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Sulphur in Assam coal

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Abstract

Research carried out on sulphur in Assam coals are reviewed. It is intended to provide a general overview with some recent advances on the forms of sulphur in these coals and their desulphurization and recovery in the forms of elemental sulphur or useful compounds. Greater emphasis is given on a new form of sulphur, i.e., secondary sulphur, in Assam coals. Studies on sulphur in Assam coals would be potentially useful in coal utilization.

Keywords: Assam coal; Sulphur; Removal; Recovery

1. Introduction

Coal is the world's most abundant fossil fuel. The existing accessible stock of gas and oil will last for approximately another 50 years while the coal resources will be able to supply power at least for three centuries. The world demand for coal with low ash and low sulphur is due mainly to environmental pressure and is already changing the value of coals [1].

High-sulphur coals have a deleterious effect on the environments specially when these are used as a fuel. There are vast deposits of high-sulphur coals throughout the world, i.e., in countries where coals have been found. Australia is an exception in which most of the coals are low in sulphur content [2]. In India although we have coal reserves that are likely to last for 200 years at the present rate of consumption, the present thermal power plants are able to achieve only 38–40% efficiency since nearly 71% of Indian coals contain high ash and high sulphur [3]. Inefficient use of these coals is also unacceptable to our present environmentally conscious society [3]. The high-sulphur Indian coals occur in the North Eastern part of the country; the reserves of Assam coals predominate over the others. Even though the proximate and ultimate

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analyses of Assam's coals have been published elsewhere [4], their average values are listed in Table 1.

Assam coals are unique in various respects relative to other high-sulphur coals:

(1) Assam coals occur in the same geographical locations where petroleum has been found;

(2) Assam coals have high-sulphur percentage whereas the sulphur content of the petroleum from the same area is very low;

(3) although Assam coals are known as low-rank coals, the occurrence of low oxygen content indicates that these coals should be of higher rank.

(4) tar obtained from these coals is quite high; and

(5) the best chance for conversion of coal to oil in India is in Assam where coal characteristics and the amenability for conversion of coal to oil are unique in the world [5].

It is evident that, establishment of various coal-based industries and innovation of technologies are necessary for the development of the Indian economy. Sulphur is an important raw material in industry and it is presently imported because India does not have native deposits of sulphur. Therefore, if an efficient method of desulphurization of Assam coal can be developed, utilization of both sulphur and desulphurized coal would help the economic prosperity of India. Moreover, environmental pollution caused by the emission of sulphur dioxide could be minimized. Thus, a precise insight into the forms of sulphur and their associations in Assam coal are essential. Considerable progress has been achieved with regard to the forms of sulphur, their associations in coal bodies and methods of desulphurization. A review of these topics is the subject matter of the present paper.

2. Location and Geology

Prior to the early 1960s, coals from the North Eastern Region of India were commonly known as Assam coals. With the separation of the region on grounds of religion, language and political interest into different states, namely, Assam (capital – Dispur), Meghalaya (capital – Shillong), Tripura (capital – Agartala), Mizoram (capital – Aizawl), Manipur (capital – Imphal), Nagaland (capital – Kohima) and Arunachal Pradesh (capital – Itanagar), the geographical boundary of the present day Assam became much smaller (see Fig. 1).

Assam is composed of the Brahmaputra valley, the Borak Valley, and the hilly districts of Karbi Anglong and North Cachar Hills. The major coal reserves of the state are confined to two major coal belts, i.e., the Makum coal fields and the Dilli–Jaipore coal fields. Some small deposits of coal also exist in the Karbi Anglong and North Cachar Hills districts.

The Makum coal fields are situated in the Dibrugarh district and extend over an area 30 km long and 5 km wide which includes four major mines, e.g., Namdang, Boragolai, Ledo and Tipong. The area is within the latitudes 27°16' and 27°18' North and longitudes 95°43' and 95°55' East [6].

Table 1
Analysis of Assam coals (average value)

Items	Makum coals		Dilli-Jaipore coals		Karbi Anglong coals			
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Air dried basis								
Moisture (%)	2.1	2.5	4.6–7.5	5.3–6.3	6.7–8.9	3.3–8.3	12.7–16.1	8.6–10.9
Ash (%)	4.9	2.6–4.9	4.5–9.1	1.4–6.3	18–26	10–36	6–22	8–32
Total S (%)	5.4	1.5–2.6	3.7–6.4	1.3–4.7	3.6–6.3	3.4	2.5	2–3
C.I. (B.S.)	32	16–25	< 5–5	< 5	—	—	—	—
Specific gravity (at 40°C)	1.321	1.280–1.314	1.374–1.414	1.284–1.394	—	—	—	—
Unit coal basis								
Carbon (%)	79.11	80.44–81.63	73.63–77.55	75.71–79.21	—	—	—	—
Hydrogen (%)	5.54	5.8–6.1	5.4–6.2	5.5–5.9	—	—	—	—
Sulphur (%)	4.95	1.13–1.94	1.83–3.82	1.18–2.69	—	—	—	—
Nitrogen (%)	1.45	1.35–1.47	1.25–1.69	1.50–1.56	—	—	—	—
Oxygen (%)	8.95	9.74–10.36	12.37–17.40	12.29–14.23	—	—	—	—
V.M. (%)	45.3	44.4–46.0	45.4–48.8	45.2–48.1	39.7–49.0	42.0–62.1	29.3–36.5	30.0–50.4
Calorific value	14490	14630–14800	13040–14220	13480–14150	7940–8570	7605–8630	8630	7250–7480

(1) Boragolai colliery, (2) Tipong colliery, (3) Jaipore colliery, (4) Dilli colliery, (5) Kailajan, (6) Khumbaman range, (7) Manje area (8) Nambur river area & Selvetta area.

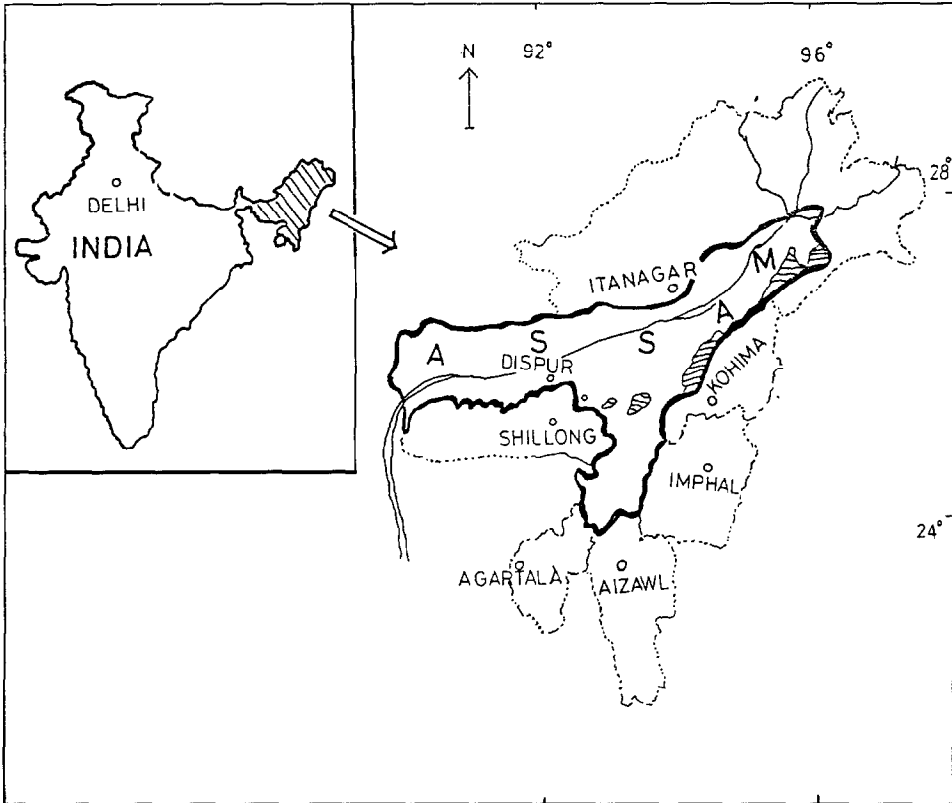


Fig. 1. Major coal bearing areas of Assam.

The coal fields mentioned are situated along the outermost flank of the Patkai range. The southern and south eastern sides of the fields are hills which rise abruptly to a height of 300–500 m from the alluvial plains of the Buridihing and the Tirap rivers. These hilly ranges are traversed by the Namdang, Ledopani and Tirap rivers, whose courses expose sections of the coal-bearing Tikok Parbat Formation.

The Dilli–Jaipore coal fields are located in the Dilli–Jaipore area of Dibrugarh and Sibsagarh districts. These coal fields extend over an area 23 km long and 0.5 km wide from Bimolpore on the west and Jaipore in the east [6]. The coal fields fall within the latitude of 27°04' and 27°19' north and longitude of 95°15' and 95°25' east. The general elevation of these coal fields varies from 120–475 m above sea level.

The coal-bearing areas of the Karbi Anglong district are situated on the south of the river Brahmaputra and are bound by the Jayantia hills of Meghalaya in the west and Nagaland in the east. The height of the coal fields varies between 220–1237 m above sea level. There are at least nine coal-bearing areas, located within this coal belt, which are within the longitudes of 93°8' and 96°45' east and latitudes 25°44' and 26° north. The coal-bearing areas of Karbi Anglong district are scattered throughout the hills

[7]. The coal fields of the North Cachar Hills district were recently discovered and are found to extend to an area of 1.5 km². The area lies at 25°45'25" north and 92°54'50" east [6].

A detailed study on the geology of Assam coals region has been reported by various workers [8–15]. Raja Rao [16] presented a stratigraphic succession of Assam coal and reported that the coals of the Makum coal fields are both of Pliocene and Eocene ages. The coal fields of Karbi Anglong were formed during the Paleocene to Eocene ages [17]. The geologic history of the area is fragmentary up to Tertiary time. The Paleozoic and Mesozoic strata do not occur in the Karbi Anglong district. Here the sandstones are mostly ferruginous and are of brown, red, and violet colours which are found interbedded with the coal seams.

3. Forms of sulphur and desulphurization

The presence of high-sulphur content in Assam coals has been reported in 1931 by Fox [18]. Sulphur in these coals generally occurs in the range of 2.7–7.8% [19]. Iyenger et al. [20] termed the Assam coals as abnormal coals and suggested that the abnormal behaviour is attributed to high-sulphur content. The distribution of sulphur in these coals has been reported by various workers [20–22]. The upper seams of these coals contain more sulphur than the seams lying below [21]. However, chemical studies have revealed that there is no uniformity in the variation of sulphur in the seams in the lateral or in the vertical directions [15].

In regard to the incorporation of sulphur, two groups are of the same opinion that the presence of high sulphur in Assam coals is due to the atomic exchange reaction in which oxygen is substituted by elemental sulphur, however, these groups did not show any experimental evidence of such a reaction [20, 23]. On the other hand, we have ruled out the possibility of such an atomic exchange reaction [24]. Instead, we have proposed a ligand substitution reaction mechanism in aqueous solution in which hydroxo is replaced by bisulphide [25, 26]. This reaction has been experimentally verified [27]. It appears, therefore, that the presence of high-sulphur content in Assam coal is attributed to exchange reactions occurring in different manners.

Assam coal has three forms of sulphur – sulphate, pyritic and organic sulphur [28]. No elemental sulphur has been reported so far in case of Assam coal [29]. The major portion of sulphur is in the organic form [20] which is about 70–80% of the total sulphur [30]. Moreover, the occurrence of another type of sulphur in high-sulphur Assam coals has recently been established and reported elsewhere [26, 31]. This sulphur has been termed as secondary sulphur containing Fe–S moieties associated with coal organic matter [26].

Combustion of high-sulphur coal forms SO₂ which is toxic and corrosive. Sulphur dioxide is subsequently converted to SO₃ [32, 33], which in contact with water, forms sulphuric acid [32]. The presence of sulphur in coke beyond a certain limit makes it unsuitable for metallurgical purposes [32]. In weathered coal sulphur percolates with ground water making the water highly acidic and causes the problem of acid mine drainage [34]. The presence of moisture and sulphur are indications of the liability of

coal to spontaneous combustion during storage [34]. Other deleterious effects observed are—formation of acid rain, corrosion of boilers, underground pipelines, metallic installations, mine machineries, etc. [35,36]. These problems caused by the presence of sulphur in coal indicate the need for the development of an effective desulphurization method for all coals in the world.

Air pollution law specifies the permissible limit for using coals having 1% or less sulphur content [34]. No single desulphurization method has been known by which the sulphur could be removed completely without disturbing the properties of the parent coal and also be economically viable. However, various desulphurization processes have been reported for the removal of total sulphur in Assam coal and are briefly discussed below.

Various gases such as steam [19,37–40], ammonia [19,41], coal gas [38–40], hydrogen [37,39,40], nitrogen [37] and water gas [40] have been known to remove sulphur from Assam coal. A coal sample when allowed to be exposed to the atmosphere up to 106 days showed a decrease in the total sulphur content to the permissible limit of utilization [42]. The sulphur content of coal has decreased on storage under water; this could be due to bacterial oxidation of reduced sulphur [43]. Hydrogenation of Assam coal using anthracene oil has been shown to remove 90% of the total sulphur [44] whereas with tetraline, removal of the total sulphur was only as high as 40–48% [45–47]. Although the removal of sulphur using sodium alkyl or aryl has been known [48] the extent of sulphur removal by chlorinolysis (using methanol) was only 48.70 to 56.45% [49]. A large number of chemicals such as CaO and CaCl₂ [50], Na₂CO₃ and NaHCO₃, chlorides of Na, Mg, Zn and Sn [19], carbonates of Li, Na and K and sodium borohydride [51], aqueous hydrogen peroxide [52], silica [53], inorganic compounds, ore and tar [54] have been used for removal of sulphur from Assam coal. It was also observed that sulphur removal was maximum where ash in coke showed a marked increase from that of original coal [55].

3.1. Inorganic sulphur

Two forms of inorganic sulphur – sulphate and pyritic sulphur are known to occur in Assam coal. The occurrence of sulphate sulphur is very low [20] and is a lesser amount in comparison to other forms [15]. Sulphate sulphur in the form of ferrous sulphate has been reported which formed by the oxidation of pyrite [56]. Identification of melanterite (a form of ferrous sulphate, FeSO₄·7H₂O) in Assam coal by powder X-ray method has been reported [56]. In regard to distribution of sulphate sulphur in Assam coal seams, the content of this sulphur normally remains approximately constant from the floor to the roof of the seam [21]. Further, as the percentage of total sulphur increases there is a decrease in the sulphate sulphur content [58].

Pyrite is an important sulphur-containing mineral occurring in Assam coal [28,59]. Its presence has been verified by chemical [60] and physical [15,58,61] methods. The presence of pyrite in various forms like stringers, individual crystals and disseminated grains has also been reported [56].

The distribution of pyrite in Assam coal has been studied by various workers. There is an increase of pyrite content from the floor to the roof of the seam [21]. But the

occurrence of higher concentrations of pyritic sulphur in the floor and roof of the seams has also been observed [15]. While correlating sulphur with carbon, it has been suggested that the pyritic sulphur predominates in coals containing more than 81% carbon [61]. Moreover, the petrographic characteristics and sulphur genesis of Assam coal were studied and it was concluded that the amount of pyritic sulphur increases with decreasing thickness of the impermeable over burden [62].

Pyrite in Assam coal was reported to form through different ways. Most researchers agree that the constituents of pyrite formation were accumulated at an early stage of coal formation; fresh water being the main supplier of iron while sea water supplied sulphur (in the form of sulphate). A hypothesis for the formation of pyrite has been proposed, according to which iron and sulphate combine to yield ferric sulphate and the resultant product of the reaction of this ferric sulphate and hydrogen sulphide is pyrite [15].

Formation of pyrite during the progressive coalification process has been studied [26, 61]. It has been considered that secondary sulphur having Fe–S moieties associated with organic matter might crack under conditions of high temperature and pressure resulting in separation of iron disulphide, i.e., pyrite [26]. It has been suggested that the low amount of pyritic sulphur in Assam coal is due to incomplete rupture of Fe–S moieties from the coal organic matter and release of H₂S from pyrite during the formative stage of this coal [63].

Desulphurization of inorganic sulphur was done by using hydrogen peroxide, ammonium hydroxide, glacial acetic acid, cupric salt, etc. Hydrogen peroxide could remove 50–90 wt% of inorganic sulphur [64]; however, reduction of sulphate sulphur was 82% at 10% solution and 57–97% pyritic sulphur was removed at 15–20% solution [51]. Moreover, hydrogenation with tetralin as a solvent could remove pyritic and sulphate sulphur in the range of 75–88% and 74–80%, respectively, [44–46]. When coal was exposed to air, oxygen was absorbed and this chemisorbed oxygen formed peroxides on the surface of coal [37]. Peroxide and hydroxide complexes were capable of oxidizing the coal and so oxidation of pyrite to soluble sulphate took place. Further, ferric ion thus formed also oxidized pyrite to sulphates.

Microbial removal of sulphur from Assam coals has been reported in 1977 by Gupta et al. [34]. They used two flora, namely, *Thiobacillus* and *Ferrobacillus*. When *Thiobacillus thiooxidans* was used, the leached liquor was found to increase the acidity and soluble sulphates. A high amount of sulphur was leached from the coal that was assumed to be present as pyritic sulphur [34]. *Thiobacillus ferrooxidans* can also effectively remove pyritic sulphur from coal [21]. Reduction of pyritic sulphur was observed and this was possibly due to bacterial oxidation of reduced sulphur by *Thiobacillus ferrooxidans* [65].

3.2. Organic sulphur

The nature of organic sulphur in Assam coals has not yet been precisely determined and the literature on this is meager. Some workers reported that organic sulphur in Assam coal occurs as mercaptan and disulphide [66] whereas others believed that thiol, sulphide, disulphide and ring compounds are the types of organic sulphur in

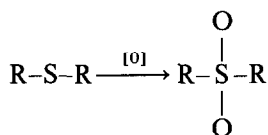
these coals [19]. However, these workers could not show any precise experimental evidences of the nature of organic sulphur in Assam coals.

Iyenger et al. [20, 67] while studying aerial oxidation of Assam coals, identified three different types of organic sulphur:

(a) sulphur estimated during the initial stage of oxidation. The workers could not identify the types of sulphur but observed that the value increased with increasing sulphur content of coal,

(b) the second type, on oxidation, resulted in sulphonic acids and was identified as thiophenol, and

(c) a type resistant to oxidation and assumed by them to be thiophene. Further, if sulphur were present as R–S–R, then this type, on oxidation, would convert into sulphane by



If sulphane was formed by oxidation of sulphide, the oxygen content of the product should have been higher, which was not the case, thus eliminating the possibility of the occurrence of sulphide in coal. It was further reported that the sulphur as thiophenol is remarkably constant and thiophene is particularly constant in coals containing less than 3% organic sulphur. In coals with more than 3% sulphur, organic sulphur generally increases with an increase in the total sulphur content [20, 67]. The possibility of the occurrence of organic sulphur as disulphide was also reported [28]. Recently, the presence of five types of organic sulphur functional groups in the Tipong coal of Assam, namely disulphide, thiol, sulphide, thiophenic and thioketonic have been reported [68].

In studying the nature of sulphur forms in Assam coal by photoelectron spectroscopy, some peaks at 164–165 eV were observed which were assigned to both iron sulphide compounds such as pyrite, marcasite, etc., and organic sulphur compounds [58]. The precise nature of organic sulphur could not be identified. In regard to the nature of distribution of organic sulphur in Assam coals, there is an increase of organic sulphur content from the floor to the roof of the seam [21]. Organic sulphur predominates in these coals containing less than 81% carbon [61].

Some workers believed that it would be easy to desulphurize Assam coal due to its abnormalities related to chemical composition (resulting from depositional environment) and of high organic sulphur content. However, removal of small amounts of organic sulphur by *Thiobacillus ferrooxidans* and certain microorganism present in Assam coal was reported [65, 69]. Removal of organic sulphur was slightly better in sterilized coal samples. Some organic sulphur was also removed along with the pyritic sulphur when *Thiobacillus thiooxidans* was used [34].

Assam coals with high-sulphur content were desulphurized by a hydrogenation process using tetralin as a solvent. The removal of organic sulphur was reported to be in the range of only 27–31% [46, 47]. An increase (> 31%) of the removal of organic

sulphur was observed by increasing the reaction temperature from 300 to 370°C and pressure 40–80 kg/cm². Chlorinolysis in a methanol medium could desulphurize organic sulphur to a lesser degree (< 50%) this is due to the presence of thiophenic sulphur which is resistant to chlorinolysis [48]. Moreover, chlorinolysis was carried out in the presence of NaOH and CaO at 70°C followed by hydrothermal quenching and hydrolysis at 80°C for 2 h [70]. It was observed that in the absence of water less removal of organic sulphur took place than in the presence of water. Two mechanisms, for the removal of organic sulphur proposed were – (1) the formation of coal-bonded alkyl chlorosulphides, which were hydrolyzed to sulphate and coal-bonded alkyl chloride intermediates which were hydrolyzed in situ and (2) the formation of SCl₂ [70]. High-sulphur Assam coal was also chlorinated with Cl₂ at 60–64°C for 2–3 h in the presence of methanol and then dried [44]. The product of this reaction was hydrolyzed with water for 1–2 h at 70–80°C with constant stirring and dechlorination with steam at 300–450°C for 1–3 h, with 50% of the organic sulphur removed by this process. Removal of 26–46% organic sulphur was also reported by using a 5–10% solution of hydrogen peroxide [52].

3.3. Secondary sulphur

It is well-known that sulphur present in coal-forming vegetations cannot account for high-sulphur percentage in coal. Therefore, an adventitious sulphur source must have existed in peatbogs and this sulphur incorporated into the coal precursor under suitable environmental conditions leading to the occurrence of secondary sulphur in coal. The occurrence of secondary sulphur in coal was reported in the late 1950s. Three groups have been known so far to work on secondary sulphur in high-sulphur coals. According to the Russian group, the major portion of secondary sulphur in coal came from elemental sulphur [71, 72]. This secondary sulphur could vulcanize the coal substance during the formation of pyrite [57, 73]. The American group [74, 75] reported that humic acid (a coal precursor) could take up sulphur from an environment containing elemental sulphur [75] or hydrogen sulphide [74] to form organic sulphur. This group could not show any probable mechanism for sulphur incorporation into the coal precursor.

In India, extensive investigation on the organo-geochemical aspects of the formation of different forms of sulphur in coal have been carried out by Baruah [24–27, 31, 61, 76, 77]. A mechanism for incorporation of adventitious sulphur in coal organic matter was hypothesised which involves interaction of humic acid with bisulphide, in the presence of iron, forming coordination compounds containing Fe–S bondings [26]. This concept has been experimentally verified and it has been demonstrated for the first time that the chemical bonding and thermal stability of products formed by incorporation of sulphur in coal precursor [27] can occur. It has been observed that sulphur distribution in coal is dependent on iron distribution [27]. Moreover, metalloproteins such as ferredoxin (containing Fe–S clusters) and related compounds, derived from sulphate-reducing bacteria [78], has also been presumed to contribute a certain percentage to the Fe–S moieties associated with coal [25, 31, 77].

After the death of bacteria, the metalloproteins might accumulate with the organic matter at the formative stage resulting in Fe–S moieties in coal.

Iron (as Fe^{3+}) is preferentially taken up by humic acid relative to other metal ions likely to be present in peat-bogs [79], and organically bound iron present in coal has been reported [80]. In Assam coal, the organically bound iron occurs as Fe–S moieties which has been verified by infrared studies [26, 27, 31, 81]. However, no infrared absorption peaks were detected in Assam coals between 2600 and 2550 cm^{-1} [31, 82] which is the region for S–H stretching vibration. Surprisingly, one Assam coal showed a weak absorption at 2300 cm^{-1} signifying that –SH groups, whether from thiophenol or from bisulphide complex, are bonded to a metal and as a result the band was observed at a lower frequency [26, 27]. Thus, the occurrence of Fe–S moieties in Assam coal is confirmed.

The chemical structure of secondary sulphur in Assam coal has recently been reported [26]. A coal sample when heated at 180°C formed higher amounts of pyritic and sulphate sulphur than the original coal. It was concluded that an unknown form of sulphur could be present in Assam coal which is neither purely organic nor strictly pyritic sulphur; this form of sulphur has been termed as secondary sulphur [26]. It has also been proposed that pyrite could be formed from the secondary sulphur (having Fe–S moieties) during later development of the coalification process [26, 63]. Thus a genetic relation between secondary sulphur and pyrite is proposed.

It is true that thermal treatment of high-sulphur coals of the other regions of the world could also release pyrite. Formation of pyrite by heating an Illinois bituminous coal at 175°C for 6 h in nitrogen was reported [80]. Moreover, it was mentioned that the chemical treatment of coal at high temperatures resulted in an apparent decrease in organic sulphur while the pyritic sulphur apparently increased [83]. If it is true that pyrite can be formed from Fe–S moieties, at a certain stage of the coalification sequence: peat \rightarrow lignite \rightarrow bituminous coal \rightarrow anthracite coal, high amounts of pyrite should be observed. Typically, bituminous coals have higher pyrite contents than lignitic, subbituminous and anthracite coals [84]. Recently, the nature of bondings of Fe–S moieties have been proposed and these moieties upon thermal treatment may remove different Fe–S compounds with varying number of iron and sulphur atoms [76]. The occurrence of secondary sulphur having Fe–S moieties in coal and the formation of pyrite from these moieties by thermal treatment are very significant as far as coal sulphur chemistry is concerned. The presence of such moieties could be the reason why Miller and Given [85] observed that low-rank coal, i.e., lignite, contains more inorganic matter in organic associations and low contents of minerals than is the case for high rank, i.e., bituminous coal.

In regards to the removal of secondary sulphur, not much work has been done because this form of sulphur has been identified only recently in Assam coal. The organic sulphur is always calculated by difference. Yurovskii [57] has indicated that “organic sulphur” as a vague term. It has been presumed that if varying amounts of iron is bonded with the sulphur atom of the Fe–S moieties, then it is not possible to get the actual amount of pyritic sulphur from the soluble quantity of iron in dilute nitric acid [76]. It is also quite likely that some of the secondary sulphur may not be soluble when treated with nitric acid because of the nature of association of the Fe–S moieties

with coal organic matter. Therefore, while claiming the removal of organic sulphur, there is a probability that some amount of secondary sulphur might have removed. This presumption is strongly supported by Rumyantseva [86], who found that most of the sulphur in coal determined as organic sulphur by chemical analysis is pyritic sulphur.

4. Recovery of sulphur

Sulphur is an essential raw material for many chemical industries. Most of the sulphur requirements for Indian chemical industries has to be satisfied by importing sulphur or its compounds. In fact, in the year 1967–68 India imported sulphur worth rupees forty crores approximately [87]. The major sources of Indian import of sulphur are Canada, USA, Poland and Mexico. India imported 199 000 tonnes of sulphur in 1969 which became double in the year 1978 and 350% in the year 1981. In this way it can be projected that in this last decade of the century, the yearly Indian requirement of sulphur will be approximately 25 000 000 tonnes. Thus, high-sulphur Assam coal is a promising source for extraction of elemental sulphur [87, 88], while the H_2SO_4 , so obtained from it, is used as a fertilizer.

Ghose and others [89] mainly investigated the recovery of sulphur from Assam coal. High-sulphur coal combustion in air releases sulphur dioxide. The gas was allowed to be absorbed in limestone and Na_2CO_3 with maximum recovery of sulphur in the form of CaSO_4 at 30% while as Na_2SO_4 , the value increased to 42%.

Two different processes, namely, dehydrogenation and carbonization have been known for extracting sulphur from Assam coal [90]. In the first method, flue gas, obtained from burning high-sulphur Assam coal, was dehydrogenated and passed through iomax, a by-product of Gauhati Refinery, Assam, which was found to absorb SO_2 selectively. The absorbed sulphur dioxide was recovered from gas solution by slight warming. The efficiency of SO_2 absorption varied inversely with the temperature. In the second method, sulphur was recovered by blending coal with suitable proportions of sodium carbonate and then subjecting it to low temperature carbonization. The resultant char was leached with water to recover sulphur as sodium sulphide and sodium sulphate. It was also reported that sulphur was recovered as calcium sulphite or calcium bisulphite from flue gas, obtained from combustion of pulverized Assam coal [91]. These chemicals are useful for the paper industry.

Recovery of sulphur in elemental form from Assam coal was done by passing gaseous products of combustion through an iron pyrite slurry [92]. In this reaction, SO_2 and H_2S react to give free sulphur. By steaming the coal, after slurring into 20% of sodium hydroxide solution for 2 h at 775°C , the sulphur was recovered as H_2S .

Other methods have also been known for the recovery of sulphur from Assam coal [93]:

(a) selective oxidation of Assam coal in the presence of catalysts such as, Al_2O_3 or $\text{Al}_2\text{O}_3 + \text{ZnS}$,

- (b) absorption of SO_2 in sodium aluminate solutions,
- (c) carbonization with Na_2O_2 ,
- (d) carbonization after refluxing with $\text{NaOH}/\text{H}_2\text{O}_2$, and
- (e) digestion of coal with 30% alkali solution at 100 atmosphere pressure.

Among these methods, (e) and steaming were found to be most effective to recover sulphur as H_2S .

The Regional Research Laboratory, Jorhat (RRLJ) made various attempts to improve the recovery of sulphur by burning coal on a grate. It was observed that only 80% of sulphur was recovered in the scaled-up unit, by maintaining the lime stone in fluidized condition around 550°C , though in the laboratory scale, 75% sulphur was reported to be recovered [93]. Moreover, powdered sodium carbonate was used as an absorbent in the pilot plant trial where coal was burned on a furnace grate using excess air. The gas was passed over Na_2CO_3 under fluidised conditions. An excess amount of 40% of Na_2CO_3 was used to absorb SO_2 evolved during the combustion of coal. In this process the percentage of recovery of sulphur was enhanced to 40% at 450°C [94]. The entire process developed at RRLJ, was summarized by Ghose et al. [89]. It was concluded that the process can be taken up in large scale as integrated process in a coal power complex.

5. Conclusion

Four forms of sulphur – sulphate, pyritic, organic and secondary sulphur are present in Assam coal. The first three forms of sulphur are well-known but the occurrence of the last form has only recently been reported. Sulphate and pyritic sulphur occur as separate entities while organic sulphur (C–S bonded) and secondary sulphur (having Fe–S moieties) are found to associate with the coal organic matter.

Desulphurization of Assam coal indicates that maximum removal of inorganic sulphur could be possible whereas organic sulphur could be removed to a less extent. The method of removal of secondary sulphur is not precisely known. The recovery of sulphur from Assam coals shows promising results. Therefore, further research on the forms of sulphur, particularly organic and secondary sulphur, in Assam coal and their removal aspects are desirable.

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