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RESEARCH ARTICLE

THE EFFECTS OF HYDROGEN ON SOME CONSTITUENTS ELEMENTS IN THE TARFAYA OIL SHALE LAYERS (MOROCCO)

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Abstract

The elements calcium, magnesium, aluminum, silicon and potassium are part of oil shales, precisely they are found in the mineral matrix. In this work, hydrotreating in a dynamic regime (21°C/min) and under standard hydrogen pressure (1atm) was carried out and these elements were followed quantitatively before and after reaction by the dispersive X-ray diffraction technique (RXD). The compounds formed are hydrides which are mainly fuels, indeed, calcite, an element of oil shale, under hydrogen produces hydrolith (CaH₂), dolomite under hydrogen produces magnesium hydride (MgH₂), similarly kaolinite produces monosilane (SiH₄) also carbon under hydrogen produces methane. It should be noted that oil shale around the world vary in their oil production capacity and quality. For example, the Green River shale in the western United States contains a high concentration of hydrogen relative to organic carbon and yields a high yield by simple decomposition using a conventional inert gas. However, much other shale that resembles to the Devonian shale in the eastern United States contains a lower concentration of hydrogen than the Green River (**J.C. Janka: 1984**).

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Introduction:-

Hydrogen deficiency prevents much of the kerogen from converting to hydrocarbons (**J.C.Janka et al: 1979, R.D.Matews et al 1981**), as in the case of oil shale in the eastern United States (Devonian)

MASS IN %	DEVONIEN	GREEN RIVER	TARFAYA*	TIMAHDIT*
Organiccarbon	13,7	13,6	10,62	10,9
Hydrogen	1,6	2,1	1,2-1,4	1,84

The yield from conventional shale decomposition can be improved by adding more hydrogen during the decomposition process. This allows more of the kerogen to be converted to hydrocarbons rather than remaining in the ash as coke.

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The effects of hydrogen have been studied before by authors (**O.M.Larson et al: 1981**) who have shown that degradation under hydrogen pressure decreases the H/C ratio in the residue.

Authors (**W.G.Schlinger et al: 1967**) have shown that by using hydrogen they can improve the Fisher test. The same beneficial effects of hydrotreating have been reported by other authors (**M.G.Q.Huntington: 1966, P.B. Tarman et al: 1977, S.A. Weil et al: 1976 and N. Toreis et al: 1986**) studied the effect of some transition metals (Mo, Rn, Pd, Co, Ni, Co/Mo) on oil shale under hydrogen, they noticed that the presence of these metals does not affect the order of the kinetics of kerogen decomposition but it decreases the activation energy.

1/Literature Review:-

The Institute of Gas Technology has conducted pressurized fluidized bed hydrolysis (PFH) tests of six oil shale in the eastern United States in batch and continuous reactors at laboratory scale (**M.J.Roberts et al: 1991**).

In order to mitigate the environmental impacts of HFP for oil production from shale, the types of potential pollutant sources need to be quantified. Therefore, one of the objectives of the mission was to provide analytical data on process streams from the hydroprocessing unit at bench scale for pollutants, including trace and minor organic compounds. The distribution of pollutants in the process streams was also quantified, including product oil, sour water, product gas and shale. Finally, the readability of spent shale determined whether its evaluation as a hazardous material should be considered as well as its disposal. It is during exposures that the most significant environmental impacts (**F.Register: 1990**) could be realized through the leaching of trace metals.

The BSU (bench scale unit) serial grouping unit is used under conditions at temperatures and pressures up to 870°C and 7.0 MPa for the analysis of shale from two zones. Using different reactors of varying inner diameter of the BSU from 15.2 to 30.5 cm, test samples were taken periodically in steady and unsteady state. These solid residues (spent shale), or produced gases and liquids (oil and water) after each test, are submitted to the IGT analytical laboratory for analysis. At the start of the test, the reactor and the tailings receiver were all pressurized with hydrogen. Then the compressor recycle gas was started and the hydrogen flow through the reactor was brought to the desired speed. The gas was filtered and then cooled indirectly (with water) in the liquid condenser products. The condensed oil and water were the liquid collection pot. This pot was sampled at intervals during the test. The product gas was then passed through a coalescing filter to remove the fine droplets of oil and water. The product gas was then passed through a pneumatic compressor and recycled to the reactor. High pressure hydrogen was added just downstream from the recycle compressors. The make-up stream and the recycled hydrogen stream were heated to the required temperature in a preheater. The product gas from the BSU was metered to the orifice and back pressure control valve. The hydrocarbon content of the product gas was continuously monitored by a hydrocarbon analyser. The product gas and the gas recycled through the BSU system usually contained 98-99% hydrogen. Thus, organic compounds and trace elements in the product gas were present at low concentrations. Part of the product gas stream, typically about 1.13 m³ /h was passed through the environmental (**M.J.Roberts et al: 1991**). The hydrotreating results increased the overall carbon conversion rate for the Alabama shale from 64.5 to 72.9%. The fraction of feed carbon appearing in the oil increased from 44.0 to 58.1%. Indiana shale conversions similar to Alabama shale at 7.0 MPa. The enriched Indiana shale showed a higher carbon forming oil and lower carbon forming gas with an overall carbon conversion of 80.8%. The final analyses of the feed shale are presented in Table 1. The carbon contents were 15.94% for the Alabama shale, 12.95% for the raw Indiana shale and 28.05% for the enriched Indiana shale. At 9.05%, the sulphur content. The Alabama shale was significantly higher than the crude and enriched Indiana shale (2.93% and 2.77%, respectively). Analyses of the feed shale for the elements are presented in Table 2, as the data shows. The analysis of the feed shale for 20 trace elements is presented in Table 1. Of the 20 elements, eight (arsenic, barium, cadmium, chromium, mercury, lead, selenium and silver) were analyzed in the TCLP test. One of the objectives of the oil shale programme is to develop efficient and environmentally acceptable model mechanisms that provide a predictive approach to the conversion of oil shale to combustion. The development of a predictive model requires a fundamental but detailed understanding of the "primary" and "secondary" chemical reactions, including the role of minerals in the pyrolysis of oil shale. During the decomposition process, shale oil vapors pass and contact mineral surfaces, particularly in the hot recycling process, particularly in the hot recycling process.

Table 1:- Chemical analyses of the product oil from hydrotreating tests in the BSU.

	Alabama	Indiana	Beneficiated Indiana
Moisture (wt%)	0.94	1.56	1.88

Ultimate analysis (wt %)	Organic carbon	15.94	12.95	28.05
	Mineral carbon	0.07	0.08	0.05
	Hydrogen	1.57	1.48	2.81
	Oxygen	2.90	3.16	5.41
	Nitrogen	0.49	0.35	0.74
	Sulphur	9.05	2.93	2.71
	Ash	73.59	80.25	61.11
Gross calorific value	MJ / Kg	7.60	5.81	12.52
	Btu Ib ⁻¹	3266	2497	5385
Fisher assay	Fisher assay'	53	54	108
(gal ton- I)	(gallon ton- I)	12.7	12.9	25.9

Table 2:-Component analyses of the products oils from hydroretorting tests in the BSU.

Elémentwt%	Alabama	Indiana	Beneficiated Indiana
Calcium	0.24	6.88	0.34
Le fer	7.49	0.34	7.49
Potassium	2.70	3.99	3.00
Magnésium	0.64	3.00	0.70
Sodium	0.34	0.70	0.34
Silicium	22.10	0.41	22.10
Titane	0.36	24.80	0.41
Aluminium	4,89	6,88	5,32

Minerals are known to catalyze primary and secondary reactions in oil shale reactions (A.K.Burham et al: 1984). Products from the decomposition of kerogen during retorting can react on the surface of shale particles resulting in secondary reactions that alter oil yield and composition. To understand the effect of minerals on oil shale and how they affect oil yield and composition, it is necessary to know which oil shale constituents are catalytically active. This information is not only of theoretical interest, but should also assist in the design and scale-up of improved retorting processes. Studies comparing the pyrolysis of oil shale and kerogenes have shown that the mineral material in oil shale provides surfaces that can crack a high molecular weight and produced by thermal or catalytic mechanisms (J.B. David et al: 1982). These studies indicate that reactions involving the cleavage of carbon-carbon bonds and carbon-hydrogen bonds on mineral surfaces were presented in a paper by the authors (R.A.Regtop et al: 1985). These same authors provided evidence that carbonized residues in spent shale can increase the extent of secondary reactions. These researchers based their conclusions on the examination of pyrolysis of model hydrocarbon scaling compounds under different conditions on waste shale, minerals and charcoal.

2: Experimental study:

2.1:X-ray diffraction indispersive for the crude and hydrotreated samples at 550°C.

The two techniques used in this experimental work are:

Dynamic thermogravimetry, samples belonging to the oil shale layers Z0, Z1, Z2, Z3 and Z4 were hydrotreated under hydrogen (1atm) at a heating rate of 21°C/min to 550°C.

Dispersive X-ray diffraction coupled with SEM, the same samples mentioned above were analysed first to get the pictures and then to get the elemental analysis spectra. Figures (1, 2, 3, 4 and 5) represent these elemental analyses in the raw state and the following figures (6, 7, 8, 9 and 10) represent the analyses of the samples when they were treated under hydrogen:

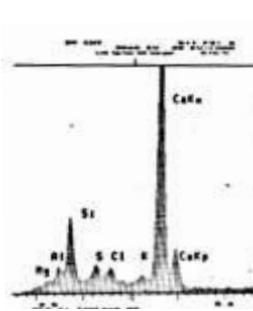


Fig1: Raw Z0 layer

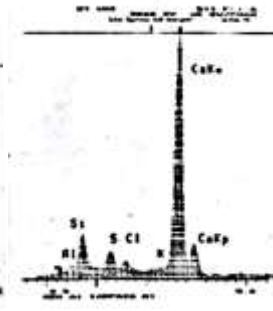


Fig2: Raw Z1 layer

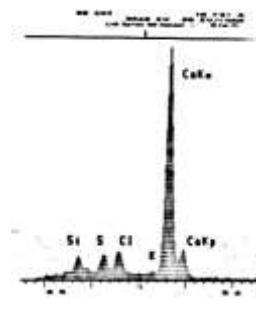


Fig3: Raw Z2 layer

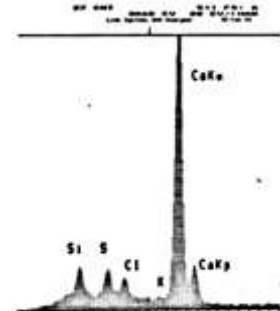


Fig4: Raw Z3 layer

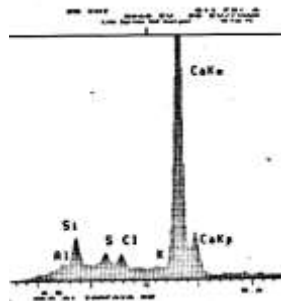


Fig5:- Raw Z4 layer.

For the hydrogen treated samples, their XRD analysis can be found in the following spectra:

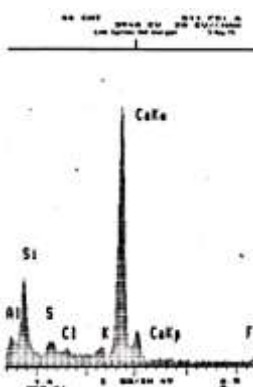


Fig6: Z0 hydrotreated at 550°C

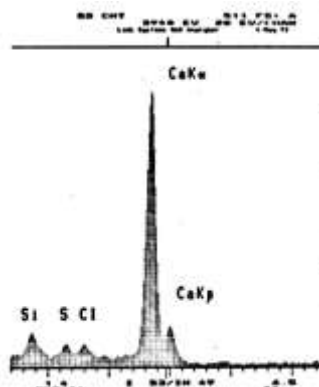


Fig 7: Z1 hydrotreated at 550°C

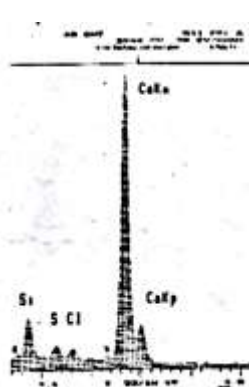


Fig8: Z2 hydrotreated at 550°C

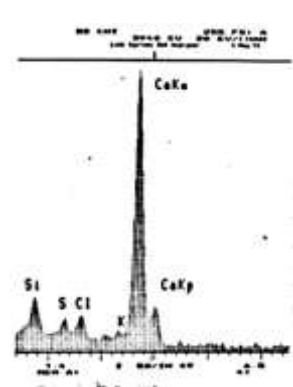


Fig9: Z3 hydrotreated at 550°C

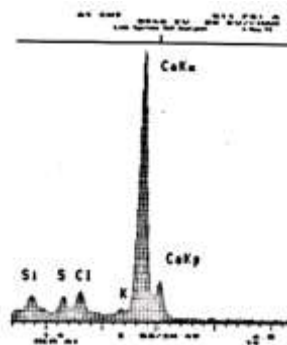


Fig10:- Z4 hydrotreated at 550°C.

2.2: Experimental results.

The results of these spectra are shown in the following table 3. It should be remembered that the spectra with which the measurements and calculations were made have A4 forms, the spectra in the text are reduced forms. The same spectra were used for hydrodesulphurization in a previous work (M.Hafid and A.Attaoui: 2022).

Table 3:- Percentage of chemical elements in the Tarfaya oil shale.

Composition	Type of 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
Aluminium	Crude	2,35	1,2	1,4	1,15	0,8	5,46	3,69	3,72	3,18	2,67
	Treated by H ₂ at 50°C	1,9	0,95	0,8	1,35	0,8	6,13	3,15	2,98	3,97	2,66
Silicom	Crude	6,5	3,6	3,4	3,1	1,95	15,11	10,97	9,57	8,58	6,52
	Treated by H ₂ at 50°C	5,4	3,25	2,1	3,65	1,8	17,42	10,78	7,83	10,75	5,99
Sulphur	Crude	2,4	2,15	2,15	2,9	2,1	5,58	6,55	5,72	8,03	7,02
	Treated by H ₂ at 50°C	1,6	1,5	1,45	2,2	1,75	5,16	4,97	5,41	6,48	5,82
chlorine	Crude	2,2	1,5	2,05	2,3	2,3	5,11	4,57	5,45	6,37	7,69
	Treated by H ₂ at 50°C	1,1	1,3	1,45	2,4	2,1	3,54	4,31	5,41	7,07	6,98
Potassium	Crude	1,6	1,0	1,1	1,0	0,8	3,33	3,04	2,92	2,77	2,67
	Treated by H ₂ at 50°C	1,2	0,8	0,8	1,5	1,00	3,87	2,65	2,98	4,42	3,32
Calcium _α	Crude	22,3	19,6	22,6	21,2	18,5	51,86	59,75	60,1	58,72	61,87
	Treated by H ₂ at 50°C	15,8	18,6	16,6	18,6	18,8	50,97	61,69	61,94	54,78	62,56
Calcium _β	Crude	3,85	2,8	3,75	3,2	2,5	8,9	8,53	9,97	8,86	8,36
	Treated by H ₂ at 50°C	2,2	2,8	2,45	3	2,85	7,09	9,28	9,14	8,83	9,48
Magnesium	Crude	1,15	0,6	0,8	0,7	0,6	2,67	1,8	2,12	1,93	2,01
	Treated by H ₂ at 50°C	1,15	0,6	0,8	0,7	0,6	3,71	1,99	2,98	2,06	1,99
iron	Crude	0,65	0,35	0,35	0,55	0,35	1,51	1,06	0,93	1,52	1,17
	Treated by H ₂ at 50°C	0,65	0,35	0,35	0,55	0,35	2,09	1,16	1,3	1,62	1,16

It should be noted that the percentages present are relative to each other for the same oil shale layer.

3: The elements of the layers in the raw state, treated under hydrogen and analyzed by RXD

3.1: Calcium element

According to the spectra we have two kinds of calcium, CaK_{α} and CaK_{β} , CaK_{α} increases with depth while the more stable CaK_{β} decreases with depth (figure 11 and figure 12):

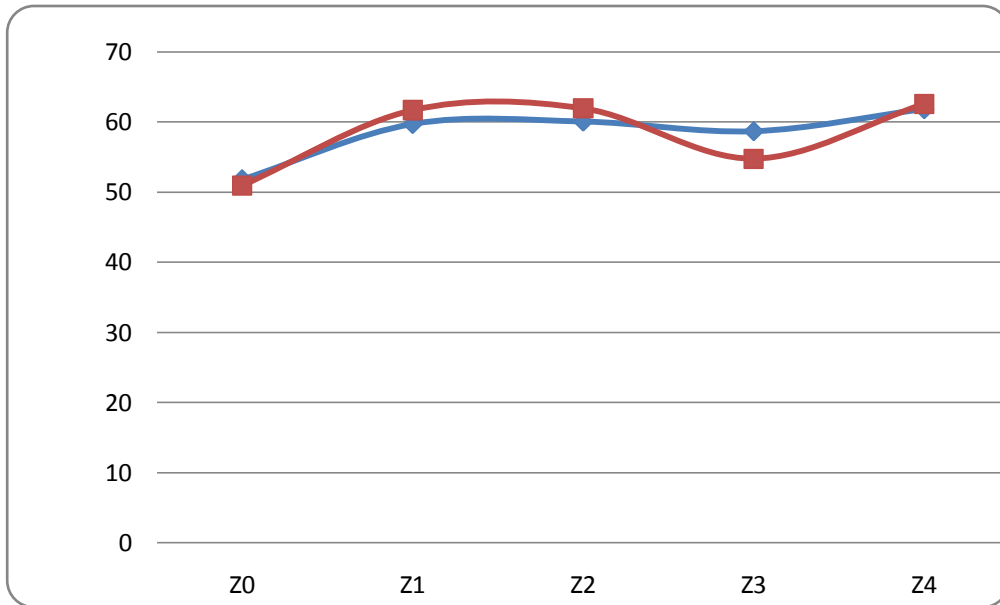


Fig 11:- Raw CaK_{α} and CaK_{β} and CaK_{α} hydrotreated at 550°C

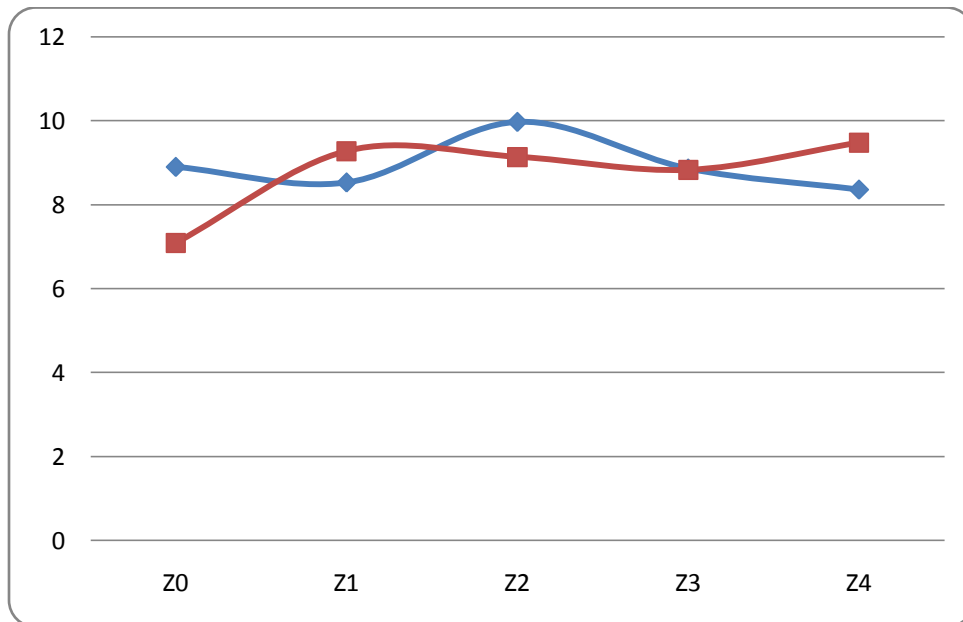


Fig 12:- Raw CaK_{α} and CaK_{β} and CaK_{α} hydrotreated at 550°C

For CaK_{α} it is the Z3 layer that reacts best to hydrotreating because of its high reactivity. For CaK_{β} it is the Z0 and Z2 layers that react to hydrogen. Total calcium (CaK_{α} , CaK_{β}) occurs in the case of the Tarfaya shale either as calcite, calcium chloride dolomite, free calcium or oxidized calcium stored in the form of sedimentary rocks or originating from erosion and sedimentation, the concentration of this element is almost the same in the different oil shale layers.

3.2: Silicon and aluminum elements

The elements silicon and aluminum are the constituents of clays. Figures (13, 14) show these elements, silicon and aluminum, in their raw and hydrotreated states. These elements have different percentages with the fact that silicon is more concentrated than aluminum, in fact silicon also comes from quartz and sand which are very abundant in the marine environment whereas aluminum is generally found in clays.

We can see that the percentage of these two elements decreases with depth. For the action of hydrogen, we notice that it is less sensitive, nevertheless, we observe the same effect whether it is for silicon or for aluminum concerning all the layers.

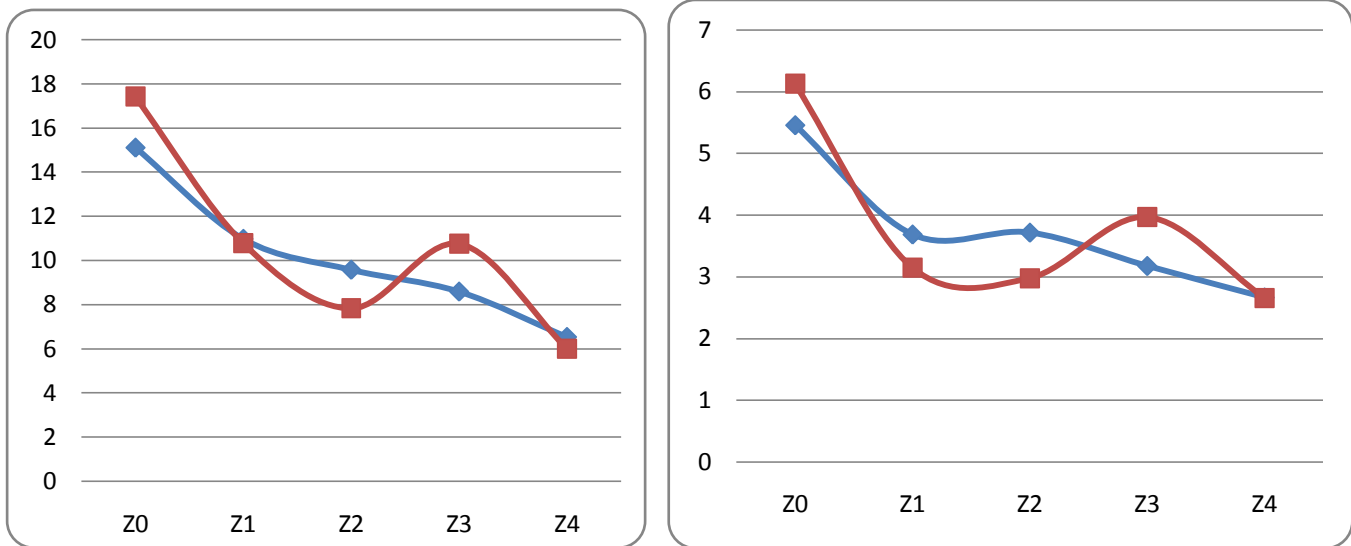


Fig 13: Raw silicon percentage ■ ■ ■ **Fig 14:** Raw aluminum percentage ■ ■ ■ and silicon hydrotreated at 550°C ■ ■ ■ and aluminum hydrotreated at 550°C ■ ■ ■

3.3: Chlorine element:

According to the percentages of chlorine we observed that this element chlorine increases with depth, in the order Z0, Z1, Z2, Z3, and Z4. So we can say that the increase of chlorine concentration with depth is caused by the infiltration and solubility of salt (NaCl) present by rainwater through the oil shale layers.

Concerning the element chlorine in the hydrotreated state at the different layers we noted a low activity, this compound generally formed from calcium chloride and free chlorine up to this considered temperature (550°C) reacts weakly with hydrogen. A slight reactivity for the Z0 and Z4 layers

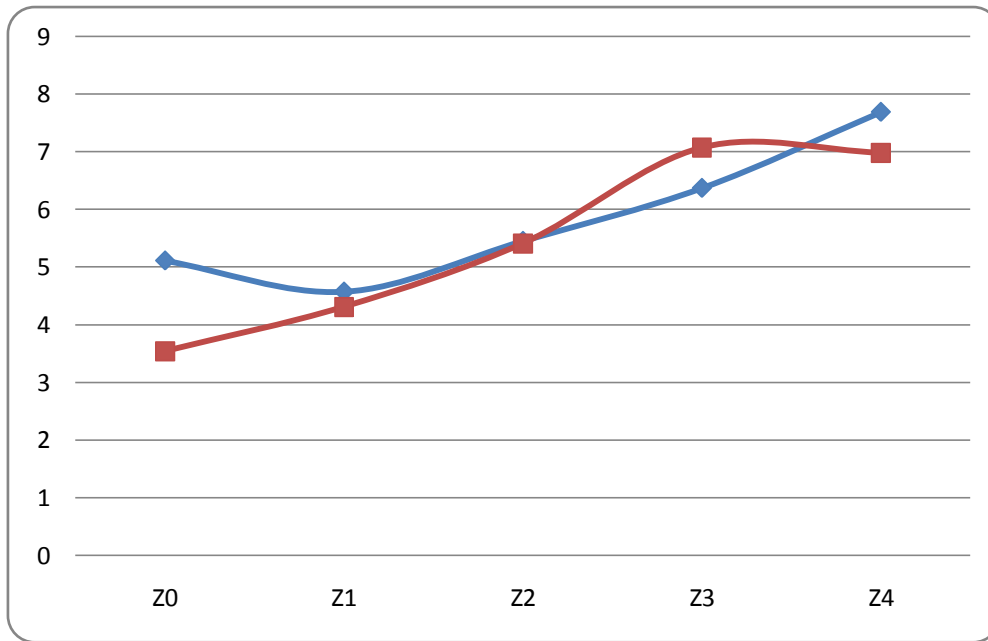


Fig 15:-Raw chlorine percentage ■■■ and chlorine hydrotreated at 550°C ■■■

3.4: Element magnesium and element potassium:

According to the percentage of magnesium we observed a classification of the presence of magnesium as follows Z0> Z2> Z1> Z3> Z4. From this classification we can see a high concentration of magnesium in the layers Z2, Z0, these layers are formed in the cold geological stage i.e. concentrated in mineral matter, on the contrary for the layers Z3, Z1, Z4 formed in the warm geological stage and which are concentrated in organic matter. From this we conclude that the magnesium in the oil shales comes from mineral matter (Figure 16).

We note that the oil shale layers formed in the warm geological layers (Z1, Z3, Z4) react well with hydrogen, unlike the Z0 and Z2 layers (cold zone) where we observe a certain increase in the presence of magnesium, thus proving an inertia to hydrogen. Thus hydriding is strongly observed in the Z1, Z3 and Z4 layers.

It should be noted that the peaks of the corresponding elements are relative to each other for the same oil shale layer, when the percentage of an element increases for some layers and keeps the same value for others it means that we have a hydrogen inertia for the former and a hydrogen reactivity for the latter.

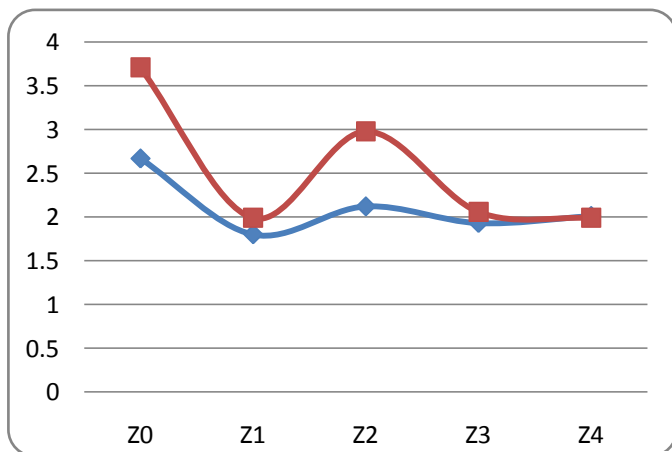


Fig 16: Raw magnesium percentage ■■■ and magnesium hydrotreated at 550°C ■■■

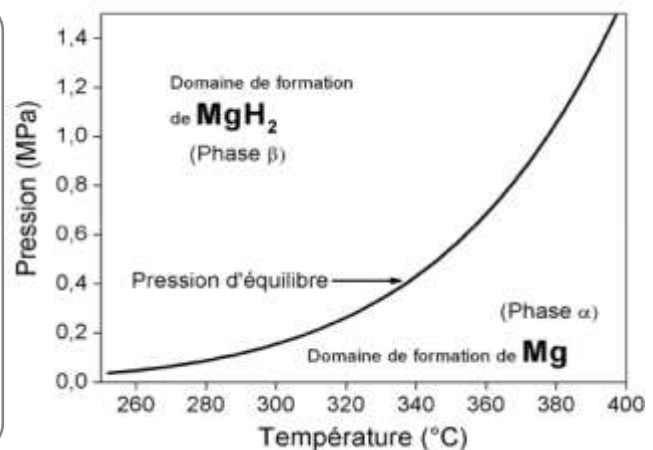


Fig 17: Domains of existence for Mg and MgH2 and equilibrium curves in the P - T diagram (P.De.Rango et al: 2016).

For the element potassium, a decrease in concentration is observed in the raw state from the layer Z0 to the deep layer Z4 (Figure 17). Thus, the raw potassium decreases with depth.

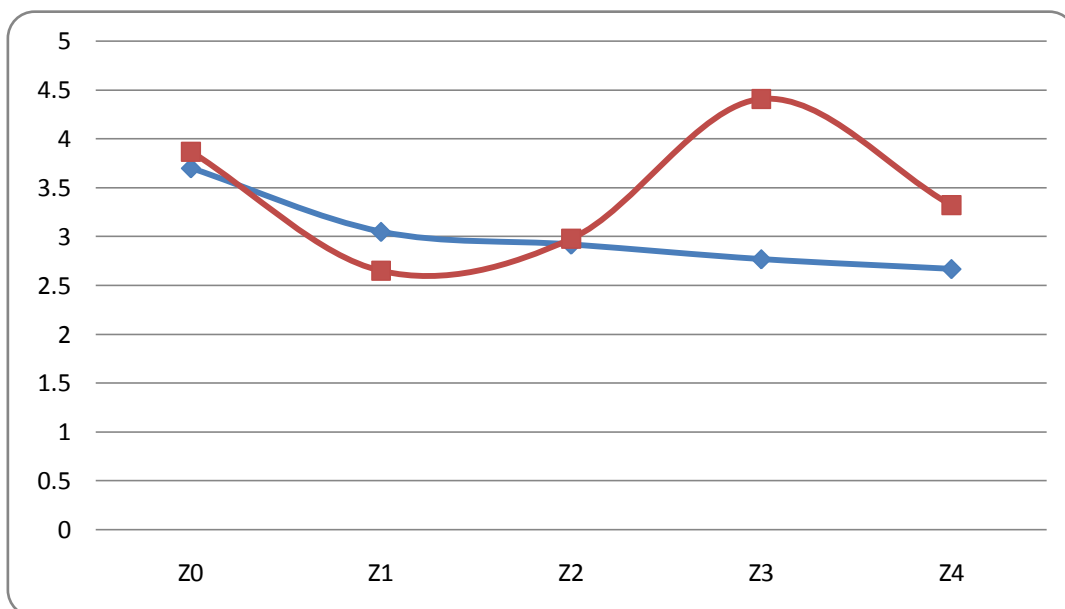


Fig 18:-Raw potassium percentage ■ ■ ■ and potassium hydrotreated at 550°C ■ ■ ■

Conclusion:-

The contribution of hydrogen even at atmospheric pressure finds its interest in several effects. During the dynamic regime chosen up to a temperature of 550°C, we have noted the interest of the use of hydrogen, firstly an increase in reactivity compared to the use of nitrogen (A. Attaoui et al: 1992), then in the context of the elimination of the corrosive element sulphur (HDS), we have a sensitization to the presence of hydrogen (M. Hafid and A. Attaoui: 2022).

The effect of hydrogen does not stop at the organic matter, but it also extends to the mineral matrix, as the production of hydrides, which are fuels, is achieved by the reaction of hydrogen with all metallic elements. We also note that although the curves are very close between the crude samples and the hydrotreated ones, the peaks are relative to each other as well as their decomposition as a whole.

The calcium hydride CaH_2 (the majority element) is produced between 300°C and 400°C, which is verified in our working conditions, this calcium comes from calcite and dolomite. CaK_α increases with depth, unlike CaK_β , which is the most stable element and decreases with depth. For CaK_α it is the Z3 layer that reacts best to hydrotreating because of its high reactivity. For CaK_β it is the Z0 and Z2 layers that react to hydrogen.

For magnesium we observed a classification of presence as follows $\text{Z0} > \text{Z2} > \text{Z1} > \text{Z3} > \text{Z4}$. and according to this classification we can observe a high concentration of magnesium in the layers Z2, Z0, these layers are formed in the cold geological stage i.e. concentrated in mineral matter, on the contrary for the layers Z3, Z1, Z4 formed in the warm geological stage and which are concentrated in organic matter (A. Malal, D. Lahmadi and A. Attaoui: 2022). From this we conclude that the magnesium in the oil shale comes from mineral matter, so the magnesium decreases with depth. We note that the oil shale layers formed in the warm geological layers (Z1, Z3, Z4) react well with hydrogen (formation of magnesium hydride MgH_2) in contrast to the Z0 and Z2 layers (cold zone) where we observe a certain increase in the presence of magnesium, thus proving inertia to hydrogen. Hydriding is therefore strongly observed in the Z1, Z3 and Z4 layers.

For silicon and aluminum, which are the constituents of clays, silicon and aluminum, in their raw and hydrotreated states. These elements have different percentages with the fact that silicon is more concentrated than aluminum, in fact silicon also comes from quartz and sand which are very abundant in the marine environment whereas aluminum is generally found in clays. We can see that the percentage of these two elements decreases with

depth. For the action of hydrogen (formation of SiH_4 and AlH_3) we notice that it is less sensitive, nevertheless, we observe the same effect whether it is for silicon or for aluminum concerning all the layers.

Chlorine increases with depth, in the order Z0, Z1, Z2, Z3, Z4, so we can say that the increase of chlorine concentration with depth is caused by the infiltration and solubility of salt (NaCl) present by rainwater through the oil shale layers. For the element chlorine in the hydrotreated state (HCl formation) at the different layers we noted a low activity, this compound generally formed from calcium chloride and free chlorine up to this considered temperature (550°C) reacts weakly with hydrogen. A slight reactivity for the Z0 and Z4 layers.

For the element potassium, a decrease in concentration from the Z0 layer to the deep Z4 layer is observed in the raw state. Potassium hydride KH, which has a boiling point of 316°C, is formed by the direct combination of molecular hydrogen and the alkali metal potassium.

References:-

- [1] J.C. Janka, R.C. Rex. AICHE.1984 August.19-22.
- [2] J.C. Janka and J.M. Dennison, Paper presented at 10T Sympo on synthetic. Fuel.From oil shale, Atlanta, Georgia. Dec. 3-6. 1979.
- [3] R.D. Matews and all.AAPG. Bulletin Vol. 65. N° 5. 1981. 53.
- [4] O.M. Larson and C.S. Wen. Proceeding of the 14th oil shale symposium Colorado school of Mine 1981. 161.
- [5] W.G. Schlinger and D.R.Q. Jess.Colo.Sch. Mines 62. 1967. 133.
- [6] M.G.Q. Huntington. Colo. Sch. Mines.61. 1966. 135.
- [7] P.B. Tarman and all AIME.EasternRegMeeting.Pittsburg P.A. 1977. Oct.
- [8] S.A. Weil and all D. US Patent 4003821. 1977.
- [9] N. Toreis and all.Ind. Eng. Chem. Process.Des.Dev. 25. 1986. 552.
- [10] Michael J. Roberts, David M. Rue and Francis S. Lau, Pressurized fluidized-bed hydroretorting of six eastern shale in batch and continuous laboratory-scale reactors, Received 3 April 1991; revised 23 August 1991;
- [11] Federal Register, Thursday March 29, 1990, Part II Environmental Protection Agency, 40 CFR Part 261, pp. 11845-1 1846
- [12] Burnham, A. K.; Happe, J. A. On the Mechanism of Kerogen Pyrolysis. Fuel 1984, 63 (10), 1353
- [13] Davis, J. B.; Stanley, J. P. Catalytic Effect of Smectite Clays in Hydrocarbon Generation Revealed by Pyrolysis-Gas Chromatography. J. Anal. Appl. Pyrol. 1982, 4, 227.
- [14] Regtop, R. A.; Ellis, J.; Crisp, P. T.; Ekstrom, A.; Fookes, C. J. R. Pyrolysis of Model Compounds on Spent Oil Shale, Minerals and Charcoal. Fuel 1985, 64, 1640.
- [15] M. Hafid and A. Attaoui, Behaviour of the different layers from Tarfaya deposit (Morocco) in thermal hydrodesulphurization at 550°C, Int. J. Adv. Res, DOI : 10.21472/IJAR01/15199, August, 2022, 10(08), 459-472
- [16] P. De Rango, P. Marty and D. Fruchart, Hydrogen storage systems based on magnesium hydride, From laboratory test to fuel integration, Applied Physics A. 122.(2), DOI : 10.1007/S00339-016-9646-1, February. 2016.
- [17] A. Attaoui and L. Belkbir journal of Alloys and compounds, 188(1992) 202-205.
- [18] Ahmed Malal, Doha Lahmadi and Abdeljabbar Attaoui, "Type of burial and adaptation of the geological ages with the sedimentation of the organic matter for the different layers for the Tarfaya's oil shale deposit (Morocco)", Int. J. Adv. Res. 10(04), 372-382, April 2022, DOI: 10.21474/IJAR01/14557.