

The Leachability Propensity of El-Lajjun Jordanian Oil Shale Ash

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Abstract

This work reports the leachability of heavy metals and major anions from Jordanian spent oil shale after combustion. Oil shale samples were combusted at temperatures of 550°C, 650°C, 750°C and 850°C. Characterization of the produced solid ash was performed based on XRD analyses. Leaching tests on the ash samples were conducted for different periods of time. Experimental results indicate that the level of heavy metals such as Cd, Pb, Zn, Cu, Cr in the leachate is below the maximum levels set by the Environmental Protection Authority (EPA). For instance, the maximum level of Cd measured in the leachate solution was 0.14 ppm, which is below the EPA limit. Results also indicate that even though the level of heavy metals in all samples was below the EPA limits, yet the level of heavy metals increases as the temperature of the ashing process increases. The effect of ashing temperature on ash cation exchange capacity (CEC) and the pH of ash solution were studied and found to increase with increasing ashing temperature.

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Keywords: Oil Shale; Ash; Leachability; Heavy Metals. Introduction

1. Introduction

Jordan has limited energy resources such as crude oil or natural gas compared to its neighboring countries. However, oil shale is an important and unutilized energy source in the country. More than 50 billion tons of oil shale deposits are discovered in different areas especially in the middle and southern parts of the country (Dabbas, 1997). The soaring prices of oil have led many investors to consider oil- alternative energy resources. The oil equivalent of oil shale around the world is estimated to be around 30 times the reserve of the crude oil (Russell, 1990). Commercialization of Jordanian oil shale in the form of utilizable oil is being studied. The high percentage of ash in the Jordanian oil shale (50-60%) makes the future of utilization of oil shale as a source of liquid fuel uncertain (Jaber *et al.*, 1999). One method is widely used in utilizing oil shale is the retorting process. This process involves extraction of bituminous oil at elevated temperatures in non-oxidizing conditions.

There are growing concerns over the fate of spent shale after retorting process. One of these concerns is mainly the

leachability propensity of trace elements of the spent oil shale into underground water.

The chemical nature of the minerals in the spent shale can change considerably during both the retorting and the combustion stages. These chemical changes will affect both the physical and chemical stability of the spent shale and are important when determining disposal strategies for the waste solid (Bell *et al.*, 1986).

Disposal of mining wastes, spent shale (semicoke) and combustion ashes needs additional land use. According to the study of the European Academies Science Advisory Council (Francu *et al.*, 2007), after processing, the waste material occupies a greater volume than the material extracted, and therefore cannot be wholly disposed underground. The primary threat to water quality is generally considered to be the leachate from spent, i.e. retorted, oil shale. Typically oil shale retorting result in the generation of slightly over one tone of spent shale per barrel of shale oil (EASAC, 2007).

In order to study the migratory behavior of trace elements in oil shale at retorting, tests were performed in laboratory with oil shale of the Huadian deposit of China at different temperature from 360 to 560°C (Bai *et al.*,

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2008)). Results indicate that trace elements are richer in oil shale than earth crust. Also, for most of the elements, their release from oil shale can be promoted by higher heating rate.

The physical and thermal properties of spent shale affect the design and characteristics of embankments used for storing the material prior to ultimate disposal. Leaching tests are used to determine if spent shale must be treated as a hazardous material for disposal. The Institute of Gas Technology and the Illinois Institute of Technology conducted tests to determine some physical and thermal properties and leaching characteristics of spent shale samples from six states in the Eastern United States (Michael and Surendra, 1991). The samples were processed in the continuous, laboratory scale, pressurized fluidized bed hydro-retorting (PFH) reactor at 4.2 MPa (600 psig) and a temperature of 482°C. The physical and thermal properties determined included particle size distribution, permeability, compressibility, compatibility, consolidation, shear stress, cohesion and thermal conductivity. The samples of spent shale were also agglomerated with air at a temperature of 1093°C to determine the effects on leachability. The results showed that the physical and thermal properties of the six spent PFH shales differ considerably. The results also showed that none of the spent shale samples exhibited any

significant metals leachability under the acidic test conditions. In general, thermal agglomeration further reduced the levels of metals leached from the spent shales.

Recently the leachability of retorted Jordanian oil shale at a temperature of 500°C was studied (Ibrahim and Jaber, 2007). They found no detectable release of heavy metals from the ash to percolating water. However, to the authors' best knowledge there was no single study which investigated the release of heavy metals from Jordanian oil shale ash after combustion.

The main objective of this work is to study the leachability propensity of spent oil shale after ashing process at different temperatures. The release of trace elements such as cadmium, lead, zinc and copper from oil shale ash was investigated.

2. Methods

2.1. Samples Locations

Samples were collected from El-Lajjun oil shale area, which is located in the central part of Jordan as shown in Figure (1), with an estimated area of 33.6 km². The oil shale deposits in El-Lajjun area are shallow, near the surface and can be utilized by open cut mining method (Ibrahim and Jaber, 2007).

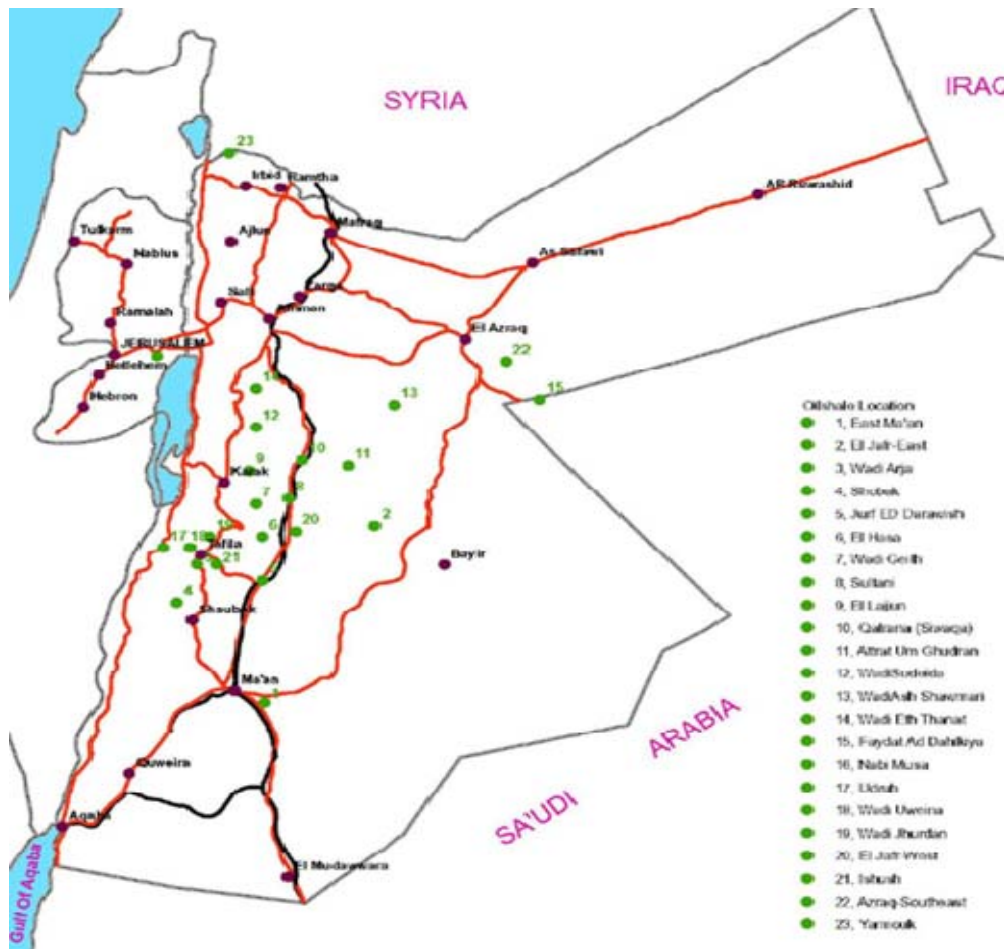


Fig 1.Oil shale Location map (Ellajun No 9) (NRA, 2011)

2.2. Experimental Work

2.2.1. Materials

A representative fresh oil shale samples were obtained from the outcrop of El-Lajjun deposit. These samples were collected from several positions of the outcrop. They were mixed together and crushed and milled. A representative sample (about 5 kg) was then taken by cone and quartering method which was then sieved to several particle size fractions. A size fraction of 125-250µm was used in this study. Typical characteristics of El-lajjun oil shale samples are presented in Table (1).

Detailed analysis of the oil shale samples used in this study has been obtained in a previous study (Al-Otoom *et al.*, 2005). The content of some heavy and trace elements of prepared oil shale ash at 850 °C was measured according to standard procedure and the obtained data are illustrated in Table 2.

Table (1) Proximate analysis (air dried) for the El-Lajjun oil shale deposit used in this study according to ASTM D 5142 (Al-Ottom *et al.*, 2005).

| Property | Proportions (wt%) |
|-----------------|-------------------|
| Moisture | 1.1 |
| Volatile Matter | 44.0 |
| Ash | 54.5 |
| Fixed Carbon | 0.4 |

Table 2. Chemical composition of El-lajjun oil shale Ash in terms of heavy metals.

| Element | Ni | Cu | Pb | Fe | Zn | Cr | Cd | Mo |
|--------------------|-----|------|----|-------|------|-----|----|-----|
| Concentration, ppm | 331 | 1645 | 85 | 14204 | 1035 | 790 | 2 | 540 |

2.2.2. Ashing Process

Oil shale samples were placed in a ceramic crucible, which were then heated in a carbolite furnace to different temperatures of 550°C, 650°C, 750°C and 850°C. A heating rate of 10°C/min was used for this purpose. Samples were kept isothermally at the required temperature for 30 minutes and then cooled to room temperature.

2.2.3. Leaching Process

Dried spent oil shale samples collected by ashing (approximately 10 g) were placed in a volumetric flask (200 ml) and filled with distilled water to the 200 ml mark. Samples were soaked for different time intervals with regular shaking. After each leaching time, the mixture was then filtered out using 0.5 micron filter paper and liquid solutions were then analyzed using ICP. Distilled water was used as the blank.

3. Results and Discussion

3.1. Effect of Temperature and Time on Heavy Metals Leachability.

The level of trace elements such as cadmium, lead, copper, zinc as obtained by ICP (Optima 2000, from Perking) was compared to the maximum levels as set by the EPA. As shown in the Figures (2-6) below, all the

above mentioned trace elements were below the maximum level as per the EPA for drinking water within the whole temperature range used. It can be observed that the level of heavy metals in all samples was below the EPA limits. The level of cadmium, as shown in Figure 2, increases with increasing the combustion (ashing) temperature while this level remains almost constant irrespective of the leaching time. On the other hand, the level of lead did not show any significant change with increasing the combustion temperature, while increasing with increasing the leaching time (Figure 3).

Shawabkeh *et al.* (2004) has shown a propensity of the same oil shale ash to be adsorbing both copper and zinc. Similar observation was obtained in this study; this propensity was found to increase if ash was treated with nitric acid. This result explains the disappearance of zinc and copper from samples of the leachate at all ashing temperatures (Figure 4 and Figure 5)

With regards to chromium leachability from ash (Figure 6), it seems that the highest release of Cr is from oil shale combusted at 650°C, regardless of soaking time. The release on Cr from oil shale combusted is minimal compared to that ashed at higher temperature. Shawbkeh (2006) observed that Cr adsorption is highest at lower pH. At ashing temperature 550°C, the pH of the slurry is the lowest as can be seen later (Figure 8). At temperature 650°C, where the pH is higher, there is no decomposition of carbonates to their oxides (Al-Harashseh *et al.*, 2011). At temperature 750°C and higher all carbonates should have been decomposed to oxides like CaO which contribute to formation of more hydroxide groups. At the same time, at high pH values, Cr presents in trivalent state and therefore, with the present of high OH⁻ concentration there is little chance for Cr to be released from oil shale ash.

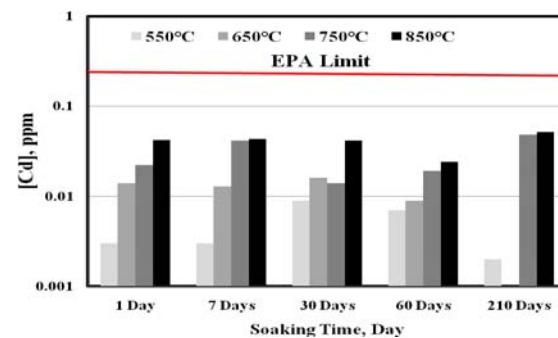


Fig 2. Concentration of cadmium (in ppm) in the leachate at different temperatures as determined by ICP.

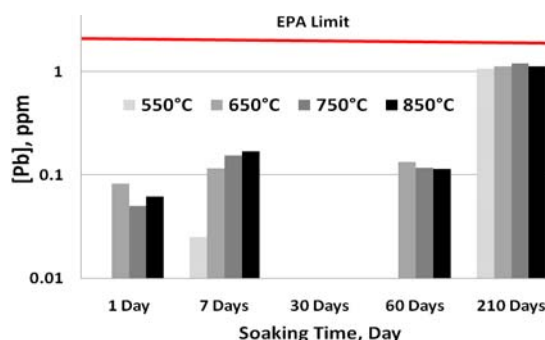


Fig 3. Concentration of lead (in ppm) in the leachate at different temperatures as determined by ICP.

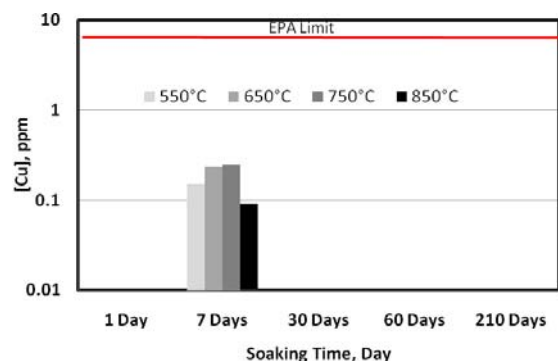


Fig 4. Concentration of zinc (ppm) in the leachate at different temperatures as determined by ICP.

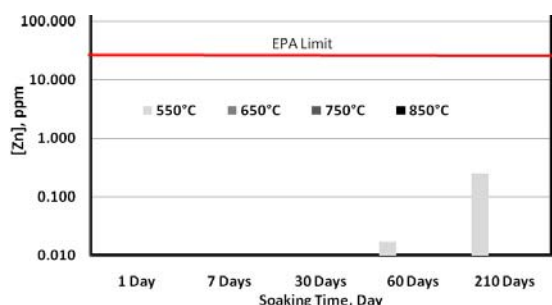


Fig 5. Concentration of copper (ppm) in the leachate at different temperatures as determined by ICP.

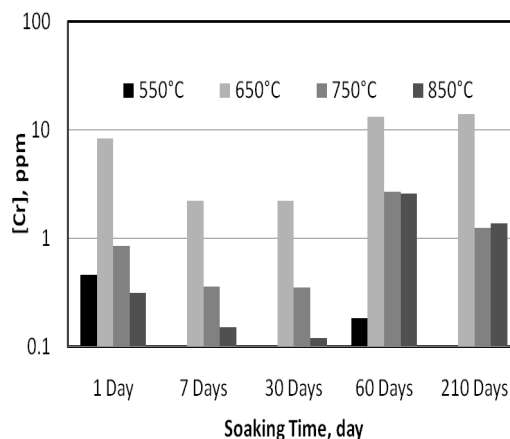


Fig 6. Concentration of chromium (ppm) in the leachate at different temperatures as determined ICP.

3.2. Effect of Ashing Temperature on Ash Cation Exchange Capacity (CEC)

It was found that the cation exchange capacity of oil shale ash increases with the increase of ashing temperature. This could be explained based on the increase of surface area due to release of carbon dioxide and combustion of organic matter present in oil shale. Additionally, due to removal of these compounds the content of Ca and clay matter present in the ash increases which consequently increases the electronegativity of the ash therefore the CEC increases.

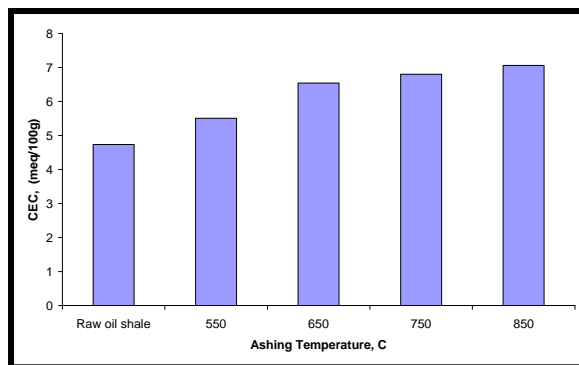


Fig 7. Variation of CEC of oil shale ash as a function of ashing temperature.

3.3. Effect of Ashing Temperature on Ph Value

Figure (8) shows the effect of ashing temperature on the pH of ash mixture with water. It was found that the pH of solution mixture increased considerably when ashing temperature increase from 550 to 650°C then remains almost constant with further increase of ashing temperature demonstrating high level of alkalinity of the ash (pH ≈ 12). This could be explained by the fact that above the temperature of 600°C calcium carbonate present in oil shale starts to decompose to CaO and CO₂. The solubility of CaO is much higher than that of CaCO₃. The presence of CaO in water leads to formation of Ca(OH)₂. Soaking time was found to marginally affect the pH value of the mixture.

The decomposition temperature of CaCO₃ was confirmed by Thermogravimetric Analysis (TGA) of raw samples as shown in Figure (9). Oil shale TG and DTG curves show several stages in the mass loss profile. Some clay minerals may lose their interlayer water from 200°C up to 550°C depending on their crystal structure. Kaolinite, for example loses its bound water at about 430°C (Al-Otoom *et al.*, 2009). The main mass loss occurring in the temperature range of about 320 to 550°C is due to pyrolysis of bitumen and kerogen present in oil shale. The last region of mass loss (~17%) from oil shale sample occurs in the temperature range from about 630 to 780°C due to the decomposition of carbonates (Aboulkas *et al.*, 2008).

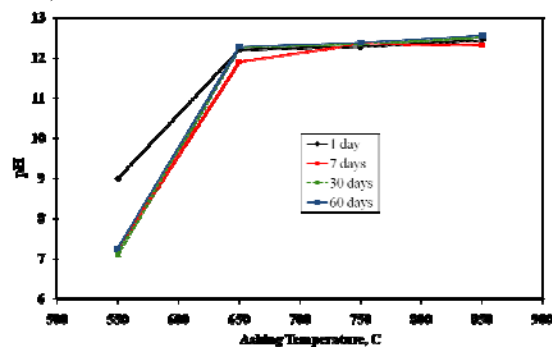


Figure (8). Effect of ashing temperature on the pH of solution mixture

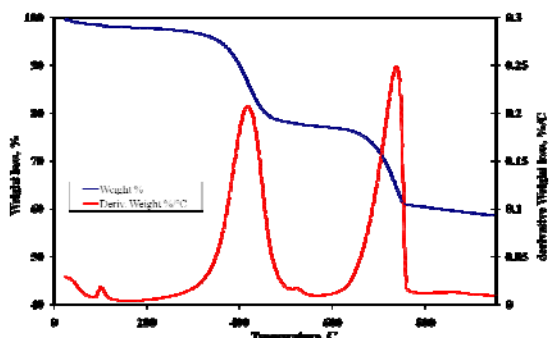


Fig 9. TGA and DTG of oil shale sample at a heating rate of 10C/min.

The high content of calcite in Jordanian oil shale, which varies between 30 to 70% of its mass ((Hamarneh *et al.*, 2006), and the subsequent high content of calcium oxide after combustion at temperatures higher than 650°C

is considered as advantageous. This is because of the formation of high pH when oil shale ash comes into contact even with acidic mine drainage (AMD). It is well known that AMD is normally neutralized by the addition of lime to increase the pH and reduce the release of heavy metals by AMD, which would reach the ground water (Johnson and Hallberg, 2005; Dutta *et al.*, 2009).

3.4. Characterization of Solid Products

Ashing of oil shale at 850°C leads to complete combustion of organic matter. Decomposition of carbonates present in the sample in large quantity and volatilization of both organic and inorganic sulphur as can be seen from the XRD pattern of oil shale ash (Figure 10) Anhydrite (CaSO₄) was formed as a result of reaction between SO₃ (product of organics and CaO (product of calcite decomposition).

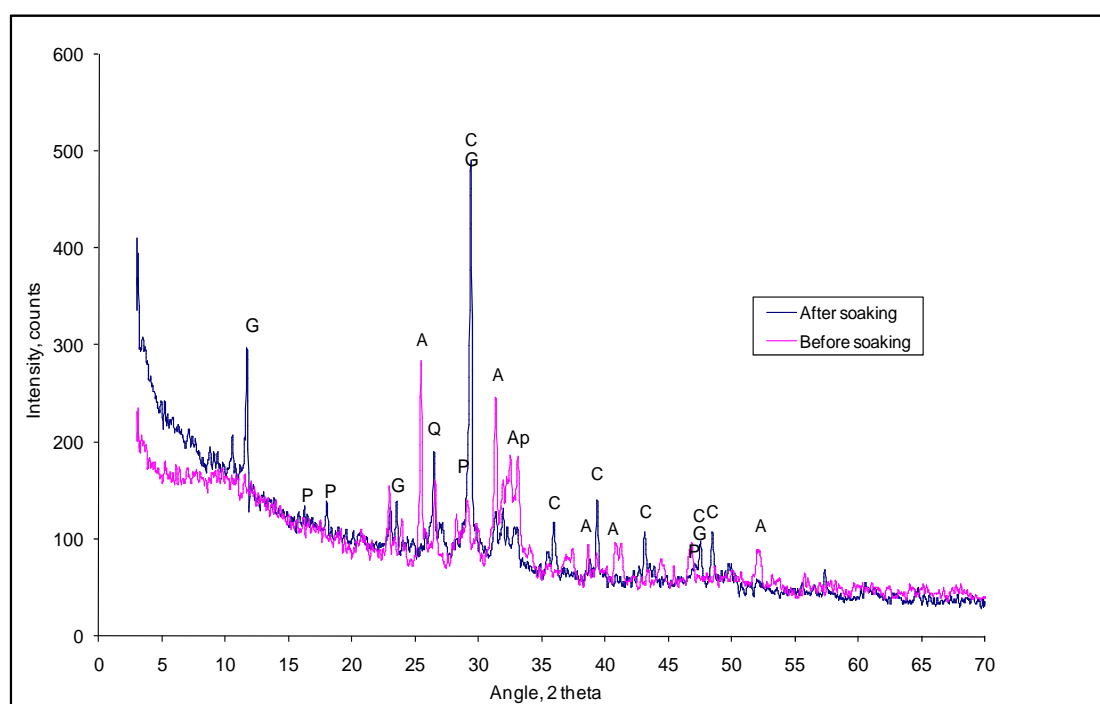
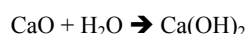


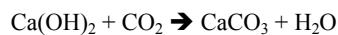
Fig 10. XRD patterns of oil shale ash (850°C) before and after soaking in water for 7 months (G-Gypsum, A-Anhydrite, Ap- Apatite, C-calcite, Q-Quartz, P-portlandite).

The analysis of XRD pattern of oil shale ash after soaking shows that almost all anhydrite was transformed to gypsum (Figure 10). More importantly, it was observed that CaO (the product of calcite decomposition) was also transformed into calcium carbonate again. There is no evidence of the calcite in the ashed sample before soaking, however after soaking very intense calcite peaks appear in the XRD pattern (Figure10). This phenomenon can be explained as follows:

The quicklime formed as a result of ashing hydrolyzes in water according to the following reaction:



The presence of CO₂ available in surrounding environment (the soaking vessel was not tightly closed, dissolves in the slurry solution. As a results this dissolved CO₂ reacts with portlandite (Ca(OH)₂) according to the following reaction:



The mechanism of carbonate formation from quicklime was described earlier by Bruno *et al* (2009) and Cizer *et al* (2008).

At ashing temperatures of 550, 650 and 750°C, the anhydrite XRD peaks are less intense and they also disappear after soaking in distilled water. Furthermore, the peaks of gypsum appear after soaking with much lower intensity compared to that ashed at 850°C.

3.5. Release Anions From Spent Shale.

The release of (Cl⁻) and (SO₄⁻²) was measured by ion chromatography after 7 months soaking of ash in distilled water. Table 3 shows the level of these anions in leachate for ashes combusted at different temperatures. The release of (SO₄⁻²) from ash combusted at a temperature of 550°C is considerably higher than that at temperatures 650, 750 and 850°C. It can be seen from the TGA curves that the

dissociation of calcite starts at temperature above 620°C. Upon the formation calcium oxide sulphate ions will be captured to form anhydrite as it is evident from XRD patterns shown in Figure 10 which was transformed to gypsum after soaking. However, at an ashing temperature of 550°C there was no CaO to react with sulphur oxides. Therefore, it was easy for (SO₄²⁻) to be released.

4. Conclusion

Experimental data indicate that none of the spent shale samples exhibited any significant metal release and have indicated low concentrations of trace elements when compared to the EPA limits for drinking water. This could be explained by the low level of these elements in El-lajjun oil shale and more importantly due to the high level of alkalinity of the ash produced. High ashing temperatures have led to decomposition of calcite present in large quantity and the formation of anhydrite and amorphous CaO. Anhydrite was transformed in gypsum after soaking in water, whereas, CaO was partially transformed into portlandite leading to high level of alkalinity. Additionally, CEC was found to increase with the increase of ashing temperature due to the increase of surface area of ash as a result of carbon dioxide release and combustion of organic matter present in oil shale. The removal of these compounds also increases the content of Ca and clay matter present in the ash which consequently increases the electronegativity of the ash therefore the CEC increases.

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