Chemical and Physical Properties of Solid Salt Fluxes

Solid salt fluxes are inorganic compounds that are added during the treatment of molten aluminum to improve the final quality. An understanding of the chemical composition of the flux is essential for the assessment of the physical and chemical behavior of the flux. The chemical composition of the flux can be tailored to adjust properties such as density, viscosity, reactivity, and wettability. Such properties, in turn, will impart different functions to the flux.

1. Chemistry of Salt Fluxes

The compounds usually found in solid fluxes can be classified into four major groups based on the main effect of the characteristics of the flux. The four major groups are chlorides, fluorides, oxidizing compounds, and solvents of aluminum oxide. They are described in the following sections.

1.1. Chlorides

Chlorides usually consist of NaCl and KCl. They mainly act as fillers, given their lower cost compared to other compounds for which chlorides act as carriers, such as fluorides. Chlorides are also used in high percentages for their fluidizing effects. When used individually, they act as passive fluxes, meaning that their reactivity with molten aluminum is negligible, and their effect on the surface tension is trivial if compared to fluorides. As aforementioned, the most common NaCl-KCl ratios are 50–50 and 70–30. Higher NaCl contents lead to a higher melting point of the flux; however, it can be economically convenient given the highest cost for KCl. Furthermore, a limited reduction of the amount of KCl in the flux does not seem to significantly affect the metal recovery [1].

Another binary mixture used as flux is $MgCl_2$-KCl. Sodium-free fluxes are preferred by producers of Al-Mg alloys, especially when the Mg content is high, to avoid the introduction of Na in the aluminum melt. If sodium-containing fluxes are used, the higher the Mg content in the alloy, the more Na is introduced in the melt by fluxes. Furthermore, some flux additives such as NaF or Na_3AlF_6 can also increase the residual content of Na in the aluminum melt [2]. Nowadays, chloride fluxes such as $MgCl_2$ and $CaCl_2$ are also gaining more attention for the possibility of removing alkali and alkali-earth metals from molten aluminum. Purification of aluminum melt was once carried out through the injection of chlorine gas, but the practice has been abandoned due to environmental concerns for the release of chlorine gas, and it was replaced by solid chloride fluxes [3].

1.2. Fluorides

Fluorides, as previously explained, play an essential role in stripping the oxide layer and assisting the coalescence of metal droplets by acting as surfactants for wettability adjustments between salt, oxide, and molten aluminum. Common fluoride compounds include simple fluorides such as CaF_2, NaF, KF, MgF_2, and AlF_3 and double fluoride compounds such as Na_3AlF_6, $KAlF_4$, K_3AlF_6, Na_2SiF_6, and K_2SiF_6 [4][5][6]. Fluorides are usually present in small amounts in flux mixtures, typically around 5 wt %, although their amount varies to a great extent depending on several factors, including the type of scrap, the desired metal quality, the level of inclusions in the melt, as well as the environmental regulations.

Nonetheless, too much fluoride addition can result in a degradation of flux properties because, usually, the fluidity and density increase because of fluoride additions. This results in poor coalescence and reduced metal recovery, as previously mentioned according to Stokes' law (see Equation (2)). Additionally, an excessive increase in density may also lead to poor metal-slag separation. Thus, the amount of fluoride in the flux should be just enough to improve the wettability properties without excessively compromising the fluidity and density of the salt. Limiting the use of fluorides also implies economic and environmental benefits. As a matter of fact, not are only fluorides more expensive than chlorides, but they also cause health and environmental concerns due to dust and fumes as well as toxic and polluting

compounds [7]. Most of them are classified according to EC Regulation No. 1272/2008 [8] as harmful to the environment, toxic, or both. Their amount in the salt flux should be minimized for environmental and health reasons; however, their presence is essential since fluoride-free fluxes do not yield the same efficiency for metal recovery [9].

1.3. Oxidizing Agents

Oxidizing agents promote exothermic chemical reactions, which assist the release of entrapped aluminum from the dross back into the molten metal bath. The mechanism is the improvement of fluidity due to the heat released by exothermic reactions [4]. Moreover, when added with fluorides, the heat released facilitates the chemical reactions between fluorides and inclusions [10]. Examples of oxidizing agents include nitrates such as KNO_3 and $NaNO_3$, carbonates such as $CaCO_3$ and K_2CO_3 and sulfates such as K_2SO_4 and Na_2SO_4 [6].

1.4. Solvents of Aluminum Oxide

Solvents of Al_2O_3 can also be included in the fluxes. Cryolite is extensively used for the electrolytic conversion of Al_2O_3 to commercially pure aluminum metal in the Hall–Heroult process because alumina shows good solubility in cryolite melts. However, aluminum oxide has slight solubility in chloride melts with fluoride additions [11]. Some studies [12][13][14] suggested that the alumina solubility in some fluorides plays a key role in the mechanism of stripping the oxide layer, facilitating its dissolution, and improving the wettability [4]. The solvents of aluminum oxide are cryolite (Na_3AlF_6), borax ($Na_2B_4O_7$), and potassium borate ($K_2B_4O_7$) [6]. The chemical compounds used in salt fluxes are presented in **Table 1**.

Table 1. Chemical compounds used in salt fluxes and grouped according to the chemical type. The melting point ™ and hazardous classification are also reported for industrial relevance. Data were collected and elaborated from [4][6][15][16][17].

Compound Type		Molecular Formula	T_m (°C)	Hazardous Classification [1]
Chlorides		NaCl	801	×
		KCl	770	×
		$MgCl_2$	714	×
		$CaCl_2$	782	✓
		LiCl	605	✓
		$BaCl_2$	962	✓
		$AlCl_3$	190	✓
Fluorides	Simple	KF	858	✓
		NaF	993	✓
		CaF_2	1418	×
		LiF	848	✓
		MgF_2	1263	✓
		AlF_3	1290	×
		BaF_2	1368	✓
	Double	$KalF_4$	-	✓
		Ka_3AlF_6	-	✓
		Na_2SiF_6	-	✓
		K_2SiF_6	-	✓

Compound Type		Molecular Formula	T_m (°C)	Hazardous Classification [1]
		$CaCO_3$	1339	×
		K_2CO_3	894	✓
	Carbonates	Na_2CO_3	851	✓
		$MgCO_3$	990	×
		Li_2CO_3	723	✓
		KNO_3	339	✓
Oxidizing Compounds	Nitrates	$NaNO_3$	307	✓
		$LiNO_3$	264	✓
		K_2SO_4	1069	×
		Na_2SO_4	897	×
	Sulphates	Li_2SO_4	859	✓
		$CaSO_4$	1450	×
		$MgSO_4$	11,424	×
		$Na_2B_4O_7$	743	✓
Solvents of aluminum oxides		$K_2B_4O_7$	-	✓
		Na_3AlF_6	1010	✓

[1] According to EC Regulation No. 1272/2008 [8].

2. Physical Properties and Reactivity of Solid Salt Fluxes

The chemical composition of salt fluxes determines their physical properties and reactivity. The key properties of fluxes include density, fluidity, melting temperature, wettability, and reactivity. These features are described in the next sections with a focus on how they are affected by the chemical composition of the fluxes.

2.1. Density

The density of the fluxes affects the slag-metal separation and the coalescence of metal droplets as described by Stokes' law shown in Equation (2). The higher the density difference between metal and slag, the faster the droplets settle through the slag and back into the aluminum melt. The density of aluminum decreases linearly with temperature, and at 800 °C, it ranges between 2.33 and 2.39 g/cm^3 [18][19]. At 800 °C, the density of an equimolar NaCl-KCl mixture is approximately 1.53 g/cm^3, whereas, if the content of NaCl increases in the mixture up to 90 mol %, the density increases up to 1.55 g/cm^3 [20]. Roy et al. [21] investigated the effect of some common fluoride (NaF, LiF, KF, Na_3AlF_6) additions up to 30 mol % on the density of an equimolar NaCl-KCl mixture at 740 °C. The results showed an increase of the density up to 1.63 g/cm^3. Because the density difference between the molten aluminum and the salt mixtures is about 0.7 g/cm^3, this is enough to ensure sufficient separation between the two phases [22]. Proper salt-slag separation ensures that the salt floats over the melt without joining it to avoid adhesion of salt granules or lumps which would result in a deleterious effect on the final product and to facilitate the removal of the slag at the end of the melting process.

Nonetheless, the effect of impurities and inclusions in the slag on its density cannot be neglected, as in the case of the effect on viscosity.

2.2. Viscosity

The viscosity of fluxes should also be low to assist the settling of metal droplets through the slag layer according to Stokes' law. Few studies are available regarding the viscosity of molten NaCl-KCl with fluoride additions. Roy et al. [21] found how, after a critical amount of fluoride, the addition of LiF, NaF, and CaF_2 increases the kinematic viscosity of an equimolar NaCl-KCl flux. Before reaching this critical amount, the viscosity showed a decreasing trend. Exceptions to these findings include the addition of Na_3AlF_6 up to 2 mol %, which results in a decrease in viscosity, and KF, which leads to a maximum value of viscosity for 5 mol % addition before declining. Tenorio et al. [23] found how the viscosity of an equimolar mixture decreases with NaF and KF additions, in contrast with the previous study. Milke et al. [24] investigated

the solubility of CaF_2 in NaCl-KCl at 750 °C and concluded how it decreases drastically, thus increasing the viscosity of the flux when the CaF_2 concentration exceeds the solubility limit in the chlorides.

Nevertheless, the viscosity of the salt is only representative of the beginning of the process at the industrial scale. When the salt starts to collect oxides and inclusions, its viscosity increases significantly [22][25]. Xiao et al. [26] found that the presence of non-metallic particles in the slag impacts viscosity more than fluorides, especially when the volume of non-metallic particles in the slag exceeds 10 vol %. The impact of oxides in the flux during the remelting of aluminum chips with a lab-scale rotary furnace was studied by Thoraval and Friedrich [25]. The findings showed a significant decrease in the metal recovery, which was attributed to increased slag viscosity and density resulting from oxides, thus hindering the coalescence and metal-slag separation.

2.3. Melting Point

The melting point of the salt is another significant parameter, as the flux should be molten at the processing temperature. Preferably, the melting point of the salt should be close to the melting point of aluminum. If the melting point of the salt is too low, it may result in evaporation of the salt, whereas if it is too high, it may lead to excessive metal oxidation. Furthermore, an excessively high melting temperature leads to increased costs related to higher energy requirements to melt the salt. As previously noted, adding more NaCl to NaCl-KCl mixtures results in a higher melting temperature. However, certain operators, particularly in Europe, choose to prioritize cost savings by using more NaCl, which is less expensive than KCl. Flux mixtures based on KCl and $MgCl_2$ allow obtaining even lower melting points, as the binary system presents eutectic points that melt at temperatures below 500 °C. The KCl-$MgCl_2$ binary phase diagram is shown in **Figure 1**.
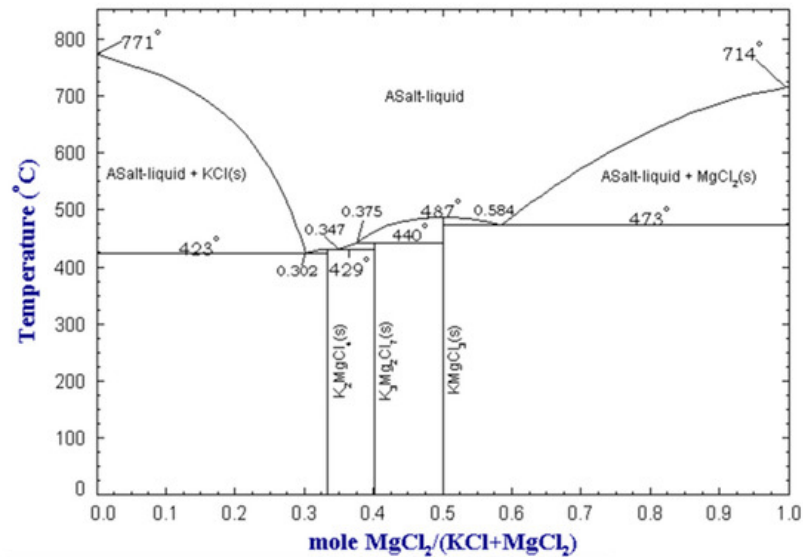

Figure 1. $MgCl_2$-KCl binary phase diagram at atmospheric pressure, obtained from the FactSage™ FTsalt database [27].

Although the binary systems of NaCl-KCl and KCl-$MgCl_2$ have been extensively studied in the literature, to the author's best knowledge, there is a lack of experimental evidence of the effect of the fluorides' addition on the melting point of salt mixtures. Although generally, fluorides show melting points above 1000 °C, some of them show the presence of eutectic points melting below 750 °C when combined with NaCl, as in the case of NaF [27], CaF_2 [24], and Na_3AlF_6 [28]. Even though binary systems of NaCl and fluorides may contribute to the understanding of the melting behavior, they are not representative of common flux mixtures because they are usually constituted by several compounds.

2.4. Wetting Properties

The wetting characteristics of a flux determine its ability to envelop inclusions and transfer them into the slag. It is widely recognized that the ability of flux to strip away and suspend oxides is largely influenced by the degree of wetting between (i) the liquid salt and aluminum melt and (ii) solid oxide and flux. A low value of interfacial tension between flux and oxide assists in the removal of inclusion by wetting. The interfacial tension between flux and aluminum melt should be sufficiently low to allow the spreading of the flux on the melt surface but not excessively low to avoid incomplete separation [29]. As previously explained, fluorides adjust interfacial tensions by promoting chemical reactions which produce surface-active elements (such as Na or K). Enrichment of these surface-active elements at the interface flux/aluminum is responsible for changes in the interfacial tensions. Wan et al. [29] and Shi et al. [5] investigated the effect

of several fluoride additions to a commercial salt flux on the interfacial tensions between aluminum melt, oxides, and flux. The results are summarized in **Figure 2**.
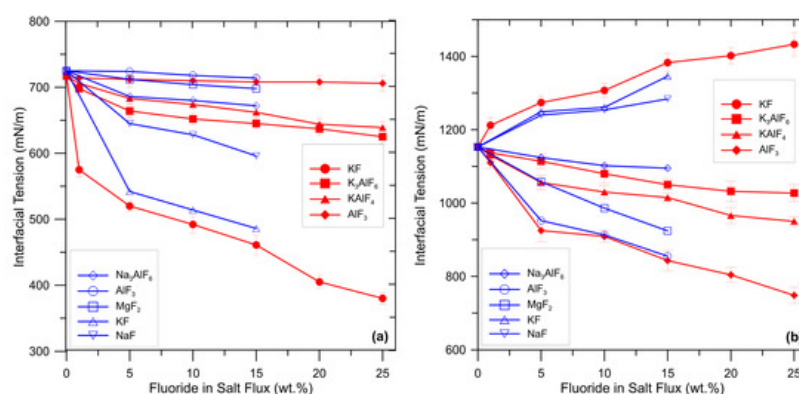

Figure 2. Effect of some fluoride additions in the flux on the interfacial tension (**a**) between flux and aluminum melt and (**b**) between flux and aluminum oxide. Data collected and elaborated from [5][29].

2.5. Reactivity

The reactivity of a flux determines the ability to affect the chemical reactions, which lead to the removal of impurities from the aluminum melt. Simulation studies [30][31] based on thermodynamic calculations investigated the possibility of removing dissolved chemical impurities by considering the relevant parameters of the remelting process. The studies have shown how the salt fluxes containing $AlCl_3$ affect the equilibrium constant of elements such as Mg, Ca, Be, Zn, Hg, Cd, Li, and Sr, allowing their removal either by chlorination into the salt flux, oxidation into the slag phase or by evaporation. However, low efficiency in the removal of such impurities and the impossibility of reducing other harmful impurities such as Cu, Si, Fe, and Mn by fluxing was revealed.

In the past, the injection of chlorine gas, i.e., chlorination, was a common strategy to remove alkali and alkali-earth metals. The tramp elements react with Cl_2 forming more stable chlorides than aluminum chloride, assisted by the bubbling of the gas. Elements such as Mg, Na, Ca, Li, and K react with fluxes and form compounds which will either settle or float into the slag [32]. The toxicity of chlorine has led to its replacement with other methods, such as the use of fluxes. Nowadays, the most popular technology for the removal of inclusions and alkali from molten aluminum is through the addition of chlorine or fluorine-containing compounds to the salt flux, namely $MgCl_2$ and AlF_3, and $AlCl_3$ [3][33]. Replacement of chlorination with solid fluxes can reduce environmental concerns without excessively compromising the efficiency of impurities' removal; however, to replace the mixing due to bubbles, mechanical agitation is necessary [34]. Even though the use of $MgCl_2$ is effective in the removal of alkali, it is not easily handled due to its high reactivity and tendency to absorb moisture. Thus, it is usually pre-melted in mixtures such as NaCl-KCl to obtain easier handling.

Impurities such as Zn, Si, Fe, Mn, and Cu are extremely difficult to remove from molten aluminum using fluxing [4][31]. Nonetheless, some experimental studies [35][36][37] have shown the possibility of reducing the Fe content in aluminum alloys by treating the melt with a flux mixture containing $Na_2B_4O_7$. The methodology has shown promising efficiency at the lab scale, even when compared to other strategies, such as filtration and centrifugal separation. Furthermore, the addition of $Na_2B_4O_7$ not only reduces the Fe content but also shapes Fe intermetallic compounds into less detrimental morphologies and promotes the formation of compounds such as AlB_2, which act as grain refiners.

Particular attention should be dedicated to the treatment of Al-Mg alloys, especially for Mg content above 3 wt %, with fluxes containing Na, Ca, or K, as some chemical reactions may lead to the contamination of Al with Na or K. This is due to the exchange reactions of Mg with the impurities which preferentially stabilize Na, Ca, and K in the molten aluminum rather than in the flux [3][4]. Huang et al. [2], by treating an Al-Mg alloy with a NaCl-KCl flux with NaF and Na_3AlF_6 additions, concluded that the extent of Na contamination increases due to the increasing content of both Na in the flux and Mg in the Al alloy.

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