

A fused magnesium chloride containing refining flux

The performance of a fused magnesium chloride-potassium chloride refining flux, in a paper presented to the 2012 TMS Conference by **John Courtenay***, **Michael Bryant****, MQP, reviews.

Fused magnesium chloride-potassium chloride refining fluxes are used as an environmentally acceptable means for removing alkali metals and oxides from molten aluminium than injection of chlorine gas.

These refining fluxes¹ were initially based on the classic binary system magnesium chloride-potassium chloride, which exhibits two low melting point eutectics, one at about 55.5% mole magnesium chloride and another at 36.5% mole magnesium chloride.

Later a revised binary diagram² was accepted that showed three eutectics with the two 'classic' eutectics and a third eutectic occurring at 31% mole.

Today, commercial products are supplied based on all three eutectics with magnesium chloride contents ranging from the slightly hypo eutectic 25% by weight up to the hyper eutectic 75% by weight. In addition, a product with enhanced efficiency, containing 25% magnesium chloride with potassium chloride and a small amount of alkali metal fluoride is also available.

Economics

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. Prices are starting once again to move upwards (**Fig 1**).

The rising price of potassium chloride and the likelihood of further increases has given impetus to a programme aimed at developing an alternative flux where the potassium chloride is partially replaced with sodium chloride.

This paper summarises the results of a thermodynamic study together with laboratory measurement of viscosity, and differential thermal analysis and sodium removal casthouse trials of a flux product where 25% of sodium chloride is introduced to replace potassium chloride.

Developing a new flux

In constituting a new flux it was important to understand some of the thinking that originally went into devising a refining flux.

Two conventional wisdoms were in place. The first held that performance in terms of sodium removal would be higher as the percentage of magnesium chloride increased. Second, that the amount of sodium chloride permitted in the product must be below 1%. In reality neither of these beliefs is correct as demonstrated by the theoretical arguments and evidence from the series of results and investigations presented below.

Influence of % magnesium chloride on efficiency

Test data was collected under controlled conditions at a number of casthouses. Comparisons were made between a 40% MgCl₂ and a 60-65% MgCl₂

containing product applied manually in two identical 50t furnaces at a smelter casting 5xxx alloy.

Results showed the 40% MgCl₂ product performed slightly better than the 60-65% product. In a separate series of tests, results were obtained from production use for a 40% MgCl₂ product and a 25% MgCl₂ product at a smelter casthouse. The average % sodium removal for the 40% MgCl₂ product was 76% while the result for the 25% MgCl₂ product was 77% sodium removal.

More recently a study of MgCl₂ fused salt reagents applied in the salt flux ACD, showed there was no significant difference in alkali removal efficiency with a 60% MgCl₂ or a 75% containing composition. Further confirmation came from results of an investigation carried out at the Alcoa Technical Centre³ showing that varying the % MgCl₂ between 10% and 90% had no influence on the rate of sodium removal (**Fig 2**).

All the evidence from practical evaluations and published research from different sources shows alkali removal efficiency is not influenced by the % of MgCl₂ in the fused salt, contrary to some widely held views.

In an explanation of this Dietze² has proposed the concentration of MgCl₂ in the molten salt droplet has little influence on the kinetics because the rate of salt addition applied in practise is ten times that needed to satisfy the requirement for stoichiometric reaction and therefore there is always an excess present.

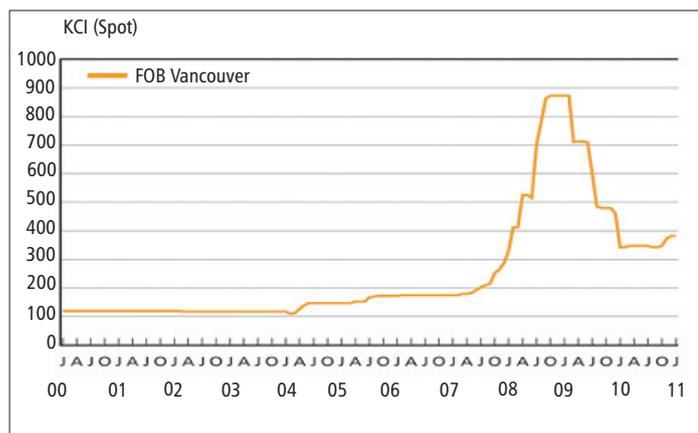


Fig 1 Price \$/t for KCl from 2000-2011

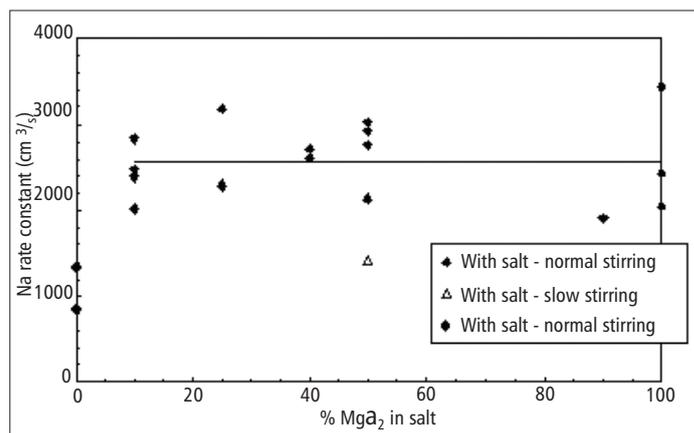


Fig 2 Effect of Magnesium Chloride content in flux on Sodium removal

Influence of sodium chloride on sodium removal

In terms of cost NaCl would be welcome as a substitute or partial substitute for KCl in fused salts.

The reaction $MgCl_2 + 2 Na = 2NaCl + Mg$ can be considered to move strongly to the right. If this was not the case then the sodium removal process by $MgCl_2$ would not be practically effective. Ellingham diagrams show the high stability of NaCl with respect to $MgCl_2$. Therefore it was anticipated there would be no increase in sodium in the aluminium if quantities of NaCl were introduced into the flux composition.

The above hypothesis was tested by thermodynamic modelling at IME Aachen⁴, under Prof Friedrich.

FactSage databases were used to investigate the effect of NaCl content in Refinal on the reaction between $MgCl_2$ in Refinal and Na from the aluminium melt.

In terms of selecting the product, composition consideration was given to selecting a ternary composition, with an appropriate addition of NaCl to an existing proven formulation (Fig 3).

The eutectic low melting point area of the system can be seen on the diagram and the composition selected was:

- Magnesium Chloride 37-42%
- Potassium Chloride 21-26%
- Sodium Chloride 27-32%

The thermodynamic study was based on the following conditions:

A standard salt flux composition with 35% $MgCl_2$ + 65% KCl. Additions of 1%; 5%; 10% or 25% NaCl into the flux.

Starting with an initial Na content of 30ppm or 10ppm in the melt and targeting a final Na content of 10ppm or 2ppm respectively.

Application of 0.05 – 0.1 % Refinal based on melt weight. Melt temperatures of 700 and 750°C.

The modelling results showed that after completion there was no sodium remaining in the melt. Therefore it can be concluded that up to 25% NaCl can be substituted for KCl in Refinal 350 and Refinal 352XF without effect on the residual Na content after treatment.

Given that KCl plays no active part in the alkali removal reaction, substitution or partial substitution with an alternative stable alkali metal chloride should not influence the alkali removal kinetic.

Viscosity measurements

The objective of the work was to get a better understanding of the variation in viscosity with temperature and composition of the flux with a view to connecting this with performance in molten aluminium.

In the context of performance it has been proposed that the beneficial influence of fluoride additions to the flux, as in Refinal 352XF, is due to its propensity to reduce interfacial surface tension.

This leads to the formation of smaller diameter liquid salt flux droplets giving rise to an increase in the surface area for reaction. Prof Friedrich believes the presence of F ions in Refinal 352 is the reason for the better performance due to F ions reacting with Na better than Cl ions.

The following compositions were studied in (Table 1):

Viscosity was measured by oscylographic viscometer in conjunction with density measurement, and confirmed with a high degree of probability the following initial conclusions:

Refinal 352XF has a higher viscosity than Refinal 350 or 555XF.

Refinal 352XF has a higher change-rate of the viscosity than Refinal 350 or 555XF. The viscosity of all fluxes becomes equal > 600°C. The precision of the absolute values is difficult to estimate.

Since the viscosities, although quite different at low temperatures, become equal at >600°C it can be determined there is no negative effect from the addition of NaCl as a ternary addition to the standard binary product in terms of viscosity.

Differential thermal analysis

DTA measurement was carried out on the ternary composition, Refinal 555XF and the result showed a sharp peak at 402.7°C in the heating up cycle and 405.6°C when cooling down. The sharpness of the peak indicates eutectic melting (Fig 4).

This data was then compared with the DTA curve for a typical binary composition, Refinal 350 which showed a similar sharp peak at 438.8°C.

The conclusion was that both products exhibited sharp eutectic melting points with the ternary composition having a lower melting point by 30°C and that there was no negative effect from the addition of NaCl as a ternary addition in terms of melting characteristics.

Trials in a casthouse

With the favourable outcome of thermodynamic calculations and

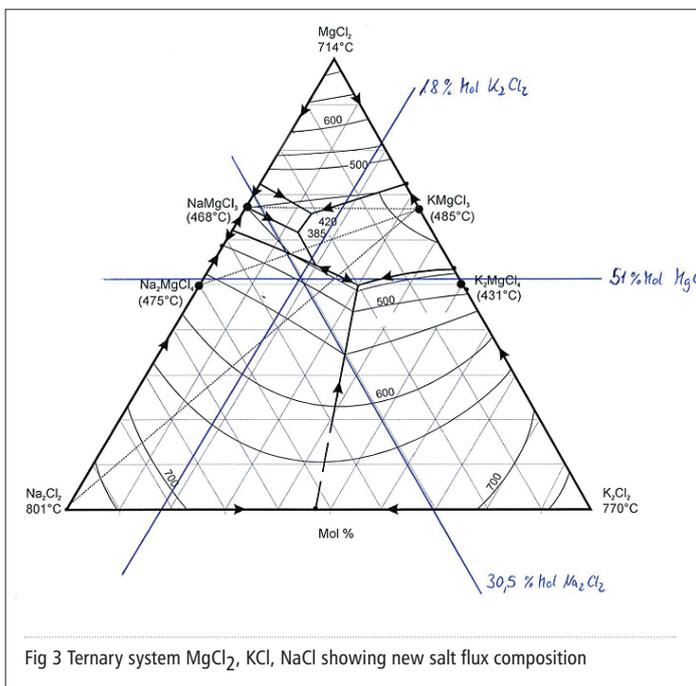


Fig 3 Ternary system $MgCl_2$, KCl, NaCl showing new salt flux composition

Product	$MgCl_2$ %	KCl %	NaCl %	CaF_2 %
Refinal 350	30-35	60-65	1-3	
Refinal 352XF	30-35	60-65	1-3	1-3
Refinal 555XF	36-41	21-26	26-31	1-3
Refinal 750	40-45		55-60	

Table 1 Compositions

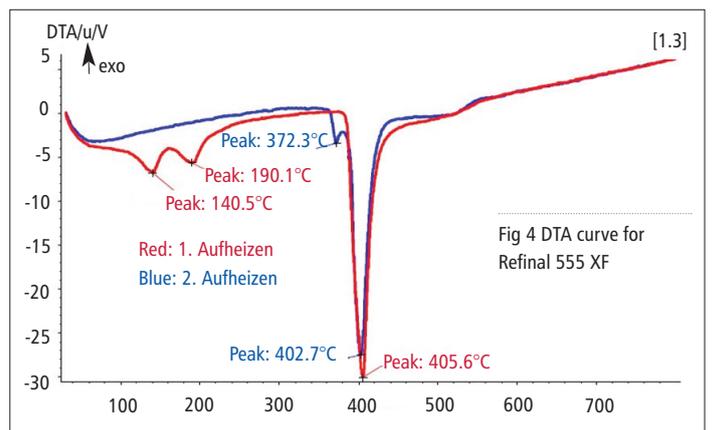


Fig 4 DTA curve for Refinal 555 XF

laboratory tests it was decided to proceed with full-scale casthouse trials at a major casthouse in Europe.

Trials were carried out by substituting the trial product, Refinal 555XF into standard practice and comparing results to those obtained with standard practice using a 35% MgCl₂ – 65% KCl salt flux.

During 87 furnace preparations an average Na-level of 6.5ppm at first time of batching was achieved.

The conclusion was the results were comparable to their standard practice of applying Refinal 350.

Subsequently Refinal 555XF has been adopted into regular production with over 100kt of aluminium having been successfully produced.

Summing up

Not for the first time widely held beliefs have been challenged by technical investigation.

In the case of the effect of MgCl₂ content reaction kinetics are of overriding importance and simply matching the stoichiometrically required amount does not ensure that the reaction goes to completion.

In the case of the effect of NaCl additions, here the thermodynamics confirm that, irrespective of reaction kinetic considerations, NaCl cannot be

reduced again to Na. Furthermore laboratory characterisation of the ternary composition has confirmed that there is no adverse effect from the NaCl addition in terms of both the viscosity and melting characteristics of the product.

Conclusions

– A fundamental study involving thermodynamic modelling databases has demonstrated it should be possible to add up to 25% of NaCl to a MgCl₂ – KCl salt flux by substituting KCl without any effect on the residual Na content in the treated aluminium melt.

– A composition, corresponding to the ternary eutectic in the MgCl₂, KCl, NaCl system has been produced, characterised in laboratory testing and trialled on a production scale in a large casthouse in Europe.

– The results of the laboratory characterisation confirmed there were no adverse effects from the ternary addition of up to 25% NaCl to a MgCl₂ – KCl binary composition in terms of viscosity and melting characteristics.

– The casthouse results confirmed the thermodynamic prediction and showed a satisfactory performance in terms of sodium removal, compared with standard practice, over a monitored series of 87 production casts. ■

Acknowledgement

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