



Sulfate Aerosol Formation During Pyrolysis And Mining Of High Sulfur Indian Coals

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Abstract:

The sulphur deposition and atmospheric sulphates are detrimental to ecosystems, harming aquatic lives and plants, and damaging to a wide range of terrestrial plant life. This also results in creation of yellow clouds that reflect sunlight, reducing the atmospheric transparency which can be measured by Aerosol Optical Depth (AOD) index. The sulphate particles also influence the formation of clouds by acting as Cloud Condensation Nucleus (CNN). In the present study, investigation into SO₂ emission and sulfate aerosol formation during pyrolysis and mining of high sulfur NE coals has been discussed. The North Eastern Region (NER) of India has a substantial deposit of high sulfur (2-8%) coal with low ash, high volatile matter (35-45%) and high vitrinite maceral contents. During combustion and carbonization of these coals, sulfur is emitted to the atmosphere as SO₂ mainly in the temperature region 600-850°C which is further oxidized to SO₄²⁻ and this process is catalyzed by the metal ions present in the environment. In the present investigation gas and particulate samples were collected from different environments viz, coke oven (pilot plant of 100kg/batch) and from coke industries and mine site in winter season in between January to February. The SO₂ concentrations was found in the range 0.29-97.83 µg/m³, 0.23-0.56 µg/m³ and 0.147-0.62 µg/m³ in coke oven, coke industries and mine site respectively. While the SO₄²⁻ concentrations observed were 0.002-0.533 µg/m³, 0.029-0.21 µg/m³ and 0.06-0.14 µg/m³ in coke oven, coke industries and mine site respectively. In coke industries both SO₂ and SO₄²⁻ concentrations lower than that of coke oven pilot plant because in coke industry, washed coal were used for coke production when in coke oven unwashed coals were used. Moreover, it has also been observed that in the mine site, SO₂ and SO₄²⁻ concentration mainly contributes from the coal burning and nearby coke ovens. Hence, the present study on SO₂ emission and SO₄²⁻ aerosol formation has made a significant contribution towards the national as well as global emission inventories.

Keywords: SO₂, SO₄²⁻ aerosol, pilot and industrial coke ovens, catalytic effect of metal ions.

Introduction

Coal-fired power plants currently provide about 41 % of global electricity and are major emitters of CO₂ along with SO₂, NO₂, and NH₃ [1]. Coal, the most important fossil fuel in India is vital for its low cost and energy security. While coal is poised for significant growth, it faces significant and mounting social and environmental challenges. Relative to other fossil fuels, coal is less energy efficient and pollutes more. In India, a good deposit of high sulfur coals is found in the northeastern (NE) region. These low rank coals have different physicochemical attributes in comparison to other Indian coals. The general char/coke characteristics, which restrict their usage in the domestic as well as industrial sectors, are that the coal is high in sulfur, high in volatile matter, and mostly caking and friable in nature. Atmospheric released of sulfur compounds in both gaseous and particulate phases has the potential to cause adverse health effects and other environmental damages (acid rain, etc.) [2]. The sulfur content in these coals is in the range of 2–8% in general, and the majority of the sulfur is in an organic matrix (70–95%), which is aliphatic or aromatic disulfides, heterocyclic compounds of the thiophenic types etc. and these are not easily removable [3]. Sulfur is a major factor in regard to inhibiting the extensive utilization of coal. In pyrolysis, both inorganic sulfur and organic sulfur can be removed, and most sulfur goes into the gas phase in the form of H₂S, which is easily recovered as sulfur. During pyrolysis, pyrite will decompose to the sulfide and sulfur. The nascent sulfur is very active and can capture hydrogen from coal to form H₂S that is converted to gas and/or is captured by an organic matrix to form organic sulfur that remains in char or tar and/or is fixed by mineral matter in coal (mainly calcium, sodium, or iron compounds) to form sulfides that remain in the char [4]. The SO₂ produced can be directly converted to H₂SO₄ after the reaction with the OH⁻, H₂O₂ or by the oxidation catalyzed by transition metals like Fe (III), Mn (II) etc followed by condensation onto aerosol particles [5]. The most important factor affecting the transformation of sulfur during coal pyrolysis are temperature, heating rate, time, pressure, velocity of carried gas, type of reactor, etc [3,4]. This chemical transformation process is generally referred to as gas-to-particle conversion and involves many factors, viz., meteorological parameters, site characteristics, etc The sulfate formation results in creation of yellow clouds that reflect sunlight which reducing the atmospheric

transparency. The sulphate particles also influence the formation of clouds by acting as Cloud Condensation Nucleus (CNN) [5].

Materials And Methods

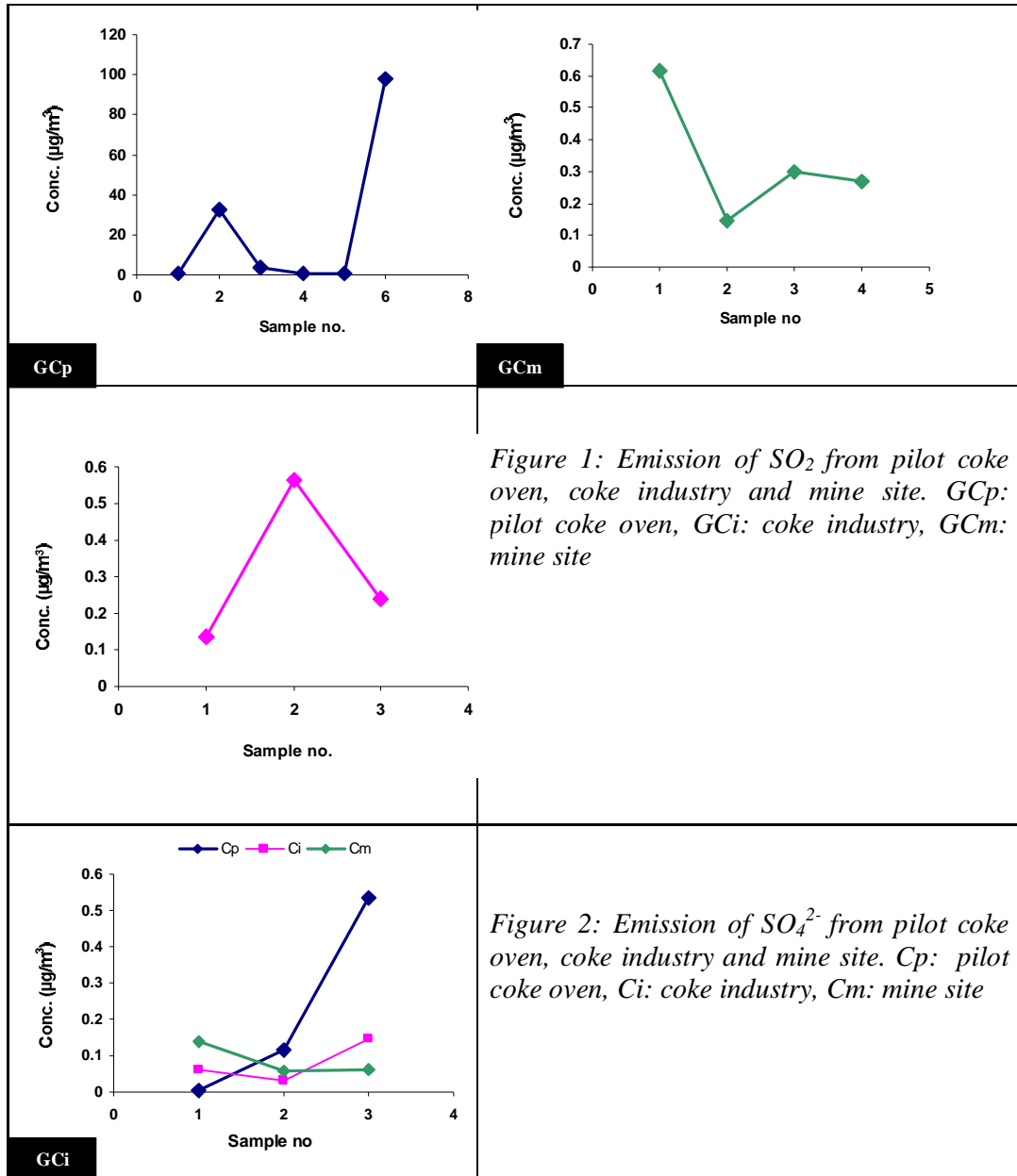
Gaseous sulphur dioxide samples (N=6) and PM_{10} (N=3) were collected during sampling at non-recovery type of experimental coke oven (100Kg/batch) in between September to October of 2010 using stack gas sampler (Vayubadhan Pvt Ltd, India), APM-550 (Envirotech, India), and PEM-ADS25 (Poll Tech., India) respectively. At pilot coke oven, samples were collected SO_2 samples were collected on a 4 hourly basis, while particulate samples were collected on a 24 hour basis.

The mine site sampling was carried out at Tirap colliery, Ledo, Tinsukia District, Assam. Gaseous sample (N=4) and PM_{10} (N=3) were collected using impinger technique using Envirotech Respirable Dust Sampler (APM 460NL), EPM 2000 glass fiber filter using a single stage open face diameter 20.3×25.4 cm (Cat No- 1882-866) filter holder in February, 2011 during day time at a flow rate of $1.3 \text{ m}^3/\text{min}$. In the site, coal mining was carried out by open cast method; where mining, transportation and stacking were carried out simultaneously.

Gaseous SO_2 (N=3) and PM_{10} (N=3) were collected from coke industrial site situated in Guwahati on November, 2011 during day time using Envirotech High Volume Sampler (APM 430NL) T and Envirotech Fine Particulate Sampler (APM 500) respectively. The Coke Oven Industry produces coke from Meghalaya (NER) coals. In both mine and industrial site SO_2 samples were collected on a 4 hourly basis, while particulate on a 6 hourly basis. SO_2 samples were collected in 0.04 M Potassium tetrachloromercurate (K_2HgCl_4 ; TCM) and analyzed by Modified West & Gaeke method by recording UV-visible absorption at 560 nm (SPECORD 200 UV-Visible Spectrophotometer) [7]. SO_4^{2-} were analyzed (Turbidimetric Method at 420 nm) from the water extracts prepared from particulate matters [8].

Results And Discussion

From the observation, it has been found that concentrations of SO_2 in 13 gaseous samples ranged between 0.147 to $97.83 \mu\text{g}/\text{m}^3$ (Figure.1).



Its concentration in pilot coke oven site was found in the range 0.29-97.83 µg/m³ while, 0.23-0.56 µg/m³ in coke industry and 0.147-0.62 µg/m³ in mine site. The SO₂ concentration was found highest in pilot coke oven mainly during combustion followed by industrial and mine site. The emission of SO₂ depends on percentage of sulfur contents in coal and on the time of pyrolysis due to the dependence on thermal stability of sulphurous compounds present in coals. In pilot coke oven coals were used directly without washing, while in coke industrial site before feeding into the coke oven, coal was washed in a hydro-cyclone producing three types of coal samples

depending on their size of the feed. Due to the aqueous leaching sulfur of these coals removes as sulfate [9]. Only the final washed product having low ash and sulfur content were used for coke making. Before washing ash % and sulfur content in the coal were 16.8% and 4.50% but, after washing it reduces to 4.73% and 3.76% respectively (Table 1).

Name of coal	%M	%VM	%Ash	%FC	%S
Tirap (Margherita)	1.8	43.8	2.5	51.9	3.33
Bapung (Meghalaya)	4.63	37.3	16.8	41.2	4.50
Bapung (after washing)	2.52	41.5	4.73	51.3	3.76

Table 1: Physico chemical characteristics of coals

Therefore, SO₂ emission from coke industrial site much lower than that from pilot coke oven. Since maximum sulfur release was found in between 600-850°C and has a decreasing tendency from 850-1000°C which might be due to the incorporation of sulfur released into coal matrix [3]. So, in industrial site second sample has higher concentration followed by third and first. On the other hand, in the mine site SO₂ concentration found higher on first day mainly due to coal burning near the sampling for sometime. Here the coke ovens situated almost one and half kilometer away from the sampling sites, vehicles used for coal loading and mining also have contribution to SO₂ concentration in mine site. The colliery is surrounded by several tea gardens using coal for tea drying and brick kilns using coal for firing.

While the SO₄²⁻ concentrations observed were 0.002-0.533 µg/m³, 0.029-0.21 µg/m³ and 0.06-0.14 µg/m³ in coke oven, coke industries and mine site respectively (figure 2). In all the three sites SO₄²⁻ concentration is lower than SO₂ concentration which shows slow rate of gas to particulate conversion of SO₂ to SO₄²⁻. SO₄²⁻ concentration was found higher in pilot coke oven due to higher emission of SO₂. The higher SO₄²⁻ concentration in mine site is due to more release of fine particulate and coal fines which are smaller in size. Besides this Table 2 shows the higher concentration of Fe and Mn released from mining activity with the particulates which further catalyses the SO₂ to SO₄²⁻ conversion.

Name of coal	Fe (mg/l)	Zn(mg/l)	Mn(mg/l)	Cu(mg/l)	Cr(mg/l)
Tirap (Margherita)	2.40	0.24	0.10	0.02	0.04
Bapung (Meghalaya)	1	1.04	0.04	0.04	0.02

Table 2: Metal analysis from the particulate matter

Conclusion

The comparison study of sulfur released from different environment using high sulfur NE coals shows the high SO_2 and SO_4^{2-} released from experimental coke oven than from industrial coke oven where washed coal were used. These emissions from above two sites also compared with mine site emissions. The SO_4^{2-} released from mine site was found higher than coke industrial site due to more release of fine particulate and coal fines from mining activity and also due to catalytic effect from higher concentration of mainly Fe and Mn. Hence, the study of SO_2 emission and sulphate aerosols formation significantly shows the role of coal mine area, coal based industries particularly coke oven industries towards the global warming scenario.

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