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RESEARCH ARTICLE

Quantitative discernments of the different calcium compounds in the Tarfaya oil shale (Morocco)

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Abstract

Calcium exists in several compounds, calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), calcium oxide (CaO) and calcium chloride dihydrated ($CaCl_2$, $2H_2O$). All of these calcium compounds occur in oil shale. This work consists of using some physical and reaction analytical methods to try to discernthese calcium constituents quantitatively. By the methods of this work, which are the complexometry reaction using dimethyl tetra acetic acid (EDTA), the hydrochloric acid etching reaction and dispersive X-ray diffraction, we have tracked these calcium qualities. Pure calcite and pure hydrated calcium chloride were the references used. By combining the three analytical methods and making calculations, we were able to identify calcium chlorides and free chloride in the Tarfaya oil shale. The material account of the calcium compounds mentioned in addition to calcite and dolomite was established.

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Introduction:-

The oil shale of Spain **(M.A. Kruge and I.S. Ruize: 1991)** was studied by the geochemical and petrographic method; three of the samples are of lacustrine nature and one of maritime nature. The petrographic method shows a dominance of liphodetrinite associated with the bitumen contained in the mineral matter, as well as a similarity of the tertiary structure concerning the organic matter. As for the geochemical method, it shows the presence of organic matter which is a mixture of tertiary and aquatic derivatives. We mention beforehand the works carried out on kerogen isolated from their mineral matrix **(J. Espitalie et al: 1973, B. Tissol et al: 1973, B. Durand et al: 1972, B. Durand and J. Espitalie: 1973)** which showed that it is possible to classify the different types of kerogen and to follow their physico-chemical transformations during burial. The author **(Van Krevelen: 1951)** was able to show that certain shale lineages can be classified using a diagram showing the atomic composition of the three main elements (C, H and O) of the kerogen as H/C and O/C. He had assigned that the samples corresponding to the same type of organic deposit, group together on a curve called "evolutionary path". Several of these evolutionary paths can be distinguished, which correspond to different natures of organic matter, kerogen, composed almost exclusively of algae, are located on a path with a high H/C ratio and a low O/C ratio. On the contrary, kerogen, consisting mainly of higher plant debris and continental material, has a high O/C ratio and a low H/C ratio. Mineral matter is identified by X-ray diffraction and dispersive X-ray diffraction.

1/ Bibliographical study

The catagenetic evolution of this kerogen during burial results in an early decrease in the O/C ratio and therefore the elimination, mainly under the action of temperature, of a certain number of oxygenated compounds (CO_2, H_2O, etc.).

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Then, this evolution of the kerogen continues with a progressive elimination of hydrogen (decrease of the H/C ratio) mainly in the form of hydrocarbons.

When the evolution paths of two shale lines are different, the physic-chemical properties will be modified. Authors **(C. Sauron et al: 1974)**, by carrying out pyrolysis studies in true thermogravimetry, in a nitrogen atmosphere at 4°C/min and on kerogen belonging to two distinct evolutionary lineages, have shown that the percentages of weight loss, at 600°C, vary from simple to double for the least evolved samples and these percentages decrease as the evolution of these kerogene proceeds.

Authors **(C. Wen and T. Yen: 1978)** compared the thermal behavior and properties of two varieties of shale (Devonian, Green River (USA)) according to the two analytical methods TGA (Thermogravimetry) and DSC (calorimetry). They found that the activation energy and kerogen concentration are higher for the Devonian than for the Green River. In addition, the heat absorption peak at 550°C was attributed to the presence of pyrite in the Devonian. By removing the pyrite, the peak disappears and thermal decomposition takes place at 450°C, a relatively low temperature compared to the decomposition of the Green River shale.

The interest of knowing the chemical or physical characteristics is that it allows the value of this shale. Table (1) shows some of the characteristics of two average samples from the two deposits.

Table 1:- Characteristics of two average samples from Tarfaya and Timahdit.

Deposit Characteristics	Moyen sample of Timahdit	Moyen sample of Tarfaya*
density	2,21	2,24
Superior calorific powerSCP Kcal/kg	1340	1228
% Cendre	64	59,46
CO_2	20,4	26,07
Organicmatter	15,8	14,47
% C_{tot}	18,34	17,74
% C_{min}	5,57	7,72
% C_{org}	12,77	10,62
% S_{tot}	2,26	1,92
% S_{org}	1,54	1,6
% S_{pyr}	0,60	0,31
% S_{sul}	0,12	-

* Communication from the Ministry of Energy and Mines and ONAREP

The identification of the phases of the mineral matter of the shale during this study was carried out on powder using a C.G.R Theta 60 X-ray diffractometer formed of a copper anti-cathode with a wavelength of 1.54051Å. X-ray diffraction is a qualitative analysis technique; to obtain the quantity of the rock's constituents, other techniques must be used, such as thermogravimetry and dispersive X-ray diffraction, which make it possible to identify the constituent elements. We will gather in table (2) the mineralogical composition made by some authors **(M. Taibi and B. Kaye: 1985, O. Bikri and R. Bouchta: 1981, C.Y. CHA: 1981)** respectively for the deposits of Tarfaya, Timahdit and Colorado.

Table 2:- Composition of mineral matter of three varieties of shale:Timahdit; Tarfaya and Colorado.

I. Deposit constituents	Tarfaya	Timahdit	Colorado
Dolomite($CaMg(CO_3)_2$)%	4,1	15,9	32
Calcite ($CaCO_3$)%	59,2	41,5	16
Quartz (SiO_2)%	-	19,5	15
Clay (Illite.Kaolinite)%	28,4	13,4	0
Pyrite (FeS_2) %	2,4	1,8	1

$FeCO_3 + Fe_2O_3$ %	-	1,8	-
TiO_2+phosphate %	1,2	2,4	-
Otherelement %	4,7	3,7	-

Considerable attention is being paid to the use of water in the super fluid SFE extraction of organic matter from fossil fuels. Deshpande et al found that supercritical water acts not only as a solvent but as a reagent in the conversion of coal to gases and liquids **(Deshpande, G. V et al: 1984)**. Also, Houser et al found that supercritical water (SC) is an active participant in the decomposition of organic compounds **(Houser, T. J et al: 1986).**

Compared to the considerable amount of work done on coal EFS, little work has been done on oil shale EFS. Qin et al and Zhu et al studied the ELA of Chinese oil shale with toluene **(Qin, K. Z et al: 1984, Zhu, Yet al: 1982)**. Standard Oil Company (Indiana, USA) patented a process for the enhanced recovery of hydrocarbons from oil shale with SC water and with a mixture of SC water, hydrogen and a catalyst **(Standard Oil Company: 1978)**. McKay et al studied EFS of Green River oil shale with water and with a mixture of water and various organic solvents, and found a mixture of water and methanol effective for extraction **(McKay, J. F., Chong, S. L. and Gardner, G. W: 1983, McKay, J. F. and Chong, S. L: 1983)**.

In this study, SFE of Chinese oil shale was carried out with water and toluene, separately, in a batch autoclave. The oil shale was also subjected to pyrolysis in argon and Soxhlet extraction with tetrahydrofuran (THF).

Crushed particles of (0.35-0.84mm) Chinese Maoming oil shale, whose chemical compositions are shown in Table 1, were placed in a 0.7 dm3 autoclave equipped with an agitator. After the air in the autoclave was removed by a vacuum pump, a solvent (water or toluene) was introduced: the weight ratio of oil shale to solvent was 0.08 to 0.3: 1. The autoclave is heated by an external heating element from room temperature at a rate of 8.5 k min-1 to the final temperature, which was maintained for a specified time. The autoclave is then rapidly cooled with a fan and opened. In some cases, as soon as it reached the final temperature the autoclave was rapidly cooled and opened. The results of this study for samples B1, B2, B3, B4 and B5 of oil shale from Maoming in China treated under the selected conditions **(T.Funazukuri et al: 1988)** are given in the following table 3.

Table 3:- Hydrogen distribution of the extracts.

Extraction conditions		B1	B2	B3	B4	B5
Solvent / atmosphere		Eau	Eau	Toluène	Argon	THF
Finale température (K)		673	673	673	673	-
Final pressure (MPa)		23	23	23	0.15	-
Time (h)		0.75	3.75	0.75	0.75	-
Solventdensity (kg m^{-3})		200	200	540	1.1	-
Weight loss of oil shale (wt %)		48.6	78.4	33.5	47.6	22
Oilrecovred (wt%)		28.9	55.9	32.7	30.2	22
	Chemical shift (ppm)					
Aromatichydrogens	>6	6.0	3.3	8.1	10.8	6.2
Oléfininichydrogens	4.0-6.0	0	4.8	2.6	2.4	1.4
Methylene hydrogensα to aromatic ring	2.3-4	10.0	13.2	8.4	6.4	7.5
Methyl hydrogensα to aromatic ring	1.9-2.3	5.7	9.0	5.1	5.1	6.7
Naphtalenichydrogensβ Toaromatic ring	1.6-1.9	7.3	7.8	4.4	2.9	5.1

β –CH_3 and β –CH_3, to aromatic ring,straight-chain alkane methylene hydrogens	1.0-1.6	57.1	51.8	53.0	53.1	56.6
γ -CH_3 to aromatic ring and straight-chain or branched alkane metrylhydrogens	< 1.0	13.8	10.1	17.8	29.8	15.9

2/ Experimental study

By the methods of this work, which are the complexometry reaction using dimethyl tetra acetic acid (EDTA), the hydrochloric acid etching reaction and dispersive X-ray diffraction, we have monitored the calcium qualities. Among the calcium compounds in oil shale we have calcite $CaCO_3$ which is the most present. Calcium also exists either in the elemental state Ca^{2+} or in the form of chloride, which is quite evident from the presence of chlorine in the marine environment. A study of the two substances $CaCO_3$ and $CaCl_2$, $2H_2O$ in their pure state was carried out in a complexation reaction and used as a standard connector.

2.1/ Analysis methods

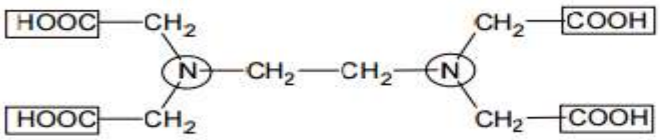
2.1.1/ Complexometry reaction

Complexometric titrations are volumetric assay methods based on the formation of complexes and on the ability of certain molecules to complex ions. During the assay, a complexing agent (EDTA), capable of trapping the ions to be assayed, is gradually added to the solution to be assayed. When all the ions to be measured are trapped, a complexometric indicator changes color, making it possible to visualise the equivalence **(G. Schwarzenbach: 1951).**

- **Complexing Agents**

The complexing agent or chelator is a ligand capable of trapping ions. Ligands used in cation assays must have at least one pair of non-bonding electrons available to bind to the trapped (so-called "core") ion via a dative (or coordinative) bond.

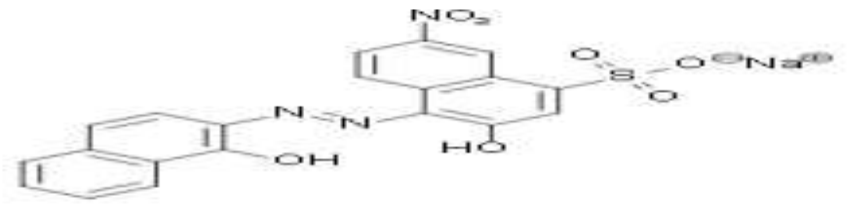
EDTA is a powerful complexing agent with 6 possible binding sites for metal ions: 4 COOH (circled) and 2 tertiary amines (encircled).



- **Color indicators**

Color indicators are also complexing agents whose color changes according to the presence or absence of certain ions in solution.

Eriochrome Black T (NET) is a coloured indicator with the chemical formula:
$HOC_{10}H_6N{=}NC_{10}H_4(OH)(NO_2)SO_3Na$.



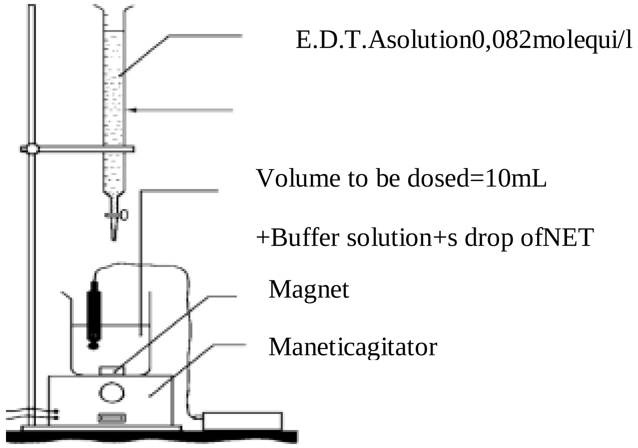


Fig 1:- Complexexometry assay setup.

2.1.2/ Dispersive X-ray (coupled with SEM)

Dispersive X-ray is an elemental analysis technique coupled with SEM, which allows the elements to be followed quantitatively. The following XRD spectra (figure 2 and figure 3) represent the Z0 and Z1 layers in the raw state to highlight the presence of chlorine and the non-presence of sodium, which proves that chlorine forms other compounds besides Na.

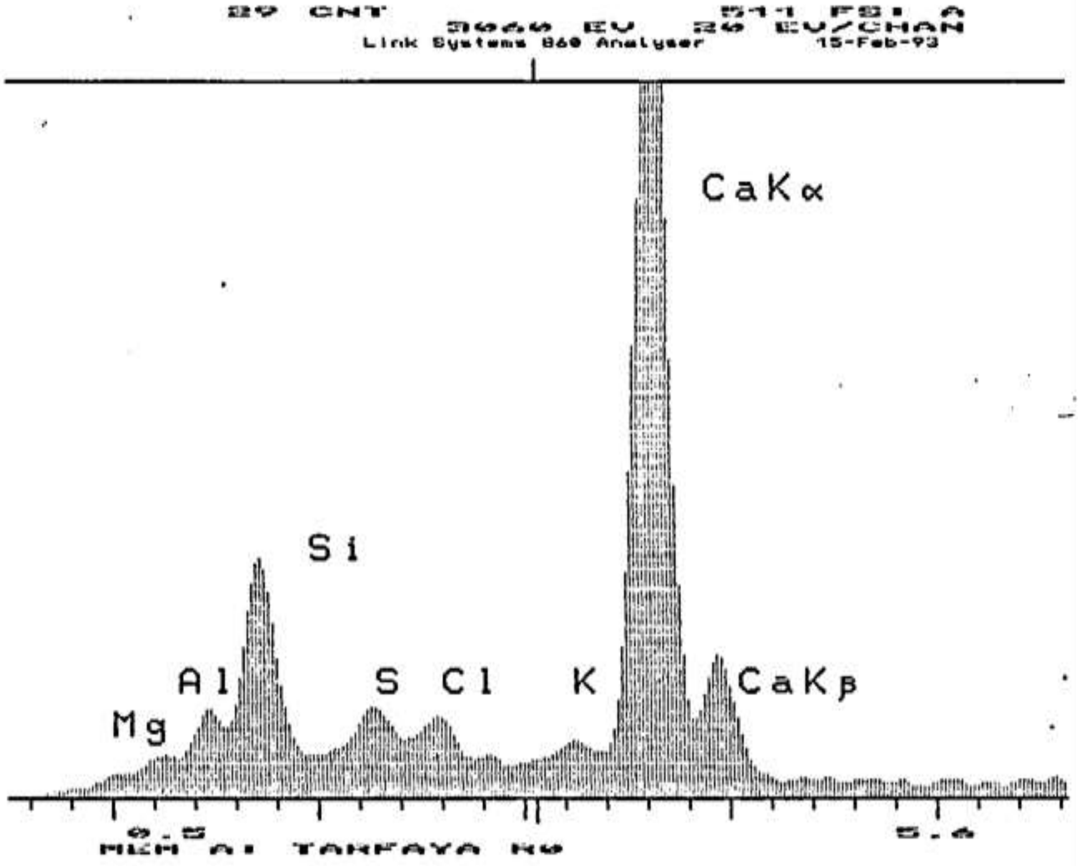


Fig 2:- Dispersive X-ray spectrum for sample Z0.

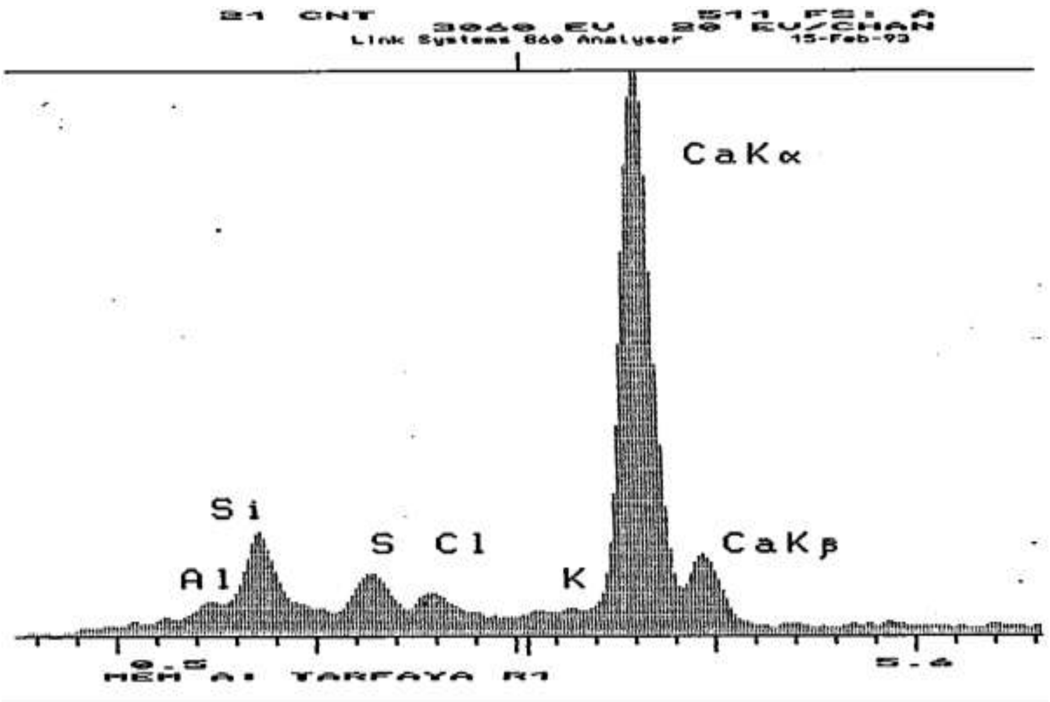


Fig 3:- Dispersive X-ray spectrum for sample Z1.

3/ Experimental results

3.1/ Percentage completion of the complexation reaction for pure $CaCO_3$ and $CaCl_2$, $2H_2O$

The following two compounds taken in pure state are used as reference or standard as follows. One gram of $CaCO_3$ was cold solubilized in 50 cm^3 of distilled water, after filtration we measured 10 cm^3 of the filtrate with EDTA (0.082 N). The volume of neutrality being 0.7 cm^3 this fact brings us to the mass concentration C'_{Ca2+}= 0.115 g/l and a percentage of 1.44% of realization of the reaction.

In the same way we solubilized one gram of $CaCl_2$, $2H_2O$ in 50 cm^3 of cold distilled water, after filtration and dosing of 10 cm3 of the filtrate with EDTA. The volume of neutrality is 34.9 cm^3. This brings the reaction to 100% completion with some fluctuation in the rate of chloride hydration. The volumes of the assay are given in the following table:

Compound	Volume of dosage in cm^3
$CaCO_3$	0,7
$CaCl_2$, $2H_2O$	34,9

3.2/ Presence of calcium varieties in oil shale

In this section we are interested in the quality of calcium present in the shale whether it is in the form of calcite $CaCO^3$ and calcium chloride $CaCl_2$, dihydretedor oxidized calcium CaO.

The same assay was adopted (complexation reaction) for:

One gram of Tarfaya oil shale (Z0 and Z1 layer) cold solubilized in 50 cm^3 of distilled water, after filtration 10 cm^3 of the filtrate was dosed with EDTA (0.082N).

The volumes of neutralization are:
- For Z0 V1=1.2 cm^3
- For Z1 V2=1 cm^3

As the mass concentrations are relatively higher than when pure calcite was studied, this forces us to consider calcium in other forms (chloride, free calcium .....). Hence the need to use other analytical technics.

The volumes bring us to the mass concentrations of calcium is:
- 0.197 g/l for Z0
- 0.164 g/l for Z1

If we take these values to 50 cm^3 as the working volume we have:
- m_0= 0.00985 g in 50 cm^3 for Z0 and
- m_1=0.0082 g in 50 cm3 for Z1

The percentage of presence of calcium calcite was found by acid etching in a previous work it is 52.9% for Z0 and 31.1% for Z1 **(H.Mokhlis and A.Attaoui: 2022).**
Similarly for dolomite it is 11.8% for Z0 and 9.3% for Z1
We gather the volumes, of the different compounds in the shaleor in a pure way, from the EDTA:

Compound	Volume of dosage in cm^3
Couche Z1	1,2
Couche Z2	1
$CaCO_3$	0,7
$CaCl_2$, $2H_2O$	34,9

3.2.1/Presence of hydrated calcium chloride in oil shale

Sedimentation during the formation of the Tarfaya oil shale took place in the marine environment where the presence of chlorine is high.

According to the hypothesis assigned in paragraph (3.1) that the complexation reaction occurs at 100% for the case of calcium in the form of chloride, it is admitted that the difference in volume of neutralization 1.2-0.7cm^3 (Z0) can only be explained by the presence of these chlorides in the shale. This leads us to find this quantity of calcium chloride in the Tarfaya shale.

We will look for the volumes of neutralization by complexometry taking into account the percentages of calcite in Z0 and Z1, by simple correspondence.
100% pure calcite (1g) →V we have 0.7 cm^3
52.9% calcite (1g of Z0) → V (calcite) Z0=0.37 cm^3
31.1% calcite (1g of Z1) → V (calcite) Z1=0.22 cm^3
Assuming that dolomite behaves in the same way as calcite and assuming that it consumes the same volume.
11.8% dolomite (1g of Z0) → V dolomite (Z0) = 0.083 cm^3
9.3% dolomite (1g of Z1) → V dolomite (Z1) =0.065 cm^3

Thus the reaction volume by EDTA dosage for the presence of calcium chloride will be the difference between the total volume of the dosage with the previously calculated volumes for the presence of calcite and dolomite for each oil shale layer.

3.2.2/ Inertia to acid attack HCl for calcium chlorides $CaCl_2$, $2H_2O$

Under the same conditions carried out for the calcite and the different layers of the Tarfaya deposit, we attacked the hydrated calcium chloride (m=0.2g) with HCl (0.1N).

The curves of the determination of the remaining acid as well as the determination of HCl alone by NaOH (0.1N) are shown in the following figures at different thermal treatments of the compound.

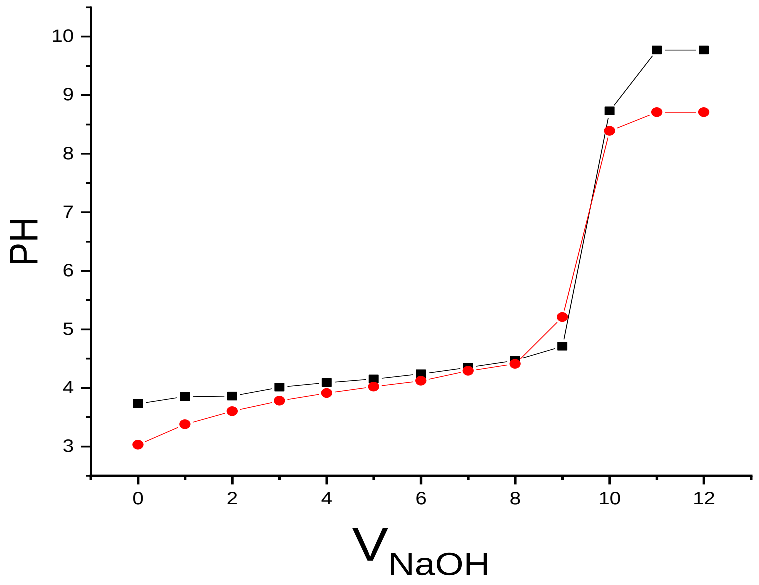


Fig 4:- Dosing of the acid alone at room temperature ----- ■----- and dosing of the acid remaining after attack acid of calcium chloride at room temperature ------■------

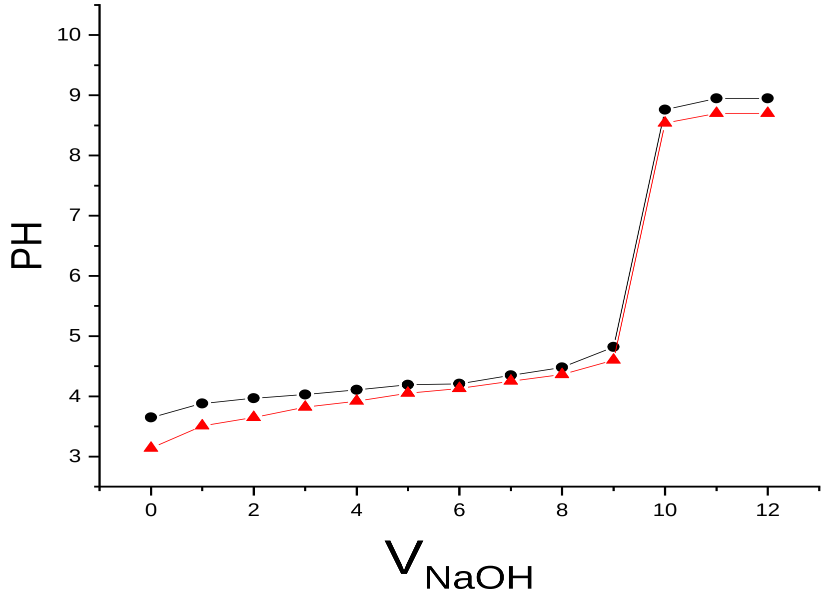


Fig 5:- Dosing of the acid remaining after acid attack of calcium chloride hydrated treated at 400°C ----- ■----- and 500°C----- ▲----- in a muffle furnace

A conservation of volume of neutrality was observed for the four assays, this is explained by the inertia of the acid attack for calcium chloride.

This finding is very important to highlight that the acid attack HCl only reaches calcite and dolomite whether they are pure or part of the composition of shale**(H.Mokhlis and A.Attaoui : 2022).**

4/ Interpretation

4.1/ Determination of the percentage of presence of hydrated calcium chloride and free chlorine in oil shale (Z0 and Z1)

In paragraph 3 we found the volumes by correspondence that was used in the complexation reaction to identify calcite and dolomite. If we make the difference of the total volume of the realization of the complexation reaction for the layer Z0 and Z1, and those preventing calcite and dolomite separately we have:

■1.2 - 0.37 - 0.083=0.747cm3 for Z0
■ 1 - 0.22 - 0.065=0.715 cm3 for Z1
These volume values lead us to determine the presence of hydrated calcium chloride in these layers, as the complexation for these calcium chlorides is 100% (paragraph 2).
We have:
■ (0.082×0.747/10×2)×147=0.450 g/l for Z0
■ (0.082×0.715/10×2) ×147=0.431 g/l for Z1
With 2 being the equivalent number.
Corresponding to the 50 cm_3 prepared at the beginning we have:
0.0225 g in 50 cm^3 for Z0
0.0216 g in 50 cm^3 for Z1
The presence of hydrated calcium chloride is presented in percentages of
2.25 % for Z0
2.16 % for Z1
We will also calculate the presence of free chlorine in the shale of the first two layers using dispersive X-ray diffraction:
The percentage of presence of chlorine **(M.Hafid and A.Attaoui: 2022)**, according to these dispersive peaks is:
● 5.11% chlorine for Z0
● 4.57% in chlorine for Z1
We can therefore calculate the percentage of free chlorine in the two layers.
In 2.25% of the calcium chloride we have 1.09% of chlorine for the Z0 layer, and in 2.16% of the calcium chloride we have 1.04% of chlorine for the Z1 layer.
Differentiating between these two percentages, this gives.
● 5.11-1.09=4.02% of free chlorine in Z0 and
● 4.57-1.04=3.53% of free chlorine in Z1.

We also note that this free chlorine includes a light fraction of NaCl, this light fraction is due to the fact that the sedimentation was done in a marine environment, as well as being light due to the non-identification of sodium in the X-ray spectra.

Looking at both values we can assume a certain static equilibrium of the compounds and elements during their natural sedimentation.

4.2/ Conformity of the method for another layer (Z2) of the Tarfaya deposit

The same assay was adopted (complexation reaction) we solubilized one gram of Tarfaya oil shale (layer Z2) in 50 $cm^3$of cold distilled water, after filtration and dosing of 10 ml of the filtrate with EDTA.

The volume of the neutrality is 1.25 cm3, which brings us to the mass concentration of calcium, which is 0.205g/l

If we reduce this to 50 cm^3 as the working volume we have found 0.0103g in 50 cm3.

The percentage presence of calcium calcite was found by acid etching in a previous work to be 48.4% (Z2). Similarly for dolomite it is 6.8% (Z2) **(H.Mokhlis and A.Attaoui: 2022).**

We will look for the volume of neutralization by complexometry taking into account the percentage of calcite in Z2, by simple correspondence.
100% pure calcite (1g) → 0.7 cm^3
48.4% calcite (1g of Z2) → (calcite) Z2=0.339 cm^3
Assuming that dolomite behaves in the same way as calcite and assuming that it consumes the same volume.
6.8% dolomite (1g of Z2) →Vdolomite (Z2) = 0.048 cm^3
For the determination of the percentage of presence of calcium chloride and free chloride in the oil shale (Z2), we make the difference of the total volume of the realization of the complexation reaction for the layer Z2, and those coming from calcite and dolomite separately we have :
● 1.25-0.339-0.048=0.863 cm3
This volume value leads us to determine the presence of hydrated calcium chloride in this layer, as the complexationrealisation for this calcium chloride is 100%.

We have:
- $(0.082\times0.863/10\times2)\times147=0.520$ g/l for Z2

With 2 being the equivalent number
Corresponding to the 50 cm3 as the working volume we find 0.026g.
The percentage presence of calcium chloride hydrate in this layer is 2.6%.
We will also calculate the presence of free chlorine in this layer (Z2) from dispersive X-ray diffraction:

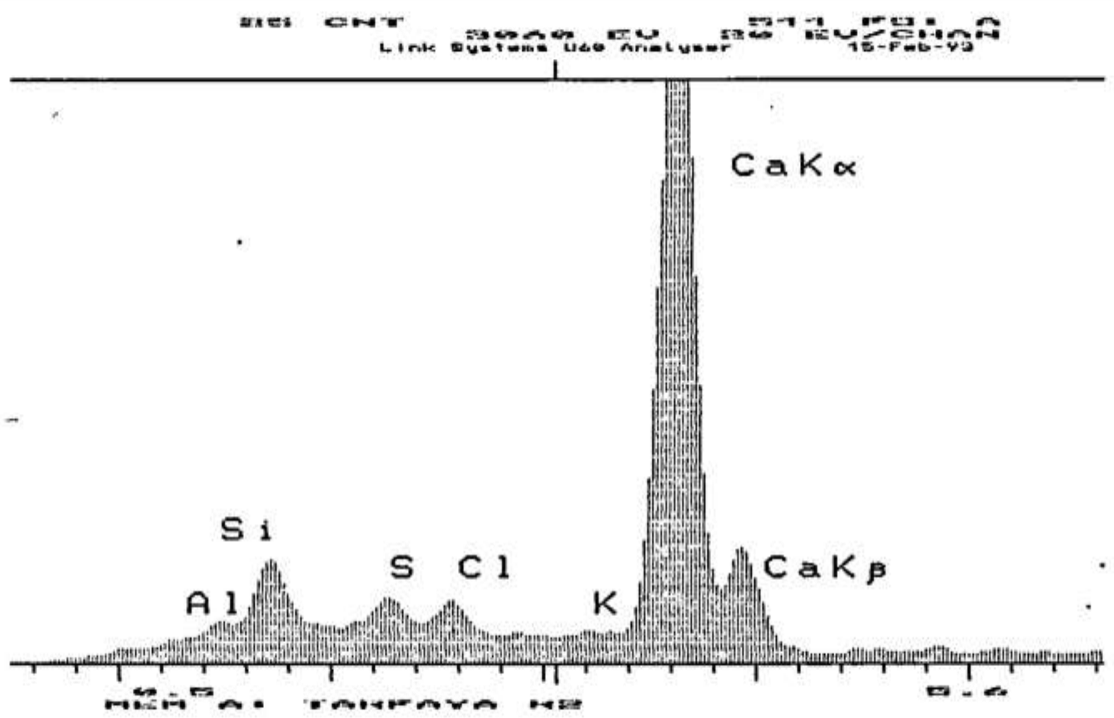


Fig 6:- Dispersive X-ray spectrum for sample Z2.

We observe the presence of the chlorine peak and the non-identification of sodium, so that the chlorine present, apart from a fraction of NaCl, can only be hydrated calcium chloride and free chlorine. We will also calculate the presence of free chlorine in this layer (Z2) from dispersive X-ray diffraction:

The percentage presence of chlorine according to these dispersive peaks is: 5.45% chlorine **(M.Hafid and A.Attaoui: 2022).**

We can therefore calculate the percentage of free chlorine in this layer.

In 2.6% of the calcium chloride we have 1.26% of chlorine (Z2).
The difference between these two percentages gives
- 5.45-1.26=4.19% of free chlorine in (Z2).

According to these results we can estimate the concentration of chlorine in the different layers of the Tarfaya deposit, which varies between 4 and 5%, due to the natural static equilibrium caused by the preservation of the chlorine concentration in the Atlantic Ocean.

Conclusion:-

For oil shale, an energetic material with multiple constituents, whether mineral or organic, we chose calcium in this study based on three analytical methods (complexometric dosing, acid etching and dispersive X-ray diffraction).

This calcium as determined is present in several forms: calcium calcite, calcium dolomite, calcium chloride and oxidized calcium.

Three layers of the Tarfaya oil shale deposit were analyzed by these complementary methods to discern these calcium qualities.

By simple difference in volume of the complexometric assay with the pure reference which is calcite we have highlighted the presence in the shale of the calcium chloride type.

By combining the three methods of analysis and developing the calculation designed we were able to determine the calcium chloride as well as the free chlorine in the three layers mentioned. The following table shows the mass percentages for each layer.

Sample	Z_0	Z_1	Z_2
Mass percentage of calcium chloride hydrate	2.25%	2.16%	2.6%
* Free chlorine mass percentage	4.02%	3.53%	4.19%

According to this table we conceive a static equilibrium between free chlorine and calcium chlorides, as in each geological period the chlorine concentration was the same.

It has been noted that the concentration of chlorine has been decreasing since that time.

*We also note that this free chlorine includes a light fraction of NaCl, which is present because the sedimentation was done in a marine environment, as well as being light due to the non-identification of sodium in the XRD spectra.

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