Effect of SO_2 Concentration and Humidity on the Removal of SO_2 from Cell Effluent Gases Using Hydrated Lime

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Abstract

To reduce the release of pollutants to the atmosphere, including SO_2, the control of atmospheric emissions can be necessary to respect air quality standards. In this work, a semi-dry method was used for the removal of SO_2 from the effluent gases of the aluminum electrolysis cells. The experimental investigation presented in this research work is to examine the possibility of the removal of low-concentration SO_2 from the gas with hydrated lime ($Ca(OH)_2$). The reaction was carried out between the hydrated lime and the gas containing different concentrations of SO_2 under dry and humidified conditions. The results indicate that the humidity plays a key role in the enhancement of the reaction between lime and SO_2. Furthermore, the surface area and morphological analyses suggest that the reactants have a strong interaction on the lime surface, which subsequently decreases the lime surface area available for further reaction with SO_2. The X-ray photoelectron spectroscopy (XPS) provided information on the chemical interactions taking place between lime and SO_2 species along with their conversion to $CaSO_3$/$CaSO_4$ products. The experimental results permitted the evaluation of the product ($CaSO_3$/$CaSO_4$) formation and the SO_2 removal efficiency with hydrated lime from a gas containing a low concentration of SO_2.

Keywords: Effluent gas desulfurization, Sulfur dioxide, Hydrated lime, Calcium sulfate.

1. Introduction

Due to the sulfur content in petroleum coke used in the anode manufacturing, aluminum smelters emit SO_2 to the atmosphere [1]. Depending on the quantity released and the airshed capacity, SO_2 emissions could have detrimental effects on human health and environment. To control the emissions of SO_2, the effluent gases from a process are desulfurized. A number of methods are used by the industry [1]. The desulfurization processes can be separated into two categories depending on the sorbent can be reused in a loop or not: regenerable and non-regenerable. The regenerable processes release the SO_2 from the sorbent which can be reused to capture other SO_2. In the non-regenerable processes, the sorbent reacts irreversibly with SO_2 to produce a byproduct such as gypsum that can be valorized. Both regenerable and non-regenerable processes are further classified into three types: dry [2], wet [3], and semi-dry [4]. In the wet process, the effluent gas is bubbled through a liquid column, thus producing a liquid product such as Na_2SO_4(aq). In the dry process, the effluent gas is put in contact with a dry sorbent. In the semi-dry process, the

sorbent is injected in the form of a slurry; the water vaporizes creating a highly humid environment [4]. The products containing the captured SO_2 may be subjected to further processing for valorization.

Alternative calcium sulfate raw materials are being developed due to increased industrial gypsum use. Calcium sulfate hemihydrates (β - $CaSO_4 \cdot 0.5\ H_2O$), known as high-intensity gypsum, have become increasingly popular because of their exceptional thermal stability, chemical resistance, and mechanical strength. The use of calcium sulfate is significant in construction materials, molding works, alternate binders [5,6]. The beneficial nature of gypsum produced as a byproduct of desulfurization process truly depends on its final quality. The presence of supplementary hazardous elements such as arsenic, mercury, lead, selenium, etc. could pose a threat to its applications. Researchers tried various approaches, including chemical modification, to produce good quality calcium sulfate materials [6]. However, it involves high cost, skilled manual labor, and special laboratory requirements, which would be difficult for construction applications where large quantities are needed. Also, the transformation of calcium containing raw materials to high-intensity gypsum should address the environmental challenges of pollution, sustainability and minimize the hazardous output as well as consider the economic viability [7] . The efficiency of product formation also reported to be based on the SO_2 adsorption rate by calcium containing particles. Many parameters, such as pH, additives, organic acids, help improve the adsorption rate on the surface of the particles. Seo et al. [8] reported that certain acids provide both the adsorption of SO_2 and a higher efficiency of the desulfurization product[8] Similarly, additives such as Na_2CO_3 and MgO have enhanced the alkalinity[9][10]. Liu et al. [11] studied the role of CO_2 in effluent gases containing SO_2 at concentrations of greater than 1000 ppm using lime[11]. However, their aim was to enhance the CO_2 capture along with SO_2. Though several researchers have investigated the removal of higher concentrations of SO_2 from a gas for the industrial applications, the removal of lower SO_2 concentrations remains difficult to achieve.

Due to the low cost and high abundance, lime (CaO), $Ca(OH)_2$, and limestone $Ca(CO)_3$ are used as a common source material to adsorb SO_2 [1,12]. However, because of the low thermal stability of limestone, it needs additional grinding steps before using it as an efficient desulfurization source. Thus, lime is preferred as the most common and effective sorbent source in desulfurization. Dasari et.al. [13] and Ruhland et al. [14]have studied the kinetic and absorption behavior of SO_2 in $Ca(OH)_2$ solutions. The instantaneous reaction with a low resident time yields the product $CaSO_3$. Kikkawa et al. [3] have investigated the role of the granular limestone size via wet desulfurization process. An SO_2 removal efficiency of 90 % has been achieved because of the use of granular limestone, but needed a neutralization column to ensure the rubbing of the limestone particles in order to expose a fresh lime surface to gas.[3]

In the current work, the desulfurization of effluent gas via a semi-dry process using hydrated lime ($Ca(OH)_2$), which produces calcium sulfite/sulfate as products, were explored. The concentration of SO_2 in the effluent gas coming from the electrolysis cells is much lower compared to that of the other processes such as power generating stations. The lower concentration of SO_2 could significantly change the composition of the final $CaSO_3/CaSO_4$ product. The quantity of specific components of the product was estimated through chemical species analysis. Physiochemical characterizations of the desulfurization product were performed using BET surface area analysis, X-ray photoelectron spectroscopy, and SEM analysis.

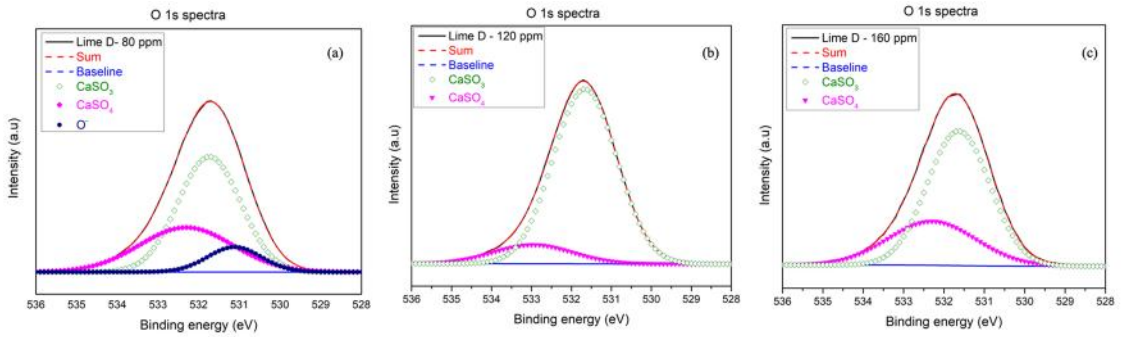

Figure 9. XPS analysis of O 1s spectra for experiments with gas containing different inlet SO_2 concentrations (a) 80 ppm (b) 120 ppm (c) 160 ppm.

Table 4. Summary of Oxygen 1s spectra.

Details	Peak area (%)		
Binding Energy (eV)	*532.3*	*531.6*	*529.2*
Sample details	$CaSO_4$	$CaSO_3$	O^-
SO_2 inlet – 80 ppm	32.8	56.7	10.5
SO_2 inlet – 120 ppm	11.9	87.8	0.3
SO_2 inlet – 160 ppm	31.4	68.4	0.2

4. Conclusions

The semi-dry gas desulfurization reactions were carried out with hydrated lime to study the desulfurization of effluent gas containing low SO_2 concentrations. The experiments were carried out to better understand the desulfurization process. The results could be helpful to develop technologies to eventually reduce SO_2 emissions coming from aluminum production. The hydrated lime with an average particle size of about 10 µm was used to carry out the reactions. It was found that the relative humidity plays a key role in the reaction of SO_2 with hydrated lime. The surface structural properties from BET analysis showed that the adsorbed SO_2 molecules modify the surface structure significantly. The experimental results indicated also that the higher the inlet SO_2 concentration is, the greater the amount of reacted lime particles is. The corresponding XPS results show that the product formed even at lower concentrations of SO_2 (such as 80 ppm). The chemical species at respective binding energy values indicated that the product contains a lower quantity of $CaSO_4$ and a greater quantity of $CaSO_3$. However, $CaSO_4$ formation increased with increasing inlet SO_2 concentration. According to the best of our knowledge, for low SO_2 concentrations (a few hundred ppm), this is the first study which identifies the different components of effluent gas desulfurization products through chemical composition analysis.

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6. References

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