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華煤中硫質種類之分析

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華煤中硫質種類之分析

楊珠灝

（一）緒言

近世鋼鐵事業盛興，而焦煤（Coking Coal）遂見重于世。蓋焦煤云者，謂可供煉焦（Coke）之煤也。然完善之焦煤，頗不多覯。缺乏粘性者有之，灰份過高者有之。即或粘性強，灰份低，則又以硫份稍多之故，亦每爲煉焦者所屏棄。然硫之性質不同。有時有可以人力減低其含量者。則雖有較高之硫份，仍不失爲良好焦煤，故未可偏廢也。中國煤礦雖富而煉焦之煤則殊非甚多。其中所含硫份之性質尤向未有詳細研究。著者特就重要烟煤十五種詳加分析。費時半載，始告厥成。于中國焦煤問題或能有少補乎。

（二）煤中硫質之分類

焦炭內之硫質，係由原煤而來。是以原煤中之硫質及其成分，關係于焦炭者，至密且巨。因擇是節，茲將煤中硫質之分類以及炭化（Carbonization）作用影響於焦炭中之硫質及其成分者，簡述如次：

I 基於化學性質之分類，亦即本篇之藍本也。

a. 硫與碳，氫，氧，氮或磷諸原素，形成含硫之有機化合物，是爲有機硫質（Organic Sulphur）。

b. 硫與鐵經化合成爲二硫化鐵，是爲硫鐵礦硫質（Pyritic Sulphur）。

c. 硫礦硫質再經化學作用，轉變爲硫酸亞鐵（Ferrous Sulphate），是項硫酸亞鐵同極少量之硫酸鈣（Calcium Sulphate），合稱硫酸硫質（Sulphate Sulphur）。

煤中之硫酸硫質，大抵含量不高，似不致顯著的影響于煉焦，茲從略。二硫化鐵則又以其比重較大，大抵能以冲洗法（Washing Process）或浮游法（Flotation Method）削減或分除之。且是項硫質，於煉焦爐中，經分化作用變爲一硫化鐵（Ferrous Sulfide）

及原質硫（Elementary Sulphur）。後者經再度化學作用，成硫化氫（Hydrogen Sulphide）而揮發。其一硫化鐵則轉變爲易揮發之二硫化炭（Carbon Disulphide），或少量不易揮發之含硫有機物。蓋後者可由焦中硫化硫份之減低，及有機硫份之增高，而得證實焉。總之是項硫鐵礦硫質，確能以相當方法，減低其含量，則毫無疑問矣。是以焦煤中之硫質，其於焦炭之硫份，所最舉足重輕者，厥惟有機硫質耳。且後者含量既高，化除亦難。或謂此項硫質，亦能於煉焦爐中，分解其一部而揮發。蓋全部有機物質，就廣義言之，皆屬於揮發物質故也。然證諸事實則有大謬不然者。前已言之：即硫鐵礦硫質，經炭化作用，而成有機硫質是也。著者以爲炭化作用，與其謂減低有機硫份，毋寧謂增加該項硫份之爲愈耳！究以衆說紛紜，莫衷一是。是故有澈底測驗之必要。茲有下列分類。

II本分類係小規模之煉硫試驗。其子目如下。

a.揮發硫質(Volatile Sulphur)。—此項硫質，以其能揮發於煉焦爐中，故不甚爲害。就煉焦觀點言，此項硫質愈多則減低該焦炭之硫份愈易。

b.固定硫質(Fixed Sulphur)—是項硫質與實用分析中之固定炭同一意義，即由全硫份減去揮發硫份及不燃燒硫份（灰內之硫份）之和。是類硫份之鑑定於含高量硫份之焦煤最關密切，亦絕對必要。設某煤含硫過多時，則藉以固定硫份之鑑定，以明其炭化後之是否減低其硫份，抑減低至何種程度，而決定各種硫質之鑑定，以及沖洗浮沈諸法之應用是否必要。匪特此也，由此鑑定亦可概見各焦之粘性硬度等，是故著者以爲是項工作對於煉焦堪稱首要。此次惜以時間關係未得向此方研求不無遺憾。

(三)本試驗所選之煤樣說明

本試驗所選之煤樣，係採自中國南北各重要之烟煤礦。大多數可以煉焦。所選計十有五種，要亦可進窺中國一般焦煤對此各種硫質之存在，及成分之梗概焉。茲將所選之煤樣，詳實表出之如後：

表一——煤樣之來源及其類別

試驗室號數	省份	縣名	產地	煤礦	俗名或煤層	種類符號	時代
三〇六	山東	博山	西河岳家莊	同興公司	小石炭	AB	二疊石炭紀
三一九	河北	磁縣	西佐村	怡立公司	頭煤	Bm	二疊石炭紀
三二一	河北	磁縣	西佐村	怡立公司	一坐煤	Bh	二疊石炭紀
三四九	察哈爾	宣化	玉帶山桑溝	厚豐公司	甲號(全層)	Bl	侏羅紀
三六二	河北	井陘	崗頭村	井陘礦務局	南大井第五層	Bm	二疊石炭紀
三六五	河南	安陽	六河溝	六河溝煤礦		Bm	二疊紀上
三六九	山東	嶧縣	韭莊	中興煤礦	已洗煤末	Bm	二疊紀上
三七三	河北	灤縣	趙各莊	開灤礦務局	洗煤	Bm	二疊紀上
三七四	河北	灤縣	趙各莊	開灤礦務局	特別洗煤	Bm	二疊紀上
四四八	安徽	宣城	大汪村	水東官礦	烟煤	Bl	二疊紀上
四八五	安徽	懷遠	舜耕山	淮南礦務局	三四號井南三槽	Bc	二疊紀
五二三	山西	大同	口泉格格塔			Bi	侏羅紀
五九一	湖南	湘潭	譚家山	有利公司		Bh	二疊紀
五九七	浙江	長興	大煤山	長興煤礦	大煤山樣	Bc	二疊紀上
六五五	江西	萍鄉	安源	萍鄉煤礦	洗焄煤	Bl	侏羅紀

表二——各煤之實用分析及發熱量

試驗室號數	水份	揮發份	固定炭	灰份	公熱單位	英熱單位
三〇六	〇·五一	一六·八一	七三·九七	八·七二	七九三八	一四二八八
三一九	〇·二五	二一·二〇	七二·一〇	六·四六	八一五三	一四六七五
三二一	〇·三二	二一·一〇	七三·六三	四·九六	八一七九	一四九〇二
三四九	一·九六	三六·〇二	四八·三八	一三·六四	六六一二	一一九〇二
三六二	〇·一四	二三·七〇	六五·〇一	一一·一五	七七三三	一三九一九
三六五	〇·四六	二三·七九	六〇·七三	一五·〇七	七三五五	一三二三九
三六九	〇·四〇	三一·七五	六一·〇五	六·八〇	八〇〇九	一四四一六
三七三	〇·三一	三一·九四	五七·三九	一〇·三六	七六三六	一三七四五
三七四	〇·七六	三一·二七	五五·六九	一二·二六	七五〇三	一三五〇五
四四八	〇·一〇	三三·三四	四六·六六	一九·八八	六三四八	一一四二六
四八五	二·一一	三六·三二	四八·六七	一二·九〇	六六四六	一一九六三
五三三	二·〇〇	三五·六三	五八·一一	四·二六	七七九四	一四〇二九
五九一	〇·六五	二二·〇三	七〇·九八	六·三七	八一二五	一四六二五
五九七	〇·四六	三三·四九	四五·五一	二〇·五二	六一八〇	一一一二四
六五五	〇·九二	三〇·二八	五三·〇三	一五·六七	七二一九	一二九九四

(四)各種硫質之鑑定

a. 全硫份之鑑定，由來已久，方法亦夥。要皆不外以相當之氧化劑，使煤中之全部硫質成爲硫酸基（Sulphate Radical），而鑑定以氯化鋇焉。茲將其最重要之方法摘錄之如下：

1. 愛氏法（Eschka method）。—以愛氏混合劑（Eschka mixture）燒之。後者係由一份之無水炭酸鈉二份之養化鎂及五分一份之硝酸鉀三者混合而成。

2. 過養化鈉法（Sodium Peroxide method）。

3. 氧氣法（Oxygen Bomb washing method）—養氣法定量似不甚精確，過養化鈉法亦覺不甚適用，最近又有人以養化鈣代替愛氏混合劑中之養化鎂。就經濟觀點言，意至善矣。但以尚無充分之證實，著者遂不得不依舊沿用愛氏之法。

b. 硫質分類之鑑定，以鮑氏及巴氏法（Powell and Parr method）爲最重要，亦最準確。著者於後部之分析，亦一本此法。

II 試驗法

a. 全硫份之鑑定—先以三克之愛氏混合劑，盛於一適當之乾鍋或蒸發皿內；繼之以一·三七三六克之煤末而攪勻之；再以一或二克之愛氏混合劑覆於其上。如吾人確知某煤含硫過多時（超過百分之二），該煤末宜減半用之。卽〇·六八六八克是也。而上層之愛氏混合劑，則應加倍覆之。蓋恐硫質之不及養化而揮發，致結果低於實際之硫份也。將此乾鍋置於電爐內，漸漸燒之。以鍋內黑色之炭質完全揮發爲度。如無電爐，燒以無硫焰之氣燈或酒燈，亦無不可。此殆視試驗室之設備而定耳。該鍋內之混合物，俟冷却後取出研碎之，傾於摺就之濾紙上，冲以熱水至濾液之體積約達二百立方公分（cc.）。傾入此濾液以二或三立公分之溴水（Bromine water），繼之以充分之鹽酸，使其酸化後，煮沸之。一俟溴氣全部揮發，卽以十立公分之氯化鋇（百分之十），漸漸滴入該沸騰之濾液內，頻攪以玻棍（Glass Rod）。使沸騰約五分鐘，將該杯置於暖處渡夜，而以定量濾紙濾之，先洗以淡鹽酸（百分之一），繼之以熱水者約六次，或以無氯基（Chloride Radical）爲度。此項濾過之洗澱，置於精確秤過之乾鍋內燒之。硫酸鋇之克數乘以十卽得該煤之全硫份（百分比）。其用〇·六八六八克者，須乘以二十方可。

b.全無機硫份之鑑定—煤內之硫礦硫質與硫酸硫質合稱爲無機硫質。是項硫質能全部溶解於淡硝酸中，而有機物質則否。故依鮑氏及巴氏法，前者易於鑑定之如次：

一克之煤末置於百五十立公分之燒杯內，傾入以八十立公分之淡硝酸，（酸比水爲一比三）而攪勻之，隨時攪以少許之溴水，於二十四小時後濾之。而置該濾紙及末被硝酸溶解之煤末於該原燒杯內，以備後部全有機硫份之鑑定。而於此濾液內，加入少許之濃鹽酸，置諸蒸汽鍋（Water Bath）上蒸發之使乾。而將此乾燥物，溶解於二十五立公分之水，及五立公分之鹽酸中，繼以熱氫氧鹽水(Ammonium hydroxide)使該酸液內之鐵質沈澱而後濾之。由此沈澱，鑑定鐵份以高錳酸鉀法（Potassium Permanganate Titration）。此項鐵份卽爲硝酸鐵量(Nitric Acid soluble Iron)。同時由該濾液中，鑑定硫份，一如前述。惟所得硫酸鋇之重量，須乘以一三·七三六，始得該煤之全無機硫份。

c.硫酸硫質之鑑定—煤內之硫酸硫份大都甚低。新出井之煤樣，甚至缺乏是項硫質。其出井時間較久者，則受外界之養化作用，形成少量之硫酸硫質。茲將此項硫質之鑑定法，簡述之如後：

置五克之煤末於五百立公分之燒杯或同容量之大口三角玻瓶（Wide Mouthed Erlenmeyer Flash）內，傾入以三百立公分之淡鹽酸（百分之三）而攪勻之，置於溫度約達六十度之電熱鐵板上，使其浸蝕，四十小時後濾之。由此濾液內鑑定鐵量及硫份，一如前述。而以所得之硫酸鋇乘以一·七四七二，卽爲該煤之硫酸硫份。該鐵份則爲該煤之鹽酸鐵量。

d.硫礦硫份之鑑定—此項硫份之鑑定方法有二：

1.由全無機硫份減去硫酸硫份卽得。

2.由硝酸及鹽酸溶液中之鐵量，計算得之—硝酸鐵份（Nitric acid Soluble Iron）減去鹽酸鐵份（Hydrochloric acid Soluble iron）乃爲鐵含於二硫化鐵內之鐵量。由此鐵量，與二硫化鐵之公式(FeS_2)，卽可得相當於該鐵量之硫份焉。是爲硫礦硫份。

e. 全有機硫份之鑑定—全有機硫份之鑑定方法亦有二：

1. 由全硫份減去硫酸硫份及準確硫磺硫份之和，卽爲全有機硫份。

2. 以直接方法鑑定之。法以前經硝酸侵蝕而未溶解之煤末及濾紙，一併置諸該原燒杯內，加以足量之濃硝酸，置諸蒸氣鍋上乾之，約三四次。再加以濃氫氧鉀水於該乾燥物上，提勻而後濾之。該濾液經再度乾以蒸氣鍋，而以愛氏法鑑定該乾燥物內之硫份焉。所得之硫酸鋇乘以一三·七三六，卽爲該煤之有機硫份。

f. 有機硫質之分類及其鑑定—有機硫質約分爲二種：一爲膠性硫質(Phenolic or resinous sulfur)，係溶解於石炭酸(Carbolic acid or phenol)之有機硫質。一爲不溶解於石炭酸之有機硫質，名曰腐植硫質。(Humus Organic Sulphur)。其鑑定之方法如次：

盛一·三七三六克之煤末於五十立公分之三角玻瓶(Erlenmeyer Flask)內，傾入以二十五立公分之熱石炭酸。瓶口塞以軟木(Cork)，並通以長二尺許之玻管(Glass Tubing)，以防石炭酸氣體之揮發。置此瓶於油鍋(Oil Bath)或電爐(Electric Oven)內，熱之至溫度約達百五十度，並在此溫度下經二十小時後用顧氏濾器(Gooch Crucible)乘熱濾之。洗以純酒，並使乾之。嗣將此乾燥物及石棉一併磨以二或三倍之愛氏混合劑。依法鑑定其硫份焉。是項硫份係不溶解於石炭酸之混合硫質之成分。故由全硫份減去是項硫份，始得溶解於石炭酸之膠性硫份。次由全有機硫份減去該膠性硫份，則得腐植硫份焉。

(五)分析之結果

I 無機硫份—分析之結果，第一步當屬各煤之全硫份。著者爲避免重複起見，將此部並入表四。本節所列者，則爲無機硫份之部。有機硫份則不及焉。

表三—各種無機硫質之成分，與由兩種不同之方法，所得之硫磺硫份及其比較。各煤之鐵量，亦一并列入。

試驗室號數	全無機硫份	硫酸硫份	硫磺硫份	硝酸鐵量	鹽酸鐵量	硫磺鐵份	硫磺硫份	相差

三〇八	一·四〇	〇·二五	一·一五	一·八三	〇·八六	〇·九七	一·一一	增〇·〇四
三一九	〇·一一	〇·〇二	〇·〇九	〇·二三	〇·一四	〇·〇九	〇·一〇	減〇·〇一
三二一	〇·九二	〇·〇八	〇·八四	〇·八八	〇·一八	〇·七〇	〇·八〇	增〇·〇四
三四九	〇·四九	〇·〇六	〇·四三	〇·五九	〇·二二	〇·三七	〇·四二	增〇·〇一
三六二	〇·二五	〇·〇二	〇·二三	〇·四〇	〇·二〇	〇·二〇	〇·二三	無增減
三六五	〇·三二	〇·〇八	〇·二四	〇·四八	〇·二七	〇·一九	〇·二二	增〇·〇二
三六九	〇·二五	〇·二三	〇·〇二	〇·五五	〇·五三	〇·〇二	〇·〇二	無增減
三七三	〇·三〇	〇·一二	〇·一八	〇·四二	〇·三〇	〇·一二	〇·一四	增〇·〇四
三七四	〇·六〇	〇·一七	〇·四三	〇·六八	〇·三二	〇·三六	〇·四一	增〇·〇二
四四八	三·八八	〇·〇五	三·八三	三·六四	〇·二七	三·三七	三·八六	減〇·〇三
四八五	一·〇四	〇·〇七	〇·九七	一·〇〇	〇·一六	〇·八四	〇·九六	增〇·〇一
五二三	〇·一二	〇	〇·一二	一·五七	一·五〇	〇·〇七	〇·〇八	增〇·〇四
五九一	〇	〇	〇	〇·一九	〇·一八	〇·〇一	〇·〇一	減〇·〇一
五九七	一·七七	〇·二二	一·五五	一·七五	〇·四二	一·三三	一·五二	增〇·〇三
六五五	〇·一〇	〇	〇·一〇	〇·三五	〇·二八	〇·〇七	〇·〇八	增〇·〇二

或謂有機硫質之一部，亦往往溶解淡硝酸。以試驗度之，不爲無因。蓋上表所列之硫礦硫份由硝酸浸液所鑑定者，大抵高於該項硫份由各該煤之鐵量計算所得之數字。著者遂亦以後項數字爲準確之硫礦硫份焉。

煤中之硫酸硫份，大抵甚少，前已道及。但證諸上表，似不盡然。此殆係某數種煤樣之出井時間較久所致。

II全有機硫份—由兩種不同之方法所得之全有機硫份，稍有出入。茲列表四以比較之。並以各平均值爲各該煤之全有機硫份之准確數字云。

表四—全有機硫份，包括比較及其平均值。

試驗室號數	全硫份	硫礦硫份	硫酸硫份	全有機硫份(間接)	全有機硫份(直接)	相差	全有機硫份(平均)
三〇六	二·八六	一·一一	〇·二五	一·五〇	一·四六	增〇·〇一	一·四九
三一九	〇·六五	〇·一〇	〇·〇二	〇·五三	〇·五六	減〇·〇三	〇·五五
三二一	一·四三	〇·八四	〇·〇六	〇·五五	〇·五二	增〇·〇三	〇·五四
三四九	〇·七五	〇·四二	〇·〇六	〇·二七	〇·二六	減〇·〇一	〇·二六
三六二	〇·七六	〇·二三	〇·〇二	〇·五三	〇·五七	減〇·〇四	〇·五五
三六五	〇·八四	〇·二二	〇·〇八	〇·五四	〇·五二	增〇·〇二	〇·五三
三六九	〇·七九	〇·〇二	〇·二三	〇·五四	〇·五六	減〇·〇二	〇·五五
三七三	〇·九七	〇·一四	〇·一二	〇·七一	〇·六九	增〇·〇二	〇·七〇
三七四	一·三九	〇·四一	〇·一七	〇·八一	〇·八二	減〇·〇一	〇·八二
四四八	五·四七	三·八六	〇·〇五	一·五六	一·六〇	減〇·〇四	一·五八
四八五	一·六六	〇·九六	〇·〇七	〇·六三	〇·六六	減〇·〇三	〇·六五
五二三	〇·五七	〇·〇八	〇	〇·四九	〇·四六	增〇·〇三	〇·四八
五九一	〇·六五	〇·〇一	〇	〇·六四	〇·六三	增〇·〇一	〇·六四
五九七	三·三五	一·五二	〇·二二	一·六一	一·五八	增〇·〇三	一·六〇

六五五	〇·五四	〇·〇八	〇	〇·四八	〇·四八	無增減 〇·四八

兩種全有機硫份，雖少有出入。然究未出乎可能的試驗之錯誤。故以各平均值爲準確之數字。庶與理論之數字，更近似矣。

III 兩種有機硫質之分析：

表五—兩種有機硫質之成分。

試驗室號數	全硫份	石炭酸不溶硫質	膠性硫質	全有機硫份(平均)	腐植硫質
三〇六	二·八六	二·七二	〇·一四	一·四九	一·三五
三一九	〇·六五	〇·六四	〇·〇一	〇·五五	〇·五四
三二一	一·四三	一·四二	〇·〇一	〇·五四	〇·五三
三四九	〇·七五	〇·七〇	〇·〇五	〇·二八	〇·二三
三六二	〇·七八	〇·七二	〇·〇六	〇·五五	〇·四九
三六五	〇·八四	〇·七六	〇·〇八	〇·五三	〇·四五
三六九	〇·七九	〇·五九	〇·二〇	〇·五五	〇·三五
三七三	〇·九七	〇·七七	〇·二〇	〇·七〇	〇·五〇
三七四	一·三九	一·一五	〇·二四	〇·八二	〇·五八
四四八	五·四七	五·〇三	〇·四四	一·五八	一·一四
四八五	一·六六	一·五二	〇·一四	〇·六二	〇·四八
五二三	〇·五七	〇·五六	〇·〇一	〇·四八	〇·四七

五九一	〇·六五	〇·五七	〇·〇八	〇·六四	〇·五六	
五九七	三·三五	二·八六	〇·四九	一·六〇	一·一一	
六五五	〇·五四	〇·四八	〇·〇六	〇·四八	〇·四〇	

由上表可知有機硫質中之腐植硫質占絕對多量。

分析之總結：

表六—總結各項分析之結果。並比較各煤內諸硫份之和與各該煤之全硫份。

試驗室號數	硫礦硫份	硫酸硫份	腐植硫份	膠性硫份	諸硫份和	全硫份	相差
三〇六	一·一一	〇·二五	一·三五	〇·一四	二·八五	二·八六	減〇·〇一
三一九	〇·一〇	〇·〇二	〇·五四	〇·〇一	〇·六七	〇·六五	增〇·〇二
三二一	〇·八〇	〇·〇八	〇·五三	〇·〇一	一·四二	一·四三	減〇·〇一
三四九	〇·四二	〇·〇六	〇·二三	〇·〇五	〇·七六	〇·七五	增〇·〇一
三六二	〇·二三	〇·〇二	〇·四九	〇·〇六	〇·八〇	〇·七八	增〇·〇二
三六五	〇·二二	〇·〇八	〇·四五	〇·〇八	〇·八三	〇·八四	減〇·〇一
三六九	〇·〇二	〇·二三	〇·三五	〇·二〇	〇·八〇	〇·七九	增〇·〇一
三七三	〇·一四	〇·一二	〇·五〇	〇·二〇	〇·九六	〇·九七	減〇·〇一
三七四	〇·四一	〇·一七	〇·五八	〇·二四	一·四〇	一·三九	增〇·〇一
四四八	三·八六	〇·〇五	一·一四	〇·四四	五·四九	五·四七	增〇·〇二
四八五	〇·九六	〇·〇七	〇·四八	〇·一四	一·六五	一·六六	減〇·〇一

五三三	〇·〇六	〇	〇·〇四	〇·〇一	〇·三六	〇·三七	減〇·〇一
五九一	〇·〇一	〇	〇·三六	〇·〇六	〇·六五	〇·六五	無增減
五七七	一·三三	〇·三三	一·二一	〇·四七	三·二四	三·二五	減〇·〇一
六五五	〇·〇六	〇	〇·四〇	〇·〇六	〇·五四	〇·五四	無增減

總上分析結果，頗稱近似。此殆充分表現鮑氏及巴氏法之應用矣。

(六)結論

I 沿用鮑氏及巴氏法所得之結果，頗稱精確。該法之詳細步驟，已一并列入本文。

II 淡硝酸能溶解一部分有機硫質。故鐵量之鑑定極爲重要。

III 淡硝酸能溶解全部二硫化鐵，及其他溶解於淡鹽酸之鐵質。故由鐵量計算所得之硫礦硫份，較爲準確。

IV 全硫份中大抵以有機硫質之成分爲最高。

V 有機硫質內之膠性硫質，含量頗少。且少於腐植硫質。

VI 硫酸硫質之含量應極低，惟以某數煤暴露於空氣中時間較久之故，以致其成分稍高。

VII 半烟煤及低級烟煤浸蝕於濃硝酸之時間應久，次數應多。俾使全部有機物質得溶解於濃氫氧化鉀水，以便鑑定。

(七)志疑

淡硝酸能溶解全部二硫化鐵，及一應鹽酸所能溶解之鐵質，而不能溶解矽酸鐵，此爲事實。著者並假設華煤中之鐵質惟有二硫化鐵能溶解於硝酸，而不溶解於鹽酸，而有前項之結論焉。究於實際，是否如此，猶是疑問。蓋煤內或有與二硫化鐵同性質之鐵質：即溶解於硝酸而不溶解於鹽酸之時，則其由鐵量所計算之硫礦硫份，應高於實際之硫礦硫份矣。若然則前項結論，將無以自立矣。惟著者僅就試驗之結果，下該斷語，初未顧及是項可能之事實。且試驗所及，亦未發現類似該項之事實。其所可疑者則

有三一九，四四八，及五九一，等三煤樣。因該三煤之由硝酸侵液所得之硫礦硫份，小於由該煤鐵量所計算之該項硫份。惟以各該煤之硫礦硫份，相差無幾（百分之〇·〇一—〇·〇三）。或屬可能之試驗錯誤，抑確有與二硫化鐵同性質之鐵質存在，未審孰是，茲誌以存疑。

（八）鳴謝

著者甚荷本所技師金開英先生之熱心指導與匡正，特此鳴感。又洪會荃女士供給本篇以煤之實用分析表，亦一併申謝。參攷書目已列入英文篇，不另述。

4. Pyrite in coal can be quantitatively extracted by the same acid.

5. Semibituminous coals and the low volatile bituminous coals must be digested for a longer time with concentrated nitric acid in order to render the organic matter completely soluble in ammonia.

6. The percentages of phenolic sulphur are always lower than those of humus organic sulphur.

6. BIBLIOGRAPHY.

1. Beitrag zur Bestimmung der verschiedenen Schwefelformen in südafrikanischen Kohlen und Schiefern, Von P. E. Rousseau. Brennstoff-Chemie 12, 446-9 (1931).

2. Zur Kenntnis der Verbindungsformen des Schwefels in einigen tschechoslowakischen Steinkohlen und Braunkohlen. Von H. Ditz und H. Wildner, Brennstoff-Chemie 13, 192 (1932).

3. The Powell and Parr Method for the Determination of Sulphur in Coals. By T. G. Woolhouse. Fuel in Science and Practice IV, 454 (1925).

4. Quantitative Determination of Sulphur Forms in Coke. By A. R. Powell. Ind. Eng. Chem. 15, 951-3 (1923).

5. Sampling and Analysis of Coal, Coke and By-Products. By U. S. Steel Corporation, 3rd Ed., pp. 77-86.

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5. Sampling and Analysis of Coal, Coke and By-Products. By U. S. Steel Corporation, 3rd Ed., pp. 77-86.

4. Summary of Analytical Results.

The following table gives in condensed form the results of the analyses for the various forms of sulphur and a comparison of the total of these with the total sulphur in the coal.

TABLE 6. SUMMARY OF ALL ANALYSES FOR SULPHUR FORMS IN COAL:—

Lab. No.	Pyritic Sulphur	SO_4 Sulphur	Humus Org. Sulphur	Phenolic Sulphur	sum	Total Sulphur	Total Difference
306	1.11%	0.25%	1.35%	0.14%	2.85%	2.86%	−0.01%
319	0.10%	0.02%	0.54%	0.01%	0.67%	0.65%	+0.02%
321	0.80%	0.08%	0.53%	0.01%	1.42%	1.43%	−0.01%
349	0.42%	0.06%	0.23%	0.05%	0.76%	0.75%	+0.01%
362	0.23%	0.02%	0.49%	0.06%	0.80%	0.78%	+0.02%
365	0.22%	0.08%	0.45%	0.08%	0.83%	0.84%	−0.01%
369	0.02%	0.23%	0.35%	0.20%	0.80%	0.79%	+0.01%
373	0.14%	0.12%	0.50%	0.20%	0.96%	0.97%	−0.01%
374	0.41%	0.17%	0.58%	0.24%	1.40%	1.39%	+0.01%
448	3.86%	0.05%	1.14%	0.44%	5.49%	5.47%	+0.02%
485	0.96%	0.07%	0.48%	0.14%	1.65%	1.66%	−0.01%
523	0.08%	0.00%	0.47%	0.01%	0.56%	0.57%	−0.01%
591	0.01%	0.00%	0.56%	0.08%	0.65%	0.65%	0.00%
597	1.52%	0.22%	1.11%	0.49%	3.34%	3.35%	−0.01%
655	0.08%	0.00%	0.40%	0.06%	0.54%	0.54%	0.00%

It is evident from this table that the sum of the several analyses checks very closely with the total sulphur content of each coal.

5. CONCLUSION.

1. The organic sulphur content of coal is generally known to be greater than pyritic sulphur content. This statement is proved to be correct with Chinese coals.

2. The method of Powell and Parr is well applicable to Chinese coals and values on duplicate determinations mutually agree.

3. Dilute nitric acid will extract small amounts of organic sulphur from certain coals. In order to avoid this error in laboratory determinations, it is recommended that the pyritic sulphur be calculated from the pyritic iron content.

TABLE 4. PER CENT REPRESENTING TOTAL ORGANIC SULPHUR:—

Lab. No.	Total Sulphur	Pyritic Sulphur	SO_4 Sulphur	Total By diff.	Organic S. Dir. Det.	Difference	Average
306	2.86%	1.11%	0.25%	1.50%	1.48%	+0.02%	1.49%
319	0.65%	0.10%	0.02%	0.53%	0.56%	−0.03%	0.55%
321	1.43%	0.80%	0.08%	0.55%	0.52%	+0.03%	0.54%
349	0.75%	0.42%	0.06%	0.27%	0.28%	−0.01%	0.28%
362	0.78%	0.23%	0.02%	0.53%	0.57%	−0.04%	0.55%
365	0.84%	0.22%	0.08%	0.54%	0.52%	+0.02%	0.53%
369	0.79%	0.02%	0.23%	0.54%	0.56%	−0.02%	0.55%
373	0.97%	0.14%	0.12%	0.71%	0.69%	+0.02%	0.70%
374	1.39%	0.41%	0.17%	0.81%	0.82%	−0.01%	0.82%
448	5.47%	3.86%	0.05%	1.56%	1.60%	−0.04%	1.58%
485	1.66%	0.96%	0.07%	0.63%	0.60%	+0.03%	0.62%
523	0.57%	0.08%	0.00%	0.49%	0.46%	+0.03%	0.48%
591	0.65%	0.01%	0.00%	0.64%	0.63%	+0.01%	0.64%
597	3.35%	1.52%	0.22%	1.61%	1.58%	+0.03%	1.60%
655	0.54%	0.08%	0.00%	0.46%	0.46%	0	0.46%

3. Two Forms of Organic Sulphur.

TABLE 5. PHENOLIC AND HUMUS ORGANIC SULPHUR IN COAL:—

Lab. No.	Total Sulphur	Nonphenolic Sulphur	Phenolic Sulphur	Aver. Total Org. sulphur	Humus Org. Sulphur
306	2.86%	2.72%	0.14%	1.49%	1.35%
319	0.65%	0.64%	0.01%	0.55%	0.54%
321	1.43%	1.42%	0.01%	0.54%	0.53%
349	0.75%	0.70%	0.05%	0.28%	0.23%
362	0.78%	0.72%	0.06%	0.55%	0.49%
365	0.84%	0.76%	0.08%	0.53%	0.45%
369	0.79%	0.59%	0.20%	0.55%	0.35%
373	0.97%	0.77%	0.20%	0.70%	0.50%
374	1.39%	1.15%	0.24%	0.82%	0.58%
448	5.47%	5.03%	0.44%	1.58%	1.14%
485	1.66%	1.52%	0.14%	0.62%	0.48%
523	0.57%	0.56%	0.01%	0.48%	0.47%
591	0.65%	0.57%	0.08%	0.64%	0.56%
597	3.35%	2.86%	0.49%	1.60%	1.11%
655	0.54%	0.48%	0.06%	0.46%	0.40%

According to the above table the majority of organic sulphur would be of humus type.

forms of the sulphur alone. The data from these experiments are given in the following table (Table 3).

TABLE 3. SULPHUR AND IRON IN COAL AND ALSO WITH A COMPARISON OF THE PYRITIC SULPHUR AS OBTAINED WITH THE PYRITIC SULPHUR AS CALCULATED FROM THE PYRITIC IRON CONTENT:—

Lab. No.	Inorg. Sulphur	SO_3 Sulphur	Pyritic Sulphur	HNO_3 Sol. Fe	HCl Sol. Fe	Pyritic Iron	Pyritic Sulphur	Differ.
306	1.40%	0.25%	1.15%	1.83%	0.86%	0.97%	1.11%	+0.04%
319	0.11%	0.02%	0.09%	0.23%	0.14%	0.09%	0.10%	−0.01%
321	0.92%	0.08%	0.84%	0.88%	0.18%	0.70%	0.80%	+0.04%
349	0.49%	0.06%	0.43%	0.59%	0.22%	0.37%	0.42%	+0.01%
362	0.25%	0.02%	0.23%	0.40%	0.20%	0.20%	0.23%	0.00%
365	0.32%	0.08%	0.24%	0.46%	0.27%	0.19%	0.22%	+0.02%
369	0.25%	0.23%	0.02%	0.55%	0.53%	0.02%	0.02%	0.00%
373	0.30%	0.12%	0.18%	0.42%	0.30%	0.12%	0.14%	+0.04%
374	0.60%	0.17%	0.43%	0.68%	0.32%	0.36%	0.41%	+0.02%
448	3.88%	0.05%	3.83%	3.64%	0.27%	3.37%	3.86%	−0.03%
485	1.04%	0.07%	0.97%	1.00%	0.16%	0.84%	0.96%	+0.01%
523	0.12%	0.00%	0.12%	1.57%	1.50%	0.07%	0.08%	+0.04%
591	0.00%	0.00%	0.00%	0.19%	0.18%	0.01%	0.01%	−0.01%
597	1.77%	0.22%	1.55%	1.75%	0.42%	1.33%	1.52%	+0.03%
655	0.10%	0.00%	0.10%	0.35%	0.28%	0.07%	0.08%	+0.02%

It is claimed that a small quantity of organic sulphur may have been taken into solution by dilute nitric acid. According to the present data it seems correct since the per cent of pyritic sulphur obtained by direct extraction method are generally higher than those calculated from the pyritic iron content. For this reason the latter figures are considered as the correct per cent of the pyritic sulphur in coal.

2. Total Organic Sulphur. The following table (Table 4) gives the per cent of total organic sulphur obtained in two ways. A comparison of the totals and their average values are also given.

4. Pyritic Sulphur Content.

The per cent. of the pyritic sulphur in coal may be found in two ways, namely:

a. By subtracting the per cent of sulphate sulphur from the per cen of total inorganic sulphur.

b. By calculating from pyritic iron content of the coal. The difference between nitric acid soluble iron and hydrochloric acid soluble iron is the pyritic iron content and by means of the latter the pyritic sulphur is readily computed.

5. Total Organic Sulphur Content.

The total organic sulphur content of the coal may be estimated as follows:

a. By difference. The per cent. representing the sulphate sulphur in the coal is added to the correct per cent. representing the pyritic sulphur, and the sum is subtracted from the per cent., representing the total sulphur in the coal.

b. By direct determination. The sulphur is determined by Eschka method from the residue of the dilute nitric acid extraction.

6. Two forms of Organic Sulphur.

One gram, or the factor weight, 1.3736 grams, of the coal sample is extracted with 25 cc. of phenol at a temperature of about 150°C. for twenty hours. The mass is filtered hot and washed with alcohol and sulphur is determined from the residue by Eschka method. This amount of sulphur, in per cent, represents the phenol insoluble, non-phenolic, sulphur of the coal, while the per cent of the phenol soluble, phenolic, sulphur is obtained by subtracting the per cent of non-phenolic sulphur from the total sulphur content of the coal. The total organic sulphur minus the phenolic, resinous organic, sulphur both represent in per cent, gives the per cent of humus organic sulphur.

4. ANALYTICAL RESULTS OF EXPERIMENTS.

1. The first set of experiments was, of course, the determination of the total sulphur in coal, the data of which were already given in Table 2. Now comes the second which was performed with regard to the analysis of the sulphate and pyritic

3. METHODS USED.

The method developed by Powell and Parr* has been well known and considered as a reliable and practical procedure. For that reason, their method was entirely adopted for this study. The procedure is abstracted below.

1. Total Sulphur Content.

One gram, or, preferably, the factor weight, 1.3736 grams, of the coal sample is heated with about three grams of Eschka mixture (one part of anhydrous sodium carbonate, two parts of calcined magnesium oxide and one-fifth part of ammonium nitrate) in a muffle furnace and the sulphur is determined in the water extracts as sulphates by barium chloride method. In case the sulphur content is exceedingly high, say over two per cent., one half the factor weight, 0,6868 gram, is used.

2. Total Inorganic Sulphur Content.

One gram of the sample is digested with 80 cc. of dilute nitric acid (1:3) with occasional addition of bromine water for a period of 24 hours at room temperature. The filtrate, after getting rid of the nitric acid by evaporating with hydrochloric acid, is taken up in dilute hydrochloric acid and treated with ammonium hydroxide to precipitate iron and the latter is determined by potassium permanganate titration. The sulphur is determined by usual method from the filtrate from which the iron is just removed. This amount of iron, in per cent., is termed as the nitric acid soluble ron content of the coal while that of sulphur, also in per cent., is known as the total inorganic sulphur content, that is, the pyritic sulphur plus sulphate sulphur.

3. Sulphate Sulphur Content.

A five-gram portion of the sample is extracted with 300 cc. of dilute hydrochloric acid (3%) for a period of 40 hours at a temperature of about 60°C. The extract is analyzed for iron and sulphur, the sulphur representing the sulphate sulphur present in the coal.

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* Forms in which Sulphur Occurs in Coal. By A. R. Powell and S. W. Parr. Bull. Am. Inst. Mining Met. Eng. 1919. 2041-9; C. A. XIV, 112.
The Analysis of Sulphur Forms in Coal. By A. W. Powell. U. S. Bureau of Mines, Technical Paper 254.

TABLE 1. SOURCE OF COALS USED IN EXPERIMENTS.

Lab. No.	Province	District	County	Co. operating mine	Symbol
306	Shantung	Poshan	Hsiho	Tunghsing Co.	AB
319	Hopei	Tzuhsian	Hsitsochun	Yili Co.	Bm
321	Hopei	Tzuhsian	Hsitsochun	Yili Co.	Bh
349	Chahar	Hsuanhwa	Yutaishan	Houfeng Co.	Bl
362	Hopei	Chinghsing	Kangtouchun	Chinghsing Mining Adm.	Bm
365	Honan	An-yang	Liuhokou	Liuhokou Co.	Bm
369	Shantung	I-hsian	Tsaochuang	Chunghsing Co.	Bm
373	Hopei	Lanhsian	Chaokouchuang	Kailan Mining Adm.	Bm
374	Hopei	Lanhsian	Chaokouchuang	Kailan Mining Adm.	Bm
448	Anhwei	Hsuancheng	Tawangchun	Suitung Mine	Bl
485	Anhwei	Hwaiyuan	Shunkengshan	Hwainan Co.	BC
523	Shansi	Tatung	Kakata	———	Bl
591	Hunan	Hsiangtan	Tanchiashan	Youli Co.	Bh
597	Chekiang	Changhsing	Tameishan	Changhsing Co.	BC
655	Kiangsi	Pinghsiang	An-yuan	Pinghsiang Co.	Bl

TABLE 2. PROXIMATE ANALYSIS AND CALORIFIC VALUES OF COALS USED IN EXPERIMENTS.

Lab. No.	Moisture	Vol.Mat.	F. Carbon	Ash	Sulphur	Calories	B.T.U.
306	0.50%	16.81%	73.97%	8.72%	2.86%	7923	14288
319	0.24%	21.20%	72.10%	6.46%	0.65%	8153	14675
321	0.32%	21.10%	73.62%	4.96%	1.43%	8279	14902
349	1.96%	36.02%	48.38%	13.64%	0.75%	6612	11902
362	0.14%	23.70%	65.01%	11.15%	0.78%	7733	13919
365	0.46%	23.79%	60.73%	15.07%	0.84%	7355	13239
369	0.40%	31.75%	61.05%	6.80%	0.79%	8009	14416
373	0.31%	31.94%	57.39%	10.36%	0.97%	7636	13745
374	0.78%	31.27%	55.69%	12.26%	1.39%	7503	13505
448	0.10%	33.34%	46.68%	19.88%	5.47%	6348	11426
485	2.11%	36.32%	48.67%	12.90%	1.66%	6646	11963
523	2.00%	35.63%	58.11%	4.26%	0.57%	7791	14029
591	0.62%	22.03%	70.98%	6.37%	0.65%	8125	14625
597	0.48%	33.49%	45.51%	20.52%	3.35%	6180	11124
655	0.92%	30.38%	53.03%	15.67%	0.54%	7219	12994

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THE SULPHUR FORMS IN CHINESE COALS

By C. H. Young

1. Introduction.
2. Description of Coals Used.
3. Methods Used.
4. Analytical Results.
5. Conclusion.
6. Bibliography.

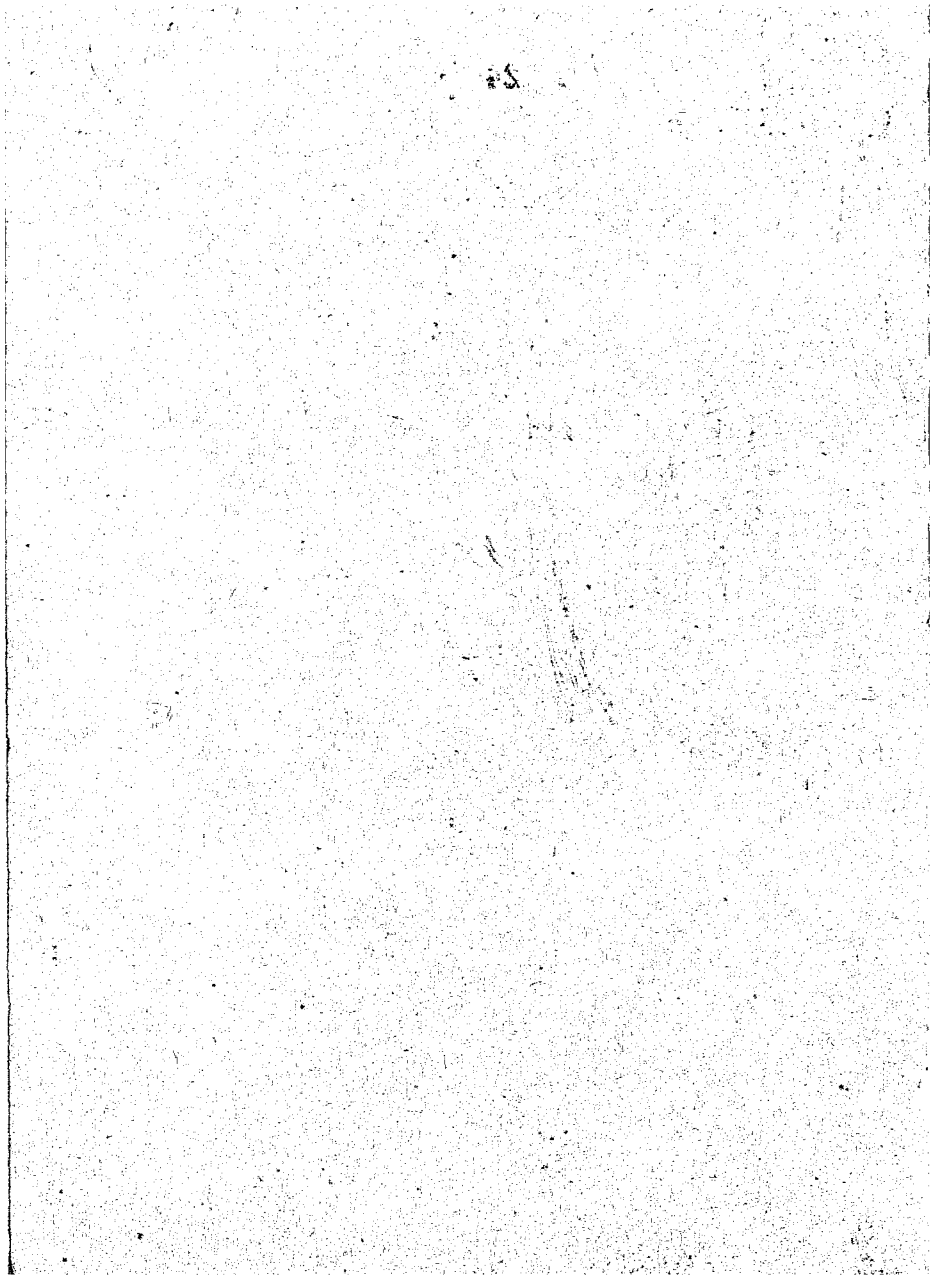
1. INTRODUCTION.

Methods for the analysis of total sulphur in coal have been in use for many years. It depends on the general principle of complete oxidation of the sulphur present in coal, followed by the gravimetrical estimation of the sulphate as barium sulphate. From technical stand-point a total sulphur determination is useful as it fixes the value of a particular coal for particular use. However in determining the value of coking coals it is usually desirable to know not only the total sulphur content, but also how the sulphur is distributed in the coal and the exact amount of each form present. Work of this kind would be useful in indicating how much of the sulphur-containing material can be removed from the coal by washing, what effect the sulphur has on the coking value of the coal, how the various sulphur forms behave during the coking processes.

Though China is well known for her enormous resources of coal, yet no work along this line has been done, consequently no data are available so far on the exact forms of the sulphur present in the Chinese coals. It is the intention of this paper to study these forms which would be useful to those who are interested in the coking coals in the country.

2. DESCRIPTION OF COALS USED

The coals analyzed were all gathered from important and working mines located at different parts of the country. With a few exceptions, they are limited to good and well-known coking coals. Their total sulphur contents vary from 0.5 to over 5 per cent. The following tables (Table 1 and Table 2) give a general description of each coal used in these experiments.



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