

Electrolyte Compositions for Aluminium Production

- Options and Desirable Properties

Halvor Kvande

Hydro Aluminium a.s

N- 0240 Oslo, Norway

Tel: +47 22 73 9155

Fax: +47 22 73 7778

Key Words: aluminium, cryolite, electrolyte properties, electrolyte optimisation.

ABSTRACTS

In the last decade there has been little change in the electrolyte compositions of modern, high-amperage aluminium electrolysis cells. They all appear to use similar compositions now, with 10 to 12 % AlF_3 , 4 to 6 % CaF_2 and 2 to 4 % Al_2O_3 and with temperatures in the range from 955 °C to 965 °C. Have we really reached the "optimum" electrolyte composition for these cells? Older prebake and Söderberg cells use different compositions, including LiF and MgF_2 as additives in some cases. Particularly, the effects of AlF_3 content, temperature and superheat have been studied in recent years. This paper discusses the options and the desirable electrolyte properties, and their relationships with cell operational performance.

INTRODUCTION

The electrolyte is the heart of the Hall-Héroult process. Cryolite, Na_3AlF_6 , is the main electrolyte constituent because of its unique capacity as a solvent for alumina. AlF_3 is usually present at 10 to 12 % (by weight) in excess of the cryolite composition. CaF_2 is seldom added intentionally, but originates from the CaO impurity in the alumina feed, which gives typically 4 to 6 % CaF_2 in the electrolyte. The alumina content is usually kept between 2 and 4 %.

The electrolyte is not consumed during the electrolysis process, but some losses occur, mainly by vaporisation and by penetration into the cathode lining. Modern cells may contain between 4 and 6 tonnes of liquid electrolyte, and the temperature during normal cell operation is typically between 955 and 965 °C.

The interpolar distance, or the average vertical distance between the bottom side of the anode and the surface of the pool of liquid aluminium, is between 4 and 5 cm. Thus, in addition to its main functions of passing electricity from the anode to the cathode and being a solvent for alumina to enable its electrolytic decomposition to form aluminium, the electrolyte also provides a physical separation between the cathodically produced aluminium metal and the anodically evolved carbon dioxide gas.

COMPOSITION CHANGES BY USE OF ADDITIVES

The reason for using additives to modify the composition of the electrolyte is to improve its physico-chemical properties, which in turn will improve the operational results of the cells. Traditionally, the target has been to increase current efficiency and reduce energy consumption of the process. Recently, many smelters have shifted their focus to higher productivity by increasing the cell amperage. At present, more emphasis is now put on economic factors such as maximum return on investment and increased shareholder's value.

Knowledge of the physico-chemical properties of cryolite-based electrolytes is essential for technological progress, and a lot of excellent research work has been done in different laboratories to measure these properties accurately and to establish a fundamental database. It has been attempted to develop empirical equations that may be used to calculate and predict physico-chemical properties as a function of temperature and composition for these electrolytes. The most important group of properties is liquidus temperature, alumina solubility, electrical conductivity and density, but also vapour pressure, interfacial tension and viscosity have been measured more accurately during the last two decades.

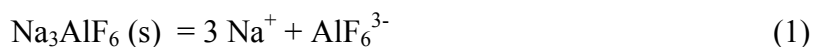
All additives reduce the melting point of the electrolyte and thereby the cell operating temperature, but unfortunately they also reduce the alumina solubility. However, with modern alumina feeding techniques it is easier to control the alumina content in the electrolyte, so the reduced solubility is not as critical as in previous years.

The electrolyte composition is rarely a design criterion for aluminium electrolysis cells. Thus, most cells can use widely different electrolyte compositions, but within the limits set by stable cell operation (stable cell voltage and energy balance). One important design criterion is the heat losses through the sidewalls and the bottom of the cell, which, in addition to the type and quality of the cathode refractory and insulation materials used, also are determined by the bath temperature and superheat. Superheat is defined later.

Thus, the electrolyte composition is clearly important for cell operation and performance. Optimisation of the electrolyte is one of the key operating features that have to be addressed for maximum performance of industrial cells, both economically, energetically and environmentally.

The structure of NaF - AlF₃ melts

The system NaF - AlF₃ is a typical ionic molten salt mixture. The most important solid compound is cryolite, Na₃AlF₆, which melts at 1011 °C. Molten cryolite is completely ionised into sodium cations and hexafluoroaluminate anions:



It is also well established that the hexafluoroaluminate ion dissociates further. The existence of tetrafluoroaluminate ions, AlF₄⁻, was suggested already in the 1940s (1). Thus, the dissociation scheme then will be:



Until 1990 this reaction was considered as the main dissociation scheme in cryolite melts. Then Dewing (2), on the basis of NaF and AlF₃ activity data, concluded that also AlF₅²⁻ ions might exist in these melts:

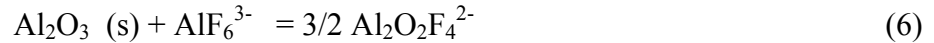
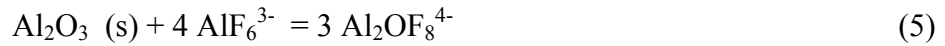
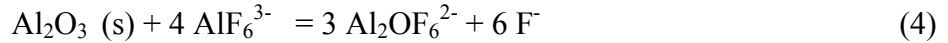


Raman spectroscopic studies by Gilbert and co-workers (3) also have indicated the presence of AlF_5^{2-} ions, and in much higher concentration than the AlF_6^{3-} and AlF_4^- ions.

While research studies of the structure of NaF- AlF_3 melts continue, it seems fairly well established that the main anions are AlF_6^{3-} , AlF_5^{2-} , AlF_4^- and F^- . The relative concentrations of the anions still remain to be established as a function of the NaF/ AlF_3 ratio in the melt. The only cation present in this system is Na^+ . Furthermore, Ca^{2+} ions are present, but possibly as Ca-Al-F complex ions in these melts.

The structure of NaF - AlF_3 - Al_2O_3 melts

When alumina is added to NaF- AlF_3 melts, it dissolves via reaction. Alumina then reacts with AlF_6^{3-} ions to form various anionic Al-O-F species (4,5). Measurements of the freezing point depression of cryolite by addition of Al_2O_3 have shown that the main complex species are of the type $\text{Al}_2\text{OF}_x^{4-x}$ at low alumina concentrations and of the type $\text{Al}_2\text{O}_2\text{F}_x^{2-x}$ at higher contents towards alumina saturation. The main species may be formed by the following reactions:



The maximum concentration of the latter two species will occur at the cryolite composition.

The structure of the melt then becomes more complex by adding alumina and is not as well established. The concentrations of the major ions present depend on the contents of Al_2O_3 and AlF_3 .

The structure of cryolite-alumina melts has been one of the most widely investigated subjects in the field of molten salt chemistry. In spite of the considerable progress that has been made from this research work, we have not yet reached a complete understanding of the structure of these complex melts. Irrespectively, however, it is true to say that the changing views on the nature of the ionic species present in these melts have had no impact whatsoever on the industrial process.

ALUMINA DISSOLUTION

The dissolution of solid alumina in cryolitic melts involves several steps before the added powder is transformed into a homogeneous solution in the electrolyte. These steps may be summarised as follows:

- Heating-up of the cold alumina powder to the temperature of the electrolyte.
- Transformation of the added gamma alumina to the alpha alumina phase.
- Dissolution of the alpha alumina and chemical reaction with Al - F ions in the electrolyte to form complex Al - O - F ionic species.
- Mixing and dispersion of the dissolved solution uniformly in the electrolyte.

The mixing and dispersion are extremely important. The alumina feeding should therefore be done in a turbulent area in the cell, and the amount of alumina added per electrolyte volume

should be minimised. Small additions are therefore desirable. Furthermore, a rapid transfer of heat to the alumina powder added is crucial to prevent formation of agglomerations.

When alumina gets in contact with the electrolyte, three basic mechanisms may occur:

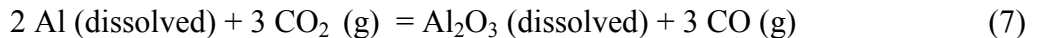
1. It rapidly disperses as discrete grains and dissolves easily.
2. It agglomerates and freezes electrolyte around it. This may float on the surface of the electrolyte, or sink as a dense crust to the top of the liquid aluminium, or it may sink to the bottom of the cell.
3. It can sink to the bottom without dispersing, which is typical for alpha alumina.

Because of these three different alumina dissolution mechanisms, meaningful laboratory measurements of dissolution rates of aluminas are difficult to perform.

Measurements in industrial cells have shown the effects of different cell operating variables. The best conditions for good alumina dissolution would be for an electrolyte with a relatively low AlF_3 content, low alumina concentration and high superheat. Most of these criteria are not in agreement with the requirements for optimum cell performance, however, as will be discussed later.

METAL SOLUBILITY IN THE ELECTROLYTE

All metals are soluble in their molten salts. Thus, the cryolite-containing electrolyte in equilibrium with liquid aluminium contains dissolved reduced metal species. These reduced species are very important electrochemically because they may be deoxidised by the anode gas to form alumina and CO (g), and they are the main cause of reduced current efficiency by what is commonly called "the back reaction":



It is generally agreed that two different types of dissolved ionic species are formed, one containing aluminium and one containing sodium in some form or another. The structurally most probable aluminium-containing species is monovalent AlF_2^- ions. The problem of the nature of the reduced sodium-containing species still remains unsolved. There are some recent work, however, that suggests that sodium may dissolve to give "free" electrons in the electrolyte, as indicated by the reaction:



The dissolved electrons that are formed, may be trapped in anion positions in the melt, but also impart electronic conductivity on the melt. Sodium has a significantly higher solubility than aluminium at the usual industrial electrolyte compositions

The best literature data for the total metal solubility are those of Ödegård et al. (6) and Wang et al. (7). The latter authors have used their measured solubility data to predict current efficiency data, as shown in Figure 1. It is seen that higher cryolite ratio, or higher AlF_3 content, reduces the solubility. In addition, Al_2O_3 has been found to have only a small reducing effect, and LiF also lowers the metal solubility in cryolite melts.

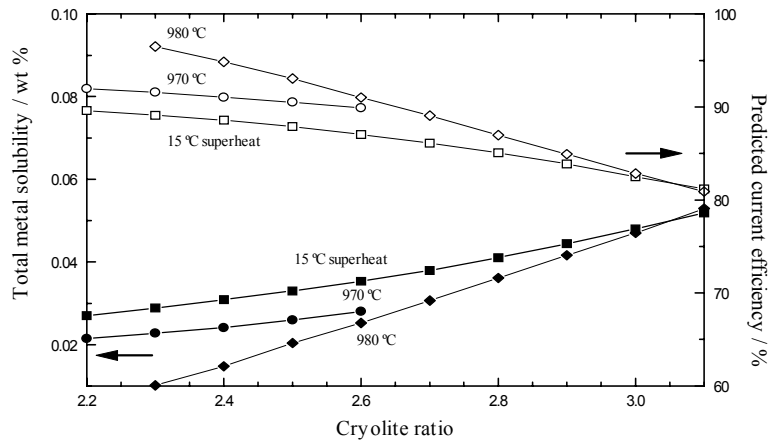


Figure 1. Effect of cryolite ratio on total metal solubility (left-hand y-axis) and predicted current efficiency (right-hand y-axis) in cryolitic melts, according to Wang et al. (7). Cryolite ratio is defined here as the molar ratio of NaF to AlF_3 .

EFFECT OF ADDITIVES ON CURRENT EFFICIENCY

The positive effect of a high content of AlF_3 in the electrolyte on cell performance can be viewed as a combination of low metal solubility and low liquidus and electrolyte temperatures. However, many practical industrial tests in recent years have shown that it does not seem to be possible to increase the AlF_3 content in the electrolyte above a certain value without experiencing cell operational problems. At the present time this composition seems to be about 12 or 13 % AlF_3 . Attempts to go to higher AlF_3 contents have given considerable variations in electrolyte composition and temperature, due to difficulties in maintaining the energy balance in the cell. In some cases the attempt to keep the cell voltage constant may give a low anode-cathode distance, because the electrical conductivity of the electrolyte decreases with increasing AlF_3 content. A thinner side ledge in the melt phase above the electrolyte/metal interface will then be the result, and the risk of formation of undissolved alumina sludge and bottom freeze will increase, because of lower alumina solubility and lower electrolyte temperature.

Up to the limit indicated above, high AlF_3 contents in the electrolyte has been shown to be a sure way to improve the cell performance. This is illustrated by tests on 180 kA and 280 kA cells that have been operated at different AlF_3 and LiF contents (8,9). Figure 2 shows that the current efficiency was found to increase linearly with increasing AlF_3 content in the whole measured range from 4 to 12 % AlF_3 . Laboratory cell measurements by Solli et al. (10) have shown the same trend.

Increasing content of CaF_2 has a positive effect on current efficiency, according to recent literature data from a laboratory cell study (10). However, in practice the small variation in the CaF_2 content in the electrolyte of industrial cells has often been insufficient to show any clear trend.

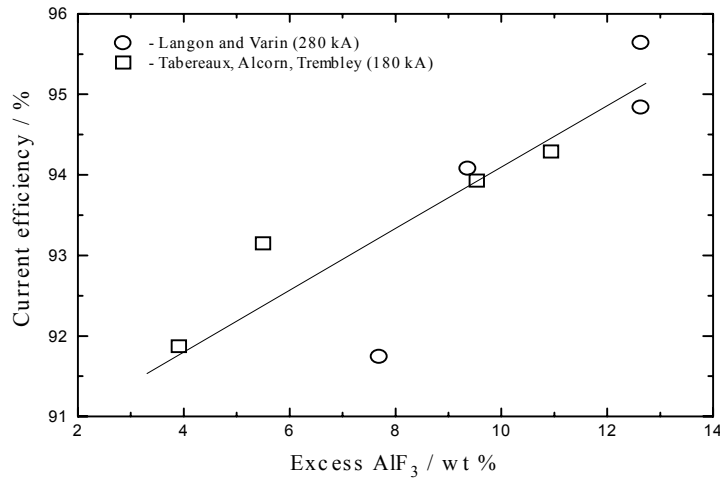


Figure 2. The change in current efficiency with aluminium fluoride content in lithium-modified electrolyte tests, from Tabereaux et al. (8).

The true effect of LiF is more controversial. Several smelters have reported improved operational performance with the use of LiF-containing electrolytes (11-15). For modernised and older prebake anode cells, as well as Söderberg cells, this alternative electrolyte composition may be an interesting choice. The effect of LiF may be cell dependent, however. In modern high-amperage cells its positive effect is questionable. Comprehensive plant tests have been reported for modern 180 kA and 280 kA cells operated with lithium-modified low-ratio electrolyte chemistry (8,9). The current efficiency was then reduced when the electrolyte contained 2 to 3 % LiF. It should be mentioned here that attempts to operate cells with both high AlF_3 and high LiF contents failed because of problems with electrolyte composition instability. From these tests it was concluded that lithium carbonate addition to these modern cells could not be technically and economically justified, because current efficiencies exceeding 95.0 % could be achieved without it.

Effect of electrolyte temperature

The electrolyte temperature is an important parameter for cell operation. In fact, the temperature has been claimed to be the most important factor influencing current efficiency (16). Typically, five degrees reduction in electrolyte temperature causes 1 % improvement in current efficiency (17). This improvement may not be the case when the temperature change is caused by changes in electrolyte composition, however.

An interesting relationship is illustrated in Figure 3, which shows data for current efficiency versus electrolyte temperature in various 180 kA cells of the same technology and electrolyte composition. The data show a considerable scatter by 3 % in current efficiency, even in the narrow temperature range of 957 °C to 966 °C. From these data one may be tempted to draw the conclusion that electrolyte temperature does not matter much for the cell performance. However, this is not correct. Tarcy's (16) explanation of the fact that some plants operate at both high current efficiency and high temperature was that the higher temperature improves cell stability. In

other words, these high temperatures gave good cell voltage stability and correspondingly low cell voltage noise, and also a stable energy balance in the cells.

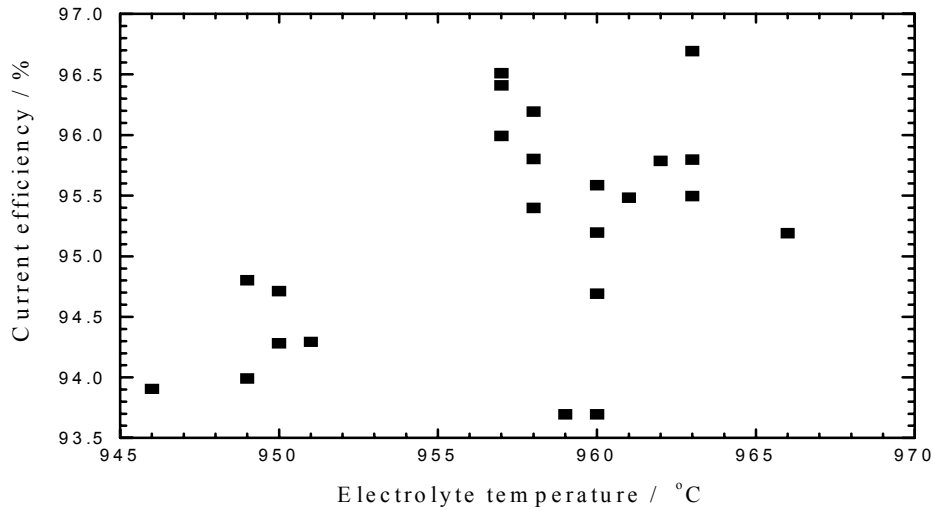


Figure 3. Current efficiencies versus electrolyte temperatures for various 180 kA cells, according to Cutshall (18).

Effect of the superheat

While textbooks and technical papers hardly mentioned the expression superheat about ten years ago, it has now become an important parameter for cell operation. It is defined as the difference between the electrolyte temperature and the liquidus temperature for the given electrolyte composition. Typical values are in the range from about 5 °C in point-fed cells and up to 15-20 °C in centre or side-fed cells. Its relationship with current efficiency is illustrated in Figure 4, where it is shown that the current efficiency clearly increases with decreasing superheat.

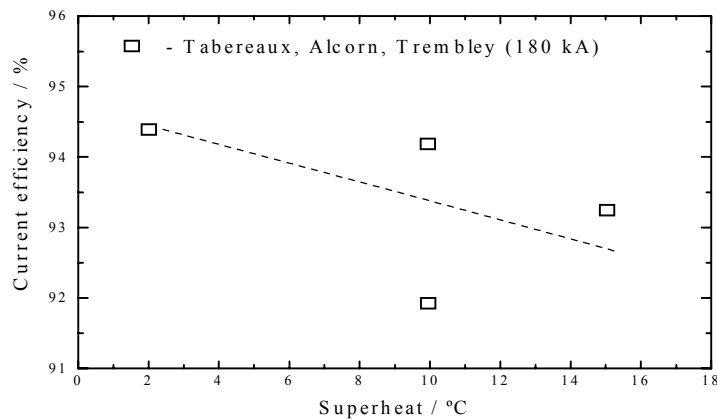


Figure 4. Current efficiency as a function of electrolyte superheat, from Tabereaux et al. (8). The dashed line is calculated from Dewing (19), but his data has been normalised at 2 °C superheat to agree with the experimental data.

Superheat is an important parameter, because it controls the thickness of the side ledge, and it provides the heat necessary for heating and dissolution of the alumina added. Thus, the superheat should not be too low. Previously, one had to base the superheat data on electrolyte analysis and calculated liquidus temperatures from equations developed in laboratory investigations. Sometimes the calculations could give low or even negative superheats. This so-called "liquidus enigma" has been discussed in the literature, and possible explanations have been given (20,21). More recently, new equipment for direct measurement of superheat has been developed (22,23), based on the principle of thermal analysis. This is now the most reliable method of determination of this parameter, and it is claimed to give superheats with an experimental scatter of less than 1 °C.

INDUSTRIAL ASPECTS

Choice of electrolyte composition

The choice of electrolyte composition can be made from several reasons. In practice the composition may be a result of management decisions and goals, but also the background and experience of the operators, their flexibility for changes, and the tradition of the smelter. Cost factors are always important. Acquisition of new cell technology can imply a change in electrolyte composition, and it can be an important part of a modernisation and retrofitting program for older cells. In some cases environmental problems, like high fluoride emissions from the cells, and also customer requirements for a better metal purity, can be reasons for changing the electrolyte composition.

There are many different electrolyte compositions that can be used in the primary aluminium industry today. For a given cell there can be several compositions that give equivalent technical, but different economical results. As discussed by Kvande (24) and Tabereaux (25), there is no universal optimum electrolyte composition for aluminium electrolysis cells. The composition is often customised to fit the needs of each individual smelter to maximise cell performance and productivity. The basis for the choice of electrolyte composition is the excellent database for the fundamental bath properties, as has been discussed earlier, and the known theoretical and empirical relationships between these properties and cell operational parameters. Still, relatively little may be found in the open literature about the practical effects of electrolyte composition on cell performance. At least a part of the reason may be the difficulty in quantifying the specific effects, and many of the papers published on cell modernisation have not emphasised the importance of the electrolyte composition for the reported operational results.

Short history of industrial electrolyte compositions

Fifty years ago the typical electrolyte compositions consisted of 1 to 3 % AlF_3 and up to 8 % CaF_2 . Apparently, Alcoa has been one of the pioneers in the development of modern electrolyte compositions. Already in 1954 the Wenatchee smelter went up from 1.5 to 6 % AlF_3 and experienced 3 % increase in current efficiency (26). With the introduction of the first point feeders in Rockdale in 1961, where small amounts of alumina were added in each feeding dump, the conditions were right for further increase in the AlF_3 content. A large-scale test at 11 % AlF_3 in the Badin smelter in 1965 was a failure, as described vividly by Holmes (26), but eleven years later electrolytes with 11.5 % AlF_3 gave 91 % current efficiency. At the end of the 1970s Pechiney (27) tried compositions with 13 to 14 % AlF_3 in their 180 kA test cells. However, at

present the Pechiney cells are operated at 11 to 12 % AlF_3 (28). This may mean that there appears to be a limiting AlF_3 content in the electrolyte, above which no further gain in cell performance seems to be achieved.

Some more industrial experiences

Many if not all of the older smelters have changed their electrolyte compositions since the time of start-up of their potlines. This has been a gradual and slow process, and in most cases the observed effects on cell performance have not been published. But there are a few exceptions. Jeltsch and Franklin (29) have published the results from the modernisation of the Kaiser Mead smelter. These cells were of World War II technology, and the smelter was faced with a shutdown if not modernised. The electrolyte composition was then increased from 5 to 13.5 % AlF_3 , and a 5.7 % increase in current efficiency was achieved, together with a nearly 3 kWh/kg Al reduction in energy consumption.

In Dubal (30) the improvements in cell performance was 0.9 kWh/kg Al lower energy consumption and 3.8 % higher current efficiency, with an increase in AlF_3 content of 3-4 %. Of this current efficiency improvement, 2.5 % was attributed to the change in electrolyte composition, while 0.8 % was due to an anode size increase, and 0.5 % was caused by what the authors called an anode quality optimisation.

In the Boyne smelter (31) the predicted performance by increasing the AlF_3 content from 7 to 13 % was a reduction in energy consumption from 14.2 to 13.8 kWh/kg Al, an improvement in current efficiency from 88.9 to 93.1 %, and a reduction in electrolyte temperature from 972 to 955 °C.

Intalco (32) has changed from cell operation at 6-7 % AlF_3 and 970-975 °C to 8 % AlF_3 and 2 % LiF at 940-945 °C, and they then achieved an increase in current efficiency of up to 3 %. A similar change from an electrolyte with 10 % AlF_3 to a lithium-modified electrolyte with 4 % AlF_3 and 4 % LiF, together with higher cell amperage and wider anodes in Söderberg cells, was estimated to increase current efficiency from 88 to 92 % and reduce the temperature from 965 to 950 °C (33). The increase in current efficiency was estimated on the basis of lithium-modified electrolyte, point feeding, computer control and process stability. Authors from Venalum (34) have described the opposite case; the changeover from lithium-modified to a high AlF_3 -containing electrolyte.

CATEGORIES OF ELECTROLYTE COMPOSITIONS

Somewhat simplified, but still realistic, it seems that there are now three main categories of electrolyte compositions used in three different types of cells:

1. Modern high-amperage side-by-side prebake cells (175 to +300 kA) use electrolytes with 10 to 12 % AlF_3 and are operated at energy consumption between 13 and 14 kWh/kg Al.
2. Modernised or retrofitted cells (100 to 175 kA) with energy consumption above 14.0 kWh/kg Al, have a choice between an electrolyte with high AlF_3 content (10 to 12 %) or a lithium-modified bath.

3. Older cells constructed 30 to 40 years ago with low amperage (below 100 kA) and high energy consumption (above 15.0 kWh/kg Al), often use electrolytes with AlF_3 contents below 7 %, but also lithium-containing baths are employed.

Again, it is emphasised that these three categories are not very strict, and variations occur. However, the trend for the last two decades has clearly been towards electrolytes with higher AlF_3 contents for most cell types. It has been claimed that the biggest stumbling block preventing use of electrolytes with high AlF_3 contents is centre or side feeding with bar breakers. Point feeders have been believed to be necessary for AlF_3 contents above 9 to 10 %, but this is probably not the limit. With a good alumina feeding strategy higher values may be reached, even with bar breakers.

ELECTROLYTE OPTIMISATION

The focus of electrolyte optimisation has been to reduce the metal solubility and to increase or maintain the electrical conductivity. The majority of the electrolyte modifications have been made by adding more AlF_3 , because this gives much purer aluminium and has a slightly lower deposition potential. Some companies have preferred to use LiF additions to reduce the dissolved metal solubility and increase the electrical conductivity of the electrolyte. This is counteracted, however, by the tendency for a limited co-deposition of lithium in the aluminium produced, thus necessitating having a specific type of metal treatment facility to meet many metal quality standards. Therefore, plants having this will be able to utilise LiF-containing electrolytes, whereas other smelters can only do that at a cost penalty.

On the other hand, the use of high AlF_3 contents in the electrolyte presents several challenges, as a consequence of the following unwanted changes in physico-chemical properties:

- reduced electrical conductivity,
- reduced saturation solubility of alumina (also for modified electrolytes),
- increased electrolyte loss through vaporisation and HF (g) formation,
- increased solubility of aluminium carbide.

The latter can lead to accelerated wear of the cathode and thereby reduced cell lives.

FUTURE CHALLENGES

At present the greatest challenge is to control the electrolyte composition at levels above 11 to 12 % AlF_3 that is used in most modern cells. One problem is the inherent variation in AlF_3 content with time, which makes it difficult to keep the composition constant. Better control of the heat balance and possibly a redesign of the cathode insulation are needed to achieve this. The greatest problem, however, is the tendency to form bottom freeze or ridge, because of the high melting temperature of sludge and the low operating temperature in cells with high excess AlF_3 electrolytes. Welch and co-workers will discuss the subject of AlF_3 control in detail at this conference (35).

It is also important to control the alumina concentration. Larger cells will continue to be developed. When cells are getting larger, it is expected that it will be more difficult to disperse

the alumina sufficiently to avoid aggregation and sludge formation, and there will be a disturbed fluid flow due to alumina not dissolving well. Thus, it will be an increasing problem to distribute the dissolved alumina evenly, and the concentration of dissolved alumina may vary from place to place in these large cells. The present point feeding is not the optimum method, because it introduces a process disturbance in the cell (36). The ideal would be completely continuous feeding of homogeneous preheated alumina.

The increasing demand to minimise the occurrence of anode effects and the corresponding perfluorocarbon gas emissions will require better alumina feeding control. Perhaps it may be advantageous to increase the average alumina concentration in the bath, for this and other reasons (37).

A really radical change would be if inert or non-consumable anodes could be developed to become technically and economically viable. Such anodes would probably consist of a mixture of various ceramic materials (oxides) and/or metal alloys, and in all cases the electrolyte then has to be saturated with alumina to minimise anode dissolution. This could also change the overall electrolyte composition in such cells. Inert anodes would really represent a revolution of the Hall-Héroult process.

CONCLUDING REMARKS

The continuous progress in the electrolysis process has reduced the relative effect of increasing AlF_3 content in the electrolyte compared to the effects of cell design and operation. This is illustrated in Figure 5, taken from Welch (36). Although these curves are based on estimated data, they show the great progress made by the increase from 3 to 13 % AlF_3 . At higher AlF_3 contents the two other factors are becoming more important, and particularly cell operation. Anyway, it is believed that the electrolyte composition and its effect on cell performance will continue to be a focal aspect also in the years to come.

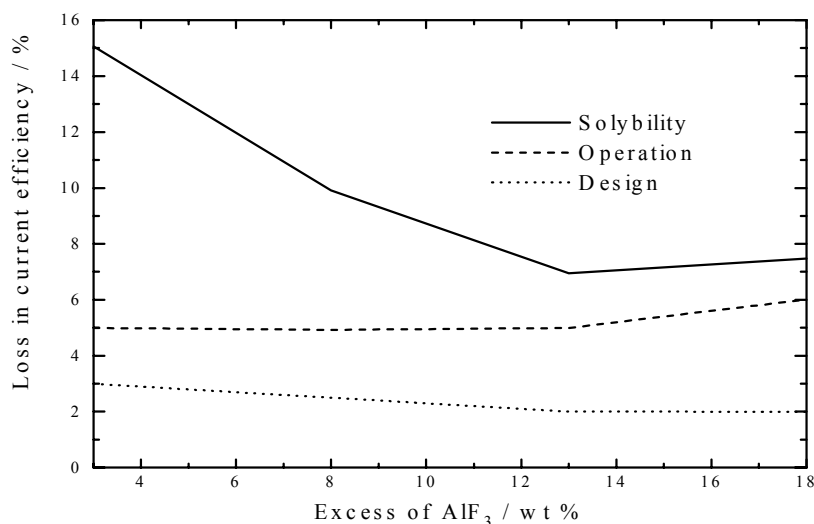


Figure 5. Contributions to loss in current efficiency as the AlF_3 content in the electrolyte increases, according to Welch (36).

Even though the Hall-Héroult process has been studied, used and continuously improved for more than a century now, there is still a great deal that we do not know about the technology. The process has long been characterised by incremental process improvements. The electrolyte for the aluminium electrolysis cells is then an area that also has undergone little evolution. All electrolytes are still based on cryolite, with additions of some alkali and/or alkaline earth fluorides. It is reasonable to expect that this will continue also in the future, since cryolite is essential to dissolve the alumina. No new additives are expected to appear, and low-melting electrolytes (below 900 °C) is still a dream.

It is clear that for most modern cells today, the gain in current efficiency by changes in electrolyte composition is limited. Still small, but significant improvements in cell performance are possible even in the best operating cells and this may be worth striving for. In the majority of the existing older cells the potential improvements are considerably greater.

REFERENCES

1. Grjotheim, K., Krohn, C., Malinovsky, M., Matiasovsky, K. and Thonstad, J., *Aluminium Electrolysis - Fundamentals of the Hall-Héroult Process*, 2nd edition, Aluminium-Verlag, Düsseldorf, Germany, 1982.
2. Dewing, E. W., "Thermodynamics of the System NaF-AlF₃: Part IV, Revision", *Met. Trans.*, 21B (1990) 285 – 294.
3. Gilbert, B., Robert, E., Tixhon, E., Olsen, J. E. and Östfold, T., "Acid-Base Properties of Cryolite Based Melts with CaF₂, MgF₂ and Al₂O₃ Additions. A Comparison between Raman and Vapour Pressure Measurements", *Light Metals 1995*, 181-194.
4. Grjotheim, K. and Welch, B. J., *Aluminium Smelter Technology - A Pure and Applied Approach*, 2nd edition, Aluminium-Verlag, Düsseldorf, Germany, 1988.
5. Grjotheim, K. and Kvande, H., *Introduction to Aluminium Electrolysis - Understanding the Hall-Héroult Process*, Aluminium-Verlag, Düsseldorf, Germany, 1993.
6. Ödegård, R., Sterten, Å. and Thonstad, J., "The Solubility of Aluminium in Cryolitic Melts", *Light Metals 1987*, 389 - 398.
7. Wang, X., Peterson, R. D. and Richards, N. E., "Dissolved Metals in Cryolitic Melts", *Light Metals 1991*, 323 - 330.
8. Tabereaux, A. T., Alcorn, T. A. and Trembley, L., "Lithium-Modified Low Ratio Electrolyte Chemistry for Improved Performance in Modern Reduction Cells", *Light Metals 1993*, 221-226.
9. Langon, B. and Varin, P., "Aluminium Pechiney 280 kA Pots", *Light Metals 1986*, 343-347.
10. Solli, P. A., Haarberg, T., Eggen, T., Skybakmoen, E. and Sterten, Å., "A Laboratory Study of Current Efficiency in Cryolitic Melts", *Light Metals 1994*, 195-203.
11. Tschopp, T., Franke, A. and Bernhauser, E., "Improvement in Operational Results by Using Lithium Carbonate in the Reduction Plant at Essen", *Light Metals 1979*, Vol. 1, 457 - 465.

12. Adams, J. H., "Electrolyte Composition for High Current Density Aluminum Reduction Cells", in *Extended Abstracts from The Electrochemical Society, Inc. Spring Meeting*, Electrochemical Society, Pennington, NJ, USA, 1980, 9 pp.
13. Cheney, R. G., "Potline Operation with Lithium Modified Bath", *Light Metals 1983*, 519 - 536.
14. Shirley, D. R., "Potline Conversion to Lithium Bath", *Light Metals 1985*, 471 - 484.
15. Hawkins, R. A., "Intalco Potlines' Operation with Lithium-Modified Bath Chemistry", in *Proceedings of the International Symposium on Production, Refining, Fabrication and Recycling of Light Metals*, ed. by Bouchard, M. and Tremblay, P., Pergamon Press, New York, USA, 1990, 41 - 48.
16. Tarcy, G. P., "Strategies for Maximizing Current Efficiency in Commercial Hall-Héroult Cells", in: *Proceedings from the 5th Australasian Aluminium Smelting Technology Conference and Workshop*, Sydney, Australia, 1995, 139-160.
17. Kvande, H., "Current Efficiency of Alumina Reduction Cells", *Light Metals 1989*, 261-268.
18. Cutshall, E., "Potential Improvements in Reduction Cell Operation", *Travaux ICSOBA*, 24 (No. 28) (1997) 246-256.
19. Dewing, E. W., "Loss of Current Efficiency in Aluminium Electrolysis Cells", *Met. Trans. B.*, 22B (1991) 177-182.
20. Haupin, W., "The Liquidus Enigma", *Light Metals 1992*, 477-480.
21. Tarcy, G. P., Rolseth, S. and Thonstad, J., "Systematic Alumina Measurement Errors and Their Significance in the Liquidus Enigma", *Light Metals 1993*, 227-232.
22. Verstreken, P. and Benninghoff, S., "Bath and Liquidus Temperature Sensor for Molten Salts", *Light Metals 1996*, 437-444.
23. Rolseth, S., Verstreken, P. and Kobbeltvedt, O., "Liquidus Temperature Determination in Molten Salts", *Light Metals 1998*, 359-366.
24. Kvande, H., "The Optimum Bath Composition in Aluminium Electrolysis - Does it Exist?", *Erzmetall*, 35 (1982) 597-604.
25. Tabereaux, A. T., "Bath Chemistry and Cell Performance", in: *Proceedings from the 5th Australasian Aluminium Smelting Technology Conference and Workshop*, Sydney, Australia, 1995, 108-126.
26. Holmes, G. T., "Hall Cell Ampere Efficiency up 12 % in 3 Decades", *Light Metals 1995*, 371-373.
27. Keinborg, M. and Cuny, J. P., "Aluminium Pechiney 180 kA Prebake Pot from Prototype to Potline", *Light Metals 1982*, 449-460.
28. Reverdy, M., Homsy, P. and Jolas, J. M., "AP 30 Technology and Experience Gained from the Recently Started Pots", *Light Metals 1995*, 405-411.
29. Jeltsch, R. C. and Franklin, T. W., "Retrofit of the Kaiser Mead Smelter", *Light Metals 1992*, 325-328.

30. Dhameja, R. and Sachan, G. S., "Pot Retrofit with Larger Anodes", *Light Metals 1990*, 459-462.
31. Knapp, L. L., "Prediction of Pot Performance at New Operating Conditions", *Light Metals 1992*, 537-539.
32. Newsted, G., Meyer, H., Hawkins, R. and Johnson, J., "Twenty-five Years of Progress at Intalco", *Light Metals 1992*, 307-324.
33. Forberg, H. O., "Untapped Opportunities for Improving Performance and Increasing Smelter Production", *Light Metals 1996*, 313-317.
34. Mosquera, F. and Medina, H., "The Optimum Bath Ratio in Modified Baths", *Light Metals 1987*, 303-307.
35. Hyland, M. M., Patterson, E. C., Stevens McFadden, F. and Welch, B. J., "Aluminium Fluoride Consumption and Control in Smelting Cells", paper presented at the 6th *International Conference on Molten Slags, Fluxes and Salts*, Stockholm, Sweden, June 2000.
36. Welch, B. J., "Current Efficiencies in Aluminium Smelting Cells", paper presented at the 17th *International Course on Process Metallurgy of Aluminium*, Trondheim, Norway, 1998, Chapter 15, 1-22.
37. Kvande, H., Moxnes, B. P., Skaar, J. and Solli, P. A., "Pseudo Resistance Curves for Aluminium Cell Control - Alumina Dissolution and Cell Dynamics", *Light Metals 1997*, 403-409.