Journal Homepage: -www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH (IJAR)

Article DOI:10.21474/IJAR01/15637
DOI URL: http://dx.doi.org/10.21474/IJAR01/15637

RESEARCH ARTICLE

THERMAL VARIATION OF THE DIFFERENT LAYERS FORTARFAYA DEPOSIT (MOROCCO) IN HYDRODESULPHURIZATION AS WELL AS HYDROGENATION OF CALCIUM A, □ AND MAGNESIUM AT 550°C AND 750°C.

Meryem Nadif and Abdeljabbar Attaoui
Department of Chemistry, Faculty of Sciences Ben m'sik Casablanca, University Hassan II Morocco.

……………………………………………………………………………………………….....

Manuscript Info

……………………….

Manuscript History
Received: 05 September 2022
Final Accepted: 09 October 2022
Published: November 2022

Abstract

………………………………………………………………

Hydrodesulphurization (HDS), deuteriodesulphurisation, calcium hydrogenation and deuterium treatment are reactions that occur simultaneously when oil shales are treated with hydrogen. In this work, quantitative monitoring of the target elements (sulphur, calcium and magnesium) was carried out using the dispersive X-ray diffraction technique (a technique coupled with a scanning electron microscope). The treatment of oil shale with hydrogen with the objective, either to improve the products preventing oil shale (gas, oil and solid fuel) or in the particular sense to get rid of some undesirable elements having harmful effects on the course of the exploitations of materials we quote the phenomenon of corrosion. An example of this is hydrodesulphurization, which is a reaction that is used to remove sulphur. This hydrogenation reaction was followed in a first work for the different oil shale layers of Tarfaya **(M. Hafid and A.Attaoui: 2022)** at a temperature of 550°C. However we were able to raise the temperature to 750°C for this study, in the same sense of the continuity of the action by hydrogen on elements such as calcium and magnesium in the temperature domains this study has been continued.

……………………………………………………………………………………………….....

Introduction:-

Studies of hydrodesulphurization reactions (HDS) of sulphur model compounds on eastern and western oil shale minerals have been conducted to provide a fundamental understanding of the heterogeneous catalytic behavior of minerals in oil shale pyrolysis **(A.Shamsi: 1990)**. The hydrogenation of calcite and dolomite leads to the formation of calcium hydrides called hydrolith CaH_2**(M. Hafid and A.Attaoui: 2022(2))** and magnesium (Dumas: 1880).which could be followed by raising the temperature to 750°C, which led us to extend the temperature range of the hydrogen action.

One of the objectives of the oil shale programmer is to develop mechanistic models that provide a reliable predictive capability for the efficient and acceptable conversion of oil shale into useful fuels. The development of a predictive model requires a fundamental but detailed understanding of the "primary" and "secondary" chemical reactions, including the role of minerals during pyrolysis and hydropyrolysis of oil shale. During the decomposition process, shale oil vapors pass over and come into contact with mineral surfaces, particularly on hot-solid recycling processes. The minerals are known to catalyze both primary and secondary reactions during autoclaving **(Cummins, J. J and Robinson, W. E: 1978)**.

Corresponding Author:- Abdeljabbar Attaoui
Address**:-** Department of Chemistry, Faculty of Sciences Ben m'sik Casablanca, University Hassan II Morocco.

1/Literature Review:-

Products formed from the decomposition of kerogen during autoclaving can react both within the shale particles and subsequently on the surface of the shale particles, leading to side reactions that alter the yield and composition of the oil. To understand the effect of minerals during oil shale decomposition and their influence on oil yield and composition, it is necessary to know which constituents of oil shale are catalytically active. This information is not only interesting from a theoretical point of view, but should also help in the design and scale-up of improved autoclave processes.

The Institute of Gas and Technology tested six types of oil shale in a fluidized bed reactor **(M.J. Roberts et al: 1992)** by hydroretorting (PHF) under hydrogen pressure between 2.8 and 7MPa and between 480 and 590°C.The Institute concludes that carbon conversion increases significantly with increasing hydrogen pressure for all six samples. Gas conversion increases with increasing temperature and is independent of pressure. The highest oil yield is obtained at a pressure of 7MPa. The PHF process shows an increase in oil of 200% compared to the Fisher test and over 268% for one of the six samples. During hydro-retorting (PFH), thermal and physical properties such as particle size, permeability, compression, compatibility, consolidation, stresses and thermal conductivity have a great influence on the results obtained **(M.C. Mensinger and S.K. Saxena: 1991)**. Of the six shale samples studied, none showed metal depletion under acid as a test condition. In general, thermal agglomeration further reduces metal depletion levels for raw shale. IGT was also able to track **(J. Abbasian et al: 1991)** the conversion of sulphides to H_2S during hydroretorting. The solids $CaCO_3$ (calcite) and $FeCO_3$ (siderite) were added to the shale to perform the desulphurization reaction in the bed. The effects of the operating conditions of the sulphide fixation by calcite and siderite were examined. The reactivity's of calcite and siderite with H2S were determined, in a temperature range of 480 - 565°C using an absorbing solid of approximately 0.018 cm diameter. The thermogravimetric studies prove that siderite and calcite are able to capture a significant fraction of the H_2S produced by PFH. Four heavy oils were hydropyrolyzed **(T. Hikita et al: 1989)** and converted into carbonaceous gas, liquid and solid. The reactivity of these oils towards gas depends on their aromaticity; the concentration of the reaction products is strongly influenced by the temperature around 700°C. Stable benzene is the major product at 800°C, it becomes more reactive and reduces the liquid more rapidly. Aliphatic and polycyclic aromatic hydrocarbons, with the exception of pyrene, react to produce methane and benzene as the major products. The reaction chain scheme determined is 1st order and the rate constants, for aliphatic and aromatics, are calculated.

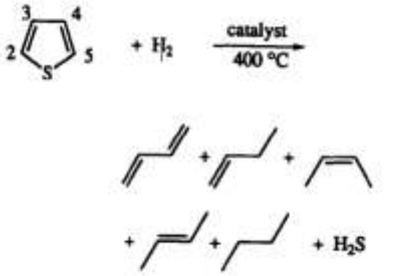
Athabasca bitumen underwent the hydrocracking reaction in a reactor at a temperature of 620 - 693K under hydrogen pressure of 7.2 MPa, the reaction products of asphaltenes, resins, aromatics, saturates and gases are separated from the coke. Three kinetic reactions are developed to arrive at the mechanism **(R.O. Koseoglu and C.R. Phillips: 1988)**:

bitumen→ gas
heavy oils →light oils→ gas
Asphaltenes→maltenes→ gas

These reactions are assumed to be of first order with respect to hydrocarbons and of zero order with respect to hydrogen and that Arrhenius' law is verified.

The existence of Bronsted acid sites during the catalytic production of sulphides**(N. Topsoe et al: 1988)** is demonstrated during hydrotreating. These acidic sites play an important role during reactions such as hydrocracking or isomerization. The hydrodesulphurization of oil shale in the western United States confirms that the thiophene reactions are those of C1 - C4 hydrocarbons. The reduction of organic carbon by chemisorbed hydrogen **(R.P. Underwood and A.T. Bell: 1988)** is catalytic and results in the dissociation of this carbon, the process evolving preferentially in the catalyst sites. Similarly, the hydrogenation of butadiene 1-3 occurs in a catalytic and supported manner **(J. Massardier et al: 1988)**. Alkaline additive improves activity and selectivity, which can be explained by the exchange of electrons during chemisorption of charged species, which reduces the band of unsaturated hydrocarbons on the metal surface.

Studies carried out by spin resonance spectroscopy on mineral groups such as nacrite, dickite, kaolinite and halloysite have shown a systematic difference **(J. Komusinski et al: 1984)** which is related to the crystallisation of kaolinite and for mutual orientations. The most important feature of the spectrum is attributed to the Fe3+ ion which occupies the different structural sites. These studies show some modifications which are due to the heat treatment which generally causes the modification of the structure. Kaolinite and smectite in the presence of steam undergo dehydroxylation which is first order for an isothermal regime and second order for a non-isothermal regime with increasing steam pressure **(J.H. Levy et al: 1993)**.Catalytic hydrodesulphurisation (HDS) is a large-scale industrial process for the removal of sulphur from oil feedstocks. Thiophene has been studied extensively as a model for this process. The reaction of thiophene with H_2 over supported HDS catalysts, Co-MO /Al_2O_3 and Ni-W / Al_2O_3 produces H_2S and a mixture of 4-carbon hydrocarbons: 1, 3-butadiene, 1-butene, cis- and trans-2-butene and butane (eq 1). Among the C4 products, bond cleavage as it is detected **(V.I. Komarewsky and E.A. Knaggs: 1951)** under reduced hydrogen pressure when its hydrogenation to butene and butane is less favorable.



(1)

Other evidence supports this proposal. Firstly, the parent amount of 1,3-butadiene produced in HDS from thiophene on MoS2, **(S. Kolboe et al: 1966)** and Chevrel Phase catalysts **(K.F. McCarty and G.L. Schrader: 1987)** increases with decreasing thiophene conversion.

2/ Method of analysis

2.1/ Energy dispersive X-ray spectrometry coupled to a scanning electron microscope (EDX)

A Quanta 200 Feg scanning electron microscope (SEM) coupled to an X-ray spectrometer (EDX) was used to study the morphology and qualitative chemical composition of the sample surfaces.

Scanning electron microscopy is a technique based on the analysis of "electron-matter" interactions. The surface of the sample is subjected to a bombardment of electrons. Some radiation (backscattered electrons, secondary electrons and X-rays) is emitted as a result of the multiple collisions between the electrons that scan the surface and the atoms of the material under test. This radiation is analyzed by different detectors to build an image of the surface and to observe the presence of elements in the analyzed area. The emission of backscattered electrons (electrons from the incident beam deflected by elastic interactions) is sensitive to the atomic number of the chemical elements present in the sample. Secondary electrons are electrons from atoms that have been ejected by the incident beam. These low energy electrons are representative of the topography of the sample. Atoms that have lost these secondary electrons will regain their stability through electron transitions that cause the emission of electromagnetic and X-ray radiation. This radiation is characteristic of the original atoms and gives information about the chemical composition of the sample.

The experimental results of dispersive X-ray identification are:

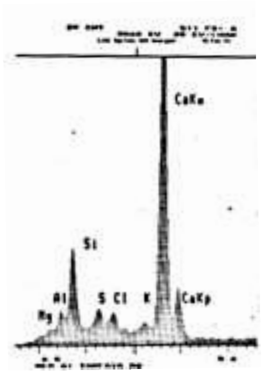
2.2/ Ambient temperature range at 550°C

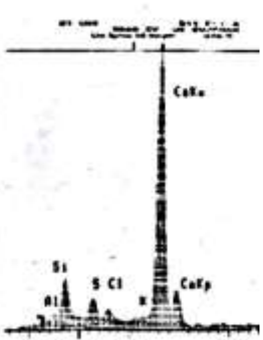
The results of the dispersive X-ray spectra for the five layers of the Tarfaya deposit were carried out in a previous work **(M. Hafid and A.Attaoui: 2022)**. These results lead to an elemental analysis of different elements constituting the shale compounds such as: sulphur, calcium, aluminum, potassium, chlorine, magnesium and iron.

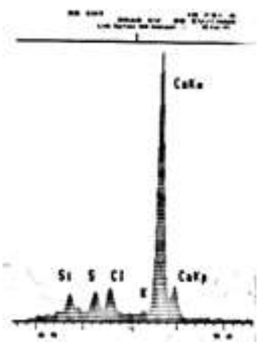
These analyses were carried out for both the raw and hydrotreated (H_2) material up to 550°C (see following figures)

2.3/ Ambient temperature range at 750°C

X-ray spectra for this temperature. The following XRD spectra represent the different layers of the Tarfaya deposit, namely Z0, Z1, Z2, Z3 and Z4, raw, hydrogen (H_2) treated (hydrogen flux = 20 cm^3/mm and PH_2 = 1 atm) up to a temperature of 550°C and hydrogen treated under the same conditions up to a temperature of 7750°C.







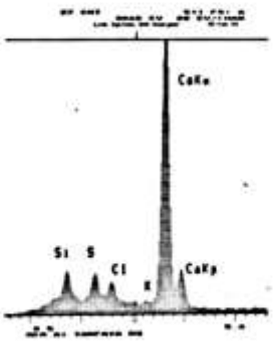


Fig1: Raw Z0 layer Fig 2: Raw Z1 layerFig 3: Raw Z2 layer Fig 4: Raw Z3 layer

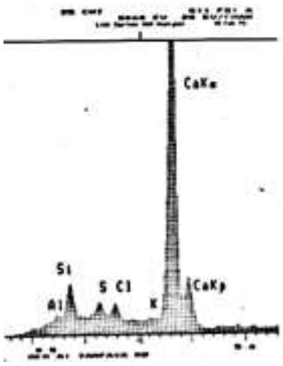
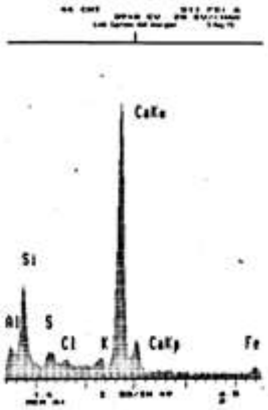
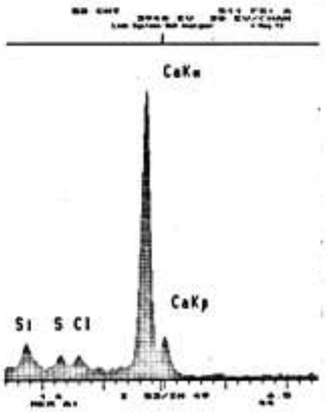
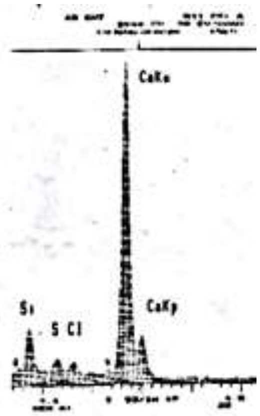


Fig5: Raw Z4 layer

For the hydrogen treated samples, their XRD analysis can be found in the following spectra at 550°C in temperature







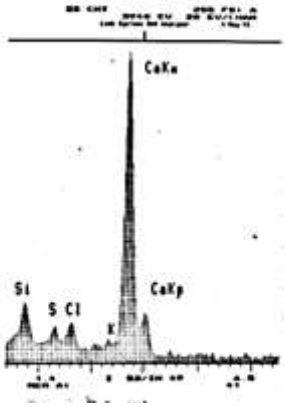


Fig 6: Z0 hydrotreatedFig 7: Z1 hydrotreatedFig 8: Z2 hydrotreatedFig 9: Z3 hydrotreated
at 550°C at 550°Cat 550°Cat 550°C

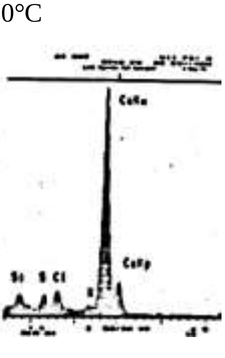


Fig 10: Z4 hydrotreatedat 550°C

Similarly, the spectra were carried out for hydrogen treatments at 750°C

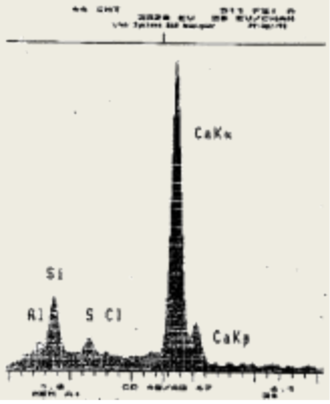


Fig 11: Z0 hydrotreated at 750°C

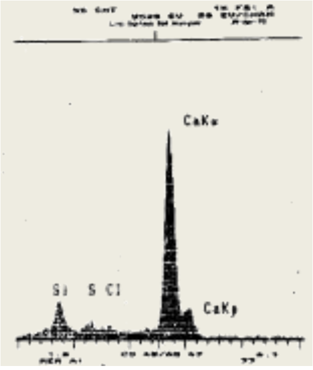


Fig 12: Z1 hydrotreated at 750°C

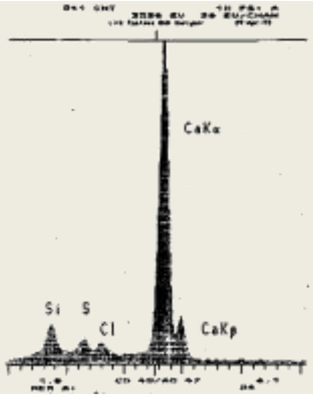


Fig 13: Z2 hydrotreated at 750°C

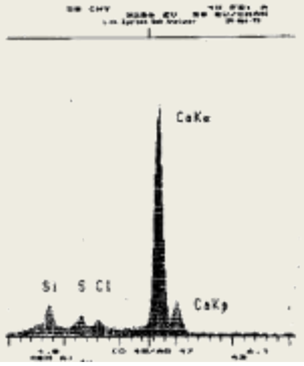


Fig 14: Z3 hydrotreated at 750°C

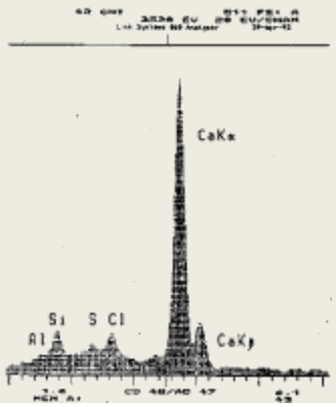


Fig 15: Z4 hydrotreatedat 750°C

3/ Table of results

The following table shows the different measurements of the peaks of the previous spectra as well as the percentages of the elements constituting the oil shale. These values are attributed to the temperatures, firstly ambient, then hydrotreating at 550°C and finally hydrotreating at 750°C.

These spectra have led to the results shown in the following table 1. It should be remembered that the spectra with which the measurements and calculations were made have A4 shapes, the spectra in the text are reduced shapes. The same spectra were used for hydrodesulphurization in a previous work **(M.Hafid and A.Attaoui: 2022)**

Table1:- PercentageofchemicalelementsintheTarfayaoil shale.at different states.

Composition	Type of oil shale	Z_0 (cm)	Z_1 (cm)	Z_2 (cm)	Z_3 (cm)	Z_4 (cm)	%Z_0	%Z_1	%Z_2	%Z_3	%Z_4
Magnesium	Raw	**1,15**	**0,60**	**0,80**	**0,70**	**0,60**	**2,67**	**1,80**	**2,12**	**1,93**	**2,01**
	Traited by H_2 at550°C	**1,15**	**0,60**	**0,80**	**0,70**	**0,60**	**3,71**	**1,99**	**2,98**	**2,06**	**1,99**
	Traited by H_2 at 750°C	**0,85**	**0,45**	**0,40**	**0,35**	**0,60**	**3,15**	**2,46**	**1,57**	**1,78**	**2,39**
Aluminium	Raw	**2,35**	**1,20**	**1,40**	**1,15**	**0,80**	**5,46**	**3,69**	**3,72**	**3,18**	**2,67**
	Traited by H_2 at550°C	**1,90**	**0,95**	**0,80**	**1,35**	**0,80**	**6,13**	**3,15**	**2,98**	**3,97**	**2,66**
	Traited by H_2 at750°C	**1,45**	**0,60**	**0,65**	**0,55**	**1,05**	**5,38**	**3,29**	**2,56**	**2,81**	**4,19**
Siliom	Raw	**6,50**	**3,60**	**3,40**	**3,10**	**1,95**	**15,11**	**10,97**	**9,57**	**8,58**	**6,52**
	Traited by H_2 at550°C	**5,4**	**3,25**	**2,10**	**3,65**	**1,80**	**17,42**	**10,78**	**7,83**	**10,75**	**5,99**
	Traited by H_2 at 750°C	**3,75**	**2,10**	**2,05**	**1,75**	**2,20**	**13,91**	**11,51**	**8,07**	**8,93**	**8,78**
Sulphur	Raw	**2,40**	**2,15**	**2,15**	**2,90**	**2,10**	**5,58**	**6,55**	**5,72**	**8,03**	**7,02**
	Traited by H_2 at550°C	**1,60**	**1,50**	**1,45**	**2,20**	**1,75**	**5,16**	**4,97**	**5,41**	**6,48**	**5,82**
	Traited by H_2 at 750°C	**1,65**	**1,05**	**1,35**	**1,20**	**1,50**	**6,12**	**5,75**	**5,31**	**6,12**	**5,99**
chlorine	Raw	**2,20**	**1,50**	**2,05**	**2,30**	**2,30**	**5,11**	**4,57**	**5,45**	**6,37**	**7,69**
	Traited by H_2 at550°C	**1,10**	**1,30**	**1,45**	**2,40**	**2,10**	**3,54**	**4,31**	**5,41**	**7,07**	**6,98**
	Traited by H_2 at 750°C	**1,00**	**0,75**	**1,10**	**0,90**	**2,10**	**3,71**	**4,11**	**4,33**	**4,59**	**8,38**
Calciumα	Raw	**22,30**	**19,60**	**22,60**	**21,20**	**18,50**	**51,86**	**59,75**	**60,10**	**58,72**	**61,87**
	Traited by H_2 at550°C	**15,80**	**18,60**	**16,60**	**18,60**	**18,80**	**50,97**	**61,69**	**61,94**	**54,78**	**62,56**
	Traited by H_2 at 750°C	**15,80**	**11,60**	**17,40**	**12,90**	**15,00**	**58,63**	**63,56**	**68,50**	**65,82**	**59,88**
Calciumβ	Raw	**3,85**	**2,80**	**3,75**	**3,20**	**2,50**	**8,90**	**8,53**	**9,97**	**8,86**	**8,36**
	Traited by H_2 at550°C	**2,20**	**2,80**	**2,45**	**3,00**	**2,85**	**7,09**	**9,28**	**9,14**	**8,83**	**9,48**
	Traited by H_2 at 750°C	**2,45**	**1,70**	**2,45**	**1,95**	**2,60**	**9,09**	**9,32**	**9,65**	**9,95**	**10,38**

4/ Interpretation of the hydrotreatment phenomenon

4.1/ Reaction of sulphur with hydrogen

The presence of sulphur in the organic matter of oil shale would constitute poisons for the catalysts used in refining as well as for the materials of the installations used for the pyrolysis or the treatment of their oil; moreover, sulphur must be eliminated from the products to preserve the environment, from the need to carry out the hydrotreatment (H_2)

Sulphur according to figure 17 can be identified in the same way for both temperatures 550°C and 750°C precisely for the layers Z2, Z3 and Z4, this proves that this kind of sulphur is part of the organic matter whose decomposition temperature in a reducing environment is around 550°C. Unlike Z0 and Z1, whose constituents are the elements Al, Si, Mg and Ca found in clays, calcite and dolomite, whose concentration is sensitive. It should be noted that the decomposition temperature in a reducing environment is lower than the use temperature (750°C) and that the departure of these elements makes the relative quantity of sulphur more accentuated for these layers Z0 and Z1 at 750°C rather than at 550°C.

As noted earlier, sulphur is an element to be extracted from oil shale by the often used reaction known as hydrodesulphurization. We note that this reaction occurred mostly (see the five layers) simultaneously during the decomposition of the organic matter at a temperature of 550°C.

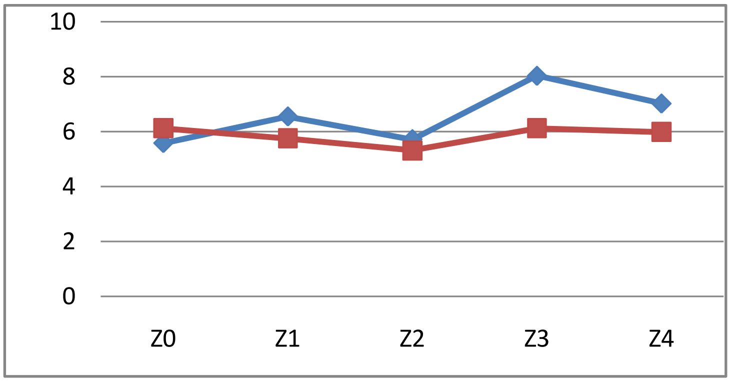


Fig 16: Percentage of raw sulphur🟦 🟦 🟦 and
sulphur after hydrotreated at 750°C 🟥 🟥 🟥

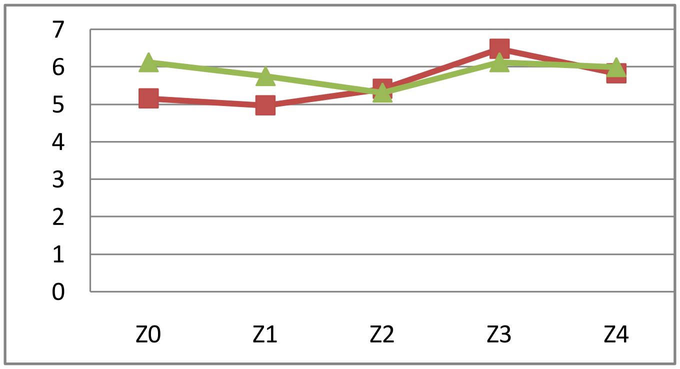


Fig 17: Percentage of sulphur after hydroteated at 550°C 🟥 🟥 🟥
andsulphur after hydroteated at 750°C 🟩 🟩 🟩

Trying to analyse figure 16 we notice the noticeable difference between the raw sulphide and when we have hydrotreated at 750°C in increasing order for the layers Z1, Z4 and then Z3. This is the same order found when we hydrotreated the oil shale layers at 550°C (hydro article). This similarity in behaviour is attributed to the climate of the geological stage of sedimentation of the given layer, i.e. a warm climate for the Z1, Z4 and Z3 layers (Type and adaptation article).

Comparing what happens when the temperature is varied between 550°C and 750°C (figure 17) we notice that the two curves are juxtaposed for the curves at the Z2, Z3 and Z4 layers samples. This means that the partial reaction effect of hydrodesulphurisation is maintained between the temperature of 5560°C and 750°C.

Concerning H2S from mineral pyrite, its decomposition in the presence of hydrogen is catalytic according to the authors **(E.R. Bissel: 1983)**. This decomposition takes place at two temperatures 385°C and 440°C.

4.2/ Hydrotreating of calcite and dolomite compounds at different temperatures

RDX spectra carried out for calcium and magnesium, which are elements of calcite and dolomite, have led to the findings, according to figures (18, 19, 20 and 21), of the percentages of the element considered. Calcium is present in two forms CaK$_{\alpha}$ and CaK$_{ß}$:

- For CaKα :

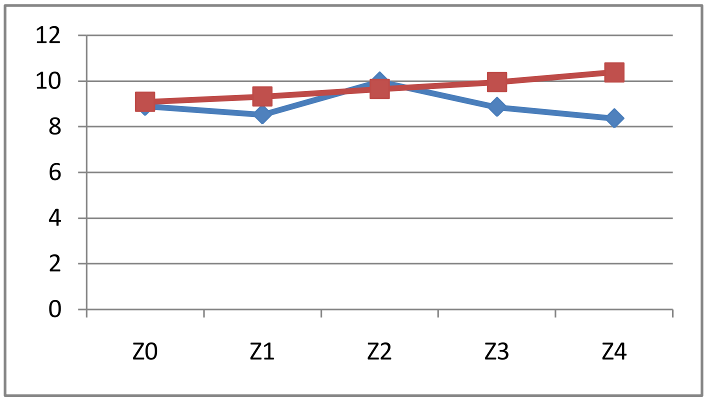


Fig 18:- Raw CaK$_{\alpha}$🟦 🟦 🟦 and CaK$_{\alpha}$hydrotreated at 750°C 🟥 🟥 🟥

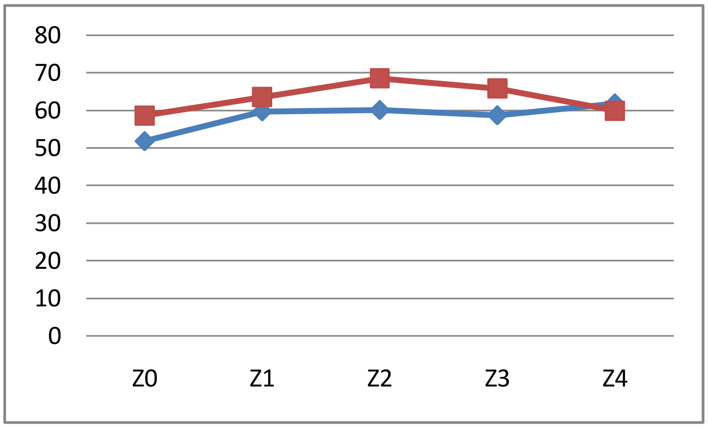


Fig 19:-CaK$_{\alpha}$ hydrotreated at 550°C🟦 🟦 🟦 and CaK$_{\alpha}$ hydrotreated at 750°C 🟥 🟥 🟥

- For CaK$_{ß}$

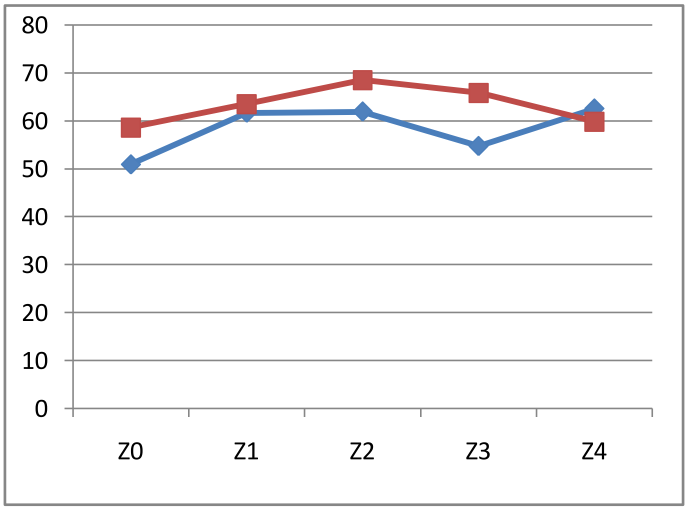


Fig 20:- Raw CaK□ 🟦 🟦 🟦 and
CaK□ hydrotreated at 750°C 🟥 🟥 🟥

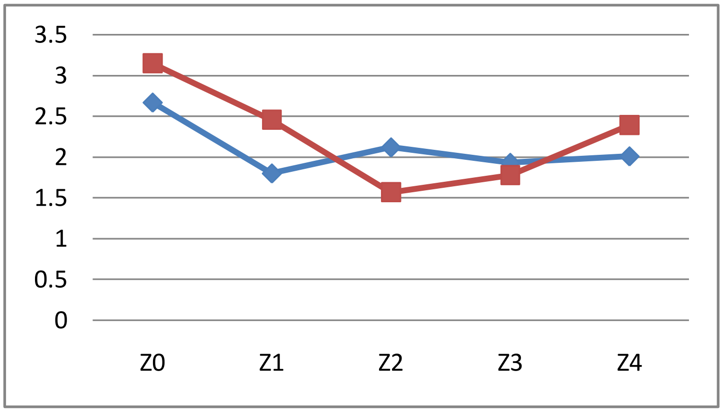
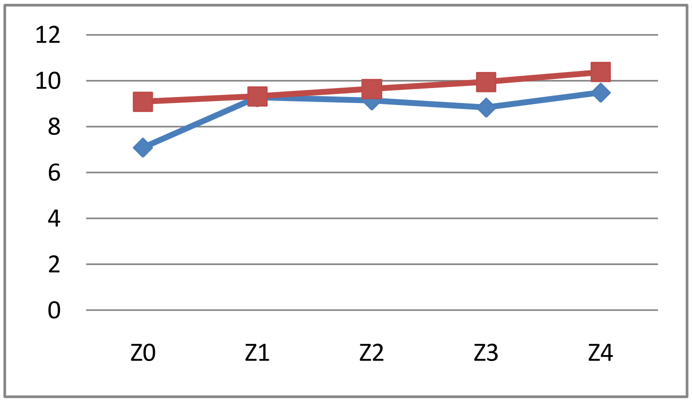


Fig 21:- CaK□ hydrotreated at 550°C🟦 🟦 🟦 and
CaK□ hydrotreated at 750°C 🟥 🟥 🟥



The two layers Z0 and Z2 are the least concentrated in organic matter, conversely we notice according to the figure that they are concentrated in calcium

For magnesium we have figures 22 and 23

Fig 22: Percentage of raw magnesium 🟦 🟦 🟦 et
and after hydrotreated at par à 750 °C 🟥 🟥 🟥

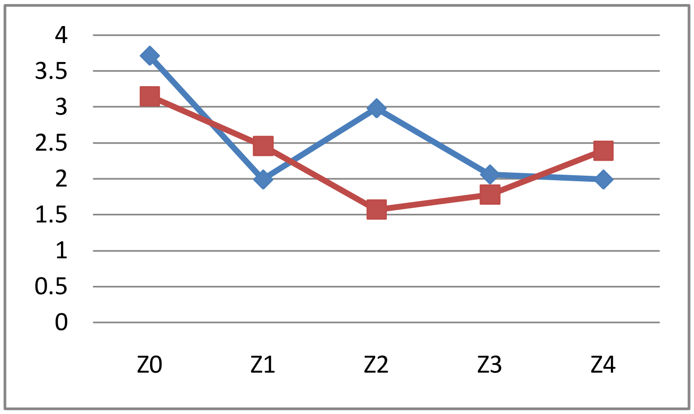


Fig 23: magnesium hydrotreated at 550°C🟦 🟦 🟦
and magnésiumhydrotreated at 750°C 🟥 🟥 🟥

We calculated the ratio of peak dimension (cm) / applied voltage in another way. We have collected the ratios in the following two tables (2 and 3), one representing CaKα and the other magnesium.

Table 2:- The ratio of peak dimension (cm) / applied voltage for calcium at different layers.

Peak d (cm) / V.a Layer	CaKα (Raw)	Cakα (550°C)	Cakα (750°C)
Z_0	0,0073	0,0040	0,0045
Z_1	0,0064	0,0047	0,0033
Z_2	0,0074	0,0042	0,0049
Z_3	0,0069	0,0047	0,0037
Z_4	0,0060	0,0048	0,0043

According to this table, the decomposition gap between 550°C and 750°C is accentuated for the layers Z1 and Z3 and Z4 which are layers of hot geological stages

Table 3:-The ratio of peak dimension (cm) / applied voltage for magnesium at different layers

Peak d(cm) / V.a Layer	Mg (Raw)	Mg (550°C)	Mg (750°C)
Z_0	0,00038	0,00029	0,00024
Z_1	0,00020	0,00015	0,00013
Z_2	0,00026	0,00020	0,00011
Z_3	0,00023	0,00018	0,00010
Z_4	0,00020	0,00015	0,00017

According to the tables we find that calcium decomposes more in the 550°C ambient temperature range, for dolomite the decomposition range is extended towards the higher temperatures of 500°C -750°C, this is confirmed for samples Z2 and Z3. It should be noted that the hydrides formed during the treatment are the hydrolith CaH_2 and the magnesium hydride MgH_2. The reactions of hydrogen with the constituents of the mineral material are of different kinds depending on the compounds of the mineral material:

- With calcite

$CaCO_3Ca\ H_2 + C\cancel{O2 + 6H_2O}\rightarrow$ 500 < T < 750°C
Hydrolith

- With dolomite:

H_2

$Ca\ (Mg)\ (CO_3)_2Ca\ H_2 + MgH_2 \rightarrow + CO2 + 6H_2O$ $500 < T < 750°C$

- With kaolinite:

$2Al_2Si_2O_5\ (OH)_4 \xrightarrow{H_2} SiH4 + 2Al_2Si_2O_7 + Al_2O_3 + 4H_2O$ $300 < T < 750°C$

monosilane

- With pyrite:

$H_2FeS_2\quad FeSFe \xrightarrow{H_2}$ $300 < T < 600°C$

- With magnétite

$Fe_3O_4 + 3H_2S \xrightarrow{H_2} 3FeS + 4H_2O$ $550 < T < 750°C$

Conclusion:-

Dispersive X-ray diffraction is an elemental analysis technique coupled with the scanning electron microscope, which was used in this work to analyses the different layers of the Tarfaya deposit. The elements monitored are, in order, sulphur, calcium, aluminum, chlorine and magnesium.

Sulphur is an element to be extracted from oil shale by the often used reaction called hydrodesulphurization. In the Z2, Z3 and Z4 layers sulphur is identified in the same way for both temperatures 550°C and 750°C, unlike the Z0 and Z1 layers where the decomposition temperature in a reducing environment is below the use temperature (750°C).

Calcium and magnesium are elements of calcite and dolomite, there are two forms of calcium (CaK_{α}, $CaK_{ß}$). By simple calculation we have given the ratio of peak size (cm) / applied voltage for calcium α and magnesium. We find that calcium decomposes more in the 550°C ambient temperature range, for dolomite the decomposition range is widened towards higher temperatures i.e. 500°C -750°C, this is confirmed for samples Z2 and Z3.

As mentioned earlier, sulphur exists in two forms, organic and inorganic sulphur. Hydrodesulphurization occurs over the temperature range with the exception of the Z2 layer where we observe certain inertia when comparing the percentage of crude sulphur at 550°C and 750°C. This layer, with a lower concentration of organic matter, is the only one where the sulphur content is lower than in the Z3 layer. This layer, less concentrated in organic matter and having a geological formation stage in the Upper Cretaceous with a cold climate.

Calcium and magnesium form hydrides in reaction with hydrogen, such as hydrolith (CaH_2) and magnesium hydride (MgH_2). The reaction for calcium is similar despite the temperature variation from 550°C to 750°C. The difference is that the temperature effect is noticeable due to the fact that dolomite has a higher decomposition temperature of over 600°C. For the Z0, Z2 and Z3 layers, there is a predominance of the temperature effect between 550°C and 750°C. The Z0 and Z2 layers are concentrated in mineral matter and less concentrated in organic matter, while for Z3, the catalytic effect of organic matter is manifested.

References:-

[1] M. Hafid and A.Attaoui, BehaviourofthedifferentlayersfromTarfayadeposit(Morocco)inthermalhydrodesulphurizationat 550°C, Int. J. Adv. Res, DOI : 10.21472/IJAR01/15199, August, 2022,10(08) ,459-472

[2] AbolghasemShamsi, Ind. Eng. Chem. Res., Vol. 29, No. 7, 1990

[3] M. Hafid and A. Attaoui, The effects of hydrogen on some constituents elements in Tarfaya oil shale layers (Morocco), Int. J. Adv. Res,DOI:10.21474/IJAR01/15424, September 2022,10(09), 811-820.

[4] Dumas C.R. 90. 1027. 1880.

[5] Cummins, J. J.; Robinson, W. E. Thermal Conversion of Oil Shale Kerogen Using CO and Water at Elevated Pressure. LERC-78/1 US. Department of Commerce: Washington, D.C., 1978.
[6] M.J. Roberts et al. Fuel. Vol. 71. 1992. March. 335.
[7] M.C. Mensinger and S.K. Saxena.Fuel.Vol 70.1991. Nov. 1885.
[8] J. Abbasian et al. Fuel. Vol. 70. 1991. Dec. 1342.
[9] T. Hikita et al. Fuel. Vol. 68. 1989. Sept.1140.
[10] R.O. Koseoglu and C.R. Phillips.Fuel.Vol. 67. 1988. Oct. 1411.
[11] N. Topsoe et al. Journal of Catalysis. 119. 1988. 252.
[12] R.P. Underwood and A.T. Bell.Journal of catalysis 109. 1988. 61.
[13] J. Massardier et al. Journal of catalysis 112. 1988. 21.
[14] J. Komusinski et al. Journal of thermal Analysis.29. 1984.
[15] J.H. Levy et al. Fuel.Vol 72.N°6. 1993. 873.
[16] V.I. Komarewsky and E.A. Knaggs, lnd.Eng.Chem., 43 (1951) 1415.
[17] S. Kolboe and C.H. Amberg, Can.J. Chem., 44 (1966) 2623. b) P.J. Owens and C.H. Amberg, Adv. in Chem., Ser. No. 33 (1961)
[18] K.F. McCarty and G.L. Schrader, J. Catal., 103 (1987) 26
[19] E.R. Bissell. Deprt Energy. Lawrence Livermore Labo UCID 1983.Sept. 19906.