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Hot Metal Desulphurization Using Waste Residues from the Aluminum Industry

Abstract: In this paper, the sources, properties and possible applications of waste residues from the aluminum industry as refining agents for the steel industry were investigated. Characterization of the potential fluxing agents was performed using a combination of XRD, XRF, DTA, and TGA. Experiments were carried out to examine the potential of hot metal desulphurization with fluxes made from these residue materials in comparison with those obtained from bauxite. To facilitate this comparative behavior of fluxes derived from different source materials, particular attention was given to the enhancing effects of controlled amounts of sodium oxide in contrast to the deleterious effects associated with the presence of silica and titanium dioxide on the desulphurization process. A major advantage of refining fluxes made from white mud waste products is that they contain significant amounts of sodium oxide and only very small concentrations of the oxides of silicon and titanium.

Keywords: aluminum industry, waste residues, calcium aluminate fluxes, hot metal desulphurization, steelmaking

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1 Introduction

Dr. Masanori Iwase spent two years from 1979 through 1981 as a Visiting Research Associate at the University of Toronto. During that period his research activities included a study of the thermodynamics of iron-bismuth alloys conducted in collaboration with Inland Steel Company, the application of electrochemical sensors for the evaluation of the oxygen potential in protective gas shrouds during continuous casting of steel billets at the Lake Ontario Steel Company, and a study of the thermodynamics of phosphorus behavior in metallurgical slags. Throughout his distinguished career Professor Iwase welcomed many visitors from abroad to his Ferrous Metallurgy Research Group at Kyoto University. He also had numerous visits over the years to Canada, Sweden and Australia and initiated many collaborative activities between the different research groups. He was a great teacher to his students and always emphasized the importance of the practical implications of their fundamental studies. It is a marvelous tribute to his endeavors that many of his former students have gone on to occupy leading positions within industry. It is therefore with good memories of warmest friendship and great times together that this paper is prepared in honour of Professor Masanori Iwase and his outstanding career in process metallurgy.

In order to produce one tonne of liquid steel, about 100–150 kg of slag will be produced in addition to that produced during the ironmaking process. Using hot metal low in sulphur and phosphorus contents will significantly reduce the flux consumption and waste slag disposal from the steelmaking process. In ferrous metallurgy, finding a flux with high refining capacity and low cost is of great interest. Traditionally, $CaO\text{-}CaF_2$ based fluxes are used as desulphurizing agents for hot metal pretreatment. However, it has been found that fluorine compounds can destroy ozone molecules. Also if fluorine compounds enter the water system, this can pose a problem to human health by weakening of the bones, inducing stomach problems or even bone cancer. As a result, metallurgical industries are seeking an alternative flux.

During the production of aluminum and alumina, several different types of waste materials are generated as by-products including red mud, white mud, and dross from electrolysis and casting. The storage of these waste residues constitutes a major environmental concern due to the sheer volume and causticity of the materials. The composition of the waste residues varies and often depends on the starting raw material and subsequent processing route.

The iron and steel industry could potentially utilize these materials as fluxes in refining operations, since the associated flux consumption is significantly higher than that of other industries. Preliminary research has shown that these waste materials are viable candidates to be used as refining agents in iron and steelmaking processes, since they are able to produce similar results as fluxes currently used by the industry. The resulting slag is inert, and will be safe to dispose after use for refining operations. The application of residues from the aluminum industry as a basis for metallurgical fluxes in the steel industry would be beneficial from both economical and environmental perspectives.

2 Waste residues generated by the aluminum industry

The sources of waste slags and by-products from the aluminum industry and their possible applications are summarized in Figure 1.

2.1 Red mud

Red mud is an iron-rich residue formed as a result of the extraction of alumina from bauxite. As shown in Figure 1, about 2–3 tonnes of red mud material are generated for the production of every tonne of alumina. Because of the size of this waste stream and its causticity, red mud is a major environmental concern. In most cases, the red mud is stored on location close to aluminum production establishments and a considerable amount of land is required for this purpose [1]. Development of potential applications for this bauxite residue would reduce its impact on the environment and is therefore an important consideration with respect to the management of waste materials and contaminated sites.

Currently, most alumina is produced from bauxite by three methods: the Bayer process, the Lime-Sintering process and the Combined process [2]. The choice of exact processing route largely depends on the specific composition of bauxite ores. There are four main types of bauxite in nature: gibbsite bauxite, boehmite bauxite, diasporic bauxite and combined bauxite [3]. In general, the digestion process is easier for gibbsite bauxite in comparison to boehmite bauxite and diasporic bauxite. Another important aspect that influences the quality of bauxite is the weight ratio between alumina and silica, expressed as the A/S ratio. The Bayer process usually requires gibbsite bauxite or boehmite bauxite with an A/S ratio greater than 7. On the other hand, the Lime-Sintering process is employed to cope with diasporic bauxite where the A/S ratio is often less than 7. Examples of the chemical composition of different waste materials generated during alumina and aluminum production processes are summa-

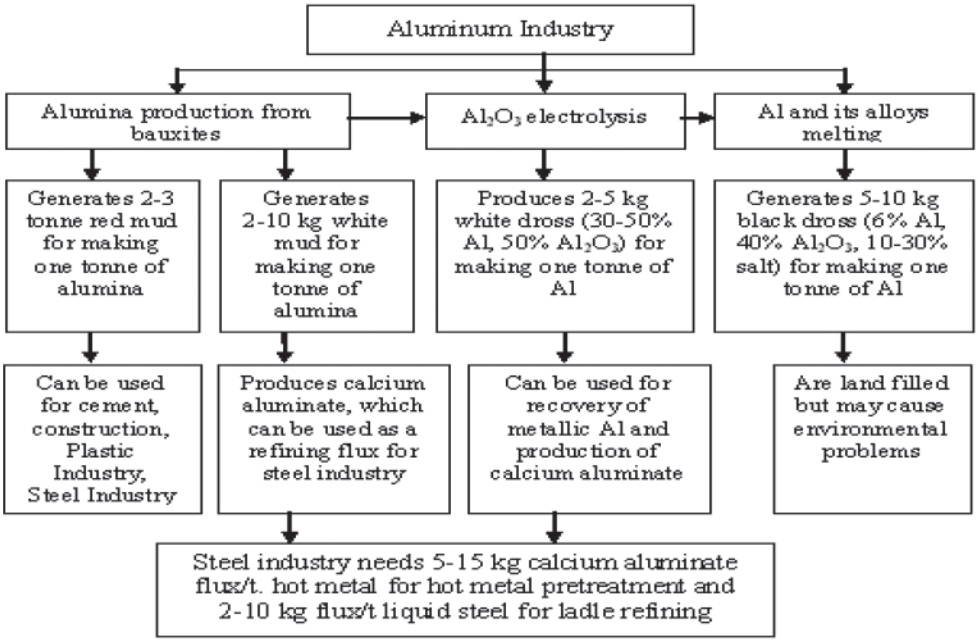

Fig. 1: Sources of waste residues from the aluminum industry and their potential applications.

	CaO	MgO	Na_2O	K_2O	Fe_2O_3	TiO_2	Al_2O_3	SiO_2	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
RM3	47.27	0.44	1.54	0.09	9.61	3.81	4.65	24.91			6.31
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
Bauxite	1.23				5.63	2.74	64.07	8.43			13.22
Dross R							60.00		15–25	6–15	

Table 1: Chemical Compositions of Various Materials containing Alumina (mass%)

rized in Table 1 where RM and WM refer to red and white muds respectively.

2.2 White mud

White mud is a by-product of alumina production by the Lime-Sintering process. For alumina production using this method, the desilication procedure is crucial as it controls the quantity and the quality of the alumina produced. To obtain high purity alumina, a two-stage desilication technique is commonly used. The first desilication stage typically achieves an Al_2O_3/SiO_2 ratio of 300 to 450 [4]. The residue left from this stage is called sodium-aluminum silicate slime ($Na_2O.Al_2O_3.2SiO_2.nH_2O$). To further increase the purity of alumina, slaked lime is added to the sodium aluminate solution during the second desilication stage. Silica and a small amount of alumina will combine with lime to form a garnet ($3CaO.Al_2O_3.xSiO_2.yH_2O$). The precipitated material from the second desilication stage is in the form of mud which is white in colour and is therefore commonly called white mud. Recycling this by-product as a charging material for alumina production would increase energy consumption and decrease the productivity of the rotary kiln. Thus from an economic standpoint, there is an incentive to develop an appropriate application for this white-mud by-product.

2.3 Dross materials

Dross is an unavoidable by-product from aluminum production. Depending on the process, it contains, on average, about 50% free aluminum metal dispersed in an oxide layer. Since aluminum production is highly energy-intensive, dross recycling is very attractive from both the energy and the economic points of view. The conventional recycling process using the rotary salt furnace (RSF) produces a non-metallic salted residue, which has to be landfilled since no commercial use for this portion of the dross has been found. To make use of the non-metallic part of the dross, salt-free dross treatment processes may be used. Such processes produce salt-free non-metallic residues, which can then be treated to produce calcium aluminates for use as refining fluxes in the steel industry. Since fluxes made from dross have already been used by the steel industry, the main focus of this paper will be on the potential application of white mud as the basis for a new refining reagent.

The bauxite material shown in Table 1 has an A/S ratio of 7.6, and can therefore be used as the raw material for alumina production by means of the Bayer process. RM1 represents a typical composition of red mud generated by the Bayer process. RM2 is typical of the red mud generated using the Lime-Sintering process. RM3 corresponds to the red mud obtained when alumina is produced by means of the Lime-Bayer process in which lime is used to digest alumina. WM1 and WM2 are white muds generated during desilication from sodium aluminate concentrated solution in the Lime-Sintering process. The notable difference between WM1 and WM2 is the sodium oxide content. Dross R is the residual of the high temperature dross treatment for recovery of aluminum metal.

As shown in Table 1, RM1 generated from alumina production by the Bayer process is characterized by high iron oxide and low lime contents which are not the most suitable conditions for hot metal desulphurization. On the other hand, RM2 generated from the Lime-Sintering process contains higher lime and much lower iron oxide content and is therefore more appropriate for desulphurization.

3 Production of calcium aluminate refining fluxes

The production of calcium aluminate fluxes can be classified based on the different sources of alumina: (1) from the by-products of alumina production, (2) from secondary dross of the high temperature dross treatment process, and (3) from bauxite.

3.1 From the by-products of alumina production

The iron oxide in red mud from the Bayer process can be recovered using smelting reduction, solid-state reduction or magnetic separation. In the smelting process, red mud is charged into the blast furnace or electric arc furnace with coke and lime or limestone. The iron oxide is reduced to generate pig iron that can be used in steel production, and the slag from the process can be used as refining flux or for construction materials after proper treatment. In the solid-state reduction process, the mud is mixed with a reducing agent or brought in contact with a reducing gas to produce metallic iron in a rotary kiln. The solid residue from this process can be used for making refining flux after adding a certain amount of lime and other additives. Magnetic separation is also an attractive option to recover iron from red mud. According to a study by Jamieson et al., [5] a wet high intensity magnetic separation (WHIMS) was employed to obtain a magnetic fraction containing around 56% Fe_2O_3 (mass percent) and a non-magnetic fraction of less than 4% Fe_2O_3 (mass percent). In China, Shandong Aluminum Company also used WHIMS to produce a concentrate containing 56%–76% Fe_2O_3 (mass percent). The recovery of Fe_2O_3 was 45%. Another method is to convert hematite or goethite in red mud to magnetite, followed by magnetic separation. Thus magnetic separation is becoming a more widely accepted approach for recovering iron from red mud, particularly in view of the increasing demand for iron ore throughout the world. Moreover, extracting iron from red mud also means lesser amounts of red mud will be stored in landfill. The residue after iron oxide recovery can be used to make calcium aluminate based flux by smelting or pelletizing with lime and other additives. Red mud from the Lime-Bayer process (RM3) or the Lime-Sintering process (RM2) contains higher lime and lower iron oxide contents. This material has a relatively low melting point and high basicity, which makes it suitable for hot metal pretreatment and steel refining. The iron oxide in the red mud can be controlled by addition of carbon and/or aluminum, or can be removed by calcination in a rotary kiln prior to its application. The compositions of RM2 and RM3 shown in Table 2, were calculated from Table 1 by removing the loss of ignition (LOI).

The white mud residues WM1 and WM2 from the Lime-Sintering process contain high lime, sodium oxide and low silica contents and therefore have a high basicity. They also have a relatively low melting point, and therefore should be an excellent base material for hot metal desulphurization.

3.2 From the residuals of dross treatment

The residues from the high temperature dross treatment processes (secondary dross) contain 6–15% aluminum, 15–25% aluminum nitride, 50–60% Al_2O_3 and other oxides. This waste contains a high-energy value. 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 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, at the hot end of the kiln, the temperature of the sintered material is increased to about 1573 K to complete the reaction between CaO and Al_2O_3 to form calcium aluminate. The energy consumption of the process is low because aluminum and aluminum nitride in the secondary dross are oxidized and the energy contained in the two components is released. The whole

	CaO	MgO	Na_2O	K_2O	Fe_2O_3	TiO_2	Al_2O_3	SiO_2	Opt.B
B1	35.10	0.40	0	0.05	2.90	2.20	53.30	6.00	0.729
B2	33.80	0.70	0	0	2.30	2.60	52.40	7.20	0.725
D1	33.60	8.80	1.90	0	0.70	0.20	49.80	3.10	0.766
RM2	42.74	1.61	8.66	1.15	14.37	4.11	6.89	20.47	0.835
RM3	51.27	0.48	1.67	0.10	10.42	4.13	5.04	27.02	0.761
WM1	39.96	1.06	7.03	0.50	0.12	0.03	48.53	2.78	0.814
WM2	39.46	1.38	13.08	0.52	0.13	0.01	42.76	2.41	0.867
HN Flux	50.57	0	0.02	0	1.16	1.90	40.13	6.22	0.771

Table 2: Compositions of Calcium Aluminate Fluxes made from Different Sources (mass%)

process from the recovery of aluminum to calcium aluminate production is a closed loop process with no waste residue. The composition of calcium aluminate flux made by dross treatment is shown in Table 2 as D1.

3.3 From bauxite

For this production route, bauxite, limestone and other raw materials are ground and pelletized then sintered in a rotary kiln at about 1573 K. The fuels used for sintering can be coal, natural gas or oil and the process can be conducted in any cement plant with no additional investment. When solid fuels are used, the residue and gangue, for example, the sulphur and ash from coal, will contaminate the calcium aluminate flux. The main drawback of the process is that the bauxite raw material must be of high quality. In Table 2, B1 and B2 are calcium aluminate fluxes produced from bauxite through the rotary kiln process. However the oxide contents of iron, titanium and silicon in these fluxes may be too high for certain secondary steelmaking processes. The calcium aluminate flux shown in Table 2 as HN was produced by fusing high-grade bauxite with lime and other additives. In this case, the fusion process is expensive and this will increase the production cost of the flux.

4 Fundamentals of hot metal desulphurization

4.1 Sulphide capacity of molten slags

The definition of sulphide capacity is commonly derived from the slag-gas exchange reaction [6]:

$$\frac{1}{2}\mathrm{S_2(g)}+\mathrm{O^{2-}}=\mathrm{S^{2-}}+\frac{1}{2}\mathrm{O_2} \tag{1}$$

$$K_1=\frac{a_{S^{2-}}\cdot p_{O_2}^{1/2}}{a_{O^{2-}}\cdot p_{S_2}^{1/2}} \tag{2}$$

The sulphide capacity of the slag is defined as:

$$C_{S^{2-}}=(wt\%S)\frac{p_{O_2}^{1/2}}{p_{S_2}^{1/2}}=\frac{K_1.a_{O^{2-}}}{f_{S^{2-}}} \tag{3}$$

By introducing the free energy change for the dissolution of gaseous sulphur into liquid iron and taking logarithms of both sides of Equation (3), the relation between slag sulphide capacity and the sulphur distribution ratio between molten slag and liquid iron is expressed as follows:

$$\log L_S=\log C_{S^{2-}}+\log f_S-\frac{1}{2}\log p_{O_2}-\frac{7055}{T}+1.224 \tag{4}$$

Considering the free energy change for the dissolution of gaseous oxygen into liquid iron, Equation (4) can be rewritten as:

$$\log L_S=\log C_{S^{2-}}+\log f_S-\log a_{[O]}-\frac{935}{T}+1.375 \tag{5}$$

4.2 Optical basicity as an indicator of slag performance

The concept of optical basicity was developed by glass scientists and introduced to the metallurgical community by Duffy, Ingram and Sommerville in the late seventies [7, 8]. This approach provides a good foundation for a better understanding of the behaviour of molten slags than conventional basicity ratios such as lime/silica or (lime plus magnesia)/silica. It has proved to be a valuable tool for designing slags or fluxes which will have the required characteristics with respect to the behaviour of, for example, sulphur, phosphorus, hydrogen, magnesia and alkalis. Optical basicity of molten slag can be calculated using the following relationships:

$$\Lambda=\sum_{i=1}^{n}\Lambda_i N_i \tag{6}$$

$$N_i=\frac{X_i n_{oi}}{\sum_{i=1}^{n}X_i n_{oi}} \tag{7}$$

Here Λ: Optical basicity of the slag
Λ_i: Optical basicity value of component “i”
N_i: Compositional fraction
X_i: Mole fraction of component “i” in the slag
n_{Oi}: Number of oxygen atoms in component “i”

Optical basicity values for oxides in metallurgical slag can be found in several publications [7–10]. The values from Duffy and Ingram [7] are based on the theory of Pauling electronegativity, while those from Nakamura et al. are based on the average electron density of the oxides [9].

Oxide	Ion-Oxygen Attraction, $I = (2Z)/d^2$	Ionic Bond Fraction	Optical Basicity, Λ Derived from Pauling Electronegativity	Optical Basicity, Λ Derived from Average Electron Density	Optical basicity, Λ, Recommended
K_2O	0.27	0.68	1.40	1.15	1.40
Na_2O	0.36	0.65	1.15	1.10	1.20
Li_2O	0.50	0.63	1.07	1.05	1.05
BaO	0.53	0.65	1.15	1.08	1.10
SrO	0.63	0.61	1.07	1.04	1.05
CaO	0.70	0.61	1.00	1.00	1.00
MnO	0.83	0.47	0.59	0.95	0.95
FeO	0.87	0.38	0.51	0.93	0.93
MgO	0.95	0.54	0.78	0.92	0.85
Cr_2O_3	1.44	0.41	0.55	0.69	0.69
Fe_2O_3	1.50	0.36	0.48	0.69	0.69
Al_2O_3	1.66	0.44	0.61	0.68	0.65
TiO_2	1.85	0.41	0.61	0.64	0.65
B_2O_3	2.34	0.31	0.42	0.42	0.42
SiO_2	2.44	0.36	0.48	0.47	0.48
P_2O_5	3.31	0.28	0.40	0.38	0.40

Table 3: Optical Basicity Values for Oxides [10]

Recommended values for the optical basicities of the oxides of interest in metal extraction are shown in Table 3 [10].

From a quantitative evaluation of desulphurization data for a number of different slag systems, Sosinsky and Sommerville derived the temperature dependence of the sulphide capacity for slags with different optical basicity as [11]:

$$\log C_{S^{2-}} = \left(\frac{22690 - 54640\Lambda}{T}\right) + 43.6\Lambda - 25.2 \qquad (8)$$

By using virtually all the experimental data for sulphide capacities available at 1773 K for CaO based slags, the following equation is obtained:

$$\log C_{S^{2-}} = 12.6\Lambda - 12.3 \qquad (9)$$

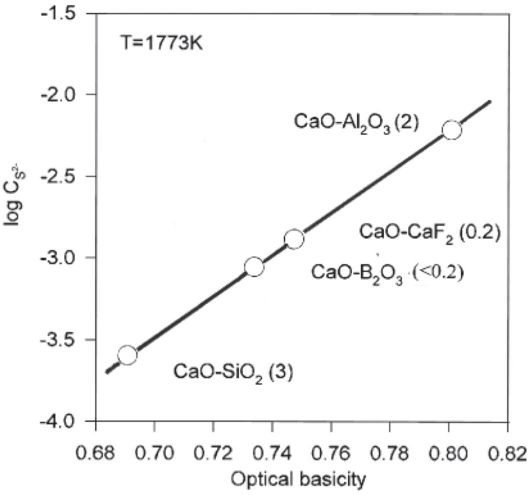

Fig. 2: Sulphide capacity of CaO-saturated binary slags with various secondary components. (The number shown within each bracket represents the viscosity of the slag in 10^{-1} Pa.s at 1773 K).

4.3 Replacement of calcium fluoride in metallurgical slags

Additives which can possibly replace calcium fluoride in metallurgical slags include Al_2O_3, SiO_2 and B_2O_3. The optical basicity and sulphide capacity of CaO-saturated binary slags with each of these different components are shown in Figure 2 together with the viscosity values for the slags at 1773 K obtained from the literature [12]. From the data in Figure 2, the optical basicity of CaO-Al_2O_3 slag at lime saturation is 0.8 with a corresponding sulphide capacity of 6.2×10^{-3}. However, the maximum optical basicity value for CaO-CaF_2 slag is only 0.75 so that the expected sulphide capacity is relatively lower at 1.3×10^{-3}. The optical basicity and sulphide capacity of CaO-B_2O_3 and CaO-SiO_2 slags are lower than those of CaO-CaF_2. Furthermore, B_2O_3 is unstable under steelmaking conditions after deoxidation and the boron released from B_2O_3 in the slag will affect the properties of steel. Based on this comparative analysis, it is evident that replacement of CaO-CaF_2 with CaO-Al_2O_3 flux is the preferred option for desulphurization during steelmaking operations.

Calcium aluminate fluxes of various compositions have been widely used as ladle slags to provide the following functions: (1) Thermal insulation of steel, (2) Protection of the steel from atmospheric reoxidation, (3) Absorption of inclusions from the steel and (4) Desulphurization. Calcium aluminate flux together with magnesium powder has also been used for hot metal desulphurization. In this case, calcium aluminate slag can protect the hot metal from atmospheric oxidation, increase the utilization efficiency of magnesium metal powder and absorb the desulphurization products. Due to the increasing importance of this flux, there is an increasing interest in finding additional sources of low-cost calcium aluminate based materials for use in iron and steelmaking.

5 Experimental aspects

5.1 Characterization of calcium aluminate fluxes

As mentioned above, calcium aluminate fluxes can be produced from various mineralogical precursors such as lime or limestone together with bauxite, red mud, white mud or aluminum dross. They can be produced in the sintered or fused condition. During this investigation, a number of different fluxes containing calcium aluminate were evaluated however as mentioned previously, the main focus of this paper is on the potential application of white mud as the basis for a new refining reagent.

The compositions of the materials were determined using X-Ray Fluorescence spectrometry (XRF) and the results obtained are summarized in Table 2. The content of Na_2O is significantly higher in WM2 compared to that in WM1. WM1 and WM2 contained 25% water in the as-received condition and had to be calcined prior to use for the desulphurization experiments. The major mineral phases present in the white mud were identified using X-Ray Diffraction Analysis (XRD) as gibbsite $\{Al(OH)_3\}$, hydrated calcium aluminum oxide $\{(CaO)_3Al_2O_3(H_2O)_6$, or C3AH6}, 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 (407 °C) respectively. Thermo-Gravimetric Analysis (TGA) confirmed that the weight loss of the white mud materials began at 526 K and was complete at 680 K. Above this temperature the weight loss of the sample was negligible. Dehydration experiments were also carried out in a muffle furnace fitted 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 experiments are shown in Figure 3. As shown in the figure, no significant weight loss occurred when the powder was heated at temperatures below 523 K. In the temperature range from 523 to 873 K, the dehydration rate increases with increasing

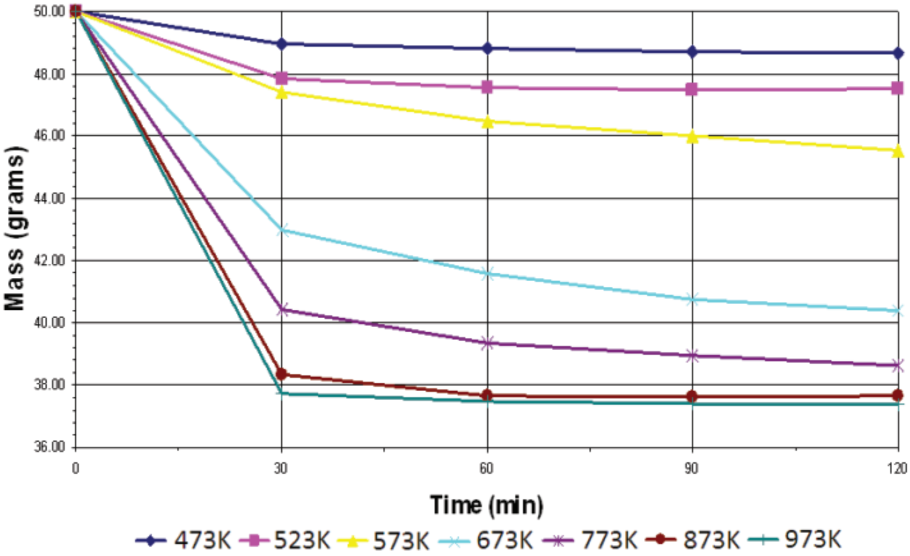

Fig. 3: Dehydration of WM2 flux.

temperature. Above 873 K, the dehydration rate remained constant. This confirms 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 from the TGA analysis.

5.2 Desulphurization experiments

These experiments were carried out in a 30 kW 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 time zero. Metal samples were taken every 5 minutes. After 20 minutes, the time interval for taking the sample increased to 10 minutes. The total time for each trial heat was 40 minutes. Desulphurization results using the fluxes made from different raw materials are shown in Figure 4.

6 Results and discussion

6.1 Comparison of the desulphurization performance of fluxes from different sources

As the initial sulphur content in the metal, $[\%S]_i$, for each trial is different, rather than plotting [%S] versus time, it is useful to plot the ratio $[\%S]_t/[\%S]_i$ against time where $[\%S]_t$ is the sulphur content in the metal at time t. The desulphurization performance of the different fluxes can then be more easily compared. The results from desulphurization trials using the five fluxes B1, B2, D1, WM1 and WM2 are plotted in Figure 4. 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 indicates 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. All of the fluxes used for these tests had the CaO to Al_2O_3 ratio adjusted to unity, however the existence of Na_2O in the WM1 and WM2 fluxes further increased the slag basicity and hence the sulphide capacity.

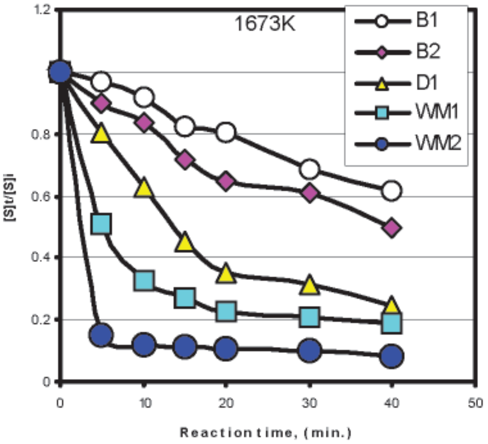

Fig. 4: Desulphurization using fluxes made from different materials.

6.2 Effects of sodium oxide on the desulphurization reaction

Sodium oxide is a common component of the by-products from alumina production using low-grade bauxite. For some applications a high sodium oxide content is not required. Sodium oxide 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 sodium oxide in the flux, experiments were conducted to study the effects of sodium oxide content on desulphurization and on the working environment. For these experiments, the fluxes made from B2 (as base flux) with appropriate amounts of CaO and Na_2O were used. The ratio of CaO to Al_2O_3 in the fluxes was adjusted close to unity (C/A = 1) and sodium oxide content changed from 0 to 15%. As shown in Figure 5, desulphurization rate increased with increasing sodium oxide content. When the sodium oxide content was over 10%, white vapour was observed during the desulphurization reaction indicating the loss of sodium oxide from the system and therefore a decrease in slag basicity with an associated decrease in sulphide capacity. This was confirmed by the resulphurization observed in the later stages of the process with the flux containing 15% Na_2O. Thus, 10% Na_2O in the flux may be an optimum value.

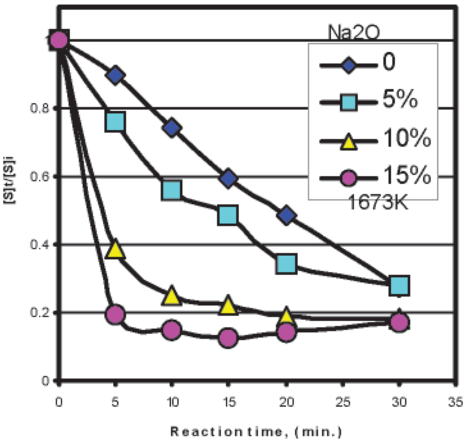

Fig. 5: Effect of Na_2O in calcium aluminate fluxes on desulphurization.

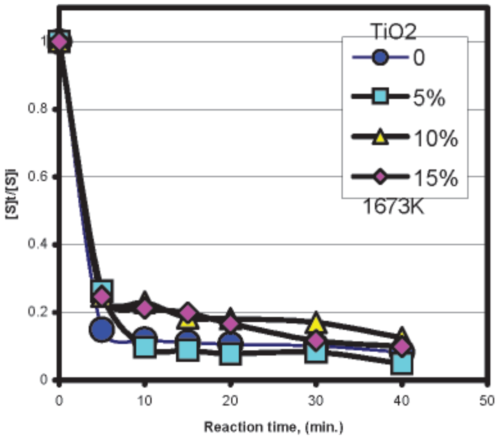

Fig. 7: Effect of TiO_2 in calcium aluminate fluxes on hot metal desulphurization.

6.3 Effects of silica and titanium dioxide on the desulphurization process

Silica and titanium dioxide can be undesirable components in the flux for some operations of steel refining, but since these oxides are common impurities found in bauxite minerals, their presence is inevitable when bauxite or red mud is used for the production of calcium aluminate. Where there is a steelmaking requirement for low concentrations of these oxides in the fluxes (e.g. $SiO_2 < 6\%$ and $TiO_2 < 2\%$), this will result in a higher price. The effects of silica and titanium dioxide in the fluxes on the desulphurization reaction are shown in Figures 6 and 7. For these experiments, the fluxes were made from WM2 as a base flux with appropriate additions of SiO_2 and TiO_2.

As shown in these figures, both silica and titanium dioxide in the fluxes have a negative effect on desulphurization. However, the negative effect of silica is more significant than that of titanium dioxide. In order to control the contents of these oxides in the fluxes made from bauxite, high quality bauxite with low silica and titanium dioxide contents must be selected. This will increase the cost of the refining flux. The fluxes D1, WM1 and WM2 made from the waste products of the aluminum industry contain 2–13% Na_2O and very low amounts of silica and titanium dioxide. This represents a major advantage for refining fluxes made from the waste or by-products of the aluminum industry.

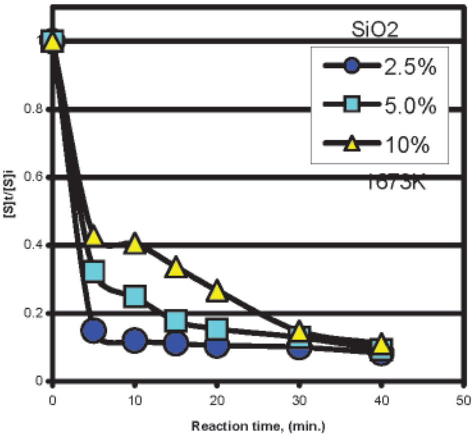

Fig. 6: Effect of SiO_2 in calcium aluminate fluxes on hot metal desulphurization.

7 Conclusions

1. The calcium aluminate fluxes made from dross from aluminum production and white mud by-products from alumina production showed excellent desulphurization performance.
2. Sodium oxide increases the flux basicity and sulphide capacity and has a beneficial effect on the desulphurization process.
3. On the other hand, the presence of silica in a flux decreases the basicity and sulphide capacity, and should be restricted to a low value.
4. The presence of titanium dioxide also decreases the flux basicity and sulphide capacity but not to the same extent as silica.
5. In light of these findings, since white mud waste materials contain significant amounts of sodium oxide and only very small concentrations of the oxides of silicon and titanium, they are highly appropriate for the custom design of desulphurizing agents and environment-friendly fluxes for hot metal pretreatment and liquid steel refining.

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