# Simultaneous addition of lithium fluoride and magnesium fluoride in the aluminium electrolysis

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The fundamental condition for increasing the current efficiency in aluminium electrolysis is the lowering of the operational temperature. This can be achieved by means of additives to the conventional electrolyte.

The requirements which must be fulfilled by the additive are formulated. The influences of various potential additives on the important physicochemical properties of the electrolyte and on the industrially important parameters of the aluminium electrolysis are compared.

It has been found that of all additives tested, LiF and MgF₂ are best suited. The possibility of their simultaneous application is discussed and tentative "optimum concentrations" of the additives are suggested.

Основным условием повышения выхода по току при электролизе алюминия является понижение рабочей температуры. Это возможно достичь с помощью добавок к обычному электролиту.

Сформулированы необходимые потребности, касающиеся добавки. Сравнены влияния различных возможных добавок на значительные физико-химические свойства электролита и промышленно важные параметры электролиза алюминия.

Обнаружено, что из всех испытанных добавок самыми удобными являются LiF и MgF₂. Обсуждается возможность их совместного применения и предложены опытные »оптимальные концентрации« добавок.

The world energy crisis in the last decade imposed a heavy pressure on the aluminium industry which is one of the biggest consumers of the most precious sort of energy — electricity. This pressure resulted in a continuous decrease in specific energy consumption per mass unit of Al produced even in the energy-rich countries where only a few years ago aluminium was produced with the aim of obtaining the maximum production of aluminium per production unit (cell) regardless of the consumption of the then cheap energy. At present, the average specific consumption [1] is about 15 kWh/kg Al and the trend is steadily decreasing.

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One of the most promising possibilities of cutting down the specific consumption and, consequently, increasing the energy efficiency (EE), appears to be an increase in current efficiency (CE) of the electrolytic process. Presently the CE is in the range [1] from 85 to 92 %. A number of previous investigations [1] indicate that the CE is lowered by the secondary reactions, mainly by the reaction between the primary products of electrolysis: aluminium, dissolved in the electrolyte, and the gaseous or dissolved $CO_2$ in the proximity of the anode

$$2Al(dissolved) + 3CO_2(g) = Al_2O_3(dissolved) + 3CO(g) \qquad (1)$$
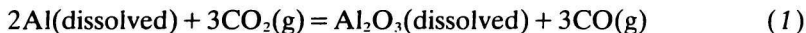
From an analysis of the literature data [1] it follows that CE is determined by the composition of the electrolyte (cryolite ratio (CR) and alumina concentration), and by the operational parameters of the electrolysis, *i.e.* working temperature, interpolar distance, and current density. The temperature apparently is the most important since it influences the equilibrium solubility and the dissolution rate of Al in the electrolyte as well as the rate of reaction (1). Although the data on the temperature dependence of CE are rather scattered, it may be assumed that the temperature gradient of CE is within $(-0.15 \pm 0.05)$ %/°C [2]. As to the dependence of CE on the electrolyte composition, the available data [1] indicate that Al losses are at a minimum at CR between 2.6—2.8. Analysis of literature data [1, 3, 4] indicates that the dependence of CE on the alumina concentration reaches a minimum with $Al_2O_3$ mass fraction within 4—8 mass %.

The possibility of lowering the working temperature is limited. The conventional electrolyte is a mixture of the system $Na_3AlF_6$—$AlF_3$—$Al_2O_3$—$CaF_2$,* operating near its liquidus temperature. The only way to decrease the temperature of primary crystallization $(\theta_{pc})$ of the electrolyte is by adding certain compounds.

The substance to be used as an additive must fulfil strict requirements [6]:

(i) It must not contain a cation with a lower deposition potential (more noble) than aluminium.

(ii) It must not be too hygroscopic, it must be thermally stable at the conditions of electrolysis, and it must not react to form volatile compounds or compounds insoluble in the melt.

(iii) It must not cause serious difficulties in cell operation, such as an increase in the strength of the crust.

(iv) Its price must be acceptable.

Further, a hypothetical "ideal" addition should improve the technologically important physicochemical properties of the electrolyte. It should:

— decrease the $\theta_{pc}$ of the electrolyte while the solubility of the alumina should be reduced as little as possible,

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* Calcium fluoride is considered to be a constant component of the aluminium electrolyte. If not added deliberately (up to about 5 mass %), it is continuously introduced into the electrolyte by the raw materials (mainly as oxide) and its mass fraction reaches from 4 to 8 mass % [5].

— decrease the density of the electrolyte in order to increase the difference between the density of the electrolyte and that of aluminium,

— increase the interfacial tension at the Al/electrolyte phase boundary to reduce the rate of Al dissolution,

— lower the solubility, both chemical and physical, of metal in the electrolyte,

— increase the electrical conductivity of the electrolyte.

The effect of the viscosity of the electrolyte on the operation still remains uncertain. Low viscosity promotes diffusion and, consequently, the transport of aluminium to the proximity of the anode where reaction (1) takes place. High viscosity makes the separation of carbon particles difficult, and will also reduce the electrical conductivity.

Several substances, mainly fluorides and chlorides of alkali and alkaline earth metals have been tested as potential additives [1]. None of them have fulfilled all the above requirements. Of all the investigated substances, only lithium fluoride and magnesium fluoride have found large-scale application. Sodium chloride has a favourable influence on the technically important physicochemical properties of the electrolyte, and has therefore been considered a promising additive [7—9]. But it was found to be a failure as it increased the solubility of aluminium in the electrolyte [9, 10] and, consequently, lowered the CE [3, 11, 12].

Industrial application of magnesium fluoride addition started in the Soviet aluminium industry more than 20 years ago [13], whereas lithium fluoride was first successfully applied by *Lewis* [14—16]. In the present paper, the influence of these additives and their possible cumulative effect on the essential physicochemical properties of the conventional aluminium electrolyte, and on some industrially important parameters of the electrolysis is discussed.

### Influence of LiF and $MgF_2$ additions on the essential physicochemical properties of the electrolyte

#### Temperature of primary crystallization ($\theta_{pc}$)

The influence of LiF, $MgF_2$, and several other substances [17], on the $\theta_{pc}$ of cryolite is shown in Fig. 1. In this respect, also the influence of lithium cryolite, $Li_3AlF_6$, is of interest, as the addition of a limited amount of lithium fluoride (dependent on the CR of the electrolyte) to an "acid" electrolyte is equivalent to the addition of $Li_3AlF_6$. The liquidus curves of the systems $Na_3AlF_6$—LiF, $Li_3AlF_6$, $MgF_2$ in Fig. 1 are those presented by *Holm* [18].

It should be pointed out that from a technological point of view additives of up to 5 mass % are of prime interest, mainly since a higher concentration of additives

may cause unacceptable contamination of the aluminium. Analysis [1] of liquidus diagrams of systems of the type $Na_3AlF_6$—$Al_2O_3$—$MA_x$ shows that the individual additives (up to 5 mass %) have essentially the same effect on the $\theta_{pc}$ as in the binary systems.

The simultaneous effect of the LiF and $MgF_2$ additives on the $\theta_{pc}$ of cryolite and cryolite—alumina melts has been investigated by *Vidyaeva et al.* [19]. Their data are apparently incorrect and should be reexamined.

Several "universal" equations have been proposed for estimating the cumulative effect of various combinations of potential additives on the $\theta_{pc}$ of the electrolyte. However, most equations have a rather limited range of application. One example is an equation proposed by *Pawlek* [20], based on relationships derived by *Dewing* [21] by a mathematical analysis of a large number of experimental data

$$\theta_{pc}/°C = 793 + 60.83 \cdot (CR) - 2.75 \cdot w(Al_2O_3)/\text{mass } \% -$$

$$- 1.125 \cdot w(MgF_2)/\text{mass } \% + 0.875 \cdot w(CaF_2)/\text{mass } \% -$$

$$- 9.31 \cdot w(MgCl_2)/\text{mass } \% - 6.19 \cdot w(LiF)/\text{mass } \% \tag{2}$$

CR is the cryolite ratio on molar basis $(n(NaF)/n(AlF_3))$. According to eqn (2), though, the addition of $CaF_2$ should increase the $\theta_{pc}$ of the electrolyte, which obviously is not the case (Fig. 1). Besides, there seems to be a systematic error in
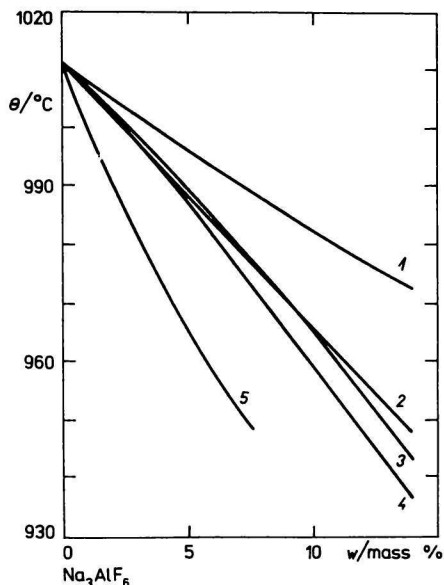


*Fig. 1.* Influence of additives on the $\theta_{pc}$ of cryolite melts.
*1.* $CaF_2$; *2.* NaCl; *3.* $Li_3AlF_6$; *4.* $MgF_2$; *5.* LiF.
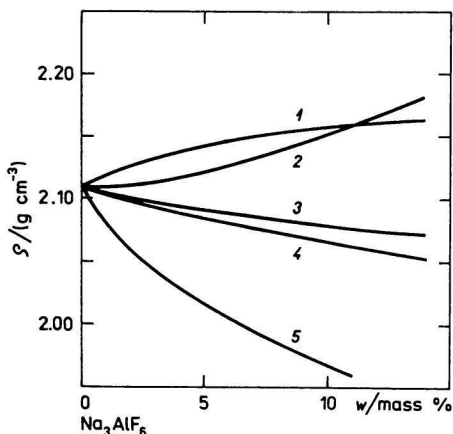
*Fig. 2.* Influence of additives on the density of cryolite melts at 1000 °C.
*1.* $MgF_2$; *2.* $CaF_2$; *3.* $Li_3AlF_6$; *4.* LiF; *5.* NaCl.

the calculated values. (One calculates a melting point of cryolite of 975.5 °C, as opposed to the experimentally determined value [18] of 1011 °C.)

## Density

The influence of LiF, $Li_3AlF_6$ and $MgF_2$, and some other additives [1] on the density of molten cryolite is shown in Fig. 2. Obviously, all the additives affect the density of molten cryolite to a minor extent only. This may be attributed to the spatial arrangement of the $AlF_6^{3-}$ complex ions. The small $Li^+$ and $Mg^{2+}$ cations as well as the $F^-$ anions occupy interstitial positions. Thus, the small increase in the density caused by an addition of $MgF_2$ may be attributed to the higher relative atomic mass and the higher polarization potential of the $Mg^{2+}$ cation compared to $Li^+$.

The effect of both these additives on the density of cryolite—alumina melts in the low-concentration range is essentially the same as in the corresponding binary systems [1]. The cumulative effect of the two additives on the density of the electrolyte has not been investigated as yet.

## Surface properties

The investigation of the influence of various additives on the surface properties of the aluminium electrolyte appears to be of prime importance, as these properties have a direct influence on some technologically and economically important parameters of the industrial process [2]. The interfacial tension at the electrolyte/ /carbon phase boundary affects the selective absorption of the electrolyte components into the carbon lining and the separation of carbon particles ("carbon froth") from the electrolyte. The interfacial tension at the electrolyte/aluminium phase boundary affects the rate of dissolution of aluminium in the electrolyte directly and, consequently, the CE of the electrolysis process.

The influence of LiF and $MgF_2$ as well as other potential additives on the interfacial tension at the electrolyte/aluminium phase boundary was investigated by *Belyaev* [13] (the additives have been applied to a melt with the composition $2.5NaF \cdot AlF_3 + 12$ mass % $Al_2O_3$ at 1000 °C). From the reported data shown in Fig. 3 it is obvious that the addition of lithium fluoride only slightly affects the interfacial tension, while the influence of magnesium fluoride is clearly superior to that of $CaF_2$. Thus it might be expected that an addition of $MgF_2$ would *directly* increase the CE of the electrolysis process, which is not the case with LiF as will be shown later.

As to the wetting of carbon by the electrolyte, the additions of LiF and $MgF_2$ according to *Belyaev et al.* [22] do not have any significant influence as shown in

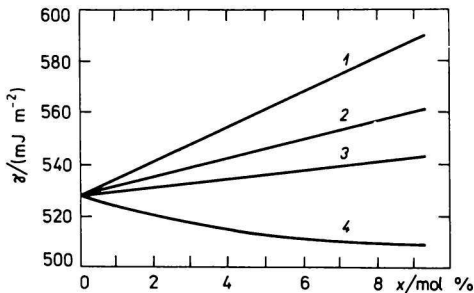Fig. 3. Influence of additives on the interfacial tension at the electrolyte/aluminium phase boundary at 1000 °C.
1. MgF₂; 2. CaF₂; 3. LiF; 4. NaCl.
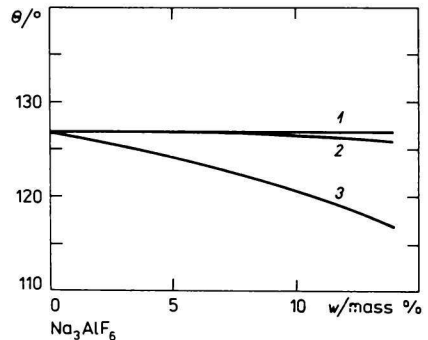
Fig. 4. Influence of additives on the wetting of carbon by cryolite melts at 1005 °C; $\Theta$ = wetting angle.
1. MgF₂, CaF₂; 2. LiF; 3. NaCl.

Fig. 4. In another work by the same author [23], however, the addition of MgF₂ was claimed to reduce considerably the wetting of carbon in cryolite—alumina melts. It should be pointed out that these measurements have been carried out in current--less conditions and the picture may be drastically changed by the polarization during electrolysis [24].

## Viscosity

The influence of LiF, Li₃AlF₆, and MgF₂, as well as some other substances, on the viscosity of cryolite, as determined by *Matiašovský* and *Votava* [25], is shown in Fig. 5.

Although their viscosity values are obviously too high because of a systematic error [1], the trends are quite obvious. Here again it may be assumed that simultaneous additions of both LiF and MgF₂ will not bring about any major change in the viscosity of the aluminium electrolyte.

## Electrical conductivity

The electrical conductivity of the melt determines the ohmic voltage drop across the electrolyte, and consequently affects the EE of the process. The influence of LiF, Li₃AlF₆, MgF₂, and other additives on the conductivity of cryolite, as presented by *Grjotheim et al.* [1], is shown in Fig. 6. Lithium fluoride is superior to all the other additives. On the other hand, the positive effect of lithium cryolite (which is, up to a certain concentration, dependent upon the CR, equivalent to an
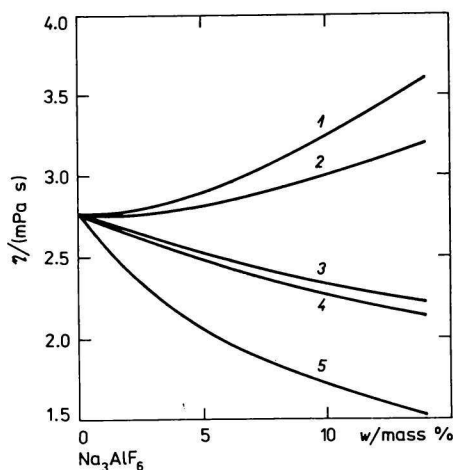
*Fig. 5.* Influence of additives on the viscosity of cryolite melts at 1000 °C.
*1.* MgF$_2$; *2.* CaF$_2$; *3.* Li$_3$AlF$_6$; *4.* NaCl; *5.* LiF.
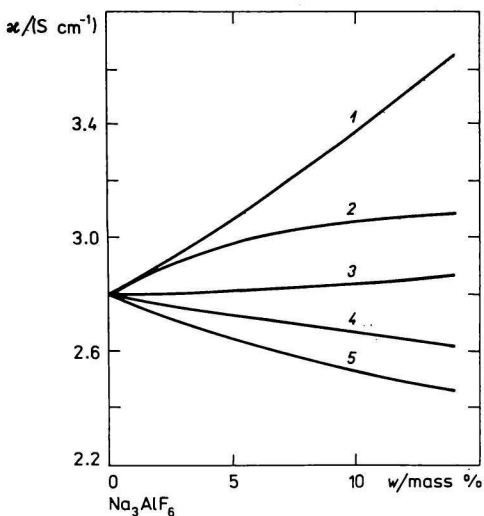
*Fig. 6.* Influence of additives on the electrical conductivity of cryolite melts at 1000 °C.
*1.* LiF; *2.* NaCl; *3.* Li$_3$AlF$_6$; *4.* CaF$_2$; *5.* MgF$_2$.

addition of LiF into an "acid" electrolyte (CR < 3)) is surprisingly low, and the addition of MgF$_2$ decreases the conductivity of the electrolyte. The effect on the conductivity of cryolite—alumina melts with the additives tested is comparable to their effect on pure cryolite (Fig. 6).

The influence of the addition of lithium fluoride on the conductivity of a melt consisting of 2.7NaF · AlF$_3$ + 5 mass % Al$_2$O$_3$ + 3 mass % CaF$_2$ + 3 mass % MgF$_2$ at 1000 °C was determined by *Vakhobov* [26]. Also in this case LiF was found to be a highly effective additive, its influence being more pronounced at higher concentrations corresponding to a basic melt with CR > 3.

For an approximate estimate of the cumulative influence of LiF and MgF$_2$ additives on the conductivity of the electrolyte, the relation proposed by *Choudhuri* [27] may be used

$$\ln x/(\text{S cm}^{-1}) = 2.0156 - 0.0207 \cdot w(\text{Al}_2\text{O}_3)/\text{mass \%} -$$
$$- 0.0050 \cdot w(\text{CaF}_2)/\text{mass \%} - 0.0166 \cdot w(\text{MgF}_2)/\text{mass \%} +$$
$$+ 0.0178 \cdot w(\text{LiF})/\text{mass \%} + 0.0077 \cdot w(\text{Li}_3\text{AlF}_6)/\text{mass \%} +$$
$$+ 0.0063 \cdot w(\text{NaCl})/\text{mass \%} + 0.4349 \cdot (\text{BR}) - 2068.4 \text{ K}/T \qquad (3)$$

Here BR is the bath ratio (mass ratio $w(\text{NaF})/w(\text{AlF}_3)$). The agreement between the experimental and calculated conductivity values is claimed to be better than ± 4 %.

*Influence of LiF and MgF$_2$ additions on the industrially
important parameters*

Solubility of Al$_2$O$_3$ in the electrolyte and the rate of its dissolution

The investigation of the influence of additives on the solubility and rate of dissolution of alumina in the electrolyte is of great importance as regards the possibility of sludge formation which may raise serious technological problems.

From the relevant phase diagrams it is obvious that all additives involving LiF, Li$_3$AlF$_6$, and MgF$_2$ reduce the solubility of Al$_2$O$_3$ in the electrolyte. Fig. 7 shows
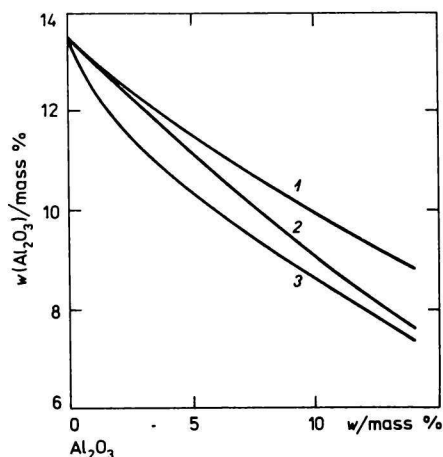


Fig. 7. Influence of additives on the solubility of alumina in cryolite melts at 1010 °C.
1. LiF; 2. CaF$_2$; 3. MgF$_2$.
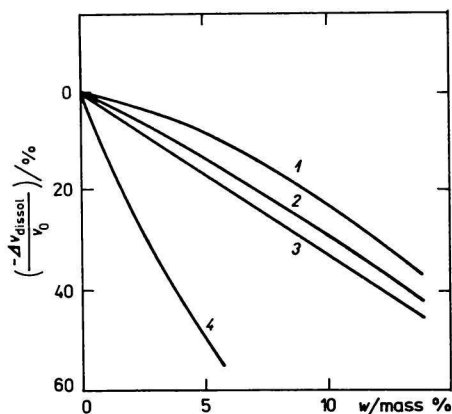
Fig. 8. Influence of additives on the rate of dissolution of alumina in cryolite + 4 mass % AlF$_3$ at 1010 °C.
1. LiF; 2. CaF$_2$; 3. MgF$_2$; 4. Al$_2$O$_3$.

the influence of the common additives on the isothermal solubility of alumina in cryolyte as determined by *Poetsch* [28]. The solubility of Al$_2$O$_3$ is obviously most lowered by the addition of MgF$_2$, mainly in the technologically interesting region with low concentrations of the additive. *Poetsch* [28] and *Gerlach et al.* [29] have also found the addition of magnesium fluoride to exhibit the most pronounced negative effect on the rate of alumina dissolution in a cryolite melt with 4 mass % AlF$_3$, as shown in Fig. 8.

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## Current and energy efficiency (CE and EE)

As mentioned in the introduction, the CE is decreased by secondary reactions, mainly by reaction (1) between Al dissolved in the electrolyte and $CO_2$ which is the primary product of the anode reaction. The most important factors governing the rate of this reaction were found to be the solubility and rate of dissolution of aluminium in the electrolyte. Usually it is assumed [1] that CE is proportional to the solubility of Al in the melt.

From an analysis of the published data [1] it follows that the CE depends on the composition of the electrolyte (see introduction) and on the operational parameters of electrolysis. It has been found that the CE increases with decreasing operational temperature and, to some extent, also with increasing interpolar distance and current density. The possibility of increasing the two latter parameters, however, is rather limited. Without changing the composition of the electrolyte, their increase brings about an increase in the ohmic voltage drop in the electrolyte. The result is an increased working temperature, and consequently a decrease in both the CE and EE.

The *direct* influence of a lithium fluoride addition on the CE was found to be negligible [17, 30, 31]. This is consistent with the data on the influence of LiF on the interfacial tension at the electrolyte/aluminium boundary [12], which determines the rate of dissolution of Al in the electrolyte. On the other hand, in a laboratory electrolytic cell the addition of $Li_3AlF_6$ (applied as $AlF_3$ and Li as carbonate) was found to be more effective, especially when applied to an "acid" electrolyte as shown in Fig. 9 [11, 12].

The literature data on industrial tests with additions of lithium fluoride agree with the results of the laboratory experiments. According to *Richards* [32], the specific influence of LiF additive on the CE was found to be negligible (CE was increased by 0.0043 %/mass % LiF). In industrial tests in GFR, an addition of 3—4 mass % LiF only increased the CE by 0.3 to 0.5 %, whilst severe operational problems due to an increased sludge formation have been encountered in several cases [33].

An increased effect of lithium fluoride on the CE can only be expected when utilizing the positive effect of this additive on the physicochemical properties, mainly on the $\theta_{pc}$ of the electrolyte. The reported data are contradictory, however. According to *Potylitsyn et al.* [34], an addition of 4 mass % LiF made it possible to lower the working temperature by 13 °C (from 965 to 952 °C) which resulted in a CE increase of 1.5 %, whilst *Botor* and *Suchánek* [35], with the same addition, reported an increase of the CE by 3.4 % which seems rather improbable. The data in a patent by *Lewis* [14] seem more reliable. He claims that an addition of 4 mass % LiF increases the CE by 2.5 % due to a decrease in the working temperature. At the same time less carbon and fluorides are consumed. According to another patent

by *Lewis* [15], the application of a high concentration of LiF (up to 20 mass %) makes it possible to achieve a substantial increase in the CE and the productivity of industrial cells due to the positive influence of lithium fluoride on the specific conductivity of the electrolyte. This makes a substantial increase of current density possible without increasing the working temperature. A consequence may be the contamination of Al, as will be shown later. *Lewis* [16] has reported an increase of the CE by 3 % with an addition of 5 mass % LiF to an electrolyte with CR = 2.6.

The specific influence of the $MgF_2$ addition on the CE, determined in a laboratory electrolytic cell [11], is obviously superior to that of $CaF_2$ (Fig. 10), most probably due to the more pronounced influence of magnesium fluoride on the interfacial tension at the electrolyte/aluminium phase boundary. The positive influence of magnesium fluoride on the CE has also been reported by *Belyaev* [36]. In industrial cells it has been found [13, 37] that an addition of 4 to 6 mass % $MgF_2$ increases the CE by approximately 1 %. In a paper presented by *Dzierva* [38], the same increase in the CE has been claimed for an addition of 3 mass % $MgF_2$, whereas *Qiu Zhu-Xian* [24] reported that the CE increased by about 3 % with an addition of 5 mass % $MgF_2$. This was mainly ascribed to the decreased working temperature.
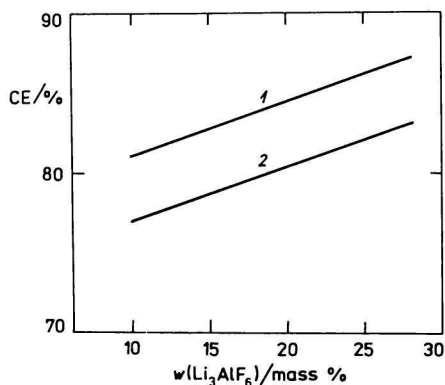


Fig. 9. Influence of the $Li_3AlF_6$ addition on the current efficiency.
Operational parameters: $\theta = 950$ °C, $d = 5$ cm, $i_\lambda = 1.2$ A cm$^{-2}$.
Electrolyte: *1.* $Na_3AlF_6 + 5$ mass % $AlF_3 + 5$ mass % $Al_2O_3$; *2.* $Na_3AlF_6 + 5$ mass % $Al_2O_3$.
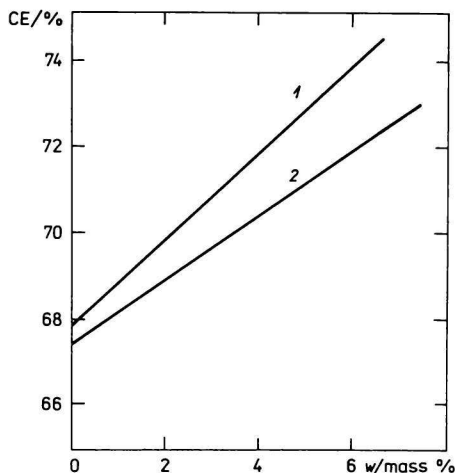
Fig. 10. Influence of the $MgF_2$ and $CaF_2$ additions on the current efficiency.
Operational parameters: $\theta = 980$ °C, $d = 4.5$ cm, $i_\lambda = 0.85$ A cm$^{-2}$.
Electrolyte: $2.8NaF \cdot AlF_3 + 5$ mass % $Al_2O_3$: *1.* $MgF_2$; *2.* $CaF_2$. (The dependences do not have a common origin as they were obtained by two independent measurements with an experimental error of ± 1 %.)

When one looks at the energy efficiency aspect of the aluminium electrolysis in addition to the CE, the influence of additives on the deposition potential of Al (decomposition voltage of $Al_2O_3$) and on the ohmic voltage drop in the electrolyte is important. Theoretically this influence may be expected to follow the Nernst law. According to *Grjotheim et al.* [12, 17] and *Matiašovský* and *Malinovský* [39] the additions of LiF and $Li_3AlF_6$ in laboratory experiments only slightly affected the deposition potential of aluminium. This observation is consistent with the results of industrial experiments where an addition of 4 mass % LiF was found to have no influence on the decomposition voltage of alumina [40]. The influence of $MgF_2$ on the deposition potential of aluminium should also be negligible. According to *Ushakov et al.* [41], the decomposition voltage of alumina increased by 27 mV/ /mass % $MgF_2$, whilst *Haupin* [42] states that the addition of magnesium fluoride has practically no effect on the value of the decomposition potential of alumina.

The ohmic voltage drop in the electrolyte is a function of the electrolyte conductivity, current density and the interpolar distance. The cumulative effect or the LiF and $MgF_2$ additives can be estimated on the basis of their influence on the conductivity of the electrolyte. Here it should also be assumed that the industrial electrolyte contains suspended carbon particles which may substantially decrease conductivity [1]. Hence, the negative influence of $MgF_2$ on the conductivity may partially be compensated for by its positive effect on the interfacial tension at the electrolyte/aluminium phase boundary. This effect may be more pronounced in cells with Södeberg anodes where the carbon dust content in the electrolyte is substantially higher than for prebaked anodes.

## Contamination of aluminium

According to *Dolling et al.* [43], an increased Li content in aluminium adversely affects its casting and rolling properties and resistance to corrosion. Consequently, it is important to know the effect of a LiF addition on the Li contamination of the cell metal. The Li content of aluminium obviously depends on the concentration of LiF in the electrolyte. According to *Sparwald* [44], the lithium content in the metal was 12 mass p.p.m. with 5 mass % LiF in the electrolyte, compared to about 2 mass p.p.m. when no lithium fluoride was added. These values, however, seem to be too low compared to the values calculated using the equation based on experimental data which was presented by *Tschopp* [45]

$$y = 6.63 + 2.64x \qquad (4)$$

where $x$ is the $w$(LiF)/mass % in the electrolyte and $y$ is the $w$(Li in Al)/mass p.p.m. Substantially higher Li contents are given by another equation of the same type presented by *Pawlek* [20].

Based on theoretical considerations supported by industrial testing, *Dewing* and *Gilbert* [46] suggested a dependence between the mass fractions of Li and Na in the metal, the ratio $w(\text{Li})/\sqrt{w(\text{Na})}$ being proportional to the mass fraction of LiF in the electrolyte and independent of the CR. For a LiF content of $(2.5 \pm 0.5)$ mass % LiF and CR values between 2.3—3.0, the ratio $w(\text{Li})/\sqrt{w(\text{Na})}$ was found to be fairly constant. As Na values varied from 45 to 200 mass p.p.m., the Li values varied from 12 to 34 mass p.p.m.

Whereas the deposition potential of Li is much higher than that of Na in fluoride melts, the deposition potential of Mg is lower than that for Ca, and only slightly higher than the deposition potential of aluminium. (The difference between the values of the standard decomposition potentials of $Al_2O_3$ and MgO at 1300 K is only 30 mV [1].) Therefore a substantial increase in the Mg content of aluminium can be expected when $MgF_2$ is used. This has been confirmed in industrial practice [1]. According to *Yasakov* [47], the dependence of the Mg content in the metal on the $MgF_2$ concentration in the electrolyte is given by the equation

$$y = (3.68 + 2.38x) \cdot 10^{-3} \tag{5}$$

where $y$ is the Mg content of aluminium/mass % and $x$ is $w(MgF_2)$/mass % in the electrolyte. A value of 150 mass p.p.m. Mg in aluminium found by *Sparwald* [48] in an electrolyte containing 5 mass % $MgF_2$ agrees with the value calculated according to eqn (5).

### Interaction between carbon and electrolyte

The influence of the LiF addition on the carbon cell lining was first investigated by *Rapoport et al.* [49] and *Panebianco* and *Bacchiega* [50]. It was found that lithium reacts with carbonaceous materials with formation of lamellar intercalation compounds, like other alkali metals. The lithium carbide, $Li_2C_2$, a stoichiometric compound $LiC_6$, and two nonstoichiometric compounds with an average composition $LiC_{12}$ and $LiC_{18}$ are formed [51]. Because of the small atomic radius of lithium, its destructive effect on the carbon lining is much less than of sodium and especially of potassium. Besides, according to *Wilkening* [52], the additions of LiF and $CaF_2$ decrease the activity of sodium in the electrolyte. Consequently, it can be expected that the application of LiF to the electrolyte may result in prolonged life of the carbon lining. No relevant data have been found concerning the $MgF_2$ additive.

### Other technological aspects

One of the persistent imperfections of the Hall—Héroult process is the problem of fluoride emissions. The effect of LiF appears to be of interest in this respect

whereas the effect of $MgF_2$ is considered negligible. The specific influence on the fluorine losses of the LiF additive, as reported by *Wendt* [53], is shown in Table 1.

From the reported data it follows that the addition of LiF substantially decreases the fluorine losses. Similar trends have been reported in several papers discussed by *Grjotheim et al.* [1].

Table 1

Influence of the LiF additive on the fluorine losses
$(\varrho/(mg \cdot (N\ m^3)^{-1}))$

| $w(LiF)$/mass % | F in gaseous phase | F in solid phase (particulate) | Total F losses |
|---|---|---|---|
| 0.0 | 42.9 | 9.0 | 51.9 |
| 3.5 | 31.3 | 8.0 | 39.3 |
| 4.5 | 24.5 | 6.2 | 30.7 |

Because of the high price of lithium fluoride, the LiF losses in the electrolysis process are of definite importance. According to *Balashova* and *Anufrieva* [54], when using the LiF additive, the Li losses reached an average value of 71 g Li/t Al in the first 14.5 months of electrolysis and dropped to 34 g Li/t Al in the following 12 months. Most of the difference is obviously due to the selective absorption of LiF into the carbon lining. The F content of the "carbon froth" is given, according to *Pawlek* [20], by the equation

$$y = 0.48x - 0.026 \tag{6}$$

where $y$ is the LiF loss in the froth ($m$/kg LiF/t Al) and $x$ is the $w(LiF)$/mass % in the electrolyte.

It has already been mentioned that severe problems resulting from an increased sludge formation with the addition of LiF have been encountered in several cases. The addition of $MgF_2$, on the other hand, was found to facilitate cell operation in giving an improved separation of the carbon froth and a softening of the crust [24].

## Conclusion

It is obvious from the above analysis that the *sine qua non* for increasing current efficiency in aluminium electrolysis is the greatest possible suppression of the secondary reactions. This can be achieved by lowering the working temperature and, consequently, the solubility of aluminium by application of additives to the conventional electrolyte.

Neither LiF, nor $MgF_2$ are "ideal" additives (see introduction). The addition of lithium fluoride is the most effective of all substances tested for lowering the $\theta_{pc}$ and increasing the conductivity of the electrolyte, and it is also reported to slightly increase the interfacial tension at the electrolyte/aluminium phase boundary and lower the fluorine emissions. The Li contamination of aluminium, however, adversely affects the casting and rolling properties and the corrosion resistance of the metal. This limits the applicable mass fraction of this additive. The economic factor (high price of LiF, added as $Li_2CO_3$) must also be considered.

Magnesium fluoride, on the other hand, is second only to LiF regarding its influence on the liquidus temperature of the electrolyte. While lowering the conductivity of a pure melt, it is assumed to have an indirectly favourable effect on the conductivity of industrial electrolytes, as it improves the separation of the carbon particles suspended in the melt. This may play an important role especially for Södeberg anodes where the concentration of loose carbon dust particles is substantially higher than in cells with prebaked anodes. What is still more important, however, is the substantial increase in the interfacial tension at the electrolyte/aluminium phase boundary effected by an addition of $MgF_2$. This results in a reduced solubility of Al in the electrolyte and eventually in reduced metal loss by secondary reactions. Any contamination of aluminium by Mg does not appear to have such a deleterious effect as does lithium. However, high mass fractions of magnesium fluoride above 5 mass % may still cause deterioration of the quality of the metal, mainly as regards its electrical conductivity.

Regarding the specific effect of additives, it seems worthwhile considering the possibility of the simultaneous application of both additives using $MgF_2$ as the major additive. The complementary addition of LiF is mainly intended to suppress the negative influence of $MgF_2$ on certain physicochemical properties of the electrolyte (electrical conductivity, viscosity). Let us consider an electrolyte containing 4 mass % $MgF_2$ and 2 mass % LiF. Owing to a decrease of the $\theta_{pc}$, such a combined addition would make it possible to lower the temperature of electrolysis by about 30 °C. This, together with the specific influence of $MgF_2$ on the aluminium solubility, might bring about an increase of the CE of 3 to 5 %. Besides, the lowering of the working temperature, together with the specific influence of LiF, might substantially reduce fluorine emissions.

On the other hand, decreasing the operational temperature lowers the conductivity of the electrolyte. The higher ohmic resistance heat counteracts the intended temperature reduction. It cannot be expected that the temperature can be lowered so much simply by application of additives. Most probably the heat losses must be increased, e.g. by reducing the thermal insulation of alumina on the crust under normal operating conditions or by reducing the thickness of the refractory layer at the cell bottom when completely overhauling the cells. Both reduce the energy efficiency. Another possibility is the lowering of the current density in the

electrolysis. Though such a step will result in a lower aluminium production per cell, it is attractive taking into consideration the increased CE and the present situation of the world market for aluminium.

Another problem which must be taken into account is a decrease of alumina solubility in the electrolyte effected both by the specific influence of additives and the lower temperature. Considering, however, the general trends in the aluminium industry which involve continuous feeding at fairly low alumina concentration (possibly between 3—4.5 mass %), this effect should not present any serious problems.

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