

# TREATMENT OF HOT METAL AND LIQUID STEEL WITH WASTE MATERIALS FROM THE ALUMINUM INDUSTRY

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## ABSTRACT

*Traditionally, fluxes containing calcium fluoride and other additives are used for the treatment of hot metal and molten steel. However, the use of calcium fluoride has been restricted due to environmental concerns. For this reason, calcium aluminate fluxes are a possible alternative to replace slags containing calcium fluoride. Calcium aluminate fluxes can be produced from three different raw materials:*

- *High-quality bauxite*
- *Residuals from aluminum dross treatment processes*
- *Waste products from alumina production.*

*Due to the limited amount and high cost associated with high-quality bauxite, the other two sources are preferred based on both economic and environmental considerations. The objective of this paper is to examine the use of waste slags and by-products from the aluminum industry as potential refining fluxes for the steel industry so that waste disposal from the aluminum industry can be reduced with economical and environmental benefits for both industrial sectors.*

**Key Words:** *Aluminum industry, Calcium aluminate, Environment, Hot metal desulphurization.*

## INTRODUCTION

Waste slag is a major source of environmental pollution within the metallurgical industry. In the steel industry, about 100-150 kg of waste slag is produced in making one tonne of liquid steel from iron in addition to that produced during ironmaking. The amount of waste slag from the steelmaking converter can be significantly reduced when charging hot metal with low phosphorus and sulphur contents. Hot metal pretreatment is known as an effective means of preparing high quality charge material for the converter, thus limiting the generation of waste slag during the steelmaking process. Traditionally, CaO-CaF<sub>2</sub> based fluxes are used as fluxing material in the steel industry. However, the use of CaO-CaF<sub>2</sub> flux at low temperatures is difficult due to its high melting point and low reaction rate. Furthermore, slag containing a high CaF<sub>2</sub> content can attack the refractory lining and cause environmental problems. There is great interest in searching for fluxes for hot metal pre-treatment and liquid steel refining which produce high efficiency, low cost and environmentally friendly processes.

In the aluminum industry, about 2-4 tonnes of waste slag, including by-products (red mud and white mud) from alumina production and dross from aluminum electrolysis and casting, are generated during the production of one tonne of aluminum. The waste product from alumina production is the largest environmental concern of alumina refineries mainly because of the size of this waste stream and its causticity. Dross is of concern to environment scientists because it is produced in many steps during aluminum processing from electrolysis to the casting of aluminum and its alloys. In recent years, reuse of waste slag or by-products from the aluminum industry is a topic that is receiving increasing attention. In this context, the main concentration will be focused on the treatment of white mud from alumina production using a low-grade bauxite and dross from aluminum refining and melting. The production of calcium aluminate fluxes using the by-product from alumina production and residues of dross treatment will be introduced. A comparison of calcium aluminate fluxes made from the white mud and dross with those made from other sources for hot metal desulphurization will be carried out.

## SOURCES OF CALCIUM ALUMINATE FLUXES

There are several kinds of minerals and by-products containing alumina, but only some of them can be used for calcium aluminate production. The chemical compositions of the raw materials and by-products available in the aluminum industry are given in Table 1.

Table 1: Chemical compositions of raw materials and by-products containing alumina(wt%)

	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	AlN	Al	LOI
RM1	3.63		7.77		36.27	5.70	20.73	15.54			10.15
RM2	29.65	1.12	6.01	0.80	9.97	2.85	4.78	14.20			30.00
Bauxite	1.23				5.63	2.74	64.07	8.43			13.22
Dross R							50.00		15-20	6-12	Other
WM1	26.48	0.70	4.66	0.33	0.08	0.02	32.16	1.84			33.00
WM2	26.89	0.94	8.91	0.52	0.09	0.01	29.14	1.64			31.00

RM1 is the red mud generated during alumina production using high-grade bauxite (Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>>12) in the Bayer process; RM2 is the red mud generated in aluminum production using low-grade bauxite (Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>=8-12) and the lime-sintered process; WM1 and WM2 are white muds generated during desiliconization from sodium aluminate concentrated solution. The difference between the two kinds of white mud is the Na<sub>2</sub>O

content. Dross R is the residual of dross treatment at high temperature for recovery of aluminum metal. Since the contents of  $\text{SiO}_2$ ,  $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$  are high, red mud is not suitable for making calcium aluminate flux for steel refining. According to the sources of alumina the production of calcium aluminate fluxes can be classified based on three different methods:

- From bauxite
- From secondary dross of the high temperature dross treatment process
- From the by-product of alumina production.

### **From Bauxite**

Bauxite, limestone and other raw materials are ground and pelletized. The balls or pellets, 5-25 mm diameter, are then sintered in a rotary kiln at about 1573 K. The fuels used for sintering can be coal, natural gas or oil. The process can be conducted in any cement plant and no additional investment is necessary. The main drawback of the process is that bauxite of high quality is required. The contents of  $\text{FeO}$ ,  $\text{TiO}_2$  and  $\text{SiO}_2$  in the calcium aluminate fluxes are high, which is undesirable for certain secondary steelmaking processes. When solid fuels are used, the residue and gangue from the fuels, for example, the sulphur and ash from coal, will contaminate the calcium aluminate fluxes. In some companies, high-grade bauxite is fused together with lime and other additives in a furnace heated by electricity, oil or natural gases. This fusion process will increase production cost of the calcium aluminate flux.

### **From the Residuals of Dross Treatment**

The residuals from the high temperature dross treatment processes (secondary dross) contain 6-12% aluminum, 15-20% aluminum nitride, 50%  $\text{Al}_2\text{O}_3$  and other oxides. This waste contains a high-energy value. The calcium aluminate can be made by sintering the secondary dross with limestone at a temperature of 1573 K in a rotary kiln. Inside the kiln, three different reaction zones are present. The decomposition reaction of limestone to lime and  $\text{CO}_2$  occurs in the first zone. As the temperature reaches 1073 K, the oxidation of aluminum in the secondary dross starts to take place. Finally, in the hot end of the kiln, the temperature of the sintered materials is increased to about 1573 K to complete the reaction between  $\text{CaO}$  and  $\text{Al}_2\text{O}_3$  to form calcium aluminate. The energy consumption of the process is low because aluminum and aluminum nitride in the secondary dross will be oxidized and the energy contained in the two components will be released. After this processing step, waste slag or by-product from aluminum melting can be converted to useful and high added value products. The whole process from the recovery of aluminum to calcium aluminate production is a closed loop process for waste treatment with no waste residue.

### **From the By-product of Alumina Production Using Low Grade Bauxite**

During alumina production using the sintering method, sodium aluminate is made from bauxite through wet grinding of raw materials, sintering and digestion of sodium aluminate. After desiliconization, the ratio of  $\text{Al}_2\text{O}_3$  to  $\text{SiO}_2$  in the sodium aluminate solution is in the range from 400 to 500. In order to continuously increase the purity of alumina,

slaked lime is added to the sodium aluminate solution. Silica and a small amount of alumina will combine with CaO to form a garnet ( $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot x\text{SiO}_2\cdot y\text{H}_2\text{O}$ ). The precipitated material from the desiliconization process is in mud form with a white colour and therefore is called white mud (WM in this paper) or white powder (WP) after drying and grinding. Recycling this by-product as a charging material for alumina production could result in an increase in energy consumption and a decrease in the productivity of the rotary kiln. The ideal way is to develop a new application for the by-product. In practice, this by-product will be dried in a furnace at a temperature in the range from 573 to 773 K. After drying, the materials can be sold to the customers directly or mixed with the white dross from aluminum melting to form a self-heating refining flux. The compositions of calcium aluminate fluxes made from different processes and raw materials are given in Table 2.

Table 2: Compositions of calcium aluminate fluxes made from different sources (wt%)

Sample	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO	MgO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	SrO
B1	2.90	2.20	35.10	0.40	6.00	53.30	0	0
B2	2.30	2.60	33.80	0.70	7.20	52.40	0	
D1	0.70	0.20	33.60	8.80	3.10	49.80	1.90	
WM1(WP1)	0.20	0	41.80	1.10	2.70	46.70	6.40	
WM2(WP2)	0.20	0	41.20	1.40	2.50	42.60	10.40	0.00
HN Flux	1.16	1.90	50.57	0	6.22	40.13	0.02	0.00
SrO-Al <sub>2</sub> O <sub>3</sub>	0.73	0.10	0.43	0	0.49	51.96	0.00	46.31

B1 and B2 are fluxes made from bauxite using a sintering method, while HN is from high purity bauxite and alumina in the fused condition. D1 is a flux produced by using a residual from dross treatment. WM1 and WM2 are white mud materials after removing water. Obviously, the fluxes made from the residual of dross treatment and the by-product of alumina production using low-grade ore are environment-friendly products, and should be recommended for industrial application. In this work, D1, WM1 and WM2 are tested and compared with other products.

## THEORETICAL CONSIDERATIONS

### Desulphurization Reaction and Slag Sulphide Capacity

In steelmaking processes sulphur is removed from liquid iron and steel as sulphide according to the following reaction:



The definition of sulphide capacity is commonly derived from the slag-gas exchange reaction [1]:

$$K_1 = \frac{a_{\text{S}^{2-}} \cdot a_{[\text{O}]}}{a_{\text{O}^{2-}} \cdot a_{[\text{S}]}} \quad (2)$$



$$K_3 = \frac{a_{S^{2-}} \cdot p_{O_2}^{1/2}}{a_{O^{2-}} \cdot p_{S_2}^{1/2}} \quad (4)$$

The sulphide capacity of the slag is defined as:

$$C_{S^{2-}} = (\text{wt}\% S) \frac{p_{O_2}^{1/2}}{p_{S_2}^{1/2}} = \frac{K_3 \cdot a_{O^{2-}}}{f_{S^{2-}}} \quad (5)$$

### Desulphurization Rate and Rate Constant

Desulphurization rate is the most interesting parameter to compare different fluxes. Several studies have indicated that reaction (1) can be regarded as a first order heterogeneous reaction [2, 3]. On that basis, the change of sulphur concentration with reaction time can be expressed as:

$$\frac{d[\% S]}{dt} = \frac{K_s A}{V} \cdot [\% S] \quad (6)$$

Integrating Equation 6, the following equation is obtained:

$$\ln \frac{S_t}{S_i} = -\frac{K_s A}{V} t = K_a t \quad (7)$$

where  $K_s$  is the sulphur mass transfer coefficient,  $A$  is the reaction area between molten slag and liquid iron,  $V$  is the volume of hot metal and  $K_a$  is the apparent desulphurization rate constant.

Plotting  $\log(S_t/S_i)$  against time will yield a relatively linear relationship. The slope of this line is the desulphurization rate for a particular desulphurization experiment. Since the slope of the line may change slightly with reaction time, the slope of the curve from zero time to final time is called the average desulphurization rate.

### Replacing CaO-CaF<sub>2</sub> with Calcium Aluminate Fluxes in the Steel Refining Process

The compounds, which can possibly replace CaF<sub>2</sub> in metallurgical slags, are Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub>. The optical basicity and sulphide capacity of CaO-saturated binary slags with different secondary components are shown in Figure 1.

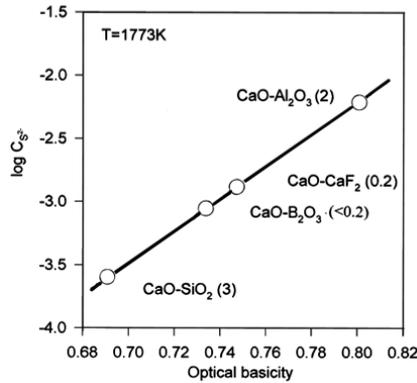


Figure 1: Sulphide capacity of CaO-saturated binary slags with various secondary components at 1773 K (the data shown in each bracket represent the viscosities of the slags in poise at 1773 K)

The values of viscosity of these slags at 1773 K obtained from reference [4] are also shown in the same figure. As shown in the figure, the optical basicity of CaO-Al<sub>2</sub>O<sub>3</sub> slag can reach 0.8 and sulphide capacity can reach  $6.2 \times 10^{-3}$ . However, the maximum value of the optical basicity of CaO-CaF<sub>2</sub> slag can reach 0.75 so that the sulphide capacity can reach only  $1.3 \times 10^{-3}$ . The optical basicity and sulphide capacity of CaO-SiO<sub>2</sub> and CaO-B<sub>2</sub>O<sub>3</sub> slags are lower than those of CaO-CaF<sub>2</sub> slag. Furthermore, B<sub>2</sub>O<sub>3</sub> is not stable under steelmaking conditions after deoxidation and the boron released from B<sub>2</sub>O<sub>3</sub> in the slag will affect the properties of steel. Therefore, it is more reasonable to replace CaO-CaF<sub>2</sub> with calcium aluminate flux in steelmaking.

Calcium aluminate fluxes of various compositions have been widely used as ladle slags to provide the following functions:

- Thermal insulation of steel
- Protection of the steel from atmospheric reoxidation
- Absorption of inclusions from the steel and
- Desulphurization.

Recently, calcium aluminate flux has also been used for hot metal desulphurization together with magnesium powder. In this case, calcium aluminate slag can protect the hot metal from atmosphere oxidation, increase the utilization efficiency of magnesium metal powder and absorb the desulphurization products. Due to its increasing importance, searching for the cheapest sources for calcium aluminate production is of great interest for metallurgists.

## EXPERIMENTAL ASPECTS

### Characterization of Various Aluminate Fluxes

As mentioned above, calcium aluminate fluxes can be produced from various mineralogical precursors such as lime or limestone together with bauxite or aluminum dross. They can be produced in the sintered or fused condition. During this investigation, six different fluxes containing calcium aluminate were evaluated. One flux consisting of strontium aluminate was also examined in order to compare the sulphide capacity with the other potential flux materials. The compositions of the materials were determined using X-Ray Fluorescence spectrometry (XRF) and the results obtained are shown in Table 2.

The content of  $\text{Na}_2\text{O}$  is significantly higher in WM2 compared to that in WM1. All fluxes shown in Table 2 were considered as possible materials for replacing  $\text{CaO-CaF}_2$  flux that is traditionally used in steelmaking. WM1 and WM2 contained 25% water in the as-received condition and had to be calcined prior to use for desulphurization experiments. The major mineral phases present in the white mud were identified using X-Ray Diffraction Analysis (XRD) as gibbsite  $\{\text{Al}(\text{OH})_3\}$ , hydrated calcium aluminum oxide  $\{(\text{CaO})_3\text{Al}_2\text{O}_3(\text{H}_2\text{O})_6\}$ , or  $\text{C}_3\text{AH}_6$ , and hydrated sodium aluminum oxide. Differential Thermal Analysis (DTA) was performed to study the behaviour of the materials during heating. The results showed that dehydration reactions occurred at 526 K (253°C), 592 K (319°C) and 680 K (407°C) respectively. Thermo-Gravimetric Analysis (TGA) confirmed that the weight loss of the white mud materials began at 526 K (253°C) and was complete at 680 K (407°C). Above this temperature the weight loss of the sample was negligible. Dehydration experiments were also carried out in a muffle furnace heated with molybdenum disilicide heating elements. An alumina crucible with 50 grams of white mud powder was placed in the furnace at the desired temperature and the crucible and contents weighed after being heated for 30, 60, 90 and 120 min. The process was repeated at different temperatures in the range from 473 K to 973 K. The results obtained from the dehydration tests are shown in Figure 2. As shown in the figure, no significant weight loss occurred when the powder was heated at temperatures below 523 K (250°C). In the temperature range from 523 to 873 K, the dehydration rate increases with increasing temperature. Above 873 K, the dehydration rate remains constant. It can be concluded that all of the combined water in the white mud material was removed after heating at 873 K for 30 to 60 minutes. These results are in accord with the findings of the TGA analysis.

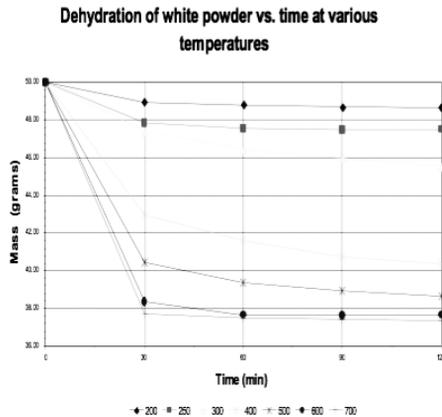


Figure 2: Results of dehydration of WM2 flux

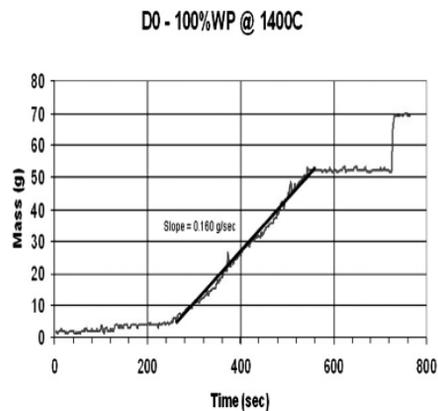


Figure 3: Drip test result of WM2 flux at 1673 K

### Melting Rate Study of Calcium Aluminate Fluxes

A drip test method was used to compare the melting rates of different fluxes. Experiments were carried out in a 30 kW induction furnace. Details of the experimental set up are given in references [5, 6]. A graphite crucible, 70 mm in diameter, was used as the container for the fluxes. The bottom of the crucible contained a 5mm diameter hole, which allowed the molten slag to flow from the crucible and drop into a pan-receiver, which was located on a load cell. The signal from the load cell was transferred to a computer and the change in weight as a function of time was obtained. The melting rate was defined as the weight

of liquid flux produced per unit time. A typical result obtained during the evaluation of flux WM2 at 1673 K is shown in Figure 3 where three regimes can be observed. The first regime is essentially flat because the fluxes are still in a solid state while being heated to the melting point. The second regime begins when the flux becomes liquid and drips through the crucible opening onto the pan. The slope of this region is used to calculate the melting rate of the flux. The final regime corresponds to the time when all of the flux that can exit the crucible has done so.

### Desulphurization Tests

These tests were also carried out in a 30 kWh induction furnace. During each trial, 500 g of hot metal in a graphite crucible was heated in the induction furnace. After melting, a certain amount of FeS was added to the hot metal to adjust the initial sulphur content. When the hot metal temperature reached the desired value, the first metal sample was taken. After sampling, 58 g of flux containing different amounts of calcium aluminate and lime was added to the top surface of the hot metal, the time of this addition was taken as zero time. Metal samples were taken every 5 minutes. After about 20 minutes, the time interval for taking the sample increased to 10 minutes. The total time for the test was about 40 minutes. Desulphurization results using the fluxes made from different raw materials are shown in Figure 4.

## RESULTS AND DISCUSSION

### Comparison of the Desulphurization Fluxes from Different Sources

As the initial sulphur content in the metal for each trial is different, rather than plotting [%S] versus time, it is useful to plot the ratio  $[\%S]_t/[\%S]_i$  against time. The desulphurization performance of the different fluxes can now be compared. The results from the desulphurization trials using the five fluxes B1, B2, D1, WM1 and WM2 are plotted in Figure 4.

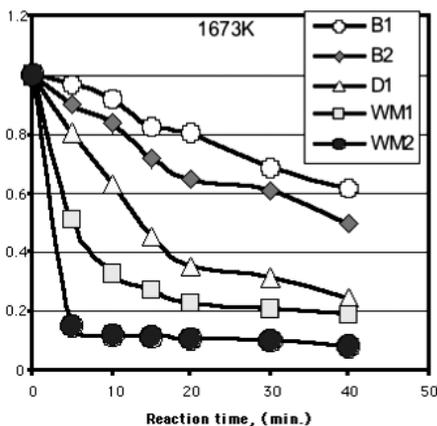


Figure 4: Desulphurization using fluxes made from different raw materials

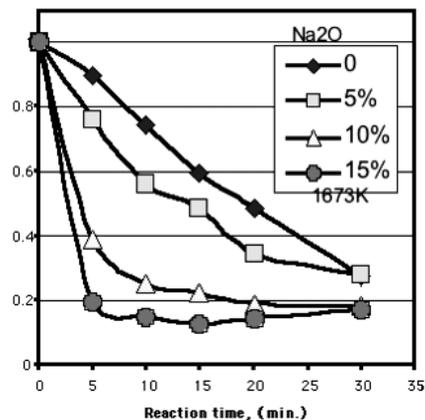


Figure 5: Effect of Na<sub>2</sub>O in calcium aluminate fluxes on desulphurization at 1673 K

It can be seen that in the first 10 minutes the sulphur content in the hot metal is reduced to 85-90% of its original value with fluxes B1 and B2, to 65% with flux D1, and to 33-12% with fluxes WM1 and WM2. This suggests that the fluxes made from the white mud have the best desulphurization performance. All fluxes made from the waste or from by-products of the aluminum industry showed good desulphurization behaviour. The main reason for the good performance of flux WM2 is the slag composition. In Figure 4, all of the fluxes used in the test have the CaO to Al<sub>2</sub>O<sub>3</sub> ratio adjusted to unity, however the existence of Na<sub>2</sub>O in the WM1 and WM2 fluxes further increased the slag basicity and hence the sulphide capacity.

### Effect of Na<sub>2</sub>O on Desulphurization

Na<sub>2</sub>O is an unavoidable component of the by-product of alumina production using low-grade bauxite. For some applications, where a high Na<sub>2</sub>O content is not required, Na<sub>2</sub>O can be removed by washing with water. This washing operation will increase the cost of the WM flux. In order to study the effect of sodium oxide in the fluxes on desulphurization and maintain an optimum content of Na<sub>2</sub>O in the flux, experiments were arranged to study the effects of Na<sub>2</sub>O content on desulphurization and on the working environment during the desulphurization treatment. For these experiments, fluxes made from B2 (as base flux) with appropriate amounts of CaO and Na<sub>2</sub>O were used. The ratio of CaO to Al<sub>2</sub>O<sub>3</sub> in the fluxes was adjusted close to unity (C/A=1) and Na<sub>2</sub>O content changed from 0 to 15%. As shown in Figure 5, desulphurization rate increased with increasing Na<sub>2</sub>O content. When Na<sub>2</sub>O content is over 10%, resulphurization was found in the later stages of the process. A strong white vapour was observed during the desulphurization operation. Therefore, 10% Na<sub>2</sub>O in the flux may be an optimum value.

### Effects of SiO<sub>2</sub> and TiO<sub>2</sub> in Fluxes on Desulphurization

SiO<sub>2</sub> and TiO<sub>2</sub> are undesirable components in the flux for some operations of steel refining, but they are unavoidable when bauxite or red mud are used for the production of calcium aluminate. In the market the requirement for low SiO<sub>2</sub> and TiO<sub>2</sub> contents in the fluxes (SiO<sub>2</sub><6%, TiO<sub>2</sub><2%) will result in a high price. Therefore, the study of optimum SiO<sub>2</sub> and TiO<sub>2</sub> contents in calcium aluminate flux is related to the production cost of steelmaking, and is therefore interesting for steel companies. The effects of SiO<sub>2</sub> and TiO<sub>2</sub> in the fluxes on desulphurization are shown in Figure 6 and Figure 7 respectively. As shown in the Figures, both SiO<sub>2</sub> and TiO<sub>2</sub> in the fluxes showed a negative effect on desulphurization. However, the negative effect of SiO<sub>2</sub> is more significant than TiO<sub>2</sub>. Both SiO<sub>2</sub> and TiO<sub>2</sub> are common impurities found in the bauxite mineral. In order to control SiO<sub>2</sub> and TiO<sub>2</sub> content in the fluxes made from bauxite, high quality bauxite with low SiO<sub>2</sub> and TiO<sub>2</sub> content must be selected. This will increase the cost of the refining flux. The fluxes made from the waste products of the aluminum industry (D1, WM1 and WM2) contain 2-10% Na<sub>2</sub>O and very low amounts of SiO<sub>2</sub> and TiO<sub>2</sub>. This is a major advantage of the refining fluxes made from the waste or by-products of the aluminum industry.

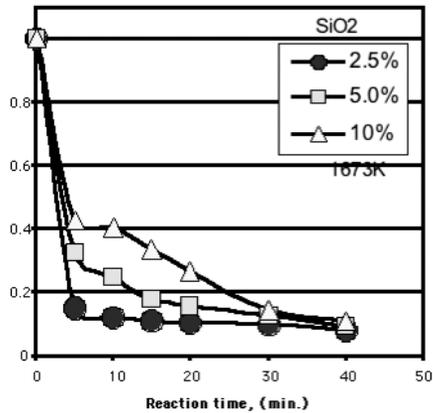


Figure 6: Effect of  $\text{SiO}_2$  in calcium aluminate fluxes on hot metal desulphurization

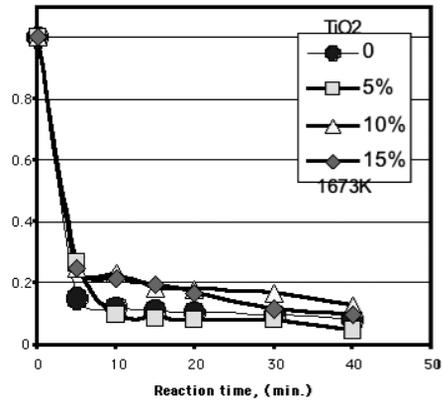


Figure 7: Effect of  $\text{TiO}_2$  in calcium aluminate fluxes on hot metal desulphurization

### Correlation of Desulphurization Rate with Melting Rate

Considering the relatively low temperature of hot metal and the limited time available for hot metal treatment, a high desulphurization rate is always desirable. The apparent desulphurization rate constant,  $K_a$ , derived from Equations 6 and 7 is a good parameter to compare different desulphurization fluxes. Traditionally,  $K_a$  has been viewed as a kinetic factor to evaluate desulphurization. In this context, fast melting of the fluxes should be the main factor for increasing the desulphurization rate. In order to study the effect of slag melting rate on desulphurization rate, experiments were carried out with six different slag mixtures. The change in sulphur content of hot metal with reaction time for the six flux mixtures are shown in Figure 8. In this Figure, WP2 corresponds to the flux WM2 in Table 2, HN China sintered is B1, HN China fused is HN flux, PV is the pure  $\text{SrO} \cdot \text{Al}_2\text{O}_3$ . The melting rates for all six mixtures used in the tests shown in Figure 8 were measured. The relationships between desulphurization rate,  $K_a$ , calculated from Figure 8 and melting rate,  $K_m$ , are plotted in Figure 9. As shown in this figure, for fluxes with the same optical basicity, the desulphurization rate increases with increasing melting rate. For slags with the same melting rate, desulphurization rate increases with increasing slag basicity. This means that desulphurization rate is a composite index for evaluating the desulphurization performance of different fluxes, and it depends on both thermodynamic and kinetic factors. Since WM2 slag has a high basicity and a low melting point, the best desulphurization performance was achieved using this flux. Thus, WM2 flux should be a good choice for hot metal desulphurization.

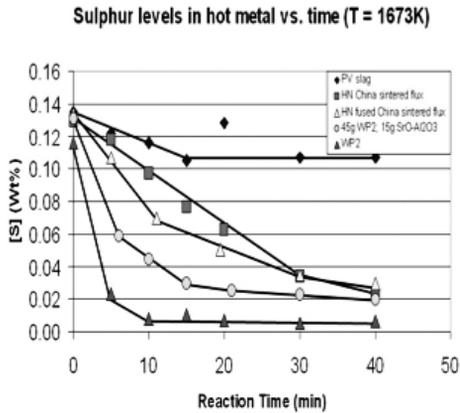


Figure 8: Changes of sulphur content in hot metal with reaction time at 1673 K

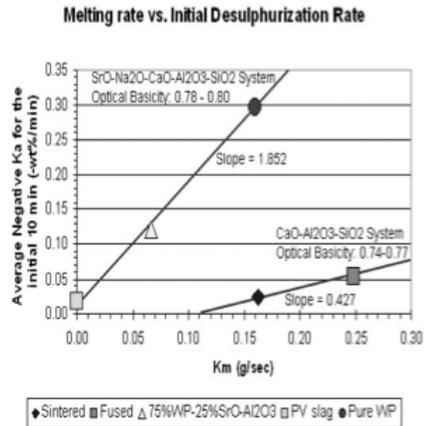


Figure 9: Correlation of desulphurization rate with flux melting and also basicity at 1673 K

In order to study the effect of thermodynamic factors on the desulphurization rate, more experimental results are shown in Figures 10 and 11. Figure 10 shows the dependence of desulphurization degree on slag optical basicity. A linear relationship is found between the two parameters as expected. However, in the high optical basicity region ( $\Lambda=0.78-0.82$ ), the slope of the curve declined slightly. Since the flux with high basicity has a strong desulphurization capacity, the sulphur content in hot metal could be reduced to below 0.01% within 10 minutes. When sulphur content in hot metal is very low, sulphur diffusion within the hot metal becomes the rate controlling step for the desulphurization reaction. This results in a lower desulphurization rate during a limited period of time. Figure 11 shows the relationship between the apparent desulphurization rate constant,  $K_a$ , and slag optical basicity. As shown in the Figure, the  $K_a$  value increases with increasing slag optical basicity. A break point is found at an optical basicity of  $\Lambda=0.75$ . The reason for this is that the fluxes with  $\Lambda>0.75$  contain a certain amount of  $\text{Na}_2\text{O}$ , which not only increases the slag optical basicity but also reduces the slag melting point. Both factors help to increase the slag desulphurization rate and therefore the rate constant. In the case of  $\Lambda<0.75$ , these fluxes are essentially  $\text{CaO-Al}_2\text{O}_3$  binary slag. With the increase in slag basicity, the components that reduce the slag melting point, such as  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , will decrease, which will affect the desulphurization rate. Thus it can be concluded that  $K_a$  is not only a kinetic factor as generally understood, it is also a composite index that is indicative of desulphurization performance.

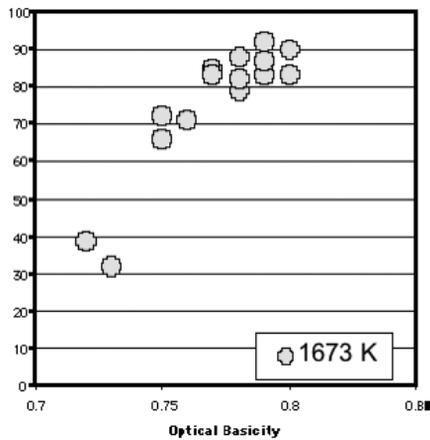


Figure 10: Dependence of desulphurization degree on slag optical basicity at 1673 K

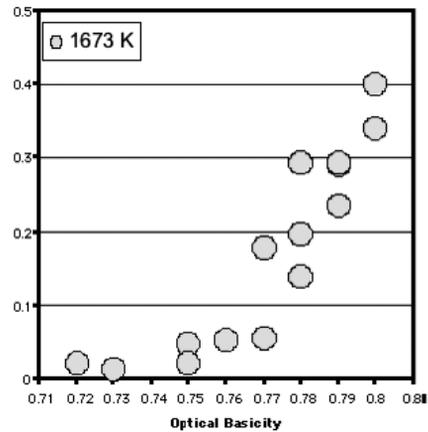


Figure 11: Dependence of  $K_a$  value on optical basicity of calcium aluminate fluxes at 1673 K

## CONCLUSIONS

- Both aluminum and steel are energy intensive and environmentally sensitive industries. A comprehensive use of the waste slags and solid residuals from the aluminum industry by the steel industry can significantly reduce the disposal of waste, increasing the economic benefit within the industry and reducing the impact on the environment.
- The calcium aluminate fluxes made from dross and the by-product of alumina production showed high melting rate and good desulphurization performance. It is suggested that this is an excellent desulphurization reagent and environment-friendly flux for hot metal pretreatment and liquid steel refining.
- The apparent desulphurization rate constant is a composite index to evaluate the desulphurization performance of different fluxes. This parameter is influenced by both thermodynamic and kinetic factors within the reaction system.

## NOMENCLATURE

- A = Total reaction area between molten slag and liquid iron.  
a = Activity of a component of molten slag or liquid metal.  
B = Basicity.  
 $C_S$  = Sulphide capacity of molten slag.  
f = Activity coefficient related to wt%.  
K = Equilibrium constant of chemical reaction.  
 $K_a$  = Apparent desulphurisation rate constant.  
 $K_m$  = Melting rate of solid flux or slag.  
 $K_S$  = Sulphur mass transfer coefficient.  
 $P_{O_2}$  = Oxygen partial pressure.  
 $P_{S_2}$  = Sulphur partial pressure.  
 $S_i$  = Initial sulphur content in hot metal.  
 $S_t$  = Sulphur content in hot metal at any reaction time.  
t = Reaction time.

- V = Volume of hot metal.  
 ( ) = Solute in molten slag.  
 [ ] = Solute in liquid metal.

## REFERENCES

- Wagner, C.** (1975). *The Concept of the Basicity of Slags*. Metall. Trans. B, Vol. 6B, pp. 405-409. [1]
- Sommerville, I. D., Grieveson, P. & Taylor, J.** (1980). *Kinetics of Reduction of Iron Oxide in Slag by Carbon in Iron*. Part 1: Effect of Oxide Concentration, Ironmaking & Steelmaking, Vol. 47, No. 1, pp. 25-32. [2]
- Pomfret, R. J. & Grieveson, P.** (1983). *The Kinetics of Slag-Metal Reactions*. Canadian Metallurgical Quarterly, Vol. 22, pp. 287-299. [3]
- Slag Atlas.** (1981). Verlag Stahleisen M.B.H., (Dusseldorf), pp.196-198. [4]
- Yang, Y. D., Sommerville, P. I. D. & McLean, A.** (2004). *The Use of Waste Materials from Aluminum Production as Refining Fluxes for Hot Metal and Liquid Steel*. Proc. of Waste Processing and Recycling in Mineral and Metallurgical Industries V, pp.143-154. [5]
- Yang, Y. D. & Sommerville I. D.** (2001). *Comparison of Various Calcium Aluminate Fluxes for Hot Metal and Liquid Steel Desulphurization*. 84<sup>th</sup> Steelmaking Conference Proceedings, pp. 493-502. [6]

