

Thermal Analysis: A Complementary Method to Study the Shurijeh Clay Minerals

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Abstract

Clay minerals are considered the most important components of clastic reservoir rock evaluation studies. The Shurijeh gas reservoir Formation, represented by shaly sandstones of the Late Jurassic-Early Cretaceous age, is the main reservoir rock in the Eastern Kopet-Dagh sedimentary Basin, NE Iran. In this study, X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopic (SEM) studies, and thermal analysis including differential thermal analysis (DTA), and thermogravimetric analysis (TGA) techniques were utilized in the characterization of the Shurijeh clay minerals in ten representative samples. The XRF studies showed that silica and aluminum oxides are present quantities. The XRD test was then used to determine the mineralogical composition of bulk components, as well as the clay fraction. The XRD patterns indicated the presence of dominant amount of quartz and plagioclase, with moderate to minor amounts of alkali feldspar, anhydrite, carbonates (calcite and dolomite), hematite and clay minerals. The most common clays in the Shurijeh Formation were illite, chlorite, and kaolinite. However, in very few samples, glauconite, smectite, and mixed layer clay minerals of both illite-smectite and chlorite-smectite types were also recognized. The XRD results were quantified, using the elemental information from the XRF test, showing that each Shurijeh exhibited low to moderate amounts of clay minerals, typically up to 21%. The amount of illite, the most dominant clay mineral, reached maximum of 13.5%, while the other clay types were significantly smaller. Based on the use of SEM and thermal data, the results of the identification of clay minerals, corresponded with the powder X-ray diffraction analysis, which can be taken into account as an evidence of the effectiveness of the thermal analysis technique in clay typing, as a complementary method besides the XRD.

Keywords: *differential thermal analysis (DTA), Shurijeh formation, thermogravimetric analysis (TGA), X-ray fluorescence (XRF), X-ray diffraction (XRD).*

1. Introduction

It is believed that the quality of clastic reservoir rocks is typically controlled by the type, amount, and distribution pattern of clay minerals [1-4]. Hence, having had a comprehensive knowledge of clay minerals in the reservoir, many significant reserves can be added to the existing hydrocarbon fields in order to help in the rapid identification of bypassed pay zones more efficiently.

For many years, the whole-rock X-ray diffraction (XRD) technique has been the most widely used laboratory technique for clay mineral identification in sandstone reservoirs [5]. However, some shortcomings in sample preparation and treatment, peak selection and weighting factors make it necessary to use other complementary analytical techniques to examine the accuracy of XRD results [6]. Thermal analysis consists of a series of methods which are suitable for studying all compounds that gain or lose energy/weight upon heating [7]. It has been proven that the thermal analysis is a sensitive, specific and relatively rapid technique for the detection of small amounts of minerals [6]. It is also of great value as a complementary method besides X-ray diffraction, which can provide a better knowledge of clay minerals and their associated minerals, simultaneously, able to detect the presence of organic matter as well [8-11].

Among all the different thermal analysis methods, differential thermal analysis (DTA) and thermogravimetric analysis (TGA), have gained the most attention [7]. The DTA analysis is carried out based on the temperature difference between the sample and a witness (control) sample, while TGA uses the weight gain/loss upon heating as an identification factor [7]. In DTA analysis, the difference-thermocouples are used to monitor the temperature difference between the sample under test and a reference sample against time or temperature, while the temperature, in a specified atmosphere, is programmed [7]. It is worthy to mention that heat flow to both samples remains the same, rather than the temperature in this method [7]. In the TGA method, having decomposed the various components of the sample as the heat increases, the weight percentage of each resulting mass change is measured [7]. The sample configurations such as the particle sizes, mass

and heating rate can greatly affect the DTA and TGA curves [7]. Therefore, to ensure optimum peak resolution, samples should be fine-grained into powders and the time at any temperature must be long enough to complete the reactions [7]. The principle of DTA was first used by Frankenheim (1837, 1854) for geological purposes [7]. Since then, geological materials have had considerable influence on the development of the DTA method [7]. The application of both methods has a long history in the identification of clay minerals, e.g., the DTA study of the chlorite minerals in 1927, revealed the broad application of this method in aiding the characterization of complex mineral series [6-17].

Furthermore, all the different groups of clay minerals undergo thermal reactions when heated and their unique thermal curve features make them distinguishable for the most parts in thermograms [10]. Loss of adsorbed water in illite, the most dominant clay mineral in sandstone reservoirs, begins from 50 to 300°C [18-19]. An endothermic reaction extends from 50 to 195°C, followed by a definite inflection at 300°C showing the beginning of the decomposition for hydroxyl water [18-19]. A second inflection occurs at 385°C, which completes at 925°C [18-19]. Another endothermic reaction begins at 485°C, attaining a maximum at 560°C, and is essentially completed at 740°C [18-19]. The last endothermic reaction attains a peak temperature at 900°C and is immediately followed by a small exothermic reaction at 920°C with a decrease in slope at 925°C [18-19]. Thermograms of smectite group are similar to illite, which begins with endothermic peaks between 100 and 200°C (loss of adsorbed water) [18-20]. This can be continued by several endothermic reactions from 200 to 260°C [18-20]. Further, the next slight endothermic reaction occurs between 510 and 650°C, due to the loss of hydroxyl units from lattice structure, followed by a third endothermic reaction between 750 and 930°C [18-20]. The exothermic reaction above 930°C is accompanied by the loss of negligible amounts of water [18-20]. A large variety of curves have been published for chlorite [12, 19, 21-22]. Dehydroxylation starts in chlorite between 550 and 600°C and the remaining octahedral sheet dehydroxylates between 810 and 870°C [21].

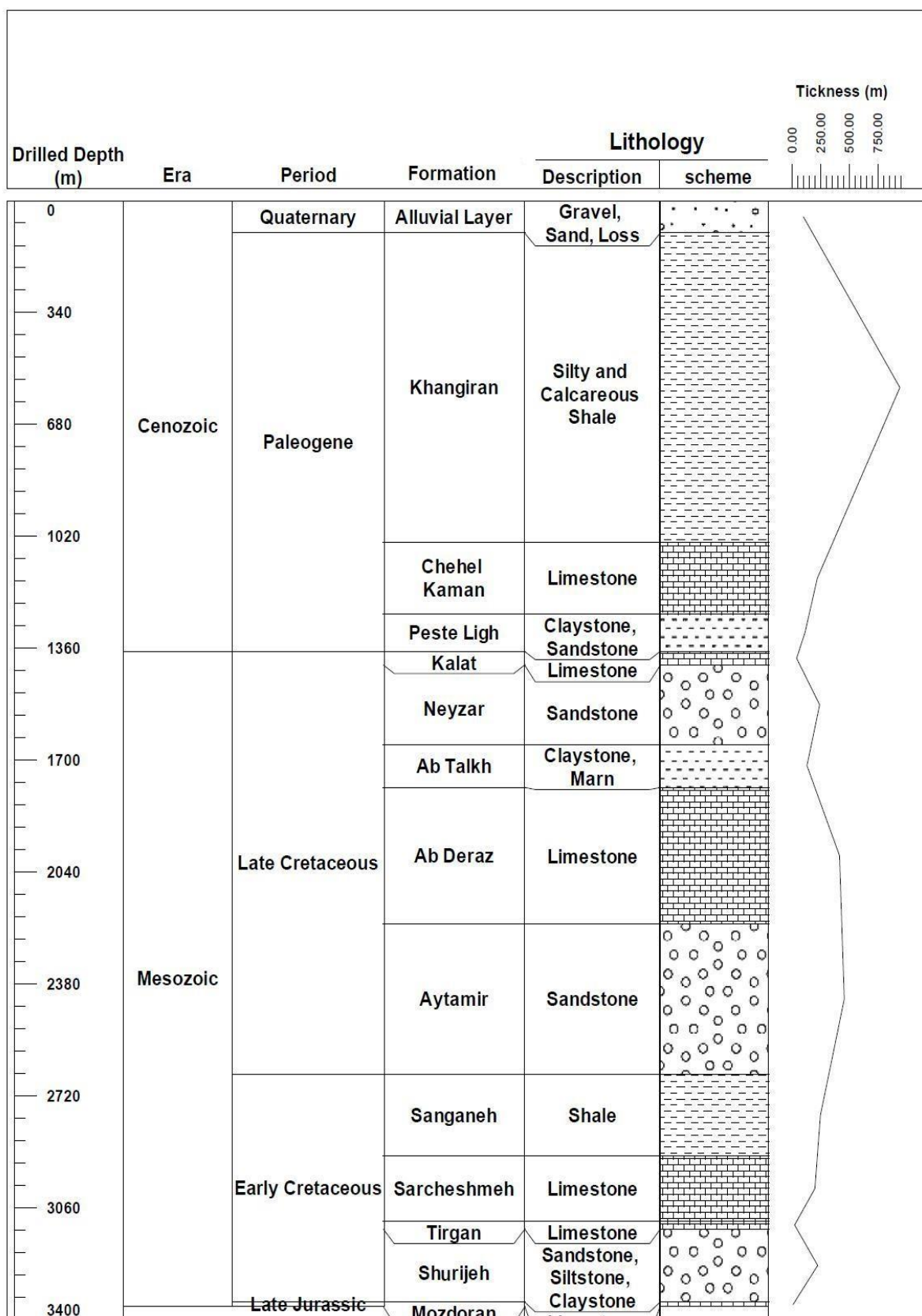


Fig. 2. The stratigraphic column in the understudy gas producing well, Kopet-Dagh sedimentary Basin (NIOC, 1986)

3. Materials and Methods

3.1. Materials

Ten core samples were taken from two wells in an Eastern Kopet-Dagh gas field. Four of the samples labeled with "G", were taken from depths of 3204.6 to 3289.6 m in a gas producing well and the remaining six samples labeled with "N", were taken from depths of 3181.21 to 3206.83 m in other non-producing wells. The samples were then crushed in order to pass through a 0.2 mm sieve and mixed to obtain a homogeneous mixture.

3.2. Methods

The clay minerals characterization in the Shurijeh Formation was carried out using a number of instrumental methods such as X-ray

diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM), and thermal analysis including differential thermal analysis (DTA), and thermogravimetric analysis (TGA).

3.2.1. X-ray fluorescence (XRF)

The core samples were first subjected to the XRF test on an automated Philips MagiX PRO wavelength-dispersive X-ray fluorescence spectrometer facility, meanwhile the loss on ignition (LOI) at 950°C was determined by the standard method [30] as well. Both tests were carried out at the laboratories of the Iranian Mineral Processing Research Center (IMPRC). The chemical composition and relevant LOI of the core samples are shown in Table 1.

Table 1. The results of XRF test for the Shurijeh samples

Code	MgO (%)	Al ₂ O ₃ (%)	SiO ₂ (%)	SO ₃ (%)	K ₂ O (%)	CaO (%)	Fe ₂ O ₃ (%)	Na ₂ O (%)	LOI (%)
G-1	1.20	11.28	74.21	0.65	2.50	3.76	0.72	3.26	2.42
G-2	0.64	11.32	75.56	1.06	2.90	3.23	1.31	2.83	1.15
G-3	3.25	11.20	56.69	3.12	3.70	7.46	7.62	0.76	6.20
G-4	3.61	4.32	78.46	0.00	0.79	5.35	1.02	0.50	5.95
N-1	1.59	10.56	70.34	2.29	2.55	5.86	1.03	2.10	3.68
N-2	1.99	8.65	66.34	6.12	2.07	8.56	1.00	1.09	4.18
N-3	1.39	7.55	42.78	22.76	1.95	18.46	0.99	1.24	2.88
N-4	1.01	14.38	62.70	2.29	5.03	5.90	3.41	1.07	4.21
N-5	1.69	8.53	48.47	17.41	2.24	15.46	1.47	0.91	3.82
N-6	1.59	13.44	57.56	8.29	3.03	8.03	2.64	2.46	2.96

3.2.2. X-ray diffraction (XRD)

The X-ray diffraction patterns were obtained on a Bruker AXS D8-Advance powder X-ray diffractometer, with Ni-filtered Cu K_α radiation having a 2θ scanning speed of 0.02/s at 40 kV and 30 mA at the X-Ray laboratory of school of Mining Engineering, University of Tehran. Thus step scanning from 4 to 70 and 4 to 35 (2θ) degrees were used for the bulk and clay mineralogy purposes, respectively. The main mineral constituents of the samples were identified (Fig. 3a) by comparing 'd' values of diffraction patterns obtained from analyzing randomly oriented samples [31]. A series of simultaneous equations were then formulated, using the whole-rock major elemental analyses from the XRF data (Table 1), to quantify the XRD results. Tables 2 and 3 show the quantitative results of bulk mineral contents of samples, as well as each clay mineral contents,

respectively. Table 4 shows the minimum, maximum and the average values for each clay mineral in both wells.

To enhance the weak peaks of clay minerals, all the identified non-clay minerals were removed with both standard physical and chemical treatments [5], and in each removal stage, clay minerals were dispersed into individual colloidal particles in the suspension, using a 0.1% solution of Na(PO₄)₆ to avoid the aggregation of submicroscopic polymineralic flocculates. A paste of <2 μm fraction was smeared onto three glass slides with a homogeneous size distribution and similar thickness. The X-ray diffraction test was then conducted on oriented clay glass slides under three separated states of air-dried, saturated with the vapor of ethylene glycol for at least 24 h at 60°C, and heated at 550°C for 1 h (Fig. 3b).

Table 2. The mineral content of the Shurijeh core samples, quantified using XRF data.

Code	Quartz (%)	Plagioclase (%)	K-feldspar (%)	Anhydrite (%)	Carbonate (%)	Hematite (%)	Clays (%)
G-1	65.5	17.1	4.6	1.1	4.0	0.0	7.7
G-2	64.0	19.6	7.3	1.8	2.0	0.0	5.3
G-3	46.8	8.7	1.5	5.3	15.2	1.5	21.0
G-4	72.2	5.5	0.3	0.0	15.6	0.4	6.0
N-1	56.9	18.4	5.3	3.9	7.3	0.0	8.2
N-2	56.7	12.6	3.6	10.4	8.8	0.3	7.6
N-3	32.4	12.5	3.4	38.7	5.0	0.0	8.0
N-4	49.7	12.4	4.8	3.9	6.1	2.1	21.0
N-5	40.0	10.7	2.3	29.6	6.3	0.9	10.2
N-6	38.0	23.9	3.3	14.1	3.5	1.2	16.0

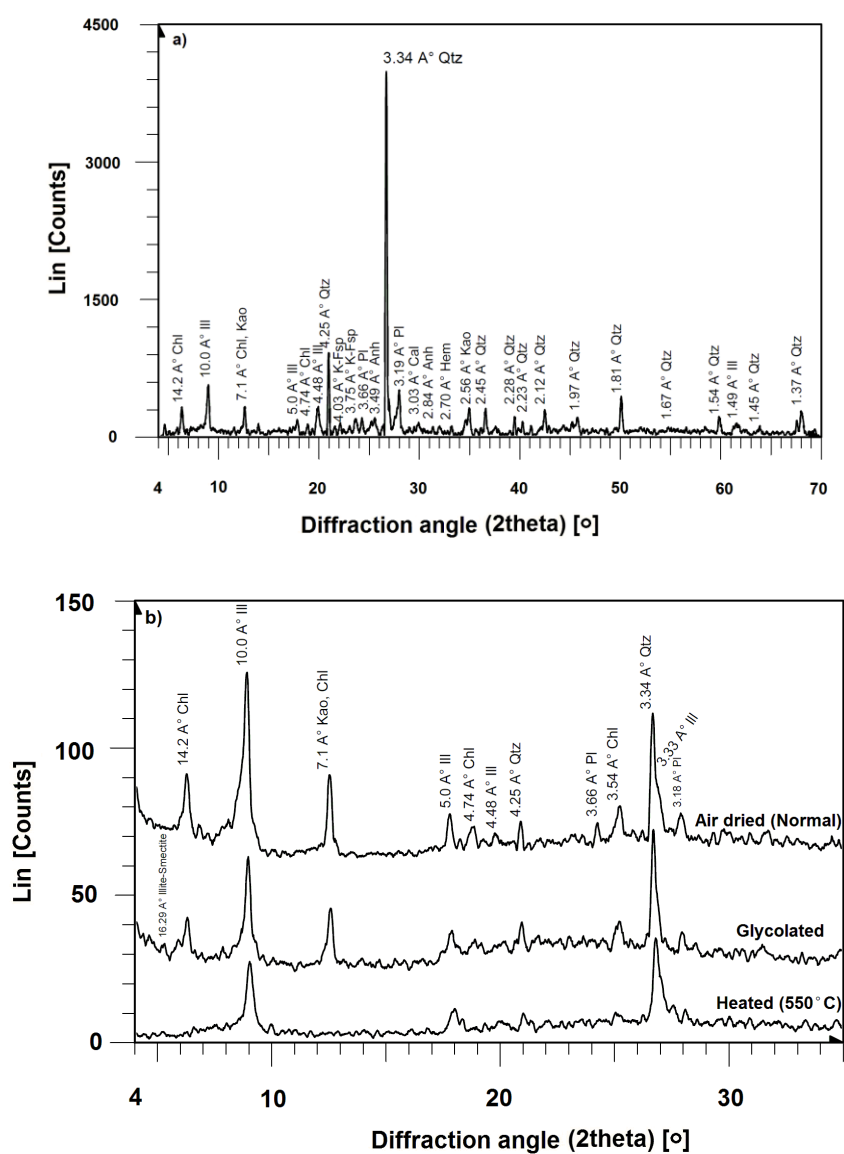


Fig.3. a) The typical bulk powder XRD diffraction pattern, b) The typical clay fraction XRD diffraction pattern of the Shurijeh samples (Sample code: N-4); Chl=Chlorite, Ill=Illite, Kao=Kaolinite, Qtz=Quartz, Pl=Plagioclase, Hem=Hematite, Anh=Anhydrite, Cal=Calcite

Table 3. The clay minerals contents of the Shurijeh core samples, quantified using XRF data

Code	Kaolinite (%)	Chlorite (%)	Illite (%)	Glauconite (%)	Smectite (%)	Mixed layer Clays (%)
G-1	1.6	1.3	2.8	2.0	ND	ND
G-2	1.7	1.3	1.1	1.2	ND	ND
G-3	1.8	4.7	13.5	ND	1.0	ND
G-4	1.6	1.5	2.9	ND	ND	ND
N-1	2.5	2.5	3.2	ND	ND	ND
N-2	2.3	1.7	3.6	ND	ND	ND
N-3	2.2	2.4	3.4	ND	ND	ND
N-4	2.4	3.2	13.6	ND	ND	1.8
N-5	1.4	1.4	6.2	ND	ND	1.2
N-6	3.8	3.5	8.1	ND	ND	0.6

ND=None detected

Table 4. The minimum, maximum and the average values for each clay mineral in the gas producing well

	Gas producing well			Non-producing well		
	Minimum (%)	Maximum (%)	Average (%)	Minimum (%)	Maximum (%)	Average (%)
Kaolinite	1.6	1.8	1.7	1.4	3.8	2.4
Chlorite	1.3	4.7	2.2	1.4	3.5	2.5
Glauconite	1.1	13.5	5.1	3.2	13.6	6.4
Smectite	ND	1.0	0.3	ND	ND	ND
Mixed layer Clays	ND	ND	ND	0.6	1.8	1.2

ND=None detected

3.2.3. Scanning electron microscopy (SEM)

The clay fraction prepared from two samples (G-4 and N-1) were selected and examined using a LEO 1450VP scanning electron microscope (SEM) equipped with the energy dispersive micro analysis system, at the SEM

laboratory of the Iranian Mineral Processing Research Center (IMPRC). It is worthy to mention that the samples were first carbon coated to make the surface conductive. The SEM photomicrographs are shown in Figure 4.

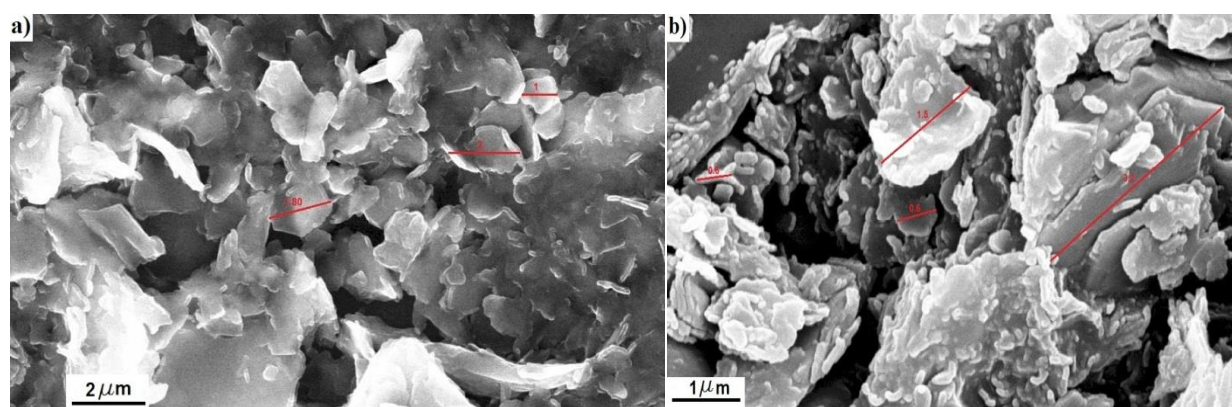


Fig. 4. The SEM photomicrographs. a) The magnesium rich chlorite in the gas producing well at X7000 magnification (Sample code: G-4), b) The booklet type kaolinite in the non-producing well at X15000 magnification (Sample code: N-1). The identifications were based on the EDX analysis and the morphology of grains.

3.2.4. Thermal Analysis: Differential Thermal Analysis (DTA), and Thermogravimetric Analysis (TGA)

Simultaneous thermal analysis including differential thermal analysis (DTA) and thermogravimetric analysis, were obtained with the thermal instrument STA 409 PC LuxxO manufactured by NETZSCH-Germany by applying a heating rate of 30 K.min⁻¹, and

final temperature of 1200°C (Fig. 5). The thermal analysis was carried out at the relevant laboratory in the Iranian Mineral Processing Research Center (IMPRC). An amount of approximately 51.5 ±1.5 mg from each powder sample was analyzed. The thermograms of DDTA-DTA and DTGA-TGA are shown in Figures 6 and 7, respectively.

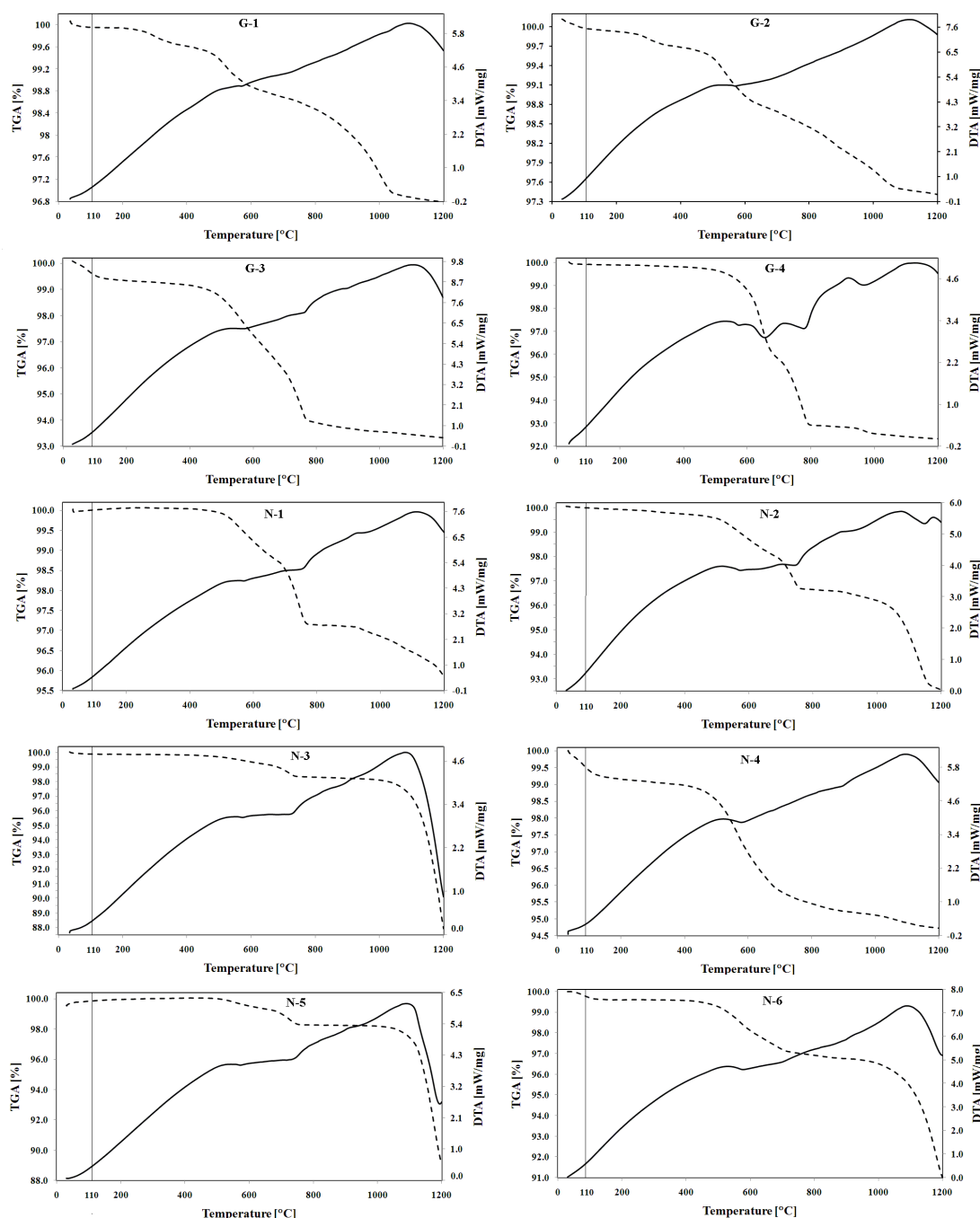


Fig. 5. Simultaneous Shurijeh thermograms. The TGA analysis is shown by dashed curvilinear lines (---) on the left side, and DTA analysis is shown by solid lines (____) on the right side.

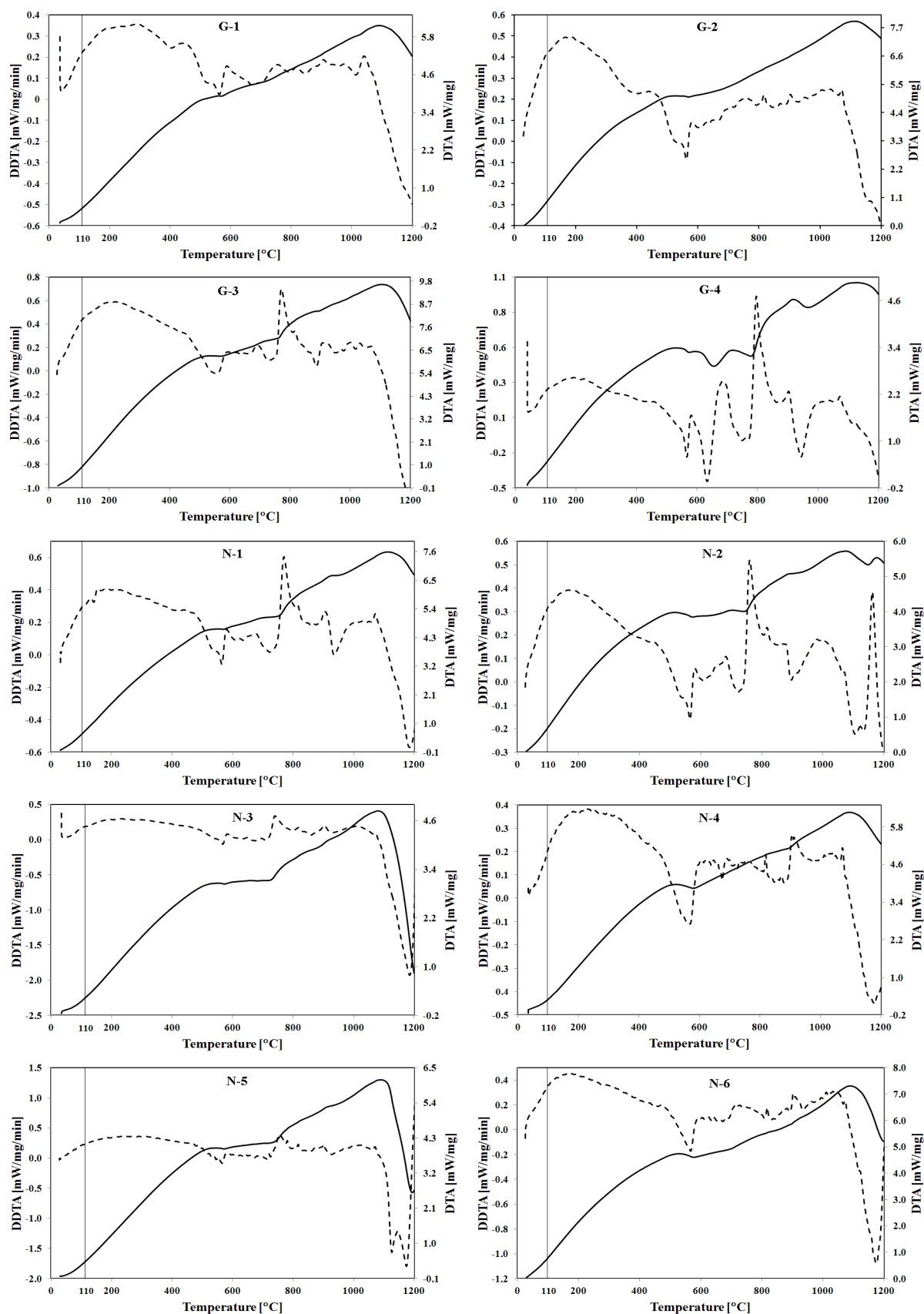


Fig. 6. The DDTA-DTA Shurijeh thermograms. The DDTA analysis is shown by dashed curvilinear lines (---) on the left side, and DTA analysis is shown by solid lines (____) on the right side.

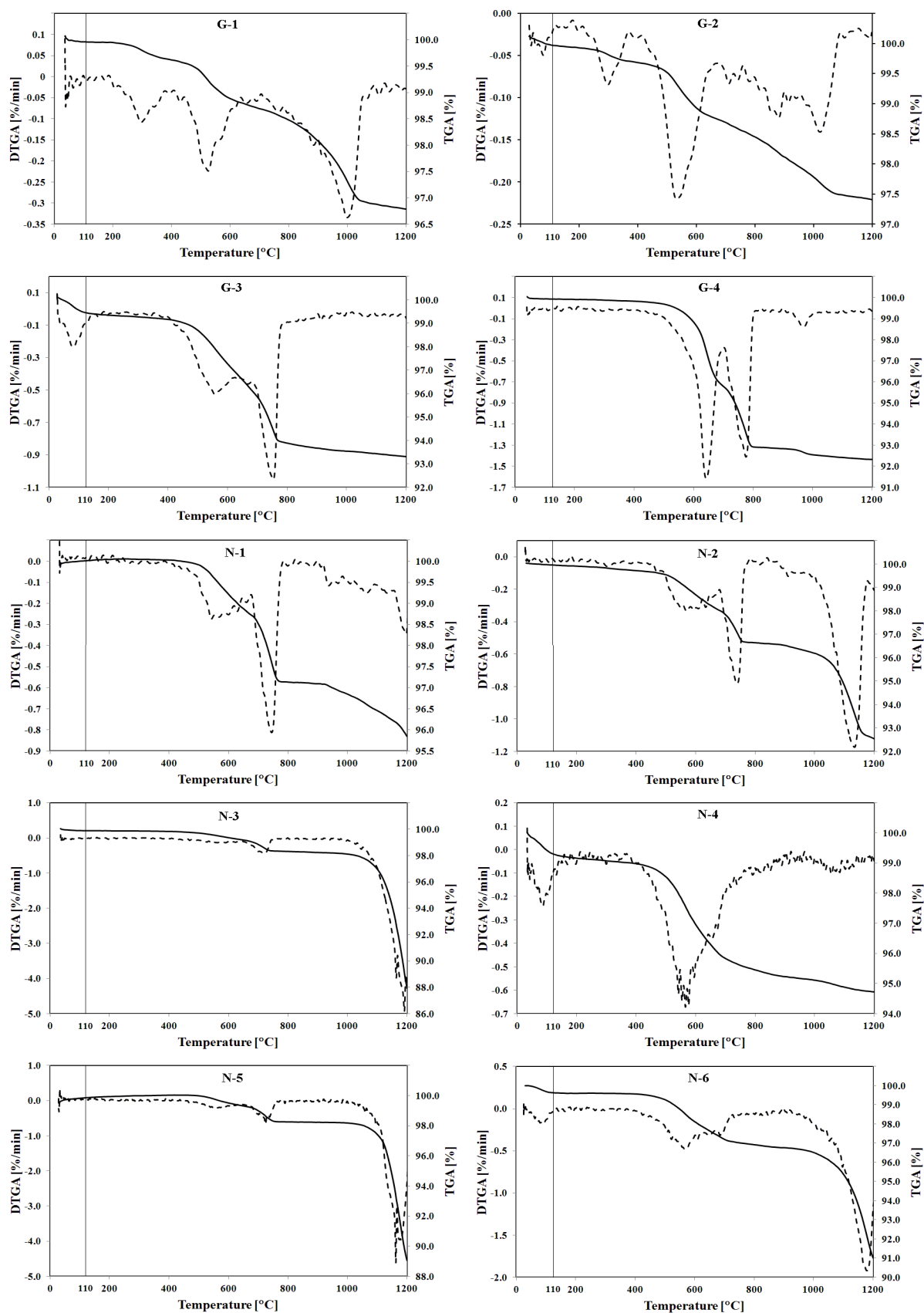


Fig. 7. The DTGA-TGA Shurijeh thermograms. The DTGA analysis is shown by dashed curvilinear lines (---) on the left side, and TGA analysis is shown by solid lines (____) on the right side.

4. Results and Discussion

As shown in Table 1, it is obvious that the chemical analysis of the Shurijeh samples contained silica and alumina in major quantities and the other elements in minor to trace quantities. The loss on ignition (LOI) values indicated that the core samples had very small amounts of organic or carbonaceous matter.

Fundamentally, characterization of XRD patterns indicated the presence of quartz and plagioclase as the major components, along with moderate to small amounts of clay minerals, anhydrite, carbonates (calcite and dolomite), K-feldspars and hematite. The clay minerals in both wells were dominated by illite, chlorite and kaolinite. While illite is the most dominant clay mineral in each well, in very few samples, the mentioned clay types were accompanied with the subsidiary glauconite, smectite and mixed layer clay minerals such as illite-smectite and chlorite-smectite. Smectite and glauconite were only found in one and two samples of the gas producing well, respectively. In contrast, the mixed layer clays were only found in a few samples from the non-producing well. According to the quantitative XRD analysis, the average contents of total clay minerals varied from a minimum of 5.3 weight percent to a maximum of 21.0 weight percent in the Shurijeh Formation. The amount of illite, the most dominant clay mineral, typically reached 13.6% in both wells, while the other types of clays did not exceed 4.7 weight percent. According to the quantitative XRD results (Table 4), the non-producing well was more shaly with a clay quantity of 1.18 orders of magnitude larger than that in the gas producing well.

The SEM analysis of clay fractions in both wells showed that the clay minerals in the selected samples consisted of illite, magnesium rich chlorite and kaolinite. The vast majority of the pores were filled with kaolinite; however, some pores were lined with chlorite in both wells. The distribution pattern of clay minerals in the gas producing well was structural and dispersed (pore-filling and pore lining) and in the non-producing well was structural, dispersed (pore-filling, pore lining and pore bridging) and laminar.

The DTA and TGA curves shown in

Figures 5, 6 and 7 shared some common features, e.g., characteristic peaks responsible for the water loss, hydroxides and organic matter decomposition, transformation of quartz and carbonates loss; all were observed more or less in the tested samples. However, in each sample, the intensity of peaks was different. Thus slight dehydration peaks were observed at some TGA curves by raising the temperature up to about 110°C, followed by two stages of weight loss, both with continual mass loss, especially in the case of G-3, N-4 and N-6. The maximum weight losses of up to 110°C were observed in N-4 (0.65%), G-3 (0.51%), and N-6 (0.36%), this may be attributed to the fact that they have the highest clay content (mostly illite), consequently the highest absorbed water on the surface of clay minerals, and the highest pore water. The lowest weight loss in this region occurred in the samples with a lower concentration of clay minerals, e.g., G-2 (0.03%), and G-4 (0.07%).

All samples taken from the gas producing well, showed signs of organic substance oxidations from 200 to 500°C with characteristic broad exothermic peaks. Having lost the largest mass by heating up to 500°C, G-1 had the highest organic matter among the samples from the gas producing well. The earliest exothermic maximums at thermograms were observed at about 500°C for all the samples, which is an obvious sign of dehydroxylation (removing water from the structure) of illite (and smectite in G-3). In carbonate rich samples (G-3 and G-4), a very slight drop was observed at temperatures at which breakdown of clay minerals occurred. The α -Quartz (trigonal) into β -Quartz (hexagonal) transformations occurred at 573°C, as endothermic peaks were shown in all sample thermograms. Similarly, the β -Quartz was transformed into tridymite at 873°C. The quartz content in different samples could not be compared because of some overlapped peaks from different minerals. The quartz was recognized by its gradual disintegration in the range of 800–1100°C, with a significant decrease in the content at 1100°C. Although, the actual temperatures at which carbonate decomposes can vary to a certain extent [32-33], but usually they are seen at 650-850°C. In the Shurijeh samples,

carbonate peaks started at about 600°C and all finished before 800°C. It is believed that carbonate rich samples with low amount of clay minerals are expected to gain much complex mineralogy during the thermal analysis [24]. If dolomite is present in the samples, it reacts with quartz at higher temperatures (about 900°C) building diopside, $\text{CaMgSi}_2\text{O}_6$ [24]. The slight endothermic reaction of smectite between 510 and 650°C was overlapped by burning of carbonates in G-3. Chlorites are normally stable at 700°C, magnesium rich chlorites show a thermal peak at about 720°C, while iron rich ones show thermal peak at about 610°C [33-34].

Generally, thermal analysis showed the presence of quartz (573 and 870°C), carbonates (600 and 760°C), organic matter, only in samples from the gas producing well (200 to 500°C), kaolinite (569 and 988°C), illite (89, 566, and 966°C), magnesium rich chlorite (410 and 720°C), and smectite (110, 650, and 900°C). Although, the identification process based on the thermal data, had a problem of some similarities or overlapping in thermal effects of different clay minerals and was not able to resolve the mixtures of different clay minerals alone, but when it was accompanied with X-ray diffraction technique, it served as a valuable complementary method for distinguishing the clay minerals.

5. Conclusions

In this study, the clay mineralogy of ten selected core samples collected from the Shurijeh gas reservoir rock, NE Iran, was studied using the X-ray diffraction, X-ray fluorescence, scanning electron microscopy (SEM) and the simultaneous thermal analysis. The combination of all methods showed consistency in the characterization of the Shurijeh Formation clay minerals. The samples were rich in silicon, with SiO_2 mainly hosted with quartz, plagioclase, K-feldspar and clay minerals. Moreover, the associated minerals were carbonates (calcite and dolomite), anhydrite and hematite. To confirm the presence of identified minerals, SEM studies and thermal analysis were carried out. The SEM micrographs and the thermograms of tested core samples indicated similar mineral composition. On the basis of DTA/TGA curves, the clay minerals were illite, magnesium rich chlorite and kaolinite. Of the total identified clay minerals,

illite was the most dominant type, which was evident in the period of 450–750°C, most in the case of G-3, and N-4.

In general, the results show that differential thermal analysis (DTA) and thermogravimetric analysis (TGA) could yield complementary information on clay minerals, which lead to a better understanding of clay minerals in the hydrocarbon reservoirs.

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