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Article

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CHARACTERIZATION OF SHALE FORMATION OF ABANDONED PETROLEUM WELLS AND TREATMENT USING ACID SIMULATION TECHNIQUE

The object of research is shale, which is a combination of carbonate (calcite or dolomite), and non clay minerals such as silica (quartz) and clay minerals such as kaolinite. Characterization of various minerals in shale formed in six abandoned petroleum wells was done using Energy Dispersive X-ray (EDX), X-ray diffraction (XRD) and Fourier Transformation Infra-Red (FTIR). Shale may contain a wide variety of minerals. The shale formation within the abandoned wells in the current study is at a deep of about (2600±300) meters. Three shale formation samples were collected from each of the abandoned wells. Characterizing the constituents of the clay minerals of the shale is important in the drilling and the treatment process.

The analyses declared that, some shale formation samples are similar. The study was continued on three abandoned petroleum wells (I, II and III). The XRD and FTIR obtained results of shale analysis show the existence of calcite ($CaCO_3$) and quartz (SiO_2) in the shale samples. Dolomite $CaMg(CO_3)_2$ is present in well (II) and well (III), and muscovite $H_2KAl_3Si_3O_{12}$ is present in well (I). Also, Kaolinite $Al_2Si_2O_5(OH)_4$, and barite ($BaSO_4$) components are detected in the FTIR results. Mg, K, Al and Ba trace elements are detected by EDX analyses and may contribute chemically.

Shale technology and research development is concern with three steps: Characterization, simulation, and permeability stimulation. The present study focusing on the characterization and simulation of the shale formed in six abandoned (non-producing) petroleum wells for enhancing the productivity of carbonate reservoirs.

Keywords: *shale technology, carbonate reservoirs, Energy Dispersive X-ray, X-ray diffraction, Fourier Transformation Infra-Red.*

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1. Introduction

Mineral recognition and measuring the substance components desires explicit explanatory strategies, providing further chemical information. Mineralogical portrayal of convoluted minerals like soils or clays is a principle subject so as to define their chemical and physical manners [1]. X-ray diffraction (XRD) is the usually utilized tool, giving far reaching information on the structure of the shale rock composition [2, 3].

The organic matter and fine grain mineral particles are considered the main components of sedimentary rock. Shales are a collection of sedimentary rocks. They have considerable potential as a natural supply of hydrocarbon [4].

For dolomite in marine cores the Fourier Transformation Infra-Red (FTIR) is the convenient technique. Priority involve quick analysis (≈2 min), little sample size (≈0.3 g), and matched to alternative techniques like XRD, comparatively low cost instrumentality. The FTIR was used to determine absorption features distinctive to dolomite [5]. These features help in qualitatively recognize dolomite in sediment specimens. Observation of a sample constituents using XRD or FTIR is a function of the concentricity of that constituents and the matrix material within which the constituents are found [6].

In order to perform the XRD quantitative analyses in minerals, they must be in high crystallinity. Whereas, the XRD technique can't deliver perfect quantitative data for the amorphous or roughly crystalline minerals [7]. Indian origin shale oil (hydrocarbons, minerals and metals) was identified using X-ray diffraction, Infra-Red and Nuclear magnetic resonance techniques [8]. The application of the FTIR-analyses together with thermal analyses – Differential thermal analysis (DTA)/Thermogravimetric analysis (TG) for evaluating clay minerals in sediments are performed. These techniques had been linked for a deduction of mineral constitution in sample sediments in Northern Moravia, Czech Republic [9].

Throughout the petroleum industry, physicists, reservoir engineers and chemists are engaged in increase their understanding of reservoir behavior and carbonate formations [10].

The accumulation of clay minerals, calcite and dolomite in the formation led to the closure of the well, a decrease in reservoir pressure and natural permeability [11]. In petroleum industry, as cheaper alternatives to drilling and re-drill, permeability stimulation techniques were adopted for geothermal application [12]. The technology of acidizing has progressed over the years with the development of methods, additives and to improving the coverage of areas during the acidizing process and systems to address different problems related to acid injection [13]. The productivity of the matrix acidized wells is estimated using the latest updated wormhole propagation models according to field conditions [14].

Thus, *the object of research* is shale, which is a combination of carbonate (calcite or dolomite), and non-clay minerals such as silica (quartz) and clay minerals such as (kaolinite). *The aim of research* is to investigate the usefulness of XRD and FTIR spectroscopic data combined with the Energy Dispersive X-ray (EDX) elemental analysis to obtain an evaluation of the mineral composition of complex mineral mixtures. Also, the work concern with, how to overcome the shale formation damage in the abandoned wells and to facilitate a deeper understanding of the controls on oil distributions.

2. Methods of research

2.1. Material. Shale is normally arranged from the composition of clay and silt minerals. It is a sedimentary rock. The samples were collected from six abandoned petroleum marine wells in the south Sinai fields (Egypt). The analyses declared that some shale formation samples are alike. The study was continued on three abandoned petroleum wells. The shale formation in the abundant wells in the current study at a deep of about 2000±400 m. Three shale formation samples were collected from each of the abandoned well.

2.2. Techniques

2.2.1. Energy Dispersive X-ray (EDX). Scanning Electron Microscope (SEM) JEOL-5400 (Germany) was used to perform the elemental analysis of the collected shale samples. The samples were exposed to 20 keV energetic electron beam leading to the creation of characteristic X-rays of each sample. The elemental formation of the shale rock samples from the six abandoned wells was deduced qualitatively and semi-quantitatively through the emitted X-ray spectrum using the EDX spectrometer.

2.2.2. X-ray diffraction (XRD). Identifying the material is a crystalline or amorphous can be done using XRD analytical technique. Shimadzu diffractometer XRD-6000 (Japan) was used to achieve the X-ray diffraction patterns at an electric current of 30 mA, a copper target (λ=0.1542 nm) and the operating voltage is 40 KV. The pattern was registered at a 2θ-scan range of 4° to 90° and the scanning rate of 2°/min.

2.2.3. Fourier Transformation Infra-Red (FTIR). Infrared spectrometer Bruker vertex 70/70v (Germany) was used to accomplish FTIR spectra of the shale samples. In the range of 400 to 4000 cm^{-1} all the measurements were done. FTIR transmission bands as a function of wavenumber were recorded.

2.2.4. Simulation for de-carbonization of shale. Apparatus, supplies, preparation of test samples and procedure are reported in the lab manual of the ASTM Designation D 3042 [15, 16]. Each sample shall have a minimum weight of 100 g.

3. Research results and discussion

3.1. Energy Dispersive X-ray (EDX). The characteristic X-ray spectrum is the element fingerprint, which assures the type of the constituent element nevertheless of its chemical bonding. The elemental analyses of the samples collected from six abandoned petroleum wells under implementation are obtained using EDX analysis. The results are shown in Fig. 1. As seen in the figure, the EDX analyses of some shale formation samples are similar. The study was continued on three abandoned wells (I, II and III).

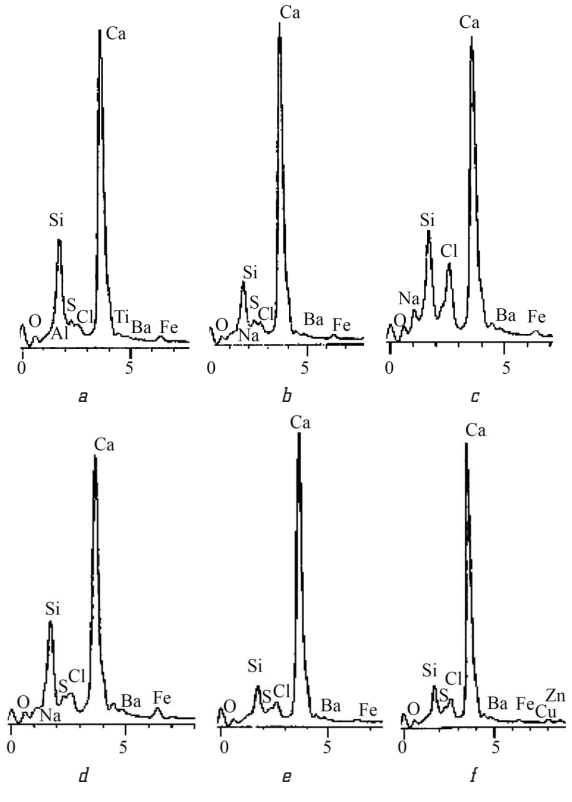

Fig. 1. Represents the EDX analysis results and the elemental composition arranged in the samples of the six abandoned petroleum wells: *a* – well 1; *b* – well 2; *c* – well 3; *d* – well 4; *e* – well 5; *f* – well 6

For every component element, the elemental analysis are accomplished with anticipated error <±0.5 %. In Table 1, the atomic weight percentages (at. %) are reported (after normalizing to unit mass) for every element.

Table 1

The EDX analysis for the three abandoned petroleum wells (I, II, III)

Elements	Well (I) (at. %)	Well (II) (at. %)	Well (III) (at. %)
Ca	65.7	73.8	74.7
Si	19.8	13.9	12.8
O	3.9	2.7	2.8
S	1.6	1.2	0.6
Al	2.6	1.9	0.8
Mg	0.4	2.3	2.9
Ba	2.2	2	0.6
Cl	0.6	0.5	1.3
Fe	1.1	0.9	1.9
K	1.8	0.6	0.4
Ti	0.3	0.2	1.2

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The above results are normalized to 100 % of the sample constituent elements which represent the total atomic percentage. EDX analyses demonstrated that Calcium and Silicon at. % values are the most abundant elements in the shale structures.

However, carbon is hard to be detected because of its low atomic number. The result is a weak signal from that element and longer wavelength X-ray generated by this light element atom. EDX device model OXFORD-ISIS (year 1995) attached to scanning microscope JEOL-5400 is not able to detect such lines.

3.2. X-Ray Diffraction Analyses (XRD). Study of the structure of the samples collected from the abandoned petroleum wells was accomplished using XRD technique. Shimadzu diffractometer XRD-6000 was used to achieve the X-ray diffraction patterns at 30 mA, 40 KV and a copper target (λ=0.1542 nm). The analyses were performed at a 2θ-scan range of 4° to 90° and the scanning rate of 2°/min at room temperature. The XRD spectra for the shale formation samples are shown in Fig. 2–4. Shale composes several amounts of various minerals. Calcite, quartz and muscovite were observed in the samples of the well (I) as shown in Fig. 2. The XRD results represent that, 31.09° and 50.26° combine small dolomite peaks shown in Fig. 3, 4 and muscovite peaks (8.91°, 17.72°, 26.85°, 31.89°) shown in Fig. 2.

Fig. 2–4 show the search and match analysis of calcite, quartz, dolomite and muscovite. Diffraction spectra record X-ray intensity in relation to 2θ. Fig. 2–4 display the diffraction pattern for the shale samples in the three abandoned wells with the standard diffraction marked peaks of these minerals. The peaks are produced in the diffraction pattern of the diffracted X-rays from a crystalline material.

The XRD figures display the matched peaks of the minerals. Calcite shows a better crystalline form with the highest peaks in comparison with the other minerals.

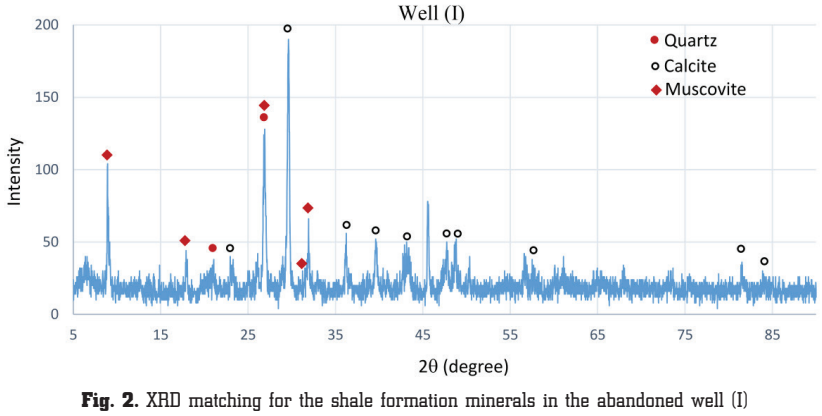

Fig. 2. XRD matching for the shale formation minerals in the abandoned well (I)

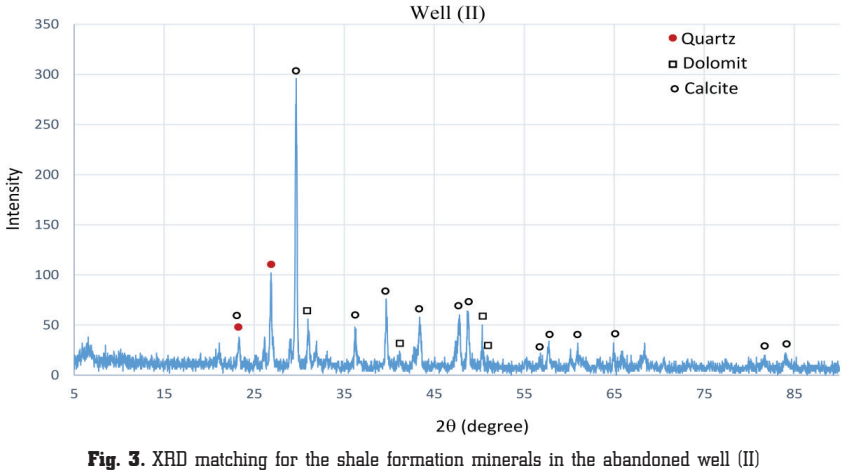

Fig. 3. XRD matching for the shale formation minerals in the abandoned well (II)

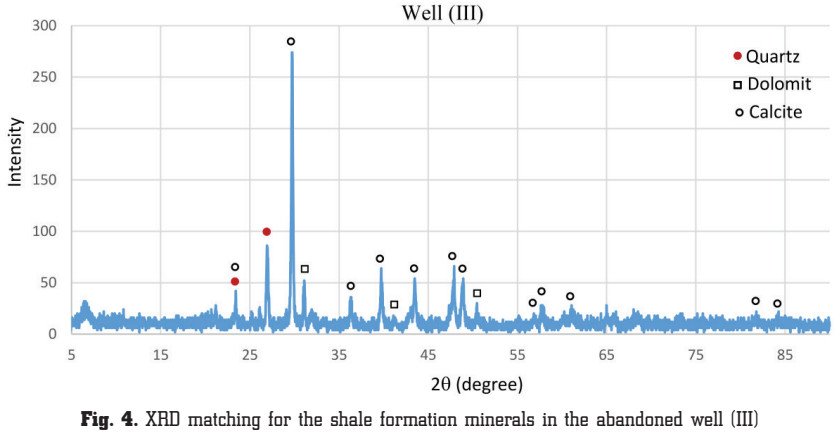

Fig. 4. XRD matching for the shale formation minerals in the abandoned well (III)

3.3. Fourier Transformation Infra-Red (FTIR). The chemical bonds in a molecule were identified using FTIR analyses. It may be either inorganic or organic. Investigation of the shale formation sample's composition and identification of the compounds were performed using infrared spectrometer Bruker vertex 70/70v to accomplish FTIR spectra of the shale samples in the range of 400 to 4000 cm^{-1}.

The spectral details of shale formation minerals in the abandoned wells are displayed in Fig. 5, indicates a wide transmission peak for CO_3 at ≈2514 cm^{-1}, 1797 cm^{-1}, 1404 cm^{-1}, 1043 cm^{-1}, 871 cm^{-1}, and 705 cm^{-1}. These values are close to that reported [17, 18] to be the essential modes of oscillation for the carbonate ions in calcite ($CaCO_3$) and are the typical traits for this molecule. Fig. 5 also indicates that, the calcite is in abundance (with various quantities) in the shale formation of the three abandoned petroleum wells.

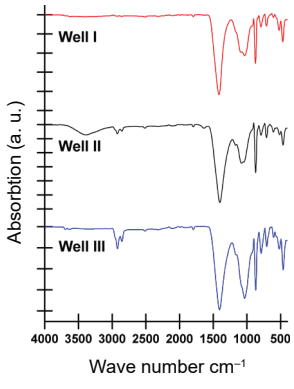

Fig. 5. FTIR spectra of the shale formation minerals in the abandoned wells

Analogize to calcite, dolomite demonstrates particular FTIR transmittance closed to the calcite bands, 2625 cm^{-1} and 729 cm^{-1}, and the presence of a band at 1114 cm^{-1} in the samples confirms the participation of dolomite as in Fig. 5. Dolomite thus occurs in well (II) and in wells (III).

The FTIR spectra are characterized by the presence of strong bands at 1163 cm^{-1}, 1079 cm^{-1}, 1057 cm^{-1}, 796 cm^{-1}, 777 cm^{-1}, and 511 cm^{-1}. These bands are at nearly the same positions as reported [17] for the quartz SiO_2.

The location of the high-frequency OH-stretching bands at 3692 cm^{-1}, 3650 cm^{-1} and 3620 cm^{-1} is in good agreement to Raman and FTIR published spectra [19, 20] of kaolinite $Al_2Si_2O_5(OH)_4$. In the wells (I, III), Barite ($BaSO_4$) shows (S–O) a stretching vibration band in the range of 1050–1200 cm^{-1}. Another narrow band present close to 1000 cm^{-1} and also, slightly stronger bands at 700–600 cm^{-1} similar to database report [17]. A summary for the Characterization of Shale Formation of Abandoned Petroleum Wells is reported in Table 2.

Table 2

Chemical structures, elements and compounds of EDX, XRD and FTIR analyses

Chemical Structure	Element (EDX)	Mineral (XRD and FTIR)
$CaCO_3$	Ca	Calcite
$CaMg(CO_3)_2$	Mg	Dolomite
SiO_2	Si	Quartz
$Al_2Si_2O_5(OH)_4$	Al	Kaolinite
$H_2KAl_3Si_3O_{12}$	Al, K, Si	Muscovite
FeS, FeS_2	Fe	Pyrite
$BaSO_4$	S, Ba	Barite

The chemical structures in Table 2 are the same as determined from the search and match software XRD analysis on the shale samples.

3.4. Simulation for de-carbonization of shale. For the solubility analysis, three shale samples were collected from every well, each sample have a weight of 100 g. All samples are deal with 8 % hydrochloric acid (HCl) to calculate the soluble and insoluble minerals percentages by insoluble residue technique. For every well, the average values of the solubility test for the three samples from each well were calculated using equation (1) and reported in Table 3.

Acidizing in calcite:

$$2HCI+CaCO_3 \rightarrow CaCl_2+CO_2+H_2O.$$

Acidizing in dolomite:

$$4HCI+CaMg(CO_3)_2 \rightarrow CaCl_2+MgCl_2+CO_2+H_2O.$$

Percent Insoluble Residue [15, 16]:

$$(A-B)\cdot 100/C, \quad (1)$$

where A – the final insoluble residue with the filter paper weight; B – the weight of the initial filter paper; C – the weight of the original sample.

Table 3

Average values of the solubility tests for three samples from each well by quantitative insoluble residue method

Solubility tests for the collected shale samples (8 % HCl)			
Well No	Average Solubility % ± <1 %		Total
	Soluble weight %	Insoluble weight %	
Well I	48.45	51.55	100
Well II	56.46	43.54	100
Well III	63.63	36.37	100

From the obtained data in Table 3 it is clear that, the average solubility value of the samples from well (III) is more than for well (II) and well (I). The third well samples have a high content of calcite are shown in the characterization analyses figures and the calcium element shown in EDX analysis. Whereas, the samples from well (I) have the lowest ratio of solubility and high ratio of insoluble weight percent. This is due to the presence of quartz and muscovite in addition to the calcite. The solubility of quartz and muscovite in HCl is neglected compared with the solubility of calcite in HCl. Quartz need more specific treatment to be dissolved [13].

When acids add to a carbonate formation, certain minerals in the rock dissolve which creating high permeability canals or wormholes. This is to improve the flow properties of the rock. Wormholes increase production not by eliminating damage, but by dissolving the rock and creating pathways. With the most effective use of acid for any treated formation, there is an optimum set of treated parameters which creates wormholes.

4. Conclusions

EDX, FTIR and XRD were used to confirm that the shale samples include quartz, calcite and other minerals. Calcite and quartz are the dominant minerals in the shale samples of all abandoned petroleum wells. In the shale samples, the

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type of the arranging elements and their atomic percentage were obtained for the six abandoned petroleum wells by the EDX analysis. Mg, K, Al and Ba trace elements are detected by EDX analyses and may contribute chemically.

The XRD results demonstrate the existence of the muscovite in the well (I). But, by the FTIR, It was difficult to recognize the muscovite $H_2KAl_3Si_3O_{12}$ bands, because these bands may be masked by the bands be associated with the other constituent minerals in the shale samples collected from that well.

The dolomite peak intensities in well (II and III) as established by FTIR and displayed in Fig. 5 is regular with the dolomite peak heights as produced using XRD and displayed in Fig. 3, 4. This regular correlation is supportive of the relevance of FTIR information.

So, FTIR technique is able to identify each component in the mineral through transmittance measurements at certain wavenumbers. Kaolinite and barite have a very small peaks suggesting they are beyond the resolution of the detection limit of the XRD analyses.

Calcite and quartz were found in all samples. Dolomite is present in well (II) and well (III), and Muscovite is present in well (I). Kaolinite and barite components may present in some shale samples, although values barely exceed the background level. Low concentrations of some minerals were detected in some samples analyzed using XRD and FTIR. Characterizing the constituents of the clay mineral of the shale will be helpful in the stimulation of the abandoned wells with various techniques for maximum oil reproduction rate.

The results of the XRD and FTIR analyses show that, the main constituent of the shale formation in the wells is the calcium carbonate (as calcite and dolomite). Also, EDX analyses data in Table 1 indicate that, the major element with a high concentration is calcium (Ca), and remain elements are minority. So, the problem of wells is concerning in the formation damage by the carbonate constituent which caused in lowering the natural permeability and so the productivity rate of the wells decreased. Accordingly, the issue of abandoning wells occurred.

The solubility test method of the shale formation samples was done on insoluble residue for determination of carbonate minerals. This method makes it possible to predetermine the weight percentage of insoluble residues in carbonate minerals utilizing a solution of hydrochloric acid to dissolve carbonate minerals. The weight percentage of insoluble material in carbonate is of interest.

Finally, the Insoluble residue simulation process for the samples of each well in the lab was applied on the Abandoned Petroleum Wells in the production field and the results were convenient with the results in the lab.

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