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Properties of Low-Temperature Melting Electrolytes for the Aluminum Electrolysis Process: A Review

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The traditional electrolyte for aluminum electrolysis is composed of molten cryolite (Na_3AlF_6) and alumina (Al_2O_3). One of the objectives of the industry is to lower the operating temperature of the electrolytic process, which is currently around 960 °C. The benefits commonly evoked of a temperature decrease in the aluminum plotlines are multiple: reduction of the energetic consumption and thus of the global environmental footprint, increase of the cell life due to limited corrosion, reduction of production costs, etc. In this work, an overview of some properties of molten fluoride systems (Na−cryolite-based electrolytes ($NaF-AlF_3$) and K−cryolite-based electrolytes ($KF-AlF_3$)) is presented. To a lesser extent, the case of all-chloride and mixed chloro-fluoride salts is also discussed. Many physicochemical properties of salt mixtures are of major importance to evaluate the potential of a given electrolyte. When available, the following properties are reported and compared: the liquidus temperature, the electrical conductivity, the density, the vapor pressure, the solubility of alumina, and the solubility of liquid aluminum.

Introduction

The Hall−Héroult process, named after its inventors, is devoted to the production of primary aluminum from alumina in an electrolysis cell, at a temperature of around (950 to 960) °C. It has been running and optimized for more than a century. The electrolyte is mainly composed of cryolite (Na_3AlF_6) and alumina (Al_2O_3), together with some aluminum fluoride (AlF_3) and calcium fluoride (CaF_2) and in some cases other additives. One of the current trends in R&D, as can be observed from the large amount of recent scientific articles, is to try to lower the operating temperature of the electrolytic process. The benefits commonly evoked of a temperature decrease in the aluminum plotlines are multiple: reduction of the energetic consumption and thus of the global environmental footprint, increase of the cell life due to limited corrosion, reduction of production costs, etc. There has been quite a large amount of work done in recent years concerning the properties of new electrolytes for the alumina reduction process, both in view of using the regular carbon-based anodes and also in the frame of the development of oxygen-evolving anodes. In this latter case, the temperature decrease is also expected to greatly reduce the corrosion rate of the anodes.

The major objective of the present paper is to review the main physicochemical properties of some selected electrolytes supposedly suited for use in the electrolytic process. As hundreds of systems can be envisaged, the study was first refined to salt mixtures containing Al(III) as a main constituent, to avoid mass-transfer limitation of the cathodic reaction. The temperature range of the melting point of the considered salt mixtures was chosen to be comprised between 950 °C (current electrolytes) and 660 °C (melting temperature of aluminum), so that aluminum is formed in the liquid phase. Finally, only the systems operating with an alumina feed were considered, which involve an oxygen-containing anodic product (either CO_2 or O_2). These criteria lead to an electrolytic process not so different from the Hall−Héroult process, in the way that dissolved alumina is reduced into liquid aluminum.

An initial overview of the published papers led to a refinement of the present review to two major systems: Na−cryolite-based electrolytes ($NaF-AlF_3$) and K−cryolite-based electrolytes ($KF-AlF_3$), which are the topics of many recently published works. To a lesser extent, the case of all-chloride and mixed chloro-fluoride salts is also discussed. The use of aluminum sulfides, nitrides, or bromides as a feeding material is not discussed: no work has been published on this topic since the mid eighties, and it seems that this kind of process has been discarded. Many physicochemical properties of salt mixtures are of major importance to evaluate the potential of a given electrolyte. The following properties have been considered: the liquidus temperature, the electrical conductivity, the density, the vapor pressure, the solubility of alumina, and finally the solubility of liquid aluminum. The main impact of each of them is described in short in the following (much more details are available in reference books, e.g., *Aluminum Electrolysis*[1,2]):

- Alumina solubility: the solubility of alumina in the electrolyte is a key parameter in the running of the process since a sufficient concentration of alumina must be maintained to control the anodic reaction. Indeed, alumina depletion in the vicinity of the anode leads to the so-called anode effect, which consists of the blockage of the anode surface and the production of significant amounts of powerful greenhouse gases, the perfluorocarbons.

- Vapor pressure: the determination of the total vapor pressure above the molten salts is a good indication of their stability, a high vapor pressure indicating that the electrolyte tends to evaporate. Knowledge of the compounds constitutive of the vapor phase and their partial vapor pressure also helps to predict the evolution of composition of the liquid salt phase.

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- Electrical conductivity: the electrical conductivity of the electrolyte is of great importance in the energetic balance of the Hall−Héroult process since the bath resistivity represents more than half of the ohmic drop of industrial cells (~1.35 V out of ~2.50 V). This ohmic drop allows the temperature of the cell by the Joule effect to be maintained, but most of the energy is lost and dissipates. The highest electrical conductivity is then required.

- Aluminum solubility: the liquid aluminum solubility in the molten salt influences the faradic efficiency of the process and needs to be minimized. Indeed, dissolved aluminum gets oxidized in the vicinity of the anode (where it reacts with $CO_{2(g)}$) and is responsible for some current loss.

- Salt density: the Hall−Héroult process operates well because aluminum is heavier than the molten salt, which allows confining the liquid metal at the bottom of the cell. A maximal density gap between aluminum and salt is thus required to ensure optimal phase separation.

While the Na−cryolite mixtures have been widely studied, it is not the case of some of the other systems presented here. A summary of the current knowledge available in the literature is established in this review: first, standard industrial cryolite mixtures are considered, and then the properties of modified cryolite mixtures, K-based cryolites and chloro-fluoride salts, are presented.

Na−Cryolite Systems

Standard Cryolite Melts. The usual industrial electrolyte composition range is, in mass fraction (w): $w(AlF_3) = 0.10$ to 0.12, $w(Al_2O_3) = 0.02$ to 0.04, $w(CaF_2) = 0.03$ to 0.05, and the balance Na_3AlF_6. To compare the properties of the various lower-temperature melting salt mixtures, a summary of the properties of the industrial electrolyte is presented in this first section. The influence of the common additives (CaF_2, LiF, MgF_2, and KF) is also discussed.

Liquidus Temperature and Alumina Solubility. The liquidus temperatures of the cryolite melts are highly dependent on their composition. As a general trend, stoichiometric cryolite has a melting point of about 1011 °C, and any modification of composition in the system $Na_3AlF_6-AlF_3-Al_2O_3-CaF_2-MgF_2-LiF-KF$ leads to a decrease of the liquidus temperature. Many detailed studies on the evolution of the liquidus temperature and alumina solubility in cryolite melts have been carried out.[1] Among them, the work of Solheim et al.[3,4] is noticeable since it proposes analytical formulas in the (850 to 1050) °C temperature range. A thermochemical modeling of most of these data has also been performed and included in the Hall−Héroult database (FTHall[5]) of the FactSage software.[6] This database has been used in this article to calculate some phase diagrams.

Industrial mixtures contain an excess of AlF_3. The molar ratio NaF/AlF_3, called cryolite ratio (CR), is the usual way to write the cryolite composition: a CR equal to 3 indicates stoichiometric cryolite, while a CR below 3 refers to mixtures containing an excess of AlF_3. Standard industrial mixtures usually have a CR of about 2.2. As illustrated in Figure 1, the increase of the AlF_3 concentration leads to a sharp decrease of the liquidus temperature. The liquidus temperature of industrial baths is around 955 °C.

The evolution of the liquidus temperature of the industrial bath composition versus the alumina content is plotted in Figure 2. It shows a major property of the cryolite mixtures: alumina is highly soluble, up to $w = 0.07$ at 950 °C, which is a key parameter for operating the electrolysis cells. Furthermore, alumina additions decrease the liquidus temperature by about −5 °C per mass percent of Al_2O_3.

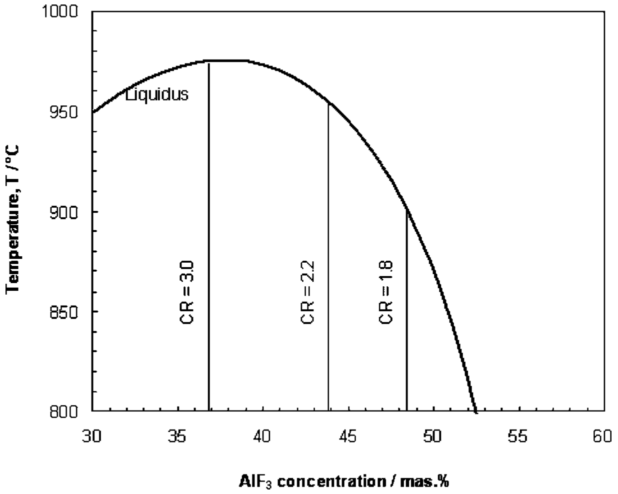

Figure 1. Influence of the AlF_3 content on the liquidus temperature of a cryolite mixture containing $w(Al_2O_3) = 0.03$ and $w(CaF_2) = 0.05$ (calculated with the FTHall database).

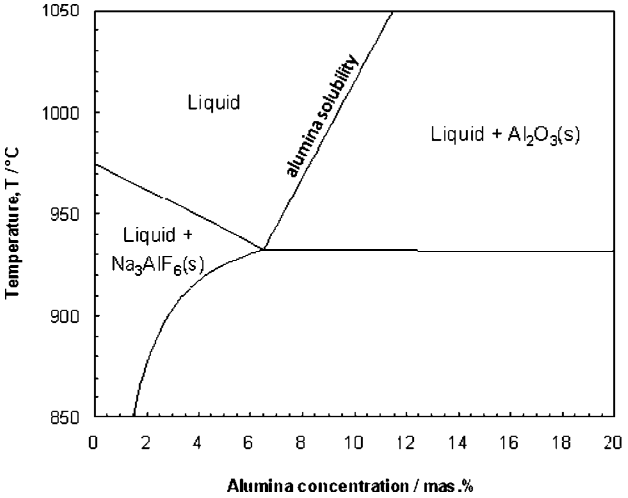

Figure 2. Part of the cryolite−alumina system for CR = 2.2, $w(CaF_2) = 0.05$ (calculated with the FTHall database).

CaF_2, KF, and LiF reduce the liquidus temperature of cryolite melts. The order of influence (on the mass scale) is $AlF_3 < CaF_2 < KF < LiF$, LiF leading to the strongest decrease of liquidus temperature. As it will be discussed later, the presence of these compounds also has a drawback since they diminish the solubility of alumina.

Vapor Pressure. The total vapor pressure of the $NaF-AlF_3-Al_2O_3$ mixtures is in the range of (5 to 10) mbar. The gaseous phase is essentially composed of the $NaAlF_4$ compound.[1] For a mixture with a CR equal to 3, an increase of the alumina concentration is linked to a slight decrease of the total vapor pressure. This trend is verified in the CR range 1.8 to 3.0.[7]

As shown in Figure 3, additives like CaF_2 and KF have only a slight influence on the vapor pressure. On the other hand, at constant temperature, an excess of AlF_3 noticeably increases the vapor pressure due to an enhanced formation of $NaAlF_{4(g)}$. Even if, on first thought, it seems that the most acidic compounds (like MgF_2 and AlF_3) implicate an increase of the vapor pressure due to AlF_4^- stabilization (which enhances the formation of $NaAlF_{4(g)}$) on detriment of AlF_5^{2-}, Gilbert[8] indicates that this way of thinking is not always true, due to the formation of mixed AlF_x-MF_x compounds.

Electrical Conductivity. The electrical conductivity of industrial baths is about 2.1 $S\cdot cm^{-1}$. This conductivity is

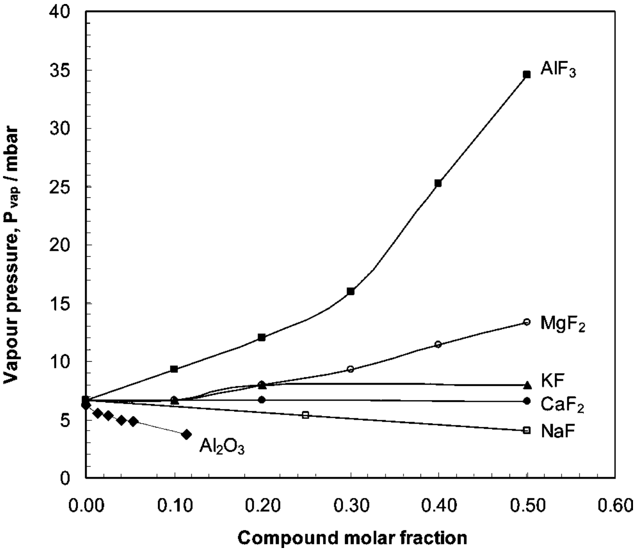

Figure 3. Total vapor pressure above Na_3AlF_6−M mixtures at 1027 °C (plotted from refs 1 and 7).

essentially driven by Na^+ cations, which are the most mobile due to their small size compared to larger ionic entities composing the salt.[1] The evolution of the electrical conductivity slightly depends on the alumina concentration:[9,10] a decrease is observed with increasing alumina content (about (−0.04 to −0.06) $S\cdot cm^{-1}$ per mass percent of Al_2O_3). This is likely due to the formation of large $Al_2OF_6^{2-}$ and $Al_2OF_8^{4-}$ anions which decrease the ions' mobility in the electrolyte.

In a similar way, the increase of AlF_3 content, which enhances the formation of AlF_4^- and AlF_6^{2-} entities, has a deleterious effect on electrical conductivity, as well as most of the additives (KF, CaF_2, MgF_2). Conversely, LiF and NaCl, which dissociate into small Li^+ and Na^+ cations, improve the conductivity of cryolite mixtures.[11]

Aluminum Solubility. Aluminum solubility in industrial melts is about $w(Al) = 0.0005$. Even though measurements are quite scattered, it is admitted that the aluminum solubility decreases with higher AlF_3 contents. This is why, as explained by Holmes[12] in a historical review of the Alcoa potlines evolution, the excess amount of AlF_3 has been increased throughout the optimization of the faradic efficiency of the process. It has also been shown that a temperature decrease reduces the aluminum solubility, which goes in favor of a decrease of the operating temperature of the cells.

Density. The usual density of the industrial baths is about 2.1 $g\cdot cm^{-3}$ at 960 °C,[1] while aluminum density at the same temperature[13] is 2.3 $g\cdot cm^{-3}$.

Common additives do not have a great influence on the density of cryolite melts compared to the density of liquid aluminum: in any case, in the (950 to 1050) °C temperature range, the salt density is comprised between (1.9 and 2.1) $g\cdot cm^{-3}$, while aluminum's is always above 2.3 $g\cdot cm^{-3}$. A few examples are plotted in Figure 4.

Modified Na−cryolite Systems ($T_{liquidus}$ < 950 °C). To decrease the melting temperature of the cryolite-based mixture below 950 °C, two options (which can be coupled) are possible: either increase the AlF_3 excess or increase the additive concentration. An outlook of the knowledge concerning the physicochemical properties of these modified cryolite mixtures is provided in this section.

Accessible Temperature Range. The phase diagram of the NaF−AlF_3 system indicates a eutectic composition at an AlF_3 molar ratio of 0.46 (corresponding to a CR of 1.7) at a temperature of 698 °C.[1] It is then possible, by an increase of the AlF_3 content, to reach a liquidus temperature of about 700 °C.

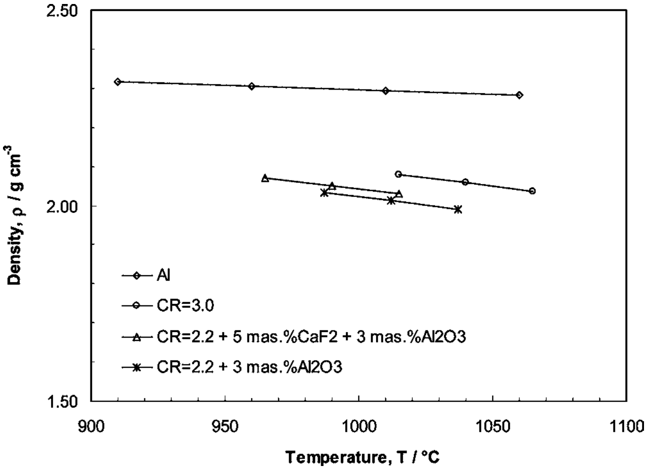

Figure 4. Influence of temperature and composition on the density of cryolite melts.[1,13,14]

The addition of additives like KF, LiF, CaF_2, or MgF_2 also allows decreasing the liquidus temperature. The review of the various analytical formulas presented in ref 1 indicates that the best fit available to estimate the liquidus temperature of such mixtures is the one proposed by Solheim et al.[4]

$$\begin{aligned} t = {} & 1011 + 0.50[AlF_3] - 0.13[AlF_3]^{2.2} - 3.45[CaF_2]/ \\ & (1 + 0.0173[CaF_2]) + 0.124[CaF_2][AlF_3] - \\ & 0.00542([CaF_2][AlF_3])^{1.5} - 7.93[Al_2O_3]/ \\ & (1 + 0.0936[Al_2O_3] - 0.0017[Al_2O_3]^2 - \\ & 0.0023[AlF_3][Al_2O_3]) - 8.90[LiF]/(1 + 0.0047[LiF] + \\ & 0.0010[AlF_3]^2) - 3.95[MgF_2] - 3.95[KF] \end{aligned}$$

where t is the liquidus temperature in °C, and all concentrations [] are related to 100 w. The formula is valid for $[AlF_3]$, $[CaF_2]$, $[LiF] < 20$ and $[MgF_2]$, $[KF] < 5$.

The liquidus temperature of various mixtures is plotted in Figure 5, according to the AlF_3 excess (w up to 0.2) for Na_3AlF_6-based salts containing $w = 0.03$ of alumina and either $w = 0.05$ or 0.15 of additives. At a concentration of AlF_3 equivalent to the industrial one ($w = 0.12$), the chart shows that the liquidus temperature can be decreased down to 900 °C, depending on the nature of the additive and its concentration.

As illustrated by the above equation and Figure 5, the mixture combinations allowing a given liquidus temperature to be reached are infinite. However, the properties of the melt (and specifically the alumina solubility and the electrical conductivity) clearly depend on the chemical nature of the additives: the addition of basic compounds like LiF and KF does not have the same influence as CaF_2 or AlF_3, which have an acid behavior.

Alumina Solubility. The solubility of alumina in the Na_3AlF_6−AlF_3−CaF_2−MgF_2−LiF system has been notably studied by Skybakmoen et al.[3] in the (850 to 1050) °C temperature range. The analytical formula proposed in their work indicates the alumina solubility according to the melt composition

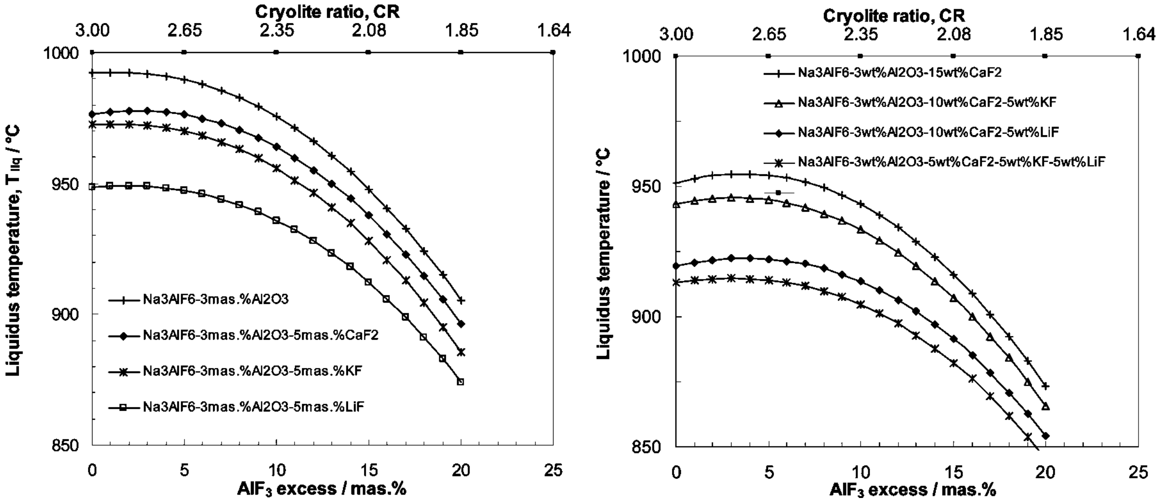

Figure 5. Liquidus temperature versus AlF_3 excess (up to CR = 1.85) for mixtures containing $w = 0.05$ (left) and $w = 0.15$ (right) of additives ($CaF_2-KF-LiF$) and $w = 0.03$ of alumina (calculated from ref 4).

$$[Al_2O_3]_{sat} = A(t/1000)^B$$

with

$$A = 11.9 - 0.062[AlF_3] - 0.0031[AlF_3]^2 - 0.50[LiF] - 0.20[CaF_2] - 0.30[MgF_2] + (42[LiF][AlF_3])/(2000 + [LiF][AlF_3])$$

$$B = 4.8 - 0.048[AlF_3] + 2.2[LiF]^{1.5}/(10 + [LiF] + 0.001[AlF_3]^3)$$

where t is the temperature in °C and all concentrations [] are related to 100 w.

This equation highlights the coupling between the AlF_3 content and the temperature decrease on the alumina solubility in the $NaF-AlF_3$ system. Indeed, as illustrated in Figure 6, the solubility of alumina sharply decreases at constant overheating, while the CR decreases: from more than $w = 0.10$ in pure cryolite (CR = 3), the solubility drops to about $w = 0.04$ in a mixture of CR = 1.6 at 850 °C. It is however noticeable, when extending the CR = 3 curve at lower temperature, that the solubility decrease is mostly due to the temperature effect rather than to the AlF_3 content.

For more acid mixtures exhibiting a liquidus temperature below 850 °C, the published formulas (both for the liquidus[4] and for the alumina solubility[3]) are not applicable according to their authors. However, since the FTHall database is claimed to be valid down to CR = 1.5, some liquidus lines were calculated using the FactSage software in the CR range 2.2 to 1.5, according to the alumina concentration. These calculations, presented in Figure 7, are in excellent agreement with the data of Skybakmoen[3] down to CR = 1.8 and slightly differ for more acid mixtures and temperatures below 850 °C.

The use of the FTHall database (Figure 7) confirms that the alumina solubility continues to decrease with decreasing CR and temperature. For a cryolite mixture of CR = 1.5, this solubility does not exceed $w = 0.025$. Below 750 °C (CR = 1.3), the solubility is expected to be lower than $w = 0.02$.

The addition of LiF, CaF_2, and MgF_2 also leads to an alumina solubility decrease. Indeed, the A term of the equation proposed by Skybakmoen et al., which is directly proportional to the alumina solubility, linearly decreases (at constant temperature) with the increase of CaF_2 and MgF_2. Some selected examples are presented in Figure 8, in which the alumina solubility is plotted versus the additive concentration at various CR and temperatures.

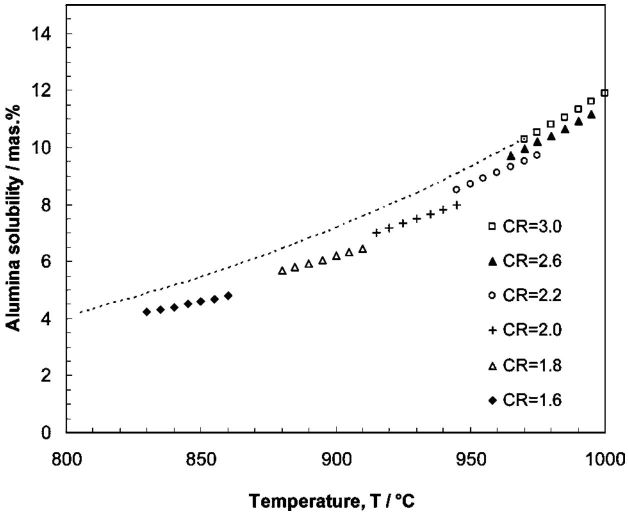

Figure 6. Solubility of alumina versus temperature at constant overheating in the system $Na_3AlF_6-AlF_3$, for various CR. Temperature range is comprised between the liquidus temperature T_{liq} and $T_{liq} + 50$ °C (calculated from ref 3).

As taken into account in the cross terms of the Skybakmoen equation, a specific interaction between LiF and AlF_3 is driving the alumina solubility. The chemical reason for the interaction still has to be explained, but the practical consequence is that, converse to MgF_2 or CaF_2, the LiF influence on the alumina solubility is related to the AlF_3 content of the melt. For a given mass, the LiF influence is much more detrimental to the alumina solubility than AlF_3.

Another way of understanding the influence of additives on the alumina solubility consists of fixing a target liquidus temperature, choosing a set of mixture compositions corresponding to this liquidus temperature, and calculating the alumina solubility. The solubility of alumina for various mixtures having a liquidus temperature of 850 °C is presented in Table 1. The data show that the best way of decreasing the temperature, as long as the highest alumina solubility is the only criterion, is to stay in the $Na_3AlF_6-AlF_3$ system since a melt with CR = 1.68 exhibits an alumina solubility of $w = 0.048$, while all other combinations have a lower solubility. A high LiF content leads to the lowest alumina solubility (below $w = 0.02$ for a LiF content of $w = 0.15$).

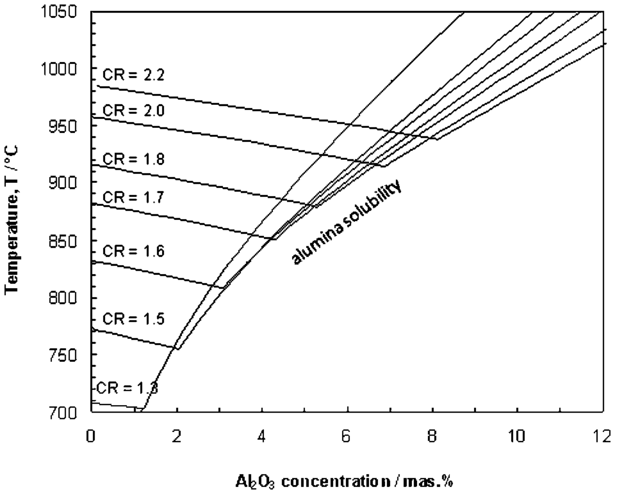

Figure 7. Solubility of alumina in the NaF−AlF$_3$−Al$_2$O$_3$ system, in the range CR = 1.3 to 2.2 (calculated with the FTHall database).

Electrical Conductivity. Several studies propose analytical formulas for the calculation of the electrical conductivity of cryolite melts in the (850 to 1020) °C temperature range. The fits from Chrenkova et al.[14] and Hives et al.[10] are among the most recent and take into account older data. One of the equations proposed by Hives[10] is

$$\ln \sigma = 1.977 - 0.0200[\mathrm{Al_2O_3}] - 0.0131[\mathrm{AlF_3}] - 0.0060[\mathrm{CaF_2}] - 0.0106[\mathrm{MgF_2}] - 0.0019[\mathrm{KF}] + 0.0121[\mathrm{LiF}] - 1204.3/T$$

where σ is in S·cm^{-1}; T is in K; and all concentrations [] are related to 100 w.

Figure 9 indicates the electrical conductivity according to the CR at constant overheating. This figure includes additional data from Hives et al.[15] concerning a mixture of CR = 1.22. It is shown that the electrical conductivity decreases due to the common decrease of the CR and the temperature: from 2.8 S·cm^{-1} in pure cryolite, the conductivity decreases to 2.0 S·cm^{-1} for a mixture with a CR of 1.8 at 900 °C and to 1.2 S·cm^{-1} for a mixture of CR = 1.22 at 715 °C.

The formula proposed by Hives shows that with the exception of LiF all additives have a detrimental effect on the electrical conductivity of cryolite melts. To illustrate the influence of each of them, the electrical conductivity of some mixtures is evaluated in Table 1: at 850 °C and without LiF, the conductivity of the mixtures is about (1.6 to 1.7) S·cm^{-1}, which represents about 75 % of the conductivity of the industrial mixtures. However, the addition of LiF allows this conductivity decrease to be fully balanced.

Density. An analytical formula proposed by Chrenkova[14] provides the density of cryolite mixtures in the (850 to 1050) °C temperature range, for an AlF$_3$ excess between $w = 0$ and 0.30 (CR = 3.0 to 1.45)

$$\rho = 2.938 - 8.466\cdot10^{-4}t - 3.373\cdot10^{-4}[\mathrm{AlF_3}]^2 - 3.201\cdot10^{-3}[\mathrm{LiF}] - 4.762\cdot10^{-3}[\mathrm{Al_2O_3}] + 2.781\cdot10^{-4}[\mathrm{AlF_3}][\mathrm{LiF}]$$

where ρ is in g·cm^{-3}; t in °C; and all concentrations [] are related to 100 w.

This formula has been applied to calculate the density of the mixtures at constant overheating (up to 50 °C), as illustrated in Figure 10. It shows that the decrease of the CR induces a decrease of the density of the mixtures and, as a consequence, an increase of the difference of density with liquid aluminum. This trend is confirmed by the measurements of Silny et al.[16] for a mixture of CR = 1.22 at lower temperatures [(700 to 850) °C].

This trend is in contradiction with earlier results published by Utigard et al.,[17] which indicate that the melt density at constant overheating exhibits a minimum at CR = 2.1. However, as mentioned in ref 1, these measurements are in disagreement with all other published data.

Vapor Pressure. At constant temperature, the increase of the AlF$_3$ content leads to a noticeable increase of the total vapor pressure of the cryolite melts. However, this phenomenon is essentially due to the fact that when the AlF$_3$ concentration increases the liquidus temperature of the mixture sharply decreases: the isothermal representation of the vapor pressure is then not really adapted to evaluate the evolution of the volatility of the cryolite mixtures.

An analytical formula derived by Haupin[18] is

$$\log P = B - A/T$$

$$A = 7101.6 + 3069.7R - 635.77R^2 + 51.22[\mathrm{LiF}] - 24.638R[\mathrm{LiF}] + 13.2[\mathrm{CaF_2}]$$

$$B = 7.0184 + 0.6844R - 0.08464R^3 + 0.010805[\mathrm{LiF}] - 0.005489R[\mathrm{LiF}] + 0.047124[\mathrm{Al_2O_3}]/(1 + 0.1893[\mathrm{Al_2O_3}]) + 0.0068[\mathrm{CaF_2}]$$

where P is the vapor pressure in kPa; T is in K; R is the bath ratio (R = CR/2); and all concentrations [] are related to 100 w.

Indeed, as illustrated in Figure 11, the vapor pressure at constant overheating is almost not sensitive to the influence of CR, with a maximal volatility at around CR = 2.4. AlF$_3$-rich mixtures are finally not more volatile than industrial melts.

This behavior was confirmed by Qiu et al.,[19] which showed that for a constant overheating of 10 °C the mass loss of acid mixtures (CR = 2.35 to 1.6) decreases with the AlF$_3$ content. The addition of Al$_2$O$_3$ and LiF also tends to decrease the volatility of the salt.

Solubility of Aluminum. The data concerning the solubility of liquid aluminum in the molten salt are quite scarce at low temperatures. The data which were compiled in ref 1 only show the effect of the CR at constant temperature and not at constant overheating. Nevertheless, Qiu et al.[20] have shown that, on top of the CR effect, the temperature decrease leads to a decrease of the aluminum solubility. In a mixture of CR = 1.5 at 820 °C, this solubility is reported to be seven times lower than industrial melts at 975 °C.

Conclusions. The use of additives (LiF, CaF$_2$, KF) as well as an increase of the AlF$_3$ excess allows decreasing the liquidus temperature of the cryolite melts down to about 700 °C. The evolution of the main physicochemical properties of these mixtures, which have been widely studied, is due to two main parameters, namely, the chemical composition and the operating temperature.

The temperature decrease has some beneficial effects (decrease of the aluminum solubility in the salt, decrease of the vapor pressure, increase of the density of the aluminum−molten salt difference) as well as negative ones (decrease of the alumina solubility and of the electrical conductivity).

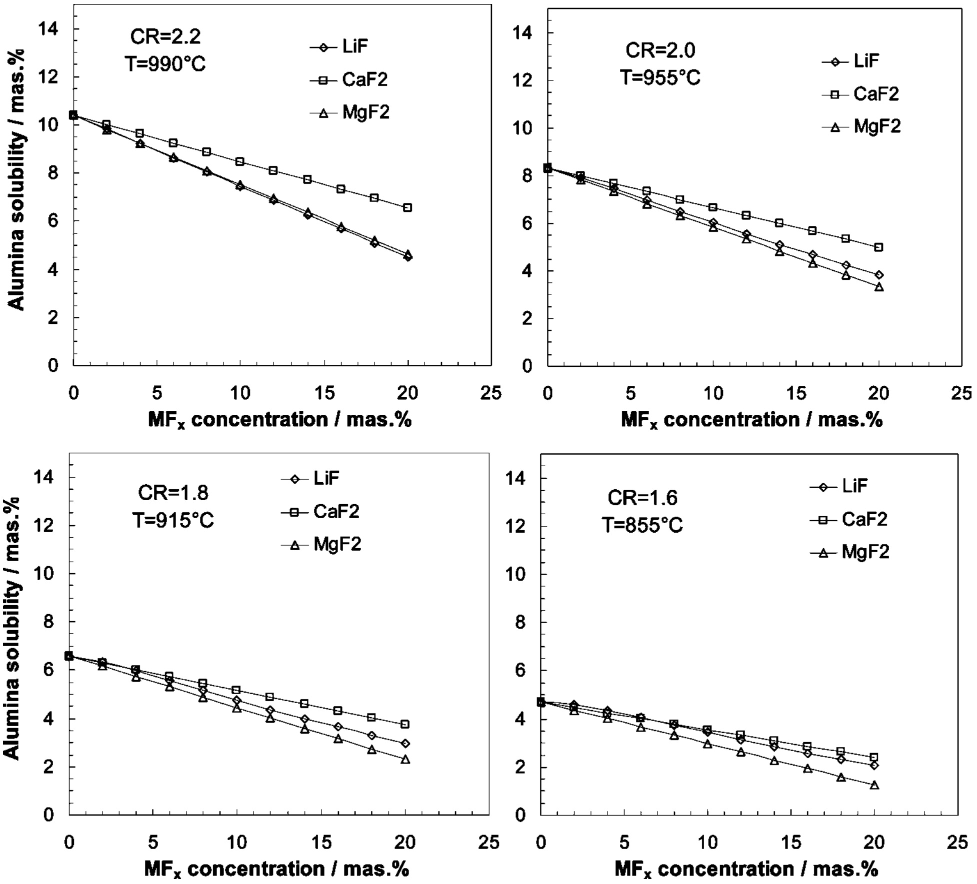

Figure 8. Alumina solubility in mixtures of various CR versus the LiF, CaF_2, and MgF_2 content, at the liquidus temperature of the $Na_3AlF_6-xAlF_3$ system (calculated from ref 3).

Table 1. Alumina Solubility (Mass Percent, 100 *w*) and Electrical Conductivity of Various Mixtures Having a Liquidus Temperature of 850 °C, in the $Na_3AlF_6-AlF_3-CaF_2-MgF_2-LiF$ System

compd	composition/100 *w*							
LiF				5	5	10	5	15
CaF_2		5			5		10	
MgF_2			5		5		5	
AlF_3	24	23.5	22.7	21.7	19.6	19.4	18.6	15.5
CR	1.68	1.70	1.73	1.77	1.86	1.87	1.91	2.06
Al_2O_3 solubility/ 100 *w*	**4.8**	**2.3**	**4.05**	**4.1**	**2.9**	**2.9**	**2.4**	**1.8**
electrical conductivity/ $S \cdot cm^{-1}$	**1.64**	**1.68**	**1.61**	**1.82**	**1.76**	**2.04**	**1.75**	**2.33**

The chemical composition of the melts, at an equivalent liquidus temperature, mostly influences the electrical conductivity and the alumina solubility. LiF addition is almost an obligation in view of maintaining the electrical conductivity at a value equivalent to the industrial melts conductivity, mixtures like $Na_3AlF_6-Li_3AlF_6-AlF_3$ having for instance an electrical conductivity of about 2.0 $S \cdot cm^{-1}$ at 850 °C.[21] Regarding the alumina solubility, it seems almost impossible to keep it high in such systems, the temperature effect dominating the chemical effect. The increase of the AlF_3 excess, preferably to the use of additives, seems the best solution to enhance alumina solubility.

An illustration of the LiF influence on the liquidus temperature, the alumina solubility, and the electrical conductivity of two mixtures is proposed in Figure 12. It finally seems unlikely to find a composition in the Na−cryolite system that allows an operating temperature below 900 °C without reducing the alumina solubility below $w = 0.05$, all other parameters (electrical conductivity, density, vapor pressure) being constant or improved.

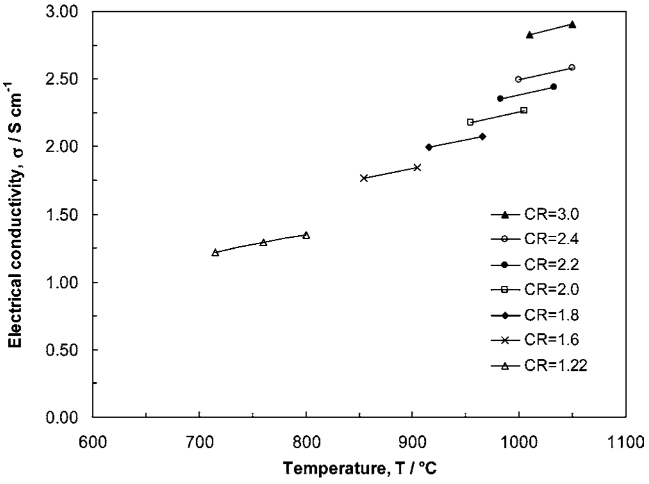

Figure 9. Electrical conductivity in the $NaF-AlF_3$ system at various CR, in the temperature range $T_{liq} - T_{liq} + 50$ °C (calculated from refs 10 and 15).

K−Cryolite Systems

The $KF-AlF_3$-based salts have been widely studied recently. These mixtures are attractive since the system has a eutectic point at 560 °C and an improved alumina solubility compared to $NaF-AlF_3$ melts. The available data (liquidus temperatures, alumina solubility, vapor pressure, and electrical conductivity) are presented in this section.

$KF-AlF_3-Al_2O_3$ System. Liquidus Temperature. As indicated in Figure 13, the phase diagram of the system $KF-AlF_3$ is comparable to the $NaF-AlF_3$ system. Similar to the Na−cryolite system, the cryolite ratio (CR) is defined here as

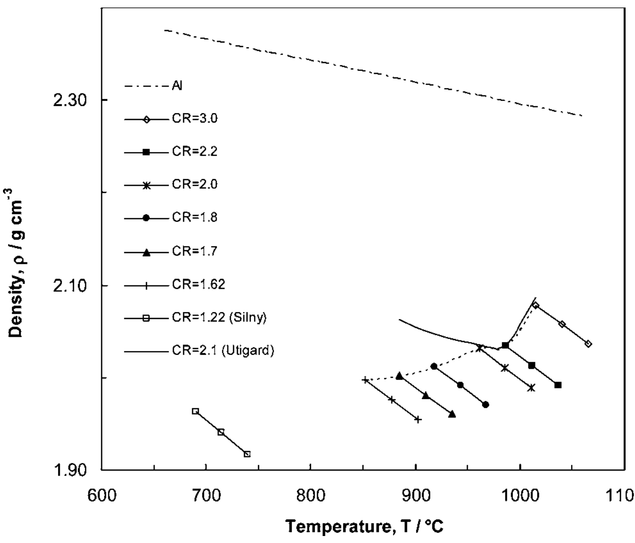

Figure 10. Aluminum density compared to cryolite mixture density in the temperature range $T_{liq} - T_{liq} + 50$ °C (from Chrenkova,[14] Silny,[16] and Utigard[17]).

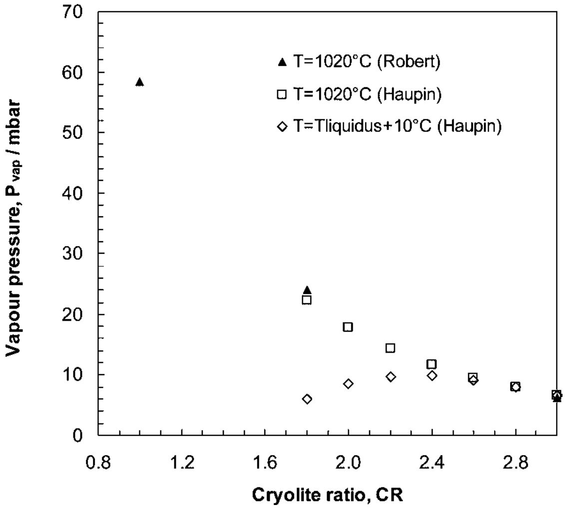

Figure 11. Evolution of the total vapor pressure above $NaF-AlF_3$ mixtures versus the CR isotherms at 1020 °C and constant overheating (from Haupin[18] and Robert[7]).

the KF/AlF_3 molar ratio. For a CR of about 1.20, the liquidus temperature is decreased by about 140 °C ($T_{liq} = 560$ °C at CR = 1.22) compared to the $NaF-AlF_3$ system. AlF_3-rich compositions are required (CR < 1.50) to decrease the liquidus temperature below 800 °C.

Several recent studies[22−26] have been devoted to the establishment of the liquidus line in function of the CR and the alumina concentration. The main results, summarized in Figure 14, show that in the 1.2 to 3.0 CR range the increase of the alumina concentration slightly decreases the melting point of the $KF-AlF_3$ mixtures, similar to the Na−cryolite system.

Alumina Solubility. Alumina is highly soluble in $KF-AlF_3$ mixtures: at 1000 °C, the solubility exceeds $w = 0.20$ for CR = 3.0. In any case, as illustrated in Figure 15, alumina is more soluble in K−cryolite mixtures than in Na−cryolite ones, for equivalent CR and temperature.

As shown in Figure 16, from data established by Robert et al.[7] and Yang et al.,[27] alumina solubility decreases with CR and temperature. It is noteworthy that alumina solubility is higher than $w = 0.05$ at 750 °C for CR above 1.3. Such a solubility is not reached in Na−cryolite melts at temperature below 850 °C (see Table 1).

Vapor Pressure. Similar to Na−cryolite mixtures, when the AlF_3 content increases in the $KF-AlF_3$ system, the vapor pressure at constant temperature greatly increases due to the increase of the $KAlF_4$(g) activity.[28]

At constant overheating, the only available data seem to be those from Robert et al.[7] They do not allow the vapor pressure at very low CR to be evaluated but indicate that the presence of alumina slightly decreases the vapor pressure. As illustrated in Figure 17, the K−cryolite mixtures are slightly more volatile than the Na−cryolite ones: for instance, at CR = 2.0, the vapor pressure of the $KF-AlF_3$ system is 14.2 mbar, while it is 8.5 mbar for $NaF-AlF_3$.

Electrical Conductivity. Conductivity measurements in the $KF-AlF_3$ system have been performed only for very low CR (i.e., CR = 1.22[15] and CR = 1.30[24]). At an equivalent temperature, as indicated in Figure 18, the electrical conductivity of K−cryolite melts is smaller than Na−cryolite melts. For instance, at 750 °C and for a comparable CR of 1.22, the electrical conductivity of the K−cryolite melt is 1.04 $S \cdot cm^{-1}$, while it is 1.27 $S \cdot cm^{-1}$ in the Na−cryolite mixture. These data show the influence of the substitution of Na^+ by K^+ ions: the ionic radius of the latter is indeed slightly bigger, and thus K^+ ions are less mobile.

The effect of alumina additions, illustrated in Figure 19, is similar to the $NaF-AlF_3$ system: the electrical conductivity decreases with alumina additions.

Density. The density of $KF-AlF_3$ melts has not been evaluated very much. Nevertheless, Silny et al.[16] have published data obtained at 750 °C for CR = 1.22: the density is 1.77 $g \cdot cm^{-3}$, while it is 1.92 $g \cdot cm^{-3}$ in the same conditions for Na−cryolite. K−cryolite mixtures are then slightly less dense than Na−cryolite mixtures.

Influence of Additives. The influence of three main additives is evaluated in this section: LiF, which was shown to improve the electrical conductivity of Na−cryolite mixtures; CaF_2, which is an inevitable additive since CaO is contained in the alumina feed; NaF, in the case of mixed $Na_3AlF_6-K_3AlF_6$ systems. For these systems, the available data are mainly restricted to the alumina solubility and the electrical conductivity.

Influence of LiF. The work from Kryukovsky, Apisarov, and Dedyukhin[24,30,31] shows that, similar to the Na−cryolite system, the electrical conductivity of K−cryolite mixtures increases with increasing LiF content. The case of CR = 1.3 is illustrated in Figure 20. Nevertheless, the conductivity of LiF-containing systems remains quite low (below 1.3 $S \cdot cm^{-1}$ for CR = 1.3). The measurements performed by Kryukovsky et al.[24] also show that the addition of $w = 0.05$ of LiF allows compensation for the decrease of conductivity induced by $w = 0.035$ of alumina.

It is also reported that LiF additions decrease the alumina solubility of K−cryolite mixtures, but very few data are available. Yang et al.[27] indicate that a concentration of $w = 0.015$ of LiF decreases the alumina solubility by about $w = 0.001$ at 700 °C.

Since LiF additions allow partial compensation of the decrease of electrical conductivity due to the temperature decrease, additional experimental data on the alumina solubility in the system $KF-AlF_3-LiF$ would be valuable.

Influence of CaF_2. Dedyukhin et al.[32] reported that the CaF_2 solubility in a K−cryolite mixture of CR = 1.3 at 700 °C is almost negligible. It reaches $w = 0.023$ in a system containing $w = 0.05$ of LiF and $w = 0.031$ for a LiF content of $w = 0.10$. Their measurements regarding electrical conductivity indicate a noteworthy phenomenon: at constant temperature, CaF_2

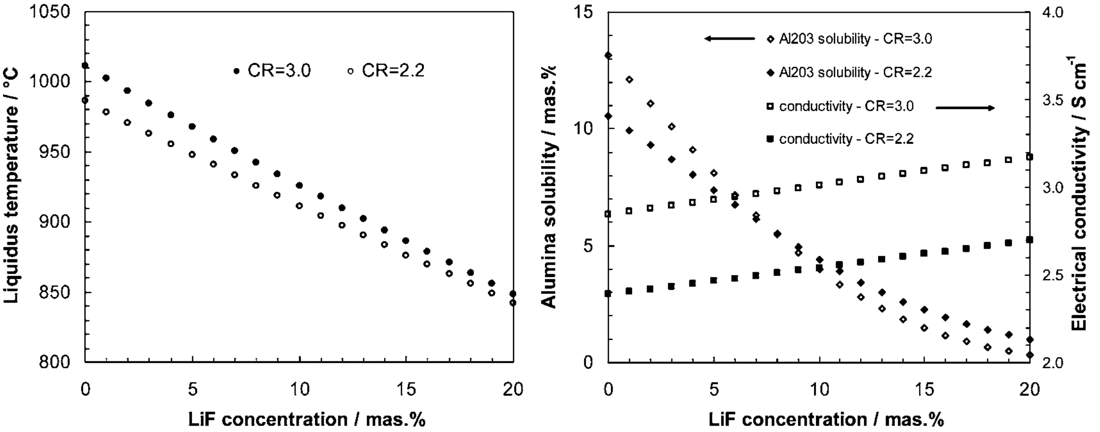

Figure 12. Evolution of the liquidus temperature, the alumina solubility, and the electrical conductivity in the $NaF-AlF_3-LiF-Al_2O_3$ system versus the LiF content, at constant overheating (+10 °C).

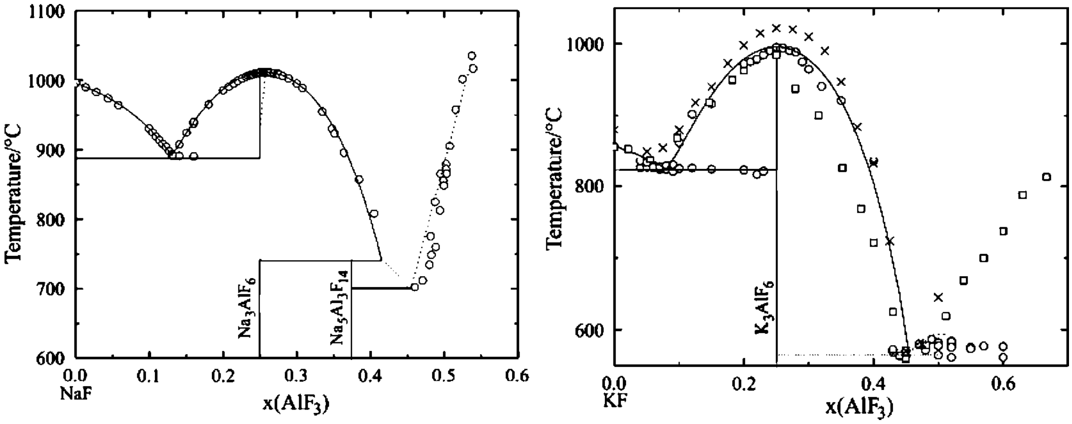

Figure 13. Comparison of the $KF-AlF_3$ and $NaF-AlF_3$ phase diagrams.[22]

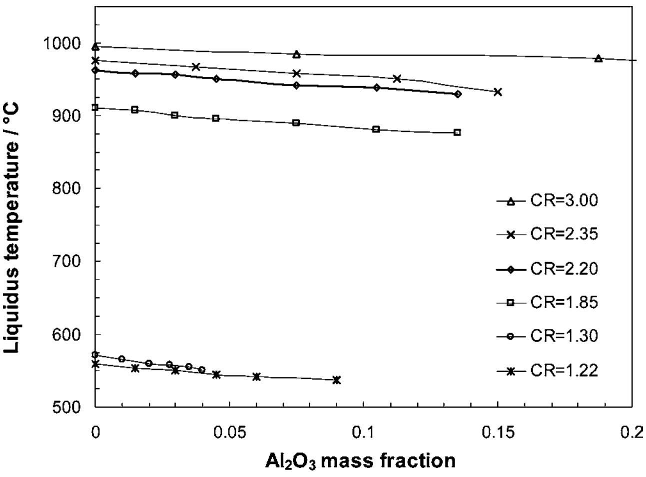

Figure 14. Liquidus temperatures in the $KF-AlF_3-Al_2O_3$ system versus the CR and the alumina concentration (plotted from refs 23, 24, and 26).

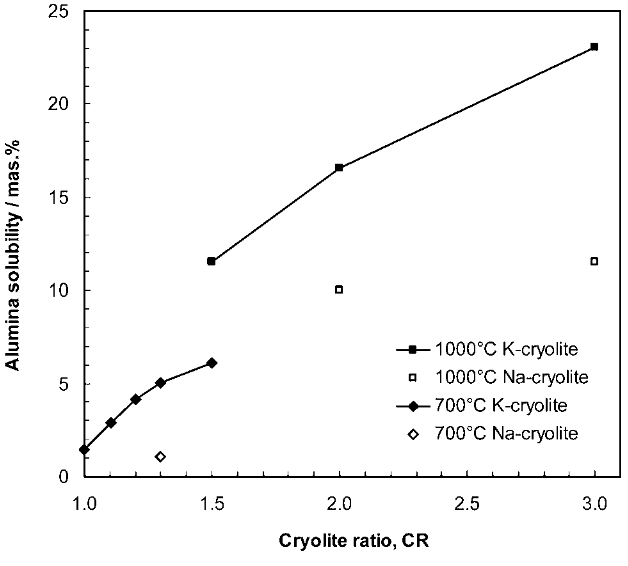

Figure 15. Alumina solubility in K−cryolite mixtures versus CR at 700 °C (Yang[27]) and 1000 °C (Robert[7]). Comparison to alumina solubility in Na−cryolite mixtures.

enhances slightly the electrical conductivity. Nevertheless, this effect is quite small (amplitude of about 0.1 $S \cdot cm^{-1}$).

The presence of CaF_2 in K−cryolite mixtures also decreases the alumina solubility: at 700 °C, Yang et al.[27] have measured that the alumina solubility is around $w = 0.038$ in a mixture of $CR = 1.22$ containing $w = 0.044$ of CaF_2, while this solubility is $w = 0.048$ in the same melt without CaF_2.

$KF-AlF_3-NaF$-Based Systems. The expected benefit of using $NaF-KF-AlF_3$ mixtures is the combination of the good electrical conductivity of Na−cryolite with the enhanced alumina solubility in K−cryolite melts. The liquidus lines of the ternary system are reported in some recent studies,[27,28] and the system was integrated in a thermodynamic model by Heyrman and Chartrand.[33] As illustrated in Figure 21 from the latest measurements from Apisarov et al.[34] and older data from Grjotheim et al.,[35] the whole range of liquidus temperature between (650 and 1000) °C is attainable in the system $NaF-KF-AlF_3$ (CR is defined here as the molar ratio $(NaF + KF)/AlF_3$). Up to now, there are quite few data concerning the

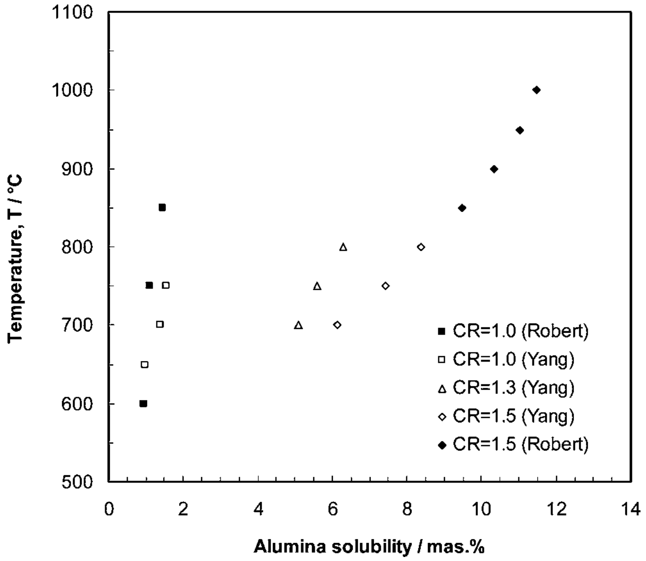

Figure 16. Evolution of alumina solubility versus temperature and CR in $KF-AlF_3$ mixtures (data from Robert[7] and Yang[27]).

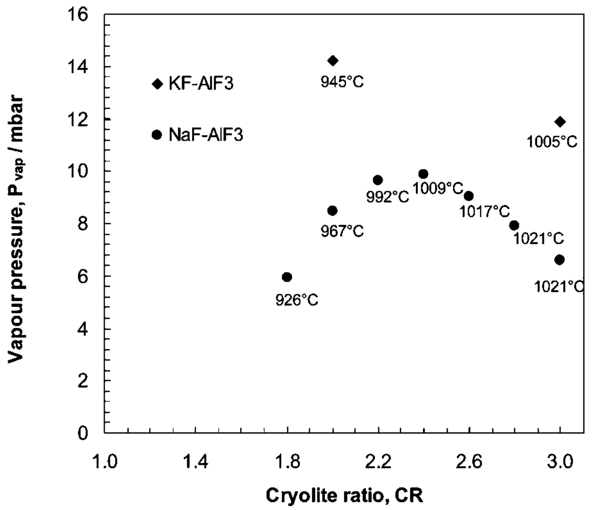

Figure 17. Comparison of the vapor pressures of $NaF-AlF_3$ and $KF-AlF_3$ mixtures versus CR, at constant overheating, T_{liq} + 10 °C (from refs 7 and 18).

properties of such ternary mixtures, but as indicated by the available measurements of alumina solubility and electrical conductivity, the properties of the melts are intermediate between those of Na−cryolite and K−cryolite.

Indeed, some alumina solubility measurements have been published by Yang et al.[27] in $KF-AlF_3$ systems with small NaF content. As indicated in Table 2, NaF additions decrease the alumina solubility, similar to LiF and CaF_2.

As for the electrical conductivity, data published by Huang et al.[36] indicate that $NaF-KF-AlF_3$ mixtures with a NaF/(NaF + KF) molar ratio equal to 0.65 exhibit an intermediate conductivity between K and Na−cryolite systems in a (1.4 to 3.0) CR range. This trend, illustrated in Figure 22, was confirmed by Dedyukhin et al.,[31] who measured the electrical conductivity of $KF-AlF_3-NaF$ systems at constant CR = 1.3 in the whole NaF/(NaF + KF) composition range. It is noteworthy that this work also provides conductivity data for the complex system $KF-AlF_3-NaF-LiF-Al_2O_3$.

Conclusions. The most obvious advantages of the K−cryolite systems are that they allow low-melting temperatures to be reached and exhibit, at an equivalent temperature, a much higher alumina solubility than Na−cryolite systems. However, on top of a slight increase of their vapor pressure, the major drawback is that the electrical conductivity of K−cryolite systems is noticeably lowered: a conductivity of about 1.0 $S\cdot cm^{-1}$ is reported at 700 °C, which has an expected consequence of a doubling of the ohmic drop in the salt compared to industrial mixtures (2.2 $S\cdot cm^{-1}$ at 960 °C).

The majority of the studies on the properties of K−cryolite mixtures has been performed at very low CR, in view of operating temperatures of about 700 °C. However, it would be interesting to characterize some melts having a liquidus temperature of about 800 °C since they should have a high alumina solubility (w = (0.07 to 0.08) % by mass) and an intermediate electrical conductivity that could be improved by LiF additions.

More data on the $NaF-KF-AlF_3-Al_2O_3$ system would also allow a better evaluation of the systems involving KF as a major component. However, with increasing number of components in the cryolite systems (for which LiF and CaF_2 are also of interest), experimental investigation becomes almost endless. An interesting approach based on an empirical evaluation involving the molar volume of the bath components is being carried out by Redkin and co-workers.[32,37,38] This modeling may

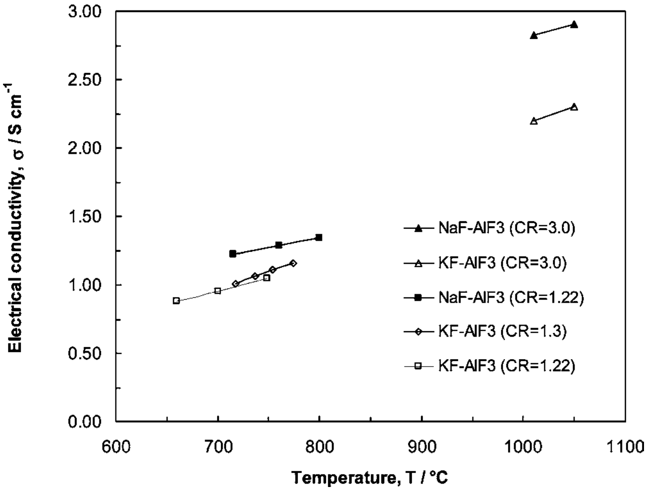

Figure 18. Comparison of the electrical conductivity of Na and K cryolite melts versus temperature at CR = 3.0 and CR = 1.22 (data from refs 15, 24, 26, and 29).

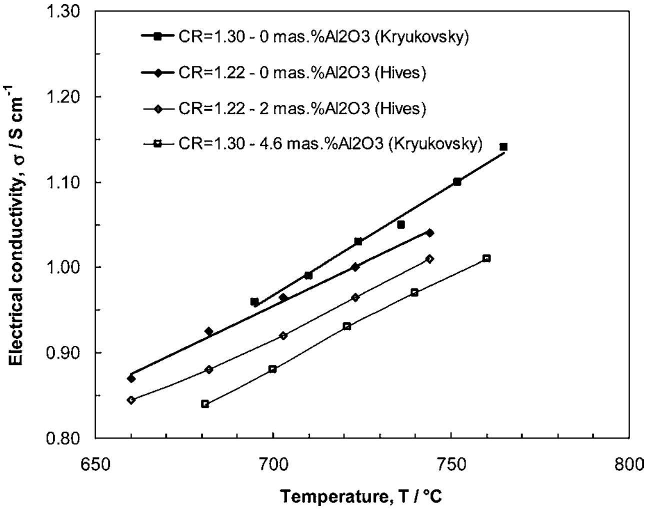

Figure 19. Electrical conductivity of $KF-AlF_3$ mixture versus temperature at low CR: influence of the alumina content (from Hives[15] and Kryukovsky[24]).

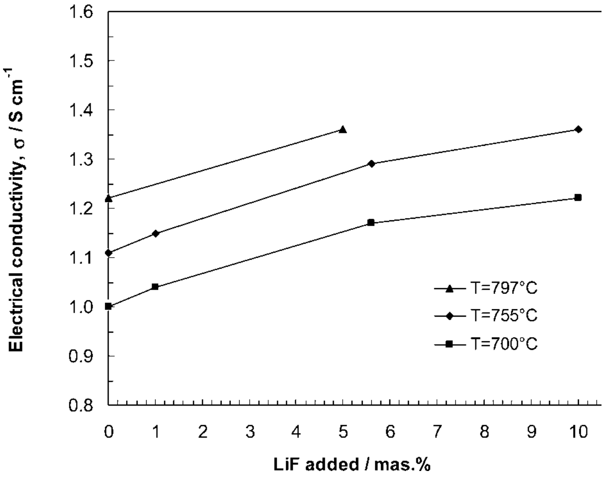

Figure 20. Influence of the LiF content on the electrical conductivity of K−cryolite melts (CR = 1.3).[24,30]

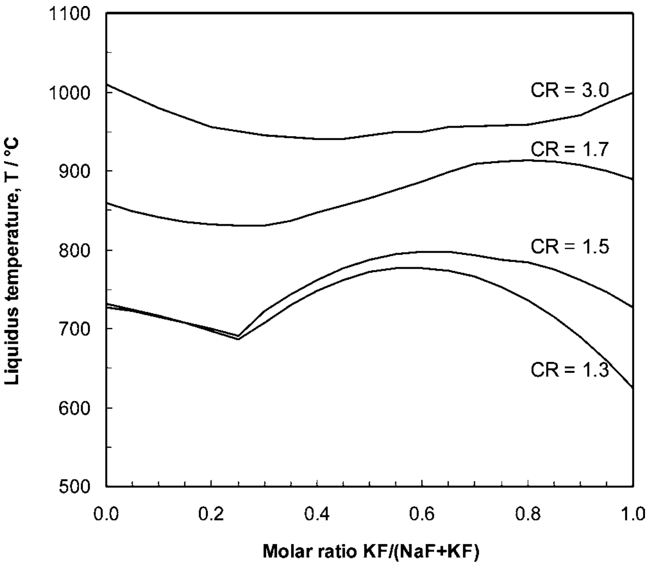

Figure 21. Liquidus temperature in the NaF−KF−AlF_3 system with different CR (from Apisarov[34] and Grjotheim[35]).

Table 2. Alumina Solubility (Mass Percent, 100 *w*) in Mixed Na−K−cryolite Melts at 700 °C[27]

composition (molar)	alumina solubility (100 *w*)
KF−AlF_3−NaF/CR	
48.0−48.0−4.0/CR = 1.08	2.51
50.0−46.0−4.0/CR = 1.17	3.57
52.5−43.5−4.0/CR = 1.30	4.49
44.0−48.0−8.0/CR = 1.08	2.46
56.5−43.5−0.0/CR = 1.41	5.04
KF−AlF_3−NaF−CaF_2	
50.0−42.0−4.0−4.0	4.30

help time to be spared in view of the evaluation of the electrical conductivity and alumina solubility of such complex cryolite mixtures.

Chloro−Fluoride Systems

Due to the very low solubility of alumina in pure chloride salts, the production of aluminum in such electrolytes requires the use of $AlCl_3$ instead of Al_2O_3 as a feeding compound. A process operating with NaCl−KCl−$AlCl_3$ salts was developed by Alcoa in the seventies, of which the main features were summarized by Layne and Huml.[39] Its advantages are the absence of carbon consumption (Cl_2 is formed on an inert carbon anode) and the high solubility of $AlCl_3$ which allows continuous feeding, while its main drawbacks are the high $AlCl_3$ volatility above 700 °C, the sensitivity to moisture, and the low electrical conductivity of the salts.

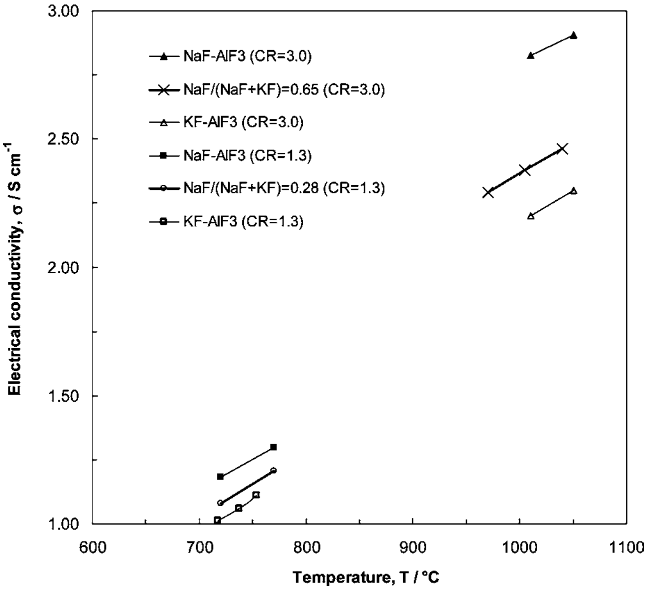

Figure 22. Electrical conductivity versus temperature for NaF−KF−AlF_3 mixtures at CR = 3.0 (from Huang[36]) and CR = 1.3 (from Dedyukhin[31]). Comparison to the NaF−AlF_3 and KF−AlF_3 systems.[15]

This process, which produces chlorine gas at the anode, was abandoned, noticeably because of high maintenance costs of the plants and the difficulty of producing oxide-free $AlCl_3$. Considering that carbon dioxide production becomes an environmental problem in the current Hall−Héroult process, chlorine gas handling seems quite a challenge, and all-chloride baths have not been studied further since that time.

Some work was also performed on the properties of mixed chloro-fluoride baths, which may allow the use of alumina feed and consumable carbon anodes. Many phase diagrams obtained from thermodynamic modeling in the system NaF-KF-AlF_3−NaCl-KCl-$AlCl_3$ are compiled in a paper by Heyrman and Chartrand:[33] several combinations allow for a decrease in the melting temperature, reaching the (700 to 800) °C temperature range.

However, a critical drawback of the chloro−fluoride mixtures is that the presence of chlorides induces a decrease of the alumina solubility. As a consequence of the small oxide concentration, a mixed anodic reaction is observed, and as mentioned for example by Fellner et al.,[40] chlorine evolution may occur at the anode. Indeed, alumina solubility is reported to be almost negligible (about $w = 0.0001$) in KCl−NaCl−NaF mixtures containing about one-third NaF,[41] as well as in LiCl−KCl−NaF mixtures.[42]

Some properties of the NaF−KCl−Al_2O_3 mixtures have been studied by Balaraju et al.,[43] and the alumina solubility seems to be enhanced in this system. Nevertheless, as indicated in Table 3, the alumina solubility does not exceed $w = 0.012$, and the production of chlorine gas can be expected at industrial current densities. The electrical conductivity of the NaF−KCl (0.5−0.5) mixture, determined by Balaraju et al., is quite high, i.e., about 2.2 $S \cdot cm^{-1}$ in the (700 to 800) °C temperature range.

The properties (melting point, electrical conductivity, density) of the Na_3AlF_6−AlF_3−$BaCl_2$−NaCl−Al_2O_3 system were also recently published by Lu et al.,[44] to evaluate a heavy electrolyte with floating aluminum. The solubility of alumina is however not mentioned in this work, nor is the nature of the anodic reaction.

Table 3. Solubility of Alumina (Mass Percent, 100 *w*) in Molten NaF−KCl Mixtures[43]

composition (molar) NaF−KCl	alumina solubility (100 *w*)
20−80	0.5 (740 °C)
30−70	0.9 (760 °C)
50−50	1.1 (740 °C)
70−30	1.2 (650 °C)
80−20	1.2 (670 °C)

Conclusions

The present review shows that the physicochemical properties of Na−cryolite and K−cryolite mixtures are well established, notably thanks to recent studies which filled some gaps. The influence of additives in K−cryolite mixtures is however not completely covered, as well as the aluminum solubility in low-temperature electrolytes.

It is noteworthy that K−cryolite mixtures have been mostly studied at a low-temperature range [(700 to 750) °C] and much less in the (800 to 900) °C temperature range, where they exhibit a large alumina solubility. The interest of a temperature decrease of about (100 to 150) °C should be evaluated, to determine if the target temperature is necessarily 700 °C or if intermediate operating temperatures may bring improvements compared to the current process.

On another hand, data concerning chloro−fluoride mixtures are quite scarce. It is probable that this kind of system has not been largely studied because of the concern of the anodic reaction: chlorine gas management will necessarily raise heavy operational troubles.

Finally, apart from the salt mixture properties presented in this article, it is obvious that many other parameters have to be taken into account to operate electrolysis cells at lower temperature than the current Hall−Héroult process. As discussed for instance by Thonstad and Rolseth[45] in the case of AlF_3-rich Na−cryolite mixtures, the purity of aluminum, the cell voltage, the handling of the thermally insulating frozen ledge, and the corrosion resistance of lining materials are some of the many problems to be studied with alternative electrolyte compositions for aluminum electrolysis.

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