

THE ROLE AND FATE OF SO₂ IN THE ALUMINIUM REDUCTIONIntroduction

CELL DRY SCRUBBING SYSTEMS

William D. Lamb

Alumina Company of Canada, Ltd
Kingston Research Centre
Kingston, Ontario, Canada

Samples of six smelter grade aluminas with different surface areas from 41 to 85 m²g⁻¹ were equilibrated with 500 ppm of SO₂ in dry air at 80°C. The amount of adsorbed SO₂ tends to increase with surface area, being in the range 0.40 to 0.70% as S. The presence of up to 2% of water vapour in the gas did not affect the amount of SO₂ adsorbed. The addition of 500 ppm of HF to the gas prevented SO₂ adsorption and SO₂ previously adsorbed on the alumina could be desorbed by passing HF. Tests run on a full scale plant dry scrubber tend to confirm laboratory results in that the alumina saturates with SO₂ at rather low concentrations of S and the adsorbed S can be displaced by fluoride. Comparison heating tests on alumina saturated with SO₂ in the laboratory and plant scrubber catch samples suggest the presence of other forms of sulphur. Further heating tests suggest that carbon is involved in removing sulphur from the catch, probably by reducing sulphates. The implications of the work on scrubber and cell operations are discussed.

The exhaust gases from the Hall-Héroult (H-H) aluminium reduction process contain particulate matter and trace amounts of both HF and SO₂ gases. The most common modern approach for removal of particulate matter and HF gas is a dry scrubbing process. This utilizes the active surface of smelter grade alumina to adsorb the HF, followed by a bag filter to collect the hydrofluorinated alumina and particulate matter from the gas. A number of papers have been published concerning the reaction of HF and alumina, e.g. Lobos and McGeer⁽¹⁾, Cochran et al⁽²⁾ and Lamb⁽³⁾. However, little attention has so far been focussed on the reaction of SO₂ and alumina and further knowledge of the reaction of smelter alumina with SO₂ is therefore important. This paper describes the work done to determine the maximum adsorption of SO₂ to be expected, how this is affected by the presence of HF and H₂O vapour and how this is related to the removal of SO₂ in a dry scrubber.

Equipment(a) Description

Figure 1 is a schematic diagram of the equipment. A supply of 5% SO₂ in nitrogen and/or 5% HF in nitrogen is mixed with dry laboratory air under positive pressure. The flow of the three gases can be controlled by the metering valves V₁, V₄ and V₅, to provide low concentrations of SO₂ and/or HF in air at a total flow of 14 l/min (0°C and 1 atm.). The flows of SO₂/N₂ and HF/N₂ are metered continuously with linear mass flow meters while the total gas flow is set up at the start of the experiment with a wet test meter. The gas can be supplied dry or humidified by appropriate setting of valves V₂ and V₃. The humidifier is simply a flask containing water at controlled temperature through which the air bubbles. The humidity is measured with a wet/dry bulb hygrometer. The gaseous mixture then passes through 2-way valve V₆ either to gas washing bottles for concentration measurement or to a cylindrical section fluorocarbon polymer-lined mild steel reactor. Across the diameter of the reactor a 10 cm diameter filter paper is held in place by a split flange with a Teflon gasket. The filter paper supports 4 g of the alumina under test in a thin layer. The experimental conditions were chosen to simulate a filter bag with gas passing through at about 1.9 m/min (6 ft/min) at 21°C with an alumina loading of 0.5 kg/m² (0.1 lb/ft²). After the humidifier, the gas lines and reactor are lagged and electrically heated to provide a gas temperature of 80°C and to prevent condensation. Before the experiment, the alumina is loaded on to the filter paper by opening the ball joint A, and feeding the alumina via a funnel in the opening, into a stream of air obtained by attaching a vacuum source to the bottom of the reactor.

After the alumina bed, the residual SO₂ and HF are measured by passing the gas through two gas washing bottles in series containing a solution of H₂O₂ for a 5 minute period. Total acidity is determined by titration with standard NaOH. This

result is related to both the HF and the SO₂ absorbed. The fluoride is separately determined with the specific ion electrode and from the 2 results, the HF and SO₂ in the gas can be separately calculated.

(b) Application

1. Equilibrium Data

After the alumina was loaded on the filter paper as described above, the gas flows were started and allowed to bypass the reactor via valve V₆, to the gas washing bottles for flow measurement and analysis. Using dry gas, the SO₂ concentration was adjusted to 500 ppm (vol) with the total flow as above, and the gas temperature at 80°C. When these values were steady as shown by repeat measurements, the flow of gas was directed via V₆ to the reactor and gas sampling and analysis commenced at the base of the reactor. This was continued until the SO₂ concentration in the exit gas reached 50 ppm. This usually occurred quite rapidly, within 30 min and at this point the alumina was considered at equilibrium with the SO₂ and the gas flow was then stopped. The alumina was removed from the reactor and analyzed for total sulphur. This was done for six smelter grade aluminas and then repeated with 500 ppm of HF in place of SO₂ with subsequent determination of fluoride. The results are shown in Table 1, which also gives the surface area and alpha-alumina for each of the six aluminas.

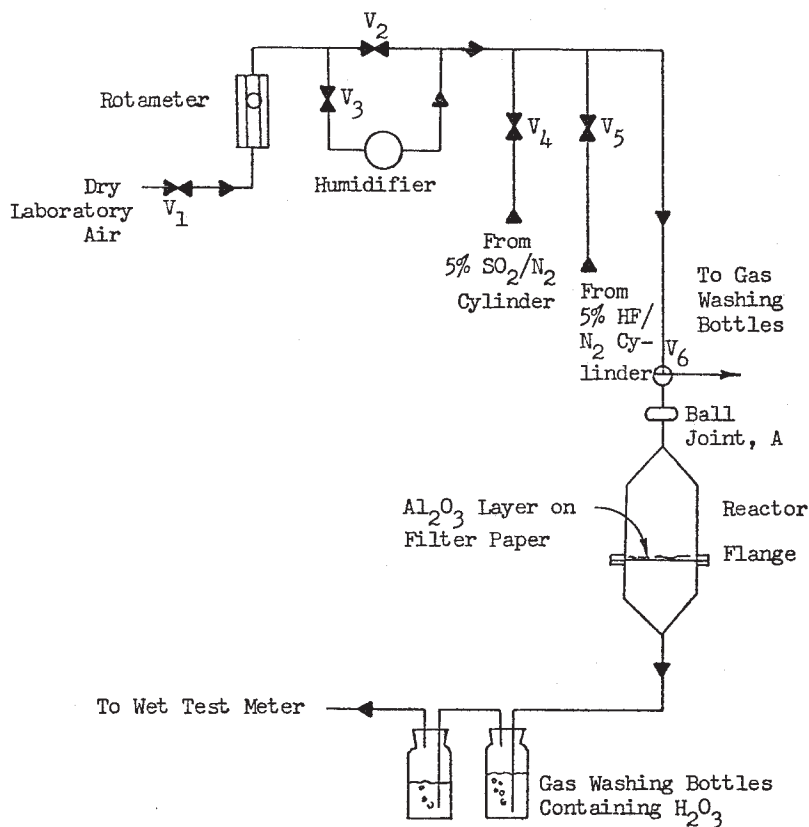


Fig. 1 - SO₂/HF Adsorption Apparatus

Table 1

Results of HF and SO₂ Equilibrium Measurements at 80°C

Alumina	Surface Area (m ² g ⁻¹)	Alpha-Alumina (%)	Equilibrium Concentration	
			S (%)	F (%)
Alcan	41	27	0.52	3.90
A	44	17	0.44	3.03
B	45	12	0.46	2.49
C	52	30	0.40	3.05
D	72	18	0.51	4.43
E	85	12	0.70	4.97

The relation between equilibrium fluoride concentration and surface area has been demonstrated previously (3) and is clearly seen again here. The results also show that the equilibrium sulphur concentration tends to increase with surface area, however, the relative accuracy of analysis at about 0.5% is probably not much better than ±10%, which may tend to blur the relationship.

2. Effect of Water Vapour on the SO₂ Equilibrium

Equilibrium tests were made with the Alcan alumina at 500 ppm SO₂, with two levels of water vapour in the gas at 80°C. Other conditions were as specified above. Table 2 shows that water vapour up to 2.2% vol has no significant effect on the SO₂ equilibrium, which contrasts strongly with its effect on HF adsorption⁽³⁾.

Table 2

Effect of Water Vapour Using Alcan Alumina With 500 ppm SO₂ at 80°C

Water Vapour Concentration (% Vol)	% S After Test
NIL	0.52
1.2	0.53
2.2	0.47

3. Effect of HF on the SO₂ Equilibrium

Again working with the Alcan alumina, two kinds of tests were done. The first one involved running the alumina to equilibrium with 500 ppm of SO₂ and then substituting 500 ppm of HF for the SO₂. The alumina was then run to equilibrium with respect to HF. In the second test, the alumina was run to equilibrium in the presence of 500 ppm of SO₂ and 500 ppm of HF together. After both tests, the alumina was analyzed for sulphur and fluoride, with the results shown in Table 3.

Evidently, in the first test, the adsorbed SO₂ has been displaced by the HF and in the second test, adsorption of SO₂ has been prevented. Also by comparison with Table 1, it is evident that the SO₂ has not affected the HF equilibrium concentration.

In further tests, the Alcan alumina was saturated with SO₂ as above and then subjected to 500 ppm HF, the reaction being stopped at intermediate stages before equilibrium was attained. The results in Figure 2 demonstrate the relationship between sulphur and fluoride in the alumina at any stage of the reaction. For example, if the alumina is 50% of the way towards equilibrium with HF, (approx. 2% F) only 0.15% remains adsorbed, compared to 0.48% S at the beginning.

Table 3

Effect of HF Using Alcan Alumina with 500 ppm SO₂ at 80°C

Test Condition	Alumina After Test	
	%S	%F
1. SO ₂ alone	0.46	0.04
2. SO ₂ followed by 500 ppm HF	0.09	3.75
3. SO ₂ + 500 ppm HF	0.07	3.95

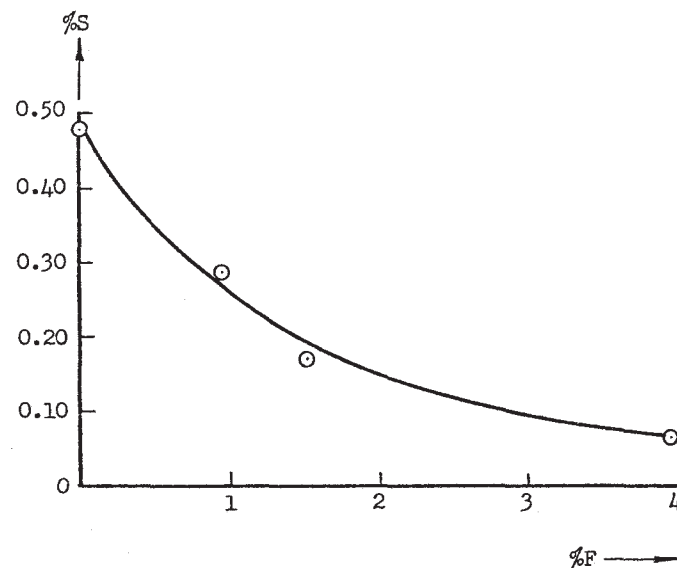


Fig. 2 - Amount of Adsorbed SO₂ (as S) Remaining on an Alcan Alumina V Adsorbed Fluoride

4. Heating Tests

(a) Laboratory Treated Samples

A sample of Alcan alumina equilibrated with SO₂ was heated for 1-1/2 h at temperatures from 400 to 900°C in a tube furnace, using 0.5 g portions in a platinum boat. The furnace was purged with a slow flow of dry air, during the heating. The residual sulphur was determined after heating and Figure 3 is a plot of the results.

(b) Dry Scrubber Catch

With similar conditions to the preceding test, a sample of catch from a dry scrubber operating with an Alcan alumina was heated at 500°C for various periods of time up to 1-1/2 h. This temperature was considered about the maximum to which scrubber catch material would be subjected while on the surface of the reduction cell. Figure 4 shows that the sulphur loss appears to level out after about 1 h and at 1-1/2 h can be compared with the laboratory treated sample. Evidently the loss is proportionately much less, amounting to about 37% of the original sulphur compared to about 75% for the SO₂-treated laboratory sample. This suggests that there are other forms of sulphur present in the scrubber catch sample in addition to adsorbed SO₂. This may explain why the original sulphur concentration is well above the SO₂ equilibrium value for Alcan alumina.

With another sample of scrubber catch alumina, two further tests were done, involving heating for different times up to 3 h (a) in air and (b) in nitrogen. Sulphur, fluoride and carbon were determined in the samples after heating and the results are displayed in Figure 5. The loss of fluoride at 500°C is small in air and appears to be almost zero in nitrogen. Of more particular interest is that the sulphur and carbon exhibit completely opposite behaviour in air and nitrogen, and that there is even a significant loss of carbon in N₂ atmosphere, where oxidation cannot take place.

5. Interaction of HF and SO₂ in a Full Scale Process Dry Scrubber

A prebake line at the Sunndalsøra Works of the Årdal og Sunndalverk (ÅSV) company in Norway is equipped with a dry scrubber. The line consists of 3 groups of cells, each of which is linked to its own section of the scrubber in a closed circuit. For a period of time in 1977, one section of the dry scrubber was operated with 33-1/3% of the normal feed rate (= 100% of reduction alumina requirements) while the other two were operated with 100% feed. The scrubber catch aluminas from the 3 sections were analyzed for F and S and with the permission of ÅSV, the results are shown in Table 4.

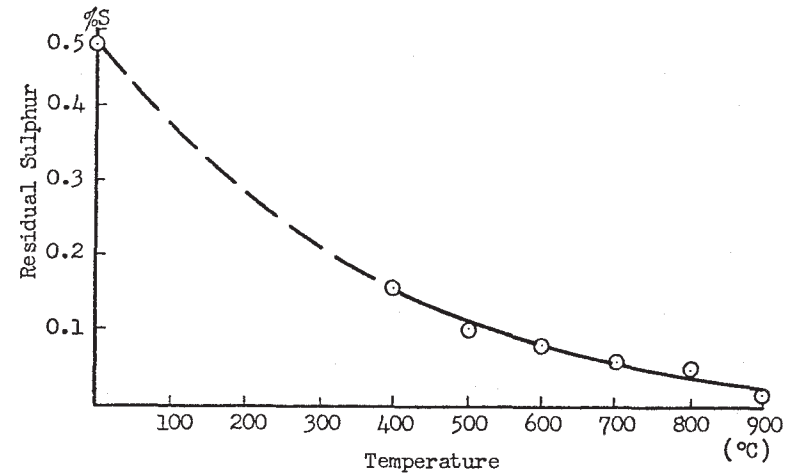


Fig. 3 - Heating Test on Alcan Alumina Equilibrated With SO₂ in the Laboratory

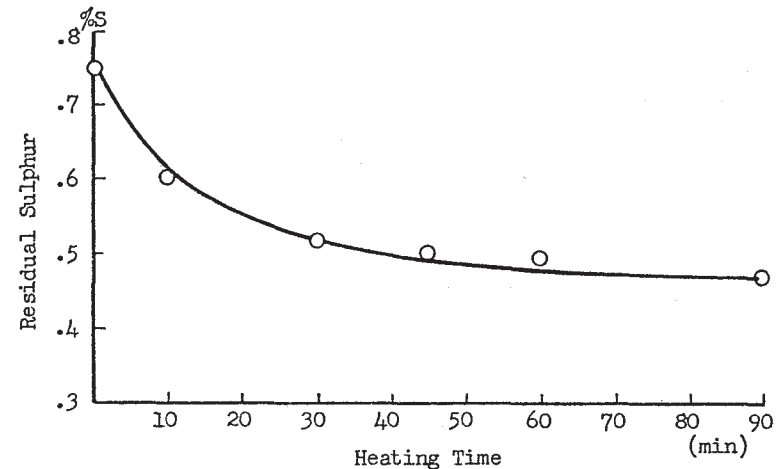


Fig. 4 - Heating Test on Scrubber Catch Alcan Alumina at 500°C

Table 4

Sulphur and Fluoride Concentration in Alumina Catch from Dry Scrubbers at Different Feed Rates

Date	Group	Al ₂ O ₃ Feed To Scrubbers	Scrubber Catch Analysis			
			%F		%S	
			Mean	Std.Dev.	Mean	Std.Dev.
13-19/6/79	I	100%	1.04	0.22	0.44	0.05
	II	100%	0.89	0.07	0.37	0.04
	III	33-1/3%	2.76	1.33	0.41	0.06
29/8 to 11/9/77	I	100%	1.14	0.31	0.47	0.09
	II	100%	1.03	0.19	0.34	0.04
	III	33-1/3%	2.02	0.29	0.41	0.09
25-31/7/77	I	100%	0.94	0.09	0.57	0.07
	II	100%	0.92	0.06	0.51	0.07
	III	33-1/3%	1.75	0.15	0.37	0.02

Whereas the fluoride concentration is significantly higher at the lower feed rate, the results show that the sulphur remains the same or is slightly lower.

Interpretation of Data

From the evidence of Table 1 the adsorption of low concentrations of SO₂ on alumina increases with increasing surface area in the range 40-85 m² g⁻¹. However, the amount adsorbed at equilibrium and at 80°C is rather small (0.4-0.7% as S) compared to HF (2.5-5% as F). Again, in contrast to HF adsorption which is strongly affected by the presence of H₂O vapour⁽³⁾ in the gas, SO₂ adsorption is unaffected with up to 2% of water vapour present (Table 2). This suggests that the mechanism of adsorption for SO₂ is different. Apart from OH⁻ ions on the surface of an active alumina Al³⁺ ions are found which act as Lewis acid sites. Since the SO₂ molecule has lone pairs of electrons on both sulphur and oxygen, it can behave as a Lewis base, which suggests that perhaps the Al³⁺ ions are the active sites for SO₂ adsorption. However, whatever mechanism is proposed, it must account for the fact that adsorbed SO₂ can be displaced by HF (Table 3). Thus if the above is true, then HF must also adsorb on Al³⁺ sites as well as on OH⁻ sites as postulated previously⁽³⁾. Another possibility is H-bond formation between OH⁻ sites and SO₂ molecules, which would be broken down in the presence of HF, which preferentially reacts with the OH⁻ ion to replace it with an F⁻ ion, eliminating H₂O and the previously adsorbed SO₂ in the process. If OH⁻ ions are implicated, however, the equilibrium concentration of SO₂ ought to be higher, unless it is adsorbed on a specific type of OH⁻ site of which there can be up to 5 different kinds on an active alumina surface^(4, 5). Without further evidence we can only speculate on the adsorption mechanism for SO₂. However, it is evident that adsorbed HF must modify the

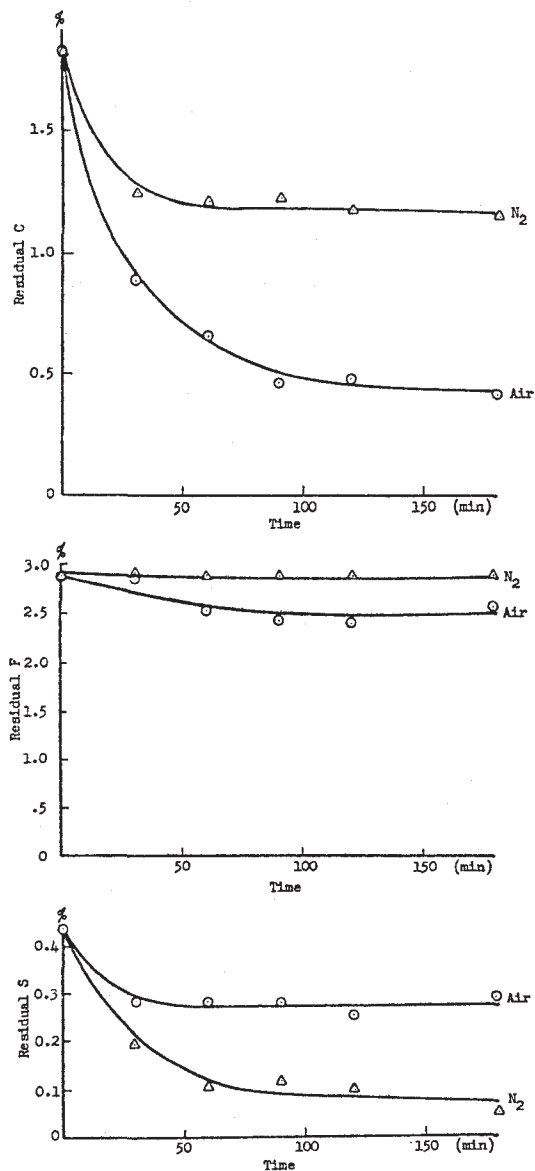


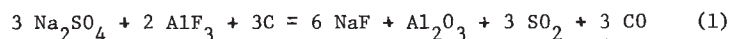
Fig. 5 - Heating Alcan Dry Scrubber Catch Alumina at 500°C in Air and Nitrogen

Implications in Dry Scrubbing and Cell Operation

surface in such a way as to eliminate adsorbed SO₂ or to prevent SO₂ adsorption, perhaps by covering the surface with F⁻ ions at equilibrium.

The behaviour of adsorbed SO₂ towards heat is also different, compared to adsorbed HF. Previous work⁽³⁾ showed that even at 900°C, about 50% of the adsorbed HF is still retained, whereas Figure 3 shows nearly all the adsorbed SO₂ is gone at this temperature and at 500°C nearly 80% is gone. This suggests that SO₂ is less strongly adsorbed on active alumina than is HF. Scrubber catch alumina shows a different behaviour at 500°C, when a substantial proportion (67%) of the original sulphur is left after heating. This sulphur is probably not due to adsorbed SO₂, but is most likely present as sodium or aluminium sulphate, both of which we have previously identified by x-ray diffraction (XRD) in fine solids collected from reduction cell gas. These undoubtedly derive from reactions of SO₂, O₂, and particulate emissions such as cryolite and alumina.

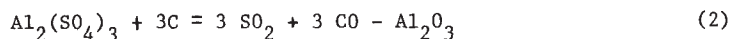
The results in Figure 5 show also how carbon behaves on heating scrubber catch. Evidently in air, oxidation takes place at 500°C and 77% of the carbon is lost. However, there is also a measurable loss (34%) in nitrogen showing that another reaction is taking place. In N₂ the sulphur loss is 84% compared to 35% in air which suggests that carbon reduces sulphate by reactions of the following type:



for which K_p = 10.7 at 500°C

and 1.7 x 10²⁰ at 900°C

and



for which K_p = 5.9 x 10²² at 500°C

and 1.4 x 10³⁵ at 900°C.

In air, the rate of carbon oxidation is probably faster than the rates for reduction by reactions, such as 1 and 2 and thus oxidation predominates. However, in N₂ atmosphere where oxidation is not possible, the reduction reactions become more important, so that the sulphur is almost entirely eliminated.

The behaviour of fluoride (Figure 5) shows about a 10% loss in air at 500°C as expected, but there appears to be no loss in N₂. There is so far no satisfactory explanation for this.

1. The Amount and Type of Sulphur Emission

A consideration of this is important if we are to relate the equilibrium SO₂ data to scrubber performance.

The amount of SO₂ in the cell gas depends on:

- (a) the amount of sulphur in the raw materials to the cell (the anode is the main source);
- (b) the proportion of the sulphur converted to SO₂ as opposed to particulate sulphates or other forms of sulphur;
- (c) the combined sulphur collection efficiency at the cell and removal efficiency at the scrubber.

If we ignore the effect of (b), for the moment and assume that other raw materials contribute negligible amounts of sulphur compared to the anode; then if there is 2% S in the latter, typical carbon consumption data for the H-H aluminium reduction process show that there will be about 10 kg S/tonne aluminium entering the process. Referring to Figure 6 and using the terminology and theoretical concepts developed by Frankenfeldt and Mannweiler⁽⁷⁾, we can break down the sulphur balance as:

S = total sulphur (kg/tonne Al) supplied to the cell

P = amount of S (kg/tonne Al) in the cell gas

G = amount of S (kg/tonne Al) returned via the dry scrubber to the cell

M = amount of S (kg/tonne Al) leaving the cell in the metal and electrolyte

A = amount of S (kg/kg Al) escaping the system into the working environment or the atmosphere

η = combined collection efficiency of cell hoods and removal efficiency of scrubber for S

k = sulphur distribution coefficient between gas phase and metal/bath.

Ignoring the effect of sulphur losses into the bath and lining, M = 0, since sulphur does not leave in the metal. Since we assume that all the S enters the gas phase, then k is not relevant in the case of sulphur. From Mannweiler's equations:

$$S = M + A \quad (3)$$

$$P = A + G \quad (4)$$

$$G = \eta P \quad (5)$$

$$A = (1 - \eta) P \quad (6)$$

For the above sulphur situation, M = 0 and so:

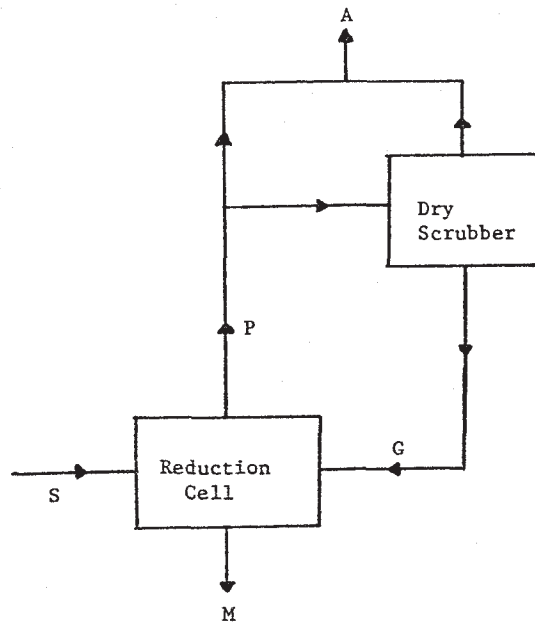


Fig. 6 - Balance of Impurities Around a Reduction Cell and a Dry Scrubber⁽⁷⁾

S = A = 10 kg/tonne Al.

In other words, all the sulphur entering the cell via the anode must escape through the scrubber stack or to ventilation air. If this is so, then for any value of η , P can be found from equation (6) and G can be found from equation (5). We can thus tabulate as in Table 5 for various values of η .

The sulphur concentration in the catch is calculated assuming that 1 tonne of Al is derived from roughly 2 tonnes of Al_2O_3 . Thus we can see that η can never be much higher than 0.5 to 0.6, otherwise the alumina would have to show much higher equilibrium values than the 0.5 to 0.7% S found in our work. This assumes that all the sulphur ends up as SO_2 . Since some of it converts to particulate forms such as sulphate, the value of S (equation 4) in terms of actual SO_2 may be lower than 10 kg/tonne in this example and this would allow somewhat higher maximum values for η , due to higher removal efficiencies for SO_2 . Sulphate formation is most likely due to oxidation of SO_2 to SO_3 and the subsequent formation of sulphates as discussed above.

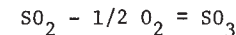
Table 5

Sulphur Material Balance Variation for Different Values of η , the Combined Collection/Removal Efficiency, When Anode Sulphur, S = 10 kg/tonne Al

η	kg S/tonne Al			% S* in Scrubber Catch
	P	A	G	
0.9	100	10	90	4.5
0.8	50	10	40	2.0
0.6	25	10	15	0.75
0.5	20	10	10	0.50
0.2	12.5	10	2.5	0.13
0	10	10	0	0

*assuming alumina feed to scrubber = 100% reduction requirements

The reaction:



$$\Delta H_{298}^0 = -23.7 \text{ k cal/mole, } K_p \text{ at } 373 \text{ K} = 6.2 \times 10^6$$

is exothermic and is therefore favoured by the low temperatures (80-120°C) found in exhaust gas. However, the kinetics of the reaction are unfavourable and some kind of catalyst or active surface is needed to obtain a measurable rate. Particulate carbon may be the important factor here, since Novakov et al⁽⁶⁾ have shown that finely divided carbon particles are a good catalyst for the oxidation of sulphur dioxide. Thus the amount and composition of the particulate matter in the exhaust gas, especially the carbon content will probably influence sulphate formation. If this is correct, then the use of cokes which release more particulate carbon from the anode will favour sulphate formation. Prebake cells release less carbon than Soderberg cells, because prebake anodes are baked outside the cell in a ring furnace. Also most of the VS cell gas is burnt in a flame which does not favour SO_3 formation due to the high flame temperature.

2. The Extent of SO_2 Adsorption in a Dry Scrubber

From the foregoing discussion, we can see that the proportion of anode sulphur remaining as SO_2 will be variable and it will be difficult to predict the SO_2 load to the scrubber and compare it with the equilibrium SO_2 concentration. An additional factor is that the latter was determined for 500 ppm SO_2 in the gas which is close to the concentration found in the gas from low exhaust VS

Soderberg cells. The gas from high exhaust HS Soderberg and pre-bake cells contains SO_2 at the 20-40 ppm level which would probably imply lower equilibrium adsorption values. Also affecting the latter, is the amount of HF to be scrubbed and the resulting gaseous fluoride concentration in the scrubber catch. This also varies for different cell gases. At the normal alumina feed-rates to a dry scrubber (= 100% of reduction alumina requirements), removal of all the HF from the gas results in gaseous fluoride concentrations of about 0.4%, 0.6% and 1.1% F in the alumina for prebake, HS and VS Soderberg cell gases respectively. We can easily see from Figure 2, therefore, that the type of cell gas will influence the equilibrium. Based on this and the previous section, we can now make a qualitative statement of the extent of SO_2 adsorption for each cell type. The following, however, takes no account of the reaction kinetics for SO_2 adsorption which we have not so far studied.

1. Prebake Cells

Here the gas contains SO_2 concentrations lower than the 500 ppm studied herein, so that the equilibrium concentration is probably lower. Based on the carbon hypothesis, the SO_2 load should be high and therefore to adsorb all the SO_2 the alumina will likely have to become fairly saturated. Adsorbed HF will have a minimal effect on the equilibrium, but it is likely that SO_2 removal efficiency in the dry scrubber will be poor. Actual plant measurements on this type of gas shows removal efficiencies which seldom exceed 50%.

2. HS Soderberg Cells

The comments above about SO_2 concentration and equilibrium also apply here. However, if carbon is important, the SO_2 load will be lower, which may offset the above to some extent. We may expect to find relatively more particulate sulphate in the catch. The effect of fluoride will be slightly more than for prebake gas and the equilibrium SO_2 concentration will be reduced further, which may offset any gains due to a lower SO_2 load. Again SO_2 removal efficiency will most likely be poor.

3. VS Soderberg Cells

Here, the SO_2 concentration is close to 500 ppm and equilibrium values for the alumina will be close to those reported herein. The particulate carbon is higher than for pre-bake and so SO_2 loading may be lower. However, the high adsorbed gaseous fluoride concentration will reduce the equilibrium SO_2 value significantly. Thus again, SO_2 removal efficiency will be poor.

So far, we have taken an anode sulphur content of 2% as a point of reference. It is evident from the above that any extra SO_2 produced by using higher sulphur raw material in the anode, is unlikely to be adsorbed and will exit in the scrubber stack gas.

Two actual samples of scrubber catch were examined in this work and we can examine their sulphur concentrations to determine their degree of SO_2 saturation. From Figure 3 about 80% of the adsorbed SO_2 was driven off at 500°C from the sample equilibrated in the laboratory. With the same conditions, 0.28% S was lost from the first catch sample (Figure 4). If we assume that all of this was due to SO_2 and that this was 80% of the SO_2 adsorbed, then 0.35% S was due to the latter out of a total of 0.75% S. This would suggest that the alumina was well on the way towards equilibrium with the SO_2 . However, the 0.35% figure may be high, since we do not know how much of the other sulphur forms was lost at 500°C . Applying the same reasoning to the second sample (Figure 5), about 0.21% of the 0.44% S present may be due to adsorbed SO_2 . This suggests again that a fair proportion of the adsorptive capacity for SO_2 has been utilized. This seems to be in line with the above discussions based on the amount of SO_2 emission.

Conclusions

1. The low equilibrium value for SO_2 adsorption on smelter grade aluminas is a limiting factor in the removal of SO_2 from aluminium reduction cell gases in a dry scrubber. The quantity of SO_2 to be scrubbed may produce S concentrations typically up to 0.5% or higher in the alumina catch, compared to equilibrium concentrations in the range 0.4 to 0.7% S for surface areas from 40-85 $\text{m}^2 \text{g}^{-1}$.
2. The presence of adsorbed fluoride from the gas will reduce equilibrium adsorption of SO_2 even further. This effect will be most important with VS Soderberg gas where HF loading and concentration is higher than for prebake or HS Soderberg gas.

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