

Toxic Metals Distribution and Extraction from Two Forms of Exhausted Oil shale

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Abstract

The distribution of toxic heavy metals in different forms of processed oil shale was investigated in this research work. Both XRF and proximate analysis were used to follow up metals distribution in processed oil shale. For comparison purposes, the levels of metals were also quantified in unprocessed oil shale. Upon processing oil shale, many heavy metals were concentrated in the final residue. The most concentrated metals were Cr, Cu, Co, and V with enrichment factor more than 2.0 in both solid forms. Compared with raw oil shale, leaching of toxic heavy metals was increased many folds and percentage of extraction was higher than 60% of all metals using HNO₃. Total characteristic leaching test (TCLT), a standard test to stimulate metals elution in the environment, confirmed that retorted oil shale was more toxic when contacted with aquatic environment. TCLT indicated that the released amount of Cr was 4.4 higher than the safe limit set by international agencies.

Keywords-Oil Shale; Retorted Oil Shale; Combusted Oil Shale; Waste Handling; Adsorption, Metals Leachability.

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I. INTRODUCTION

Compared with Gulf countries and Egypt, Jordan has limited sources of crude oil and natural gas. However, there are large deposits of oil shale (OS) in the country. Jordan is in the 8th place among countries rich in OS deposits in the world [1]. The practical utilization of OS for oil production at national level is under investigation. The high fluctuation in the prices of crude oil is the main reason behind the urgent need for utilization of OS on a global scale [2]. The most investigated OS originated from El-Lajjun as indicated in the scientific literature [1,3,2]. The estimated volume of shale oil (i.e., the oil extracted from OS) that would be produced from the global OS is 30-times higher than the available crude oil [4,5]. Increasing local demand for producing energy has initiated many national projects for OS utilization [2]. As already known, OS has been explored in Jordan since 1960 [1]. Governmental reports indicate that 65 billion tons of OS is available over Jordan, where 50 billion tons are located in the central part of the country [1]. Currently, the *Jordan Oil Shale Company* (JOSCO) has been demonstrated the efficiency of extracting oil in many locations over Al-Azraq area using in-situ retorting. Beside in-situ retorting, extraction of oil from powdered OS by organic solvents seems to be achievable on commercial scale with high percentage yield [6,7]. Using kerogen as a potential substituent for crude oil was an essential research area and received important attention in the last years [8].

Depending on utilization practices, OS often generates three types of pollutants [9]: (1) gases including S and N gases, (2) liquid residues including water saturated with un-wanted chemicals, and (3) solid residues or spent OS. Indeed, emission of N and S gases and leaching of toxic heavy metals from spent OS were listed as the top environmental issues related to full utilization of OS [1,3,2]. The previous studies confirmed that leaching of heavy metals was higher in retorted OS compared to natural OS. Accordingly, detailed chemical tests on metals leaching from spent or combusted OS are essential prior to final discharging

of the wastes of OS. A detailed literature survey was carried out to evaluate the possible utilization of retorted or combusted OS. Most studies investigated the leaching of heavy metals including Cr, Mn, Co, V, Zn and Cu from spent oil shale [10, 11, 3, 12, 2, 13]. Bai and co-workers (2008) have systematically investigated the migration behavior of toxic heavy metals from OS and other forms subjected to high temperatures (360-560°C) [12]. The reported results indicated that leaching of metals was higher for retorted OS at 560°C [12]. The authors outlined that leaching tests by different solvents are essential before the final discharge of spent OS [12]. Ibrahim and Jaber (2007) have been studied the physical and chemical properties of El-Lajjun retorted OS and outlined that the residue was rich in Ca and Si along with many heavy metals (Cr, Ni, Zn and Cu) [3]. The authors do not test the leachability of the metals from the waste, however, they outlined the best utilization was for Pb ions removal from water [3]. In an interesting study, Fu and co-workers (2013) were investigated the migration behavior of many metals including Se, Cd, Mo, As, Cs, Pb, Sr and U while combustion of marine OS for sake of heat production [14]. Al-Harashsheh and co-workers (2012) have investigated the leachability and environmental impact of combusted El-Lajjun OS. The reported results proved that combusted OS at 650°C can leach heavy metals like Cd, Pb, Zn, Cu, and Cr but in amounts below the safe levels set by the Environmental Protection Authority [2]. Moreover, the level of leached heavy metals increases with ashing temperature as a weaker matrix would generate at higher temperatures [2]. Upon extraction of heavy metals from spent residues, the other useful applications including solid adsorbent [15], carbon-based adsorbents [16], geopolymers [17], and in construction materials [18] would be judged but after detailed physical and chemical examinations.

In this work, the distribution and extraction of most toxic heavy metals from two forms of processed OS will critically investigated. The processed forms were those obtained from oil extraction and heat production.

II. EXPERIMENTAL AND PROCEDURE

A. Oil shale, retorted and combusted forms

About 5.0 kg of natural OS, provided as a hard rock, was donated by JOSCO (Amman, Jordan). The sample was obtained from Al-Azraq area. JOSCO is a leading company and has excellent experience in shale oil retorting and purification (19). The sample was crushed by a hammer and then sieved into different particle sizes and sample size less than 100 μm was used in leaching and adsorption tests. The powder was stored in a plastic bottle and tightly closed to prevent moisture uptake. The sample was used in all tests without further purification. About 3.0 kg sample of retorted OS was kindly donated from JOSCO. Combustion of OS was carried out in our laboratory as following. Before combustion process, 25.0 g of OS was crushed and sieved to homogenous particle diameter less than 1.0 mm. The powder was placed in a quartz dish and heated in an electrical muffle furnace at 750°C under atmospheric conditions. Heating rate was 10°C/min and the sample was heated for 40 min to ensure full combustion of the oil within the internal pores of the sample.

B. Reagents, solutions, and instruments

1.0 M solution of HNO_3 , was prepared by dissolving or diluting the appropriate amounts in a 1.0 liter volumetric flask and diluting by distilled water. For toxicity characteristic leaching test (TCLT), 0.1 M solution of acetic acid was prepared by diluting appropriate amount of acetic acid to final volume of 1.0 liter using distilled water. XRD pattern of samples were recorded using Shimadzu X-Ray Diffractometer (Shimadzu X-Ray Diffractometer XRD-6000). The scans were recorded over 2θ (4 to 80) with a step of 0.02 using X-ray operated at 40 kv. Scanning Electron Micrograph-Energy Dispersive X-ray spectrometry SEM/EDX (FEIINSPECT-F50-SEM/EDX) was used for viewing the surfaces at high magnification powers (x50,000) and for metals detection on the surface. The contents of heavy metals in the

solid materials was measured by X-ray fluorescence spectroscopy (Shimadzu XRF-1800 Sequential X-Ray Fluorescence Spectrometer).

C. Metals leaching from solid materials: HNO₃ extraction and TCLT

Extraction tests were carried out using 1.0 M solution and the “liquid to solid” “L/S” ratio was fixed at 50.0 cm³/ g. Typically, 200 ml solvent was agitated with 4.0 g sample. The mixture was mechanically agitated for 4.0 hrs at 25°C (±2°C). The particles of solid materials were removed by centrifugation (5000 rpm) and the clean supernatant was analyzed for metals using flame photometer for Ca, Na, and K ions and atomic absorption spectrometer for Cr, Ni, V, Co, and Cu ions. Due to the hydrophobic nature of OS particles, methanol (1.0 ml) was added as a wetting agent and this helped for soaking the floated fine particles [20]. For total characteristic leaching test (TCLT), the same experimental procedure was repeated using 0.1 M acetic acid solution [21].

III. RESULTS AND DISCUSSION

A. Surface characterization of solid materials for environmental assessment

Different physicochemical tests were adopted to evaluate the environmental impact of processed OS samples that investigated in the current work.

B. XRF and XRD: Elemental and mineralogical measurements

Solid materials were analyzed by XRF to measure the contents of metals. Table 1 summarizes the final results. Enrichment factors (EFs) were estimated for metals in retorted OS and combusted OS against natural OS to assess the effect of heating conditions on metals distribution in the wastes.

Table 1: XRF outputs along with enrichment factors for the metals

Metal	OS	ROS ^a	COS ^b	Enrichment factor	
				ROS/OS	COS/OS
Na%	0.20	0.24	0.21	1.2	1.0
Mg%	0.19	0.30	0.38	1.6	2.0
Al%	1.25	2.10	2.40	1.7	1.9
Si%	15.20	21.25	21.40	1.4	1.4
P%	0.85	1.40	1.52	1.6	1.8
S %	3.28	3.48	2.88	1.1	0.9
K%	0.35	0.66	0.63	1.9	1.8
Ca%	28.32	25.55	26.88	0.9	0.9
Fe%	0.95	0.45	1.76	0.5	1.9
V ppm	204	748	13.6	3.7	0.1
Cr ppm	277	455	816	1.6	2.9
Ni ppm	237	210	395	0.9	1.7
Cu ppm	160	255	522	1.6	3.3
Zn ppm	648	895	1134	1.4	1.8
Co ppm	160	262	325	1.6	2.0

^a Heating temperature is 520°C (in-situ retorting).

^b Direct combustion at 750°C in atmosphere.

ROS: Retorted OS.

COS: Combusted OS.

As indicated in Table 1, natural OS has high inorganic nature where Ca and Si are making 40% of the material and this was also observed in El-Lajjun OS [5]. As Ca making about 28%, then the current OS was categorized as carbonate-oil-shale [8]. As can be noted from Table 1, Si/Al was 12.5 indicating the modest content of aluminosilicate as the typical ratio of Si/Al showed to be within 1.85-3.0 [22,23]. Si content in OS also reflected the existence of quartz mineral in substantial level and this reported in other local OS like Sultani and El-Lajjun [5]. As reported in local [5,2], regional [13], and international OS [8], toxic heavy metals including V, Cr, Ni, Cu and Zn were available in large amounts (160-648 ppm).

Compared with other regional and international OS, the levels of Zn and V were high and reflecting the industrial importance of the newly discovered OS. The interesting point in Table 1 is the large variation in EF of major and minor metals. After oil extraction, EF values were ranged from 0.5 (for Fe) to 3.7 (for V). However, for COS EFs were ranged from 0.1 (for V) to 3.3 (for Cu). In fact the stable EFs (0.9) of Ca in both residues were attributed to its large fraction in the materials. It seems that both Si and Al do not leave the matrix upon retorting and combustion as their EFs were higher than 1.0. Both metals would involve in other phase changes rather leaving with other combustible materials. The possible migration of Fe and Ni with oil is possible as inferred from their low EF. The low EF of S atom (0.9) in combusted OS has indicated S removal from the matrix as SO₂ gas. After retorting, the interaction of S with other elements is possible as EF of S was higher than 1.0. The extremely high EF of V in ROS would indicate the accumulation of this metal in the solid residue rather leaving with oil. However, the same metal (V) seems to leave the matrix upon combustion with O₂ as inferred from the low EF (0.1). The best source of V, of course, is ROS not COS. The metals (Cr, Cu, and Co) have high EF in COS indicating the formation of stable oxides upon heating at 750°C in presence of O₂. Accordingly, the best source of (Cr, Cu, and Co) is COS. Following the above conversation, XRF analysis was significant for selection of proper residue for metals recovery.

Although ROS and COS were enriched with Ca, K, and Na, the direct application as fertilizer is not possible unless toxic metals were removed in a separate step. Accordingly, application of COS and ROS as potential fertilizers would be economically not feasible.

The mineralogical constitutions and possible phase changes in OS and other residues were monitored by recoding XRD scans. Labeled XRD scans of the samples are depicted together in Fig 1.

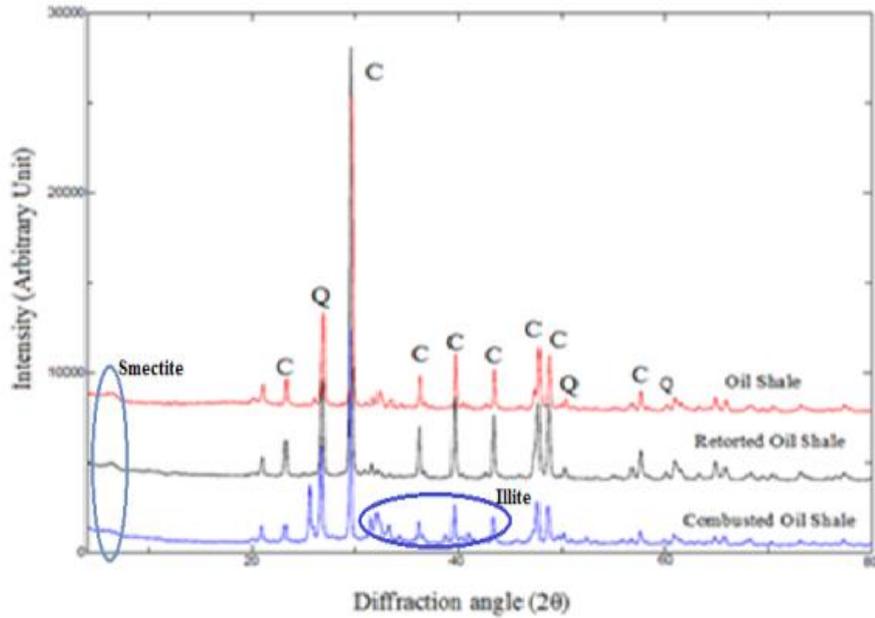


Figure 1: XRD patterns of OS and other solid wastes (Note: C: Calcite, Q: Quartz)

In fact, XRD is the most adopted technique for surface characterization of OS [8]. For better detection of crystalline phases, the scanning was carried out at high power of 40kV. At high scanning powers, the detection of low-level crystalline phases is possible and can give detectable diffraction peaks in XRD pattern [24]. Stable and noise-free scans with sharp peaks were obtained as indicated from Fig 1. From the XRD scans, the crystalline phases in the samples were identified by the search match program available with the instrument. Identification of phases is based on inter-planer distances and intensity of the peak value. Moreover, identification of phases was also made by comparing XRD pattern of pure phases with those shown in Fig 1. XRD analysis indicated the domination of crystalline phases compared to amorphous phases as confirmed from the sharp XRD lines over the entire range (4°-80°). For the three samples, almost identical XRD pattern was observed and the main difference was the new peak of high intensity that observed in the pattern of COS (diffraction angle 25.6°). Fourteen XRD peaks were positioned at 21.0°, 23.8°, 26.9°, 29.7°, 32.4°, 36.2°, 39.7°, 43.4°, 47.7°, 48.8°, 57.6°, 60.9°, 64.9°, and 65.8° and observed in the three scans. Among the detected peaks, the highest intensities were observed at 26.9°, 29.7°, 39.7°, 47.7°

and 48.8°. In fact, phase identification in real soils would be a hard geological job due to the lower content of some phases and the possible overlapping between the patterns. Based on library-search provided with the instrument, the clear peaks at (2 θ) degree 23.8°, 29.7°, 36.2°, 39.7°, 43.4°, 47.7°, 48.8° and 57.6° represent calcite (CaCO₃) mineral. Beside calcite, other major minerals that detected in the sample were clay minerals and quartz. The high intensity of the peaks revealed the high content of this mineral and this result is in agreement with XRD analysis as all samples were rich in Ca (Table 1). The significant reduction in the intensities of peaks in the range 2 θ (30°-50°) observed in the pattern of COS is an indication of partial damage of calcite under high temperature. Both OS and ROS showed comparable patterns which reflected the minerals do not highly affected under retorting conditions. The other detected crystalline phase was quartz which evidenced from the clear peaks at (2 θ) degree 26.7°, 50.3° and 60.0°. In fact, 26.7° is a characteristics XRD peak for quartz and the existence of Si was also confirmed by XRF. XRD evidenced the presence of clay minerals (in small level) in COS. The only identified peak was positioned at 2 θ (25.5°) with a good intensity as indicated from Fig 1. The characteristics XRD peaks of clay mineral were appeared at 12.0° and 25.5° [22,23]. The absence of other clay mineral peaks was attributed to low level of the minerals or overlapping with the peaks of calcite. The samples have high crystalline nature as no weak hump was observed in 2 θ (20°-30°) which is common for amorphous materials.

C. Extraction of toxic metals

HNO₃ has a strong ability for metals extraction from solid residues [25]. The overall results along with TCLT are provided in Table 2.

Table 2: Extraction efficiency of different solvents for metals elution^a

OS								
Extractant	Na	Ca	K	Ni	Cr	V	Co	Cu
HNO ₃ (pH 1.0)	24.5	6.3	43.4	25.8	21.7	15.2	25.8	20.2
TCLT-test (pH 5.5) ^b	21.8	6.8	34.6	9.4 (22.3 ppm) ^c	8.3 (23.0 ppm)	11.7 (24.0 ppm)	25.3 (41.0 ppm)	31.8 (50.9 ppm)
ROS								
HNO ₃ (pH 1.0)	72.1	80.8	64.8	61.9	96.7	67.1	64.1	62.0
TCLT-test (pH 5.5) ^b	67.2	32.1	60.4	57.1 (120 ppm) ^c	82.6 (440 ppm)	48.1 (360 ppm)	61.1 (160 ppm)	58.8 (150 ppm)
COS								
HNO ₃ (pH 1.0)	93.0	75.0	90.2	92.1	88.2	66.0	77.1	97.3
TCLT-test (pH 5.5) ^b	74.3	84.1	59.8	86.4 (15 ppm)	74.8 (22.8 ppm)	58.8 (< 1 ppm)	65.1 (7 ppm)	67.4 (12 ppm)

a. The reported results were taken as an average of three trials.

b. This test stimulates the potential toxicity of a solid waste toward aquatic environment [26].

c. Values in brackets are the concentration of released metals after extraction.

In OS, extraction efficiency of most metals (provided in %) was rather low for all solvents.

Even HNO₃ did not exhibit its common extraction power for heavy metals. Using HNO₃, % extraction was ranged from 6.3 (for Ca) to 43.4 (for K) as indicated in Table 2. The interested point in Table 2 is that OS is not a toxic material on aquatic environment. The earlier conclusion was deduced from the modest extraction of all cations (6.8-34.6%) as supported by TCLT.

United States Environmental Protection Agency (USEPA) has regulated the upper limits of many leachable heavy metals from solid residues [27]. Table 2 listed the final level of toxic metals from OS by TCLT. The maximum concentration was observed for Co and Cu with levels of 41.0 ppm and 50.9 ppm, respectively. Indeed, the elution of metals was not high when compared with the safe limits which set at 100 ppm for most metals [27]. In fact, the modest extraction of heavy metals was attributed to following two reasons; a) the presence of

high level of organic matter which may retard the direct contact with aqueous extractant. Moreover, strong interaction of heavy metals with organic matter is highly possible which retard their extraction, and b) the strong interaction of heavy metals with the inorganic moiety of OS and this would retard their simple liquid extraction.

Undoubtedly, a better extraction of metals from ROS and COS by all solvents was observed. As indicated in Table 2 for ROS, the best elution was achieved by HNO₃ with % extraction of 62 (for Cu) to 96.7 (for Cr). It was interesting to notice the better extraction of Ca (up to 80% using HNO₃) upon oil extraction, the final residue becomes more hydrophilic and this would help for better contact with aqueous solvents and hence better extraction. In fact, the release of heavy metals was substantially higher than in OS and this would make ROS as a toxic solid residue. For better environmental assessment of ROS, the amounts of leached metals were checked against regulated levels. The results indicated that the levels of all heavy metals were exceeded the safe limit (100 ppm). The level of released Cr was 4.4 times higher than the safe limit and this would make direct disposal of ROS as a questionable matter. In the meantime, extraction of heavy metals by nitric acid would be a necessary job before utilizing the spent oil shale as fertilizer or adsorbent for water purification. Finally, better extraction of all metals was observed for COS (Table 2). The best elution was observed for HNO₃, 66% (for V) and 93% (for Na). Based on TCLT, COS was rather of less toxicity than ROS as the final level of metals did not exceed the safe 100 ppm level. The poor extraction by acetic acid may reflect the strong interaction of metals with the inner matrix that subjected to high temperatures. Based on leachability test, ROS could be discharged into environment but after elution of toxic heavy metals. ROS is a good source of Cr, V, Co and Cu. As indicated from XRF measurements and extraction test, heavy metals were present in variable amounts and degree of stripping was dependent on the type of residue and nature of solvent. The majority of metals were eluted using HNO₃.

IV. CONCLUSIONS

XRD indicated that calcite and quartz were the main minerals in OS, ROS and COS. XRF analysis indicated that V was concentrated in ROS compared with OS and COS. The utilization of Ca-rich-ROS and Ca-rich-COS as fertilizer is possible but after removing of toxic heavy metals like Cr, Co, V, and Zn. Based on TCLT, OS is not a potential toxic material as the level of eluted metals was less than the safe-limit recommended by international agencies. However, both ROS and COS would be toxic residues due to the high levels of eluted metals.

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التوزيع المعدني في مخلفات الصخر الزيتي المعالج بطرق مختلفة

الملخص

يهدف هذا البحث إلى استخلاص الفلزات السامة من الصخر الزيتي المحلي ومن مخلفاته (وهي الصخر الزيتي المستنفذ ورماد الصخر الزيتي) بعد استغلاله لإنتاج النفط والحرارة. ولتحديد كيفية معالجة مخلفات الصخر الزيتي، تم إجراء عدد من التحاليل لدراسة المتغيرات السطحية على الصخر الزيتي وتشمل التحليل الكيميائي وتحديد المعادن وغيرها. أثبتت التحاليل المخبرية أن مخلفات الصخر الزيتي تحتوي على نسب أعلى من الفلزات السامة بالمقارنة مع الصخر الزيتي الأصلي. وقد بينت التحاليل وجود أكاسيد الكالسيوم والسيليكا بنسب عالية في المخلفات ، وتشير النتائج أيضاً إلى وجود عدد من الفلزات السامة كالكروم والنحاس والكوبلت والفاناديوم وغيرها، وهي متركزة بكميات عالية (معامل التركيز يعادل ٢) . وصلت نسبة استخلاص الفلزات السامة من المخلفات إلى أكثر من (٦٠٪) باستخدام حامض النيتريك، مقارنة مع الصخر الزيتي الأصلي. كما أثبت الفحص البيئي (TLCT) بأن نزوح الفلزات كان مرتفعاً، وكان مستوى الكروم أعلى أربع مرات من المستوى المسموح به عالمياً.