THE OCCURRENCE OF SULPHUR IN COAL

M. Naseem Ahmed

Central Laboratories, Pakistan Council of Scientific and Industrial Research, Karachi

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The problem of the occurrence of sulphur in coal is of considerable importance in many countries and has attracted attention at one time or another without any very precise conclusions having been drawn. Sulphur is present in coal in both organically combined and inorganic forms—the latter as pyritic and sulphate sulphur—and its content varies over a wide range, from a fraction of 1% to over 10%, but there is insufficient knowledge of the forms in which it exists in organic combination. In Pakistan a difficulty arises in the utilization of indigenous coal because the major part of the reserves consists of coals containing an unusually large proportion of organically combined sulphur which cannot be removed from the coal by means of well-known methods alone.

This article is a brief review of our present knowlegde about different forms of sulphur and their origin, with special reference to the organic sulphur compounds present in coals.

Coal occupies a unique position in world economy, and its amount produced annually exceeds that of any other single commodity; but, despite its importance, knowledge of its chemical constitution is relatively scanty. Procedures employed in the utilization of coal have been developed empirically, and there is no doubt that greater efficiency of utilization could be achieved if the chemical constitution of coal were known. In particular the direct use of coal as a chemical raw material could be greatly extended; and this is an important consideration at the present time when the demand for organic chemicals is increasing and that for coal as a fuel may be somewhat lessened by the development of sources of nuclear energy.

In Pakistan a difficulty arises in the utilization of indigenous coal because the major part of the known reserves consists of coals containing an unusually large proportion of organically combined sulphur. This cannot be removed from the coal by normal cleaning methods, and problems of corrosion, atmospheric pollution, etc., become more pressing as industrialisation of the country proceeds. In addition to the development of empirical processes for the de-sulphurization of the Pakistan coal, the problems may be approached from a fundamental standpoint by research into the way in which the sulphur is combined into the organic coal substance. Such research would lead ultimately to better utilization of the coals as fuels, and might also allow the sulphur present to be used fully as a valuable raw material.

This article is a brief review of our present knowledge about different forms of sulphur and their origin, with special reference to the organic sulphur compounds present in coals.

General Characteristics of the Pakistan Coal

The Pakistan coals are among the few examples of coals known to have been formed under marine conditions. They belong to the Tertiary age and were laid down in the early Eocene times following the uplift of this area towards the end of the Mesozoic period.[1] Some of them contain extremely high proportions of sulphur. Although in many cases this is present as pyrites, either in massive form or colloidally dispersed throughout the coal substance, in other cases the major part is present in the organic portion of the coal.[2] The proportions of sulphur, hydrogen, nitrogen, volatile matter and ash were apparently characteristic of coals like those of Pakistan, which were laid down under marine conditions from material that had been drifted in very intimate association with much mineral matter. Due to severe earth movements, some of the coals attained sub-bituminous rank. According to Seyler's classification,[3] the Pakistan coals may be termed[4] as per-hydrous metalignitic and ortho-lignitic coals.

The rational analyses of these coals is of special interest. All of the coals contain much finely divided matter, which is a characteristic of drift coals and there is occasional evidence of fusain and opaque matter. Some of these coals, particularly those from the Trans-Indus field, contain relatively high proportions of resins, which can also be observed as small pockets or partings in the lump coal.[1] Most Pakistan coals contain an extremely high "organic" sulphur content which is a characteristic of carbonaceous products, including many oil shales, that have accumulated and developed under marine conditions.

Forms of Sulphur in Coal

Wormley [5,18] was apparently the first to discover that a substantial proportion of the sulphur in coal is present in organic combination. This work was supported by the experiments of M'Creath[6] and Brown.[7]

The forms of sulphur in the Tertiary coals of the Indo-Pakistan subcontinent attracted the attention of Chatterjee,[8] La Touche[9] and Smith,[10] though in the analytical results only total sulphur was reported. Smith,[10] in discussing analyses of Makum coals, suggested that the sulphur present might occur as an organic constituent as well as pyrites and sulphate.

Wheeler[11] concluded that sulphur exists in most coals in at least three different forms: as metallic sulphides, such as pyrites; as metallic sulphates, such as ferrous sulphate and gypsum; and as a constituent of organic compounds forming part of the coal substance. The principal metallic sulphide present, iron disulphide, may exist in coal in a variety of forms; from massive cubical or octahedral crystals of yellow colour (true iron pyrites) to finely divided slat-grey or greyish-black powder. The rhombic crystalline variety of iron disulphide, known as marcasite, is of frequent occurrence in coal.

Macpherson, Simpkin and Wild[12] have classified pyrites as crystalline, massive, nodular, stringy or globular. Pyritic sulphur is very variable in its occurrence in coals, both in amount and form. Pyrites occur in the form of crystals, balls, lenses, nodules, continuous layers, thin sheets, or flakes, both in horizontal planes and in vertical cleavages and fissures.[13,14] It also occurs in microscopic particles or nodules disseminated through the compact coal.[15] Small quantities of other metallic sulphides, such as mispickel (FeS_2, $FeAs_2$) and lead, zinc and copper sulphides, are often formed in coals, in association with pyrites.

It is now generally accepted that sulphur occurs in coal in four principal forms,[16] this is because the "organic" sulphur is believed to be present in two distinct forms since part may be extracted by means of phenol (i.e. "resinic sulphur"). The insoluble portion is classified as "humic sulphur."

Elemental sulphur is present only in badly weathered coals, as a product of decomposition of pyrites or marcasite.[16,17]

2. The Origin of Sulphur in Coal

(i) Organic Sulphur

Sulphur is a constituent element of (almost all) proteins, which are essential to all living organism, plants as well as animals. Wherever there are coal deposits, living matter and therefore proteins were present.[18] By hydrolytic cleavage with mineral acids the sulphur of the protein substance is split off as cystine, the principal sulphur containing substance in plants. The sulphur in cystine may be regarded as a derivative of hydrogen sulphide, since hydrogen sulphide and some methyl mercaptan are split off in the putrefaction of proteins.[19]

The non-protein forms of sulphur in plants are mustard oils and their glucosides,[11,20,21] which are generally considered to be the probable non-cystine sources of sulphur in coal. Much of sulphur in coal is derived from the original sulphur-containing compounds in the plants from which the coal was formed.[22] The organic sulphur content of a coal seam is fairly constant and could be used as a distinguishing characteristic.[23,24] Dieulafait[25] investigated modern members of the *Equisetaceae*, a family of important coal forming plants, and found greater amounts of carbonates, than in other plants. It is also possible that certain plants of ancient times which contributed to coal formation were particularly rich in non-protein sulphur, like the onion and the mustard families of today.[15]

Some indications of the possible sources of sulphur in coals were given by Funasaka and Yokikawa,[26] who studied artificial coals prepared by heating pure cellulose (filter paper) and lignin (from a acerose tree dust) with 0.1 N hydrogen sulphide, 0.2 N sodium sulphide, 0.2 N ammonium sulphide, aqueous ferric or ferrous sulphate, or ferrous sulphide (with water) at 300°C. and 120 atm. The results indicated:—

(a) that water-soluble sulphide can give rise to organic sulphur compounds in coal;

(b) that water-insoluble sulphide and sulphate react with neither cellulose nor lignin;

(c) neither ferric sulphate nor ferrous sulphate are reduced to ferrous sulphide by organic substances, and

(d) the presence of sulphur compounds results only in minor changes in the properties of the artificial coal.

It should be remembered that most of the substances found to be inert could be converted to soluble sulphide by bacteria present in the early days.

Parallelism exists between organic sulphur and pyrites contents in that a high organic sulphur content is frequently accompanied by a high content of pyrites.[13,24]

(ii) PYRITIC SULPHUR

The origin of pyritic sulphur in coal is a matter of much speculation, mainly because the pyrites may have been formed in various ways and at different periods in the history of the coal bed. Theories have been advanced attributing the presence of pyrites both to external and to internal sources of sulphur.[27]

In connection with the presence of pyritic sulphur in peat, Thiessen[15] suggested that during putrefaction the sulphur which was present in the original plants, largely in the form of proteins, was converted to hydrogen sulphide; which was thus oxidised by sulphur bacteria to sulphonic acid. This would immediately attack any carbonates present and change them into sulphates.

Other reactions might occur which did not involve bacteria; for example, hydrogen sulphide could react with solutions or suspensions of heavy metal salts such as iron carbonate, to produce insoluble sulphides, which would oxidize to form sulphates.[11,15] Iron sulphates could subsequently be reduced through ferrous sulphate to ferric disulphide or pyrites. It is, however, doubtful whether oxidizing reactions could take place under the strongly reducing conditions which exist in peat bogs. Similarly Bischoff [29] advanced a theory that pyrites could have been formed either as a result of reduction of iron sulphate in percolating waters by the organic matter in the peat or coal bed, or by contact between iron compounds, not necessarily soluble, with the decaying organic matter. This would explain the thin coating of pyrites found on coal at shrinkage cracks.

Yourovskii [30] has recently advanced a similar theory that high sulphur coals were formed under reducing conditions with an access to iron containing ground waters. As a result, all coals with highly developed organic material, including coking coals, should contain considerable amounts of sulphur if treated underneath sandstone and limestones. Strongly coking coals of low sulphur content should be formed principally underneath argillaceous shale which insulates the deposits from the iron containing ground water.

Feld[31] on the other hand observed that iron disulphides were formed when ferrous sulphide and sulphur were warmed together in aqueous suspension, the conversion taking place under acid conditions but being hindered by basic conditions. It is also well known that with certain forms of cover such as limestone, coal will have a lower content of sulphur, particularly pyritic sulphur, than coal in the same seam under a shale cover, and that coals with marine cover frequently have high sulphur contents.

It is generally conceded that sulphur bacteria[32] and iron bacteria [33] may play an important and perhaps dominant role, and are responsible for the occurrence of finely disseminated pyrites, which represents by far the greater part of pyritic sulphur present in British coal seams. Colonies of sulphur bacteria which give rise to granules of disseminated pyrites have been formed in peat.[15] Szadoczky-Kardoss[34] has drawn attention to the influence of lime on the accumulation of sulphur in petroleum, coals and peats, which can be brought about by the action of sulphur bacteria. The activity of these is promoted by the abundant supply of calcium and by the fixation of both inorganic (sulphate) and organic (protein) sulphur as calcium sulphate and sulphide, which are then reduced and converted to organic sulphur. The high sulphur contents of coals of certain basins of the United States of America have attributed by White, Theissen and Davis [35] to the erosion of richly sulphide-bearing rocks in the basin drainage, and that of shallowly covered coal to secondary enrichment by sulphate-bearing water from overlying strata. According to Whelan[36] there is strong petrological evidence that the secondary pyrites were formed by solution and redeposition of the primary marcasite, and not by some independent mechanism.

Newhouse [37] considered that globular concentrations of iron sulphides in rocks other than coal are probably pyrites and are of syngenetic origin from gels which later crystallised, while iron sulphide forming bands and lenses in coal is probably marcasite deposited as a gel.

(iii) SULPHATE SULPHUR

The presence of sulphate sulphur in bituminous coal is the evidence of a long process of weathering. Heavy metal sulphates may arise by oxidation of insoluble sulphides previously produced as a result of bacterial activity.[15] Sulphates may generally be detected in peat, especially in the upper strata; in many instances they are present in relatively large amounts. Calcium sulphate appears to be the chief sulphate in peat bogs[15] but in regions of rapid weathering of coals rich in pyrites ferrous sulphate is also present.

Armstrong and Himus[16] found out that free sulphur occurs in very few coals, which have been extensively weathered, and appear to arise from pyrites, since no change occurs in the 'organic' or 'sulphate' sulphur on weathering. Chatterjee[8,17] studied the forms of sulphur present in fresh and weathered (exposed to air) specimens of Tertiary coals of India. Free sulphur was not found in the fresh coal, but developed on oxidation, along with ferrous sulphate, at the expense of pyrites granules. He proposed a series of oxidation reactions by which free sulphur, sulphate, sulphuric acid and ferric hydroxide (limonite) could be obtained by oxidation of pyrites.

Studies of Organic Sulphur Compounds in Coal

The problem of the nature of organic sulphur in coal has attracted considerable attention from many workers. [24, 38, 39, 40, 41, 42, 59] Attempts have been made to extract characterisable sulphur compounds from coal with various solvents. [28, 43, 44] However, even less is known about sulphur than is known about the nitrogen in coal.

In view of the known existence of phenolic groups in coal, it would be expected that the common sulphur groups present would be thiophenol, disulphides and perhaps also heterocyclic sulphur in ring structures. Difficulties are encountered in the low sulphur content of most coals, and the variety of ways in which the multivalent sulphur atom may be combined into the coal "molecule". Although many different sulphur groupings, e.g. thio-ethers, mercaptans, and cystine derivatives, have been stated to occur [43,46] the evidence for their presence is not conclusive. In addition, the majority of researches[47-52] has been directed towards the removal of sulphur rather than towards obtaining knowledge of its role in coal constitution. It is probable that a study of particular coals having a high 'organic sulphur' content will provide a valuable contribution to this knowledge.

Wheeler[28] found that pyridine and chloroform extracts, and the extraction residue, had similar contents of sulphur, and concluded that the organic sulphur compounds were distributed uniformly throughout the coal as part of its fundamental constitution. Powell, Parr and Hadley [53,54] extracted coal with phenol and distinguished between 'resinic sulphur' which was present in the extract, and 'humic sulphur' which remained in the residue. Bhatnagar and Dutt [43] have reported the recognition of mercaptans and disulphides in coal extracts; the bulk of the sulphur compounds, however, remains in the insoluble residues. As much as 24% of the Rasa coal of Istria (Yugoslavia) which contains 11% total (organic) sulphur, has been extracted by benzene under pressure, [44,45] 32% by tetralin, and 43% by pyridine. The extracts and residues all contained similar percentages of sulphur. Kimball [55] suggested that the 'organic sulphur' is combined with the organic mass of coals in the same way as sulphur in vulcanised rubber. Dieulafait, Wheeler and Donath[56] stated that organic sulphur is present in molecular combination in a form similar to that of cystine, a derivative of the albumin of the plants which were the precursors of the coal, and that 'organic sulphur' in sapropelic coals has its origin in animal albumin.

Sulphur has also been stated[46] to be present in coals partly as thiols, sulphides and disulphides and partly as ring compounds. Gusev,[57] and Postovskii and Harampovich [58] suggested that it may occur as bisthioethers and thioethers. Evidence for bisthioether groups was considered to have been supplied by the reaction of the coal with cupric chloride.

Owing to the high molecular character of the sulphur compounds and the complicated structure of the basic organic mass of coals, it is extremely difficult to investigate the chemistry of the sulphur by the usual methods of investigation, for the natural organic substances. Evidence for the existence of the thioether group rested on the reaction of the treated coal with methyl iodide, and on the diminished extent of the reaction after the coal has been treated with potassium permanganate. Kavcic[46] observed that the reaction of anhydrous methyl iodide with sulphur compounds differentiates between various types of sulphur-containing groups, since its rate of reaction with the sulphur atoms varies with the type of bond and residue attached to it. He concluded that 70% of the sulphur present in Rasa coal exists in ring structures; in the form of aromatic thiols, cyclic and aromatic sulphides, disulphides and condensed thiophenes. From an earlier study, using the statistical structural analysis methods of van Krevelen, Kreulen [60] concluded that much of the sulphur present in Rasa coal of Istria occurs in the form of ring structures.

From the consideration of the evidence described above it is clear that although certain organic sulphur-containing groups might be recognised in coal by necessarily indirect methods, the coal "molecule" is too large to allow direct determination of the way in which the sulphur atoms were combined into the carbon skeleton. The desired information could be obtained if coal are degraded to fragments which were small enough to permit characterisation by usual chemical methods, and which retained the sulphur in organic combination. The previous success of oxidative degradation methods make these an obvious choice for a study of high sulphur coal; however, a serious difficulty arises in the ease with which coal sulphur is oxidised to inorganic sulphate, because this product affords little or no information as to the chemical form of the original sulphur.

Work has therefore been undertaken with the principal object of developing improved methods for the degradation of high-sulphur Pakistan coal which would be reported in the next communication. It was required that these methods should degrade the maximum proportion of the coal substance to fragments of relatively small molecular size, while retaining the maximum proportion of the original 'organic sulphur' still in organic combination. The determination of the distribution of sulphur among these products, and ultimately, their characterisation would thus provide valuable information as to the nature of the organic sulphur present in the original coal.

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