

HYDROLYSIS OF CARBONYL SULFIDE (COS) ON SMELTING GRADE ALUMINA

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Keywords: carbonyl sulfide, COS, aluminum smelter emissions, catalyst, smelting grade alumina, catalytic COS decomposition, industrial scrubbing, emission monitor

Abstract

Carbonyl sulfide (COS) is present in aluminum smelter off-gas at low ppm concentrations. The primary source of COS is the 2-3 wt% sulfur contained in carbon-based anodes. COS is directly evolved from anode oxidation during aluminum electrolysis. Upon evolution, COS is further oxidized to SO₂, while a minor fraction of evolved sulfur is emitted in the form of COS. Very little, if any, of the evolved COS is captured by the dry scrubbing systems.

In this work, a series of laboratory experiments was conducted to characterize interactions of COS with smelting grade alumina (SGA) as a function of gas temperature and humidity. The effect of other smelter off-gas components (HF and SO₂) was also evaluated. This work suggests that SGA is an efficient catalyst for COS hydrolysis, however, the presence of hydrogen fluoride, SO₂ and humidity negatively affects its catalytic activity.

Introduction

Carbonyl sulfide is one of air pollutants present in aluminum smelter off-gas. Its chemical and physical properties, environmental exposure factors, health and welfare effects as well as environmental quality factors are reviewed in corresponding report from the U.S. Environmental Protection Agency, EPA [1].

The primary source of COS emissions in a conventional aluminum smelter is the 2-3% sulfur contained in carbon-based anodes. Sulfur, upon anode oxidation during aluminum electrolysis, is principally evolved in the form of COS and is further oxidized to SO₂ [2, 3]. A small amount of evolved sulfur is released in the form of COS. Typical concentration of COS present in smelter off-gas is on the order of 10 ppmv.

In terms of potential options for COS emissions control, one approach could be catalytic COS decomposition [4]. This approach is widely used in oil, gas, petrochemical and polymer industries to remove sulfur containing gases/compounds from process streams using metal or metal-oxide based catalysts [5-8]. Among these catalysts, alumina looks especially attractive for primary aluminum industry.

The use of alumina-based catalysts to remove COS from gaseous streams was demonstrated and patented by Dow Chemicals as early as 1962 [6]. Multiple subsequent patents describe further COS removal process modifications adapted to different types of process streams including but not limited to ref [7, 8].

In the work presented here, catalytic performance of smelting grade alumina is characterized as a function of gas temperature and humidity. In addition, the effect of SGA poisoning by key smelter off-gas contaminants, HF and SO₂, is also examined.

Experimental

A schematic diagram of the experimental setup used in this work is shown in Figure 1. A COS permeation tube (Kin-Tek Laboratories, Inc.) was used in conjunction with a temperature-controlled permeation oven (Kin-Tek Laboratories Inc., Model 491-MB) to generate a known amount of COS. Evolved COS was then diluted with dry air to produce a gas stream containing ~ 10 ppmv of COS. The resultant flow was directed to a 2" ID Teflon tube containing a ~8 g bed of smelting grade alumina supported on a 10 μm perfluorinated filter paper. Outlet reactor COS concentration was monitored using a process FTIR (Gasetm Technologies, Inc.). This instrument also provides capability to measure SO₂ and moisture levels in real time.

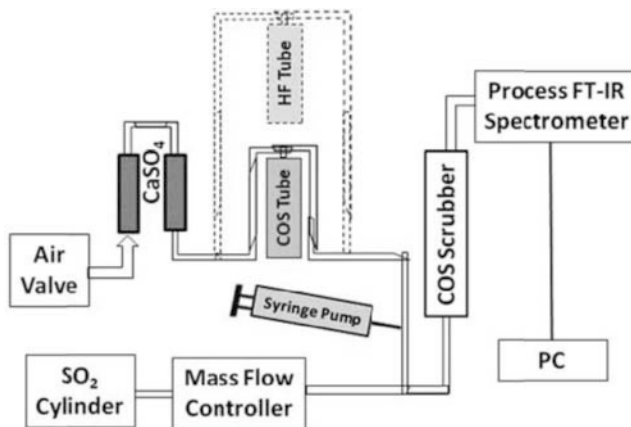


Figure 1. Schematic diagram of experimental setup used for COS scrubbing tests

In order to generate a known level of humidity in the gas stream, a controlled syringe pump injector (KD Scientific, Model #100) was used to add moisture into the stream. An electrochemical sensor (IBRID MX6, Industrial Scientific) was used in select experiments to monitor H₂S generation downstream of the bench-scale COS scrubber. COS scrubbing efficiency was calculated by rationing scrubber inlet and outlet COS concentrations:

$$\text{Efficiency} = ((\text{COS inlet} - \text{COS outlet}) / \text{COS inlet}) \times 100\%$$

Results

COS Scrubbing Mechanism

COS decomposition on SGA surface may occur through several different mechanisms including (but not limited to) the following:

- Hydrolysis: $\text{COS} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2\text{S}$ (1)
- Complete oxidation: $2 \text{COS} + 3 \text{O}_2 \rightarrow 2 \text{CO}_2 + 2 \text{SO}_2$ (2)
- Partial oxidation: $2 \text{COS} + \text{O}_2 \rightarrow 2 \text{CO}_2 + 2 \text{S}$ (3)

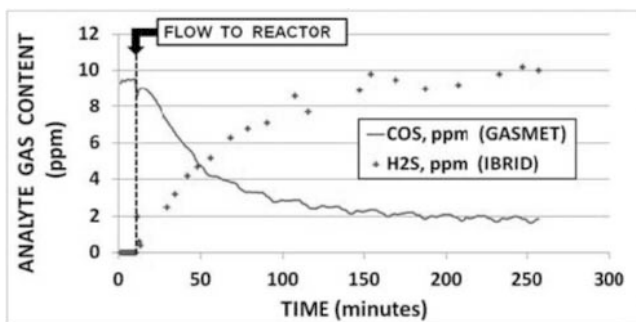


Figure 2. Alumina induces catalytic decomposition of COS through hydrolysis: $\text{COS} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2\text{S}$

Figure 2 shows temporal evolution of COS and H₂S concentrations at the outlet of the bench-scale reactor loaded with 8 grams of alumina. As can be seen from Figure 2, outlet COS and H₂S concentrations are inversely related and mass-balanced (to within the accuracy of these experiments). Hence, COS removal occurs through catalytic hydrolysis of COS on alumina surface (mechanism (1) above), where COS(g) is converted to H₂S(g). Catalytic activity of SGA was tested continuously for ~48 hours and no deterioration of scrubbing efficiency was observed in the absence of other gas impurities.

Temperature Dependence

Figure 3 shows the measured effects of gas temperature and alumina moisture content on COS scrubbing efficiency. In these experiments, SGA was either pre-dried (“Dry SGA”) by passing dry air (<200 ppmv H₂O) through a bed of SGA for ~30 minutes prior to experiment initiation, or used as is (“Fresh SGA”), equilibrated with room-temperature air at ambient humidity.

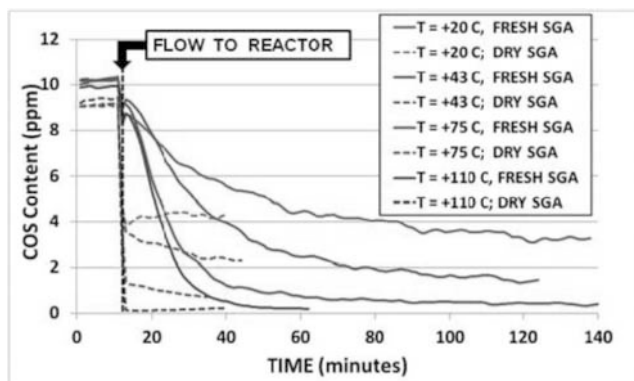


Figure 3. Temperature dependence of COS hydrolysis reaction in dry air: “Dry” vs “Fresh” alumina (see text for details).

The data plotted in Figure 3 demonstrates that even though trace amount of moisture is required for COS hydrolysis, dry SGA results in faster reaction kinetics. This is possibly due to the fact that pre-adsorbed moisture blocks active catalytic sites on alumina surface and inhibits hydrolysis reaction.

It is also noteworthy that the rate of COS hydrolysis increases with temperature. This suggests the overall positive temperature dependence for the complex heterogeneous process consisting of gas-solid mass transfer, adsorption and chemical reaction.

In summary, both “fresh” and “dry” alumina show appreciable removal of COS (>90%) in the temperature range typical of smelter off-gas, and in the absence of other gas impurities.

Effect of Air Humidity

In this section, the effect of air humidity on COS scrubbing efficiency is presented.

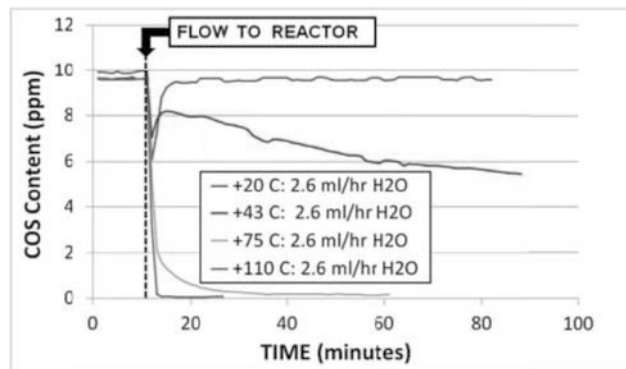


Figure 4. Scrubber outlet COS concentration as a function of temperature (20 – 110 °C) and at 2.3 vol% air humidity.

Specifically, Figure 4 shows outlet COS concentration at absolute air humidity of ~2.3 volume % and gas temperature in the range between 20 and 110 °C. This air humidity (corresponding to ~95% relative air humidity at 20 °C) is typical for summer time in the Northern US, Canada, Europe and Iceland, i.e. geographic locations with moderate climate. Figure 4 clearly shows that COS scrubbing efficiency is low (<10%) at high relative air humidity and low temperature (+20 °C curve (top, blue) in Figure 4). In contrast, the increase of internal scrubber temperature (decrease of relative air humidity) results in significant improvement of catalytic COS removal efficiency. Specifically, at internal scrubber temperatures higher than ~70 °C, COS scrubbing efficiency is greater than 90%.

Figure 5 shows scrubber outlet COS concentration as a function of temperature and at absolute air humidity of ~7.1 volume%. This humidity corresponds to ~95% relative humidity at +40 °C and was chosen to mimic climate conditions of South-Eastern USA, Brazil and other regions with sub-tropical, tropical or equatorial climate.

Consistent with the results shown in Figure 4, COS scrubbing efficiency is low at high relative humidity and low temperature (45 °C curve in Figure 5). However, an increase of internal scrubber temperature (decrease of relative air humidity) results in an improvement of COS scrubbing efficiency (75 and 110 °C curves in Figure 5).

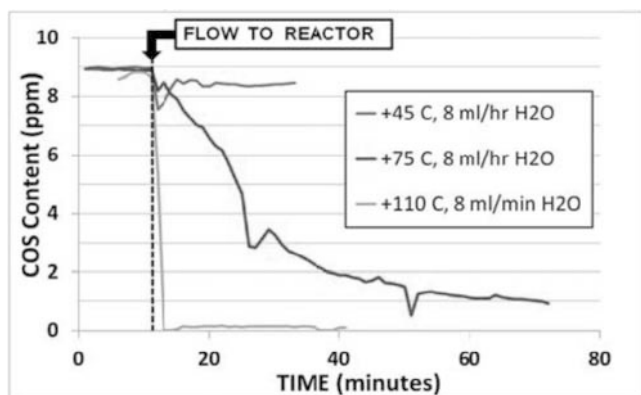


Figure 5. Scrubber outlet COS concentration as a function of temperature (20 – 110 °C) and at 7.1 vol% air humidity.

Figure 6 summarizes the data presented in Figures 3-5. Specifically, Figure 6 shows the “equilibrium” COS scrubbing efficiency (calculated based on stabilized scrubber outlet COS concentration 3 hrs upon experiment initiation) by alumina with no impurities (HF or SO₂) present in the stream. As can be seen from Figure 6, COS scrubbing efficiency is greater than 90% for typical smelter off-gas temperatures between 80 and 110 °C and absolute air humidity from 0 to 7.1 volume% (covering essentially all climate zones). Therefore, the use of SGA for COS removal from smelter off-gas could be a fairly simple and straightforward process provided that major smelter off-gas contaminants (HF and SO₂) were removed prior to COS scrubbing. Under these conditions, catalytic lifetime of SGA is expected to be high, since alumina is not consumed or poisoned in the course of COS hydrolysis reaction.

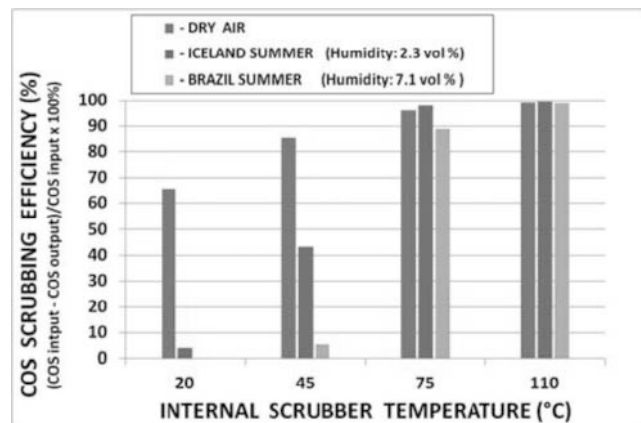


Figure 6. Summary plot: COS scrubbing efficiency at different temperatures (20 – 110 C) and air humidity (2.3 and 7.1 vol% H₂O)

Effect of HF and SO₂ on COS Scrubbing Efficiency

Figure 7 shows outlet COS concentration in the presence of 40 or 80 ppm SO₂ and 0 or 1 ppm HF at different temperatures and air humidity for both “dry” and “fresh” alumina conditions. As noted above, “dry” SGA was generated by passing dry air (<200 ppm H₂O) through the reactor for ~ 30 minutes prior to experiment initiation, whereas “Fresh” alumina was equilibrated with room air at ambient temperature and humidity. Specific experiments plotted in Figure 7 are numbered 1 to 9 and the corresponding test conditions are listed in the figure captions.

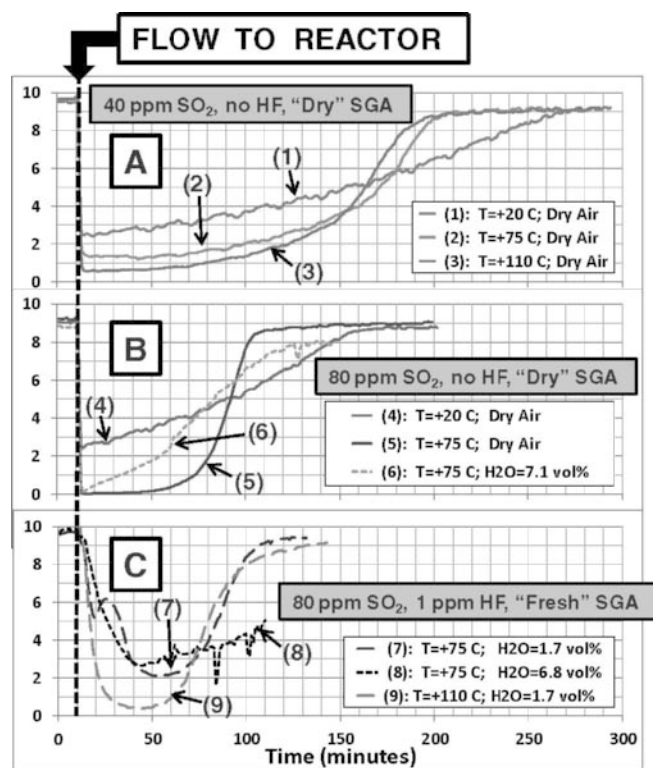


Figure 7. Effect of SO₂ and HF on catalytic performance of alumina at different temperatures and air humidities. A) 40 ppm SO₂, no HF, “dry” SGA, dry air; B) 80 ppm SO₂, no HF, “dry” SGA; C) 80 ppm SO₂, 1 ppm HF, “fresh” SGA.

It is immediately evident from Figure 7 that HF and SO₂ gas impurities have a significant negative effect on COS scrubbing efficiency. Specifically, the loss of scrubbing efficiency due to catalyst poisoning is observed after ~ 3 hrs of experiment initiation. The rate of SO₂ and HF-induced alumina poisoning depends on specific experimental conditions. For instance, COS breakthrough time in the presence of 40 ppm SO₂ appears to be twice as long as that for 80 ppm SO₂ in the gas stream.

Higher gas temperature appears to improve COS scrubbing efficiency in the presence of SO₂ and HF initially. However, the poisoning of alumina appears to proceed somewhat faster at elevated temperatures.

The effect of air humidity is not immediately discernable from the data plotted in Figure 7. It appears that gas moisture content does not dramatically affect COS scrubbing performance. Likewise, COS breakthrough time is not significantly affected by the use of “dry” vs. “fresh” alumina.

Summary and Conclusions

In this work, a laboratory alumina bed scrubber was used to evaluate catalytic efficiency of SGA with regard to COS removal. Scrubbing efficiency was characterized as a function of gas temperature, humidity and smelter off-gas impurities - SO₂ and HF.

Key findings of this work are summarized below:

- SGA catalyzes COS hydrolysis reaction in the presence of trace amounts of moisture: $\text{COS} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2\text{S}$.
- SGA is not poisoned or consumed in the reaction in the absence of gas impurities (HF and SO_2) and the scrubbing efficiency can reach >90% at elevated temperatures (>70 C) and low relative humidity (< 10% RH at 70 C)
- Both HF and SO_2 have deleterious effect on catalytic efficiency of SGA, significantly reducing its lifetime

A means to control H_2S emissions downstream of COS scrubber may be needed if no wet scrubber is already placed downstream of the dry scrubbers.

Acknowledgements

The authors would like to thank our Alcoa colleagues Luis Espinoza-Nava, Nathan Westendorf and Rajat Ghosh for their help in carrying out this work.

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