Concentration and study of the carbon-sulfur residues resulting from the thermal purification of Fracsh sulfur in the Al-Mishraq sulfur mine

Sulav S. Shareef [1], Thaeir A. H. [2] and Mote`a O. A. [3]
1,2 Department of Chemistry, collage of education for girl, University of Mosul, Mosul, Iraq
3* Mishraq Sulfur State Company, Mosul, Iraq
shareefsulav@gmail.com, Thaer.abed@uomosul.edu.iq, alojmaniojmani@gmail.com

Abstract
This research included a study of the well-known sulfur residues Blow Down to determine its exact composition, as the percentage of elemental sulfur reached 81.04 % wt., and the carbon-sulfur compounds 18.21 % wt. consisting primarily of carbon and sulfur bonded chemically. Both thermal and air-thermal treatments for the waste were then carried out with a temperature range. (130-190)°C it was observed that carbon-sulfur materials increased during heat treatment and increased before decreasing during air-thermal treatment due to the interaction of oxygen and carbon . SEM analysis revealed that they are particle formations with nanoscale sizes that are grouped in semi-spherical shapes in which the case of air-thermal treatment saw a modest increase. By using semi-industrial filtration to concentrate the sulfur residue, and its weighted percentage was 42 %wt. , and the weighted percentage of separated elemental sulfur was 58 % wt. its purity is 99.48 % wt .

Keywords: Mishraq, sulfur residue, carbon-sulfur,

1-Introduction

Al-Mishraq field is located in northern Iraq, about 320 km north of the capital, Baghdad, and 45 km south of the city of Mosul. Geological investigations have shown that this field is rich in sulfur deposits and closed to bitumen deposits, which negatively affected the quality of the extracted sulfur as a result of the presence of bituminous materials accompanying mine sulfur [1].

It was employed at the start of production in 1971 for the chemical method of carbonizing bituminous materials by adding concentrated sulfuric acid, using the rights of scientific knowledge of the Polish method developed by the Polish engineer Behan Zeki and contracting with the Polish company cntrozap for the extraction, purification, and production of sulfur [2], however, due to the occurrence of economic, technical, and environmental problems in the chemical process replaced by the thermal process and using the scientific knowledge rights of the American Free port company, which is known as submerge combustion distillate, by heating sulfur to a degree of approximately 400 c [3] ,Similar to other chemical industries, the thermal process produces industrial waste that is of a carbon-sulfur type and is referred to as blow down.

In a chemical analysis Al-Jubouri [4] founded that they are made up of 20% carbonaceous material and 80% orthorhombic elemental sulfur, carbonaceous material known as carsul, in wich sulfur and carbon have chemically bonded.

Muhammad [5] used CS2, NaOH and KOH to extracted the carsul from the blowdown wastes , and studying the carsull with XRD, XRF, BET, and SEM, it was discovered that the carsul has a structure resembling sulfur-doped graphite and is made up of layers of nanoparticles with porous structures that have a surface area of (8.2 m2/g).

The hybridization of SP2 of carbon in its allotropes, such as graphite, carbon black, fluorine, and carbon nanotubes, is necessary for the formation of carbon-sulfur materials because these materials contain c=c double bonds that can interact with sulfur through polymerization and crosslinking reactions to create materials that, when hardened, are a type of three-dimensional sulfur polymer. when the interaction In between sulfur and carbon might result in bulck materials with nanostructures[6] .

Shihab et al [7] looked at the creation of carbon-sulfur compounds by the interaction of sulfur with asphalt materials and they noticed that the ratio of sulfur and carbon depends on the ratio of sulfur to the asphalt material in a temperature range of 500-1000 C and in the absence of oxygen.

Gianfranco and colleagues [8] demonstrated that the interaction between sulfur-doped graphite and carbon results in multiple bridges of the type (c-s8-c) as a result of the interaction of the two materials. These sulfur-doped graphite properties include high stability, good electrical conductivity, and a large surface area which can access numerous technical applications thanks to it.

Both Yang and Wauy [9] suggested that the c-s-c bridges were created when sulfur and carbon broke down, creating a free radical sulfur that then reacted with the edges of the graphite to create the (c-s-c) bridge, It is significant because it permits delocalization electrons to pass across the layers of graphite, making it a form of electrical conductive material.

Adjizian and others [10] found that sulfur does not intertwine with the graphite layers, but occupies the voids formed as a result of crystalline defects in the layers, forming a hexagonal symmetry structure between the layers. The presence of sulfur in these sites leads to the stability of the graphite edges.

In order to find the best techniques to concentrate the carbo-sulfur materials in the sulfur waste and separate the elemental sulfur from them, we are studying of the sulfur wastes included an extensive study of the carbo-sulfur materials by several methods.

2-Experimental

2-1: **instruments**

1- 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 m
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 Electron Microscopy

9- FT-IR Tenser 27 Germany 2003.

2-2: **Preparing the raw materials**

The blowdown material was obtained from the General Company for Al-Mishraq Sulfur in the form of black granules that were ground to 200 mesh to conduct the required chemical analyzes.

2-3: **Chemical analysis of sulfur waste**

Chemical analyses were performed according to standard methods [11,12]

2-5: **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 analyzes 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 sulfur waste liquid at a flow rate of 2.5 Liters/min. % .

2-6 Extraction of carbo-sulfur compounds

SEM, XRD, and FTIR spectral analyses were then carried out after the carbon-sulfur compounds were extracted from the treated wastes using Mohammed's method [5].

2-6 cocentrated of sulfur waste

By using the Jubouri method, the sulfur leftovers were concentrated and removed from the sulfur[13].

2-7 Sulfur separation and concentrated residues analysis

The analyses were carried out utilizing accepted standard procedures[11,12].

3- Results and discussion

Different technologies have been developed to treat pollution at various levels in response to the significant technical advancement and the damaging industrial waste it causes to the environment and society. It was decided to investigate the concentration of carbon compounds in the Al-Mishraq field since they make up a significant portion of the waste produced by the thermal process of purifying mine sulfur.

3-1 Analysis of the sulfur residues' components (Blow Down)

Standard chemical techniques were used to determine the major sulfur residue components, and the results are shown in Table 1.

Table 1. The main components of sulfur residues

Item	parameter’s	%wt.
1	Elemental Sulfur	81.04
2	Carbonas Materials	18.21
3	Ash	0.31
4	Acidity	0.001
5	Moisture	0.42

When compared to the chemical purification process, the above table shows a high percentage of carbon-sulfur compounds, 18.21%. On the other hand, elemental sulfur makes up a large portion of the mixture. Orthorhombic, it was discovered that these materials are mostly made of carbon and sulfur with chemical bonding and nanostructures after the carbon materials (CarSul) were extracted using carbon disulfide liquid [5] . Therefore, heat and air-thermal treatments must be carried out on these materials before concentration in order to concentrate them. As follow:

3-2 Treatment of sulfur leftovers by thermal and air-thermal processes

Rhombic sulfur is thermodynamically stable up to 95 °C (Tα-β) , at which point it transforms into monoclinic prismatic sulfur [14,15], which is stable until the melting point of 119 °C (Tm) . Elemental sulfur undergoes various compositional changes at various temperatures. At 159 °C , a crucial transformation takes place(Tλ) as the viscosity of sulfur increases as a result of the fission of the eight rings into two free radicals, s-s6-s [18].The carbon-sulfur materials were removed using a 20% solution of sodium hydroxide, and the sulfur residue was heated to a temperature range of (130-190) °C, with a 10 degree increase for each treatment. The results are shown in Table No. -2.

Table 2. Percentage of carbon-sulfur materials for sulfur residues thermal-treated at (130-190) °C.

Item	Temp. range °C	Carbon-Sulfur %wt.
1	Blow Down untreated	18.04
2	130 -140	18.64
3	140 –150	18.87
4	150 -160	19.51
5	160 – 170	20.22
6	170 – 180	20.77
7	180 - 190	21.17

We can see from the table that the amount of carbon-sulfure materials is steadily increasing. This is due to the interaction of sulfur with the carbon-sulfur material, and the fact that these materials are made up of numerous layers [17].

The way sulfur interacts with carbon-containing compounds is by entering the spaces between the layers and chemically connecting with carbon atoms to form three-sided structures with the adjacent layer, as seen in the image [10].

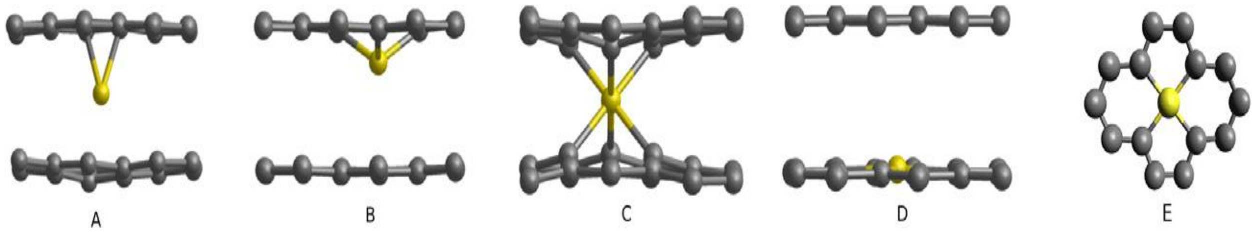

Fig.1- – Optimized structures for sulfur complexes in graphite and their point group symmetries. (A) Grafted interstitial sulfur atom, Cs. (B) Off-site substitutional sulfur atom, C3v. (C) Interplanar split-vacancy sulfur complex, D3d. (D) Coplanar splitvacancy sulfur complex, C2v. (E) As (D) but view along < 001 >.

In order to establish the ideal circumstances for the process of concentrating carbon materials, a air-thermal process at the same temperature range was also conducted, and the outcomes are shown in Table (3).

Table 3. Percentage of carbon-sulfur materials for air-thermally and thermally treated sulfur residues with a range of (130-190) C

Item	Temp.range C	Carbon – Sulfur %wt.
1	Blow Down	18.21
2	130 – 140	18.16
3	140 – 150	19.33
4	150 – 160	18.633
5	160 – 170	17.20
6	170 – 180	17.65
7	180 - 190	17.09

In the above table, we see a slight increase in the proportion of carbon-sulfur materials between (130-160) ^{o}C which is caused by the interaction of sulfur with the layers of carbon materials, as we discussed above. However, between (160-190) ^{o}C, we see a decrease in the proportion of carbon materials, which is caused by the interaction of oxygen with carbon.

4- Studying the nature of carbon-sulfur materials by scanning electron microscope

By using a scanning electron microscope to examine carbon-sulfur materials, it is possible to learn more about the changes that take place on the materials' morphology as well as their granular size.

The two processes samples were photographed and revealed to be semi-spherical bodies made of carbon-sulfur particles that had clustered together at all temperatures and at 20 nm, much like balls floating in outer space.

According to Figure 2, the granular size of the carbon-sulfur materials for heat treatment ranged from (58.22-27.64) nm.

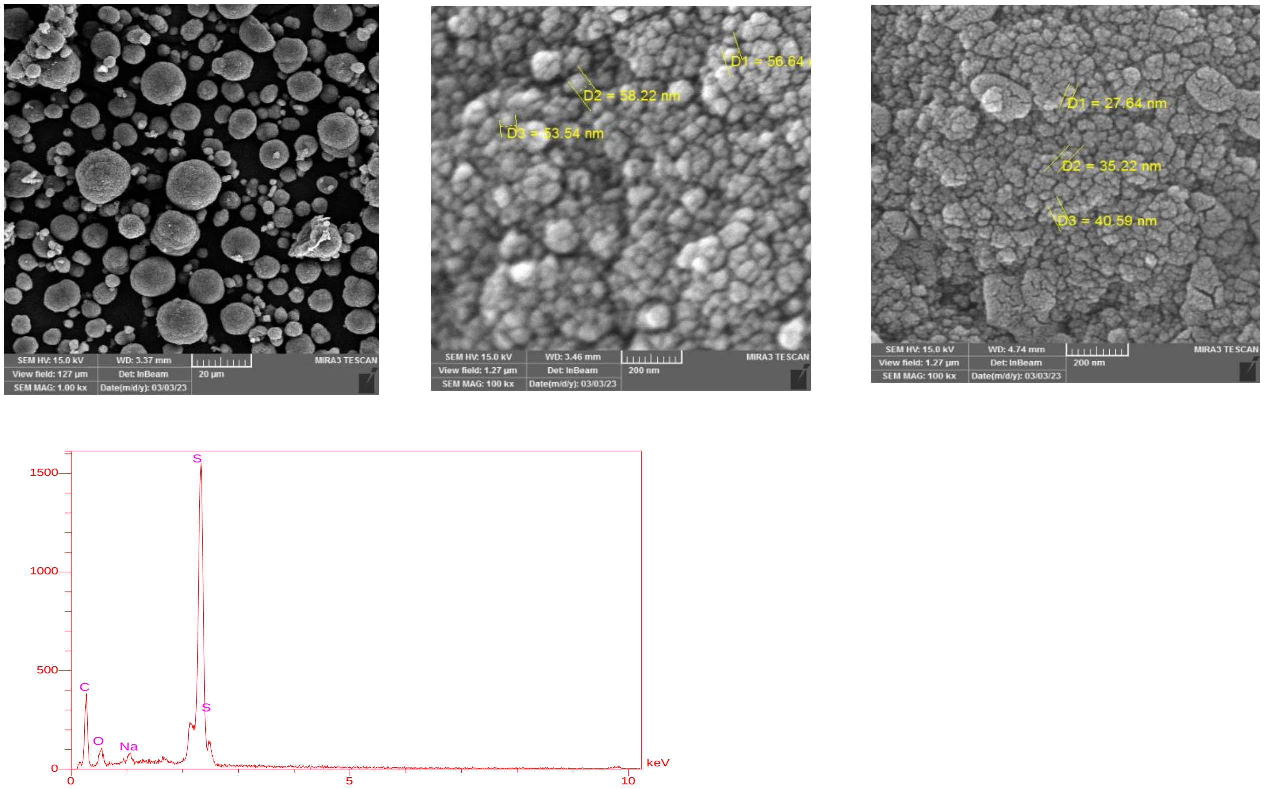

Figure -2 SEM analysis of a sample of carbon-sulfur materials taken from thermal-treated sulfur residues.

The carbon-sulfur materials produced by air-thermal
process of sulfur waste at temperatures between (130-190) C ranged in particle size from (67.38-37.75), as shown in Figure 3.

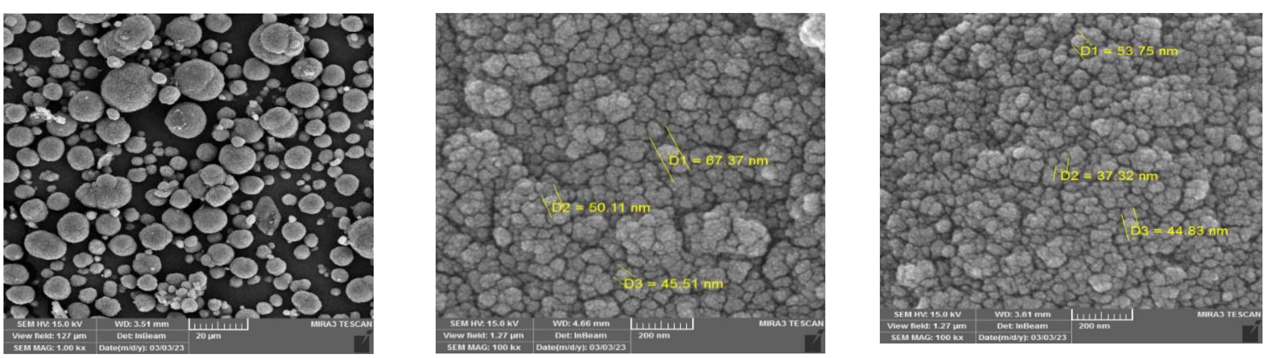

Figure -3 SEM analysis of a sample of carbon-sulfur materials taken from air-thermal-treated sulfur

The circumstances for the creation of carbon-sulfur materials during the purification of mineral sulfur by the thermal method, which reach a height of around 400 m, are to blame for the modest changes in particle size that are evident from the aforementioned.

5-3 Energy dispersive X-ray spectroscopy (EDS) study of the carbon-sulfur samples for the both treatments

All samples' energy dispersive X-ray spectroscopy spectrums showed that they are mostly composed of carbon, sulfur, and oxygen, with a minor amount of sodium, as shown in Figure -4.

a- Thermal **b- air-thermal**

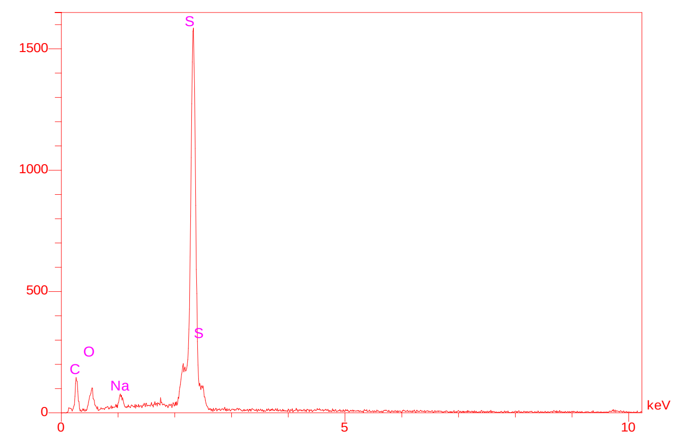

Fig.-4- eds spectroscopy of a thermal and air-thermal treated carbon-sulfur samples at a temperature of 150-160°C.

Tables -4 and 5 shows the percentage of the constituent elements of the carboxylic compounds for the both treatments.

Table 4. shows the percentage of constituent elements that compose carbon-sulfur compounds for thermal treatment

Item	Temp .range	C%	S%	O%	Na%
1	130 – 140	4.190	39.10	14.28	3.54
2	140 – 150	47.80	33.35	15.12	2.64
3	150 – 160	61.03	26.17	11.34	0.96
4	160 – 170	17.76	35.06	14.20	2.98
5	170 – 180	44.20	36.64	14.04	3.64
6	180 – 190	45.37	36.82	15.08	2.77

Table 5. shows the percentage of constituent elements that compose carbon-sulfur compounds for air-thermal treatment.

Item	Temp. range °C	C%	S%	O%	Na%
1	130 – 140	46.41	38.54	13.49	1.14
2	140 – 150	47.78	39.39	10.98	1.85
3	150 – 160	45.33	38.69	13.44	2.53
4	160 – 170	45.39	39.97	12.49	2.16
5	170 – 180	50.62	33.79	13.90	3.30
6	180 – 190	48.64	33.62	14.69	3.00

The two tables above show that, as mentioned at the beginning of the paragraph, the carbon-sulfur components of the treated samples are primarily made up of carbon, sulfur, oxygen, and a small amount of sodium. The sodium does not come from the extraction of sulfur through mining or the thermal purification of sulfur, but rather from the 20% NaOH extraction solution used to separate the carbon-sulfur materials from the treated samples. A recent study revealed the potential for employing carbon-sulfur materials (Carsul) in the adsorption of metals, particularly the hexagonal chromium ion, after one of the repeated washing processes to remove the ions in the extraction solution did not completely remove them [18] .

5-3 Study of the X-ray diffraction pattern of carboxylic compounds with a temperature range of 160-170 °C

The X-ray diffraction pattern was examined for two samples of the both treatments and in the same temperature range of 160-170C in order to determine the crystal structure of the carbon-sulfur compounds recovered from the sulfuric residues, as shown in Figures -5,6.

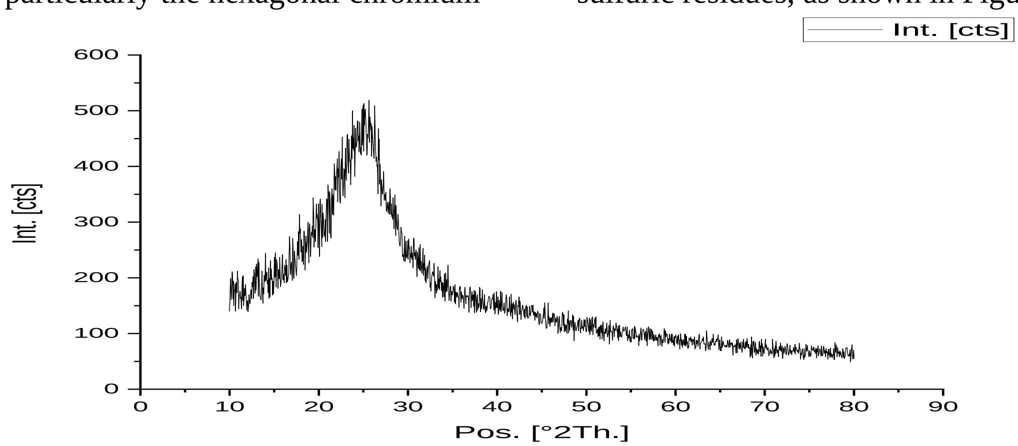

Fig. 5- X-ray diffraction pattern of the carbon-sulfur sample extracted from thermal-treated sulfur residues with a range of 160-170

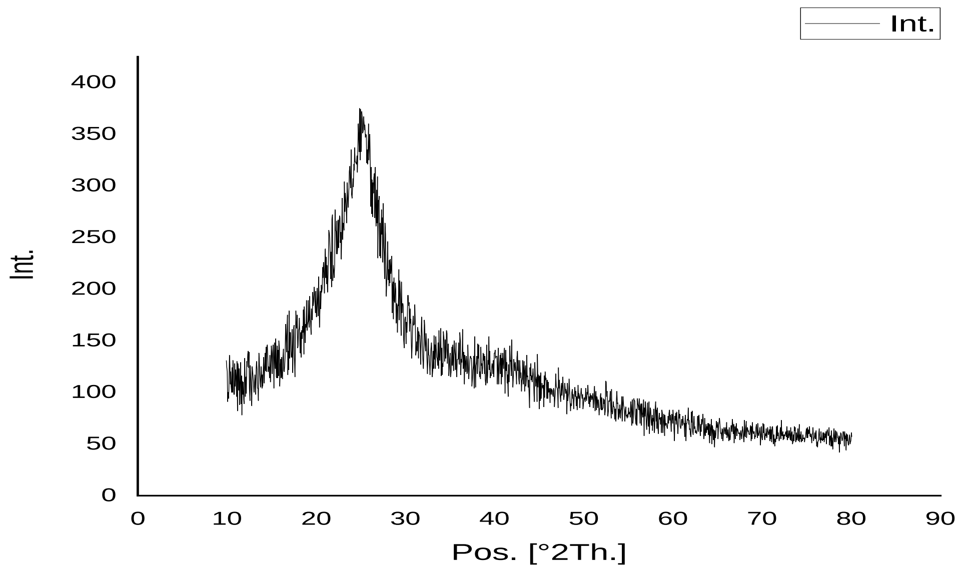

Fig. 6- X-ray diffraction pattern of the carbon-sulfur sample extracted from air-thermal treated sulfur residues with a range of 160-170

The diffraction pattern of the two samples revealed a striking resemblance between them, the presence of a mixture of crystalline and amorphous compounds, and a broad band between (2theta= 15-30) , suggesting that the carbon-sulfur materials consist of multiple layers. This is due to the reflection of (002), which is present in both samples. and a small wide band appeared at about 2theta = 42, which is caused by the reflection of (001) for carbon-sulfur materials and indicates the presence of carbon-related compounds. All these values show that the composition of carboxylic materials is very similar to that structure of graphite.

6-3 Infrared spectrum study of extracted carbo-sulfur samples at 160-170 C

At a temperature of 160–170 C, the infrared spectrum of two samples revealed a broad band at 3359 cm due to the O–H bond, two sharp and weak bands at 2850 and 2917 returning to the C–H stretch, the presence of aphatic c, and a weak band at 1474 cm due to the O–H bond. The bending of the C-H bond and its distinct and powerful band at 1032 are equivalent to the stretching of the etheric C-O bond or the stretching of the S=O bond for sulfoxides. For sulfur compounds, the 473cm band corresponds to the stretching of the S-S bond, whereas the 615cm band describes the stretching of the C-S bond. As well as in figures (7,8):

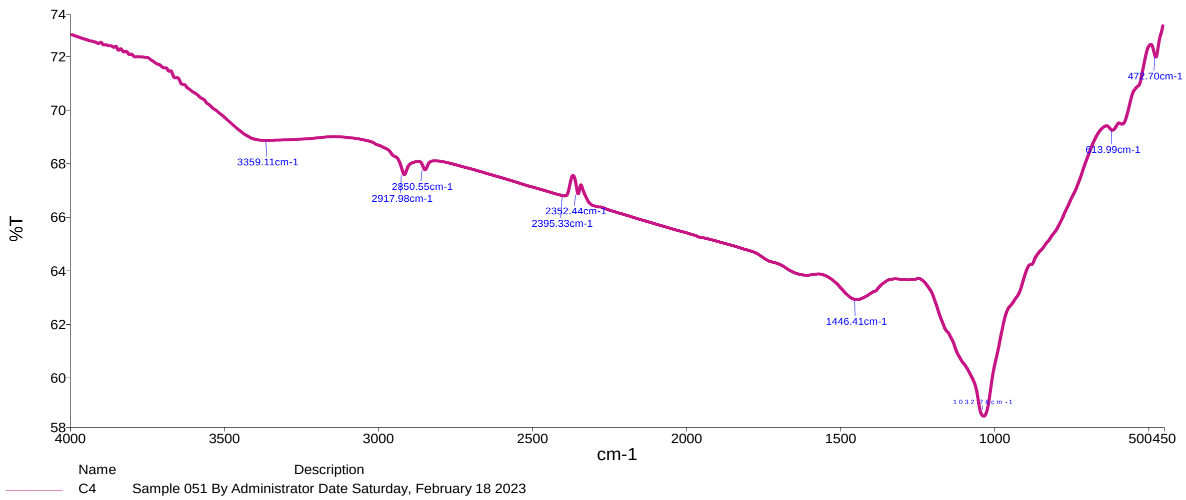

Figure -7- FTIR spectrum for carbon-sulfur materials extracted from heat-treated sulfur waste at a temperature of 160-170 °C.

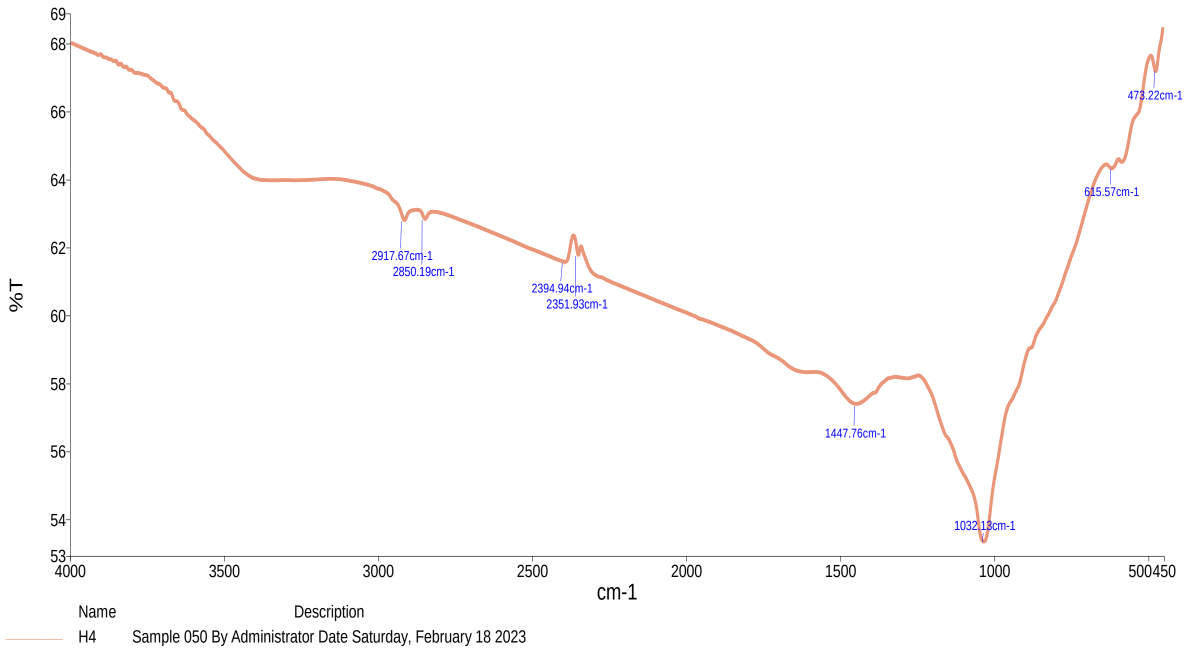

Figure -8- FTIR spectrum for carbon-sulfur materials extracted from airheat-treated sulfur waste at a temperature of 160-170 °C.

7-5 Concentration of carbo-sulfur materials and their separation from treated sulfur residues

In light of the significant and cutting-edge applications for carbo-sulfur compounds, which, among other things, offer significant opportunities for the production of lithium sulfur batteries[9], or for enhancing the rheological characteristics of asphalt [20]or as additives with other wastes in the production of activated carbon[21].

In order to utilize all the components of the BlowDown wastes and separate what can be separated from one another, we went in the direction of physical separation through a metal filtering device that simulates the commercial method of filtering industrial sulfur in the General Company for Al-Mishraq Sulfur, which has experience and long experience. Carbo-sulfur materials can be separated from the sulfuric residues in several ways, either chemically or physically. As already established, the semi-spherical, nanoscale particles that comprise up the carbon-sulfur materials were their defining characteristics. Because of this, filter aids must be utilized before filtering sulfur residues in order to create the ideal environment for the separation of the sulfur residues' constituent parts [19].

After concentrating the carbon-sulfur materials on the metal filter, a black mass that left a black trace when touched by hand and had a weight proportion of 42% of these sulfur residues was left behind. This layer was known as a cake and was the result. The details of the cake layer are shown in Table No. 5.

Table 5. Specifications of the cake layer concentrated from sulfur residues

Item	Parameter	%wt
	Elemental Sulfur	55.68
1	Bonded Sulfur	26.02
2	Carbon	17.34
3	Ash	0.54
4		

The filtered sulfur represented 58% of the filtered waste, which was separated in the form of a honey-colored liquid, and after solidification it turned yellowish-brown in color. Table - 6- Specifications of filtered sulfur.

Table 6. Specifications of filtered elemental sulfur separated from sulfur residues.

Item	Parameter	%wt
1	Sulfur	99.48
2	Carbon	0.35
3	Ash	0.17

We can see from the table that there is a slight deviation from the Iraqi standard specification 2199 [22]and this sulfur can be mixed with mine sulfur to improve the specifications of mine sulfur before performing purification operations, whether chemical or thermal, or using it in the production of concentrated sulfuric acid after making simple adjustments after burning sulfur and turning it into Sulfur dioxide gas and its entry into Cyclone rotary sorters for the production of concentrated sulfuric acid[23] Since carbon is a raw ingredient in the preparation, it may also be extracted in the production of carbon disulfide, and its presence has no effect on the product's requirements[24] .

4- conclusions

It was found by analyzing the sulfur residue left over following the thermal purification of mine sulfur in the Al-Mishraq field that they include a high proportion of elemental sulfur and a fair proportion of carbon-sulfur compounds. Their crystalline structure is similar to that of crystalline hexagonal graphite, consisting of many layers supported by sulfur atoms situated between the layers. They are semi-spherical particles of nanoscale that have in their chemical composition O-H, C-S, C-H, C-O, S=S, and S-S bonds.

By concentrating the residue components in the sulfur units and separating the elemental sulfur from them, which has numerous industrial applications, the residue components were made ready for various scientific uses.

Acknowledgment:

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References

1- Baker, J.M.; Cochran, D.E. and Semrad, R. “Economic geology of the Mishraq active sulfur deposit, northern Iraq”. Economic geology. Vol. 74, No. 2, pp. 484-495. 1979.

2-Sulphur, “Iraq Emerges as Major Sulphur Exporter, British Sulphur”, No.Ill, March/April 1974, London, p p . 36-40

3-Lipps, D.A. “Process for heat treating liquid sulfur containing carbonaceous impurities”. us. Patent: 3, 316, 563.1963.

4- 24- M. O. Al-Gobore, (1999)," Study of Sulfur Waste Obtained From Raw Sulfur Purification by Thermal Method,” Master thesis, University of Mosul - College of Education ,1999.

5- Mohammud B. K.,“ The Use of Sulfur Residues from Mishraq Sulfur as a Raw Material in the Preparation Of Nanoparticle Sulfur”. Master's thesis, University of Mosul - College of Education for Girls, 2021.

6- Ji X, Lee KT, Nazar LF: A highly ordered nanostructured carbon–Sulphur cathode for lithium–sulphur batteries. Nat Mater 2009, 8:500–506.

7- Shihab, Y.A.; Sidiq, A.A.; Tawifiqw,K.S, . “The synthesis of carbon sulfur, bulk Compounds”. Carbon, 26(6): 801-802.1988.

8- C .Gianfranco, S.N. Valentina., and N .Luigi” Graphite nanoplatelet chemical cross-linking by elemental sulfur” Nanoscale Research Letters 8:94, 2013.

9- Wang H, Yang Y: Graphene-wrapped sulfur particles as a rechargeable lithium-sulfur battery cathode material with high capacity and cycling stability. Nano Lett, 11:644–2647, 2011.

10- J.J. Adjizian , C.D. Latham , S. Oberg , P.R. Briddon d, M.I. Heggie , 'DFT study of the chemistry of sulfur in graphite, including interactions with defects, edges and folds" Carbon 63.pp 256-262. 2013.

11-M. O. Al-jubori, "Study of the purification of sulfur raw materials and its refining products and their use in the chemical industries." Ph.D. thesis, University of Mosul - College of Education ,2011.

12- Iraqi standard 1213" Insecticides sulfur and sulfur formulations".1988.

13-N. T.William, "The Sulphur Data Book" Free Port Sulphur Company. P.4.,1954.

14- Carvajal, E., P. Santiago, and D. Mendoza, Sulfur Nanowires Elaboration and Structural Characterization, in Physics of Low Dimensional Systems, K.A.P. Publishers, Editor. 2001, J. L. Morán López: New York. p. 195-201.

15- Meyer, B., Elemental Sulfur. Chemical Reviews, 1975. **76**(3): p. 367-388.

16- Scopigno, T., et al., Origin of the lambda transition in liquid sulfur. Phys Rev Lett, 2007. **99**(2): p. 025701.

17- Ramadhan, O.M. and Mote'a U.A. (2003). "Chemical nature and composition of blow down from Mishraq sulphur refinery", Natural J. of Chemistry. Vol. 9, 109-114.

18- Muhammad Muzammil Ikma, Mery Selintung, dan Rosalinda Ibrahim Pemanfaatan Limbah Carsul Sebagai Koagulan Untuk Menurunkan Konsentrasi Chrome Hexavalent Dalam Air Limbah Industri Nikel. Jurnal Ilmiah Ilmu-Ilmu Teknik Vol. 6, No. 2, September 2021

19- R. Fang, J. Xu,and D. Wang "Covalent Fixing of Sulfur in Metal-Sulfur Batteries" Energy & Environmental Science,2020.

20- A. I. Al-Hadidy Experimental Investigation on Performance of Asphalt Mixtureswith Waste Materials International Journal of Pavement Research and Technology 2023.

21- Taufiq, K.S.; Hamdon, A.A. and Thanoon, A.A., (2010). "Preparation of activated carbon by chemical treatment of spent lubricant oil with residual wastes (blow-down) of Mishraq company". National Journal of Chemistry, Vol. 39, pp. 427-434.

22 -Iraqi standard 2199" Sulphur used in industry",2002.

23- 14- D. K. Louie,: "Handbook of Sulfuric Acid Manufacturing" Canada, 1, 5-58, DKL Engineering, Inc. 2005.

24- Shereve, R.N. "Chemical Process Industries" 5th ed., McGraw Hill Book company Inc., Japan, p.1990.