



Catalytic Purification of Sulfur from Bituminous Impurity

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Abstract

The aim of this study is to build a pilot plant system working in a continuous mode to purify sulfur from bituminous impurities. This study focused on the role of the added mineral salt of view to help choose and design the right and suitable purification reactor that is capable of overcoming any future problems and getting pure sulfur. The presence of these impurities deteriorates the specification of the produced sulfur and has to be removed from it. Two different processes were used in the mine both based on the carbonization of the bitumen (in two different ways) and then the separation of the carbonized material by filtration. Both processes suffered serious technical, ecological and economic problems. Search for another purification method that can overcome these problems continued, finally, it was possible to purify sulfur from accompanied bituminous impurities by treating raw sulfur at about (125-130 °C) with certain metal salt for 10 minutes, then subjecting the mixture to a filtration step. No hydrogen sulfide gas was detected. The reaction conditions are quite mild compared with the conditions currently used in the Mishraq sulfur mine (440-500 °C for ~ 2 hours), with a large percentage of sulfur being converted to sulfurous gases. Rather than carbonizing the bitumen, it is presumed that purification is accomplished through the formation of a complex between the hydrocarbon and the metal salt that can be deposited on the surface of the filter element. It is possible to recover the spent metal salt and reuse it again.

Keywords: Sulfur, Purification, Mineral Salts, Complex, Bituminous impurities.

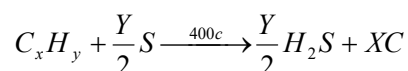
Introduction

The industry of sulfur is one of the most important extraction industries in Iraq after the oil industry. Mishraq sulfur mine is one of the biggest mines in the world with estimated reserves of about 360 million tons according to the Iraqi Ministry of Minerals and Industry. The annual production of sulfur in Iraq is approximately one million tons. Iraqi extracted sulfur from the Mishraq mine is different from other extracted crude sulfur in the world in terms that it is contaminated with about 1% [1] of heavy bituminous material which represents an obstacle toward

traditionally applied purification methods of sulfur. In the Mishraq mine [2], sulfur is extracted from underground by the Frasch process, and that causes the blending of sulfur with interfering bitumen. Consequently, the extracted crude sulfur from the Mishraq field requires the use of an unconventional purification method to get rid of the bituminous impurity. To affect efficient separation between sulfur and bitumen, all used and even proposed methods (in Mishraq), aimed to change the nature and specifications of the bituminous material in a way that

permits the isolation of this impurity efficiently. The conventional method which was applied at the beginning of the 70s of the last century (usually referred to as the Polish method) treated melted crude sulfur with concentrated sulfuric acid to oxidize and carbonize the bitumen. Then, the carbonized material was separated from sulfur after mixing with some active clays by filtration [3]. Iraq produces about 1 million ton of sulfur from the Mishraq mine located in the north near the city of Mosul. Extracted raw sulfur of this mine comes out mixed with about (0.8 - 1.0 %) of bituminous impurities [4].

Despite the capability of this process to produce sulfur with internationally accepted specifications, it suffered from high levels of corrosion in equipment and high percentages of gaseous, liquid, and solid discharged pollutants [5,6] as a result of the production process. In addition to that, the efficiency of the process was restricted to treat raw sulfur with up to 1% by wt. of bitumen as the specification of treated sulfur shows deterioration at percentages of bitumen higher than 1% by wt., on the other side, it was noticed that the percentage of bitumen in the extracted sulfur keeps increasing directly as the extraction of sulfur from the mine continues more and more. These problems were reflected strongly in the economic benefit of the whole project. The Polish unit continued its function until 1990 and stopped working due to the aforementioned problems. To avoid the previous problems, a new method was proposed at the beginning of the eighties [7,8] to set a cornerstone for a new industrial course. That method is based on the thermal treatment of crude sulfur in an air-insulated environment at 400 °C, where a portion of sulfur is reacted with the bitumen to generate H₂S and carbon according to the following equation [7]:



Pure sulfur was obtained after a filtration process to separate carbon from sulfur. Noting that, bitumen is composed of resinous and asphaltic materials of condensed aromatic structures with high molecular weight, that contained no more than 9% by wt. of hydrogen [9]. Therefore, it only requires a small portion of sulfur to carbonize according to the aforementioned reaction. This process was tested on the pilot plant level but never implemented on the industrial scale due to many reasons related to different viewpoints about the process's upper operational thermal limit and the type and quality of utilized technology.

Concerning the thermal limit, the method suggested using 400 °C and 2 hours as operational conditions to complete the carbonization reaction. While another viewpoint, based on a study by Ali et al. [10], claimed that it is possible to apply lower temperatures (280-320 °C) to minimize spent energy. The first industrial model was built by Nissan Chemicals followed by a temperature level that is approximately between (280-320 °C) with a production capacity of (1/2) ton per day. (Nissan Chemicals company report, 1986).

The only defect of this method was the fainted copper color that can be symbolized with 3A4 on the Methuen color scale[11], although the color problem can be treated by raising the treatment temperature of sulfur to 400 C° according to the first patent [7]. This fact was confirmed again by another study conducted by Aldobouni et al. [12] and Yin et al [13].which clarified the connection between the applied temperature and the remaining hydrocarbon in the crude sulfur with the quantity of liberated H₂S gas (that indicates the speed of reaction), and the resulting color. However, unfortunately, these modifications were not conducted although the reason behind building industrial pilot plants is to

carry out modifications and developments to achieve better results. Consequently, the Japanese unit failed.

Later on, another contract was made with an American company (Freeport) in 1990 to construct an integrated industrial unit. It was based on the thermal treatment of sulfur but at a higher temperature level (444.6 °C) than that proposed by Shihab et al. [7].

The American unit suffered many problems related to the adopted technology that has been used to heat sulfur. Sulfur was heated by a method called heating by submerged distillation. In this method, sulfur is subjected to the flame directly in the closed air-insulated reactor, and the quantity of fuel and air is controlled by a computer to prevent the combustion of sulfur. These problems can be summarized by the low thermal efficiency of the unit and the need for higher requirements of energy and fuel. Added to this, are the problems of the polluting and corrosive sulfurous gaseous products that require treatment to recover sulfur from them. About 30% of the sulfur feed is converted to SO₂ [14] which has to be reduced to sulfur through the Claus unit [15]. Therefore, the resulting sulfur will be obtained from two different production paths instead of obtaining it from one path. The useful life of this unit did not last long as it stopped production at the end of the nineties of the last century after a few years of construction.

After these failures, a new method of purification [16] emerged to overcome the obstacles that were the reason behind the failure of previous attempts to establish an industrial unit for purifying sulfur from the accompanying tar impurity based on the utilization of certain salts that seemed to act as

a catalyst. The method is based on treating raw sulfur with special mineral salts [18] for 10 minutes at 125-130 °C (that is approximately similar to the temperature of the extracted sulfur from the well), followed by a filtration step to obtain pure sulfur. The addition of this salt caused a noticeable decrease in the operational conditions compared with the aforementioned processes. The endorsement of the new conditions means saving a large amount of fuel required to heat and maintain the temperature of sulfur for two hours at 400 °C. Also, the shortening of reaction time to ten minutes means increasing the reactor productivity to 1200% at minimum. Unlike most catalyzed reactions, the metal salt (which is presumed to be a catalyst) was consumed in the reaction, hence it was imperative to understand how it works and affects the removal of bitumen.

This study deals with a comprehensive study for building a pilot plant system for the purification of sulfur from Bituminous impurities. The aim is to study the role of the used mineral salt in choosing the suitable purification reactor in order to overcome any future problems or obstacles during the practical industrial implementation of the method.

Materials Study area

The study area (Mishraq sulfur mine) source of this study extends from AinZala fields northwest of Mosul to Kirkuk fields, passing through the Qayarah field to the south of Mosul-Iraq, within coordinates extending West LONGITUDE=43° 17' 41.2786" W, North LATITUDE=36° 01' 33.3174" N, east LONGITUDE=43° 20' 23.1594" E, South LATITUDE=35° 58' 6.0582" S, within the coordinates extending 13.885 Km² determined by Fig. 1.

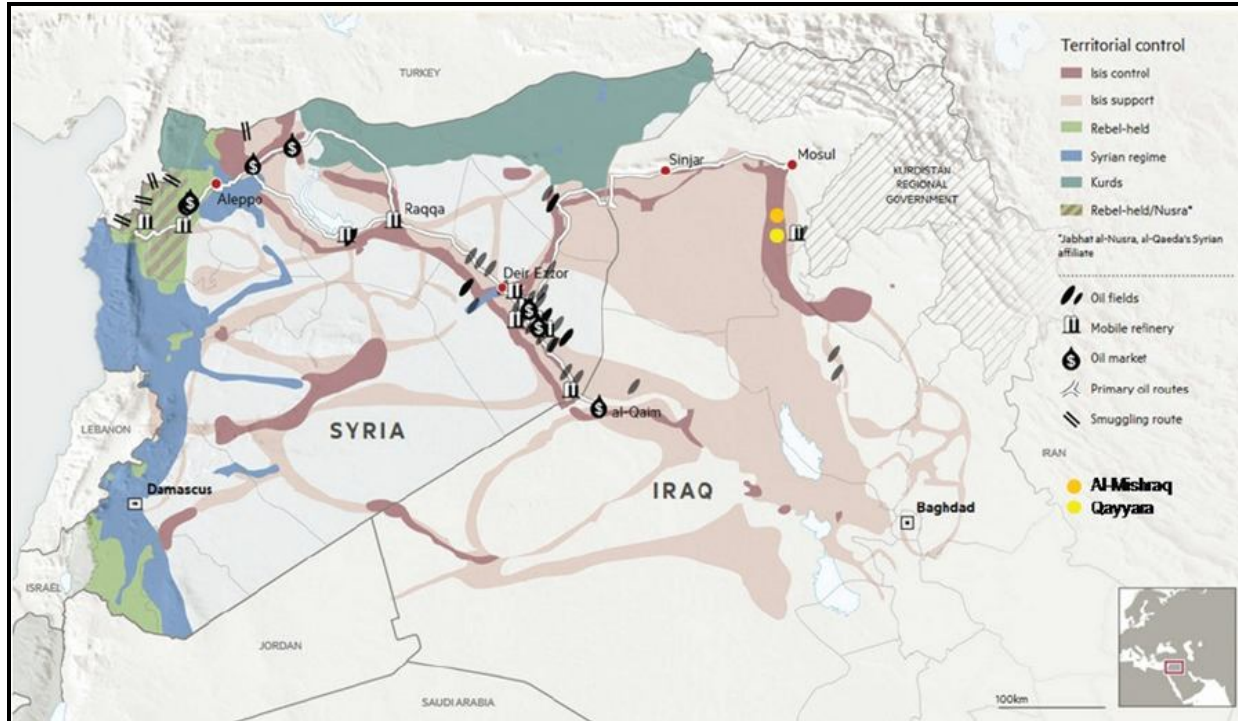


Figure 1A: Mishraq and Qayyarah fields [17]

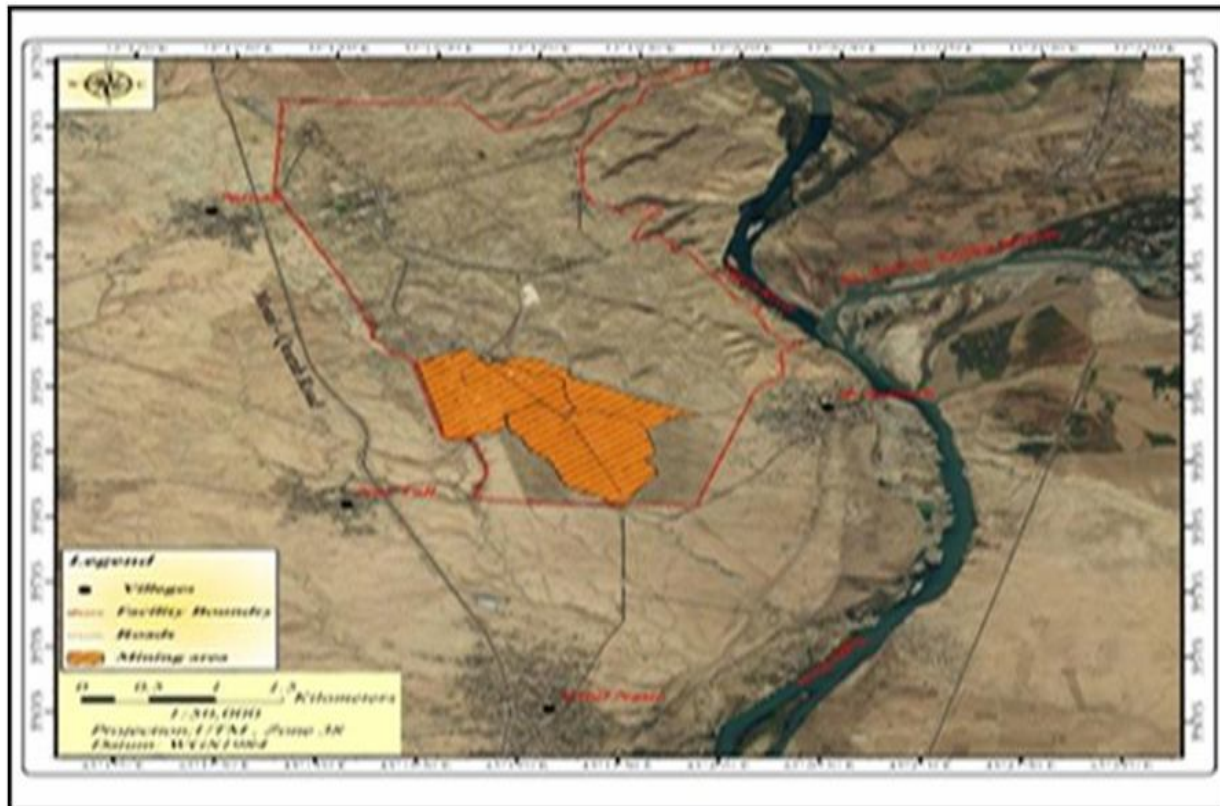


Figure 1B: GIS Study area [18]

Methods and Instruments

Analysis of a homogenized sample of raw sulfur as obtained by the existing method at the Mishraq deposit, gave the following results for its C, H, N and S contents (Table 1).

Table 1. Element analysis of raw sulfur.

Analysis of Raw Sulfur				
C%	H%	N%	S%	Ash and O ₂ by different %
1.15	0.1	0.0	97.85	1.15

100 g of Mishraq raw sulfur was mixed with a definite percentage of the mineral salt (as outlined in the results) in a suitable flask, the mixture was heated to the desired temperature with continuous stirring for a definite time then, the mixture was separated by filtration. Four variables determine the degree of purity of the resulting sulfur. These include the type and concentration of the added salt, the temperature, and the time of the treatment. To determine the optimum conditions, experiments were carried out by changing one variable and keeping the rest constant. The amount of remaining bitumen in the treated sulfur was determined preliminarily spectrophotometrically by measuring the absorbance of the samples, then the concentration was found using the calibration curve [19], using JaSCO.V630, Japan origin. This measurement was conducted at Mosul University, the color of this sample of sulfur was taken as a basis to compare the colors of other samples of treated sulfur. The hydrocarbon was also isolated from the complex by adding an organic solvent such as xylene to the complex and conducting a thermal escalation at 170 °C and then evaporating the solvent and measuring the active hydrocarbon aggregates by infrared spectrum and comparing them with the absorption spectrum of the hydrocarbon

isolated from raw sulfur using Bruker: Model: Alpha, PN:1003271, SN:102996 Germany origin. This measurement was conducted at Mosul University.

To clarify the changes resulting from the addition of the mineral salt, a scanning electron microscopy (SEM) test was conducted to know the resulting shape and morphological resulting from the ligand and complex form using TESCAN MIRA3, French origin. This measurement was conducted at Kashan University in Iran.

Relying on the foregoing data it is possible to propose a purification process for sulfur from bituminous impurities that is composed of the steps illustrated in Fig. 2.

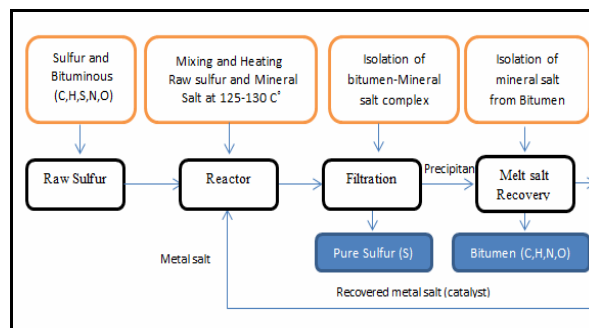


Figure 2. Flow diagram of the proposed process for the purification of sulfur from bituminous impurities

Results and Discussion

For any treatment to be recognized as a purification process for sulfur from bitumen, it requires changing the properties of one of the components of the mixture to the extent that it will be possible to permit efficient separation and isolation from each other. Also, it would be logical to focus on treating the component with a lower percentage to decrease the cost of the treatment. For this reason, bituminous impurity was the target for most of the adopted or proposed purification methods in the Mishraq sulfur mine. Accordingly, the bituminous impurity was the target of the purification method of the current study.

To clarify briefly the adopted reaction in this proposed purification method and on a laboratory scale, it is possible to obtain pure sulfur by treating crude sulfur that is contaminated with bituminous impurity (1.35% wt./wt.) with a specified percentage (3% wt./wt., w.r.t sulfur) of a metal salt at a temperature of about (125-130 °C). Fig. 3A illustrates, the dark color of raw sulfur before treatment which contains 1.35% by weight of bituminous impurity [1,4], while Fig. 3B shows the color of sulfur after the treatment, where the percentage of hydrocarbons is reduced to $\leq 0.015\%$ by weight. The great difference between the color of raw and pure sulfur enabled us to adopt the color as a rapid criterion of purity, using the Methuen color system [11].







Figure 3. Effect of the treatment on crude sulfur

It is noteworthy that the removal of bitumen was achieved by several metal salts and was not restricted to a single definite salt [20], although, the removal efficiency and the treatment conditions varied from one definite salt to another. Table 2 illustrates the color of the sulfur after being treated with four different metal salts. The salt with the best efficiency was used in the subsequent

experiments to determine the optimum conditions of the treatment.

Table 2. Color of sulfur samples purified by four different metal salts.

catalyst type	D	C	B	A
Sulfur color after catalytic treatment				
Methuen color code	2A5	2A2	4A4	2A7

On another side, it is noticed that the purity of sulfur was affected clearly by the amount of the added metal salt. The removal of bitumen was increased by increasing the amount of the added salt (Table 3). The best color was obtained at a concentration of 3% by wt. of added salt.

Table 3. Color of sulfur samples at different metal salt concentrations.





Color treated sulfur for a number of catalysts				
Metal salt Con %	0.5	1	2	3
Methuen color code	4C8	4B8	2A4	1A2

Table 4. Effect of catalyst quantity on sulfur purity.

Hydrocarbon concentration in sulfur after treatment g/g	The amount of metal salt (Catalyst) %
$0.52 * 10^{-2}$	0.5
$0.28 * 10^{-2}$	1
$0.21 * 10^{-2}$	1.5
$0.11 * 10^{-2}$	2
$0.821 * 10^{-3}$	3

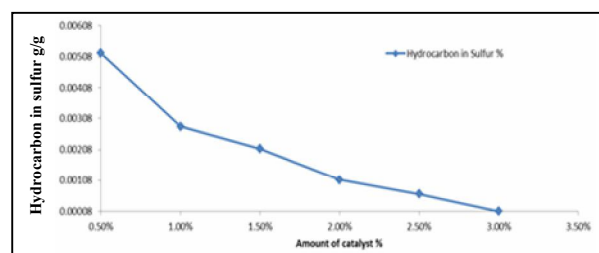


Figure 4. Relationship between the purity of sulfur and amount of catalyst at (130 °C, 5 min)

It has been observed during the many experiments that were conducted to optimize the reaction conditions that the color of the resulting sulfur begins to deteriorate gradually as the reaction temperature is raised with all other conditions kept constant (Fig. 5).

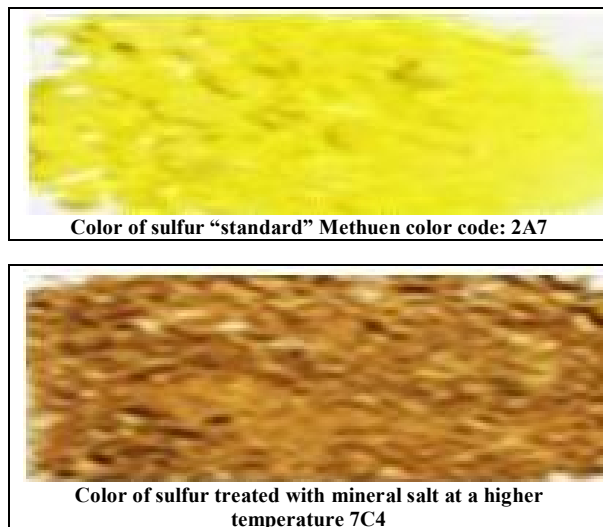


Figure 5. Effect of increasing the treatment temperature on the color of the purified sulfur, keeping all other reaction variables constant

Table 5. Effect temperature on sulfur purity.

Hydrocarbon concentration in sulfur (g)	Temperature (°C)
0.1×10^{-2}	125
0.9×10^{-2}	130
0.2×10^{-1}	140
0.4×10^{-1}	150
0.5×10^{-1}	160
0.56×10^{-1}	170

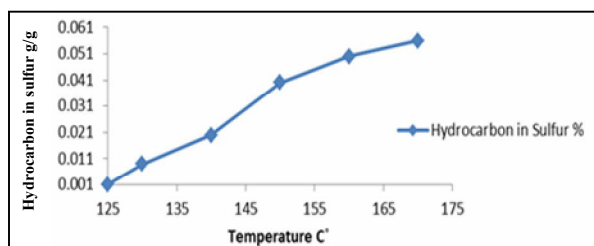


Figure 6. Relationship between the purity of sulfur and temperature at 3% (wt./wt.) catalyst, 5 min

This result attracted our attention, as it is generally supposed that rising the

temperature leads to an increase in the speed of the dehydrogenation reaction and, accordingly, an increase in the rate of formation of hydrogen sulfide gas [21, 22] which means better and more complete carbonization of bitumen which leads to the sulfur of higher purity, but the result was the opposite and the color of sulfur deteriorated greatly indicating incomplete purification and persistence of some traces of bitumen in sulfur.

To confirm this observation, the amount of liberated hydrogen gas at reaction temperature was measured and found to be insignificant and within ($\sim 3.7 \times 10^{-3} \text{ g.L}^{-1}$), [23] which is very close to the amount of hydrogen sulfide liberated at 130 °C and by the influence of heat only. This means that the rate of carbonization is low and practically useless. Relying on these results, we have to rethink the fact that the influencing reaction in the purification process will not be a carbonization reaction and that there is another reaction affecting it in this respect.

By using time to improve the purity of sulfur, it was observed that the purity of sulfur increased with the increase of time with all other conditions kept constant.

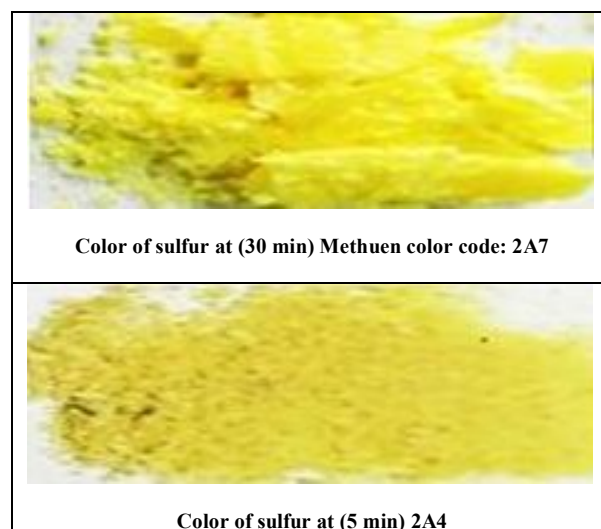


Figure 7. Effect of time on the color of the purified sulfur, keeping all other reaction variables constant

Table 6. Effect time on sulfur purity.

Time (min)	Hydrocarbon concentration in sulfur (g)	
5	0.15×10^{-3}	
10	0.00013	0.13×10^{-3}
20	0.00012	0.12×10^{-3}
30	0.0001	0.1×10^{-3}

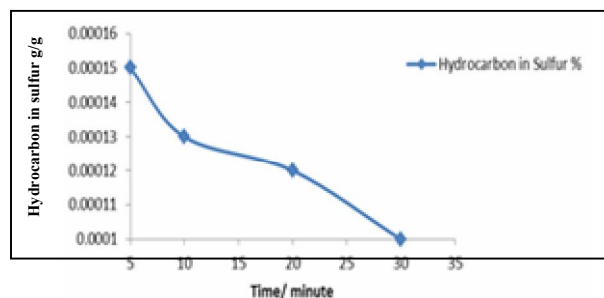


Figure 8. Relationship between the purity of sulfur and time at 3% (wt./wt.) catalyst, 130c°

Finally, experiments that were conducted to optimize the reaction conditions used the time from 5 to 20 minutes. The color of sulfur becomes purer with all other conditions kept constant.

On the other hand, during our attempts to recover the metal salt from the residue of the filtration process, it was noticed the possibility of obtaining heavy hydrocarbon products when washing these residues with carbon tetrachloride, where it was possible to remove the bulk of hydrocarbon from the metal salt. Also, after removing the hydrocarbon part from the metal salt, we did not observe any existence of carbon deposits mixed with the metal salt, confirming our previous conclusion that no carbonization occurred.

Fig. 9 shows the infrared spectrum of the hydrocarbons that were isolated from crude sulfur by washing with carbon tetrachloride (i), and that of hydrocarbons that were isolated from the filtration

residues (ii). There is a convergence in the absorption bands, especially the absorption band returning (C-H) at (2850-2940) cm-1 for the alkyl methyl group And the C-C group for vibrations at (1400, 1500, 1600) cm-1 with varying percentages of the aromatic ring. The obvious congruence in the spectra of both substances indicates that there is no change occurred like hydrocarbons before and after the treatment.

The similarity between the spectrums (i) and (ii) and the appearance of the same main structural groups in both spectrums backs up our conclusion that no carbonization had taken place.

In an attempt to reuse the filtration residue, as a substance that contains the metal salt, it was observed that there was no change in the color of raw sulfur, and no separation or removal of the bituminous impurity from the sulfur was achieved, which indicates the exhaustion of the metal salt and the need to add the amount of it. This creates a controversial problem about the role of this metal salt whether it acts as a catalyst, or that its role is in more than added reactant like any reactant added to the components of the reaction. It was possible to recover this metal salt and reuse it again in the process, and it was found that it retained its activity toward the removal of the bitumen as if it was being used for the first time. The color of the resulting sulfur was yellow (1A2) on Methuen color code [11]. There is more than one example of such a process in the petrochemical industry, one of which is the oxidation of ethylene to acetaldehyde by the Wacker scheme process[24]. In this process PdCl₂ (the catalyst) was reduced to Pd, then, in the reactivation step, pd was oxidized to PdCl₂ as shown in the following equations [25].

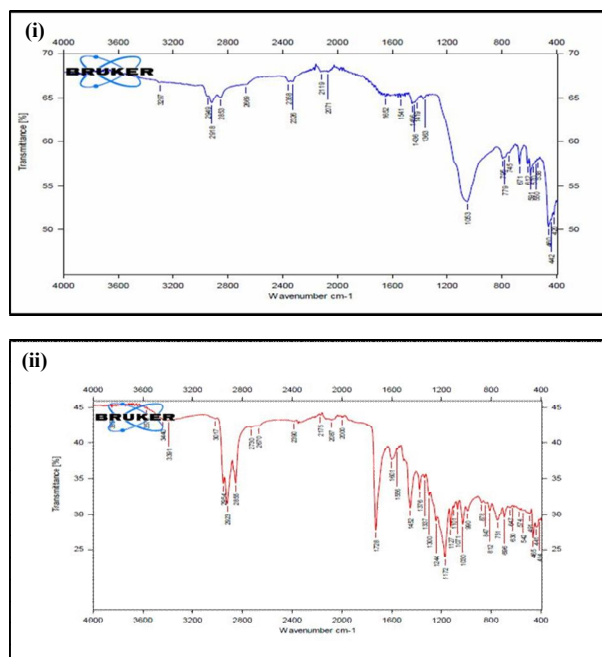


Figure 9. FTIR hydrocarbon (i), (ii)



In our case, the recovery of the metal salt can be achieved by treating the filtration residue either with organic solvent (to dissolve the hydrocarbons) or aqueous solvents (to dissolve the metal salt). The ease of the dissociation of the residue to hydrocarbons and metal salt, and the matching in the composition of the hydrocarbons before and after the treatment, besides the deterioration of the quality of the treated sulfur by rising the treatment temperature, guided us to reformulate our perceptions about the actual role of the metal salt and its way of working in this treatment, we find the most appropriate explanation which comes in agreement with the experimental data is that the purification of sulfur from the bituminous impurity takes place through a complex formation between the metal salt and the hydrocarbons[26]. Support for this assumption could be found in the results of the scanning electron microscope analysis for the hydrocarbons and

their complexes with the metal salt. This technique was used to study crystal structures and to identify the shape of surfaces, the distribution of crystals, and the size of the particles. The scanning electron microscope Technique was used to take a picture of the surfaces of the hydrocarbon particles and their complexes. It showed a clear difference in the crystal structure and surface homogeneity.

The morphological and structural properties of the hydrocarbons and the mixed hydrocarbons metal complexes were evaluated using scanning electron microscopy (SEM). The SEM micrographs are shown in Figure (10a) showing morphological and structural. The form of the hydrocarbons is in the form of large swollen crystal surrounded by a hole around the crystal with the appearance of grains on the surface of the crystal, which indicates the hydrocarbon molecules, a surface that can bond with the metal in the salt.

Figure (10b) illustrates other morphological and structural properties of complex (hydrocarbon and mineral salt), it reveals the emergence of some elevations with sharp ends indicating a none homogeneous shape containing holes between the particles which appear as semi-spherical or bean-shaped like granules of different sizes for the complex, with the presence of tissue and lamellar structures and spider threads connecting these structure indicating the presence of crystals as a result of a complex formation between the hydrocarbons with the metal salt.

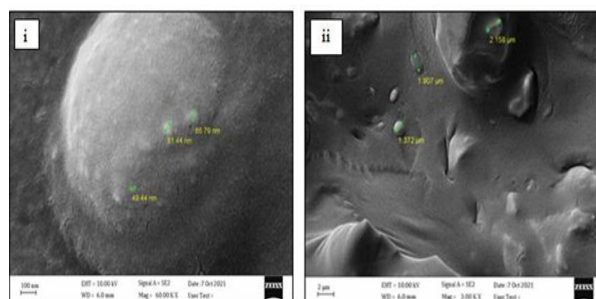


Figure 10a: SEM images of hydrocarbon (i), (ii)

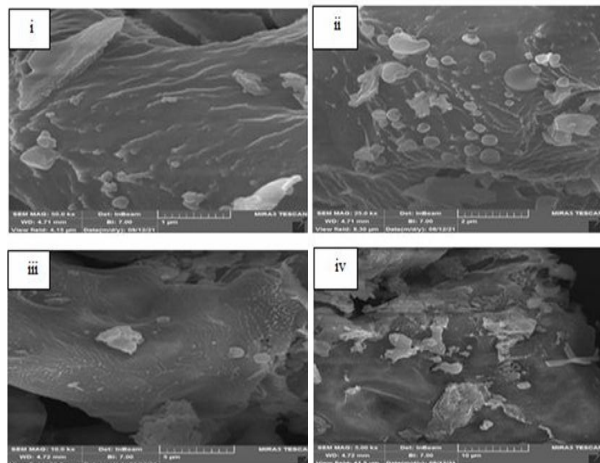


Figure 10b: SEM images of complex (i), (ii), (iii), (iv)

The utilization of complexes is quite familiar in the oil industry. In the first half of the twentieth century, mineral acids were used to treat oil derivatives, especially the heavy ones, to reduce the sulfur content in those derivatives, where the purification was achieved by the formation of complex compounds between the acids and mineral salts on one side and organic sulfur compounds on the other. Also, the process of separating straight-chain paraffin by forming clathrate complexes [27] gives another example of complexes used on an industrial scale. We also find in some recent publications those who seek to remove organic sulfur compounds from oil derivatives by extraction processes using ionic solutions of various acids, bases, and salts. Therefore, we find that the hypothesis that the separation of the bituminous impurity occurs through the formation of a complex between the metal salt and the bitumen is highly likely. However, there is no doubt that the final decision on the trueness of this hypothesis requires further studies and measurements.

It should be realized that determining the mode of action of the "catalyst" is crucial and indispensable matter when designing and choosing the type of reactor to be used in the industrial unit, for example, fixed bed reactors are unuseful for catalysts operating with

complex forming mode, and, in such a case, it is necessary to switch to other types of reactors and according to the level of technology intended to be used, where it is possible to use basin reactor with simple and available technology or to move to reactors of higher technology levels such as liquefied catalyst reactors for example.

It is necessary to design a unit to recover the "catalyst" and recycle [28] it into the reactor to avoid the cost of consuming it as a raw material, which is not desirable even if its cost is low. The easiness of the dissociation process of the complex by using either aqueous or organic solvents at relatively mild conditions will help greatly in this regard.

Conclusion

It is possible to purify sulfur from accompanied bituminous impurities through the formation of complexes between the bituminous impurities and an added metal salt then the complex was separated by filtration. The required conditions are mild compared to those currently used in the Mishraq sulfur mine. It is possible to disintegrate the complex with a solvent and recover the metal salt and reuse it again.

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Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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