

# The evolution of fused refining fluxes

The range of compositions and application technology of fused refining fluxes has come a long way since their first introduction to aluminium casthouses. Michael Bryant of MQP explores fused refining flux efficiency, reaction kinetics and application methods.

Fused refining fluxes have been in widespread use since first developed in the 1990's as a means of reducing sodium and cleaning liquid aluminium. They are an environmentally friendly alternative to chlorine gas which, although effective, presents major health and safety concerns in its usage and control in a casthouse environment. Two of the most frequently asked questions by users of fused refining fluxes are:

- "Which composition of fused refining flux is the most efficient... and why?"
- and
- "What is the optimum method of adding fused refining fluxes to molten aluminium... and why?"

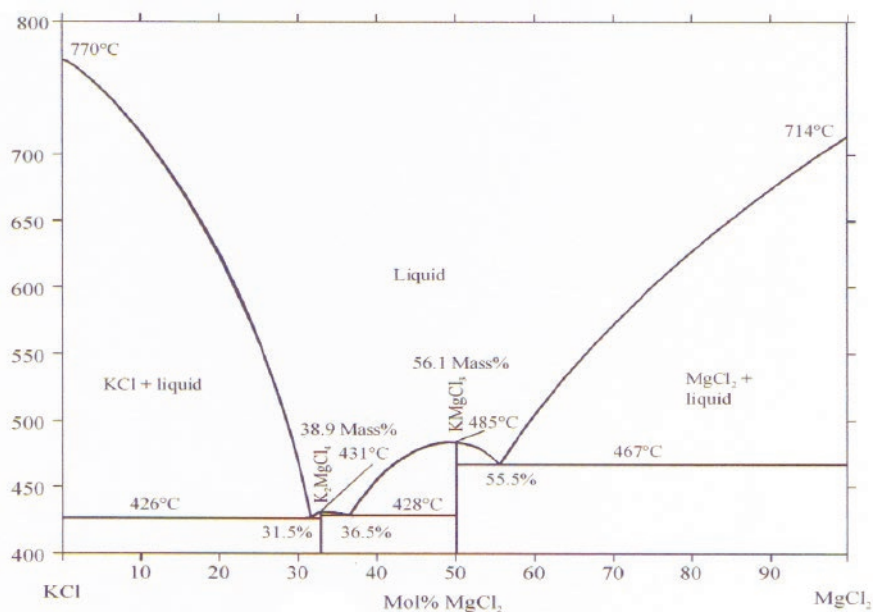
The answer to both of these questions can, as expected, be found in the field of thermodynamics and chemical reaction kinetics, as will be explained later. Firstly, let's establish something about the background and evolution of the chemical composition of refining fluxes, their relative effectiveness as alkali reducers when added to molten aluminium alloys, and the mechanism in which they are believed to operate.

## Replacing chlorine

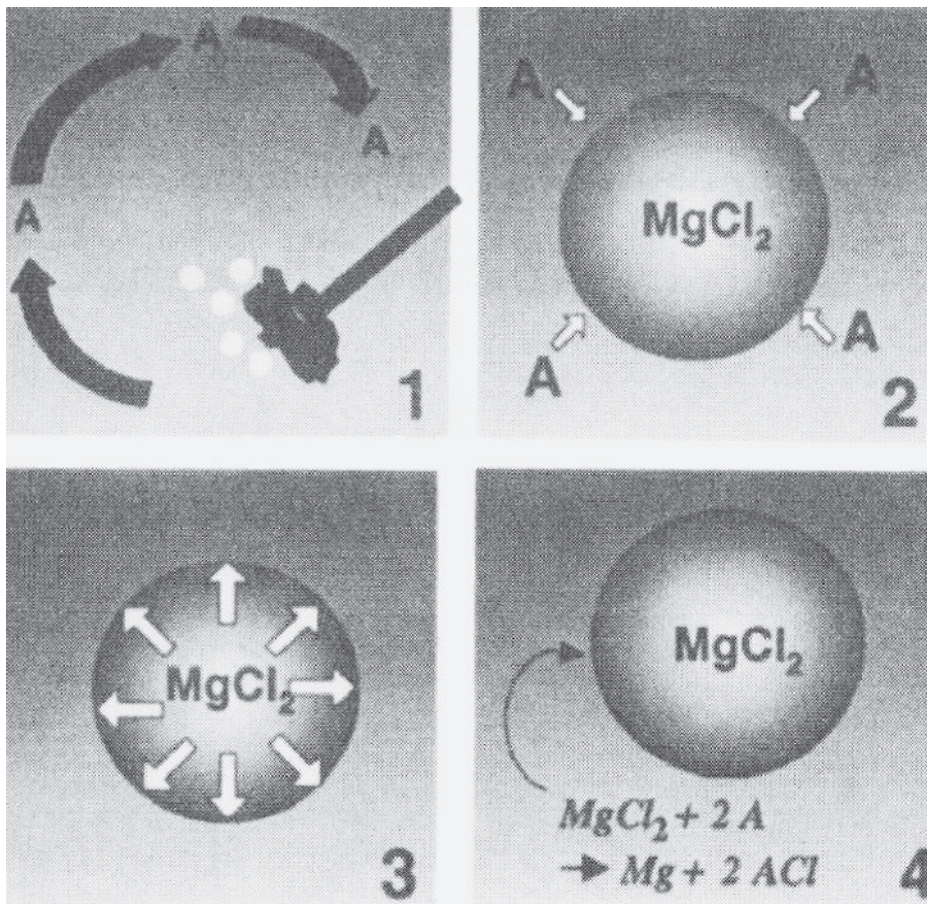
Treatment with chlorine, in the melting or holding furnace, is an effective means of reducing sodium levels and improving melt quality, but its usage in the casthouse has been subject to increasing scrutiny since the mid 1980's. (1) By the mid 1990's legislation and regulations were in force in most industrialised countries concerning the use of chlorine which imposed very low limits on emissions arising from its use. As a result, Alcan instigated an ongoing global strategy to reduce its chlorine dependency by looking at both optimisation of chlorine usage and substitution of chlorine.

The traditional practice was to inject chlorine gas, mixed with argon or nitrogen, into melting or holding furnaces, to reduce hydrogen and alkali metals and reduce metallic and non-metallic inclusions. The usual addition method was stationary lances but in shallow reverberatory furnaces this was inefficient, due to large bubbles and low residence time. The tendency was to compensate by increasing the chlorine addition well above stoichiometric levels. This led to incomplete reaction, resulting in acid gas and particulate emissions.

Attention was given to means of increasing chlorine gas bubble/metal contact time by reducing bubble size and improving bubble distribution, using improved methods of addition including multi lance systems,



1  $MgCl_2$  -  $KCl$  mole% system after Grjotheim, Holm and Roetnes, with additions by Ditze.



2 Mechanism of alkali removal after J.F. Bilodeau et al': 1. Alkali brought to the reaction zone; 2. Alkalis diffuse in external bubble/droplet boundary layer; 3. Active agents diffuse to droplet surface; 4. Reaction with alkali to form alkali chloride.

lances with porous nozzles, porous plugs installed in furnace floors, subsurface metal pumping and systems with rotors and impellers.

All of these systems brought about an improvement in chlorine efficiency to a small or greater extent, and the most sophisticated of them, subsurface metal pumping with the Alcan Jet Stirrer, gave major gains in efficiency of utilisation of chlorine, hence reduced chlorine consumption by 50% compared with lance fluxing alone. Rotors and impellers also gave greater gains in chlorine efficiency when removing alkalis.

Together with measures such as these to improve chlorine efficiency and therefore reduce emissions at source, there was also the added possibility of controlling the emissions once generated by installation of alkaline scrubbers. These are helpful but expensive, and produce noxious liquid and solid residues which still need to be disposed of.

Summing up, it was concluded that it was possible to greatly improve the efficiency of chlorine usage, and largely control emissions, but at a significant cost and without really overcoming the basic problem, the nature of chlorine itself.

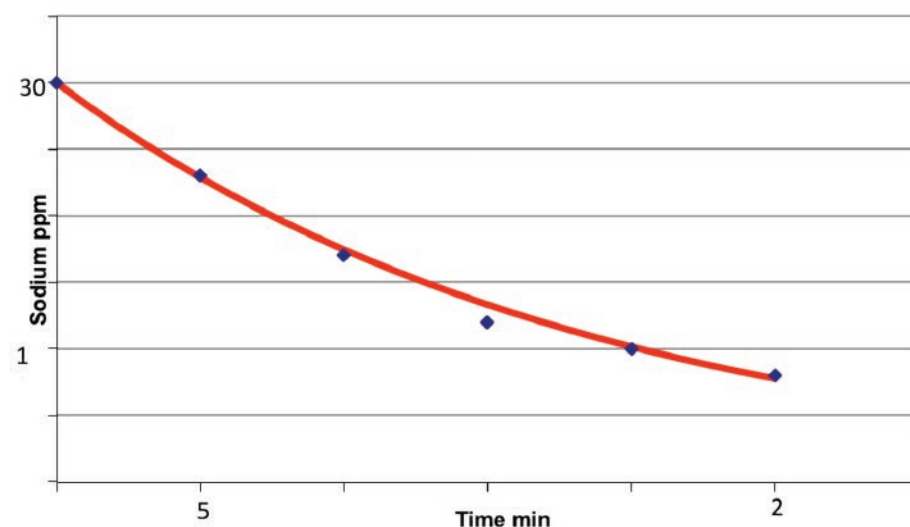
Attention was switched to looking at alternatives to chlorine. Powder fluxes based on mixtures of fluorides, chlorides, carbonates, sulphates and carbonates had traditionally been used as casthouse furnace additions as a means of dross conditioning, reducing oxides in the metal and releasing metal back into the bath by exothermic reaction. However these powder fluxes, generally added to the bath surface, were largely ineffective in cleaning the metal or reducing halides. Injection or addition to the solid charge during meltdown helped, but efficiency was still poor and emissions levels high.

The answer as pointed out in a landmark 1995 TMS paper by Béland et al (2), is to take advantage of the fact that it is the liquid magnesium chloride intermediate which is the critical rate controlling species in chlorine usage. They injected magnesium chloride based fluxes into aluminium alloy baths and obtained alkali removal rates and cleanliness improvements equivalent to or better than chlorine lance fluxing. At the same time emissions of chlorine, hydrochloric acid and particulates were substantially less than the emission levels experienced when using chlorine lance fluxing.

### Effective fluxes

Although injection of mixtures of powder fluxes containing magnesium chloride are quite effective, they suffer from three significant disadvantages. Firstly they contain very fine particles and dust which can potentially lead to emissions in handling and usage. Secondly they have a melting range rather than a single melting point, which is related to the individual components of the powder mix. Thirdly the magnesium chloride powder contained is very hygroscopic and powder mixes containing it pick up moisture quite rapidly, especially when exposed to humid, warm atmospheres.

The solution to these problems associated with powder fluxes containing magnesium



3 Typical sodium removal rate by a eutectic  $MgCl_2/KCl$  fused flux.

chloride and potassium chloride was to constitute them together as a single fused entity.

(1) Using a special fusion process, products were initially manufactured to coincide with two eutectic compositions on the magnesium chloride / potassium chloride binary phase diagram. One product coincided with the 60/40 eutectic, and another with the 40/60 eutectic. Both products can actually be regarded as synthetic anhydrous carnalite. They have single sharp melting points, below  $470^\circ C$ , and are free from fluorides, sodium and dust. They are very much less hygroscopic than mixtures containing magnesium chloride powder.

Both of these eutectic compositions were proven to be effective at removing alkalis and inclusions, but it was also thought important to know whether there were other eutectics and compounds in the system that might be of interest.

### The third eutectic

Studies into the phase equilibria of  $MgCl_2$  and  $KCl$  by Ditzel (3) predicted a system with three eutectics and two compounds, but with the absence of a peritectic and eutectoid. The positions of the two commonly referred to eutectics, corresponding to 55.5% mole and 36.5% mole respectively, are shown in Figure 1 plus a third eutectic occurring at 31.5% mole, later confirmed by thermal analysis work carried out by Seifert and Eubach.

Commercial products became accepted based on the three eutectics with magnesium chloride contents ranging from the slightly hypo-eutectic 25% by weight up to the hyper-eutectic 75% by weight. Laboratory and field test data comprising sodium removal measurements and Prefil testing confirmed that products with 40 wt %  $MgCl_2$  and 25% wt %  $MgCl_2$  provided equal alkali and inclusion removal performance to compositions corresponding to the first eutectic at 65 wt %  $MgCl_2$ .

The accepted explanation for this observation is that the amount of  $MgCl_2$  applied in practice is currently an order of magnitude higher than that required for stoichiometric removal of Na, Ca and non-metallic inclusions. This is a consequence of the need to achieve an adequate distribution of a relatively small

amount of flux in the aluminium melt. Thus the concentration of  $MgCl_2$  in the individual salt droplets, providing that it is always greater than that required to satisfy the reaction, has little influence on the reaction taking place.

### Partial substitution of KCl

The major cost factor in the production of fused refining fluxes is raw materials and in particular the cost of potassium chloride. This first became an issue in 2008/2009 as demand for potash for world food production and bio-fuels increased and gave an impetus to an MQP programme aimed at developing an alternative flux where the potassium chloride was partially replaced with sodium chloride.

To enable partial substitution of  $KCl$  with  $NaCl$  (6), a composition corresponding to the ternary eutectic in the  $MgCl_2$ ,  $KCl$ ,  $NaCl$  system was produced, characterised in laboratory testing, and trialled on a production scale in a large casthouse in Europe. The results confirmed there were no adverse effects from the ternary addition of up to 25%  $NaCl$  to an  $MgCl_2/KCl$  binary composition in terms of viscosity and melting characteristics of the flux, and the casthouse results showed a satisfactory performance in terms of sodium removal compared with standard  $MgCl_2/KCl$  fluxes.

### Alkali removal mechanism

The rate controlling step in the alkali removal process in molten aluminium by refining fluxes is believed to be transfer across the liquid salt droplet- molten aluminium interface (Figure 2) with the reaction with magnesium chloride having little effect.

It is known that certain active additives, particularly alkaline earth metal fluorides, have a strong effect in reducing interfacial tension between liquid salt droplets and molten aluminium alloys, leading to a reduction in droplet size and improved transfer across the salt droplet/ melt interface. MQP therefore undertook research into the effect of fluorides in magnesium chloride based fused fluxes on inclusion removal rates. It was found in laboratory and casthouse tests that a very small amount of calcium fluoride added to a 25%  $MgCl_2/KCl$  flux leads to a significant increase



in the inclusion and alkali removal performance over and above that of the other eutectic compositions tested.

The mechanism by which this is achieved is believed to be the effect of minute quantities of fluorine on the salt droplet interfacial tension (4) leading to a decrease in stable droplet diameter and improved transfer across the salt droplet/ melt interface.

So referring back to the question “Which composition of fused refining flux is the most efficient?”, the answer is that all three of the standard eutectic fused  $\text{MgCl}_2/\text{KCl}$  fluxes and the  $\text{MgCl}_2/\text{KCl}$  eutectic fused fluxes with partial substitution by  $\text{NaCl}$  are intrinsically equally effective in removing halides and inclusions from liquid aluminium. This is because the basic thermodynamics are the same irrespective of the  $\text{MgCl}_2$  content. However, a more effective flux is produced by adding a small quantity of calcium fluoride to an  $\text{MgCl}_2/\text{KCl}$  fused flux, because although the basic thermodynamics are unchanged the fluoride addition favourably changes the reaction kinetics.

### Reaction kinetics

In studying the removal of sodium during a melt treatment, such as with a fused eutectic  $\text{MgCl}_2/\text{KCl}$  fused flux, samples are taken at regular intervals and sodium content measured. The results are then plotted, as in Figure 3, to illustrate a reaction which is progressively taking place to reduce the melt sodium content. This sodium reduction by the fused flux can be regarded in thermodynamics as a first order chemical reaction and can accurately be expressed by the following equation:

$$[\text{Na}]_t = [\text{Na}]_0 \text{Exp} (-K \times t)$$

Where:

$[\text{Na}]_t$  = Concentration of Na at time t

$[\text{Na}]_0$  = Initial concentration of Na

and K= The reaction Kinetic Index.

If it follows that all such reactions where sodium is being reduced by the action of  $\text{MgCl}_2$  containing fluxes or chlorine gas can be described by a first order reaction equation, then it follows that the reactions can be compared solely in terms of their reaction kinetic index. In other words the kinetic index is a quantitative measure of the effectiveness of the sodium reduction process being examined.

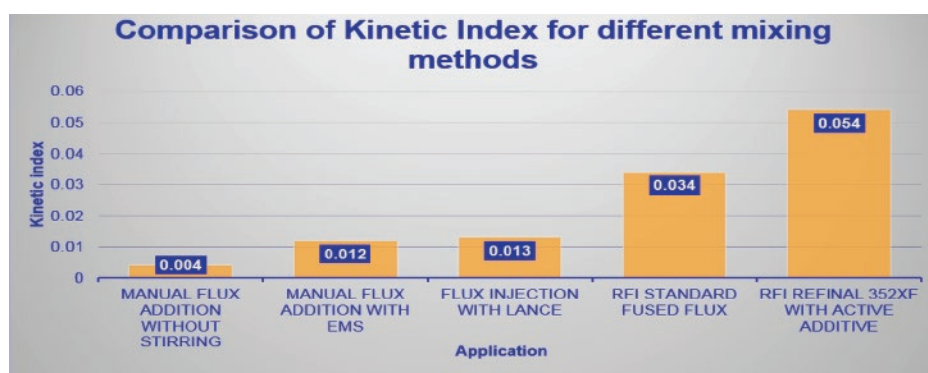
Reverting back to the finding that the effectiveness of eutectic  $\text{MgCl}_2/\text{KCl}$  fused fluxes in reducing sodium is enhanced by the addition of a small amount of fluoride, it is possible to quantify the improvement by measuring reaction kinetics. Testing carried out at a smelter casthouse applying fused flux through an RFI on an 85t furnace casting 1xxx alloy showed that the kinetic index was 0.0339 for a eutectic  $\text{MgCl}_2/\text{KCl}$  flux but increased to 0.0523 for the same flux with a 1% fluoride addition, i.e. a 54% improvement in sodium reduction efficiency.

### Addition methods

As already mentioned a lot of attention was originally given to means of increasing chlorine gas efficiency. These efforts focused



4 STAS rotary flux injector (RFI).



5 Comparison of kinetic index for different mixing methods.

on reducing gas bubble size and enhancing gas bubble distribution using improved methods of addition including multi lance systems, lances with porous nozzles, porous plugs installed in furnace floors, subsurface metal pumping and systems with rotors and impellers.

Similarly much work has since been carried out on means of increasing the efficiency of fused refining fluxes by using different addition techniques including those listed above.

In today's industrial casthouse practice around the world, fused refining fluxes are being added to furnaces in a number of different ways. These include:

- Throwing the flux in bags onto the melt surface with or without stirring
- Injecting the flux below the melt surface with a hand held lance
- Injecting the flux below the melt surface using an impeller with a spinning head rotor system, such as the STAS rotary flux injector (RFI) shown in Figure 4.

A substantial amount of information and data on the relative effectiveness of these addition methods has been developed and published over the last few years (5). The uniform conclusion is that short diffusion distances between the reacting species greatly facilitate the sodium reduction process. Diffusion is controlled by the salt-melt interfacial area, and alkali removal kinetics are highly dependent on droplet size in the reaction zone. Droplet size is influenced by shear stress. This is reflected in the kinetic indices obtained from adding  $\text{MgCl}_2/\text{KCl}$  fused fluxes using different methods as shown in Figure 5.

Rotary flux injection by an RFI is more efficient and more controlled than manual addition with or without stirring, or lance injection, and as indicated by the kinetic

indices, the most efficient process for removing sodium. The highest kinetic index as shown in Figure 5 is obtained when using an RFI to add a eutectic  $\text{MgCl}_2/\text{KCl}$  fused flux containing an active fluoride.

It is important to be aware that although an RFI is the most efficient method available to add fused fluxes, it is necessary for the operation of the RFI to be optimised to achieve maximum effectiveness. Introduction of flux through the RFI rotor bore is the ideal way of addition, and an entry angle of 45 degrees into the melt is significantly more efficient than 30 degrees. Wall effects are important and impeller rotation clockwise against the furnace far wall is the most effective. The difference in efficiency between the worst and the best practice is significant and reaction times can be reduced by up to 45% by optimisation.

Another major benefit of using the RFI for fused flux additions is that the amount of aluminium dross generated during the reaction is much less than with other addition methods, as described in an informative TMS paper by Hydro Aluminium Rolled Products. (5)

### Questions answered

It was observed at the start of this article that fused refining fluxes have come a long way since their first introduction into casthouse technology. The understanding of how they function has also come a long way, which means that the answers to the questions posed concerning the most effective formulations and most effective addition method can now be answered in a well-informed way.

The answer to “Which composition of fused refining flux is the most efficient?” is that all the three eutectic compositions of  $\text{MgCl}_2/\text{KCl}$  fused flux are equally effective as sodium

reducers because the reaction is not dependent on the amount of  $MgCl_2$  present and the reaction kinetics are the same. A more efficient fused  $MgCl_2/KCl$  is obtained when a small amount of fluoride is added to the flux because it favourably alters the reaction kinetics and increases the rate removal constant.

The answer to the question "What is the optimum method of adding fused refining fluxes?" is readily identified by comparing the kinetic indices obtained when using different addition methods. The highest rate removal constants obtained and therefore the most efficient method of adding fused  $MgCl_2/KCl$  fluxes are when using an RFI. It is important that the RFI is operating in best practice mode. Apart from giving the best sodium removal there is an added major benefit to the casthouse of a very low generation of dross from the treatment due to the low turbulence of the impeller system.

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MQP Limited was formed in the year 2000 by John Courtenay, the current Managing Director and is based in the UK and operates on a global basis through a network of consultants and distributors.

The management team at MQP consists of accomplished professionals in aluminium technology and complementary disciplines.



MQP at Aluminium Düsseldorf last year.

Several team members, like John Courtenay, were previously employed in senior roles within the Foseco organisation namely Michael Bryant, Marketing Manager, Richard Dean, European and Middle East Sales Manager, Barry Lightfoot, UK Sales Manager and MQP's Finance Director, Clive Johnson.

Richard Courtenay, is MQP Operations Director, responsible for day to day running of the business. Dr Rein Vainik, the MQP Technical Manager, based in Sweden, obtained his PhD at Stockholm University.

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