INTERNATIONAL ASSOCIATION OF BIOLOGICALS AND COMPUTATIONAL DIGEST
International & Peer-Reviewed Journal
E-ISSN: 2583-3995

A REVIEW: SULFUR IN COAL AND PETROLEUM COKE

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ABSTRACT

sulfur (S), also spelled sulphur, nonmetallic chemical element belonging to the oxygen group (Group 16 [VIa] of the periodic table), one of the most reactive of the elements.Sulfur is classified among the minor constituents of Earth's crust, in which its proportion is estimated to be between 0.03 and 0.06 percent. Coal is classified into four main types, or ranks: anthracite, bituminous, subbituminous, and lignite. Geochemical studies of sulfur in coals comprise several major aspects relating to the nature and origin of sulfur in coals, including the abundance and distribution of sulfur in coal seams, abundance of sulfur in coal lithotypes and macerals (Chen-Lin Chou, 2012). All types of coal also contain sulfur, which, when burned, releases toxic air pollution. Sulfur content is determined by the conditions under which the coal is formed. While Petroleum coke is a byproduct of petroleum refining, useful in the production of may things.

Keywords: *Coal, Petroleum, Coke, sulfur*

INTRODUCTION

When coal / Petroleum coke is burnt its sulfur content combines with oxygen to form sulfur dioxide (SO^2), which contributes to both pollution and acid rain. Sulfur dioxide emission in fuel combustion is a key problem in most of the coals and petroleum coke. Governments throughout the world have recognized the problems and moved to reduce the amount of SO^2 emission through legislation.

Ryan and Ledda 1998 reported that the acid rain destroys environment the sulphated aerosols produced by sulfur affect human health. So, by reducing SO2 we can convert the coal and petcoke into much ecofriendly energy resources.

Coal:

Coal has been accepted as a major source of energy for centuries. In addition, the International

Energy Agency has forecast a substantial increase in coal use over the next few years, rising from $3.5X10^{12}$ tonnes at present to over $5.3\ 1X10^{12}$ tonnes per year (IEA, 1998).

Coal is divided into four categories according to the carbon content

Lignite (soft) Sub-bituminous (medium-soft)

Bituminous (medium-hard) Anthracite (hard)

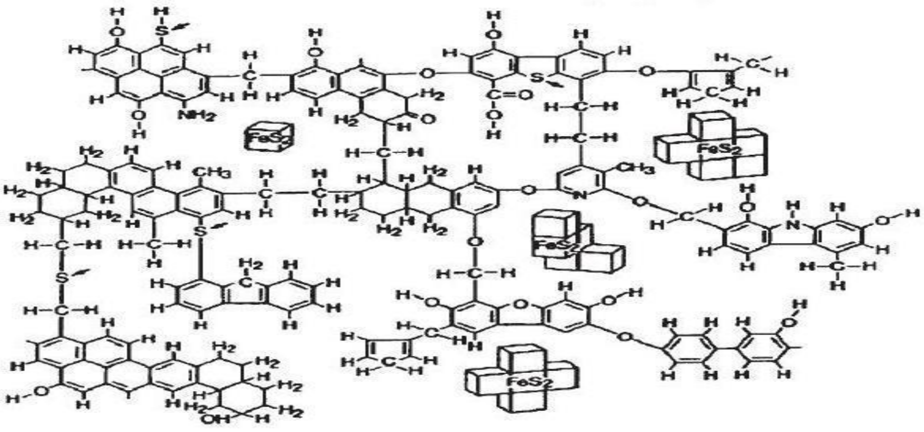
It usually depends on the geographical area from its extraction. Its typical value remains between 1% to 4% however in some coals it remains up to 10%. So higher the sulfur higher the SO2 emission.

Klein 1994 suggests there are 4 groups of aliphatic, aromatic and heterocryptic sulfur forms. The organic sulfur in coal exists as both aliphatic and aromatic or heterocyclic forms, which can be classified into four groups (Klein *et al.*, 1994)

1) aliphatic or aromatic thiols (mercaptans, thiophenols);
2) aliphatic, aromatic, or mixed sulfides (thioethers);
3) aliphatic, aromatic, or mixed disulfides (dithioethers); and
4) heterocyclic compounds or the thiophene type (dibenzothiophenes).

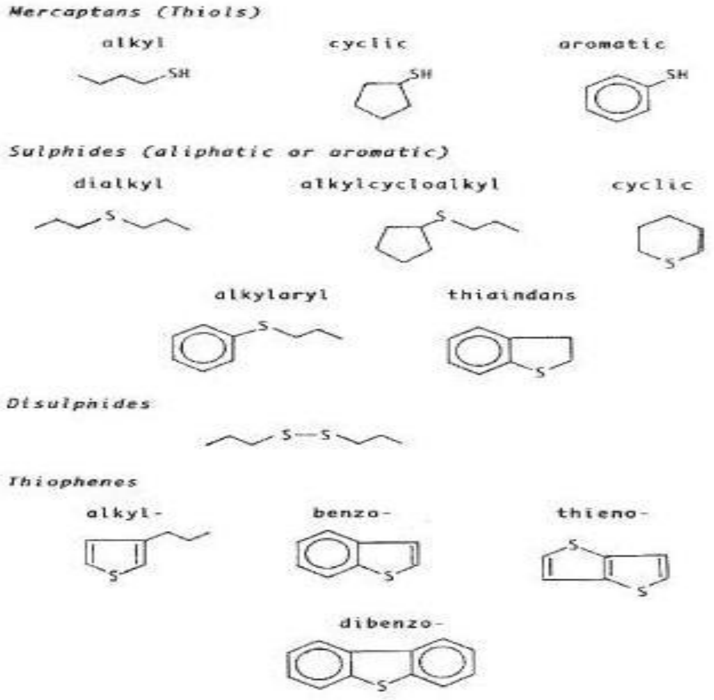
Free sulfur as such does not occur in coal at significant extent. Sulfur is present in coal in organically bound combinations, in inorganic compounds mainly as pyrite (FeS), in weathered coals as gypsum (CaSO4+.2H20) and as ferrous sulfate (FeSO4 +.7H20). inorganic sulfates and sulfides, e.g. barite (BaSO4) and sphalerite (ZnS), The three forms of sulfur commonly measured in coal are sulfate, pyritic , and organic. In physical processes coal is crushed, ground and washed. This allows for up to 90% of pyrite (predominant form of inorganic sulfur in coal) to be removed. However, depending on the type of coal, a considerable amount of finely distributed pyrite as well as organic sulfur can remain in and attach to the coal particles (Klein, 1998).

Figure 1: Structure of Coal with sulfur forms



According to Constanti *et al.*, (1994) the organic sulfur in coal is covalently bound into its large complex structure and is difficult to remove physically or chemically, in contrast to pyritic or inorganic sulfur. Organic sulphur occurs as an integral part of the molecular coal and the petroleum waste matrix and is not readily accessible for microbial attack. So, the removal of organic sulphur from coal/coke/petcoke while retaining its fuel value is most difficult.

Figure 2: The types of sulfur-containing organic compounds identified in coal (Shennan, 1996).



Petroleum coke:

US EPA, 2007 suggests Pet coke is a carbonization product of high-boiling hydrocarbon fractions obtained in petroleum processing (heavy residues). It is a product of extreme temperature and pressure treatments that convert heavy petroleum feed stocks into a solid substance composed predominately of carbon.

Thomas, 1951 reported that Pet coke is a hard, brittle, porous material with honeycomb structure. It is solid, fairly inert, low toxic material with higher oil content. It is considered as low temperature coking product at 900^0-1200^0F. Pet coke is used as a refinery and commercial fuel, in the manufacture of electrodes, abrasives, artificial graphite, and calcium carbide and as a metallurgical fuel. Low sulfur content is required if petroleum coke is to be used in the manufacture of electrodes or as a metallurgical fuel.

The Petroleum Coke category consists of two substances: green coke and calcined coke. These two substances are grouped together in a category based on their similarity of manufacturing processes, which result in similar physical chemical characteristics and chemical composition. The principal difference is the amount of residual hydrocarbon (also termed volatile matter) in the two products. Petroleum coke (both green and calcined) is a black-colored solid produced by the high-pressure thermal decomposition of heavy (high boiling) petroleum process streams and residues. Green coke is the initial product from the cracking and carbonization of the feed stocks to produce a substance with a high carbon-to-hydrogen ratio. Green coke undergoes additional thermal processing to produce calcined coke. The additional processing removes volatile matter and increases the percentage of elemental carbon, which results in a lower potential for toxicity for calcined coke.

Petroleum coke is normally characterized by its proximate analysis including the determination of its volatile matter and sulphur contents. These are of particular importance as indicators of the coke structure and quality. Removal of sulphur and volatile matter from the coke affects greatly its structure, micro porosity and its density.

(Patrick, et. al., 1991) revealed that the structure of cokes depends on the chemical composition of the parent sample and on the conditions of carbonization, especially in the course of the meso-phase formation.

It is believed that the best method to limit the amount of sulfur dioxide emitted into the atmosphere is to reduce the amount of sulfur in coal before combustion. The techniques include physical, chemical and biological processes.

Total sulfur determination:

The need for accurate methods of determining total sulfur in coal was previously noted. The Eschka and bomb washing procedures are the two most commonly used methods in the United States, both of which are given in ASTM D-3177 (6).

The Eschka procedure consists of thoroughly mixing coal with Eschka mixture (2 parts calcined MgO and 1-part anhydrous NaZC03) and ashing it in a muffle furnace at *800°* C. The ashed coal is leached with hot water, filtered, and the sulfur is determined gravimetrically in the filtrate. This method is rapid when carried out on large batches of samples; it is most accurate when used for coals containing no more than 6 or 7% sulfur.

The bomb washing procedure is convenient for laboratories that make frequent coal calorimetric determinations (ASTM D-2015). After cooling and careful venting, the bomb used for a calorific determination is thoroughly washed with water, and the sulfur is then gravimetrically determined in the bomb washings. This method gives excellent results when used for the analysis of coals containing no more than 4.

Desulfurization techniques

Leaching, chemical, extraction, flotation, oxydesulfurization are some of the techniques. Although the alkaline desulfurization is more effective.Acharya et al, (2001) revealed that the physical methods are used mostly although they do separate much of the mineral material, their yield decreases significantly. Furthermore, they have no effect on organic sulphur.

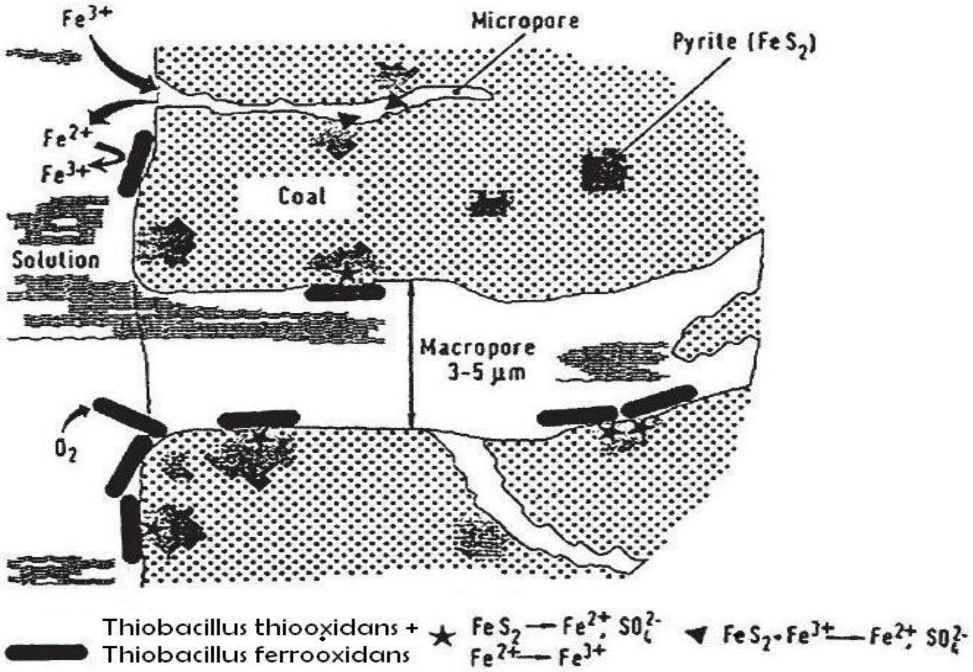
Monticello,(1998) analyzed Hydrodesulfurization a physicochemical technique needs 17-20 atmospheric pressure and approximately 200-425 °C which can affect coal quality as well as it is lengthy, costly, and hazardous in several aspects. Same suggests in compared to such physic chemical methods the microbial methods are mild and nonhazardous and not any impact on quality of coal.

The inability of physical methods to completely remove even the inorganic sulfur has led to the development of many chemical desulfurization processes. These include carbonization in different atmospheres, air oxidation, wet oxidation, Meyer's process, chlorination and extraction with sodium hydroxide, copper chloride and ethanol solutions (Yaman *et al.*, 1995). Bonyton and Abott, (1950) reported that the pet coke may contain various constituents such as V, As, Ni, Fe etc. but the most important which is causing negative impacts on natural environment and hazardous to human health. The number of totals has been reported from 0.1 to 6.4% in pet coke.

According to Beier (1987), 90% of Pyritic sulfur can be eliminated at a cost of $3 per ton. Although many others suggests that microbial desulfurization is slow as well as not feasible in larger quantities. Hence trhe combination of physical and biological desulfurization can be more effective (Pooley and Atkins 1983)

Olsson et al (1994) revealed that the both the organisms Acidianus brierleyi and Thiobacillus ferrooxidans have similar effects on S removal and rate was also similar although the rate of oxidation of pure pyrite was higher for A.B then T.F. Also gave reason for the limitation of direct mechanism of pyrite in coal is the size of microorganisms is large and can't penetrate the coal pores.

Figure 3: Bimodal pore structure of coal and pyrite oxidation (Hone *et al.*, 1987).



Hone et al (1987) reported that some microorganisms with larger body are unable to enter coal so the oxidation of pyrite is limited. Heterogeneous process in which the bacterial cell attaches itself to the sulfide crystal surface and the corrosion occurs in a thin film located in the interspace between the bacterial outer membrane and the sulfide surface. With certain coals, the direct mechanism for oxidation of pyrite may be limited because the microorganisms are too large to enter most of the coal pores as shown in Figure 3.

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