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Recovery of Sulfur from the Residues of the Chemical Method for the Purification of Sulfur from the Farsch Mine in the Al-Mishraq Mine

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Abstract

This research aims to recover sulfur from sulfur residues of the chemical method for purifying mine sulfur in the Al-Mishraq mine by studying and using thermal and air-thermal treatment with a temperature range of 130-190 °C and an increase of 10 degrees for each treatment. After being prepared in the sulfur residues (foam) by grinding it to 200 mesh and chemically analyzing it, we find that it contains a high percentage of elemental sulfur, amounting to 89.60% wt. As for its X-ray diffraction, it was found that the crystal structure of elemental sulfur is of an orthorhombic And after the completion of the two thermal and air-thermal treatments, then the extraction of the carbon-sulfur materials by using a 20% NaOH solution and analyzing them by FESEM, it was found that they have nanostructures and their granular size increased three times than the carbon-sulfur materials extracted from the untreated sulfur residue, and that they have a composition and crystal structure similar to graphite doped with sulfur. The industrial sulfur was filtered in a manner similar to the industrial method of sulfur production units, and 75% wt. of sulfur residues was recovered, and it was in conformity with the Iraqi standard specification 2199 of 2002.

1. Introduction

The Al-Mishraq Sulfur mine's Foam waste, which is produced by a chemical process, is distinguished by its high sulfur content of about 90%. Foam waste presents significant issues due to its accumulation and massive volumes, which surpass two million tons. Being a source of ongoing environmental contamination due to the substances it releases into the air, water, and soil [1]. The General Corporation for Sulfuric Acid established a factory for the manufacturing of concentrated sulfuric acid based on the recovery of sulfur from foam waste, which was the most significant endeavour to recover sulfur from these wast°es. Nevertheless, the project was shut down for technical reasons [1]. Laszezyus et al. [1] recovered 82% of the sulfur in the foam by heating it to 150 ℃ and then filtering. Al-Khafaji [3] employed kerosene as a solvent at a temperature of 160 ℃ to recover sulfur from the foam, and the recovery rate was 92%. Two fundamental facts determine the fundamental interactions of elemental sulfur with carbon. The first is that carbon is sp2 hybridized, or it has C=C double bonds, in its compounds like graphite, graphene, fluorine, or carbon nanotubes, and the second is that sulfur is found at 160 ℃, the eight (S_8) rings change into the linear free-radical polymer (˙S-S6-S˙) [4].

Gianfranco et al. [5] demonstrated through the transformation of graphite nano-doped with sulfur that the properties of this compound are stable, a good electrical conductor, and a high surface area. It was also demonstrated that the free-radical linear polymer can interact with the double bond C=C, forming poly sulfur bridges c-s8-c, which turn into mono sulfur C-S-C at 160 °C.

The formation of the results of the $C\text{-}S_8\text{-}C$ bridge in their breakdown, according to Yang and Wauy [6], which releases the free radical two-sulfur, which interacts with the edge of the graphite to produce C-S-C. These mono-sulfur bridges in graphite have an important role in both the mechanical and electrical properties of the resultant sulfur, which is important when using spongy graphite in electrical applications including high-capacity electrodes, battery cathodes, and electrodes for electrolytic cells.

Fan et al. [7] prepared high-quality sulfur-doped graphite by using sulfuric acid as a sulfur source using microwave irradiation in the solid state. This study's aim includes recovering sulfur from foam sulfur wastes, determining the kind of these materials, and analyzing how thermal and air-thermal treatment affected the particle size of carbo-sulfur materials.

2. Experimental Procedure

1. The Air blowing instrument of the Dawson Mc Dawson type.
2. An electrical furnace of the German (delto) type with a temperature range of up to 1100 °C.
3. The electric motor device Hamburhao Shaker Germany.
4. Mantel Heater.
5. Ae ADAM Sensitive Balance.
6. X-Ray Diffraction Device of Xpert Phillips Holland 9.
7. Eds Tescan Mira3 France Energy Dispersive Spectroscopy.
8. SEM Tescan Mira3 France 10-Electron Microscopy

2.1. Preparing the Raw Materials

The foam material was obtained from the General Company for Al-Mishraq Sulfur in the form of gray granules that were ground to 200 mesh to conduct the required chemical analyses

2.2. Analyses of Untreated and Treated Sulfur Residues Using Chemicals and Spectroscopy Methods

The sulfur residues (Foam) were grinded to a size of 200 mesh for the purpose of conducting chemical analyzes using known standard methods [8], [9] and X-ray diffraction. The carbon-sulfur materials were extracted using a 20% NaOH solution and heated to 90 °C from the untreated and treated sulfur residues using an approved method [10] For an hour, for the purpose of completing the interaction between elemental sulfur and sodium hydroxide, and after filtration, washing with distilled water, drying, and weight, its percentage was calculated, followed by conducting spectral analyzes, including XRD, FESEM, and EDS, for the extracted carbon-sulfur materials.

2.3. Thermal Treatment and Thermal Air-Thermal Treatment

100 gm of sulfur residues are taken and placed in a circular flask with a capacity of 500 ml. A temperature escalation is carried out on it from 130-190 °C with a range of 10 degrees for each treatment, for a period of one hour, followed by pouring the liquid wastes into special molds for solidification, and then preparing for the purposes of chemical and spectral analysis as in paragraphs 2-2, 2-3, 2-4, the same steps above are repeated for the air- thermal treatment, the air is passed into the sulphur waste liquid at a flow rate of 2.5 Litters/min. %

2.4. Recovery of Industrial Sulfur from Sulfur Waste (Foam) Treated Thermally and Air-Thermally

We adopted Al- Jubouri method [1] in recovering sulfur from the sulfur residues (foam), which is summarized as follows. Tonsil is added to the filtered sulfur molten to 140 °C, mixes well, and is passed through a metal filtration device consisting of an outer tube containing oil and heated externally to provide the appropriate temperature for the continuation of the filtration process, and an inner tube ending at the bottom with a metal net and connected from the top with a metal tube connected to an air compressor that applies pressure 4 kg/cm^2 on the surface of sulfur to speed up the filtration process, and at the end of the filtration, the filter aid is prepared. After that, the molten sulfur waste treated thermally and pneumatically is passed through the metal filter to start filtration process. As the industrial sulfur passes, solidified and chemical tests are conducted on it according to the Iraqi standard specification 2199 for the year 2002 [11] and isolate Cake layer from above the metal filter and analyze it chemically.

3. Results and Discussion

Tables The solid waste produced as a by-product of human and industrial activity is a sort of pollution, which has been made worse by the expansion of industrial progress and the continual rise in the global population [12]. Given that it is a combustible substance and exists in such large amount, it is one of the insurmountable issues for the administration of the many sulfur industries and is located 45 km south of the city of Mosul. Due to the large-scale discharge of poisonous sulfur fumes, the extinguishing efforts took many days [13]. This study sought to conduct a thorough investigation of the foam-like by-products of the chemical process used to purify mined sulfur.

3.1. Chemical Analysis of Foam

Finding the best method to extract sulfur from sulphurous foamy wastes is made simpler for us when we accurately understand their makeup. Table (1) indicates the essential components of foam material.

Table (1). Components of foam residues.

Items	Parameters	%wt.
1	Free Sulfur	89.60
2	Bonded sulfur	0.574
3	Carbon	1.640
4	Ash	0.369
5	Acidity	1.377
6	Moisture	6.44

We note from the table that despite the high percentage of elemental sulfur, which is 89.60%, attempts to recover sulfur met with limited success and faced great difficulties, especially the Japanese method that was applied industrially and then stopped until now. Foam is used as a raw material in another industry, which we observe is using undesirable elements that harm catalysts and equipment. Ash is an inorganic non-combustible material whose source is Celite used in the sulfur purification process, and these materials are divided into two categories: solid and liquid. Solid materials include carbo-sulfur materials, which are composed of carbon and sulfur with a chemical bond, and liquid materials include acidity, moisture, and the source of acidity is concentrated sulfuric acid that used for the oxidation of bituminous materials accompanying mine Frasch sulfur. The source of moisture is from the water stream used to push foam to its gathering areas and weather conditions such as rain [14], so this must be treated materials for obtaining refined sulfur suitable for industrial use.

3.2. X-Ray Diffraction of Sulfurous Residues (Foam)

Show the X-ray diffraction pattern of sulfurous foam residues shown in Figure (1), the presence of more than 30 peaks corresponding to the X-ray diffraction pattern of rhombic sulfur (orthorhombic sulfur), and Table (2) shows the most important values obtained.

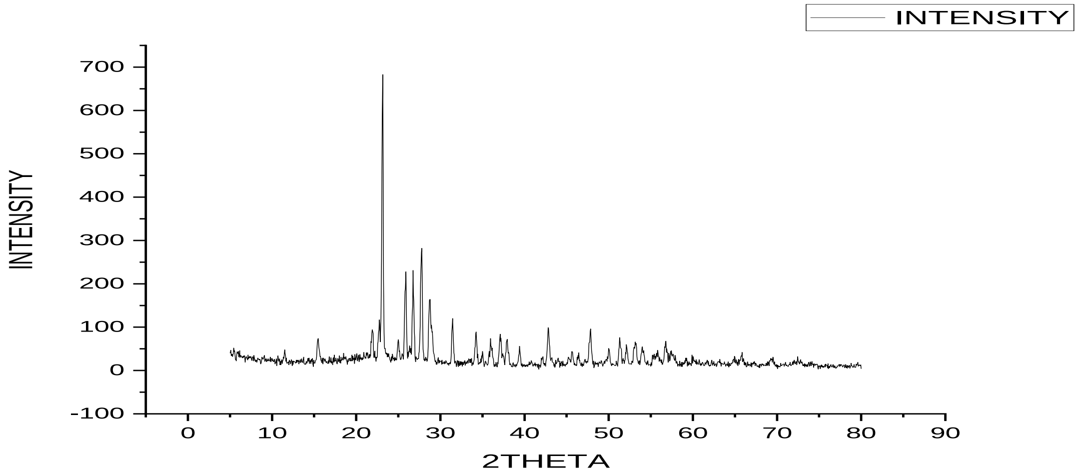

Figure (1). X-ray diffraction pattern of sulfur residue (foam).

Table (2). 2ϴ, interfacial distance d, the intensity I, and Miller coefficients nkl for foam sulfur residues.

Item	2ϴ	d	I%	n k l
1	11.509	7.6826	5.1	111
2	15.489	5.7161	9	022
3	21.908	4.0536	10.8	220
4	23.138	3.8409	100	220
5	25.883	3.4394	29.7	026
6	26.757	3.5391	29.8	311
7	27.781	3.2086	38.3	117
8	28.786	3.0989	21.8	313
9	42.811	2.1407	13.7	062
10	47.842	1.8997	13.3	428

After doing an electronic matching of the obtained results and previously stored standard values from approved literature [15], it was found, as mentioned above, that the type of free sulfur present in the foam sulfur residues is orthorhombic sulfur.

3.3. Scanning Electron Microscopy Study of Carbons Extracted from Foam

In order to complete the picture of the components of the sulfur foam residue, the carbon-sulfur materials resulting from the oxidation of bituminous materials were studied by sulfuric acid. The captured image showed that these materials are found in a spherical form grouped together with a granular size, as shown in Figure (2).

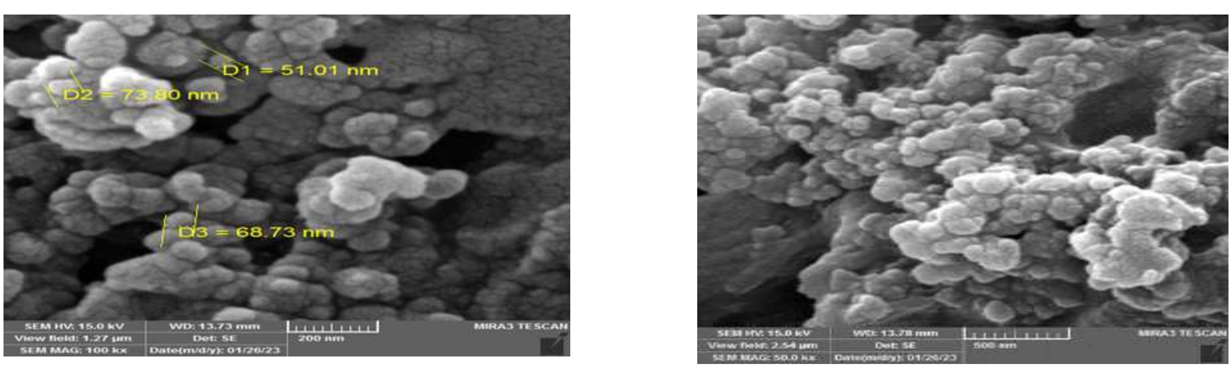

Figure (2). Scanning electron microscopy (SEM) analysis of the carbo-sulfur materials extracted from foam.

3.4. X-ray Energy Dispersive Spectroscopy of the Elemental Composition of Carbo-sulfur Compounds Isolated from Foam

According to EDS spectroscopy, the carbo-sulfur compounds are mostly composed of carbon, sulfur, and oxygen, with minor quantities of calcium and magnesium. It is associated with mining sulfur that is recovered using the Frasch process and is found as the mineral dolomite, which has the chemical formula $CaMg(CO_3)_2$ [16] and is depicted in Figure (3).

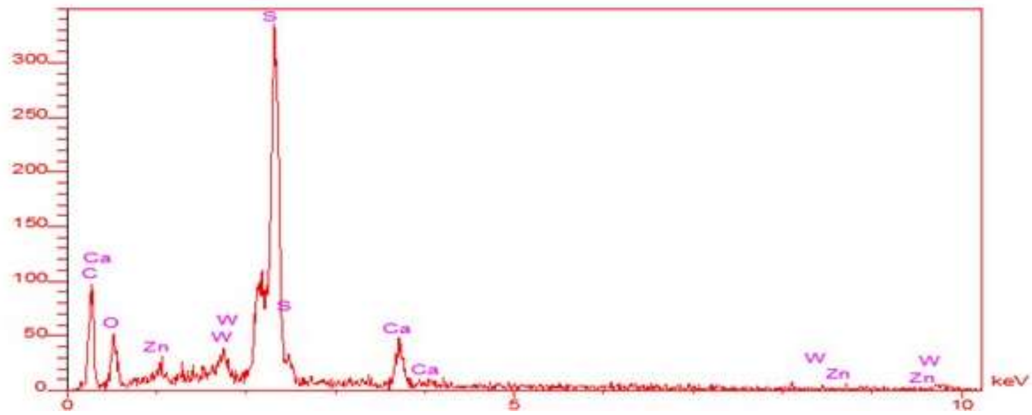

Figure (3). The energy spectrum of the dispersive X-rays (EDS) of carbo-sulfur materials extracted from foam.

The components of the carbo-sulfur materials in the foam were identified using EDS spectroscopy, and the results are shown in Table (3).

Table (3). The basic elements of sulfur-carbon materials extracted from foam.

Item	Element	%wt.
1	Carbon	40.54
2	Sulfur	14.07
3	Oxygen	22.97
4	Calcium	3.12
5	Magnesium	1.03
6	Aluminum	1.80

The empirical formula for the carbon-sulfur components of the foam, which is $C_{15}S_2O_6$, was inferred from the table. The extracted carbon-sulfur compounds show evidence of bound sulfur, which validates the chemical analysis of foam. Despite the presence of celite, which is composed of 97% silicon oxide, SiO_2, silica's interaction with sodium hydroxide results in the creation of sodium silica, which is why we could not detect (Si) in the composition of the sulfur-carbon components of the foam [17]

$$SiO_2 + 2\ NaOH \longrightarrow Na_2SiO_3 + H_2O$$

According to the above, a treatment that increases the volume of carbon-sulfur materials must be carried out.

3.5. Thermal Treatment and Air-Thermal Treatment of Foam

The thermal treatment of the sulfur residues was carried out at different temperatures from 130-190 °C in a temperature range of 10 degrees for each treatment. Carbon-sulfur materials were extracted using a 20% sodium hydroxide solution, as it reacts with sulfur and silica, leaving the carbon-sulfur materials as in the equation [18].

$$2NaOH + X\ S_{(Foam)} \longrightarrow Na_2S_x + H_2O$$

Table (4) shows the percentage of the extracted carbon-sulfur materials. The table shows that the proportion of carbonaceous materials increases as temperature increases, indicating that reactions between carbonaceous materials and sulfur occur. These interactions result in The foam also being treated by air-thermal treatment by pumping air continuously into the molten sulfur during the heat treatment. Table (5) shows the percentage of carbon-sulfur materials extracted by NaOH.

Table (4) Percentage of carbon-sulfur materials for heat treatment extracted by 20% NaOH solution.

Item	Temp-range °C	% carbon-sulfur materials
1	Foam	1.40
2	130-140	1.486
3	140-150	2.989
4	150-160	2.817
5	160-170	2.92
6	170-180	2.64
7	180-190	2.62

Table (5). Percentage of carbonaceous materials for air-thermal treatment extracted by 20% NaOH solution.

Item	Temp-range °C	% Carbon-Sulfur materials
1	130-140	2.474
2	140-150	2.372
3	150-160	2.566
4	160-170	3.896
5	170-180	3.742
6	180-190	5.111

We notice from Table (5) in the range (130-160 °C) that there is a gradual increase in the percentage of the extracted carbon-sulfur materials, as there are air oxidation reactions and sulfurization reactions that occur for the carbon-sulfur materials present in the foam, and that sulfur in this temperature range is present in the form of eight rings. While in the temperature range is 160-190 °C, we notice a sudden increase in the percentage of carbon-sulfur materials as a result of the opening of the eight rings and the formation of polymeric sulfur, a free radical, which is characterized by its very effective interaction. Figure (4) shows the transitions that occur for sulfur [19].

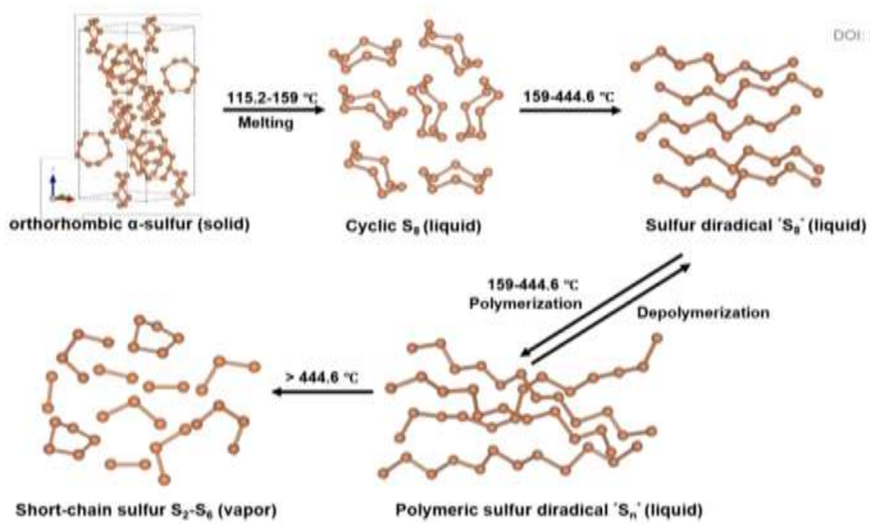

Figure (4). Structural transitions of elemental sulfur at different temperatures.

3.6. A Scanning Electron Microscope Study of the Carbon-Sulfur Materials for the Two Treatments

To find out the changes that occurred in the morphology and granular size of the carbon-sulfur materials, the samples were studied by a scanning electron microscope, and the captured images showed the heat treatment samples and for all thermal ranges, in general, they have spherical shapes gathered on each other with a size of (47.52-106.72) nm. This shows The effect of heat treatment is negligible in relation to the particle size. Figure (5) shows some images of heat treatment.

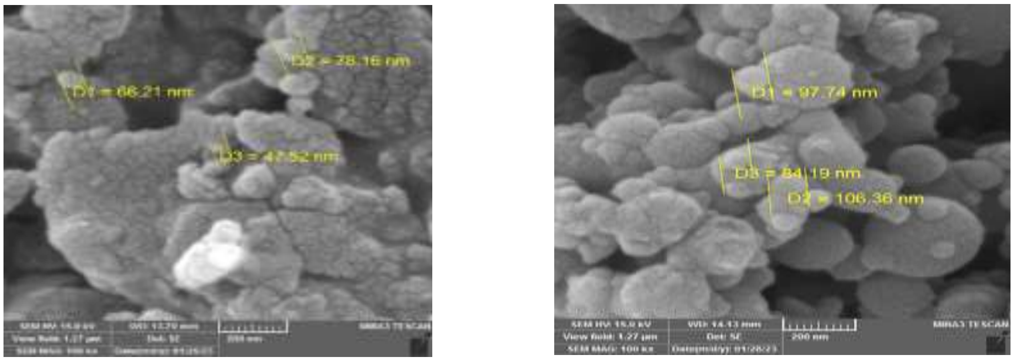

Figure (5). Scanning electron microscope analysis of heat treatment carbon-sulfur samples extracted by NaOH solution.

According to the air-thermal treatment images, all samples are observed in spherical sizes and are piled on top of one another with granular sizes of (55.78-213.69) nm. The following filtration procedure, which separates contaminants from elemental sulfur, is more effective as a result of the larger granules and their departure from the nanoscale description. The samples of carbon-sulfur for air-thermal treatment that were extracted using a 20% NaOH solution are shown in Figure (6) as SEM images.

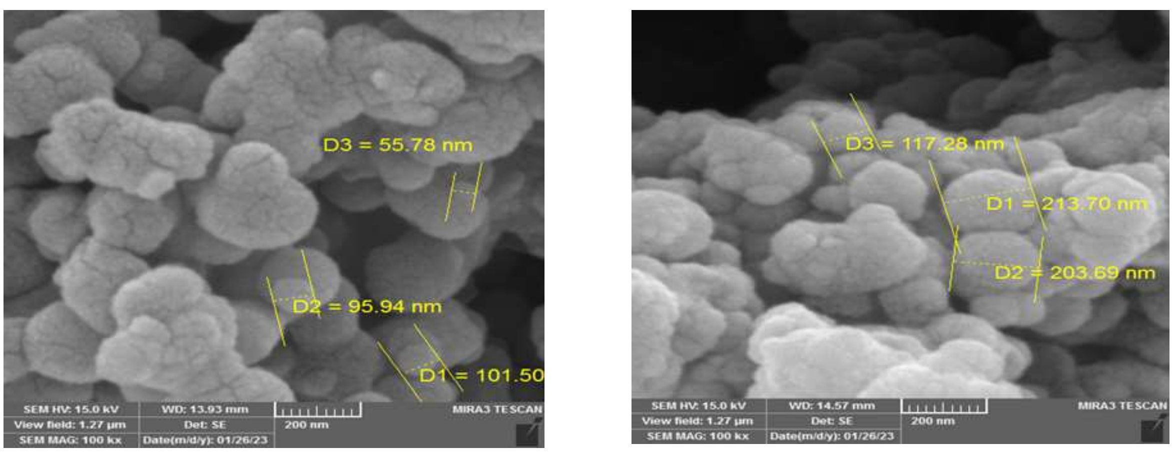

Figure (6). Scanning electron microscope analysis of carbon-sulfur samples for air-thermal treatment extracted by NaOH solution.

3.7. Studying the Elemental Composition of the Carbon-sulfur Materials of the Two Treatments by X-ray Energy Spectroscopy (EDS)

The elemental composition of the two treatments' carbon-sulfur materials was investigated, and it was evident from the EDS spectrum and for all samples that they are mostly composed of carbon, sulfur, and oxygen, with only trace amounts of magnesium and calcium, as shown in Table (6).

Table (6). Percentage of Composition of carbon-sulfur material for the two treatments.

Item	Temp-range	Thermal Treatment			Air- Thermal Treatment		
		%C	%S	%O	%C	%S	%O
1	130-140	48.34	18.17	22.31	40.28	20.32	16.57
2	140-150	43.34	18.63	22.71	40.34	20.81	15.59
3	150-160	40.37	16.21	28.76	45.30	26.61	21.22
4	160-170	43.26	15.62	22.03	43.92	23.79	12.64
5	170-180	50.31	17.64	23.16	45.05	29.90	13.63
6	180-190	39.26	22.04	12.16	46.80	28.94	14.72

As shown in the table, interactions between sulfur and carbon play a role in the development of mature carsul, whereas immature carsul is produced under the circumstances of the Frasch process to extract sulfur from molten sulfur [20]. By introducing sulfur and oxygen hybrid atoms into the composition of these compounds in one way or another, these reactions, particularly the air-thermal treatment, cause an increase in the polarity of the system, which results in an increase in the granular size of the carbon-sulfur compounds.

3.8. Study of X-ray diffraction of sulfur-carbon materials resulting from the two treatments with a temperature range of 160-170 °C.

The composition of carbon-sulfur compounds was studied by X-ray diffraction for the thermal and air-thermal treatment samples with a temperature range of 160-170 °C and as shown in the two Figures (7 & 8).

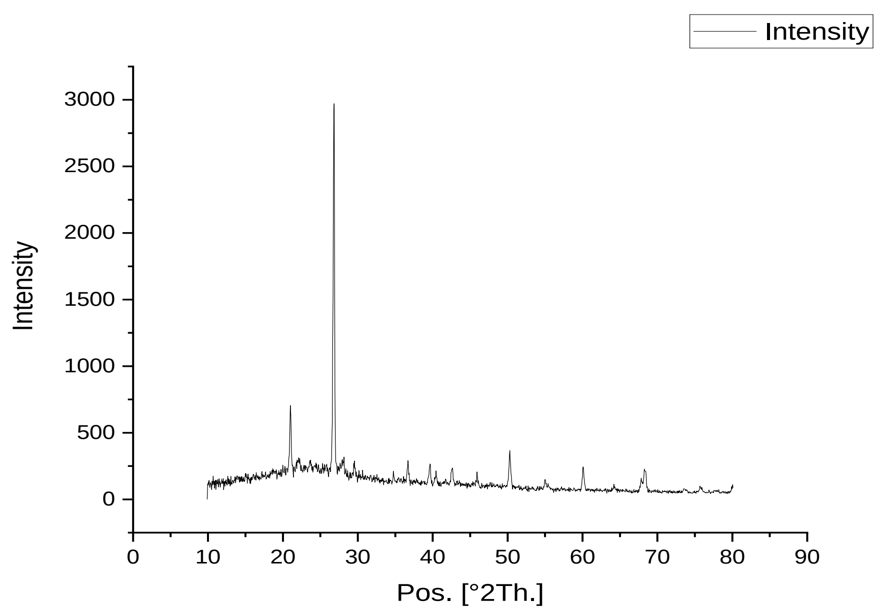

Figure (7). X-ray diffraction pattern of carbon-sulfur compounds heat treated at 160-170 °C.

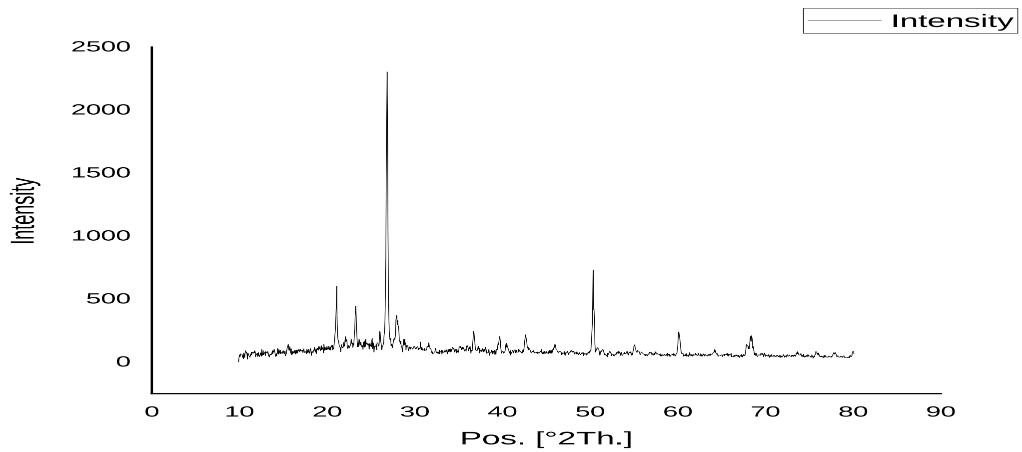

Figure (8). X-ray diffraction pattern of carbon-sulfur compounds air-thermal heat treated at 160-170 ℃.

We can observe from the two figures that the diffraction patterns of the two samples are similar, with the -air thermally treated sample having a sharper pattern than the thermally treated one. Table (7) shows the most important obtained values.

Table (7). Values of 2Ө, interfacial distance, and intensity for carbon-sulfur samples extracted by sodium hydroxide solution resulting from thermal and aerobic thermal treatment.

Item	2Ө	d-spacing	%Io
1	21.395	4.15322	5.23
2	23.2219	2.83045	14.19
3	26.7950	3.19287	100.00
4	27.0450	2.42488	29.83
5	45.9652	2.13451	4.45

The X-ray diffraction measurement instrument for the samples under research is linked to the Xpert high-score software, and after matching it with standard samples, it was discovered that they had a graphite composition identical to the graphite diffraction pattern [20]. This idea is crucial and offers up new possibilities for the usage of these substances, particularly in lithium-sulfur batteries. Li-S.

3.9. Recovery of Free Sulfur by Filtration Method Similar to Industrial Filtration

The 160-170 °C range of the 160-170 ℃ heat treatment sample was chosen for filtering because of the significant results produced by the thermal and air-thermal treatment operations. The filtration was done using a manufactured filtration device in the research lab of the General Company for Al-Mishraq Sulfur in a way that was similar to the industrial procedure that has been approved for use in sulfur purification plants. Before beginning the filtration process, a filter assist step must be carried out due to the particle nature of the carbo-sulfur compounds to boost the filtering efficiency and get pure sulfur both qualitatively and quantitatively [14]. a layer of cake that forms on the metal filter of the filtration equipment and can be used to extract carbon-sulfur compounds.

The sulfur waste (foam) was concentrated into a cake layer on the metal filter of the filtration device, from which carbon-sulfur compounds can be extracted to produce compounds with scientific and commercial value. This process recovered 75% of the elemental sulfur found in the sulfuric residues. The purified sulfur generated in accordance with Iraqi Standard Specification 2199 for the year 2002 was subjected to analysis.

Table (8). Specifications of pure sulfur resulting from the purification of the pneumatically and thermally treated sample with a range of 160 – 170 °C.

Element %wt.	Pure Sulfur Air-thermal treatment	Iraqi Standard 2199
Sulfur	99.87	99.6 % min
Carbon	0.063	0.08 % max
Ash	0.007	0.08 % max

The purity of sulfur is one of the most crucial specifications set by consuming industries, and the bituminous impurity is one of the most significant impurities affecting the purity of sulfur, which must be taken into consideration due to its impact on the equipment as the carbon-sulfur materials. We note from the above table that the filtered sulfur complies with the Iraqi standard 2199 of 2009, which is one of the most important specifications determined by the consuming industries. It coats the surfaces of burning machinery, lowering its efficiency and necessitating continuous cleaning. Together with carbon dioxide and water, the byproducts of their combustion include sulfur trioxide and water, both of which inhibit the ability of sulfuric acid, a component of sulfuric acid, to corrode metals. As for ash, it is the residue of [9] burned sulfur and is an inorganic material that is not combustible. Ash deposition and accumulation in sulfur refineries reduce the efficiency of the process, thus it is required to halt production to complete the ash removal procedure.

4. Conclusions

A significant amount of the elemental sulfur in the sulfur waste (foam) has a rhombic crystal shape. The carbo-sulfur compounds in the foam have the size of nanoparticles. The carbon-sulfur compounds' particle size is increased by the thermal and air-thermal treatment. The carbon-sulfur compounds resemble sulphated graphite in composition and are crystalline in form. The possibility of filtering sulfur residues and obtaining pure sulfur that conforms to the Iraqi standard 2199. [17]

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