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A NEW FUSED MAGNESIUM CHLORIDE CONTAINING REFINING FLUX BASED ON A TERNARY SYSTEM

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Abstract

The major cost factor in the production of fused refining fluxes is raw materials and in particular the cost of potassium chloride, which because of its role in fertilizer production has been subject to large price increases in the period 2008 – 2009, having risen by more than 350%. As demand for potash for world food production and bio-fuels is increasing again with the recovery in the global economy further price rises are expected, with the price having risen already by 43% from November 2010 to July 2011. A program of work has been undertaken to develop an alternative flux based on a ternary system comprising magnesium chloride and potassium chloride; where the potassium chloride is partially replaced with sodium chloride. The results of a study of the thermodynamics together with laboratory measurement of viscosity, and differential thermal analysis are presented.

Introduction

In 1995 Beland et al [1] described the role of the liquid magnesium chloride intermediate as the rate controlling species in removal of alkalis by chlorine fluxing. This led to the development and adoption of the alternative cleaning process of solid flux injection based around using fused magnesium chloride – potassium chloride reagent together with a newly developed rotary flux injection technique referred to as RFI. The latter process was described in detail in the 1998 paper by Beland et al [2]

Fused magnesium chloride-potassium chloride refining fluxes have therefore become widely adopted as a more environmentally acceptable means for removing alkali metals and oxides from molten aluminium than injection of chlorine gas. Refining fluxes were initially designed based on the binary system magnesium chloride-potassium chloride which exhibits two low melting point eutectics; one at about 55.5% mole and one at 36.5% mole % magnesium chloride. The understanding at the time was based on reference to the binary system according to Asinov [3] which shows only two eutectics and a peritectic. Later a revised binary diagram according to Dietze [4] was accepted as a more accurate description of the magnesium chloride system, and this showed three eutectics, the two "classic" eutectics, one at 55.5% mole and the second at 36.5% mole with in addition a third eutectic occurring at 31% mole. Accordingly commercial products have been developed and supplied based on all three eutectics with magnesium chloride contents ranging from the slightly hypo eutectic 25% by weight up [5] to the hyper eutectic 75% by weight [6]

The currently accepted binary diagram according to Dietze is shown in figure 1.

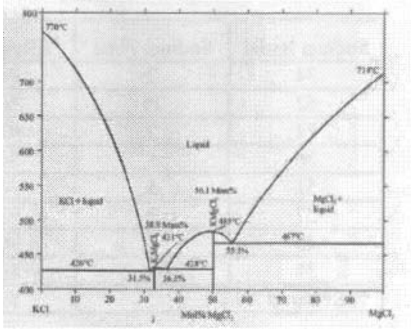


Figure 1 $MgCl_2$ – KCl binary diagram, Dietze [4]

In a further development products containing 25% magnesium chloride as a base together with potassium chloride and a small addition of an alkali metal fluoride have shown that a significant increase in efficiency as measured by the kinetic index can be obtained [5]

The influence of %$MgCl_2$ on efficiency

In presenting the development of a new composition it is important to trace the steps along the way which lead up to the new thinking that allowed such a development to take place. In considering the early development it is important to understand the influence of the % magnesium chloride on the efficiency of the alkali removal process. With initially two then later three eutectic compositions recognised in the binary system which will allow a fused composition to melt uniformly at a single and satisfactorily low melting point in the range of 400 – 450°C the question is which would provide the best base?

Beland [1] had established that magnesium chloride was the active component in the fused flux participating in the reaction:

$$MgCl_2 + 2\,Na = 2\,NaCl + Mg$$

KCl on the other hand plays no part because as is illustrated in the Ellingham diagram in Figure 5 KCl is more stable than NaCl, having a higher free energy of formation.

Accordingly conventional wisdom held that the performance in terms of efficiency of sodium removal should be higher the higher the % of magnesium chloride in the product. This is one of two widely held beliefs, the second being that the amount of sodium chloride permitted in the product should be restricted below 1%

and it will be demonstrated in this paper that in both cases surprisingly perhaps, these beliefs were not correct.

Field test data on influence of $MgCl_2$ content on sodium removal

Test data collected under carefully monitored and controlled conditions at a number of casthouses is presented as follows:

Tables 1&2 show the comparisons made between a 40%$MgCl_2$ and a 60-65% $MgCl_2$ containing product applied manually in two identical 50 tonne furnaces at a smelter casting 5xxx alloy.

Sodium Initial	Sodium Final	% Removal
34	2	94
62	15	76
24	2	92
36	5	86
51	5	90
27	2	93
40	4	90
34	4	88
% Removal Ave.		89

Table 1. A 40% $MgCl_2$ product manually applied in a 50 tonne furnace

Sodium Initial	Sodium Final	% Removal
39	14	64
46	14	70
22	2	91
25	3	88
35	7	80
36	4	89
34	3	91
42	7	83
% Removal Ave.		82

Table 2. A 60-65% $MgCl_2$ product manually applied in a 50 tonne furnace

The results show that on average the 40% $MgCl_2$ product performed slightly better than the 60-65% product.

In a separate series of tests, results were obtained from production use for 40% $MgCl_2$ product and 25% $MgCl_2$ product at a smelter casthouse. Application was by rotary flux injection via an RFI unit adding 20kg of material in a 23 minute stirring cycle. This equates to an application rate of 0.30 kg/tonne

The average % sodium removal for the first test series with 40% $MgCl_2$ product was 76% whilst the results for the second series with 25% $MgCl_2$ product gave a 77% removal. In each case a series of sodium samples were taken every 5 minutes to enable the rate curve to be plotted to calculate the kinetic index and therefore the results are based on a minimum of 25 sodium analyses in each case.

Thus it was concluded that both the 40% $MgCl_2$ and 25% $MgCl_2$ compositions were equivalent in alkali removal performance.

Therefore through a series of casthouse trials making direct comparisons under the same conditions it was demonstrated that performance of 60% 40% and 25% $MgCl_2$ containing compositions all produced equivalent results.

This was further confirmed in 2003 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% had no influence on the rate of sodium removal [7]. This is shown below in fig.2

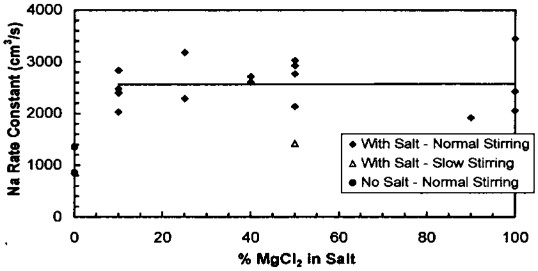


Figure 2 Effect of % $MgCl_2$ on removal efficiency, De Young [7].

More recently this question was re visited by Robichaud et al [6] when investigating the performance of $MgCl_2$ fused salt reagents applied in the Salt flux ACD, showing that there is no significant difference in alkali removal efficiency with a 60% $MgCl_2$ and 75% containing compositions.

So, the evidence from practical evaluations and published research from different sources is clearly that alkali removal efficiency is not influenced by the % of $MgCl_2$ in the fused salt contrary to the widely held view at the time.

In explanation of this Dietze [4] has proposed that the concentration of $MgCl_2$ in the molten salt droplet has little influence on the kinetics because the rate of salt addition applied is ten times that needed to satisfy the requirement for stoichometric reaction. This can be illustrated as follows: typically 0.5kg of salt flux per tonne is added to remove 20-30 ppm of sodium. This equates to 500ppm of salt flux applied to remove 25ppm of sodium. An $MgCl_2$ content of 60% corresponds to 300 ppm and an $MgCl_2$ content of 25% corresponds to 125ppm and thus in either case there is an ample amount to complete the 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 stoichometric 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 influence of the presence of NaCl in $MgCl_2$ – KCl fused salts on Na removal efficiency

The second widely held belief that is now challenged is that the amount of sodium chloride permitted in the fused salt products should be restricted below 1%.

From the time that fused salt fluxes were introduced up until the peak of the long period of economic growth ending in July 2008 potassium chloride remained a suitable low cost material to combine with the more expensive $MgCl_2$ component to provide a low melting point eutectic. Technical grades of this material were available with low < 1% NaCl contents and therefore there was no driving force to challenge the general view.

However a trend started in 2007 that dramatically changed this picture with the price of KCl increasing by more than 350% up to a peak of nearly $900/tonne in July 2009 as illustrated in Fig. 3 below.

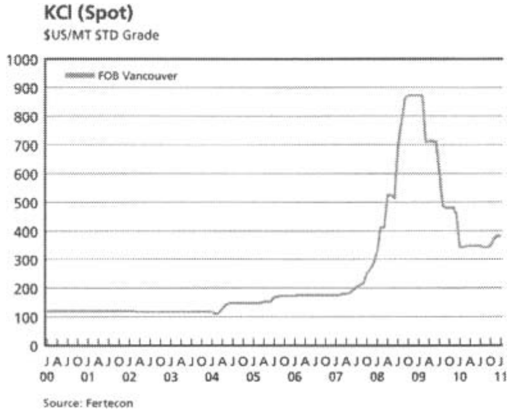


Figure 3 Price/t for KCl in USD from 2000-2011

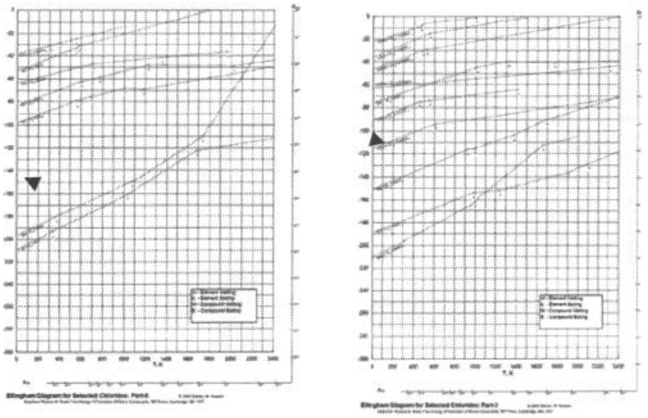
This trend is due to the increase in global demand for potash fertilizer for the production of grain crops and biofuels. Now that a recovery in the global economy is taking place the chart shows that KCl prices are starting to rise again and widespread inflation in global commodity prices is expected over the next few years. Therefore it seems likely that KCl prices may regain there former highs resulting in cost increases for both producers and users of fused salts.

This led to a review being undertaken on the role of NaCl in fused salts. NaCl would be very suitable as a substitute or partial substitute for KCl

$MgCl_2$ + 2 Na = 2NaCl + Mg

This reaction 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. The Ellingham diagrams in figure 4 show the stability of NaCl with respect to $MgCl_2$ and therefore it was anticipated that in practice there would be no increase in sodium in the aluminium if quantities of NaCl where introduced into the flux composition.

Figure 4 Ellingham diagrams for selected chlorides



Before proceeding with casthouse testing it was decided to test the above hypothesis by thermodynamic modeling of the reaction.
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 and with reference to the ternary diagram below;

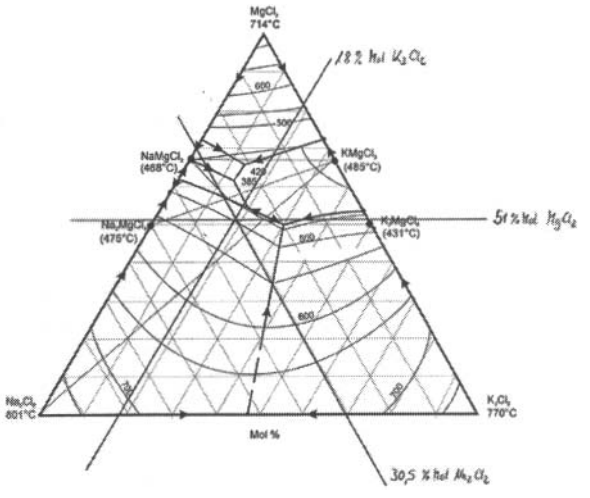


Figure 5 Ternary system $MgCl_2$ – KCl – NaCl showing new salt flux composition

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

Component	Min %	Max %
$MgCl_2$	37.0	42.0
KCl	21.0	26.0
NaCl	27.0	32.0

Table 3 Composition of ternary product (Refinal 555XF)

Results of a thermodynamic study undertaken at RWTH Aachen

A study was undertaken with IME Aachen, under Prof. Bernd Friedrich / Semiramis Akbari [8] and the following databases, Fact53, FTsalt and FSlite from FactSageTM 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 by thermodynamic modelling.

The investigation was carried out for the following conditions:

- Based on a standard salt flux composition with 35 % $MgCl_2$ + 65 % KCl
- with 1 %; 5 %; 10 % or 25 % NaCl addition in the flux
- Starting with an initial Na content of 30ppm or 10 ppm in the Aluminium and targeting a final Na content of 10ppm or 2 ppm respectively
- Application of 0,05 – 0,1 % REFINAL based on Al weight
- Two temperatures were considered; 700 and 750°C

The results of the study showed that in the two most severe conditions:

<u>Case 1</u> <u>30 ppm Na in Aluminium; 25 % NaCl in the salt flux; 750°C</u>

<u>Case 2</u> <u>30 ppm Na in Aluminium; 25 % NaCl in the salt flux; 700°C</u>

There is no sodium remaining in the melt after treatment and therefore it can be concluded on the basis of the thermodynamic calculations 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. Nonetheless FactSage does show that there is a very low equilibrium amount of Na in the metal as the %NaCl in the flux increases and that when 25% NaCl addition is exceeded this amount becomes greater than 0.02 ppm

Furthermore 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 Measurement at RWTH Aachen

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. Elsewhere [9] it has been proposed that the beneficial influence of fluoride additions to the flux where due to its propensity to reduce interfacial surface tension thus leading to the formation of smaller diameter liquid salt flux droplets in the melt giving rise to an increase in the surface area for reaction.
Prof. Friedrich commented that in his opinion the presence of F ions in Refinal 352 is the clear reason for the better performance. Because F is reacting with Na better than Cl

The following compositions were investigated:

Product	MgCl2 %	KCl %	NaCl %	CaF2 %
Refinal 350	30 - 35	60 - 65	1 - 3	-
Refinal 352 XF	30 - 35	60 - 65	1 - 3	1 - 3
Refinal 555 XF	36 - 41	21 - 26	26 - 31	1 - 3
Refinal 750 (trial)	40 - 45	-	55 - 60	-

Table 4 Compositions of products used in viscosity measurements

The viscosity has been measured by oscyllographic viscosimeter in conjunction with density measurement:
The results are compared with a viscosity measurement for molten NaCl as a reference value.

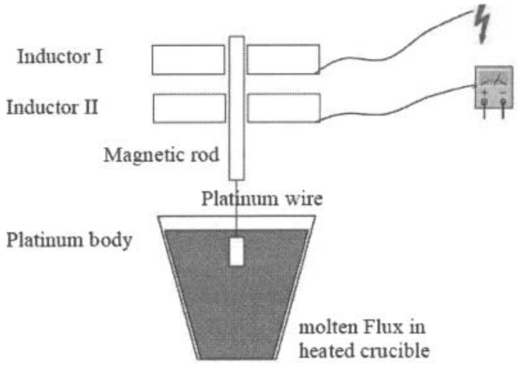


Figure 6 Oscyllographic viscometer

<u>Results</u>

The experiments 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 that there is no negative effect from the addition of NaCl as a ternary addition to the standard binary product in terms of viscosity. On the other hand when a binary product comprising MgCl2 and 55-60% NaCl, designated Refinal 750, was tested it proved to be impossible to make any measurements because a crust kept forming on the surface of the crucible preventing the magnetic rod from oscillating freely.

DTA measurement at RWTH Aachen

Differential thermal analysis 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.

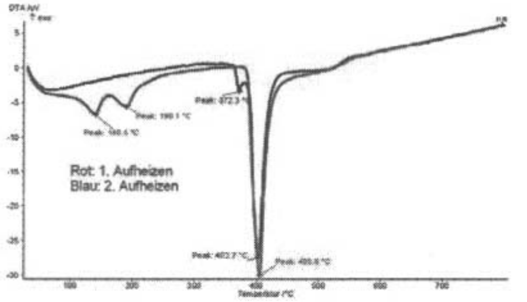


Figure 8 DTA curve for Refinal 555 XF

This data was then compared with the DTA curve for a typical binary composition, Refinal 350.

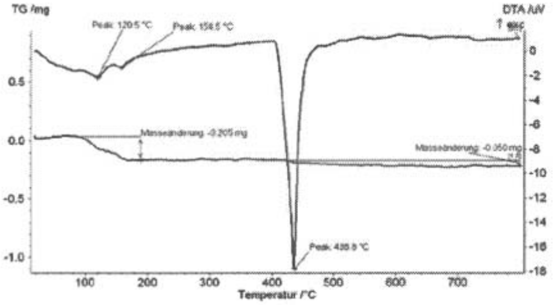


Figure 9 DTA curve for Refinal 350

The DTA curve for the binary composition shows a similarly sharp peak at 438.8°C indicating eutectic melting. This would appear to correspond to the third eutectic shown occurring at 31.5% mole or 38.9% mass in figure 1 after Dietze [4] allowing for the fact that the composition tested was a commercial composition using technical grade raw materials rather than pure reagents.

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

Results of practical trials in a casthouse

With the thermodynamic calculations and laboratory tests completed with the anticipated favourable outcome 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 practise then comparing the results to those obtained with standard practice using a 35% $MgCl_2$ – 65% KCl salt flux.

Over a total of 87 furnace preparations an average Na-level of 6.5 ppm at first time of batching was achieved. The conclusion was that the results were comparable to the ones achieved with their standard practice of applying Refinal 350. Subsequently Refinal 555XF has been adopted in regular production since May of 2011 with over 100,000 tonnes of aluminium having been cast at the time of writing.

Discussion

Not for the first time widely held beliefs have been challenged by technical investigation. It is not surprising that it was thought that the performance of a flux might be proportional to $MgCl_2$ content nor that adding NaCl to such a product when the objective is to remove Na might lead to Na pick up since this would intuitively be so, nonetheless impartial scientific investigation has confirmed otherwise. In the case of the effect of $MgCl_2$ content it turns out in practise that the kinetics are of overriding importance and simply matching the stoichometrically required amount does not ensure that the reaction goes to completion. In the case of the effect of NaCl addition, here the thermodynamics confirm that irrespective of kinetic considerations NaCl cannot be reduced again to Na in the reaction system investigated within the range of paramters studied. 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

1. A fundamental study involving thermodynamic modelling using the Fact53, FTsalt and FSlite from FactSageTM data bases has demonstrated that it should be possible to add up to 25% of NaCl to a $MgCl_2$ – KCl salt flux by substituting KCl without any effect on the residual Na content in the treated aluminium melt.
2. A composition, corresponding to the ternary eutectic in the $MgCl_2$ – KCl –NaCl system was selected, produced, characterised in laboratory testing and applied on a production scale in a large casthouse in Europe
3. The results the laboratory characterisation confirmed that 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.
4. The results confirmed the thermodynamic prediction and a satisfactory performance compared to standard practise was achieved over a monitored sample of 87 production casts in a large casthouse

Acknowledgement

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