

SULFUR SPECIES IN PARTICULATES EMITTED FROM REDUCING COAL COMBUSTION AND PYROMETALLURGICAL FURNACES

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Abstract The method of X-Ray Photo-electron Spectroscopy is used to determine the chemical state of the sulfur species present in fly-ash samples produced by burning a number of pulverized coal samples under reducing conditions in a continuous combustion furnace. The influence of submicron metallic constituents present in the flue-gases of the pyrometallurgical systems on the state of the species is also investigated. The results show that the predominant state of the sulfur species emitted from the burning chamber and produced on the surface of ZnO particulates is thiosulfate. This material, which is relatively stable at the normal workroom conditions, is not as toxic as previously seen metallic sulfur compounds produced under oxidizing conditions.

چکیده روش اسپکتروسکوپی با فتوالکترون اشعه ایکس برای تعیین حالت شیمیائی ترکیبات گوگرد در خاکستر حاصل از سوختن چند نمونه زغال سنگ تحت شرایط احیائی در یک کوره احتراق پیوسته مورد استفاده قرار گرفته است. اثر وجود ذرات فلزی کوچکتر از میکرون در گازهای خروجی سیستمهای پیرومتالورژی، بر حالت ترکیبات گوگرد نیز مورد بررسی واقع شده است. نتایج نشان می دهد که ترکیبات متصاعد شده از محفظه احتراق و تشکیل شده بر ذرات ریز اکسید روی، غالباً "به صورت تیوسولفات هستند. این ماده که در شرایط عادی داخل کارگاه نسبتاً پایدار است، به اندازه ترکیبات فلزی حاصل از سوختن گوگرد تحت شرایط اکسیدی، آنطور که قبلاً دیده شده است، سمی نیست.

INTRODUCTION

The sulfur species that form in gases emanating from coal-combustion and pyrometallurgical systems have, reportedly, substantial adverse effects on public health [1, 2]. These compounds which are generally produced under environmental conditions in the vicinity of fossil fuel power plants, non-ferrous metallurgy complexes and high density industrial areas [3-5], usually are associated with the fine airborne particulates of respirable size range. Their toxicity is therefore due to the penetration of the inhaled submicron particulates, carrying sulfur compounds deep into the lung [6]. They are also responsible for the reduction of visibility because of light scattering [2].

The sulfur, if introduced into the air as

SO₂, can be the cause of acid rainfall which has major adverse effects on aesthetics, plants, wildlife, materials, visibility, weather and climate. This phenomenon has been the matter of much concern in the recent years [7]. For this reason, many industries throughout the world have been forced to install SO₂ emission control systems, during the past ten years [8-10]. A great amount of attention has also been paid to the development and use of new control techniques for SO₂ emissions [11-16]. Still a substantial amount of sulfur species is added to the indoor and outdoor environments of the electrical, metallurgical and chemical plants throughout the world, every years.

A considerable amount of work is done on the rate of oxidation of sulfur dioxide as a function of sunlight intensity, ambient

temperature, humidity and the presence of particulate matter [17-20]. It is, for example observed that aerosoles produced photochemically in atmospheric air, contained sulfate as well as chemisorbed sulfur dioxide and sulfur trioxide [20]. The presence of Fe^{3+} cations has also increased the rate of oxidation of SO_2 and formation of sulfate [23].

Although the inorganic sulfite species present as complexes with Fe^{3+} , Zn^{2+} , Cu^{2+} and Pb^{2+} in aerosol particulates sampled in the workroom environment and the vicinity of copper and lead smelters have been found stable [24], the sulfur in fly-ash samples has generally been identified as a sulfate [17]. There has been uncertainties about whether the conventional thermometric titration method, widely used to determine the sulfite species in aerosol particulates, determines the concentration of sulfites or of other sulfur species present in the samples [25].

The prevailing condition for all investigations made so far on the production of sulfur species in airborne particulates has been that of an oxidizing atmosphere. However, the condition in some combustion systems occasionally appears to be that of a reducing one. Such a condition may also occur in some metal-

urgical furnaces. In iron-making vessels, for example, the removal of sulfur from hot metal generally occurs at reducing conditions. The production of the non-ferrous metals such as zinc and copper are also generally accomplished under reducing circumstances. However, there is not much information available on the formation of sulfur species under such reducing conditions as described above.

In this study, the method of X-Ray photo electron spectroscopy (ESCA) [26-28], is used to determine the chemical state of sulfur species present in the fly-ash samples produced by the combustion of different pulverized coal samples under reducing conditions produced by sub-stoichiometric air rates. The chemisorption of the sulfur dioxide emissions on copper oxide and zinc oxide submicron particulates were also studied by heating these materials in a reaction chamber. The stability of different sulfur species, under the indoor conditions of the work-room environments, is also studied.

EXPERIMENTS

I. Combustion Of Coal with Air Pulverized coal samples with the chemical compositions

Table 1. Chemical composition of coal samples.

Sample	Percentage								
	Moisture	Ash	Volatile	C	H	N	S	O	
A	3.1	8.6	36.5	69.8	5.1	1.4	3.0	12.0	
B	13.6	7.8	36.2	63.1	5.7	1.0	1.0	20.2	
	P_2O_5	SiO_2	Fe_2O_3	Al_2O_3	TiO_2	CaO	MgO	SO_3	K_2O
A	0.0	4.2	1.9	1.7	0.2	0.4	0.1	0.0	0.2
B	0.1	2.1	0.3	1.3	0.0	2.2	0.7	1.0	0.0

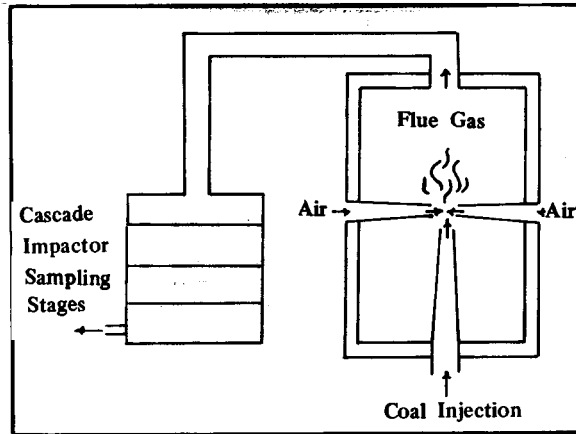


Figure 1. Apparatus used for combustion of coal.

given in Table 1 were burnt at 1600°C (particle-temperature) in a continuous oxidation furnace. The reducing condition was achieved with a sub-stoichiometric oxygen consumption. The apparatus is shown in Figure 1. The rates of injection of coal were 0.05 to 0.10 gram per minute. The size of the coal particles before burning was (A) 75-90 microns, and (B) 45-53 microns. The experimental conditions for the combustion of coal samples are given in Table 2. The stoichiometric volumes of oxygen are calculated for a complete coal burn-out resulting in the emission of CO₂, H₂O, NO₂ and SO₂.

The combustion products were led through a set of cascade impactor sampling stages and the particulates smaller than 0.6 micron in size were collected on a polyethylene filter. The percentage of these particulates is given

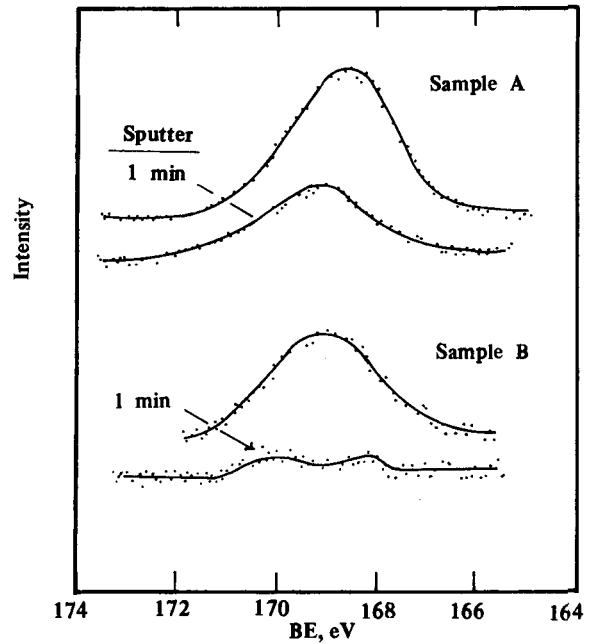


Figure 2. Sulfur 2p spectra of fly-ash samples produced by combustion of pulverized coal samples A and B.

in Table 2. Larger fly-ash particulates which were collected on cascade impactor stages were pressed onto a thin indium foil substrate. The samples were placed on a carousel-type sample tray and were analyzed under 10⁻⁹ torr by an X-Ray photoelectron spectrometer. The results obtained before and after sputtering the samples with argon ion beam are illustrated in Figure 2. The aim of the sputtering was to provide information on the state and composition of the sulfur inside the particles. Irradiation of thermal electrons from a "flood gun" was employed to minimize the

Table 2. Specifications of the combustion tests.

Sample	Coal Rate (g/min)	Oxygen Rate (cm ³ /min)	Stoichiometric Oxygen Rate (cm ³ /min)	Recovery of Particles Smaller than 0.6 micron on Filter (percent)
A	0.05, 0.1	80-160	85-170	20-30
B	0.05, 0.1	70-140	70-140	10-20

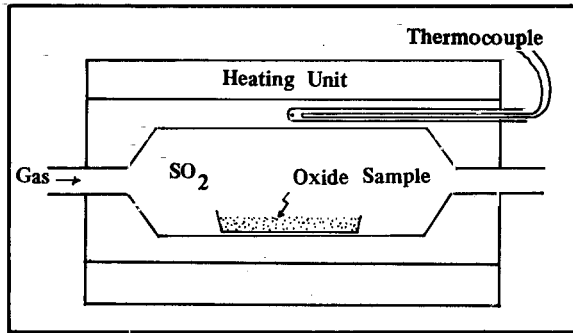


Figure 3. Capsule and furnace used for heating copper oxide and zinc oxide with sulfur dioxide.

positive charges on a number of samples.

II. Production of Sulfur Compounds in a Heating Tube The possibility of the chemisorption of the sulfur dioxide molecules on metallic oxide particulates usually present in the off-gases from coal burning systems and pyrometallurgical smelters, was studied by heating submicron ZnO and CuO powders with SO₂ in a heating tube shown in Figure 3. The oxide samples were charged in alumina boats. Each boat was weighed and inserted into a Vicor capsule that contained a very small amount of graphite. The capsule was purged with SO₂ and inserted into a resistance furnace that heated the sample by radiation. The time after insertion and the temperature of the furnace were measured. At the end of the experiment, the sample was cooled off

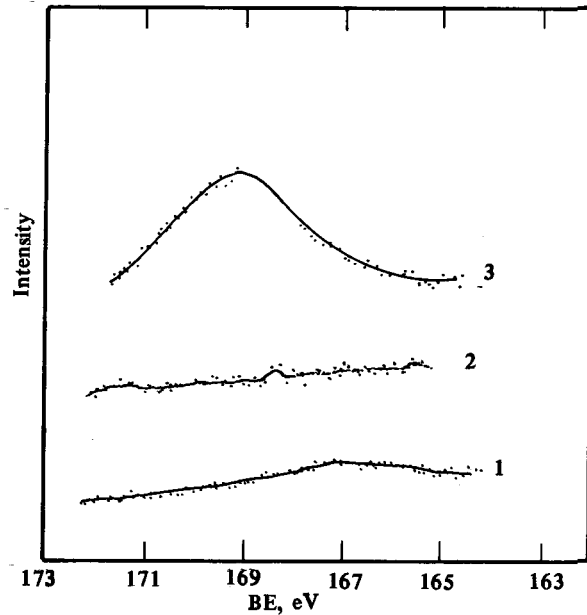


Figure 4. Sulfur 2p spectra of zinc oxide vapor particulates mixed with sulfur dioxide at (1) 430°C, (2) room temperature and (3) 530°C.

and weighed again. The results of the tests are summarized in Table 3.

A number of the samples were then scanned to determine the possibility of the adsorption of SO₂ and of the formation of sulfur compounds. The sulfur 2p spectra of three different samples produced by mixing sulfur dioxide with 0.1 micron ZnO vapor particulates at (1) 430°C, (2) room temperature and (3) 530°C are illustrated in Figure 4.

Table 3. Specifications of the tests for investigation of the formation of sulfur compounds.

No.	Material	Temperature °C	Heating Period, min	Sample Weight, g	Weight Gain g/g-sample
1	CuO + SO ₂	444	20	0.5642	0.1048
2	CuO + SO ₂	660	20	0.3977	0.2172
3	CuO + SO ₂	786	20	0.4747	0.2136
4	ZnO + SO ₂	531	20	0.0791	0.0480
5	ZnO + SO ₂	760	20	0.0999	0.4955

Table 4. The chemical states of sulfur and the corresponding binding energies.

Species	Designation	Sulfur 2p Binding Energy, eV
Sulfur Trioxide [18]	SO ₃	170.6
Sulfate	SO ₄ ²⁻	169.6
Thiosulfate	S ₂ O ₃ ²⁻	168.7 [≠]
Dithionate	S ₂ O ₆ ²⁻	168.1
Sulfur Dioxide [28]	SO ₂	167.9
Sulfite	SO ₃ ²⁻	167.4
Sulfur [28]	S	164.0
Thiosulfate	S ₂ O ₃ ²⁻	162.7 ^φ
Zinc Sulfide [18]	ZnS	162.2
Iron Sulfide [28]	FeS	161.2

[≠] Corresponding to the binding energy of central sulfur.

^φ Corresponding to the binding energy of ligand sulfur.

DISCUSSION

In Table 4, the data obtained on the binding energies of the sulfur 2p spectra of various sulfur compounds existing in a set of reference samples used for analysis of the results, is summarized. Comparing the binding energies of the peaks shown in Figure 2 with the information given in Table 4, indicates that the closest chemical state of the sulfur species present in the fly-ash samples produced by combustion of the coal samples under reducing conditions is that of a thiosulfate with a binding energy of about 168.7 eV. This material, according to a number of simple aging tests, shows to be relatively stable if kept under the conditions of the workroom

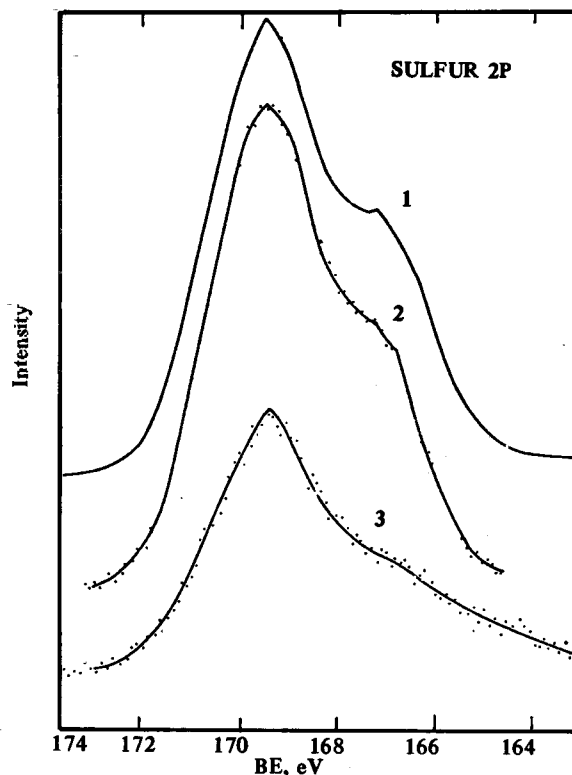


Figure 5. Sulfur 2p spectra of equi-molar sulfate/sulfite mixtures (1) as mixed, (2) after being stored for a week without access to fresh air, and (3) after being kept on indium foil for a week without access to fresh air.

environment for a few days. The mixing of the samples with the different sulfur compounds has not also affected the binding energies of the species (Figure 5).

The next closest chemical state of the sulfur present in the fly-ash samples is that of sulfate, with a binding energy of 169.6 eV. According to the information available, this latter material seems to be more toxic than thiosulfate [29, 30]. This can thus be considered a fortune, because a lot of concern has existed on the toxicity of the sulfur products emitted from combustion systems into the air during the last few years.

The experimental data illustrated in Table

3 shows that the chemisorption of sulfur dioxide on the metallic oxide samples is a function of the test temperature. This result is consistent with the information given in Figure 4, according to which the production of sulfur compounds do not occur at the temperatures less than about 500°C. At 530°C, however, a chemical compound is formed on ZnO vapor particulates, which has a binding energy close to that of thiosulfate.

CONCLUSIONS

The binding energies associated with the sulfur 2p spectra of the fly-ash material produced by the combustion of powdered coal samples under reducing conditions and submicron metallic compounds formed by heating ZnO and CuO with SO₂ under reducing conditions, have the average values of around 169.0 eV and 168.9 eV respectively. These values apparently correspond to the central sulfur S⁺⁶ atom of the thiosulfate. The next closest chemical state seems to be that of the S⁺⁶ atom in the sulfate; a substance with higher toxicity. It can therefore be concluded that from the toxicological point of view as related to the chemical state of the sulfur, the conditions of a reducing vessel should be preferred to that of an oxidizing one.

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