# SUBSTITUTION OF CHLORINE AS A FURNACE ADDITION IN ALUMINIUM INDUSTRY CAST HOUSES BY FUSED REFINING AGENTS

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**Abstract**

Increasing demand for high metal quality places greater emphasis on casthouse furnace treatments. Many furnace treatment processes today still use chlorine but there is growing concern about the environmental impact of its use. Fused refining agents based on magnesium chloride are now being introduced into a number of casthouses world-wide as an effective means of achieving high quality metal with minimal emissions.
This paper looks at the background and environmental issues surrounding chlorine substitution and outlines experiences with the use of fused refining agents as a means of reducing alkaline metals and improving melt cleanliness.

Melt quality and environmental issues are today at the top of the agenda for an increasing number of aluminium casthouses worldwide. It is well established that whatever in line treatment systems are in place, melt quality begins in the furnace.
Treatment with chlorine, in the melting or holding furnace, is a widely used and effective means of improving melt quality but there is growing concern about the environmental issues surrounding its use, including efforts by Greenpeace to link the use of chlorine with the production of dioxin.(1)
The use of chlorine in the casthouse has come under increasing scrutiny since the mid 1980's and today there is legislation and regulations in force in most industrialised countries concerning the use of chlorine. These seek to impose very low limits on emissions arising from the use of chlorine. World-wide, control of chlorine related emissions and exposure levels vary greatly, from little or no control to very stringent limits, especially in Europe and North America.

## Part 1 - Chlorine in the casthouse

### Background

Chlorine gas is widely injected, mixed with argon or nitrogen, into melting or holding furnaces as a means of controlling hydrogen and alkali metals and reducing metallic and non-metallic inclusions. The usual addition method is stationery lances but in shallow reverberatory furnaces this is inefficient, due to large bubbles and low residence time, and the tendency is to compensate by increasing the chlorine addition well above stoichiometric levels. This leads to incomplete reaction and acid gas and particulate emissions.
Comprehensive work by Celik and Doutre (1), published in 1989, studied the impact of chlorine gas concentration in the fluxing mixture and of total gas flow rates on melt quality, dross formation and acid gas emissions. Their principle findings were:

(a) that chlorine concentrations above the melts capability of reacting with it, result in stack emissions and
(b) that the efficiency of chlorine is significantly increased in magnesium containing alloys by the formation of intermediate magnesium chloride.

This work subsequently became the basis of an on going global strategy by Alcan to reduce its chlorine dependency and the subject of several excellent technical papers on both optimisation of chlorine usage and substitution of chlorine.

(1) Work to be presented at the First International Congress of the Aluminium Industry, São Paulo, 21st to 23rd of November, 2000.
(2) Chemical Engineer, ENQ-UFRJ, 1967
(3) International Product Manager of Pyrotek High Temperature Industrial Products Inc.

**Data on chlorine usage**

The effectiveness of chlorine in reducing alkali halides and improving melt cleanliness is well documented.
Béland et al (2) quote PoDFA levels of 0.091 sq.mm/kg for 1XXX series alloys after standard lance fluxing with chlorine and 0.034 sq.mm/kg for 3XXX alloys.
They also quote sodium removal coefficients of 0.091 with chlorine lancing for 1XXX alloys, calcium removal coefficients of 0.032 for 3XXX alloys and sodium plus calcium plus lithium removal coefficients of 0.033 for 6XXX alloys.
These values are in good agreement with industrial practice in many casthouses.
There is also substantial data on the emissions arising from chlorine lancing (1,2,3,4). as summarised in table I.

**Table I - Typical emissions from chlorine lance fluxing**

| **Average values** | **1XXX** | **3XXX** |
|---|---|---|
| | (mg/cubic metre) | (mg/cubic metre) |
| Particulate | >1000 | >300 |
| HCl | >1500 | >400 |
| Chlorine | 5-30 | 10-50 |

**Optimising chlorine treatment**

Single lance fluxing with chlorine is, as already discussed, very inefficient and results in excess chlorine usage and emissions, and various measures have been put forward over a period of years to address this problem.(5,6,7)
Essentially these all aim to increase chlorine gas bubble/metal contact time by reducing bubble size and improving bubble distribution.
These measures fall into the following categories:

- Double, triple and multi lance systems
- Lances with porous nozzles
- Porous plugs installed in furnace floors (8)
- Subsurface metal pumping (Jet Fluxing) with lance fluxing (9)
- Impellers with lance fluxing(10)

All of these systems bring about an improvement in chlorine efficiency to a small or greater extent.
The most sophisticated of them, subsurface metal pumping, is said to give major gains in efficiency of utilisation of chlorine and hence reduce chlorine consumption by 50% compared with lance fluxing alone. Rotors and impellers have been shown to give even greater gains in chlorine efficiency when removing alkali halides.

Together with measures, such as these, to improve chlorine efficiency and therefore reduce emissions at source there is also the alternative (or additional) approach of controlling the emissions once generated by installation of alkaline scrubbers. These are helpful but expensive and produce noxious residues, which still need to be disposed of.

Summing up it is possible to greatly improve the efficiency of chlorine usage and substantially control emissions but at a significant cost and without really overcoming the basic problem which is the nature of chlorine itself.

## Alternatives to chlorine

### Other Gases

A number of halogenated gases have been looked at as alternatives to chlorine but only sulphur hexafluoride has received any serious consideration. SF6 has proven to be reasonably suitable (11) for in line treatments, mixed with inert gases, but is expensive and unsuitable for furnace treatments (poor performance with heavy, nasty smelling dross)

### Solid fluxes

Powder fluxes based on mixtures of fluorides, chlorides, carbonates, sulphates and carbonates have 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, are largely ineffective in cleaning, the metal as measured by PoDFA (2) or in reducing halides.
Injection or addition to the solid charge during meltdown helps but efficiency is still poor and emissions levels high.
The answer as pointed out in a definitive paper by Beland et al 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 1XXX and 3XXX series 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.

## Part 2 - Casthouse experiences with magnesium chloride based refining agents

### Powder Fluxes

Although injection of mixtures of powder fluxes containing magnesium chloride can be quite effective when compared with chlorine lance fluxing, in terms of both alkali and inclusion reduction and lower emissions, these powder fluxes nevertheless suffer from a number of significant disadvantages. Namely:

- **(a)** They contain very fine particles and dust, which can potentially lead to emissions in handling and usage.
- **(b)** They have a melting range (not a single melting point) which is related to the individual components of the powder mix.
- **(c)** Magnesium chloride powder is very hygroscopic and powder mixes containing it pick up moisture quite rapidly especially when exposed to humid, warm atmospheres.

### Fused Refining Agents

The answer to the problems associated with powder fluxes containing magnesium chloride is to constitute them as a single fused entity.
Using a special fusion process, products are commercially manufactured to coincide with the eutectic compositions on the magnesium chloride / potassium chloride binary phase diagram.
The two eutectics and the commercial products, which correspond to them, are shown in Figure 1.

**Figure 1 Magnesium Chloride / Potassium Chloride phase diagram**

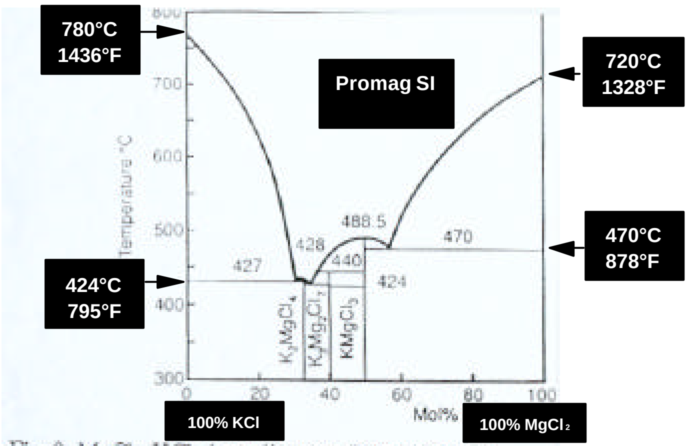



Fig. 9 $MgCl_2$-KCl phase diagram. From this work.

Promag SI, which coincides with the 60/40 eutectic, and Promag RI, which coincides with the 40/60 eutectic, can both be regarded as synthetic anhydrous Carnalite. They have single sharp melting points (below 470 degrees C), and are free from fluorides, sodium and dust. They are very much less hygroscopic than mixtures containing magnesium chloride powder.
Their physical properties are summarised in Table II.

**Table II - Promag Physical Properties**

| **Properties** | **Promag SI** | **Promag RI** |
|---|---|---|
| Chemical Compound | KMgCl3 | K3Mg2Cl7 |
| Magnesium Chloride | 65 % | 43 % |
| Potassium chloride | 35 % | 57 % |
| Melting Point | 470 degrees C | 440 degrees C |
| Form | granules | granules |
| Grain Size | 1.0-3.0 mm | 1.0-3.0 mm |

**Casthouse Experience**

Over the last years Foseco Aluminium and now Pyrotek have introduced Promag refining agents into over sixty casthouses world-wide. In many cases this has been as a substitute for chlorine lance fluxing in the furnace or the use of hexachloroethane tablets. The following examples are derived from this experience.

**Emission Data.** Obviously the primary concern when replacing chlorine with a fused refining agent is to be sure that not only is the process effective in reducing alkalis and inclusions but it is also effective in reducing emissions to the atmosphere and the local working environment. Collaborative work carried out in the casthouse of one of the world largest aluminium producers in the USA, confirmed that there were major reductions in all emissions when compared with traditional chlorine lance treatment. These results are summarised in Table III.

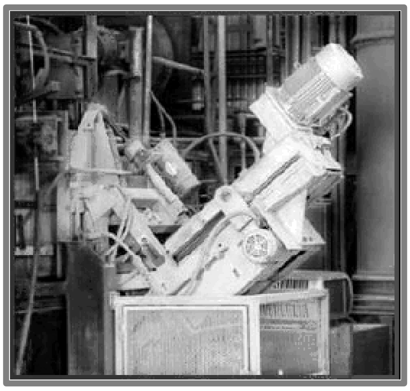
**Table III - Comparison of furnace emissions from chlorine and Promag**

| **Emission levels** | **Chlorine Treatment** | **Promag S Treatment** |
|---|---:|---:|
| Stack temperature (degrees C) | 633 | 644 |
| Air flow rate ($Nm^3$/hr) | 2,146 | 2,361 |
| Particulate(mg/$m^3$) | 937.6 | 162.4 |
| HCl (mg/$m^3$) | 2,385 | 12.1 |
| HCl emissions (kg/hr) | 4.98 | 0.03 |

**Alkali and Inclusion reduction** As pointed out in the original work by Beland et al (3) the method of addition of the fluxing agent is fundamental to its effectiveness. This is particularly true of the Promag refining agents which in order to function properly, as reducers of alkalis and inclusions, need to be mixed thoroughly into the body of the melt in their liquid phase.
When added to molten aluminium, Promag, with its low sharp melting point of 470 or 440 degrees C, melts quickly and forms a liquid layer on the aluminium bath. Unless this liquid layer is then stirred into the body of the melt the effectiveness of the refining agent in reducing alkalis and inclusions is very low.
A number of techniques and pieces of equipment have been developed in the last few years to facilitate the successful addition and mixing of fused refining agents to molten aluminium in the furnace. These range from the Rotary Flux Injector (RFI) developed by Alcan International and STAS (12), the new Pyrotek PHD50 mobile spinning rotor and the Pyrotek HD2000 fixed spinning rotor developed by Pyrotek U.S. showed in figure 2.
Sales of Pyrotek's new "in-furnace" spinning nozzles systems are under the management of the SNIF Division.

**Figure 2 - Pyrotek PHD 50 and HD2000**

Pyrotek PHD50



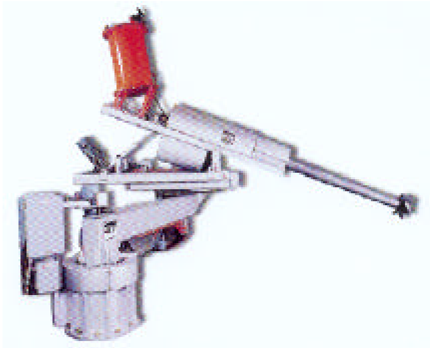
Pyrotek HD2000

The following section indicates how these methods are today being used in casthouses around the world to reduce alkali and inclusions in the furnace without the use of chlorine gas.

**Sodium Reduction**

Primary smelters often need to reduce sodium levels in their primary ingot or in liquid metal transferred to their own casthouses. These plants generally operate large reverberatory melting and holding furnaces. Traditionally chlorine lance fluxing has been used in many of these plants but a number have now changed, or are in the process of doing so, to the use of fused refining agents.
The ideal method for these large shallow bath furnaces is the injection through a spinning nozzle. The RFI, as shown in figure 3, comprises a hollow rotating shaft and impeller and a refining agent feeder. There is a separate electrical and gas control panel and the shaft is either inserted through the furnace door whilst mounted on a moveable platform or inserted permanently through a dedicated pocket door built onto the side of the furnace. This technique enables the injection and thorough mixing, below the metal surface of a precise amount of fused refining agent using a carrier gas (argon or nitrogen).

**Figure 3 - Rotary Flux Injector (RFI)**



Excellent results have been obtained in many primary plants around the world using the RFI, in conjunction with fused refining agents, for sodium reduction, inclusion reduction and emission control. The 1998 TMS paper of Beland et al (12) gave full details of experiences with 1XXX, 3XXX, 5XXX and 6XXX alloys treated with fused fluxes by an RFI technique. Metal cleanliness and alkali removal was superior to chlorine fluxing and stack emissions reduced by up to 90% compared with chlorine.
ex-Foseco Aluminium experience of using an RFI with Promag in a European primary smelter has consistently produced sodium reductions of up to 80% in 1XXX alloys.
Promag SI is used at an addition rate of 0.5kg/MT over a 30 minutes addition period, with a nitrogen carrier gas at a flow rate of 250l/min and a rotor speed of 300 rpm.
Not all primary or remelt plants, that experience sodium problems, wish to install injection equipment. Reasonable results can be obtained with the simple addition method of throwing small bags of Promag into the furnace and stirring in using a fork lift mounted tool. One European primary plant uses this technique with Promag RI in 5kg bags at an addition rate of 0.8-1.0kg/mt in a 60mt transfer furnace to reduce sodium from levels of 20 to 30 ppm to 4 to 10 ppm.

## Calcium Reduction

Many plants who produce remelt or foundry alloys, by either remelting of primary or secondary ingot or by secondary smelting processes experience problems with calcium levels being too high for the end customer specification. In the case of foundry alloys this can be due to high calcium levels in the silicon metal.
ex-Foseco Aluminium and Servimetal have developed a compact portable injector especially for Promag additions in these plants. Further to the acquisition of the Foseco Aluminium by Pyrotek, Pyrotek France has improved the original design and launched the PAL FIF50 showed in Figure 4.

**Figure 4 - PYROTEK PAL FIF50**

This unit fulfils the need for a simple, mobile, effective and inexpensive means of applying Promag refining agents by injecting accurately below the metal surface, using nitrogen or argon gas. It weighs only 200kg and has dimensions of 1400mm length, 700mm width and 1900mm length.
The hopper volume is 48 litres and the unit can be operated at addition rates from 1.0 to 2.5 kg Promag per minute.
A number of European plants are using the PF40 injection unit successfully in their operations, including a remelt plant, with a 37mt capacity channel induction melting furnace, making alloys with 2.4% magnesium, 0.25% manganese and 0.25% silicon. The furnace charge is recycled aluminium plus returns. Promag RI is injected over a period of 10minutes into the molten aluminium bath held at 710 degrees C. The rate of addition is 0.5kg Promag per mt. Significant reductions in calcium and sodium are routinely achieved by this practice, as indicated in Table IV.

**Table IV - Typical results from a European remelter using a PF40 Injector and Promag RI**

| Alloy<br>AlMg2.4% | Melting Furnace<br>35 + 7 (heel) MT<br>Induction Channel | Initial Na - Final Na<br>ppm | Initial Ca - Final Ca<br>ppm |
|---|---|---|---|
| Promag addition<br>0.5 Kg/MT | centre sweep | 13.3 - 2.9 | 13.0 - 6.0 |
| | % removal | 78.2 | 53.8 |

**Figure 5 - PYROTEK SUPER FEEDER**

In Japan, where there has been tremendous concern about the connections between hexachloroethane and dioxin, there are numerous aluminium plants that wish to have an environmentally acceptable means of reducing calcium in the production of casting alloys. ex-Foseco Aluminium has introduced the concept of Promag injection into several of these using the Pyrotek Super Feeder showed in figure 5.
As an example, one secondary smelter, making A5056 alloys (4.5-5.5% Mg), in a 22 mt furnace, now injects Promag RI at a rate of 1.0 kg/mt, at a bath temperature of 750 degrees C, and achieves an average calcium reduction of 57% ie down from 14ppm before treatment to 6 ppm after treatment, as indicated in table V.

**Table V - Typical results from a Japanese remelter using the Pyrotek Super Feeder and Promag RI**

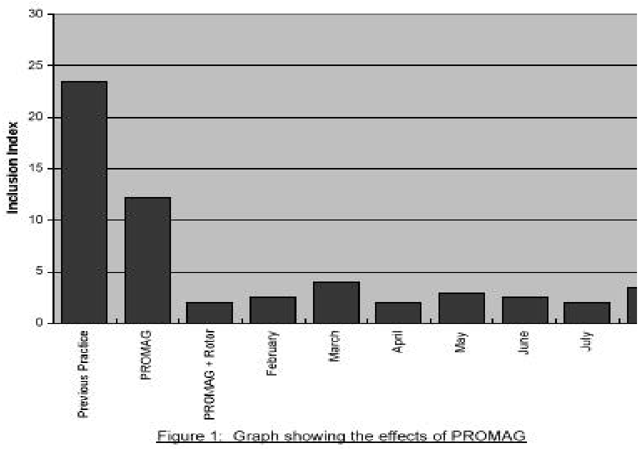
| Alloy<br>AA | Location<br>Holding Furnace<br>22 MT | Initial Na - Final Na | Promag addition<br>Kg/MT | Na removal<br>% |
|---|---|---|---|---|
| 5056 | centre sweep | 18 - 2 | 1.0 | 88.9 |
| 5056 | centre sweep | 8 - 2 | 1.0 | 75.0 |
| | | | | |
| AA | Holding Furnace<br>22 MT | Initial Ca - Final Ca | Kg/MT | Ca removal<br>% |
| 5056 | centre sweep | 16 - 6 | 1.0 | 62.5 |
| 5056 | centre sweep | 12 - 6 | 1.0 | 50 |

**Inclusion Reduction**

An excellent example of what can be achieved in metal cleanliness improvement with fused refining agents comes from a packaging foil producer in Europe. Here, reduction of inclusions from the induction furnace remelting operation of foil scrap was an urgent priority for the casthouse.
ex-Foseco Aluminium worked with the plant personnel to set up an operation involving the addition of Promag SI to the 10mt induction furnace.
The practice introduced was to add 0.5kg Promag per mt, in the form of two 2.5kg bags, during meltdown. The normal movement of the bath in the electrical induction furnace mixed the liquid Promag well into the aluminium and, after complete melting and attainment of temperature (770deg. C), resulted in a semi-liquid dross layer of oxide and unconsumed Promag on the top of the bath. This was removed and metal transferred to a holding furnace.
PoDFA evaluations indicated an immediate improvement in metal cleanliness of 50% by this technique.
However, this was still not sufficient for the plant to achieve its metal cleanliness goals and further joint work was undertaken to determine if extra stirring with argon, after Promag treatment, would remove even more inclusions.
Lance addition of argon was tried with little success but finally remarkable results were obtained by thoroughly mixing the Promag treated bath with argon injected through a spinning nozzle unit.
Metal cleanliness improved by more than a further 50%.
Today the routine practice at this plant is to add Promag during meltdown, remove the dross and then stir with argon for 15 minutes using a portable FDU/MT gas injection system which is placed in the induction furnace as shown in figure 6. Monitoring of operator exposure to hydrogen chloride emissions on the furnace platform during Promag use, gave values less than half the allowable level of 7mg/cubic metre.

**Figure 6 - FDU/MT Argon stirring unit in an induction furnace**

**Figure 7 - Metal cleanliness results from Promag usage in a foil plant**




Metal cleanliness results, by PoDFA measurement, have been carefully monitored during the two years of routine adoption of this Promag procedure and found to consistently run at levels 80 to 90% better than before Promag was introduced. (See Figure 7).
Today this foil plant, which produces 1XXX, 3XXX and 8XXX alloys, is consistently producing the cleanest casthouse metal in its history.

## Summary and Conclusions

1. Chlorine gas is a traditional and well established means of reducing alkali metals and inclusions by furnace treatment but is inefficient and the environmental problems accompanying its' use, make it increasingly unattractive to casthouses.

2. Many efforts have been made to increase the efficiency of chlorine addition methods to the furnace, and so reduce emissions problem, but with limited success.

3. Fused refining agents based on magnesium chloride can be at least as effective in reducing alkali metals and reducing inclusions as chlorine, without the environmental problems associated with chlorine.

4. The addition method used with fused refining agents is fundamental to their effectiveness. Work carried out by Foseco Aluminium and more recently by Pyrotek has clearly established that injection and thorough stirring of the furnace bath are techniques which promote excellent dispersion of Promag refining agents, maximise alkaline metal removal and inclusion reduction and minimise emissions.

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