

RESEARCH ARTICLE

PERCENTAGE OF COMPOUNDS CONSTITUTING THE TARFAYA'S OIL SHALE (MOROCCO) REACTING TO ACID ATTACK (HCL)

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| Manuscript Info | Abstract |
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| <i>Manuscript History</i> Received: 21 April 2022 Final Accepted: 24 May 2022 Published: June 2022 | The mastery of a number of chemical reactions can give us information on the constitution of compounds in the solid state. As an example, acid etching (HCl) is used for oil shale to separate the organic matrix by destroying the mineral matrix. (The use of the soxhlet). Similarly, by ashing at low temperatures (LTH) in combustion of the organic material, the mineral matrix can be kept to a minimum (A.Attaoui et al: 2022). Another way of using acid etching (HCl) at given concentrations can be carried out for oil shale in order to give the composition of the majority constituents of the latter, namely organic matter and carbonates (calcite and dolomite discerned). The objective of this study, which is carried out in a back-assay mode using the Tacussel pH meter, is to establish a table of compositions in mass percentages of the different constituents reacting to the acid attack of oil shale from the first three layers of the Tarfaya deposit (Morocco), which are Z0, Z1 and Z2.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 study of the oxidation of oil shale is important as it is the basis for the "in situ" mining process. Work by Mallon (R.G. Mallon and W.C. Miller: 1975). Tyler (A.L. Tyler: 1975) and Huang (Huang: 1977) on the air thermal behavior of shale blocks where Mallon et al observed abnormally high velocities near the center of a shale block. The mechanism known so far is not satisfactory to explain this behavior. Indeed, the transport of oxygen by diffusion through the surface of the block towards the interior is weak enough to cause an abrupt rise in temperature. Similarly, Tinen et al (S.S. Tihen et al: 1968), in calculating the thermal infusibility, showed the opposite phenomenon, i.e. the temperature rise at the surface is faster than in the interior. These authors explained this phenomenon by introducing pressure-sensitive capillaries inside the block to detect sudden combustions of hydrocarbons by the oxygen available inside the block. These combustions cause pressure pulses and of course temperature rises. The same phenomenon was observed by Sohns (H.W. Sohns et al: 1972). Carbon, which is the essential element of hydrocarbons, was oxidized by water vapor (T. Umehara et al: 1983) to find out its kinetics at 973K, the result verifying the original Langmuir-Hinshelwood equation. The reaction rate is relatively high. Auxiliary reactions by adding Na₂SO₄ indicate that the non-volatile inorganic residues of DBS (sodium dodecyclobenzenesulphonate) have a catalytic effect. Measurements of oxygen adsorption by the samples show that thermal regeneration alone is 65% of the adsorption capacity, while thermal regeneration followed by steam completely restores the adsorption energy for carbon DBS. The effect of steam and air was also studied on coal (C.

Valenzuela et al: 1987) which showed a low reactivity, this is explained by the effects of cracks when studying the textural and surface characteristics of coal. The latter, which are more reactive than its char, parent (coconut char) (S.M.J.O. Hill et al: 1989), was the subject of a kinetic study which showed that it is not possible to use the exact formula of the rate equation (G. Hakvoort et al: 1989). For this reason a step-by-step method was proposed.

1/Bibliographic study

The thermo-gas-titrimetric measurement technique (TGT) allows the determination of carbon dioxide and sulphur trioxide, respectively (**F. Paulik et al: 1984**). Although this technique has been known for a long time and has been used to clarify the kinetics and mechanisms of the decompositions of many compounds, the extension of its application to the selective determination of carbonate, organic matter, sulphide and sulphate in minerals, in the presence of another, have consisted of a series of problems. In order to eliminate these difficulties, minor modifications in the construction and operation of the derivatograph became necessary. In the present paper we describe the modified version of the apparatus and its operational technique.

Thermal reactivity's oil shale combustion at different oil fractions and oil alone have shown that the coke present has little effect in the temperature range of the reaction which is 500 - 700°C (**S.J. Day et al: 1993**), as the amount deposited is small at 700°C, at 900°C more will be formed; similarly the presence of water has no effect on the coke formed. Shale containing 3% organic carbon only undergoes 50% total combustion.

The authors (A.M. Kubet et al: 1991) have studied the interactions between water vapor and the solid. They have shown that under these conditions oxidation decreases the temperature of coke formation without changing the physical properties of the coke and the mineral matrix. The combustion temperature does not affect the reaction of the shale. The combustion of the shale was also followed using the system of coordinates that move at the same speed as the reactions. The model is obtained by the total thermal development that exists after moving a sufficient distance in the bed (M. Hiskakis et al: 1985). Of particular interest is the interpretation of the oil yield as a function of thermal order structure and operational variables. The Australian oil shale was combusted in a small reactor connected to a spectrometer, and the off-gases of sulphides and nitrogen were studied during the combustion. Cyanide hydrogen is the predominant gas (J.S. Killingley et al: 1988) which is released at around 500°C. The temperature at which sulphur dioxide is released from pyrite depends on the size of the samples. However, the binding of sulphur dioxide to oil shale is low and the ability to bind decreases remarkably with increasing temperature. It should be noted that Australia's largest pyrolysis and combustion deposit is the Condor (A. J. Gannon 1988) (9.65 trillion barrels). Various degrees of oxidation caused by surface weathering have been carried out on Australian shale (T.D. Moss et al: 1988). Analyses of the decomposition elements of kerogen after oxidation by infrared spectroscopy showed a weakening C-H concentration and an increasing C=O composition during oxidation. Oils produced from the Fischer test that underwent air weathering were compared using H1 and 13C nuclear magnetic resonance and elemental analysis (D.E. Lambert: 1988). The oils become more aromatic and less aliphatic with high oxygen concentration. The amount of reaction products such as phenols, ketones, nitrogencontaining heterocyclic compounds and sulphides during the reaction varies.

To examine the isothermal kinetics of carbon deposition a fluidized bed reactor was used during the passage of steam oil through the bed in gasification pyrolysis and combustion (S.D. Carter: 1993) of Devonian oil shale. The main silicate minerals found in Devonian shale (kaolinite, illite and quartz) was also tested. The carbon rate obtained in the solid residue decreases as the carbon deposition in the heat transfer solids increases. The activity of the firing process is ranked according to the gas used; it is higher during shale combustion than during gasification which is higher than pyrolysis. The firing temperature has a small effect on the amount of carbon deposited, which makes it an important application for the recycling of the heat transfer residue from oil shale. The quality of the products obtained depends strongly on the mineralogical composition of the shale. The association of clays and heavy metals with organic matter was studied using a soxhlet employing benzene and methanol as solvent. Series of acid treatments were carried out (M. Day et al: 1984) to dissolve the mineral support and the isolated fractions which are analyzed by oxidation. The results show that this oxidation provides insight into the refining process. The method used to extract the mineral material is the use of low temperature combustion techniques (VLTA). It is 60-70°C (A. Reza et al: 1993). To further reduce the temperature, oxygen is diluted with helium. This atmosphere regulates the amount of coal and sulphide. The Tertiary oil shale of East Queensland and Australia are an important source of liquid fuel. For this reason a study (J.H. Patterson et al: 1991) has been made of several deposits which shows that the mineral carbon included in calcite, siderite differs in concentration. Calcite and magnesium calcite are decomposed in the reactor and reduce the emission of sulphur dioxide (see following reactions). The siderite is

partially or completely decomposed depending on the conditions of the degradation. The iron oxide reacts with hydrogen sulphide to give several gases. The calcium ion replaces the ferrous ion in siderite to bind sulphur dioxide in the form of CaSO4.

Mineral compounds contained in several oil shale lines are studied during thermal degradation or during combustion (**J.H. Patterson et al: 1990**). These different mineral compounds are smectite, kaolinite, siderite and pyrite. The most important reactions that accompany combustion are:

* Smectite (200 – 900°C): $(Ca,K)_{0.65}(Al,Mg,Fe)_4(Si,Al)_8O_{20}(OH)_4 \rightarrow (Ca,K)_{0.65}(Al,Mg,Fe)_4$ (Si,Al)₈O₂₂+2H₂O(g) * Kaolinite (450 – 900 °C) : $Al_2Si_2O_5(OH)_4 \rightarrow Al_2Si_2O_7 + 2H_2O(g)$ * Siderite (450 – 900°C): $(Fe,Mg)CO_3 \rightarrow (Fe,Mg)O + CO_2(g)$ $3(\text{Fe},\text{Mg})\text{O} + \text{CO}_2(g) \rightarrow (\text{Fe},\text{Mg})_3\text{O}_4 + \text{CO}(g)$ * Pyrite (450 – 900°C): $2\text{FeS}_2 + 11/2 \text{ O}_2 (g) \rightarrow \text{Fe}_2\text{O}_3 + 4\text{SO}_2 (g)$ * Pyrrhotite (450 – 900°C) : $2\text{FeS} + 7/2 \text{ O}_2(g) \longrightarrow \text{Fe}_2\text{O}_3 + 2\text{SO}_2(g)$ * Magnetite (450 - 900°C): $4(\text{Fe},\text{Mg})_3\text{O}_4 + \text{O}_2(g) \rightarrow 6(\text{Fe},\text{Mg})_2\text{O}_3$ * Calcite (600 – 900°C) : $CaCO_3 \rightarrow CaO + CO_2$ (g) $CaCO_3 + SO_2(g) + 1/2 O_2(g) \rightarrow CaSO_4 + CO_2(g)$ * Quicklime (600 – 900°C) : $CaO + SO_2(g) + 1/2 O_2(g) \rightarrow CaSO_4$ * Anhydride (600 – 900°C) : $CaSO_4 \rightarrow CaO + SO_2(g) + 1/2 O_2(g)$

2/Experimental studies:

2.1/X-ray diffraction:

The following spectra represent the X-ray diffraction (XRD) of the first three layers of the Tarfaya's deposit (Morocco), they are classified from bottom to top respectively Z0, Z1 and Z2.



Fig1:- X-ray spectra classified from bottom to top of the Z0, Z1 and Z2 layers of Tarfaya's oil shale.

2.2/Isothermal combustion of oil shale (Z0, Z1, Z2) and Calcite (CaCO3) 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 400°C to 800°C) in an isothermal regime, the combustion was carried out for 30 minutes with air entering the furnace every 10 minutes, and finally the samples were weighed again after combustion.



Fig 2:- Muffle furnace.



Fig 3:- Balance.

The results in percentage loss for this combustion at different temperatures for the Z0, Z1 and Z2 layers as well as the pure calcite taken as reference are presented in the following table 1:

| | Z0 | | | | Z1 | | | Z2 | | | Calcite | |
|-------|-------|-----------|------|-------|-----------|------|-------|-----------|------|-------|-----------|------|
| | masse | remaining | % of |
| | (g) | masse | loss |
| | | | | | | | | | | | | |
| 400°C | 0,5 | 0,45 | 3 | 0,5 | 0,425 | 7,5 | 0,5 | 0,438 | 6,2 | 0,505 | 0,503 | 0,2 |
| 500°C | 0,5 | 0,463 | 3,7 | 0,5 | 0,42 | 8 | 0,5 | 0,445 | 5,5 | 0,5 | 0,495 | 0,5 |
| 600°C | 0,5 | 0,46 | 4 | 0,5 | 0,382 | 11,8 | 0,5 | 0,455 | 4,5 | 0,5 | 0,493 | 0,7 |
| 700°C | 0,5 | 0,371 | 12,9 | 0,5 | 0,329 | 17,1 | 0,5 | 0,4 | 10 | 0,505 | 0,48 | 2,5 |
| 800°C | 0,5 | 0,252 | 24,8 | 0,5 | 0,284 | 21,6 | 0,5 | 0,29 | 21 | 0,5 | 0,282 | 21,8 |

Table 1:- Loss percentages for combustion at different temperatures for Z0, Z1, Z2 and calcite layers.

Several remarks appeared to us, first of all the classification of the various layers with regard to their composition of organic matter, given the range of decomposition of the latter, i.e. around 400 -500°C. This classification, already known before, is increasing respectively for Z0, Z2 and Z1.

At 800°C we observe a strong loss for the Z0 layer, which is very concentrated in the presence of calcite and dolomite carbonates.

2.3/Acid etching (Hcl) of calcite that has been burnt beforehand at different temperatures from 400°C to 800°C.

Acid etching is often used for compounds that give off CO^2 , for example in gasometry.

Samples having undergone combustion at different temperatures have been the subject of this acid attack, 0.2 g of sample is attacked by 50 cm3 of HCl (0.126N) then a filtration is made and 10 cm³ of the filtrate is dosed with

NaOH (0.105N) to conceive the quantity that has been consumed during this attack (back determination). This part of the dosage is done by PH-meter (Tacussel equipped with an Orion electrode).



Fig 4:- Determination of acid attack of calcite burnt at different temperatures.

Air, which is a more reactive medium than nitrogen, will weaken the temperature range of calcite decomposition.

We note that the attack volume is similar for raw calcite and calcite burnt at 400°C as at this temperature the calcite is still intact. After this temperature, the volume decreases until 500°C, confirming the decomposition domain in air.

For the temperature from 500°C to 800°C, as the attacking mass is preserved, the phenomenon observed is more related to the thermal effect. The material leaves more activated in the pores as the temperature increases.

The following table shows the volumes of the dosage and the volumes used to etch the calcite under the conditions considered.

| | Dosage volume(cm ³) | PH | Volume of dosage of acide used for the attack(cm ³) |
|--------------------------|---------------------------------|-----|--|
| HCl alone | 12 | 7 | |
| Raw calcite | 2,5 | 7,2 | 9,5 |
| Calcite treated at 400°C | 2,2 | 7,2 | 9,8 |
| Calcite treated at 500°C | 3,4 | 7,3 | 8,6 |
| Calcite treated at 600°C | 2,5 | 7,7 | 9,5 |
| Calcite treated at 700°C | 1,5 | 7,8 | 10,5 |
| Calcite treated at 800°C | 1,2 | 7,7 | 10,5 |

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

These results will be used to estimate the amount of carbonate (calcite and dolomite) found in the different shale layers firstly in the crude state (without combustion) and then at the different combustion temperatures chosen.

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 crude state, the dosages that were made are represented in the following figure.



Fig 5:- Curves of HCl dosing by NaOH from acid etching of different layers of crude oil shale and crude calcite (Z0, Z1, Z2, and CaCO3).

The table showing the volumes of the dosage and the volumes used for the etching is as follows:

| sample | Dosage volu (cm ³) | me PH | Volume of dosage attack(cm ³) | of acide | used | for | the |
|--------------|-----------------------------------|-------|---|----------|------|-----|-----|
| HCl alone | 12 | 7 | | | | | |
| Raw Z0 layer | 4,6 | 7,1 | 7,4 | | | | |
| Raw Z1 layer | 6,2 | 6,7 | 5,8 | | | | |
| Raw Z2 layer | 5,4 | 7,2 | 6,6 | | | | |

Table 3:- Dosing volumes and acid dosing volumes used to etch different layers of crude oil shale.

By a simple correspondence it was possible to approach the composition, first of all in carbonate and MO included sensitive to Hcl for the three layers which manifests itself in this way.

| Table 4 The carbonate and organic matter composition of different on shale layers. | | | | |
|--|---|--|--|--|
| layer | Composition of carbonates and organic matter in percent by weight | | | |
| Z0 | 77,9% | | | |
| Z1 | 61,1% | | | |
| Z2 | 69,5% | | | |

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

2.5/Acid attack of oil shale samples at different combustion temperature

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

The samples are the Z0, Z1 and Z2 layers of the Tarfaya deposit.



Fig 6:-Curves of the HCl dosage resulting from the acid attack of the raw layer Z0 treated in combustion at [400°C to 500°C] by NaOH.



Fig 7:- Curves of the HCl dosage resulting from the acid attack of the raw layer Z1 treated in combustion at [400°C to 500°C] by NaOH.



Fig 8:- Curves of the HCl dosage resulting from the acid attack of the raw layer Z2 treated in combustion at [400°C 0 500°C] by NaOH.



Fig 9:HCl dosage curves from acid etching for different layers of oil shale (Z0, Z1, and Z2) and calcite (CaCO3) treated at 400°C bay NaOH.



Fig 10:- HCl dosage curves from acid etching for different layers of oil shale (Z0, Z1, and Z2) and calcite (CaCO3) treated at 500°C bay NaOH.



Fig 11:- HCl dosage curves from acid etching of different layers of oil shale (Z0, Z1, and Z2) and calcite (CaCO3) treated at 600°C bay NaOH.



Fig 12:- HCl dosage curves from acid etching for different layers of oil shale (Z0, Z1, Z2) and calcite (CaCO3) treated at 700°C bay NaOH.



Fig 13:-HCl dosage curves from acid etching of different layers of oil shale (Z0, Z1, and Z2) and calcite (CaCO3) treated at 800°C bay NaOH.

The following table (5) shows the dosing volume of $10 \text{ (cm}^3)$ 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.

| | dosage volume (cm ³) | PH | dosage volume of acide used for the attack(cm ³) |
|---------------------------|----------------------------------|-----|--|
| Hclalone | 12 | 7 | |
| Layer Z0 treated at 400°C | 4,7 | 7,8 | 7,3 |
| Layer Z1 treated at 400°C | 4,9 | 7,6 | 7,1 |
| Layer Z2 treated at 400°C | 4,5 | 8 | 7,5 |
| Layer Z0 treated at 500°C | 5,2 | 7,1 | 6,8 |
| Layer Z1 treated at 500°C | 6,5 | 7,2 | 5,5 |
| Layer Z2 treated at 500°C | 5,4 | 7,3 | 6,6 |
| Layer Z0 treated at 600°C | 5 | 8,1 | 7 |
| Layer Z1 treated at 600°C | 5,4 | 8 | 6,6 |
| Layer Z2 treated at 600°C | 4,4 | 8,1 | 7,6 |
| Layer Z0 treated at 700°C | 3,4 | 7,7 | 8,6 |
| Layer Z1 treated at 700°C | 3,8 | 7,9 | 8,2 |
| Layer Z2 treated at 700°C | 3,4 | 7,6 | 8,6 |
| Layer Z0 treated at 800°C | 3,2 | 8,1 | 8,8 |
| Layer Z1 treated at 800°C | 4,4 | 7,7 | 7,6 |
| Layer Z2 treated at 800°C | 3,5 | 7,6 | 8,5 |

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

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.

2.6/Interpretation

The selected temperature ranges are superimposed for the successive and sometimes simultaneous decomposition when it comes to the more or less answered constituents in the oil shale; in this respect we divide the material combustion ranges as follows

*Ambient-400°C: Thermal activation and beginning of the combustion of the organic matter

*400°C-500°C: End of the combustion of the organic matter and beginning of the combustion of the calcite

*500°C-600°C: End of calcite combustion and thermal activation

*600°C-700°C: The combustion of dolomite and thermal activation

*700°C-800°C: Thermal activation

We have mentioned thermal activation which means that when combustion takes place at high temperatures, it leaves more activated pores increasing with temperature. The appearance of these activated pores causes more HCl to dissipate when attacked by the latter.

To avoid this phenomenon we will adjust the values for the calculations by taking as a control the combustion of calcite under the same conditions and temperatures as the shale experiments.

2.6.1/Range: ambient-500°C

The volumes in cm^3 of the experiments carried out in Table 6 are:

|--|

| sample | Ambient | 400°C | 500°C |
|---------|---------|-------|-------|
| Z0 | 7,4 | 7,3 | 6,8 |
| Z1 | 5,8 | 7,1 | 5,5 |
| Z2 | 6,6 | 7,5 | 6,6 |
| Calcite | 9,5 | 9,8 | 8,6 |

The decomposition of the organic matter in air is finally achieved between 400°C and 500°C, taking as a reference the volume of the acid dosage for the calcite at 500°C which is 8.6 cm³, and we also observe a thermal activation close to the range of the decomposition of the calcite, we have the following differences in the volumes between 400°C and 500°C

 $Z0 \Delta V = 0.5 \text{ cm}^3$

 $Z1 \Delta V = 1.6 \text{ cm}^3$

 $Z2 \Delta V = 0.9 \text{ cm}^3$

Thus the percentage of organic matter (volume of the acid attack dosage for calcite as a control is 8.6 cm³) is.

| Sample | $\Delta V (cm^3)$ | Percentage o | Percentage of organic matter taking into account |
|--------|-------------------|---------------|---|
| Sumple | | organiematier | the HCl sensitive part |
| Z0 | ΔV=0,5 | 5,8% | 0,779×5,8=4,5% |
| Z1 | ΔV=1,6 | 18% | 0,611×18,6=12,3% |
| Z2 | ΔV=0,9 | 10,4% | 0,695×10,4=7,2% |

2.6.2/Range: 600°C to 800°C

This temperature range is designed for the end of calcite decomposition and the beginning of dolomite decomposition and the thermal activity of the reaction bath. The volumes in cm^3 of the experiments performed according to Table 5 are:

Table 7:- Dosing volumes (cm³) from 600°C to 800°C.

| Sample | 600°C | 700°C | 800°C |
|---------|-------|-------|-------|
| Z0 | 7 | 8,6 | 8,8 |
| Z1 | 6,6 | 8,2 | 7,6 |
| Z2 | 7,6 | 8,6 | 8,5 |
| Calcite | 9,5 | 10,5 | 10,8 |

*Calcite

For calcite from oil shale at the temperature of 600°C we have, taking as a reference the volume of the acid dosage for calcite alone at 600°C which is 9.5 cm^3

| Sample | V(cm ³) at 600°C | percentage | By removing the percentage of organic matter | Percentage of calcite taking into account the HCl sensitivepart |
|--------|------------------------------|------------|--|--|
| Z0 | 7 | 73,7% | 73,7-5,8=69,9% | 52,9% |
| Z1 | 6,6 | 69,5% | 69,5-18,6=50,9% | 31,1% |
| Z2 | 7,6 | 80% | 80-10,4=69,6% | 48,4% |

*Dolomite

For oil shale dolomite at the temperature of 700°C we have, taking as a control the volume of the attacking acid dosage for calcite alone at 600°C which is 10.5 cm³

| Sample | ΔV (cm ³) from 600°C to 700°C | Percentage of dolomite | Percentage of dolomite taking into account the HClsensitivepart |
|--------|---|------------------------|---|
| Z0 | 1,6 | 15,2 | 0,779×15,2=11,8% |
| Z1 | 1,6 | 15,2 | 0,611×15,2=9,3% |
| Z2 | 1 | 9,5 | 0,695×9,5=6,6% |

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 Z0, Z1 and Z2 evaluated by this method.

| Sample | Percentage of constituents insensitive to HCl | Percentage of constituents sensitive to HCl | | | | | |
|----------------|---|---|---------------|---------|----------|-------------------|--|
| | | % total | Organicmatter | Calcite | Dolomite | Otherconstituents | |
| Z ₀ | 22,1% | 77,9% | 4,5% | 52,9% | 11,8% | 8,7% | |
| Z ₁ | 38,9% | 61,1% | 12,3% | 31,1% | 9,3% | 8,4% | |
| Z ₂ | 30,5% | 69,5% | 7,2% | 48,4% | 6,6% | 7,3% | |

Table 8:- Percentages of HCl sensitive and insensitive constituents.

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 deconcentrates with depth to the same degree as all mineral matter.

Conclusion:-

An approach to the percentages of oil shale constituents sensitive to acid attack (HCl) such as organic matter, calcite and dolomite was the subject of this study.

Firstly, this work focused on the combustion of different samples of oil shale (Z0, Z1, Z2) from the Tarfaya deposit and the calcite (as a control) CaCO3 at different temperatures (400°C-800°C). This combustion is very important because it is responsible for the production of thermal energy. We noticed that the classification of the different layers Z0, Z2 and Z1, with regard to their organic matter and carbonate compositions for temperatures ranging from 400°C to 800°C, is similar to the classification made either by true thermogravimetry (Organic matter, carbonates) or by gazometry (carbonates).

Then we made acid attacks (HCl) to these samples having undergone preliminary combustions at different temperatures. This is a quantitative method to conceive the quantity that was consumed during this attack (back dosage).

Several results were obtained, which can be summarized in the following table of compositions:

| sample | Percentage of constituents | Percentage of constituents sensitive to HCl | | | | |
|----------------|----------------------------|---|---------------|---------|----------|-------------------|
| | insensitive to HCl | % total | Organicmatter | Calcite | Dolomite | Otherconstituents |
| Z ₀ | 22,1% | 77,9% | 4,5% | 52,9% | 11,8% | 8,7% |
| Z_1 | 38,9% | 61,1% | 12,3% | 31,1% | 9,3% | 8,4% |
| Z ₂ | 30,5% | 69,5% | 7,2% | 48,4% | 6,6% | 7,3% |

Two parts are noticed: HCl-insensitive and HCl-sensitive compounds. Combustion of organic matter is responsible for an accentuated production of active sites compared to carbonates. These active sites are formed when we have departures of oxidized compounds at the temperatures considered in the form of CO_2 , H_2O or oxidized volatile products.

The percentages established by the present method are of the same order of magnitude as those obtained by other techniques such as thermogravimetry(**Ouajih**, **H.**, **Attaoui**.**A**, **2022**), gazometry.....etc.

The density of the elements constituting the mineral matter during sedimentation influences the compounds produced. We cite the case of magnesium, the basic element of dolomite, whose concentration decreases as a function of depth, behaving in the same way as the overall mineral matter.

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