instability, the surface tension intervenes in the sense of hindering the growth of disturbances at the separation interface between gas and liquid i.e. of damping the capillary waves or of counteracting the instability. Thus, the critical current density results an increasing function of the surface tension, while it is well known that on the basis of the static theory of the contact angle, a reversed dependence law would be expected.  
Experimental results comply with the hydrodynamic theory predictions.

(\*\*) Corresponding to a value high enough of the ratio ; length to diameter of the wire.

The above given arguments can be considered applicable in particular to the case of anomalous phenomena on graphite anodes (or generally on insoluble anodes) in chloride melts. This case is quite simple indeed from a theoretical point of view, since only one anionic species is in the melt and thereby the anode process is only one in the whole range of the working conditions.

On the contrary, the case of the anode effect in cryolite-alumina melts is more complicated: in fact also the changes in chemical configuration of the bath in the anodic region, due to current circulation, must be taken into account a priori, because of the presence of both oxygen and fluorine donors.

As it is well known, in cryolite-alumina melts electrolysis the relative content of aluminium fluoride, as a component of the anodic bath layer, tends to increase for the electrode reaction and the transference processes (\*). In particular, the corresponding impoverishment in alumina can involve the change of the electrode reaction nature, with all the consequent effects also on the surface conditions. Thus the occurrence of the anodic anomalous phenomena could be attributed to causes quite different from the hydrodynamic instability, e.g. to anode passivation and/or change in wetting conditions. As a matter of fact the hydrodynamic interpretation does not stand at least in the case of melts with low alumina contents (including the "pure" cryolite melts), because of the very low values of the critical current density which are consistent also with interpretations following static lines.

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(\*) This phenomenon occurs, magnified, in cells having a soluble anode of metallic aluminium. In spite of the obvious differences in respect to the usual case of insoluble anode, the study with the soluble anode cells is instructive in showing - magnified again - the possible effects of the accumulation of aluminium fluoride in the anodic region. In fact also in this case, by increasing the current density, we met anomalous increments of the anode voltage corresponding to a passivity condition, due to separation of aluminium fluoride as a solid phase (6).

On the basis both of the direct evidence given by the cinematographic recording and of all the results of the electrochemical investigations we performed (7,8):

- i) on the phenomenological aspects of the occurrence and disappearance of the anode effect;
- ii) on the associated hysteresis loops;
- iii) on the influence laws of several factors, such as bath temperature and composition, anode shape and orientation, bath stirring or anode shaking, etc.; and finally
- iv) on the conditions of diffusion limiting current intervention for the oxygen containing ions discharge,

we have proposed (8) the following schema for the interpretation of the anode effect in cryolite-alumina melts.

In the range of high alumina contents, i.e. of high values of critical current density, the anode effect corresponds again to the intervention of hydrodynamic instability in the gas development; whereas for melts poor in alumina, i.e. for low values of critical current density, the anode effect corresponds to an anode passivation, due to fluorine surface compounds, which occurs as a consequence of the achievement of limiting current conditions for the oxygen containing ions discharge. The worse wetting properties in the latter case appear as a result of the anode passivation.

Finally in the intermediate range of alumina contents the occurrence of the anode effect in consequence of hydrodynamic instability in the gas development, can be quantitatively determined, as far as the critical current density values are concerned, from the variations of chemical-physical properties, due to the changes in chemical configuration of the anodic bath layer.

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## KEY TO FIGURES

Fig. 1

Schematic illustration of the current density ( $i$ ) vs. electrode voltage ( $E$ ) or specific heat flux ( $\phi$ ) vs. temperature drop ( $\Delta T$ ) from wall to liquid curves and of the typical regimes in the electrolytic gas evolution or in the boiling of liquids in contact with a heated solid surface.

- a), a') development of nucleate bubbles, corresponding to nucleate boiling.
  - b) transition period, corresponding to partial film boiling (or transition boiling).
  - c), c') anode effect, corresponding to film boiling.
- a), b), c) chlorine development on a flat, vertical graphite anode ( $0.5 \text{ cm}^2$  area) from chloride melts (50 wt% NaCl + KCl,  $850^\circ\text{C}$ ); critical current density  $900 \text{ A/dm}^2$ .
- a'), c') chlorine development on a horizontal platinum wire (0.5 mm diameter) from aqueous solutions (2N HCl,  $20^\circ\text{C}$ ); critical current density  $4700 \text{ A/dm}^2$ .

Fig. 2

Features of the anode (or cathode) effect in molten salts and aqueous solutions for various geometrical conditions.

- a) anode effect in 50 wt% NaCl + KCl melt,  $850^\circ\text{C}$ ; flat, vertical graphite anode ( $0.5 \text{ cm}^2$  area); critical current density  $900 \text{ A/dm}^2$ .
- b) anode effect in  $\text{Na}_3\text{AlF}_6 + \text{Al}_2\text{O}_3$  (sat.) melt,  $1000^\circ\text{C}$ ; flat, vertical graphite anode ( $0.5 \text{ cm}^2$  area); critical current density  $1800 \text{ A/dm}^2$ .

- c) anode effect in 2N HCl aqueous solution, 80°C ; flat, vertical graphite anode (0.5 cm<sup>2</sup> area) ; critical current density 2000 A/dm<sup>2</sup>.
- d) cathode effect in 2N H<sub>2</sub>SO<sub>4</sub> aqueous solution, 20°C ; flat, vertical platinum cathode (0.5 cm<sup>2</sup> area) ; critical current density 2100 A/dm<sup>2</sup>.
- e) anode effect in 50 wt% NaCl + KCl melt, 850°C ; flat, horizontal, downwards-facing graphite anode (0.8 cm<sup>2</sup> area) ; critical current density 500 A/dm<sup>2</sup>.
- f) anode effect in 50 wt% NaCl + KCl melt, 850°C ; flat, horizontal, upwards-facing graphite anode (0.5 cm<sup>2</sup> area) ; critical current density 800 A/dm<sup>2</sup>.
- g) anode effect in 2N HCl aqueous solution, 20°C ; filiform, horizontal platinum anode (0.5 mm diameter, 25 mm length) ; critical current density 4700 A/dm<sup>2</sup>

Fig. 3

Schematic illustration of different forms of gas development

- a) intermittent form.
- b) column-wise configuration (it may be destroyed by Helmholtz instability)
- c) film configuration (it may be destroyed by Taylor instability)

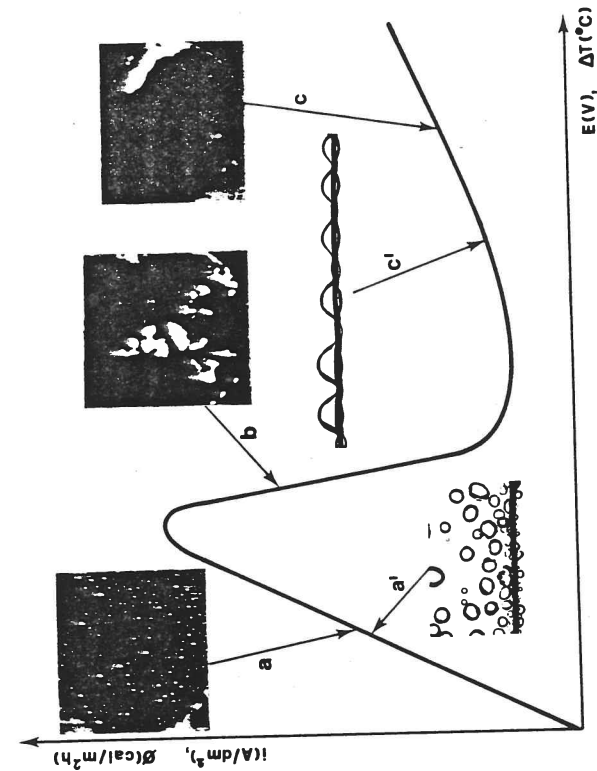
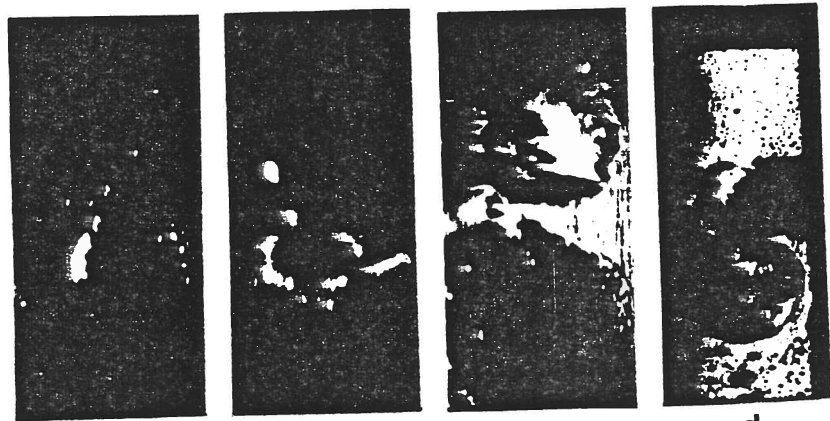


Fig. 1



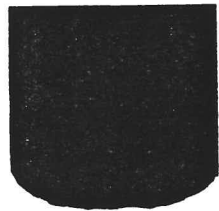


a

b

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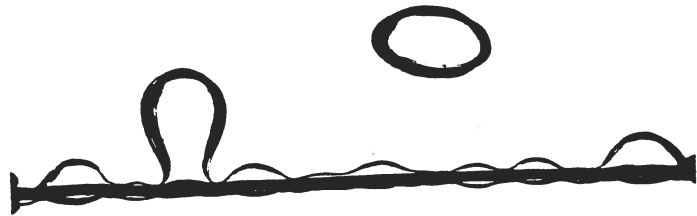
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Fig. 2

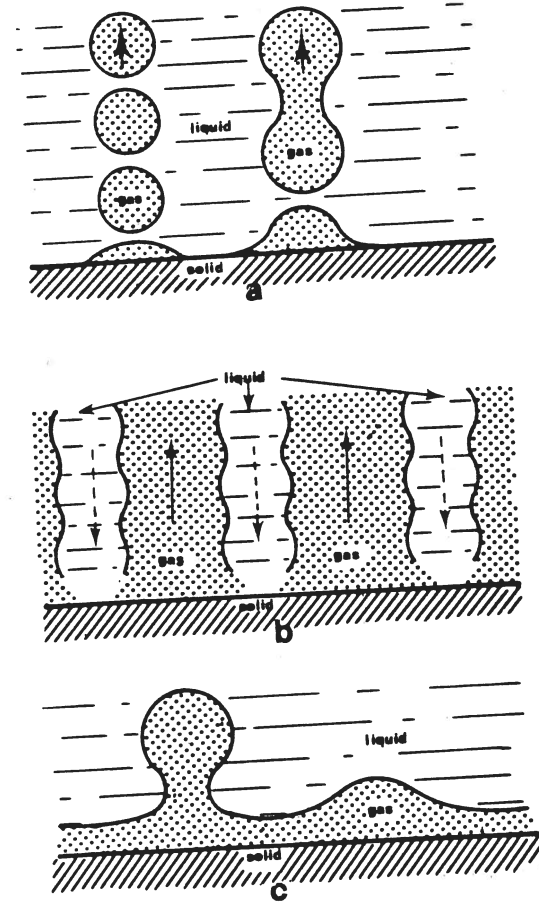


Fig 3

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# THE DEVELOPMENT OF MOLTEN SALTS APPLICATIONS

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EXTENDED ABSTRACTS & PROCEEDING