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Beliefs about fused magnesium chloride fluxes questioned

Chlorine gas has largely been replaced by magnesium chloride fluxes as a means of reducing alkalis and oxides from aluminium melts. Two widely held beliefs concerning the composition and effects of these fused fluxes have developed in recent years and this article explains why they should be questioned*.

Over the last fifteen years fused magnesium chloride fluxes have largely replaced chlorine gas as a means of reducing alkalis and oxides from molten aluminium. The change, hastened by environmental considerations, began after publication of an article by Beland in 1995. This described a refining flux based on the binary system magnesium chloride-potassium chloride, where a magnesium chloride intermediate was the rate controlling species active in the removal of alkalis.

Refining fluxes were at first based on the binary magnesium chloride-potassium chloride system with two low melting point eutectics at about 55 and 36 mole magnesium chloride. Later a revised binary diagram was accepted as a more accurate description of the magnesium chloride system with a third eutectic occurring at 31 mole. Accordingly, 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.

Two widely held beliefs, have developed about fused magnesium chloride fluxes.

**MgCl** percentage

The first belief is that the performance in terms of efficiency of sodium removal is directly related to the percentage of magnesium chloride in the fused flux. It is well established that in fused magnesium chloride-potassium chloride fluxes magnesium chloride is the active component participating in the reaction:

\[ \text{MgCl}_2 + 2 \text{Na} \rightarrow 2 \text{NaCl} + \text{Mg} \]

KCl on the other hand plays no part because as KCl is more stable than NaCl, having a higher free energy of formation and based on this the belief existed that the performance in terms of efficiency of sodium removal should be higher the higher the percentage of magnesium chloride in the product. In a number of separate series of full scale casthouse trials involving direct comparisons under the same conditions it was demonstrated that the performance of 60%, 40% and 25% MgCl\(_2\) flux compositions all produce equivalent results. Final confirmation came when David de Young published the results of an investigation carried out at the Alcoa Technical Centre into the same subject and showed that varying the % MgCl\(_2\) between 10% and 90% in fused magnesium chloride-potassium chloride fluxes had no influence on the rate of sodium removal as shown in fig.1.

In explanation of this Dietze has proposed that the concentration of MgCl\(_2\) in the molten salt droplet has little influence on the reaction kinetics because the rate of salt addition applied is ten times that needed to satisfy the requirement for stoichiometric reaction. Of far greater importance are the kinetic factors and therefore in order to achieve an adequate distribution of a relatively small amount of flux in the aluminium melt it is necessary to add considerably more than the required stoichiometric amount. 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 kinetic.

The conclusion from such comprehensive trials and examination of reaction kinetics is that the performance in terms of efficiency of sodium removal is not related to the percentage of magnesium chloride in the fused flux.

**Sodium chloride content**

The second widely held belief is that the amount of sodium chloride permitted in fused salt products for sodium removal from aluminium melts should be restricted below 1 per cent. When fused salt fluxes were first introduced potassium chloride was a suitable low cost material to combine with the more expensive MgCl\(_2\) component to provide a low melting point eutectic. However, this dramatically changed with the price of KCl increasing by more than 350% up to a peak of nearly US$ 900 per tonne in July 2009 due to global demand for potash fertiliser for the production of grain crops and biofuels. It seems inevitable that KCl prices will rise again resulting in cost increases for both producers and users of fused salts. This has led to a reassessment on the possible role of NaCl in fused salts.

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*Article based on a paper being presented by MQP at the 2011 Australian Asian Pacific Aluminium Casthouse Technology Conference, Melbourne.*
Thermserve billet heater for Vimetco in Slatina

Thermserve Limited, based at Telford in the United Kingdom have recently moved to larger premises which allows the company to not only design equipment and machinery but to also engineer and build. The company recently was awarded the Queen’s Award for Enterprise.

Vimetco Extrusion SRL, with their headquarters in Slatina, in Romania, is a subsidiary of Vimetco-ALRO S.A. which is one of the largest smelters in Europe. The smelter has been operating since 2006 and Vimetco came to Thermserve for a 2500Kg/hr 178mm billet heating furnace and hot log saw with specific performance requirements concerning throughput and fuel consumption. The equipment is currently undergoing Factory Acceptance Tests in the Thermserve fabrication shop, in the United Kingdom.

Thermserve log and billet ovens are manufactured in their own, well equipped, fabrication facility. For ease of construction, maintenance and to accommodate potential extensions to the service requirements Thermserve use modular design techniques. For this reason, the sectional mild steel casing will have readily removable top sections to access the pre cast refractory blocks and roller conveyor system which transport the log through the furnace.

These steel and precast refractory sections are designed to be an ideal substitute or partial substitute for KCl. The reaction, MgCl₂ + 2 Na = 2NaCl + Mg, can be considered to move strongly to the right which means that sodium removal by MgCl₂ is practically effective. Ellingham diagrams confirm the high stability of NaCl with respect to MgCl₂. It can be anticipated that in practice 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 modeling of the reaction. A ternary product composition was selected, with an appropriate addition of NaCl to an existing proven formula.

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Sensible beliefs

It is not surprising that it was believed that the performance of a flux might be proportional to MgCl₂ content. Nor is it surprising that it was believed that adding NaCl to a flux might lead to Na pick-up, when the objective is to remove Na. Nonetheless impartial scientific investigation has confirmed otherwise in both cases. In the case of the effect of MgCl₂, the reaction kinetics are of overriding importance and not the proportion of MgCl₂, in the product. In the case of the effect of NaCl addition, the thermodynamics confirm that irrespective of kinetic considerations NaCl cannot be reduced again to Na in the reaction system involved.

Bibliography

[3] Private communication with Dr. A. Dietze & TU Clausthal

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Thermserve main panel also houses the following:-

- Automatic temperature control for each of the fired zones of the furnace.
- Control of all log movement sequencing from storage through the heater.
- Integration of furnace and handling equipment.
- An audible alarm that will sound in the event of abnormal temperature condition in any zone.
- Full integration of a Thermserve Hot Saw

In this case, Allen Bradley PLC equipment, is specified but similar equipment by other manufacturers can be utilised if requested.

Thermserve’s in house panel shop to optimise the temperature and to manage the in feed system with the following features:-

- Interlocks with the cubicle door.
- Direct on-line motor starters, overloads, fuses, etc.
- Flame failure relay and ignition units for the fired zones.
- * HIMI – Push buttons, labels, indicator lights, etc., for control supply and emergency stops.
- The panel is fully wired to terminal strips and shop tested before despatch.

The equipment for this project has been designed and manufactured to relevant British Standards (or European Standards EN/ISO - as appropriate)

To facilitate an efficient installation the log heater is currently fully assembled in the Thermserve works and will be dismantled only to the extent necessary for efficient and safe transportation to site.

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