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Investigation of Retorted Water Produced by Direct and Indirect Methods of Oil Shale Pyrolysis

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Abstract: The oil shale retorting process produces petroleum like liquid that requires hydro treatment and refining process to produce normal distillation fractions. The retorting process produces shale oil in addition to hydrocarbon gases and retorted water. The tests have shown total water content (3.19%wt, at heating rate 5 OC/min using TGA at 400 OC. This characterization method utilized different analytical techniques. X-ray diffraction analytical techniques confirmed that the main minerals in the oil shale were calcite and quartz. On the other hand, phenol content was measured and found to be 23.7 ppm using HPLC device. Arsenic was traced in the retorted water and found to be 1.437 ppm which is lower than the Uranium which formed in 0.004 ppm. Sulphate found to be 0.45 ppm using spectrophotometer device. And the Aluminum is found 3.09 ppm of in the present work, Vanadium was formed 0.0244 ppm, Thorium is less than 0.03 ppm, and Zn present in the retorted water was found to be 1.82 ppm using ICP device. Two methods used to produce retorted water, direct method using oxygen gas, and in-direct method (absence oxygen with N2 gas). The results of the two methods are comparable.

Keywords: oil shale retorted water, direct method TGA

استقصاء المياه الناتجة من عملية التحليل الحراري للصخر الزيتي بواسطة الطرق المباشرة والغير مباشرة

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المستخلص: تنتج عملية إعادة تقطير الصخر الزيتي سائلًا شبيهًا بالبترول يتطلب معالجة وتكريرًا...للحصول على الجزيئات المنقاة... تنتج عملية إعادة التكرير زيت الصخري بالإضافة إلى الغازات الهيدروكربونية والمياه. أظهرت الاختبارات محتوى الماء الكلي (3.19% من الوزن الكلي، بمعدل تسخين 5 درجات في الدقيقة المعروف استخدم فيها جهاز التحليل الحراري باستخدام الجاذبية الأرضية (TGA7) عند

درجة حرارة 400 سيليسوس باستخدام جهاز الحيود الطيفي (X-Ray) تم الحصول على نتائج لعناصر اساسية مثل الكوارتز والكالسيت من جهة اخرى تم قياس نسبة الفينول باستخدام جهاز HPLC والتي وجدت 23.7 وتم قياس معدل الزرنيخ في العينة والذي وجد 1.437 جزء من المائة والذي كان أقل نسبة من اليورانيوم والتي كانت قيمته0.004 جزء من المائة وتم قياس بواسطة جهاز المطياف الضوئي تم كذلك قياس نسبة السلفيت في العينة والتي تقدر قيمته 0.45 جزء من المائة باستخدام جهاز المطياف الضوئي وجد كذلك نسبة للألمونيوم وكانت 3.09 جزء من المائة بالنسبة للعناصر المشعة مث الفاناديوم والثوريوم كانت نسبتها في العينة 0.244 و 0.03 على التوالي جزء بالمائة أما بالنسبة لعنصر الخارصين وجدت قيمته 1.82 جزء من المائة باستخدام جهاز ICP كلتا الطريقتين بالتحليل المباشرة والتي استخدم فيها غاز الأكسجين والغير مباشرة باستخدام غاز النيتروجين أعطت نتائج قابلة للمقارنة

الكلمات المفتاحية: الصخر الزيتي، التحليل الحراري، الطريقة المباشرة في التسخين الحراري.

1. Introduction.

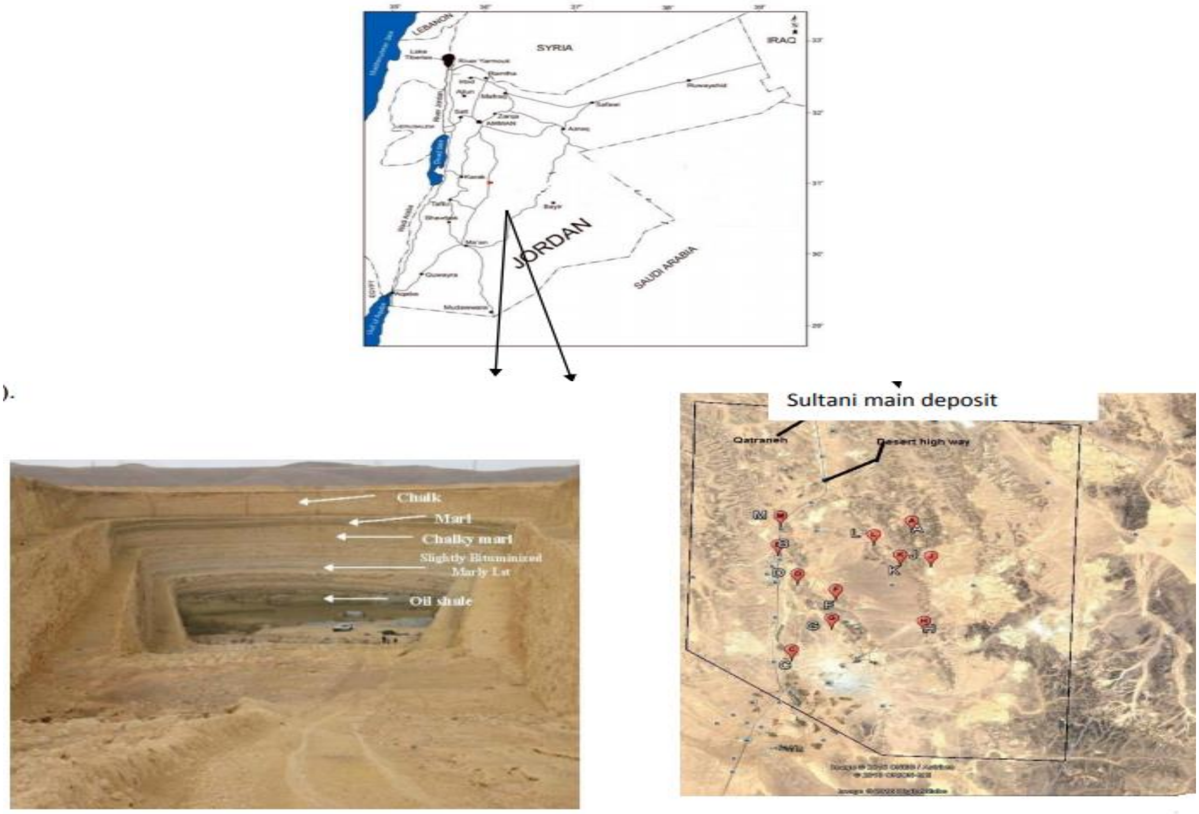
Oil shale, known as kerogen shale, is an organic-rich fine-grained sedimentary rock containing kerogen (a solid mixture of organic chemical compounds) from which liquid hydrocarbon called Shale oil (not to be confused with tight oil) can be produced (Hamrrneh, 1996). In Jordan, two-third of the country is sitting on oil shale. The oil shale deposits in Jordan (Hamrrneh, 1996) is reported to be more than 100 Billion ton scattered over the entire surface and subsurface of the kingdom. Estimates of global deposits of oil shale reserves would produce as much as 4.8 to 5 trillion barrels of shale oil in place (Dyni, 2005). The chemical composition of oil shale varies from one zone to another, the chemical formula is estimated to be (C80H10N3S1O6) (Vandenbroucke, 2007). Heating oil shale to a sufficiently high temperature 550 C0 causes the chemical process of pyrolysis to yield vapors. These hydrocarbon vapors when cooled to a sufficient low temperature produces an unconventional oil known as shale oil. Oil shale can also be burned directly as a low-grade fuel for power generation and district heating or used as a raw material in chemical and construction materials processing (Dyni, 2005). Oil shale gains attention as a potential abundant source of oil whenever the price of crude oil rises, at the same time, oil shale mining and processing raise a number of environmental concerns, such as waste disposal, water use. Among the different countries that have developed oil shale industry are Estonia, China, and Brazil. These countries have produced shale oil and it is available at the commercial level (Lynn, 2005).

2. Experimental

2.1 Study area

3.2.1 Sultani Oil Shale Deposit:

Sultani oil shale deposit is located 130 km to the south of Amman east of the desert Highway. The deposit is situated in a NNW-SSE oriented graben structure 8 km long and 2 to 5 km wide bounded and transected by faults mostly of the same orientation figure (1) show the main deposit in Sultani. The mine was excavated by the Natural Resources of Jordan for study and testing purposes by the different nominated oil shale companies for possible industrial processing. Fig (3.1) show the study area of the mine, the mine deposit located by the following coordinates (Table1).



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Fig(1): Sultani main deposit (NRA,2014)

Table (1): The coordinates of Sultani area (NRA, 2014)

Points	East	North
1	246 000	1058 000
2	246 000	1056 000
3	247000	1056 000
4	247 000	1054 000
5	247 600	1054 000
6	247 600	1053 000
7	248 800	1053 000
8	248 800	1051 800
9	253 000	1051 800
10	253 000	1055 600
11	251 600	1055 600
12	251 600	1057 000
13	250 400	1057 000

2.00Experimental

2.1 Material Oil shale used in this study was obtained from Sultana area in Jordan, two main types of analysis are conducted, and thermal Gravity Analysis (TGA); the x-ray Diffraction (XRD) analysis and the different tests performed on retorted water. The major work is the detection of Phenol, Sulphate and elements such as Al, Pb, As, Cu, Zn, Th, U, V, and Zn in elemental or compound forms.

2.1.1 Direct pyrolysis method

The Oil shale samples grained, A sample of oil shale with a size approximately 3cm and weight approximately 70 kg, is place in retort. The retort is heated externally with an external source of heating such as household cooking gas. The external heating of sample is continued until a sufficient temperature that enable sustainable combustion of oil shale. Experimental works showed that the sustainability of oil shale burning without external heating is initiated at 300 oC. After this temperature, the oil shale on the top of the combustion zone is heated by the upcoming combustion gases leading to pyrolysis of oil shale and production of hydrocarbon vapors and retorted water vapors at 330 C0. The shale oil and retorted water vapors passes through heat exchanger where liquids of both shale oil and water are collected at the bottom. In this process, the heat of pyrolysis is generated by partial combustion of oil shale; hence, it is a direct method of heating oil shale. The un-condensed gases are vented to environment. The collected water and shale oil are separated from each other after a period using Buchner funnel. The collected water is then taken to analysis. Schematic diagram of the retorting setup is depicted in figure (3).

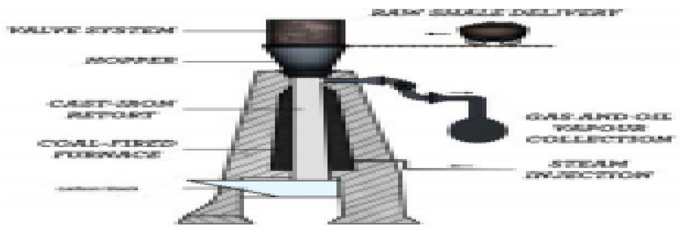


Fig (3): Direct method apparatus

2.1.2 In-direct pyrolysis method

Oil shale samples grinded, A sample of oil shale with a known size 0.5–2.1mm, is place in the retort. The retort is heated externally with an electrical heater. The oil shale pyrolysis is conducted in the temperature range between 400–500 °C. The pyrolysis process-taking place inside the retort at initial temperature of 350oC. The nitrogen gas from the retort to the heat exchanger sweeps the generated hydrocarbons. The condensable hydrocarbon and water vapors passing through the exchanger are condensed and collected in a flask, whereas the incondensable gases such as hydrogen, hydrogen sulfide, carbon dioxide and low molecular weight hydrocarbons, etc. are vented to atmosphere. The collected water and shale oil are separated from each other after a period. The collected water is then taken to analysis. The setup of the indirect method used in this work is presented in figure (4)

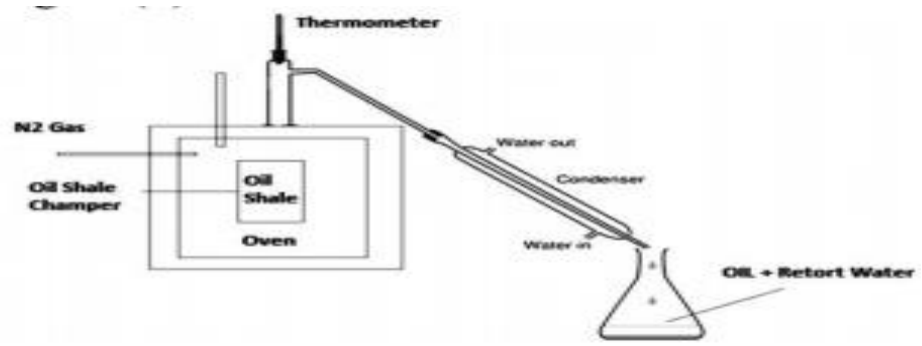


Fig (4) in-direct method apparatus

3. Result and discussion

3.1 TGA

In order to explore the mass loss of oil shale sample upon heating, the TGA is used. Two samples of raw oil shale are heated at two different heating rates. The selected heating rates are 2 and 5 oC/min. These rates are low enough to show clearly the mass loss regions at different reaction temperatures.

Temperature range, some losses occur due to softening and molecular rearrangement and associated with the release of volatile in the organic compound which known as kerogen and the water attached to mineral mater is dissociated as water vapor. Higher than 350 oC, the organic matrix of the sample start reacting to produce hydrocarbon vapors and chemical water and some clay minerals may lose their intermolecular. This process continues until 550 oC, the end of hydrocarbon evolution stage

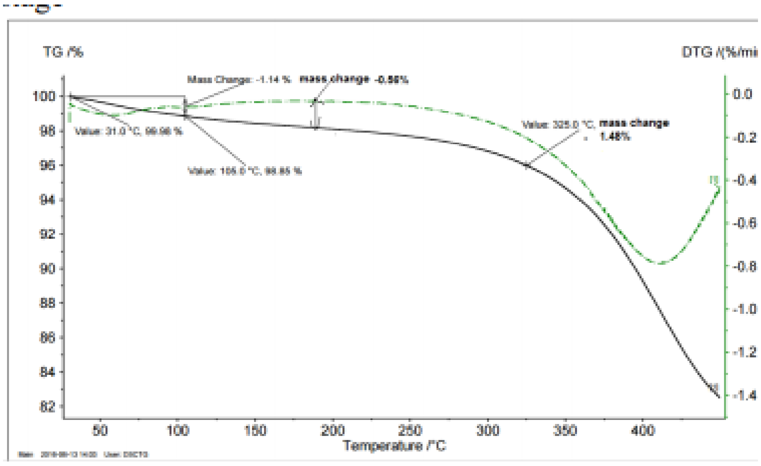
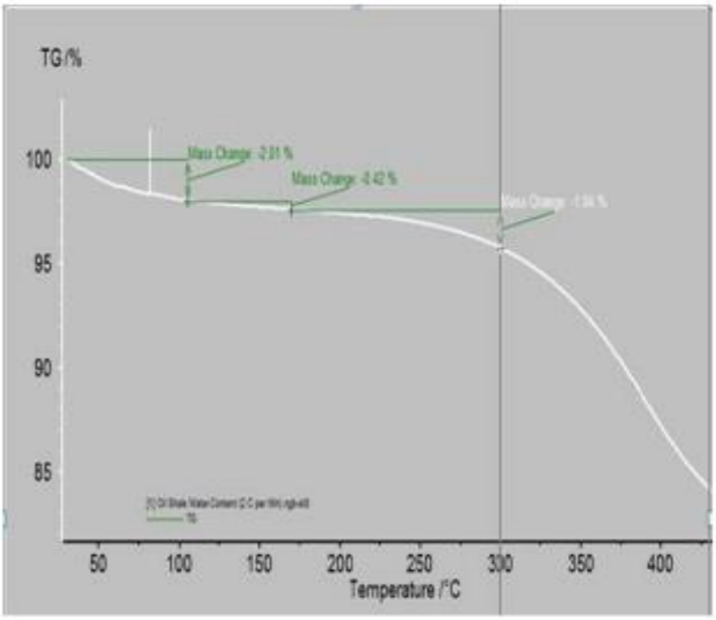


Fig (5): Oil shale water content (5/Min)

The moisture content of oil shale as calculated from figure (5), is estimated to be 1.15% mass percent. It is known that the moisture is the presence of water absorbed from environment and is driven out of sample by heating to 105 ±2 ^{o}C. This water is the moisture of oil shale that kept in the rock when the digenesis process happens. The mass percent of structural water which is known to form and evolve in 170 -300 ^{o}C temperature range is depicted in figure (5). The estimated mass loss percent of structural water is calculated to be 0.56% as indicated in figure (5). This loss is a result of heating rate because some losses occur due to softening and molecular rearrangement associated.

And formation of retorted water is the changes that occurs during heating between 170 – 300 °C. In this region, the associated mineral water is liberated from its compounds when sample is further heated from 170 to 300 °C. It assumed that the dissociation chemical reaction requires energy to proceed and liberate water from the associated compound. The amount of water produced in this region is calculated to be 1.48% mass percent. The figure (5) shows the region of evolution and the calculated mass percent. As a result, the total produced water from the three source is approximately 3.19% as mass weight percent. As it can be seen from figure (6) the total mass loss percent of sample is estimated to be 4.28% mass percent. The different magnitude of the mass loss due to water is attributed to nature of the sample and the heating rate value. If we comparable the result with fisher assay, fisher assay uses the heating rate 10 C0 /min and this is the main cause of different and the lower heating rate produced higher mass loss than high heating rate.



Fig(6): mass loss by TGA at (2°C/min)

The mass loss 2.01% at 105-170 °C and the mass loss at 170-300 °C was 0.42%. Oil shale TGA curves show several stages in the mass loss profile. At temperatures below 105–170 °C the mass loss is attributed to moisture evaporation. After that, up to a temperature of about 300 °C, depending on the heating rate, some losses occur due to softening and molecular rearrangement associated with the release of volatiles in the kerogen adding on their crystal structure. The main mass loss occurring in the temperature range of about 320 to 400°C is due to pyrolysis and kerogen present in oil shale. The increase in the heating rate is shown to shift pyrolysis to higher temperatures. For example, the maximum mass loss rate (%min) occurs at about 300 °C at a heating rate of 2 °C/min, whereas that at 5 °C/min occurs at about 340 °C. At lower temperatures, oil shale particles will have enough time to heat uniformly and for slow reactions to take place.

3.2 XRD

In the present study, taking into consideration that the peak height is directly proportional to the mineral matter content, It is clear from figure (7), that several minerals are existing as shown and indicated by the height of the peak. It is clear from XRD that clays (montmorillonite, kaolinite and illite), quartz and calcite are the dominant phase in the minerals of the oil shale. The XRD for oil shale supported the findings. It is clear from Fig. (7), calcite is the dominant phase in the minerals of the oil shale. Clays and quartz in addition to the phosphate were also present in different proportion,

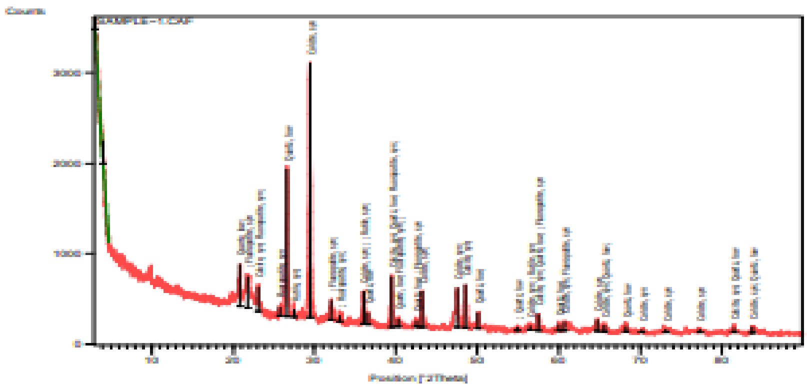


Fig (7): X-ray diffraction pattern oil shale

3.3 Water analysis

Retorted water obtained by two retorting methods, the quantity and nature of retort water is depending on the retorting process, table (1) shows the analysis of Sultani retort water. The analyzed parameters represent the major components. Which could influence of any wastewater and the most noticed pollutant, which must be removed.

Table (1): water analysis for direct method and in direct method

Element / compound	Result indirect method (ppm)	Result of direct retorting method (ppm)
Pb	0.030	0.029
Cu	0.079	0.107
As	6.211	1.437
Th	<0.03	<0.03
V	0.022	0.0244
U	0.003	0.004
Zn	1.49	1.82
Al	3.72	3.09
Sulphate	0.432	0.452
Phenol	Not tested(because need large amount of water)	23.7

The difference in quantities of the different pollutants of the retorted water is shown in table (1). As it can be seen from table, that the traced amounts of elements such Lead (pb), Thorium (Th), Vanadium (V), Uranium (U) and compounds such as Sulphate are almost the same quantities are present in both the retorting methods, whereas other elements such as Copper, Arsenic, Zinc, Aluminum and Phenol are different and depending upon the retorting method. It is clear from the data that, the direct method of heating produced more of copper, and zinc whereas, the indirect method of retorting produces more ppm values of other components. It is clear that the amount of contaminant present in the water depends upon the retorting method. In the direct method using oxygen this method making addition amount of water because there is additional reactions happened inside the furnace.

Depending on the results, a suitable way to drain the water must be found, Table 2 shows the Maximum level of contaminates in agriculture.

Table (2):Maximum level of contaminates in different type of water(http://gis.nacse.org/)

contaminates	Maximum level (ppm) in Drinking water	Maximum level (ppm) in irrigation	Maximum level ppm) in Industrial water
As	0.01	0.05	0.05
Cr	0.05	0.1	0.1
Cu	0.1	1.5	1.5
Pb	0.01	0.2	0.2
Zn	4	5.00	5.00
V	0.0000	0.1	0.1
Phenol	0.002>	0.002	0.002

Comparing the result with the table (2) we can note the retorted water specification not suitable for irrigation uses and industrial uses and not suitable for drinking water.

As it can be seen from table (5), that the traced amounts of elements such Lead (pb) its far away from the values reported by Al-Ayed's and its close value with Al-Jaradeen's and Matouq's, this is may be related to condition of experiment, examination of Cu the result seen the far of the result reported by Al-jaradeen's, Matouq's and Al-Ayed's, and for the As the result was close to Al-Ayed's, for the Thorium its close for all the searchers. As for the element of uranium, U and vanadium, V the results are close to values reported by other researchers. On the other hand, the zinc, Zn reported result is matching with that reported by Al-Ayed and Al-Jaradeen. The findings of aluminum, Al, is close to that reported by Matouq and Al-Jaradeen. For sulphate the results found in this work is close to published by Al-Ayed where the phenol findings are close to the findings of Jaradeen. This disparity in the result is ascribed to the different experimental condition employed by each worker which may include room temperature, the age of sample if it's freshly generated or not and the calibration of testing equipment

Table (5): Comparison between results of different researchers findings(ppm)

Component	Present – work	Result Aljaradin(2012)	Result in Jordan Matouq,,et al,2010)	(Al-Ayed,2015)
Pb	0.029	ND	ND	1.0
Cu	0.107	ND	ND	0.66
As	1.437	2.30	2.30	1.80
Th	<.03	ND	ND	ND
V	0.0244	ND	ND	ND
U	0.004	ND	ND	ND
Zn	1.82	1.0	4.74	0.54
Al	3.09	3.40	3.0	6.70
Sulphate	0.452	ND	0.15	0.50
Phenol	23.7	29.0	ND	64.0
Source of sample	Sultani	El-lajjun	El-Lajjun	Sultani
Method of combustion	Direct	Direct	Direct	Direct

4. Conclusions and Recommendations

Conclusions Upon completion of the present project work and the results obtained from different tests, the following conclusions and recommendations are drawn.

1- The obtained results confirm the presence of several harmful elements and organic compounds in the retorted water of oil shale.

2- The result of phenols from oil shale, that of 23.7 ppm and this very large value and its harmful and d Very dangerous to human health.

3- In direct method and direct show small differences in concentration of certain contaminants such as sulphate 0.432 ppm and 0.452 ppm

4- The method of combustion for direct method influenced on the value of element comparing by the result of combustion for in- direct method

5- Maximum mass loss rate is independent of the heating rate; the result reported by low heating rate more accuracy

6- According Irrigation water specifications we can't use this water in irrigation because the phenol value 23.7 ppm and the limit vale 0.002 ppm.

7- Sulphate showed a very high concentration which was 0.45ppm

8- Uranium and Thorium and Vanadium showed small concentration which make the water suitable for irrigation but its need treatment

Recommendations

1- Further research work is needed to fully characterize the retorted water and its entire content of contaminants

2- Several other elements and organic components must be looked for in the retorted water in order to fully investigate the harmful effect on end use of water We need to search for a suitable method for treatment of retorted water to reduce the harmful effect of the various contaminants present in water in order to make water suitable for an end use.

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