Fluxes – Is There A Panoramic View?

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ABSTRACT

Fluxes used in the following processes have been examined to determine what common features they might have: soldering, brazing, welding, electroslag remelting (ESR), ingot and continuous casting, and the production of aluminium master alloys.

The fluxes have been inspected in terms of (i) the functions that they have to perform in the process, (ii) the properties of the flux which are important to carry out those functions, and (iii) typical compositions. It was concluded that there were some common features for the fluxes; that they should (i) melt at least 100°C below the metal, (ii) form a protective layer on the metal, (iii) absorb inclusions from the metal and, (iv) usually contain halides. On the other hand, frequently, key features were specific to the type of flux and its application; for instance, powder consumption rates are essential to the performance of mould fluxes, as are factors affecting arc stability, to the performance of welding fluxes.
1 INTRODUCTION

We have been asked by the Conference Organisers to provide a panoramic view of fluxes used in the metallurgical industry. Our first reaction was "Is there a panoramic view of fluxes?"

Dictionary definitions of a flux [1]:

(i) in *Chemistry*, “a substance promoting the melting of another substance to which it is added,“
(ii) in *Materials*, “a substance used in soldering, welding and brazing to remove oxides from the surfaces to be joined,“ and
(iii) in *Metallurgy*, “in liquid metal processing, a non-metallic material used to protect the metal and remove impurities.”

A quick examination of the functions of fluxes used in a specific process (such as welding) will quickly indicate that properties such as ‘promoting arc stability’ are not covered by the above definitions.

Consequently, in this review we have examined the following types of fluxes:
- soldering and brazing,
- welding,
- electroslag refining,
- formation of master aluminium alloys containing TiB₂,
- mould and ingot fluxes for the casting of steel.

We have examined the above fluxes in terms of:

(i) the functions that the flux must perform in each application,
(ii) the physical properties which are important in carrying out these functions, and
(iii) typical compositions of the various fluxes used.

2 SOLDERING AND BRAZING FLUXES

2.1 SOLDERING

In soldering and brazing the surfaces of the metals being joined remain solid throughout the entire operation. The filler metal from the solder makes the joint by intimate attachment to the base metal surfaces. The filler metal must 'wet' the workpiece surface and must flow easily over the surfaces. These characteristics will be promoted by low surface tensions and low contact angle (solder on base metal) for the solder or braze. The fluxes are added to facilitate this process and must carry out the following tasks [2]:

(i) remove any oxide films (usually Cu₂O or SnO) present on the workpiece surfaces and protect these surfaces from any further oxidation,
(ii) any remaining left-over flux or reaction products must be easily displaced from the metal, and
(iii) promote the heat transfer from heat source to the joint.

The efficiency of the flux is controlled by its ability to promote melting and is associated closely with the reactivity of the flux. However, if the flux is reactive, it can cause corrosion of the joint in time. This is a major issue, especially in the case of soldering electronic components [2]. In some processes the fluxes are removed by washing after soldering.
Fluxes for soft soldering tend to be of two types:

(i) those soluble in organic fluids, and
(ii) those soluble in water.

In some cases activators are added to the flux to enhance the reactivity of the fluxes. Activated fluxes nearly always contain halides.

(i) Fluxes soluble in organic liquids

These are mostly based on colophony (rosin) which is a natural product derived from pine sap. The principle component of colophony is abietic acid. Colophony has a melting point (mp) of 172°C and is soluble in acetone and alcohol. It tends to have low reactivity and activators containing halides are usually added.

(ii) Fluxes soluble in water

These fluxes are frequently based on ZnCl$_2$ (mp 283°C) or NH$_4$Cl or mixtures of the two components. There is little fluxing action in the absence of moisture.

\[ \text{ZnCl}_2 + \text{Cu}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{HCl} + 2\text{Cu} + \text{ZnO} \]  

(1)

2.2 HARD SOLDERING

The principles of this process are identical to those in soft soldering but the temperatures involved are higher. In hard soldering the filler metals tend to be silver or copper to which elements such as zinc, tin etc are added to reduce the melting point. Consequently, the fluxes used must be capable of operating within temperature ranges of 600 - 800°C and 150 - 1150°C respectively. The flux must be liquid and should not decompose at the operating temperature.

Fluxes used in hard soldering contain low melting compounds such as B$_2$O$_3$, NaF, KF, KHF$_2$ boro-fluorides, borates, etc.

2.3 BRAZING

Brazing is carried out on a variety of metals Al, Mg, Ti steels and Cu/Al alloys using a variety of filter methods, each of which requires an appropriate flux. A variety of compounds are used in these fluxes (e.g. LiCl, LiF, NaF, and KF, KHF$_2$, ZnCl$_2$, KBF$_4$, B$_2$O$_3$ etc). Brazing is very similar to hard soldering and the requirements of the flux are identical to those for hard soldering.

2.4 DISCUSSION OF JOINING FLUXES

The temperatures used for soft and hard soldering and brazing vary but the role of the flux is identical in all these applications. First, and most importantly, it must promote the wetting of the filler metal and to do this, it must (i) remove the oxide films on the base metal surface to permit wetting and (ii) have a low melting point to provide a liquid layer to protect the base metal from further oxidation. The presence of halides in fluxes is interesting. The main function of the halides is the chemical attack of the oxide films on the surface of the base metal (e.g. Equation 1). However, there is evidence to suggest that Group V11 elements (e.g. I, Br, Cl, F) are very surface-active and thus the presence of F or Cl at the metal/solder (or braze) interface could reduce the surface tension of the solder (or braze) significantly and encourage spreading of the solder.

3 WELDING FLUXES
In welding the metal pieces being joined are melted. Fluxes are used to protect the metal surface from oxidation. Failure to protect the metal can lead to a weld with gas pores and poor surface appearance [3,4,5]. Fluxes are used in four welding processes:

(i) Manual - Metal Arc [MMA],
(ii) Submerged -Arc Welding [SAW],
(iii) Flux-cored wire welding, and
(iv) Electroslag – welding [ESW].

Some of the requirements are common to all the processes, but other tasks are specific to an individual welding process. Functions of welding fluxes include [3,4,5]:

(i) to melt at a temperature below (eg. 100°C) the melting point of the base metal,
(ii) to protect the weld from the atmosphere; fluxes contain (a) carbonates and fluorides which decompose to give CO₂ or F shielding and (b) in some cases, contain metals (e.g. Al) which react with oxygen to reduce the partial pressure of oxygen,
(iii) to form a slag crust which protects the weld from subsequent oxidation during cooling,
(iv) to remove impurities from both the surface (e.g. rust) and the metal (e.g. inclusions) by absorbing them into the molten slag,
(v) to encourage arc initiation and stability; sodium and potassium ions are beneficial for this task, this is very important to the welding process, and
(vi) to increase metal deposition rates of the metal electrodes; in practice this is achieved by additions of ferrous alloy powders to desulphurize the weld metal (in the case of basic fluxes).

3.1 MANUAL METAL ARC [MMA] WELDING

The core wire consists of a metallic electrode covered by a thick layer of flux (which is manufactured by an extrusion process) [3]. The welding process consists of an arc being struck between the core wire and the work pieces. [Figure 1] The flux melts and the constituents decompose to provide (i) protection against oxygen ingress and (ii) arc stability. The electrode core wire is consumed in the welding process. The arc stability is improved by Na+, K+ and iron ions but F- ions interfere with efficient metal transfer during the rapid change in polarity in AC welding. Thus, fluxes with significant F content can only be used in DC welding (where F ions migrate to the anode). The ions produced in the arc also affect the droplet size. The basic fluxes tend to produce larger metal droplets from core wire whereas more acidic fluxes (which give less oxygen protection) tend to produce ‘spray transfer’ [3]. This may also be related to the surface tension of the core wire under the welding conditions.

Several types of fluxes are available for MMA welding and the selection is dependent upon the type of weld required, for instance, practical (i.e. non-horizontal) welding, is best performed with spray metal transfer. These following fluxes are available:

(i) Acid (high SiO₂, FeO, MnO content) - high O and H content in welds with poor mechanical properties,
(ii) Rutile - (NiO₂ [30-50%], CaO, MnOSiO₂), and
(iii) Basic - (30-40% CaF₂, 25-40% CaO, 10-15% SiO₂) low O and H content in weld metals, gives large droplets, difficult to use in AC welding.
3.2 SUBMERGED ARC WELDING (SAW)

In this process [3,4,5], an arc is struck between a consumable electrode and the workpiece which is covered with a layer of flux (Figure 2). A cavern is formed in the metal (Figure 2) and its shape is maintained as the weld travels along the workpiece. The fluxes can be produced in pre-melted or agglomerated forms. The main tasks of the slag are (i) to form a liquid slag layer to protect the surface of the weld and to absorb inclusions (ii) to provide a stable arc which is very important (iii) to form a solid slag which protects the weld on cooling and which is easy to remove and (iv) to promote heat transfer. Several types of SAW fluxes are available each having its own merit and limitations. Acidic fluxes are based on eutectic MnO + SiO$_2$ slags with additions of CaF$_2$ etc.; these fluxes tend to give high oxygen levels in the weld. The oxygen content is reduced by additions of TiO$_2$ and Al$_2$O$_3$ and by SiO$_2$ being replaced by Al$_2$O$_3$ and TiO$_2$ in some formulations. They contain CaF$_2$ which is usually around 10% but can be up to 20% in more basic powders. These basic powders tend to provide some desulphurization of the weld metal but care must be taken in storage to avoid moisture pick-up, which can lead to hydrogen cracking in the weld.

3.3 FLUXED CORE WIRE WELDING

This is an automatic or semi-automatic process [3] in which an arc is struck between the reeled wire and the workpiece (Figure 3). The wire contains a core of flux. Since the wire is on the outside shielding two types of the metals is difficult and the composition of the flux reflects the importance of this function. Two types of fluxes are available:

a) **Self shielding** flux-cored wires which contain Al or Mg 10% or 50% Fe additions to deoxidise the CaF$_2$ environment of the weld along with either CaCO$_3$ or TiO$_2$ or both, providing further F and CO$_2$ shielding, and

b) **Gas-shielded** flux-cored wires, which are protected by CO$_2$ or CO$_2$/Ar, gas atmospheres. These fluxes are based on SiO$_2$ - TiO$_2$, CaO or CaF$_2$ - SiO$_2$, CaO-CaF$_2$ - SiO$_2$-TiO$_2$, all with additions of deoxidants such as Fe-Mn.

3.4 ELECTRO-SLAG WELDING (ESW)

The electroslag welding (ESW) process (Figure 4) differs from the other three processes in that it does not involve a continuous arc [3]. Once the flux is molten and a flux pool has been established, the arc is extinguished and the process relies on resistive heating due to the current flowing through the molten slag. The consumable electrode provides a stream of metal droplets, which form a molten weld pool. (Figure 4) The weld is retained by using water cooled copper plates. It is particularly suitable for welding thick sections held in the vertical position.

The principle functions of the slag are:

(i) it should melt at a temperature 100°C below the metal,

(ii) it should provide resistive heating, and

(iii) it should protect the steel from oxidisation.

The composition of ESW fluxes tends to be determined by the electrical conductivity of the molten flux [3]. The conductivity must be a balance between (i) a high conductivity to provide a suitable current between electrode and weld pool and (ii) a sufficiently low conductivity (or high resistivity) to provide the necessary power. Slag-metal reactions, such as the desulphurization of the metal, occur readily because of (a) the much longer contact times between molten metal and slag (b) the large (surface area/volume) ratios of droplets which provide fast kinetics and (c) the high sulphur capacities provided by CaF$_2$-rich slags.
ESW fluxes tend to resemble SAW fluxes but have higher CaF₂ contents to obtain the required electrical conductivity values.

4 ELECTROSLAG REFINING (ESR) FLUXES

The electroslag refining process is used for refining nickel-based super alloys, titanium alloys, and steels [6,7,8]. It is very similar to the electroslag welding (ESW) process in that it uses a consumable electrode of the required steel component cast by conventional metallurgical processes. The electrode is submerged in a molten slag held in a water-cooled copper mould (Figure 5) which serves as the other electrode. When an electrical current is passed the tip of the electrode melts and a small droplet is formed. This small droplet has a huge (surface area/mass) ratio and refining reactions occur rapidly as it falls through the molten slag and then splashes into the molten metal pool.

The principle duties of the flux are:

(i) to supply heat to the system by acting as a resistive medium for the passage of electrical current,

(ii) to remove impurities (such as S) by mass transfer across the metal/slag interface [8], e.g. Equation 2, where the underline ‘_’ indicates the metal phase,

\[
\text{S} + \text{O}^{2-} \text{(slag)} = \text{O}^{+} + \text{S}^{2-} \text{(slag)}, \quad (2)
\]

(iii) to remove inclusions by (a) dissolution of the oxide particles in the flux and (b) flotation of the particles, and

(iv) to isolate the refined product from both the atmosphere and the water-cooled mould.

The two most important of these tasks are undoubtedly the removal of harmful impurities and inclusions, since both cause a marked decrease in mechanical strength of the alloy. The kinetics of the refining reactions is rapid because of the huge (surface area/mass) ratio of the metal drop as it descends through the molten slag layer. The residence time for the descent increases with increasing flux viscosity but this must be balanced against the fact that the kinetics of the metal/slag reactions are often rate-controlled by the slag viscosity.

The kinetics of the refining reactions are also affected by the interfacial tension \(\gamma_{ms}\) between metal and slag. A low value of \(\gamma_{mi}\) favours an increase in the mass transfer rate. The classic work at IRSID showed that rapid mass transfer between metal and slag [9,10] was accompanied by a marked decrease in interfacial tension (Figure 6) which could readily lead to emulsification of metal in the slag (or slag in the metal). This, in turn, leads to rapid refining but also to entrapment of slag globules in the metal, which is very undesirable. Fortunately, the molten flux pool allows time for any flux globules to float out of the metal.

The transport of inclusions from the metal to the liquid flux is also dependent upon \(\gamma_{ms}\). Kozakevitch and Olette [9] showed that removal was favoured if:

\[
\gamma_{mi} > \gamma_s + \gamma_{ms}, \quad [3]
\]

where the subscript \(i\) refers to the inclusion

They showed that the process was nearly always favoured. However, for a refined metal in the metal pool the S and O levels will be low and consequently the surface tension of the metal will be high. The interfacial tension, \(\gamma_{ms}\) is given by Equation 4 where \(\varphi\) is an interaction coefficient.

\[
\gamma_{ms} = \gamma_m + \gamma_s \cdot \varphi \left(2 \gamma_m \gamma_s\right)^{0.5} \quad [4]
\]
The $\gamma_m$ term is typically 5 times that of $\gamma_s$ so a high $\gamma_m$ will tend to lead to a high $\gamma_{ms}$ value. Chung [11] showed that small inclusion particles cannot puncture the interface directly and require a certain rest period or residency before they can traverse the interface.

Thus, in summary, the key physical properties of ESR fluxes are the electrical conductivity, interfacial tension and the viscosity. ESR fluxes usually contain high concentrations of CaF$_2$ e.g. typical ESR fluxes contain 10% CaF$_2$ + 30% Al$_2$O$_3$, 70% CaF$_2$ + 15% Al$_2$O$_3$ + 15% CaO.

They are fundamentally unstable at high temperatures where the CaF$_2$ reacts with the various oxides or moisture with the CaF$_2$ to form gaseous fluorides:

$\text{CaF}_2 + \text{Al}_2\text{O}_3 \rightarrow \text{AlF}_3(g) + \text{CaO}$

Thus there is a tendency for the fluoride content of the ESR flux to decrease and the oxide content to increase with time. Great care must be taken in storing ESR fluxes since both CaO and CaF$_2$ tend to absorb moisture. This leads to hydrogen pick-up in the metal. Although the diffusion of hydrogen is reasonably fast, hydrogen pick-up remains a serious problem in the production of large diameter ingots.

The phase diagram of the CaF$_2$ + CaO + Al$_2$O$_3$ system indicates that there is an extensive miscibility gap and the compositions of ESR fluxes frequently border on this miscibility gap, especially, when compositional changes (e.g. Equations 5 and 6) are taken into account. The contours of the measured physical properties show a remarkable curvature in the region of immiscibility (Figure 7a,b,c). The shape of these contours has been ascribed to the problems of making property measurements on immiscible liquids [7,8]. Measurements of electrical conductivity, viscosity and surface tension tend to be made in the upper part of the crucible in order to minimise the interference from the base of the crucible. Consequently, it was proposed [7,8] that the shape of these contours (shown in Figure 7) was a result of making the measurements, predominately, in the lighter of the two liquids. It was proposed [8] that overall values for the two liquids could be obtained by extrapolating values into the two phase region as shown in Figure 8.

Fluoride emissions are a threat to health and safety, damage the environment, and can cause corrosion of plant equipment. In recent years the CaF$_2$ content of ESR fluxes have been decreased to 50% and attempts have been made to produce fluoride-free fluxes. The major problem in the development of fluoride-free fluxes is to obtain a flux with the required electrical conductivity for a successful operation.

5. FLUXES USED IN PRODUCTION OF ALUMINIUM-MASTER ALLOYS

Titanium boride TiB$_2$ and TiAl$_3$ act as grain refiners in Al alloys. The master alloy is prepared by adding fluxes of K$_2$TiF$_6$ and KBF$_4$ to the Al where it reacts to form TiB$_2$ and TiAl$_3$ and a mixture of KF and AlF$_3$. The separation of reaction products from the metal phase is a key step in any metal production process. It is easier to separate two liquid phases and so processes are usually designed to produce liquid metals and liquid reaction products.

It was mentioned above that rapid mass transfer could lead to low interfacial tension which, in turn, can lead to emulsification and rapid kinetics. However, emulsification can also lead to flux entrainment. If pure K$_2$TiF$_6$ and KBF$_4$ are used, flux entrainment in the aluminium occurs (Figure 8) which is very undesirable. However, it is known that if the K$_2$TiB$_6$ and KBF$_4$ contain as little as 40 ppm Ca then emulsification does not occur and the waste products float to the surface [12]. The extremely low levels of Ca required strongly indicate that this is probably associated with interfacial phenomena [12]. It has been suggested that
Group VII elements are highly surface active (although it is difficult to keep fluorine in the metal). One possible explanation for the effect of Ca is that Ca in addition to Al significantly reduces the soluble fluorine concentration in Al and subsequently increases the surface tension and thus the interfacial tension \( \gamma_{ms} \) of the metal phase (Al).

6 MOULD AND INGOT FLUXES

6.1 INGOT FLUXES

The traditional method of casting steel was in the form of ingots and ingot fluxes were used to prevent the steel from oxidisation and provide some lubrication. Since the flux must provide a reducing atmosphere for the entire casting period they tended to have high carbon elements and tended to be based on fly ash with other oxides added to lower the melting point. However, ingot-casting has been largely superseded by the continuous casting of steel.

6.2 MOULD FLUXES FOR THE CONTINUOUS CASTING OF STEEL

Mould fluxes play an important role in the continuous casting of steel. Molten steel from the tundish is poured through a submerged entry nozzle into a water-cooled, copper mould where the steel freezes to form a solid, steel shell. The dummy-bar filling the bottom of the mould is withdrawn and the solidified shell is further cooled by passing it through water sprays until it has completely solidified, whereupon, it is slit into lengths (Figure 9).

The mould flux is continuously added to the top of the mould where it forms various layers including a liquid slag pool (Figure 10). The mould is oscillated and molten slag is drawn into the channel between the shell and the mould during the downstroke of the mould. The slag drawn into the channel in the first moments of casting, freezes against the mould wall and forms a solid slag layer (ca. 2-3 mm thick). A thin liquid slag layer (0.1-0.3 mm thick) remains in contact with the shell and provides the necessary liquid lubrication of the steel. The mould flux must perform the following tasks:

(i) form a molten slag pool which protects the steel interface from oxidation,
(ii) provide a liquid slag film which lubricates the shell throughout the mould,
(iii) provide the right level of horizontal heat transfer between the shell and the mould, and
(iv) absorb non-metallic inclusions e.g. Al\(_2\)O\(_3\), TiO\(_2\), into the molten slag pool.

Failure to carry out any of these tasks satisfactorily will result in inferior product quality or process control problems. Providing the flux forms a molten slag pool and protects the entire steel surface from oxidation, it is usually considered that the slag infiltration and the control of the horizontal heat flux are the most important functions of the flux.

6.2.1 Powder consumption

Powder consumption is a measure of the slag infiltration into the mould/strand channel and the liquid lubrication supplied to the shell, since it is related to the thickness of the liquid slag film, \( d_l \). Originally, it was used only as a measure of the cost of mould flux and is reported as \( Q_s \) in kg (flux) tonne\(^{-1}\) but Wolf [13] pointed out that when converted to \( Q_s \) in kg (flux) (m\(^2\) of mould) tonne\(^{-1}\), it provides a measure of the liquid lubrication. It was subsequently shown [14,15] that \( Q_s \) was a sensitive function of the parameter, \( R \), which represents the ratio of the (surface area/volume) of the mould (Figure 11). Values of \( R \) are in the hierarchy: thin slabs and billets > blooms > slabs.

The liquid frictional force, \( F \), is given by:

\[
F = \eta (v_c - v_m)/d_l
\]
where \( v_c \) and \( v_m \) are the casting speed and the mould velocity and \( \eta \) is the viscosity. Thus, the frictional forces increase with increasing viscosity and decreasing slag film thickness (or powder consumption).

Several empirical rules have been reported for calculating powder consumption and these have been reviewed by Wolf [13]. Two simple rules reported by Wolf [13] are derived from relations for optimum casting conditions [16,17].

\[
Q_s = 0.7/\eta^{0.5}v_c \\
Q_s = 0.6/\eta v_c
\]

An analysis of plant data has shown [15] that these relations provide a reasonable estimate of the powder consumption with Equation 9 providing a slightly better fit. Thus, it is essential that the casting flux should have the correct viscosity for the mould dimensions and steel grade being cast. In practice, the oscillation characteristics also affect the powder consumption, \( Q_s \), which increases with decreasing frequency and increasing stroke length.

6.2.2 Horizontal heat transfer

Longitudinal cracking of the surface and the sub-surface of the continuously-cast strand is a major problem, especially for medium-carbon (MC) steel grades (0.06 - 0.18% C). This is the result of the 4% mismatch in the thermal shrinkage coefficients of the \( \delta \)- and austenite phases of iron. This, in turn, produces thermo-stresses which are relieved by longitudinal cracking. The usual strategy adopted to minimize these stresses is to ensure that the newly-formed shell is both as thin and as uniform as possible. This is achieved by reducing the horizontal heat transfer by creating a thick, crystalline slag layer [14,15].

In contrast, the shells of high-carbon (HC) steels (C>0.4% ) tend to be mechanically weak and stickier-breakouts (where molten steel pours from the mould) usually arise as a result of a lack of lubrication, but they can be minimized by creating a thicker, stronger shell to withstand the ferro-static pressure. In this case it is necessary to enhance the horizontal heat transfer through the formation of a thin, glassy slag layer. The thickness of the slag layer is partially determined by the solidification or break temperature (\( T_{br} \)) that is the temperature on cooling where there is a sharp increase in viscosity and which corresponds to the point where liquid lubrication breaks down. Figure 12 shows a plot of \( T_{br} \) as a function of viscosity (and casting speed) for (1) MC, crack-sensitive steels, (2) HC, sticker-sensitive steel grades, and (3) all other grades. Thus one can predict the \( T_{br} \) needed for casting the steel grade and casting speed.

Therefore, from the viewpoint of avoiding both longitudinal cracks and sticker-breakouts, the most important properties are the break temperature and the degree of crystallization. Consequently, the properties of the solid slag are also important.

6.3 Slag entrapment

Slag- and gas-entrapment are also major sources of defects in continuously-cast steels [18,19]. It has been shown that they are mainly caused by the casting conditions which promote turbulence in the liquid metal (Figure 13). The mould flux, however, does play some part and the problem can be alleviated by increasing either interfacial tension (\( \gamma_{ms} \)) or the viscosity of the flux; in practice, the latter approach is usually adopted, but this practice results in a lower powder consumption.

7. DISCUSSION
This study has shown that there are functions and features of mould fluxes which are common to all fluxes \( \text{viz} \)

(i) they all have melting points significantly below that of the metal phase,

(ii) they all are expected to protect the surface of the metal from oxidation,

(iii) they are expected to absorb inclusions from the metal, and

(iv) they tend to contain halides and this may be related to the surface activity of the Group VII elements.

However, the individual features, which are specific to the type of flux or application, are equally, or even more, important than those mentioned above. For instance, the powder consumption and the factors affecting horizontal heat transfer are of prime importance in continuous casting, as is arc stability in welding processes.

There is one feature of fluxes, common to all fluxes, which is becoming ever-more important, namely, the environmental concerns, health hazards and associated plant corrosion problems posed by the use of halides in fluxes. ESR slags contain up to 70% of CaF\(_2\) and are basically unstable at high temperatures. It is noticeable that the fluoride contents of fluxes have tended to be reduced to 50% CaF\(_2\) and fluoride-free fluxes are currently being developed at the present time. The challenge is to obtain a fluoride-free flux with the right electrical conductivity.

Fluoride emissions with the associated plant corrosion problems are also a source of worry in the continuous casting of the steel [20]. Consequently, some steelworks are now demanding lower fluoride levels in their mould fluxes and ever-more stringent legislation is likely to lead to lower halide levels in fluxes. The use of prefused mould fluxes would be one option for reducing halide emissions and would help to reduce the absorption of moisture.

**CONCLUSIONS**

1) Halides are used to lower the melting point, viscosity, and possibly the surface tension of fluxes, but the levels of halides are likely to be reduced in the future because of environmental and safety concerns.

2) All fluxes have melting points lower than that of the metal and the slag formed is expected to both protect the metal from oxidation and absorb inclusions from the metal.

3) The individual functions and features specific to one type of flux tend to be very important, such as arc stability in welding or powder consumption in continuous casting.

4) The high surface activity of the halides may be a reason for their widespread use in fluxes.
Table I  Property Values to be used with Figure 7(d).

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REFERENCES

Figure 1  Schematic of the manual metal arc process

Figure 2  Schematic diagram of submerged-arc welding process
**Figure 3**  Schematic diagram of the flux-cored arc welding process

**Figure 4**  Schematic diagram of electro-slag welding process
Figure 5  Schematic diagram of the electroslag remelting process

Figure 6  The effects of time (a) on interfacial tension $\gamma_{ms}$ and (b) on the mass transfer of Al from steel (to the slag).
Figure 7  Viscosity (a), Conductivity (b), Surface tension (c), and Property values (d) for the CaF$_2$-Al$_2$O$_3$-CaO system at 1600°C. Table I is to be used with 7(d).
Figure 8  Photograph showing fluoride emulsion in Al master alloy containing TiB$_2$ + TiAl$_3$. 
Figure 9  Schematic of the continuous casting process
**Figure 10**  Schematic representation of mould flux in the mould
Figure 11  Powder consumption as a function of (surface area/volume) ratio R
Figure 12  Relation between viscosity, break temperature and casting speed