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Study of Sulfur Purification from Bituminous Material in The Mishraq Sulfur Mine Using Acidic Sulfur Waste (Foam)

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Abstract: In conclusion, the sulfur wastes obtained from chemical and thermal methods for sulfur purification in the Mashreq field has been present for decades in significant quantities, approaching two million tons, with its harmful impact on the environment. Our research focused on using a different approach by utilizing the acidic sulfur wastes (foam) as a source of sulfuric acid and elemental sulfur containing bituminous materials. The goal was to make use of the sulfuric acid present in the sulfur wastes to oxidize bituminous materials. This was achieved by mixing various proportions of elemental sulfur at a temperature of 150-160 °C to achieve the best viscosity while monitoring chemical and spectroscopic changes using SEM, XRD, and FTIR devices. The aim was to eliminate the negative effects of bituminous and acidic materials and repurpose sulfur wastes, converting it into economically and scientifically valuable materials. The filtration of molten elemental sulfur from foam was conducted using a specially designed metal filter for the filtration process, along with the use of a filtration aid. This process successfully recovered 81% of the elemental sulfur, and the results met the Iraqi Standard Specification 2199.

Keywords: Wastes, Carsul, Mining sulfur, Carbosulfur.

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1. INTRODUCTION

Various methods are employed in the extraction of elemental sulfur, ranging from chemical methods using chemical substances to thermal methods using heat, or using physical methods through using clay or suitable hydrocarbon solvents Al-jubori MO (1). Jasim HS et al. (2) extracted elemental sulfur from sulfur deposits in the Mashraq mine by adding concentrated sulfuric acid within a temperature range of (130-190) °C and in the presence of air. The effect of air on the carbon particles formed due to the carbonization of organic materials by the air and sulfuric acid became evident through an increase in their size and agglomeration as a result of the increased polarity of the system. Ibrahim (3) successfully recovered sulfur from the sulfuric wastes residues left behind by the chemical method using a solvent, kerosene, with a 91%Treating molten sulfur with concentrated sulfuric acid to oxidize organic matter and then adding a type of silica earth (celite) to adsorb organic matter and facilitate separation of heavy molten sulfur from the foam layer. Alkhafaji et al. (4) employed an undisclosed hydrocarbon solvent for extracting elemental sulfur from solid sulfuric wastes residues resulting from the thermal method. Shareef et al. (5) was able to recover 75% of the elemental sulfur present in the sulfuric waste residues, known as "foam," using air-based thermal treatment within a temperature range of 130-180 °C, under industrial filtration conditions.

Patwardhan (6) was able to recover sulfur from industrial wastes rich in sulfur by raising the temperature to its boiling point and then condensing the resulting sulfur, which is characterized by high purity and direct usability for industrial and agricultural purposes. Masotta et al. (7) and others used a rotary kiln to burn the sulfur filtration residues in a concentrated sulfuric acid reactor known as "cake", which is rich in sulfur. Sulfur is burned in the range of 1100-1400 °C to obtain sulfur dioxide gas, which is used in the production of sulfuric acid. Golub et al. (8) and others recovered elemental sulfur by heating sulfur-rich residues between 120-160 °C to separate solid materials. Then, they heated the remaining substances between 450-500 °C to produce sulfur vapor, which was passed into condensers operating in the range of 120-140 °C to obtain molten sulfur. The residue left in the furnace consists of wastes materials. In our research, we used both foam-containing bituminous impurities and sulfur with organic materials in the production of sulfuric acid.

2. THE EXPERIMENTAL METHOD

1. The Air blowing instrument of the Dawson Mc Dawson type.
2. The air blowing device of the Dawson McDawson variety.
3. A German (delto) style electrical furnace that can reach temperatures of up to 1100 °C.
4. The Hamburhao Shaker Germany electric motor gadget.
5. Mantel Heater.
6. The Fifth Ae ADAM Sensitive Balance.
7. The Expert Phillips Holland X-Ray Diffraction Device 9.
8. Energy Dispersive Spectroscopy Eds Tescan Mira3 France.
9. French SEM Tescan Mira3 10. Using electron microscopy.
10. Raw materials: sulfur residues, mattress sulfur, ethanol, phenolphthalein

2.1. The Raw Materials' Preparation

Preparation of models of sulphur and sulphur residues by mixing vomit and sulfur bed ratios according to the following table.

No	%Mining Sulfur	%Foam
1	5	95
2	10	90
3	15	85
4	20	80
5	25	75
6	30	70

2.2. Oxidation Using Sulfur Residues and Air

Weigh 5 grams of powdered sulfur and 95 grams of foam. Place this mixture into a three-necked round-bottom flask. In the first neck, insert a thermometer, the second neck is connected to a condenser, and the third neck is connected to an air supply at a rate of 120 cm^3/min. Melt the sulfur at a temperature between 150 °C and 160 °C, and maintain this temperature for one hour. Monitor the temperature within the specified range. After completion, pour the resulting sample into a special mold. Repeat this process for the other proportions as specified in the table until obtaining the desired samples. After the oxidation process, perform chemical analyses on the samples, including measuring acidity, extracting organic material, and determining the carbon content. Additionally, conduct XRD (X-Ray Diffraction), SEM (Scanning Electron Microscopy), EDS (Energy-Dispersive X-Ray Spectroscopy), FTIR (Fourier Transform Infrared Spectroscopy), and mapping histogram measurements for each sample

2.3. Estimation of Acidity in Sulfur Residues and Oxidized Samples

Place 10 grams of sulfur residues, 2 mL of ethanol, and 200 mL of distilled water in a beaker. Mix the components thoroughly. Cover the beaker with a watch glass and heat it on an electric hot plate until it boils. Boil for 15 minutes. Allow it to cool to room temperature, then filter it into a 250 mL volumetric flask. Wash the residue with distilled water and complete the volume to the mark. Transfer 100 mL of the filtrate to an Erlenmeyer flask and titrate with 0.01 N sodium hydroxide using phenolphthalein as an indicator. Prepare a standard solution by dissolving 10 mL of ethanol and 90 mL of distilled water. Heat until boiling for 15 minutes, cool, and titrate with sodium hydroxide using the same indicator. Repeat the experiment for the remaining oxidized samples. Calculate the acidity based on the sulfur residues using the following equation:

$$\% \ H_2SO_4 = \frac{F\ (V - V1)}{W}$$

V = Volume of sodium hydroxide used for titrating the sample. V1 = Volume of sodium hydroxide used for the standard solution. W = Weight of the sample. F = A constant that can be determined after finding the standardized NaOH through titration with a 0.01 N HCl solution with known concentration (1).

F = N. exact × 4.9 × 2.5

2.4. To Measure the Carbon Content (Carsul) in Sulfur, Sulfur Residues, and Oxidized Samples: For Carbon Extraction from Sulfur Residues and Oxidized Samples

Place 10 grams of the sample (sulfur, sulfur residues, or oxidized samples) into a 250 mL glass flask. Add 2 mL of 96% ethanol and 25 mL of a 10% sodium hydroxide solution. Heat the mixture using a Bunsen burner to a temperature of 80-90 °C for two hours while stirring continuously. Filter the mixture through a G4-grade filter funnel. Rinse the residue several times with hot water and dry it in an oven at 80 °C for one hour. Treat the residue several times with 5 mL of carbon tetrachloride until it becomes colorless. Drip dry the organic material and dry it at 105 °C for 24 hours. Weigh the dried organic material and calculate its percentage, representing the organic material content in the oxidized samples. The remaining residue on the filter paper is dried again at 80-90 °C, collected, weighed, and its percentage calculated (9).

2.5. To Estimate the Free Sulfur Content in Mined Sulfur

Weigh 0.5 grams of finely ground sulfur and place it in a 250 mL glass flask. Add 50 mL of a 20% sodium thiosulfate solution. Attach a reflux condenser and heat for five hours while stirring. Transfer the solution to a separation funnel, allowing two layers to form (organic and water).

Separate the water layer, filter it, and transfer it to a 250 mL volumetric flask. Complete the volume with distilled water to the mark. Transfer 25 mL of the solution to an Erlenmeyer flask, add 20-30 mL of water, 1-2 drops of phenolphthalein indicator, and 5 mL of a 20% formaldehyde solution. The solution should turn gray. Leave the sample for five minutes, add acetic acid drop by drop until the gray color disappears, and titrate with 0.1N iodine solution, using starch solution as an indicator. Record the volume of iodine used in the titration and calculate the free sulfur percentage according to the given equation. Repeat the same experiment to calculate the free sulfur percentage in sulfur residues (1).

$$\textbf{Free sulfur \%} = \textbf{V.of } \mathbf{I_2} * \textbf{N.of } \mathbf{I_2} \frac{\frac{\text{Eq.wt of sulfur}}{1000} * \frac{250}{25} * 100}{Wt\ of\ sample}$$

3. RESULTS AND DISCUSSION

Considering the undesirable properties added by the bituminous materials impregnated in sulfur extracted by the Frasch method (10), such as the change in its color from yellow sulfur to dark brown sulfur, as well as their economic effects in reducing the market value of sulfur and their negative impact on reactions, various methods have been developed to eliminate these materials to obtain pure sulfur. These methods have ranged from chemical methods using oxidizing agents such as concentrated sulfuric acid and nitric acid to thermal methods, thermal oxidation methods This method is known as submerged combustion distillation The filtration unit consists of three main units: the bath burning unit, the sulfur recovery unit, and the filtration unit, and physical methods using solvents or adsorption on special carriers. In this research, sulfuric acid present in sulfur wastes (foam) was used for the purpose of oxidizing bituminous materials. The research included the following:

3.1. Study of The Composition of The Raw Materials

To monitor the changes that occur in the composition of the raw materials, represented by elemental sulfur and sulfur wastes (foam), the results recorded in Table (1).

Table 1: Main components of mining sulfur and sulfur wastes (foam).

Hem	Parometer %wt	Mine Sulfur	Sulfur Wastes (Foam)
1	Bitumenous materials	1.011	0.00
2	Carbonous materials	0.134	1.2432
3	Acidity as H_2SO_4	0.00	0.833

were obtained. From Table (1), it can be observed that elemental sulfur is characterized by a high content of bituminous materials known for their negative effects. The sulfur wastes (foam) were also characterized by its acidity as a result of the use of concentrated sulfuric acid in carbonizing and oxidizing bituminous materials (10). The above indicates the availability of suitable conditions for purifying elemental sulfur on one hand and eliminating the negative effects of both bituminous and acidic materials, as well as utilizing sulfur wastes (foam) on the other hand.

3.2. Study of Purification of Elemental Sulfur

The study of purifying elemental sulfur involved several stages as follows.

Reaction of Raw Materials at a Thermal Range of 150-160 °C To reach the minimum viscosity: Different proportions (5%, 10%, 15%, 20%, 25%, 30%) of elemental sulfur were mixed with foam and thermally treated at a temperature of 150-160 °C to maintain the viscosity within the specified limits. Changes in the carbosulfur, bituminous, and acidic materials were monitored. The results obtained are illustrated in Table (2).

Table 2: The main components of the mined sulfur mixture are foam in different proportions and heat treated with a temperature range of 150-160 °C.

No	Ratio of Mine Sulfur %	Carbon-sulfur Materials %	Acidity as H_2SO_4 %	Bitumenous Materials %
1	5	2.618	0.800	0.00
2	10	3.873	0.379	0.00
3	15	4.002	0.376	0.041
4	20	4.652	0.3675	0.024
5	25	4.996	0.316	0.025
6	30	5.249	0.235	0.012

Basic components of foam-mixed elemental sulfur at different ratios and thermally treated at a thermal range of 150-160 °C. To align the results with the required standard specifications, it is necessary for the decrease in both bituminous and acidic materials to be parallel. Therefore, different quantities of elemental sulfur were used to achieve the best conditions and results. From the table above, it can be observed that even though the percentage of bituminous materials decreased in experiments (1,2), the acidity remains high, causes a black mass that covers the equipment, and the presence of these materials causes blockage of valves and sewers and slows down the transfer of heat, which leads to corrosion of the equipment (12) which affects the quality of sulfur by impacting equipment, whether during loading or use. With an increase in the quantity of elemental sulfur, there is a presence of bituminous materials, albeit in low amounts, which can still influence the color of industrial sulfur. Despite the decrease in acidity, it did not approach the required standard specifications (Iraqi Standard Specification).

3.3. Study of Carbosulfur Materials Extracted by Sodium Hydroxide Solution

To comprehensively address the topic and propose appropriate treatments, the nature of the carbosulfur materials present in foam and the resulting reaction between sulfuric acid and bituminous materials or sulfur and bituminous materials were studied. Nature of Carbosulfur Materials of Raw Materials:

The nature of carbosulfur materials was studied using scanning electron microscopy Scanning electron Microscopy (SEM), and the images captured in sulfur wastes (foam) and elemental sulfur showed that they have nanoscale fine nature with spherical and semi-spherical shapes.

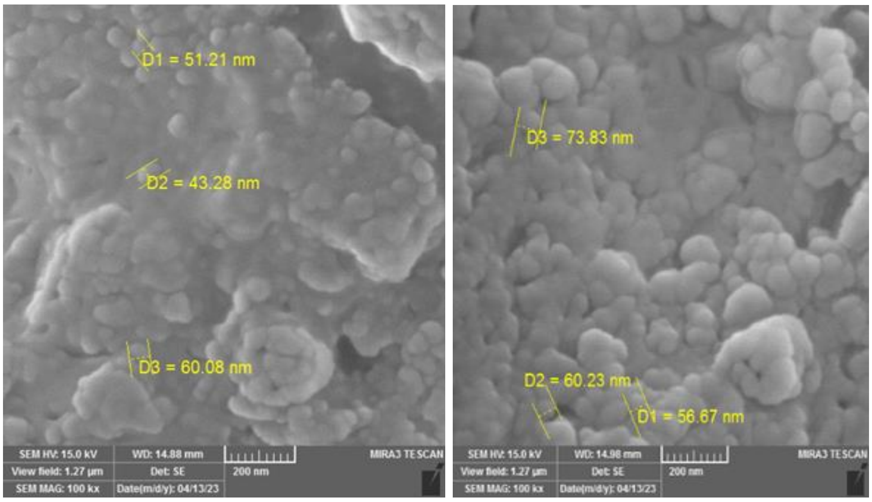

Figure 1: Scanning electron microscope (SEM) analysis of the reaction of raw materials with a temperature range of 150-160 °C in the presence of air.

The figure also indicates that the granular size of carbosulfur materials in sulfur wastes ranged from (60.08-43.28) and in elemental sulfur from (73.83-56.67). The presence of carbosulfur materials of these sizes requires special conditions for industrial sulfur filtration. X-ray Energy Dispersive Spectroscopy (EDS) study associated with SEM technology revealed the elemental arrangement of these materials. Elemental arrangement determined by (EDS) Reaction of Raw Materials at a Thermal Range of 150-160 °C in the Presence of Air: To obtain optimal conditions, the same experiments (1-2-3) were conducted in the presence of air, and the same changes were monitored.

Table 3: The main components of the mixture of mined sulfur and foam in different proportions, which are heat treated with a temperature range of 150-160 °C.

No	Ratio of Mine Sulfur%	Carbon Sulfur Materials%	Acidity %	Bitumen
1	5	3.942	0.5145	0.033
2	10	4.303	0.3185	0.028
3	15	4.948	0.3082	0.023
4	20	5.050	0.252	0.017
5	25	6.173	0.119	0.016
6	30	8.694	0.005	0.005

Illustrates the most important results obtained: Table (3): Basic components of a mixture of elemental sulfur and foam at different ratios, thermally treated at a thermal range of 150-160 °C. From the table, it can be observed that there is a parallel decrease between bituminous and acidic materials, accompanied by an increase in carbosulfur materials. The mine sulfur ratio yielded the best results, achieving two goals simultaneously: getting rid of bituminous materials in elemental sulfur and the acidity present in the foam. After obtaining positive results, before starting the filtration processes, it is essential to study the nature of the carbosulfur materials resulting from both treatments.

Table 4: Studying the nature of carboxy sulfur materials resulting from thermal and pneumatic treatment.

No	Element %wt	Mine Sulfur	Foam
1	Carbon	26.98	22.36
2	Sulfur	69.68	77.47
3	Oxygen	3.34	0.17

From the table above, it is noticeable that carbosulfur compounds primarily consist of sulfur and carbon chemically bonded (11), along with a small percentage of oxygen. One of the main objectives of purifying elemental sulfur is to separate these materials from the elemental sulfur in a suitable manner, as shown in the figure.

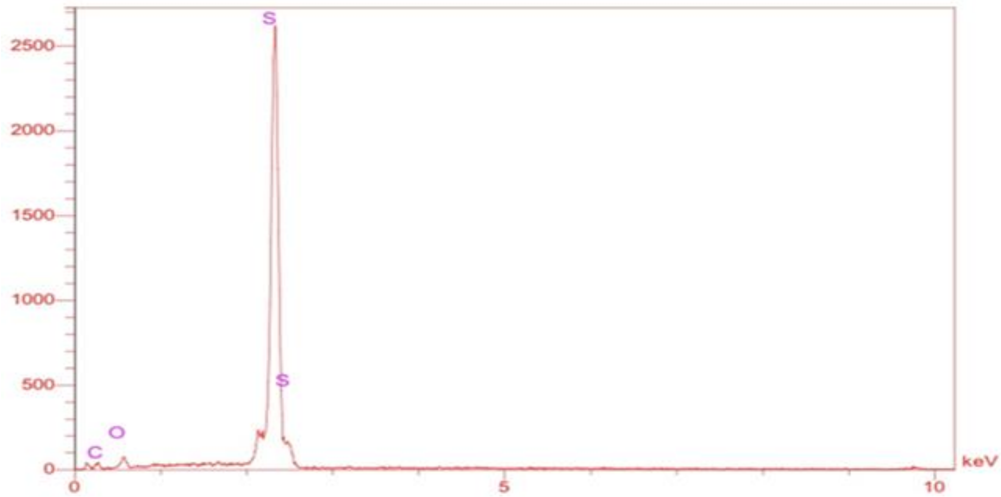

Figure 2: The X-ray power spectrum EDS for the basic components of carbs.

3.4. Study of The Nature of Carbosulfur Materials in The Thermally and Thermally-Air Treated Reaction Mixture

The percentage of the major elements in the carbosulfur materials of the mixture of elemental sulfur and foam was theoretically calculated to understand the changes resulting from the reaction conditions, we note from the table the percentages (C%. S%O%.) are not parallel due to the elements present in the device's detector and materials added to the model to increase its electrical conductivity. as shown in Table (5).

Table 5: The main components of sulfur materials for the mixture of mine sulfur and foam calculated theoretically.

% Mine Sulfur	C%	S%	O%
5	22.59	77.08	0.33
10	22.82	76.69	0.49
15	23.05	76.33	0.62
20	23.38	75.92	0.70
25	23.52	75.52	0.96
30	23.75	75.13	1.12

Major components of carbosulfur materials in the mixture of elemental sulfur and foam theoretically calculated. The carbosulfur materials resulting from the reaction between elemental sulfur and foam were separated and studied using scanning electron microscopy (SEM), as depicted in the Figure (3).

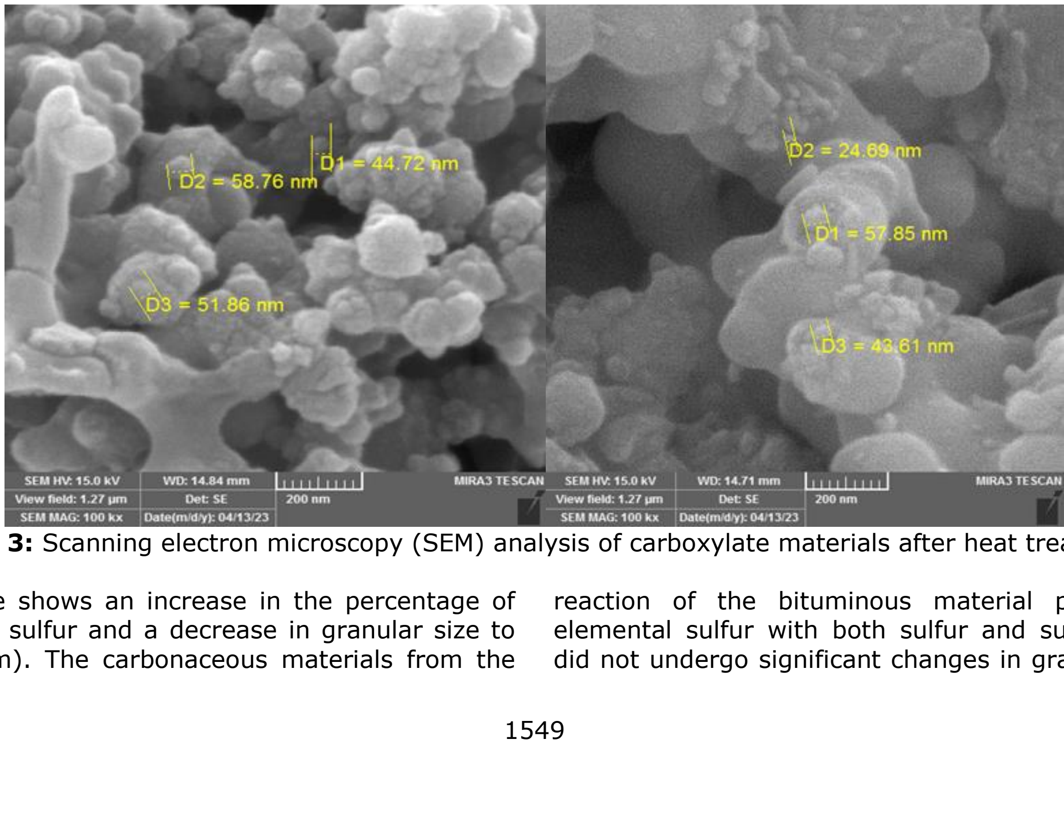

Figure 3: Scanning electron microscopy (SEM) analysis of carboxylate materials after heat treatment.

The figure shows an increase in the percentage of elemental sulfur and a decrease in granular size to (24.69 nm). The carbonaceous materials from the reaction of the bituminous material present in elemental sulfur with both sulfur and sulfuric acid did not undergo significant changes in granular size so far. In the case of thermal-air treatment, an increase in granular size was observed. This is due to an increase in the polarity of carbosulfur materials, resulting from the entry of oxygen into the structure, leading to the aggregation of molecules with each other, as shown in the Figure (4).

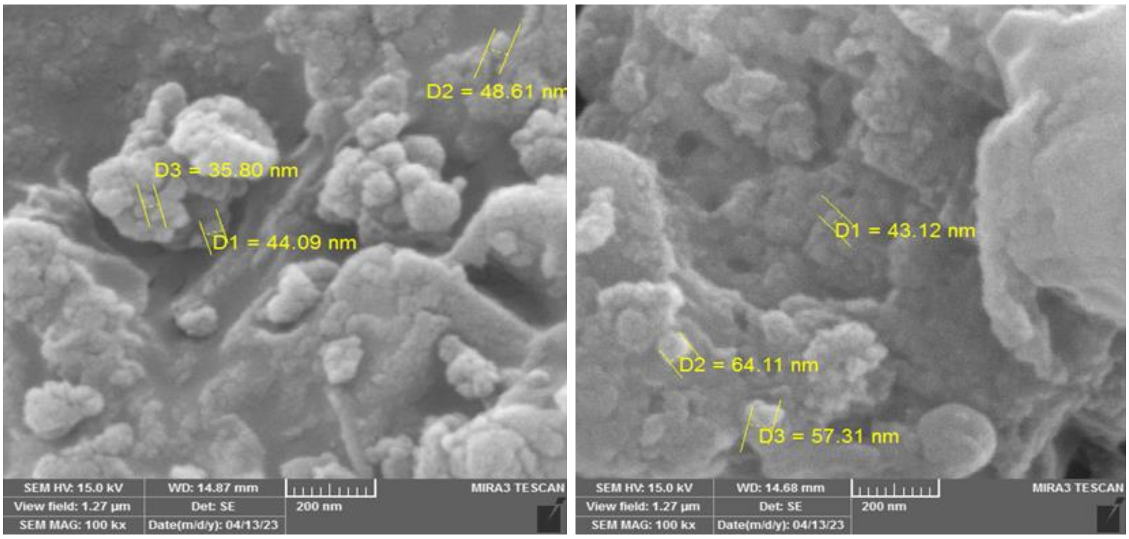

Figure 4: Scanning electron microscope (SEM) analysis of carboxylate materials after heat and air treatment.

3.5. Filtration of Molten Elemental Sulfur from Foam

The process of filtering molten sulfur differs from regular liquid filtration, requiring special conditions and equipment. To achieve this, a metal filter was used, consisting of an outer part that forms an oil bath made of carbon steel with a diameter of 3 cm and a length of 50 cm. It is externally heated and equipped with a thermostat to provide and adjust the appropriate temperature, which should be between 130-140 °C. The inner tube represents the actual filter, made of stainless steel with a diameter of 4 cm and a length of 53 cm, ending with a wire mesh made of stainless-steel grade (110*24) with a diameter of 85 microns. It is connected from above to a tube for the passage of compressed air, exerting a pressure of 4 cm3/kg on the surface of the sulfur to accelerate the filtration process. The 24/110 Stainless Steel Grade 304 Hollander Mesh offers numerous benefits for filtration applications. Its precise weave and dual wire thicknesses (0.35mm and 0.25mm) provide an excellent balance between strength and functionality, allowing for effective filtration with absolute micron retention of 110-112. Before starting the filtration process of the molten sulfur, a filtration aid, which is salt, was used to pass through the pure molten sulfur containing the filtration aid. Without this process, solid particles would quickly accumulate on the surface of the metal mesh, leading to its clogging, and the filtered sulfur would not achieve the required purity. The filtration aid is an inert material capable of forming a filtration layer, transferring the filtration process from the metal mesh to the entire mass of the filtration aid. After that, the molten sulfur was passed through for the purpose of filtration to obtain pure sulfur. Douglas managed to recover 81% of the elemental sulfur present in the fusion mixture. Table (6) shows the results obtained in comparison with the Iraqi Standard Specification 2199.

Table 6: Specifications of pure sulfur resulting from the treatment of 30% sulfur mine smelt into foam, treated pneumatically and thermally with a range of 150-160 °C.

No	Element%wt	Pure sulfur	Iraqi stardaid 2199
1	Sulfur	99.78	99.6%
2	Carbon	0.073	0.08%
3	Ash	0.006	0.08%

Table (6): Specifications of pure sulfur resulting from the treatment of a 30% mixture of elemental sulfur with foam, thermally and thermally-air treated at a range of 150-160 °C. From the table, it is evident that the filtered sulfur complies with the Iraqi Standard Specification 2199 for the year 2002. The purity of industrial sulfur is one of the most important factors determined by industries that consume it. This highlights the focus on getting rid of bituminous impurities, which are among the most significant impurities affecting sulfur purity. Bituminous materials resulting from the combustion of bituminous impurities would cover equipment surfaces, reducing their efficiency and requiring continuous cleaning. As for the sulfuric acid present, its corrosive effect on equipment is well-known.

4. CONCLUSION

Industrial sulfur has been purified, and a solution was found to eliminate critical impurities that negatively affect the quality of pure sulfur, specifically bituminous and acidic materials. These impurities were found in two different sources of elemental sulfur and elemental sulfur foam wastes. The process involved the reaction of elemental sulfur with sulfur foam wastes and a filtration procedure similar to industrial sulfur filtration, resulting in the production of pure sulfur that meets standard specifications. High-quality sulfur is produced using the Claus method and submerged combustion distillation

5. CONFLICT OF INTEREST

There is no conflict of interest.

6. REFERENCES

1. Al-jubori M. Study of the purification of sulfur raw materials and its refining products and their use in the chemical in-dustries. Doctoral dissertation, Ph. D. thesis, University of Mosul-College of Education; 2011.

2. Jasim H, halo thaer, Al jbouri M. A Study of the chemical nature of sulfur-containing rocks and Frasch sulfur in the Al-Mishraq Sulfur field. J Educ Sci [Internet]. 2021 Mar 1;30(1):1–9. Available from: <URL>.

3. Ibrahim JA. Pollution of mining industry sulfur purification plant at al mishraq. J Eng [Internet]. 2011;5(17):1159–73. Available from: <URL>.

4. Alkhafaji MW, Connan J, Engel MH, AL-Jubouri SW. Origin, biodegradation, and water washing of bitumen from the Mishraq Sulfur Mine, northern Iraq. Mar Pet Geol [Internet]. 2021 Feb;124:104786. Available from: <URL>.

5. Shareef SS, H TA, A andMotèa O. Concentration and study of the carbon-sulfur residues resulting from the thermal purification of Fracsh sulfur in the Al-Mishraq sulfur mine. J Surv Fish Sci [Internet]. 2023 May 4;10(1S):5355–67. Available from: <URL>.

6. Patwardhan A. Industrial solid waste [Internet]. NewDelhi: The Energy and Resources Institute (TERI); 2013. Available from: <URL>.

7. Masotta M, Rocchi I, Pazzagli G, D'Ambrosio R, Seggiani M. Recovery of sulfur from sulfur-rich filter cakes in a rotary kiln: Process optimization. Waste Manag [Internet]. 2021 May;126:567–77. Available from: <URL>.

8. Golub G, Subovich J, Garden O, Garden I. Recovery of sulfur from sulfur-containing waste [Internet]. United States patent US 9.216,904 B2, 2012. Available from: <URL>.

9. Mohammud B. The use of sulfur residues from mishraq sulfur as a raw material in the preparation of nanoparticle sul-fur. Master's thesis, University of Mosul-College of Education for Girls; 2021.

10. Shareef SS, Halo TA, Abdulla MO. Recovery of sulfur from the residues of the chemical method for the purification of sulfur from the farsch mine in the Al-Mishraq Mine. Iraqi J Ind Res [Internet]. 2023 Jun 14;10(1):15–25. Available from: <URL>.

11. Louie DK. Handbook of sulphuric acid manufacturin [Internet]. Ontario, Canada: DKL Engineering, Inc.; 2005. Available from: <URL>.

12. Lipps D. Process for heat-treating liquid sulfur containing carbonaceous impurities [Internet]. Vol. 316. United States patent US 3,316,063, 1967. p. 63. Available from: <URL>.