RESEARCH ARTICLE

QUANTITATIVE APPROACH OF CARBONATES, CALCITE AND DOLOMITE FROM THE TARFAYA, Z3 AND Z4 OIL SHALE LAYERS BY ACID ATTACK (MOROCCO)

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Manuscript Info	*Abstract*
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	The carbonates of the oil shale calcite $CaCO_3$ and dolomite $CaMg(CO_3)_2$ were the object of this study to determine their percentage inside the oil shales. Work has been carried out in the same context **(A.Attaoui and H.Mokhlis:2022)** for the Tarfaya shale layers Z0, Z1 and Z2. However, the Z3 and Z4 layers present a migration of matter: the light organic matter is found in the Z3 layer and the heavy one is present in the Z4 layer, and the heavy organic matter consumes more acid in the attack reaction than the light organic matter for the same mass, which is why it is necessary to follow the decomposition of this organic matter isothermally, especially at 500°C. Therefore, by combining the two reactions and by choosing well-defined isotherms (500°C, 600°C, 700°C and 800°C) we were able to approach the percentages of calcite and dolomite in these particular layers showing the phenomenon of in situ pyrolysis. The techniques used are isothermal combustion followed by HCl acid attacks and return dosing of the acid remaining after the attack. The objective of this study, which is done in return dosing using the Tacussel pH meter, is to establish a table of compositions in mass percentages of calcite and dolomite, which are the constituents of the carbonate of the Tarfaya oil shale (Morocco). Calcite $CaCO_3$ is taken as a control; it was used under the same conditions as the oil shale, i.e. combustion in an isothermal regime, followed by acid attack.

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Introduction:-

The Z3 and Z4 layers in the Tarfaya deposit present a particular behaviour due to the fact that the phenomenon of in-situ pyrolysis (catagenesis) is present **(A.Attaoui et al: 2022)**, and by means of this work we have been able to extend the method of combustion followed by acid attack and dosing already applied in the article **(A.Attaoui and H.Mokhlis: 2022)**, for the identification of the compounds of these two layers. First of all, in order to follow the evolution and decomposition of the different constituents of these two layers of Tarfaya oil shale, it is necessary to carry out isotherms in combustion at well-defined temperatures. The reference chosen is the calcite $CaCO_3$, which undergoes the same treatments as the oil shale layers. The formation of coke during the recycled combustion of oil shale (Rundle) was followed; the results are presented for the coking reactivity during combustion of oil shale to various shale oil fractions and individual oil components. The amount of coke formed is not greatly affected by the coking temperature at temperatures in the range of 500-700°C. However, the temperature at which the shale was burned had a significant effect: much more coke was deposited on shale burned at 700°C than on shale burned at

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900°C. There was no apparent difference between the amount of coke formed on shale burnt under dry conditions and the amount deposited on shale that was burnt in the presence of steam. Shale with an organic carbon content of about 3% by weight, which corresponds to material that had been about 50% by weight burnt, showed little difference in coking activity to that of fully burnt shale. The amount of char produced by separate shale oil fractions increased with boiling range, but at a rate disproportionate to the nitrogen content of the oil-derived fraction. A range of pure compounds, which are typical of oil shale components, have been examined with respect to their coking reactivities of burnt shale (Rundle). The tendency to increase coke formation as a function of chemical structure and boiling point has been observed **(Day and John S. Killingley: 1993).**

1: Literature Review:-

In one type of full-scale integrated shale oil processing plant, oil is extracted by autoclaving crude shale at about 500°C, which converts the kerogen to oil and gas. The heat for this process is provided by burning the organic material remaining during the decomposition of the shale at about 800°C in a combustor of part of the hot solids recycled back into the separate retort. This system has the advantage of not generally requiring additional fuel to provide heat to the process, and also provides good heat transfer between the shale and the raw shale burnt during decomposition. However, a major disadvantage is that hot shale particles can react with the oil vapor in the vessel to produce coke which settles on the shale surfaces. These reactions can lead to substantial reductions in oil yield which in turn can negatively affect the economic viability of the shale oil plant. It is therefore important to know the main factors that influence coke formation so that it can be minimized to increase the overall efficiency of the process.

The objectives of this study were firstly to examine how the reactivity of burnt shale coke from the Rundle deposit (near Gladstone in Queensland, Australia) and the change with combustion conditions to determine whether coke formation could be reduced by burning shale in the presence of steam rather than under dry conditions, or by recycling partially retort-burned shale, and thirdly, to measure the relative coking reactivity of a range of individual pure compounds commonly found in shale oils.

Definitive geochemical and mineralogical results have been obtained for several of the most promising mining sections of the oil shale deposits (Rundle, Condor and Duaringa) **(R.P. Cavalieri et al: 1990).**The mineralogy and geochemistry are broadly similar for the eight samples from the Queensland ternary oil shale deposit. Although there are many similarities between the mineralogy and in the various deposits, there are also some differences. Firstly, the relative amounts of the various minerals have been found to be highly variable with stratigraphic depth and ore type; and secondly, the siderite minerals have been found to be highly variable in composition, and hence in stability and heat treatment characteristics.

The most important minerals in tertiary oil shale processing are smectite, kaolinite, siderite and pyrite. The first three are relatively more abundant in eastern Queensland whereas in most other oil shale they are dehydrated, dehydroxylated or endothermally decomposed during decomposition or combustion. Pyrite is a significant potential source of sulphur gases.

Mineral characterization and thermogravimetric studies were carried out on raw and processed samples from the most prospective sections of Australia's shale (Rundle, Stuart, Condor, Duaringa, Nagoorin, South, Nagoorin, Yaamba and Lowmead oil shale deposits).The effects of processing on the minerals were determined in sufficient detail to establish the relevance of the various minerals and their reactions in the shale process oil. The minerals identified as most important in processing were smectite, kaolinite and siderite-like minerals and pyrite. Minerals such as smectite and siderite minerals are characteristic of oil shale in eastern Queensland **(J.H. Patterson et al: 1990)**.

A TG study of the effect of oil shale mineral composition on coal combustion reactions **(R.P. Cavalieri et al: 1990)** by TG was carried out. Thermal decarburization and water extraction from soluble mineral matter have a significant catalytic effect depending on the species present.

A.Iven and Jr. Jacobson **(A. Iven et al: 1980)** studied the oxidation at decomposition temperatures of shale under an atmosphere consisting of N2, O2, CO2, CO and H2O. Their mathematical model is based on the contraction of the sample volume. Furthermore, it is the diffusibility of oxygen in the shale that delimits the rate of the reaction. According to the same authors **(] A. Iven et al: 1982)**, when studying the combustion of shale in a horizontal reactor

under the same conditions, the percentage of oil production is less than 50% compared to the percentage in the Fisher test. The combustion kinetics of five Australian oil shale samples was studied at 900°C using a fluidized bed reactor. Gas analyses are determined on a continuous basis **(B.G. Charlton: 1988)**. All the degraded oil shale show that the combustion reaction follows the volume contraction model and the model is controlled by diffusion. The infusibility of the gas is controlled by diffusion and is related to the diffusion through the spent shale. The kinetic parameters and activation energies are low compared to carbon combustion, and the combustion temperatures are low compared to those of the US shale.The same author **(B.G. Charlton: 1988)** has shown that the volume contraction model applies to the Naggorin shale, and that this mechanism is attributed to the reaction of highly concentrated carbon. By similarity, Mazumar**(B.K. Mazymard et al: 1957)** oxidized coals in air and Robinson et al **(W.E. Robinson et al: 1963)** oxidized Colorado shale at a temperature of 170°C for 14 weeks also in air. They noted that the H/C ratio decreased from 1.59 to 0.63 while the O/C ratio increased from 0.1 to 0.46. J.H Levy and KI Stuart **(J.H. Levy et al: 1984)** studying the combustion of kerogen show that it evolves in two stages which are indicated by the presence of two peaks in DTG. The first peak is due to the reaction of the aliphatic compounds, while for the second peak they suggest that it is the reaction of the aromatic chains that is predominant. Similarly Uden**(P.C. Uden: 1980)** and C.M. Earnest **(C.M. Earnest: 1983)**, in oxidizing shale in air, noted the presence of two stages which vary in position and intensity in the thermogravimetric diagram, depending on the composition of the organic matter and in some cases that of the mineral matter I.C Lee and H.S. Sohn**(C. Lee and H.Y. Sohn: 1986)** studied the oxidation kinetics of Colorado shale in air using the technique of thermogravimetric analysis with a continuous linear temperature rise. Their kinetic data are analyzed at low temperatures, conditions under which they claim that the oxidation reaction occurs at the surface of the solid (kerogen) at temperatures where the kerogen does not decompose. Furthermore, the oxidation rate is first order with respect to the partial pressure of oxygen, the calculated activation energy is (11.0 2.3) KJ/mol and the frequency factor is (6.8 2.5) 10-6 m (kPa s)$^{-1}$.

2: Experimental study
2.1:X-ray diffraction:
The following spectra represent the X-ray diffraction (XRD) of Z3 and Z4 layers of Tarfaya's deposit (Morocco), they are classified from bottom to top respectively Z3 and Z4.
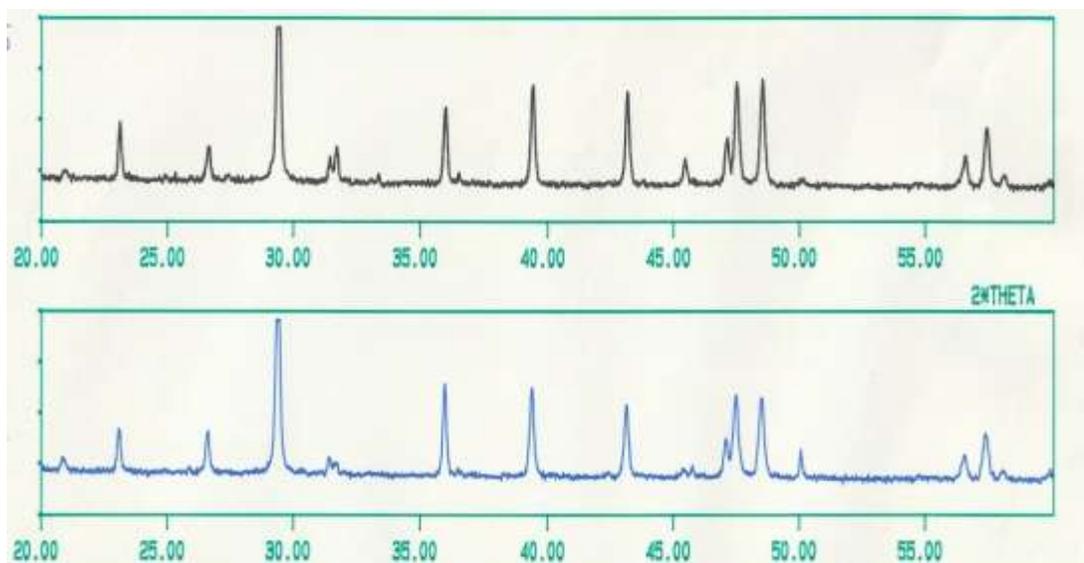
Fig1:- X-ray spectra classified from bottom to top of the Z3 and Z4 layers of Tarfaya's oil shale.

2.2: Isothermal combustion of oil shale (Z3 and Z4) and Calcite (CaCO$_3$) at different temperatures.
0.5g of each sample (oil shale and calcite) was weighed (using a balance) and placed in a crucible. The samples were then placed in a muffle furnace where they were burnt at different temperatures (from 500°C to 800°C) in an isothermal regime, the combustion was carried out for 30 min with an air access inside the furnace every 10 min, and finally the samples were weighed a second time after the combustion.

Fig 2:-Balance.

Fig 3:-Muffle furnance.

The results in percentage loss for this combustion at different temperatures for the Z3 and Z4 layers as well as the pure calcite taken as reference are presented in the following table:

Table 1:- Percentage losses for the combustion at different temperatures for the Z3, Z4 layers and Calcite.

	Z3			Z4			Calcite		
	Masse (g)	remaining masse	% of loss	Masse (g)	remaining masse	% of loss	Masse (g)	remaining masse	% of loss
500°C	0.5	0.364	13.6	0.5	0.371	12.9	0.5	0.495	0.5
600°C	0.5	0.36	14	0.5	0.359	14.1	0.5	0.493	0.7
700°C	0.506	0.337	16.9	0.502	0.308	19.4	0.505	0.48	2.5
800°C	0.507	0.289	21.8	0.5	0.27	27	0.5	0.282	21.8

We notice, first of all, the classification of the different layers with regard to their composition of organic matter, given the decomposition range of the latter, i.e. around 400 -500°C. This classification is already known and we have first Z3 which is the most concentrated in hydrocarbons followed by Z4.

2.3: Acid attack (HCl) of calcite previously combusted at different temperatures from 500°C to 800°C.
Acid etching is often used for the case of compounds releasing CO2 in gasometry. Samples having undergone combustion at different temperatures were subjected to this acid etching, 0.2 g of sample is etched by 50 cm3 of Hcl (0.1N) then a filtration is made and 10 cm3 of the filtrate is dosed with NaOH (0.077 N) to conceive the quantity which was consumed during this etching (back determination). This part of the determination is done by PH-meter (Tacussel with Orion electrode).

Air, which is a more reactive medium than nitrogen, will weaken the temperature range of calcite decomposition.
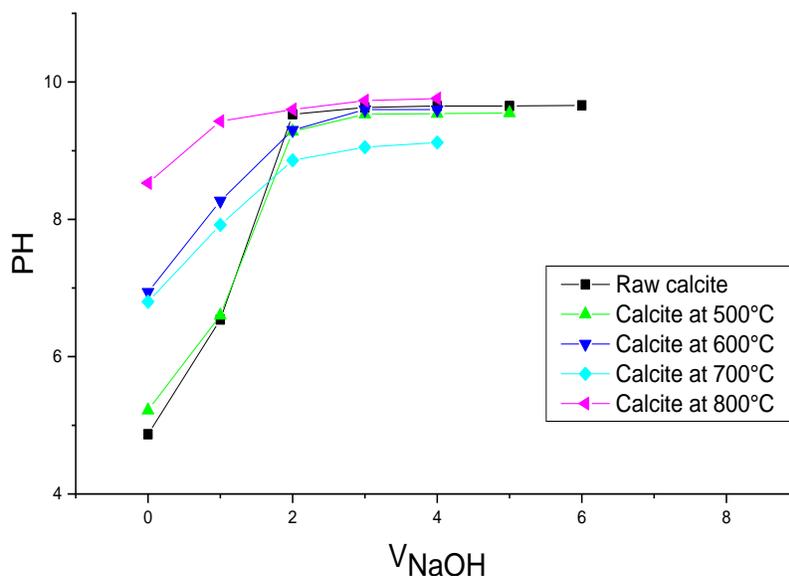
Fig 4:- Determination of acid attack of calcite burnt at different temperatures.

Table 2:- Dosing volumes and acid dosing volumes used for calcite etching for combustions at different temperature.

	Dosage volume (cm^3)	PH	Volume of dosage of acide used for the attack (cm^3)
HCl alone	13	6	
Raw calcite	1,2	6,8	11,8
Calcite treated at 500°C	1,2	7,8	11,8
Calcite treated at 600°C	1,2	8,2	11,8
Calcite treated at 700°C	1	8	12
Calcite treated at 800°C	1,5	9	11,7

2.4: Acid attack of different oil shale layers in the raw state
The same conditions were used for the study of the different oil shale layers in the raw state, the dosages that were made are represented in the following figure.2.4: Acid attack of different oil shale layers in the raw state
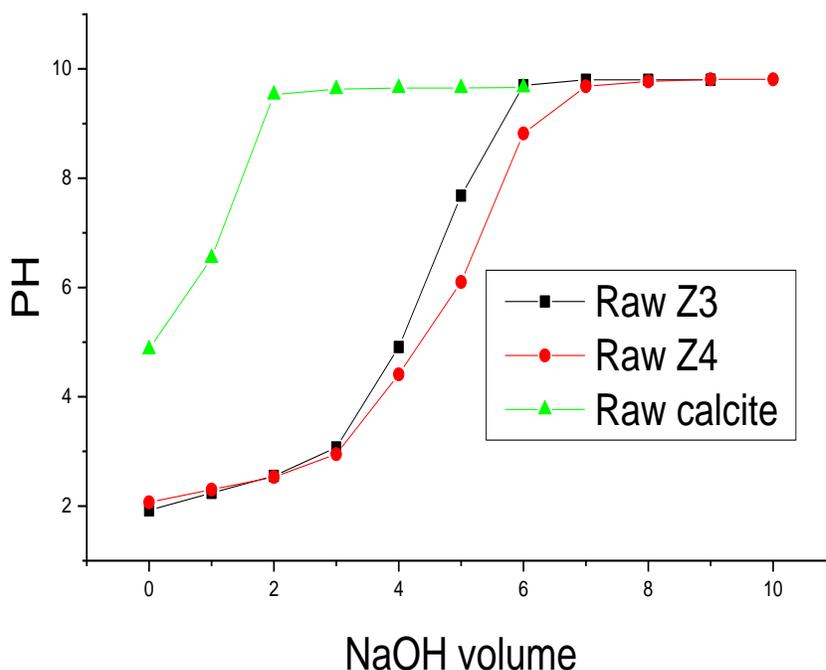
Fig 5:- NaOH dosing curves for HCl from acid etching of different layers of raw oil shale and raw calcite (Z3, Z4 and CaCO$_3$).

The table showing the dosing volumes and the volumes used for etching is as follows:
Table 3:- Dosing volumes and acid dosing volumes used to etch different layers of raw oil shale.

sample	Dosage volume (cm^3)	PH	Volume of dosage of acide used for the attack(cm^3)
HCl alone	13	6	-
Raw Z3 layer	4,4	6,2	8,6
Raw Z4 layer	5	6	8

By a simple correspondence it was possible to approach the composition, firstly in carbonates and included OM sensitive to HCl for the two layers which manifests itself in this way.

Table 4:- The carbonate and organic matter composition of the different oil shale layers.

Layer	Composition of carbonates and organic matter in percent by weight (sensitivity to HCl)
Z3	72,9%
Z4	67,8%
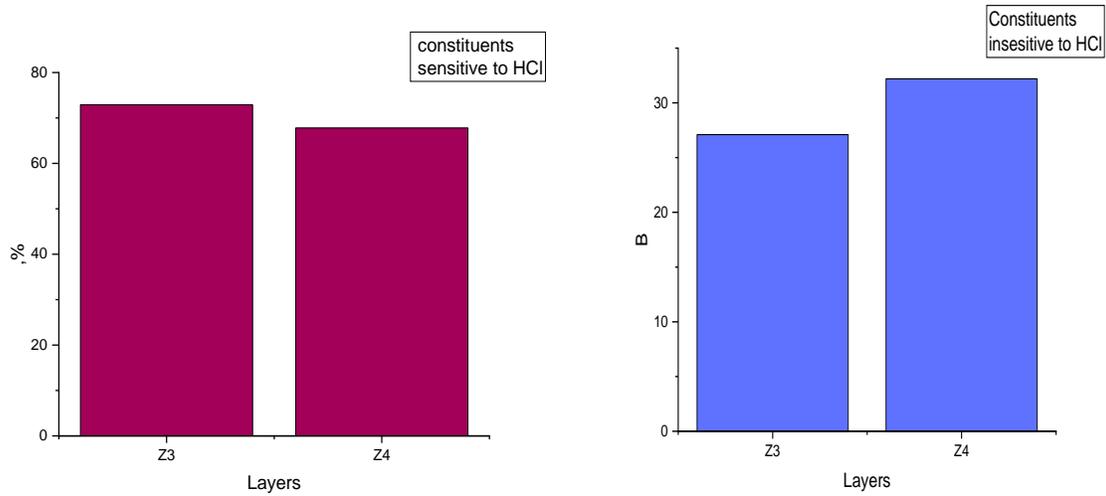
2.5:- Identification of organic matter at 500°C.

The Z3 and Z4 layers have different organic matter (**A.Attaoui et al: 2022**), heavy organic matter is concentrated in Z4, conversely light organic matter is concentrated in Z4 (catagenesis). Therefore the acid attack cannot distinguish between the two layers quantitatively; the heavy organic matter needs more HCl than the light one. To identify the organic matter we have to use table 1 of the decomposition of the layers in air at the 500°C isotherm, so we have:

Sample	Percentage of organicmatter
Z3	13,6%
Z4	12,9%
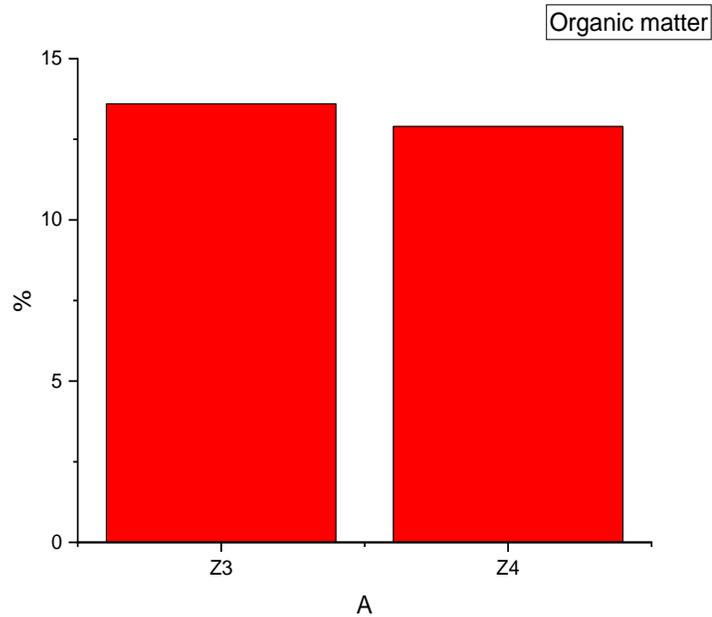
2.6:- Acid attack of oil shale samples at different combustion temperatures.

The following curves represent the return dosage (NaOH) of this acid attack for shale samples having undergone combustion at different temperatures.

The samples are the Z3 and Z4 layers of the Tarfaya deposit.
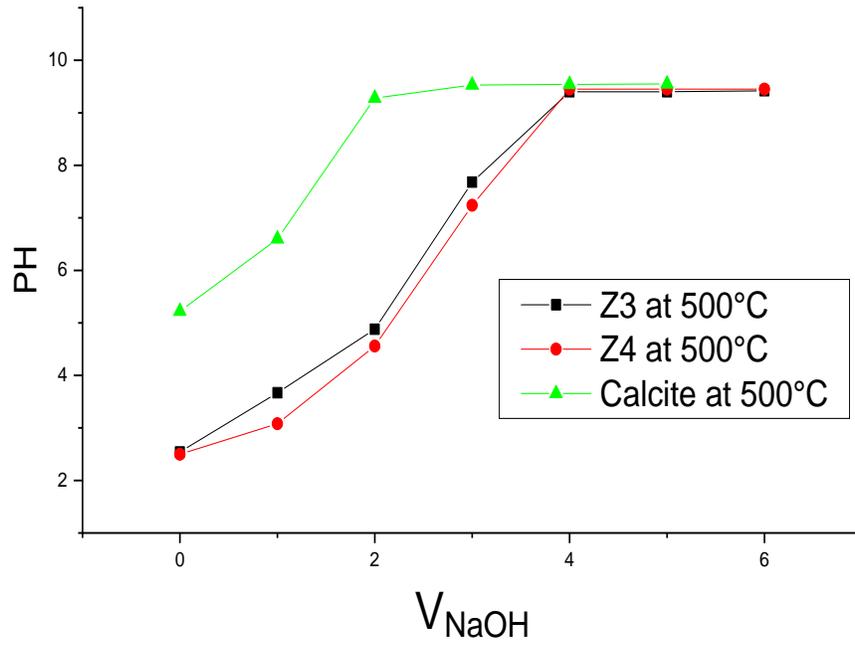
Fig 6:- HCl dosage curves from acid etching for different layers of oil shale (Z3, Z4) and calcite (CaCO$_3$) treated at 500°C.
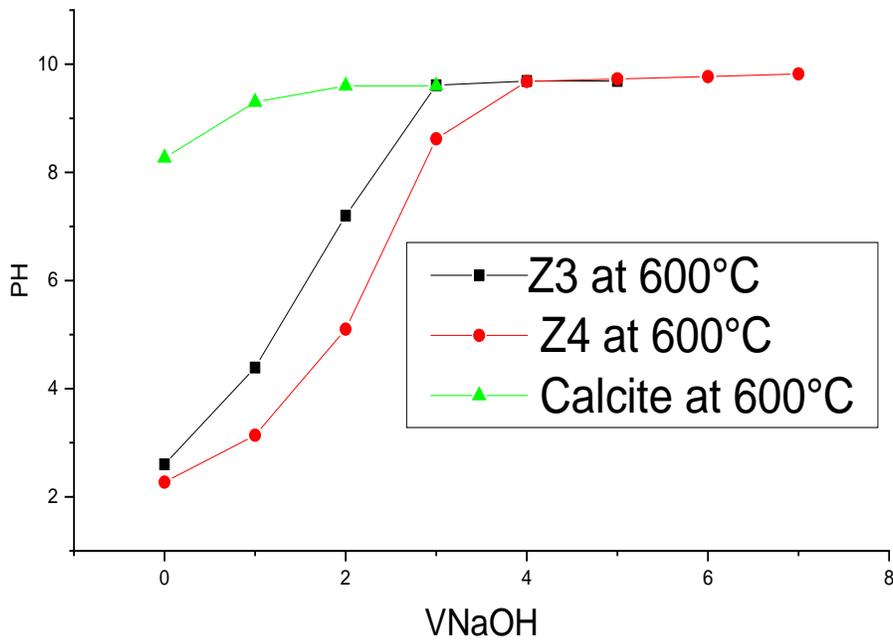
Fig 7:- HCl dosage curves from acid etching of different layers of oil shale (Z3, Z4) and calcite (CaCO$_3$) treated at 600°C.
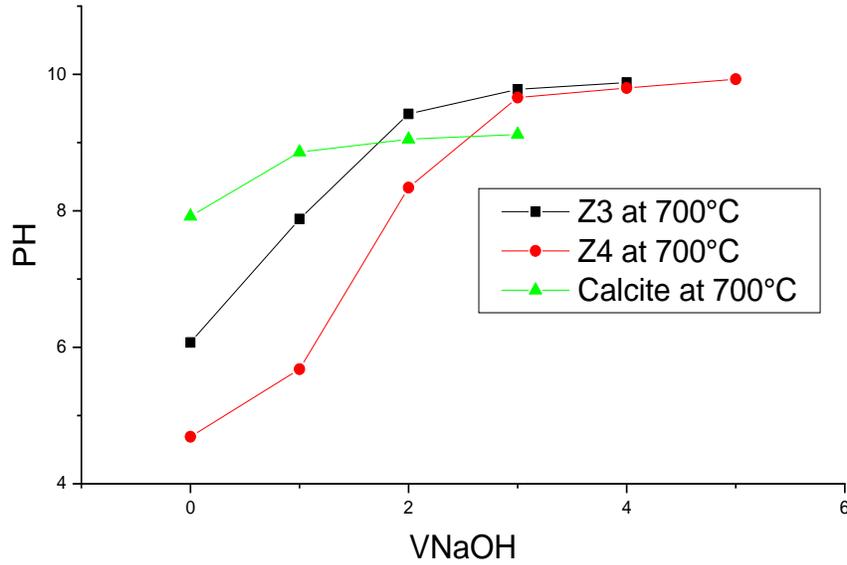
Fig 8:- HCl dosage curves from acid etching for different layers of oil shale (Z3, Z4) andcalcite($CaCO_3$) treated at 700°C.
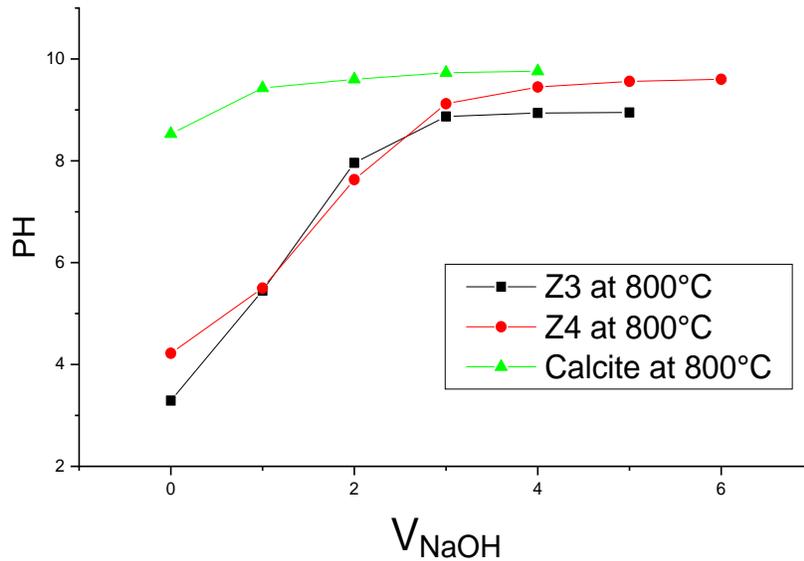
Fig 9:- HCl dosage curves from acid etching of different layers of oil shale (Z3, Z4) and calcite($CaCO_3$) treated at 800°C.

The following table (5) shows the dosing volume of 10 (cm^3) of the filtrate (same operating conditions as above), the pH at neutralization, the actual dosing volume taking into account the decomposition at the temperature considered and the actual volume of acid attack depending on the temperature.

Table 5:- Dosing volume, pH on neutralization and actual acidic attack volume according to temperature.

	dosage volume (cm^3)	PH	dosage volume of acide used for the attack(cm^3)
Hclalone	13	7	------
Layer Z3 treated at 500°C	2,6	6,4	10,4
Layer Z4 treated at 500°C	2,6	6,2	10,4
Layer Z3 treated at 600°C	1,8	6,3	11,2
Layer Z4 treated at 600°C	2,4	6,2	10,6
Layer Z3 treated at 700°C	2,4	6,2	10,6
Layer Z4 treated at 700°C	1,8	7,6	11,2
Layer Z3 treated at 800°C	1,2	5,6	11,8
Layer Z4 treated at 800°C	1,6	6,8	11,4

The decomposition stages of oil shale in an inert or reactive medium (air) are well known, they are generally composed of three temperature ranges. In the case of air, considering its reactivity, it will lower these temperature ranges compared to nitrogen. We have:

Ambient ------------- 280°C Water and volatile gases reach
280°C   -------------- 460°C reaching organic matter
460°C   -------------- 800°C reaching carbonates

To establish an approach to the composition of the different oil shale layers we will share the different combustion temperatures chosen according to the previous steps mentioned

2-7. Determination of other compounds in the different Z3 and Z4 layers of the Tarfaya deposit
The temperature ranges chosen are superimposed for successive and sometimes simultaneous decomposition when it comes to the more or less responsive constituents in the oil shale, and in this respect we divide the material combustion ranges as follows:
*Ambient-500°C: thermal activation and combustion of organic matter
*500°C-600°C: combustion of calcite
*600°C-700°C: combustion of dolomite and thermal activation
*700°C-800°C: thermal activation.
The different isotherms attacked by hydrochloric acid and dosed by NaOHare shown in the following figures for each layer Z3 and Z4 of the Tarfaya deposit in the following figures:
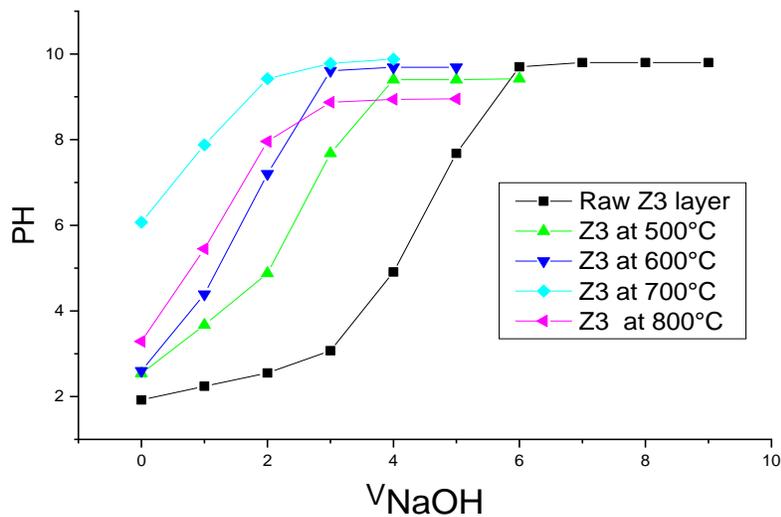
Fig 10:- Curves of HCl dosing by NaOH from acid attack of the Z3 oil shale layer, raw andtreated from 500°C to 800°C in air in isothermal conditions.
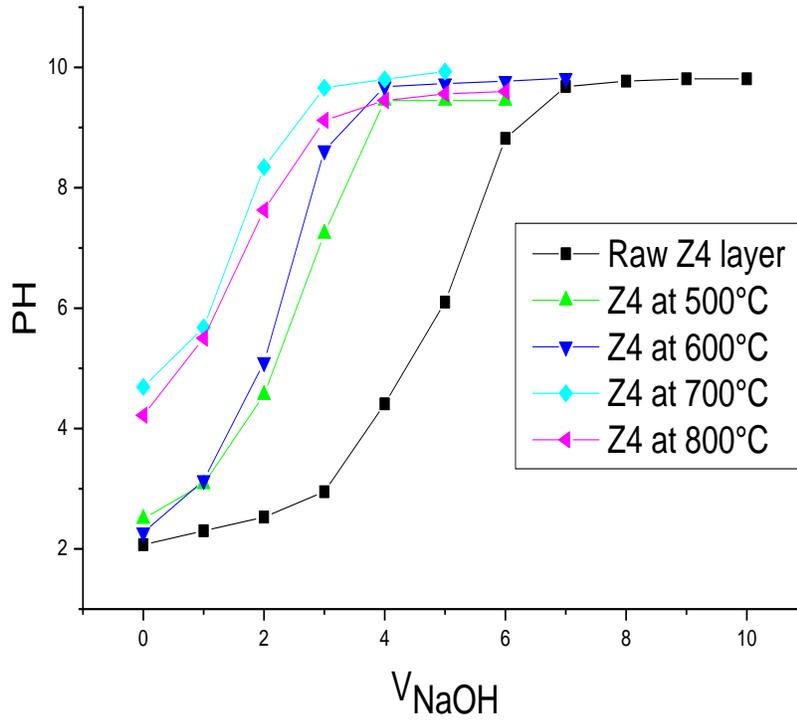
Fig 11:- Curves of HCl dosing byNaOH from acid attack of the Z4 oil shale layer, raw and treated from 500°C to 800°C in air in isothermal conditions.

We have noted that the decomposition of organic matter in air takes place at 500°C, we have calculated the percentages of this organic matter according to the decomposition in Table 1, and for the carbonates we have collected the volumes of the acid used for the attack at temperatures of 600°C, 700°C and 800°C (Table 6)

Table 6:- Dosing volumes (cm^3) from 600°C to 800°C.

Sample	600°C	700°C	800°C
Z3	11,2	10,6	11,8
Z4	10,6	11,2	11,4
Calcite	11,8	12	11,7

- Calcite:

The decomposition range of calcite is well known (**J.H. Campbell et al: 1987**), it is around 600°C. We will deal with the values in this temperature, taking also calcite as a standard:

*for Z311.2/11.8 =47.83%

*for Z410.6/11.8 =42.1%.

We gather the values in the following table considering the compounds sensitive to HCl acid attack:

Sample	Percentage of dolomite	Percentage of dolomite taking into account the HCl sensitive part
Z3	47,83 %	47,83 ×72,9 %=34,9 %
Z4	15,2 %	42,1×67,8 %=28,5 %
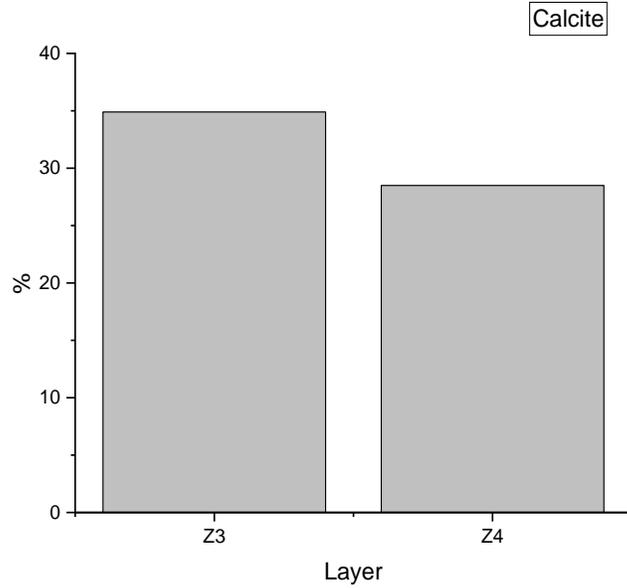
- **Dolomite**

Similarly, the decomposition range of dolomite is well known (**J.H. Campbell et al: 1987**), it is around 700°C. We will treat the values as follows: we will calculate the average of the volumes at 600°C and 700°C and make the difference with the volumes at 800°C. We will also use calcite as a standard, therefore:

Mean of the volumes at 600°C and 700°C being:

*for Z3 11.2 + 10.6 =21.8/2 =10.9 cm3

*for Z4 10.6 + 11.2 = 21.8/2=10.9 cm3

Differentiating from the volumes at 800°C:

*for Z3 11.8 - 10.9 = 0.9 cm3

*for Z4 11.4 - 10.9 = 0.5 cm3

Therefore the percentages of dolomite are;

*for Z3 0.9/11.7 = 7.6%

*for Z4 0.5/11.7= 4.3%

We gather the values in the following table considering the compounds sensitive to HCl acid attack:

Sample	Percentage of dolomite	Percentage of dolomite taking into account the HCl sensitive part
Z3	7,6 %	7,6 ×72,9 %= 5,5 %
Z4	4,3 %	4,3×67,8 %= 2,9 %

We note that the percentage of dolomite decreases with depth, as does the percentage of all mineral matter.
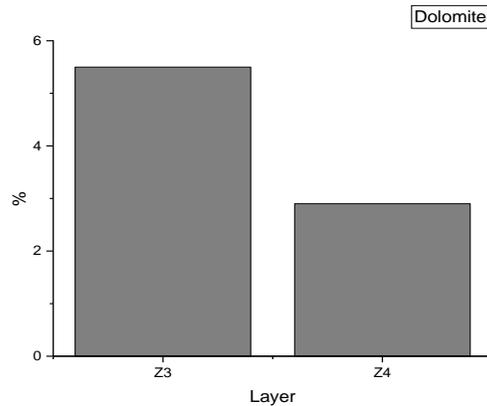
The remaining percentage compared to the crude oil can be explained by the dissipation of HCl in the presence of other material, degradable or not depending on the temperatures chosen for the experiments, i.e. clays, quartz, pyrite, etc.

In the following table we gather the different constituents of the oil shale for the layers Z3 and Z4 evaluated.

Table 7:- Percentages of HCl sensitive and insensitive constituents.

sample	Percentage of HClinsensitiveconstituents	Percentage of constituents sensitive to HCl				
		% total	Organicmatter	Calcite	Dolomite	Otherconstituents
Z3	27,1 %	72,9%	13,6 %	34,9 %	5,5 %	18,9 %
Z4	32,2 %	67,8%	12,9 %	28,5%	2,9 %	23,5 %

The composition of the organic matter probably follows the same order as the true thermogravimetric technic **(Ouajih, H., Attaoui .A, 2022)**, however combustion makes the residue heavier whereas hydrotreating makes it lighter, which is why a difference in values is observed. It should be noted that dolomite be decentralized with depth to the same degree as all mineral matter.

Conclusion:-

The carbonates of oil shale are calcite and dolomite, these two constituents when present in oil shale cannot be discerned in dynamic thermogravimetry despite having different thermal decomposition domains. In this context, it was possible to determine the percentage of their presence (therefore possible to be discernible) by a simple method which consists of carrying out combustions at given isotherms (500°C, 600°C, 700°C and 8900°C), then carrying out attacks (HCl) and then, after filtration, dosing the solution with NaOH in order to know the volume of the HCl dosing which was used for the acid attack.

If we take the curves in figures 9 and 10, we observe that the greatest difference in volume between the curve at room temperature and that at 500°C for Z3 is ΔV = 1.7 cm3 for a PH = 7.7. For Z4 the largest difference volume ΔV=2,1 cm3 for a PH=6,5. This technique makes it possible to classify the different layers of a deposit with regard to the quality of their organic matter, i.e. whether they are heavy or light in comparison. In fact, when the kerogen is formed by light hydrocarbons and when combustion is carried out, there will be a departure of gas, mainly CO2(g), so there are not many oxidized compounds in the residue, and the bath after acid attack has a relatively low strength, which leads to dosing at relatively high PH.

Conversely, when the kerogen has heavy hydrocarbons, after combustion of its oxidized compounds trapped in the bath which in the presence of hydrogen from the oil shale can regenerate formic acid as in the case of coal **(Bonnelye.v et al: 2004)**, after acid attack we will have extra acidity so the largest deviation of the PH= f(V) curves is at a comparatively low PH. Given this reasoning the hydrocarbons in the Z3 layer (PH=9.4) are lighter than those in Z4 (PH=8.5). The UV spectra of the Z3 and Z4 layers solubilized in chloroform confirm the quality of the hydrocarbons in both layers **(A.Attaoui et al: 2022)**.

Finally, we gather in the following table the percentage of calcite and dolomite identified by the present method:

Sample	Calcite	Dolomite
Z3	34,9 %	5,5 %
Z4	28,5%	2,9 %

It should be noted that dolomite be decentralized with depth to the same degree as all mineral matter.

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