

USE OF ECO FRIENDLY ALTERNATE REFINING FLUX IN ALUMINIUM CAST HOUSE - A STEP TOWARDS SUSTAINABLE DEVELOPMENT.

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Abstract

The major threat to the sustainability of Aluminium Industry is its significant contribution to global warming by way of generation of non eco-friendly gases during its production cycle from Bauxite to the finished product. Though reduction measures are taken in control and effective recovery of values from pot room gases, efforts in use of environment friendly additives in the final products production line is warranted. In this line, the present paper describes our efforts in the use of a new generation refining flux which apart from helping in effective removal of alkali metals, reduction in inclusions and ensure a better metal cleanliness shall also aide in reduction of obnoxious gases generated during the metal refining process prior to casting. The aim of the current work was to reconcile the practical results with the old generation fluxes used. Further improvements to bring in a better metal cleanliness will also be discussed.

1.0 Introduction

Process optimization is of increasing importance in order to improve quality, increase production capacity and minimize overall costs for wrought and cast aluminum alloys. For the treatment of aluminum and its alloys, various molten-metal processing steps are necessary in addition to melting and alloying. Historic practices, such as in-furnace fluxing for metal refining and degassing are being done in addition to newer in-line technologies of degassing, grain refining and filtration to obtain the best melt cleanliness. Proper melt hygiene is essential for obtaining sound cast and further good quality downstream products. Therefore use of flux for melt refining is one of the important steps of treatment of molten Aluminium. Other critical factors in managing melt quality processes include operational costs/cycle times, operational health and safety, and environmental impact/ compliance to maximize Cast House performance.

This paper discusses the development of an environment friendly technology for refining of molten Aluminium in the furnace. The environmental and operational benefits of using the new refining flux in the furnaces to remove alkali metals, non-metallic inclusions and hydrogen from molten Aluminium have been described.

1.1 The need and various measures adopted for refining of molten Aluminium

During the last 15 years metal cleanliness - specifically hydrogen, inclusions and alkaline elements - emerged as the preeminent quality detractors, for premium and commercial grade products in which high strength to weight ratios, machined surface finish, fracture toughness and low cycle fatigue performance are primary design considerations.

1.2 Impurities in Molten Aluminium

The Common Impurities in the Molten Aluminium can be listed in Table – 1 given below:

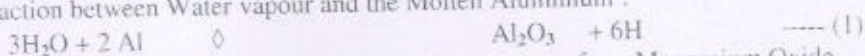
Table – 1: Common Impurities in Primary Molten Aluminium

Impurity	Concentration in primary Aluminium
Hydrogen	0.1 - 0.30 ppm (0.34 cm ³ / 100 g)
Inclusions (PoDFA Scale)	1.0 mm ² / Kg (Mainly Al ₄ C ₃)
Alkali	
→ Sodium	30 - 150 ppm
→ Calcium	2 - 5 ppm
→ Lithium	0 - 20 ppm

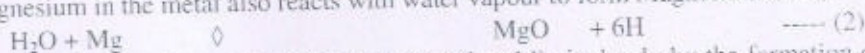
(Source: Waite. P., Light Metals, 2002, p841)

1.2.1 Hydrogen

It is well known that hydrogen is the only gas that has significant solubility in liquid Aluminium. The amount of hydrogen in the initial charge can vary due to many influences including the nature of the charge, the type of furnace and the atmospheric humidity. Hydrogen gets in to the Molten Aluminium due to the reaction between Water vapour and the Molten Aluminium:



The Magnesium in the metal also reacts with water vapour to form Magnesium Oxide.



Both the reactions are thermodynamically favoured and limited only by the formation of an oxide skin on the metal surface, which prevents further contact of water vapour with the molten metal.

Solubility of gaseous hydrogen in liquid aluminum at its melting point (660.4°C) is 2.2 cc/100gm. Solubility of gaseous hydrogen falls sharply when aluminum solidifies: solid aluminum at melting point contains only 0.05 cc/100gm). The Hydrogen values of 2.2 cc / 100gm is too high final finished product and needs to be reduced. Dissolved hydrogen in molten Aluminium results in porosity, the size and shape of which is dependent on composition of the alloy, its solidification characteristics, micro structural features and presence of porosity-nucleation sites. Interdendritic porosity, which is encountered when hydrogen content is sufficiently high (> 0.15 cc/100 g), results in reduced strength and ductility, reduced resistance to corrosion and fatigue crack propagation, bright flakes in forgings, blisters in annealed or solution treated material and leakage of pressurized casting in service. Control of dissolved hydrogen in molten Aluminium alloys is, therefore, essential to achieve the desired quality standards. Therefore aluminum alloys release excessive amount of hydrogen during solidification. This result in porosity defects distributed throughout the solid metal.

The factors that encourage these reactions and increase the dissolved Hydrogen in the molten metal include:

- A high vapour pressure of water vapour in the atmosphere (i.e., higher humidity), which drives the reaction to the right ^{2,3}.
- Metal Turbulence, which destroys the oxide skin and allows the reaction to continue ^{4,5}.
- Wet or damp charge material, which make the water vapour directly available to the melt.
- In addition to the natural humidity, the water vapour in the Products Of Combustion (POC) from the fossil fuel fired furnaces is also a source of Hydrogen ^{6,7}. As a result, extended exposure of metal to POC in transfer ladles can raise the dissolved Hydrogen content in Hot metal still further.
- Some alloying elements like Cu, Fe, Si and Zn, raise the activity coefficient of dissolved Hydrogen in the molten Aluminium, decreasing its solubility ^{8,9}.

1.2.1.1 Methods for Removal of Hydrogen from Molten Metal

For removal of hydrogen the following measures are adopted:

1.2.1.1.1 Degassing by fluxes

Solubility of Hydrogen is low at the melting point of the metal, but sharply increases with rise in temperature of the metal. Hydrogen that gets dissolved at the higher temperature of melting cycle remains supersaturated. When the temperature drops the Hydrogen gets entrapped in the molten metal and creates void and pin-hole porosities due to the physical nature of the entrapped Hydrogen. One method of eliminating the super-saturated Hydrogen is to provide suitable scavengers in the form of other gases like Nitrogen, Chlorine¹⁰, Nitrogen plus Chlorine, which facilitate heterogeneous nucleation of hydrogen requiring less nucleation energy.

Even under the best melting conditions, it is often impossible to prevent hydrogen gas from entering the melt which finally gives rise to pinhole porosity in the cast products. It is therefore necessary to remove as much hydrogen from the melt as possible prior to pouring. The Degasser product, removes the flux dissolved hydrogen through the diffusion process. Degassing with Degasser Product is superior to flushing with chlorine gas which is associated with problems of space, equipment, corrosion, health hazards etc. Degassing tablets offer the most convenient way of carrying out this operation. Some of the Degasser products contain grain refining elements also, which function as combined degassing and grain refining agents. Wherever additional grain refinement is needed as in the case of sand cast thick section castings, further treatment of the melt with the Nucleant grain refining product gives the desired effect.

1.2.1.1.2 Hexachloroethane/Tablet Degassing:

Aluminium alloys are also degassed by plunging and holding tablets containing gas evolving salts into the melt. Chlorides of Aluminium or zinc, Aluminium fluoride or Hexachloroethane are the most common ingredients. Tablets containing salt fluxes help wet oxide inclusions within the melt and thus enable some removal of the hydrogen gas associated with inclusions. The use of tablets suffers from the disadvantages of inconsistent gas removal, generation of huge amount of dross, high costs and generation of toxic fumes.

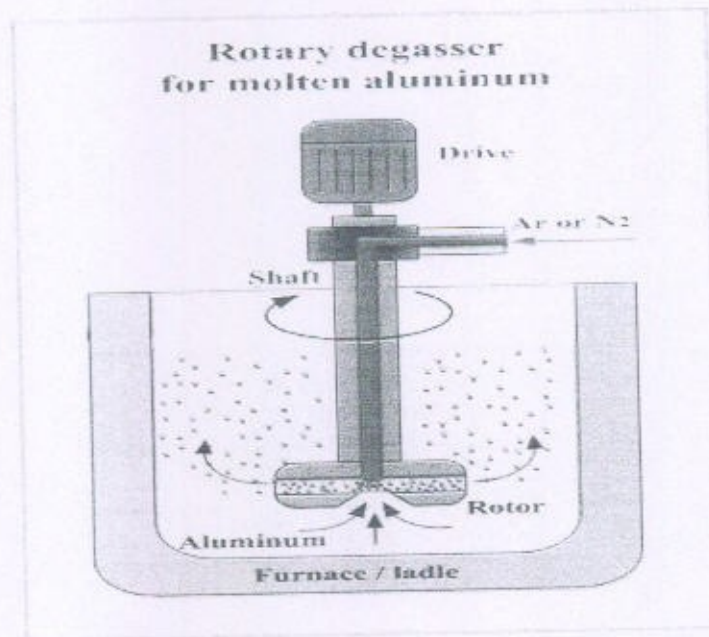
1.2.1.2 Advantages of flux injection:

- High effectiveness of flux action due to better mixing with the melt;
- Short flux treatment time;
- Controllable flux introduction;
- More environmentally friendly method of fluxing.

1.2.1.3 Gas Purging:

A simple method of degassing molten Aluminium is by injecting a purging gas or gas mixture under pressure through a flux tube, pipe or lance made up of ceramic coated cast iron, steel or graphite. A purge gas serves to collect hydrogen based on the lower partial pressure of the hydrogen imparted by the collector bubble versus the surrounding melt. Hydrogen diffuses into the purge gas bubble which rises to the surface of the melt and escapes into the atmosphere. Purge gas can either be inert (argon or nitrogen) or reactive (chlorine). Reactive gases are used in small concentration of less than 10% along with an inert gas.

Fig. 1: Rotary degasser



In the rotary degassing method an inert or chemically inactive gas (Argon, Nitrogen) is purged through a rotating shaft and rotor as shown in Fig.1.

Energy of the rotating shaft causes formation of a large number of fine bubbles providing very high surface area-to volume ratio. Large surface area promotes fast and effective diffusion of hydrogen into the gas bubbles resulting in equalizing activity of hydrogen in liquid and gaseous phases.

Rotary degasser allows achieve more complete hydrogen removal as compared to the flux degassing. Additionally rotary degasser does not use harmful chlorine and fluorine containing salts.

Rotary degasser may also combine the functions of degassing and flux introduction. In this case the inert gas serves as carrier for granulated flux. The method is called flux injection.

1.2.1.4 Methods of hydrogen content estimation:

- **Slow solidification.** In this method a small portion of liquid aluminum (about 2 in³/33 cm³) is poured into a cavity in a heated refractory brick. The alloy slowly solidifies and the released hydrogen is concentrated in the upper part of the casting in form of frozen bubbles. Quantity of the hydrogen bubbles at the sample surface is determined by the hydrogen concentration.
- **Vacuum method.** This quantitative method uses solidification of a sample portion of the aluminum alloy in a small crucible at low pressure. Hydrogen dissolved in the alloy starts to form a gaseous phase (a bubble) at a certain pressure. When the first bubble is formed both the pressure and the temperature are measured. These parameters are used for determination of the hydrogen content by means of numeric diagrams.

1.2.1.5 Combined Cleaning/Degassing Treatment:

This treatment involves the simultaneous removal of soluble (H₂, Na, Ca) and insoluble impurities (inclusions) from Aluminium/Aluminium alloy melts either by addition of special flux inside the furnace or as the metal flows from the furnace to the casting site.

1.2.2 Inclusions

Many types of inclusions are found in molten Aluminium. Carbides and oxides are generated by the turbulent electro-magnetic and chemical activity in the cells and the reactions with the cell lining materials. The bath is frequently tapped along with the metal in the crucible delivered to the Cast House. Turbulence during the transfer leads to oxide and dross inclusions in the metal. Refractory wear in transfer ladles also leads to a risk of increased inclusions.

The main inclusions found are titanium vanadium borides ($TiVB_2$), titanium borides (TiB_2) from grain refiner, aluminum carbides (Al_4C_3) and oxide films. The presence of graphites, spinel-like and refractory are also noticed. Spinel-like are formed from the reaction between liquid aluminum and the refractory materials. This reaction is faster in alloys with higher magnesium content. Spinel-like inclusions are highly detrimental to the properties of Aluminium. The rate of formation increases as the melt temperature rises. Because of their large dimensions spinel like inclusions can easily be filtered out of the metal.

While the existing types and sizes of non-metallic inclusions that are present in melting furnaces vary from foundry to foundry, their removal is essentially done for proper molten metal cleanliness. A number of commercially accepted melt treatment techniques are being used by aluminum foundries to remove inclusions from the molten aluminum alloy prior to casting. These include various methods of fluxing, degassing, and filtration.

1.2.2.1 Alkaline elements

The three main elements that can contaminate liquid Aluminium are Na, Ca and Li. Depending upon the alloy being produced each of these can be detrimental to the casting process and the finished product. Na is most common in smelter metal due to contamination in the alumina or the smelting process. Li is added to the electrolytic cells to improve current efficiency and Ca can be found as a contaminant in Si metal additions.

These alkali metals enhance edge cracking of Aluminium plates and sheets. Especially Al-Mg alloys are highly susceptible to edge cracking if higher amount (> 4 ppm) of alkaline elements are present in molten Aluminium, while these elements will oxidize to varying degrees naturally over time the levels which can be achieved are not satisfactory and the time taken is excessive. In-line treatments, such as SNIF (Spinning Nozzle Inert Floatation) Rotary Degasser, can be used to reduce the levels of alkali metals using low percentages of chlorine. It is not practical to remove large percentages using this method. To remove higher quantities of alkali metals the metal can be treated between the Cell House and the Cast House either by an active chemical reaction with chlorine, or a reactive salt for example AlF_3 , or by pouring it over charcoal. In-furnace treatments are probably the most popular and these can be achieved using low percentages of chlorine gas in an inert carrier (i.e. Argon or Nitrogen) or using reactive, non-toxic, chemicals.

1.2.3 Fluxes for Aluminium Cast House and Foundry Processes

Fluxes composed of chlorine and fluorine containing salts are used for degassing molten aluminum alloys. Degassing fluxes are commonly shaped in form of tablets. Degassing operation starts when a flux tablet is plunged by a clean preheated perforated bell to the furnace bottom. The flux components react with aluminum forming gaseous compounds (aluminum chloride, aluminum fluoride). The gas is bubbling and rising through the melt. Partial pressure of hydrogen in the formed bubbles is very low therefore it diffuses from the molten aluminum into the bubbles. The bubbles escape from the melt and the gas is then removed by the exhausting system. The process continues until bubbling ceases. Degassing flux may also be introduced by an injection method. In this case the inert gas serves as carrier for granulated flux. Besides the degassing effect the degassing treatment allows to remove non-metallic inclusions suspended in the melt (cleaning effect).

2.0 Development of the eco friendly refining flux

The most common method of reducing hydrogen in molten Aluminium is by addition of Hexachloroethane in molten metal. During degassing molten Aluminium with Hexachloroethane huge amount of toxic fumes are evolved. The alternate methods of degassing using gas lancing, gas purging through a mechanical degasser and combined methods of degassing have been reported in the literature¹¹. These equipments circulate molten metal. Accordingly, these are applicable to large sized furnaces and can be utilized as molten metal circulation system. It was confirmed that pre-fused granular formed refining flux¹², is optimum as refining flux for injection and was almost smokeless and odorless. It is also acknowledged that the Flux¹³ has the effect of removing alkaline earth/alkali metals such as Sodium, Calcium, etc. and non-metallic inclusions. Furthermore, $AlCl_3$ and molten salts generated in molten metal absorb inclusions; float up and form dry dross. Thus, it can be expected that these fluxes also enables easy dross off operation in addition to inclusion removal effect. Melting point of the new generation Fluxes is $470^{\circ}C$. It changes to molten salt readily, that absorbs inclusions and contributes to reduction of alkaline metals in molten metal and does not readily emit non-reacted hydrogen chloride.

2.1 Our Experiments

A new generation flux to reduce the generation of toxic fumes an alternative degasser was developed. Initially laboratory scale studies were carried out to establish the effects of this alternate degasser on reducing hydrogen in molten metal. After successful laboratory scale trials, degassing with the alternate degasser instead of Hexachloroethane degassing was carried out in 18 casts of Foil stock in Foundry. Without using Hexachloroethane and using only this degasser comparable hydrogen and inclusion contents of products at a lower cost of production was achieved. The quality of the products remained the same and no increase in impurity was observed. Customer's feedback on the quality of the material for use as feedstock to Aluminium Foil for Pharmaceutical applications was positive. After this a month long trial was carried out where all the foil stock casts were degassed with this degasser instead of Hexachloroethane. Not only comparable hydrogen and inclusion contents of products at a lower cost of production in an environment friendly manner were achieved, but at the same time reduction in dross generation and melt loss could be achieved. Due to the number of advantages of the innovative method of this new degassing flux over Hexachloroethane degassing this degassing method has been made a part of the Standard Operating Practice in Foundry. A month long trial was also conducted in Cast House II. Here also comparable hydrogen and inclusion contents of products were achieved. After the successful trial and positive customer feedback Hexachloroethane was replaced by the new refining flux in Cast House II. Hexachloroethane was substituted by this new flux in August 2008 and since last 1 year the quality of the rods produced at Cast House II was found to have improved.

2.1.1 Unique features of the eco friendly degassing flux:

1. During degassing of molten Aluminium no fumes are generated.
2. Simplified and less labour intensive degassing method.
3. Near zero HCl and particulate in stack emission.
4. Reduces Na in molten metal.
5. Once on the surface, prevents hydrogen pick up.
6. Reduces melt loss and dross generation.
7. Keeps the furnace, launders, in-line degassers and casting nozzles free from dross build up.

2.2 Results of laboratory scale study of the eco friendly refining flux

Laboratory scale trial of the refining flux¹⁴ was carried out in August 06. The study revealed that degassing with the new refining flux was more effective in reducing inclusions and porosity than Hexachloroethane degassing (Fig.2 and 2a).



Fig. 2-Hexachloroethane Degassed.
Lot of inclusions and porosities observed.

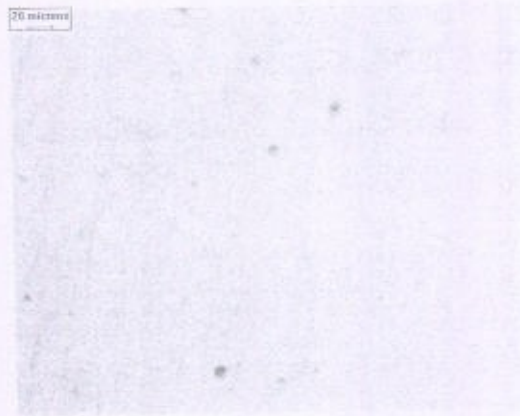


Fig. 2a –New refining flux degassed.
Few inclusions and porosities observed.

3.0 Plant Trials

Foundry trials of the refining flux in Foil Stock – 1st Phase (Before installation of SNIF in-line rotary degasser):

In March 07, in 5 Nos. of casts of Foil Stock no degassing using Hexachloroethane was done in melting and holding furnace. The new refining flux was added in all the 5 casts in holding furnace. The hydrogen and inclusion contents of the casts were measured and the results are given below in Table 2 and Table -3:

Cast No.	Holding furnace No.	Location	Hydrogen content (ml/100 gm)	Inclusion content PoDFA Index (Kg/sq. mm)
3-1841	FC2	After CFF	Top - 0.215 Bottom - 0.164	Top - 0.0790 Bottom - 0.1086
2-1797	FC1	After CFF	0.190	0.1329
5-2029	FC2	After CFF	0.209	0.0761
5-2032	FC2	After CFF	0.153	0.1528
3-1902	FC2	After CFF	0.147	0.1236

Table-2- Degassing with new flux

Cast No.	Holding furnace No.	Location	Hydrogen content (ml/100 gm)	Inclusion content PoDFA Index (Kg/sq. mm)
2-1880	FC1	After CFF	0.178	0.1160
2-1882	FC1	After CFF	0.202	0.0780
2-1884	FC2	After CFF	0.206	0.1138
3-1920	FC2	After CFF	0.221	0.1412
3-1946	FC2	After CFF	0.166	0.1589

Table-3- Degassing with Hexachloroethane

3.1 Observation:

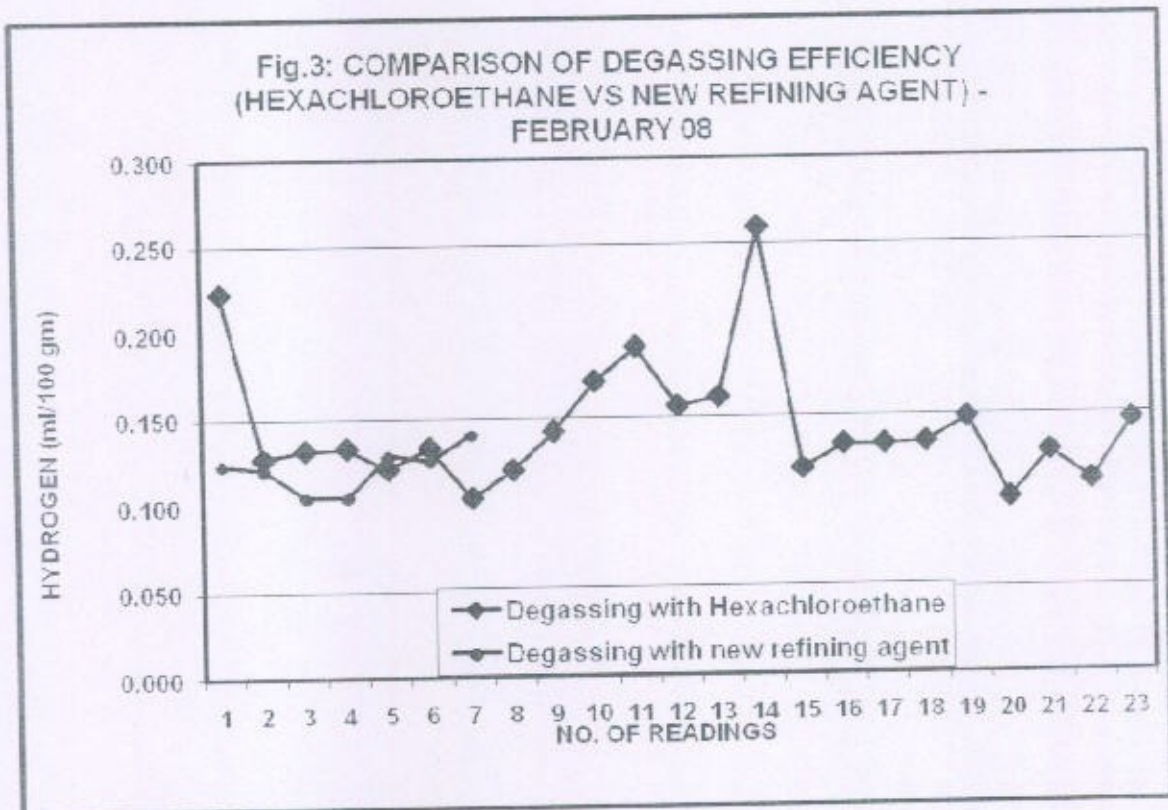
It has been observed that without using Hexachloroethane in melting furnace and holding furnace and by addition of the refining flux in holding furnace quite low levels of hydrogen and inclusion contents were achieved in the casts.

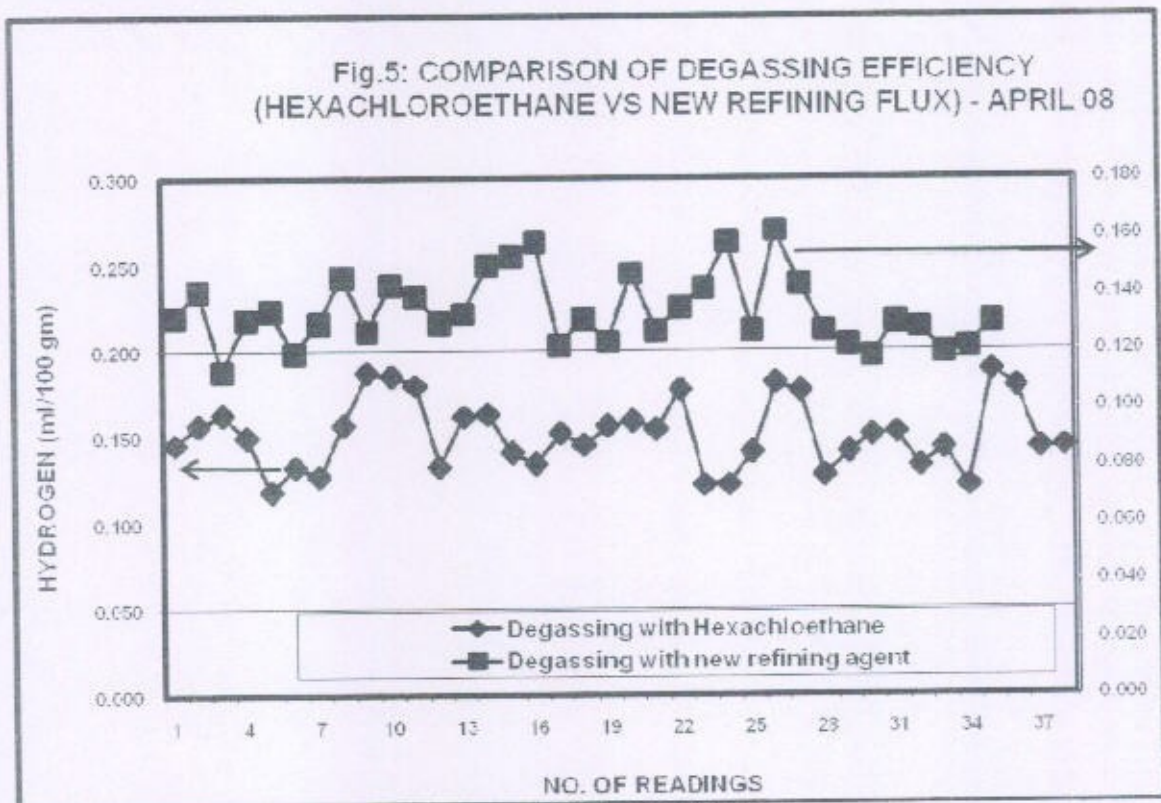
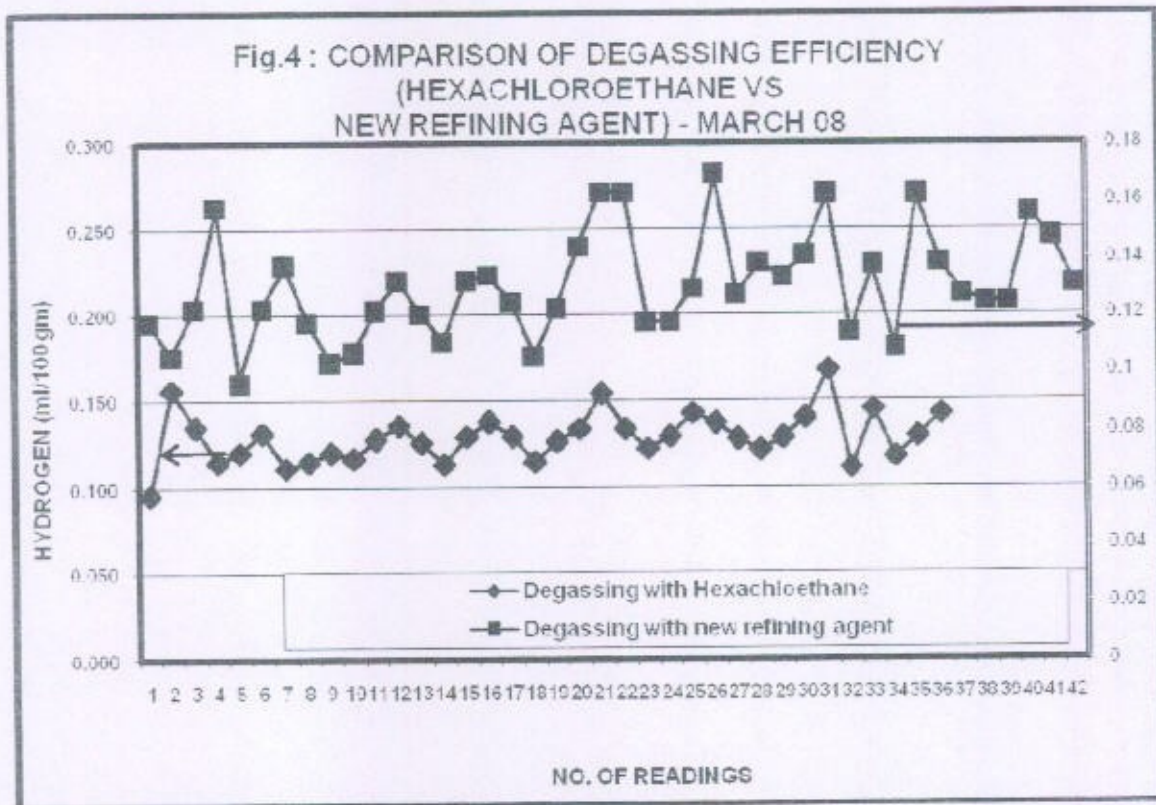
3.2 Foundry trials of the refining flux in Foil Stock – 2nd Phase:

After successful laboratory scale trial and encouraging small plant scale trial a month long trial of degassing with the new refining flux was carried out in Foil Stock casting in Foundry, in March 08, for replacing Hexachloroethane. Several combinations of flux addition and gas purging trails were conducted:

1. Casting through SNIF (in-line degasser with pure Nitrogen) through RC1 (18.5 T casting station)
2. In some casts degassing by Hexachloroethane in both Melting and Holding furnaces (MF+HF).
3. Degassing by Hexachloroethane in only Melting furnaces (MF) and
4. Degassing by the new refining flux in Holding furnace (HF).

The hydrogen contents of the casts are shown in Fig3 -5.



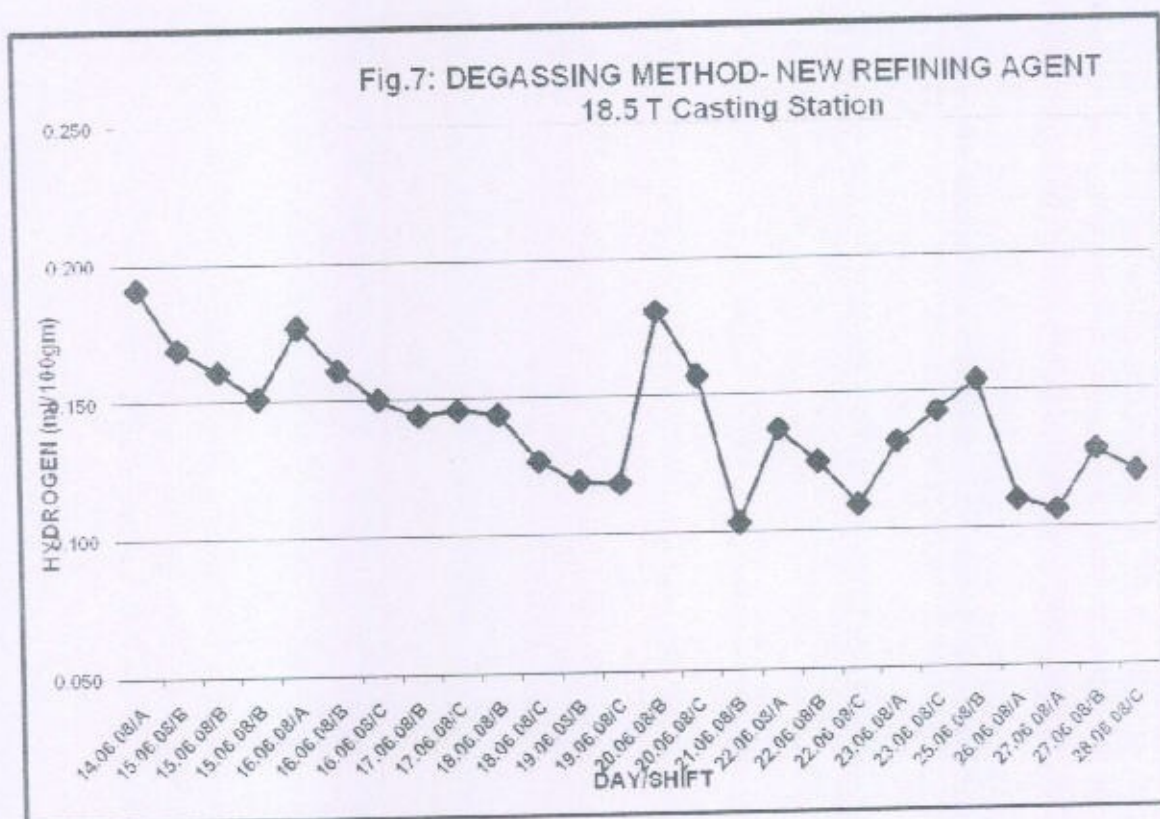
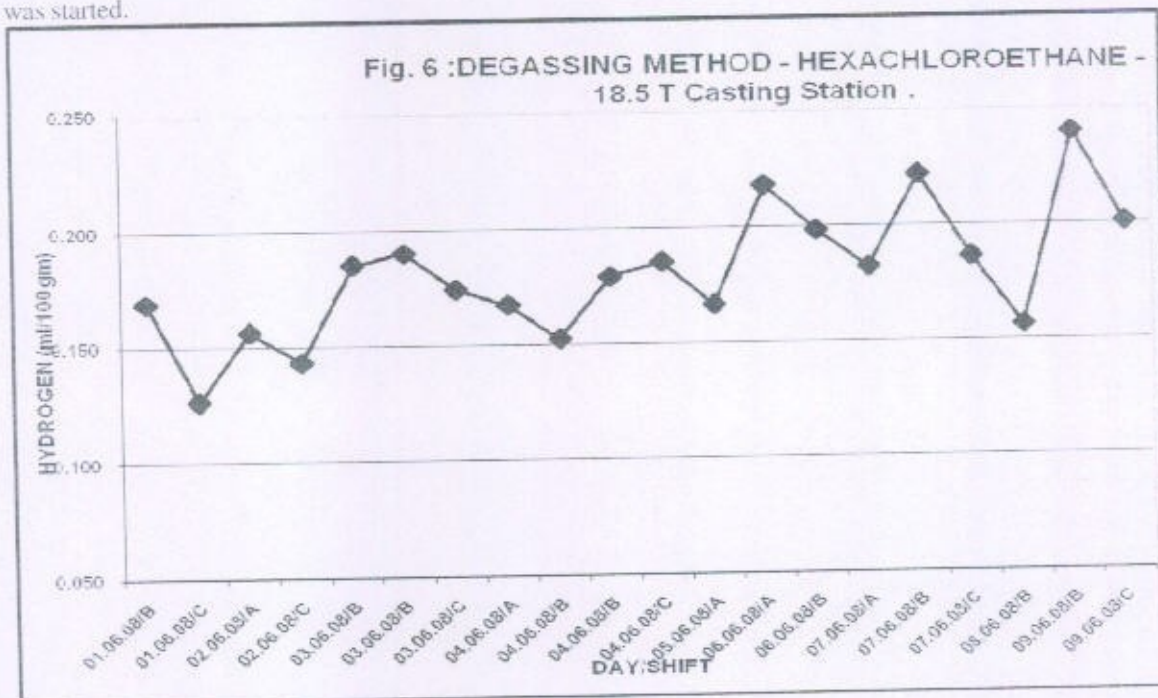


3.2.1 Observation:

It has been observed that when Hexachloroethane degassing was done the hydrogen content varied from 0.096-0.191 ml/100gm, whereas when degassing was done with the new flux the hydrogen content varied from 0.102-0.195 ml/100gm. This indicated that the two methods of degassing were equally effective.

3.3 Foundry trials of the refining flux in Foil Stock – 3rd Phase:

In June 08, it was observed that the hydrogen content of AA 8011 Foil Stock casts made in 18.5 T casting station with Hexachloroethane degassing was showing an increasing trend and number of casts were downgraded to General Engineering Quality (GEQ) casts as the hydrogen contents were above the norm. As a corrective measure Hexachloroethane degassing was stopped and degassing with the new refining flux was started.



3.3.1 Observation:

Remarkable reduction in hydrogen contents were observed by following the new degassing method. So it was recommended that for casting Foil Sock, the new degassing method instead of Hexachloroethane degassing should be carried out and this was incorporated in the SOP.

3.4 Cast House trial of the refining flux in Continuous rod casting:

After successful implementation of the new refining flux in Foundry for Foil Stock casting, a trial was conducted in August 08 in Cast House for replacing toxic fume causing Hexachloroethane degasser with the eco friendly degasser in continuous rod casting.

The results of the trials are given in Table .4:

Table.4: Results obtained on Trail of new Refined Flux in Cast House

S. No.	Period of trial	Degassing method	Furnace No.	Mill No.	Hydrogen ml/100 gm	Hydrogen ml/100 gm
					Average	Std. Dev.
1	1.8.08 – 4.8.08	New refined degassing- 1 st trial	H3	1	0.349	0.047
2	1.8.08 – 4.8.08	New refined degassing- 1 st trial	H3	2	0.371	0.052
3	16.8.08 – 19.8.08	New refined degassing- 2 nd trial	H4	1	0.333	0.051
4	16.8.08 – 19.8.08	New refined degassing- 2 nd trial	H4	2	0.330	0.058
5	5.8.08 – 8.8.08	Hexachloroethane degassing	H3	1	0.367	0.044
6	5.8.08 – 8.8.08	Hexachloroethane degassing	H3	2	0.309	0.031

3.4.1 Observation:

1. Mechanical properties and conductivity obtained in casts produced by the new generation degasser was comparable to those obtained in casts produced by Hexachloroethane degassing.
2. Though all the quality tests carried out revealed that the quality of the casts produced using the new generation degasser was comparable to that of the Hexachloroethane degassed casts, for ensuring proper wire drawing of the wire rods produced using the new generation refined degasser, wire drawing of 2 Nos. of coils was carried out at M/s Rajputana Cables, Korba, India. The wire drawability of the coils was found to be satisfactory by the customer.

4.0 Conclusion

- Degassing with the new refining flux was found to be as efficient as that with Hexachloroethane.
- Reduction in pollution causing gases resulted in improved working atmosphere.
- Low cost of degasser resulted in improved profitability.
- Less hazardous and less labour intensive degassing process made degassing operation more convenient for the furnace operators.
- Due to generation of less corrosive gas there will also be reduction in repairing cost of the structures made above the furnaces.

5.0 References

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