

## Environmental Geochemistry for Heavy Metals and Uranium Potentiality in Oil Shale Sediments, Quseir, Red Sea, Egypt

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**Abstract:** The environmental geochemistry of organic-rich uraniferous oil shale from Nakheil phosphate mine, Quseir area, Eastern Desert, Egypt is assessed in the present work. This shale provides an important example of natural geological material containing high potentially for uranium and heavy metal concentrations (Cd, Ni, Zn, V and Mo). The content of these metals exceeds the maximum permissible concentration (MPC) limits. As in most other organic-rich sediments, uranium is enriched in the oil shale where its concentration reaches 41ppm, which can be categorized as uraniferous shale. This value of uranium is higher than the average of the continental crust ( $\approx 1$ ppm). However, the reduction potential maintained by the organic matter of the oil shale reduces the soluble hexavalent uranium into the insoluble tetravalent one. Five stages sequential extraction procedure was used to fractionate uranium and the heavy metals; Cd, Zn, Ni, V and Mo. This distinguishes between the different binding forms of elements in oil shale. Conceptually; the solid material can be partitioned into specific fractions, which can be extracted selectively by using appropriate reagents. The sum of most elements present in the individual fractions shows a good agreement with the total elemental concentrations. Sequential extraction procedures (SEP) are operationally defined methods proposed for speciation in solid samples. Detailed scanning-electron microscope (SEM) study was carried out on the separated heavy minerals occurring in the oil shale. This study highlighted the mode of occurrence of the studied metals. Assembly of minerals as zircon of different varieties, non-radioactive monazite, apatite, pyrite, cerusite and gypsum, were also found and manifested by the SEM.

### Key words:

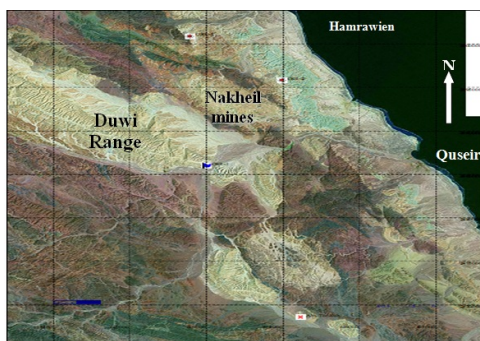
### INTRODUCTION

Thick succession of oil shale is encountered in the Upper Cretaceous – Lower Tertiary Duwi and Dakhla formations in Egypt. In resources tabulated in the Scientific Investigation Report edited by [6], the estimation of oil shale in Egypt is based on the data of [21]. The in-place shale-oil resources in Quseir-Safaga area is 4.5 billion barrels (bbls) while it is 1.2 bbls for Abu Tartur. Some of these oil shales in Quseir area are described as heavy metals-rich at economic potential level [7]. As far as the authors are aware, the data concerning the metals speciation and their mode of occurrence in the Egyptian oil shales are very insufficient. This has inspired the authors to explore the potentiality of such heavy metals-rich oil shale. Three representative samples were collected from the oil shale, its accompanied phosphorite and capping black chert from the Nekheil mines in Quseir environs.

Oil shales are an ideal material to study trace elements trapping because they show a relatively simple and homogenous mineralogical composition, including phyllosilicates, sulfides and organic matter

(OM). They are typically enriched in trace metals and iron sulfides and during the oxidative weathering of sulfides, they form large amounts of iron-rich secondary minerals often with large specific surface areas and release large amounts of trace elements during oxidative weathering, which may be significant in cycling of metals [4].

Oil shales and other sediments enriched in organic matter are one of the most important crustal reservoirs of organic carbon. They are deposited in marine and continental settings under reducing conditions. Redox-sensitive elements (e.g., uranium, vanadium, zinc, molybdenum, cadmium, chromium and selenium) are often enriched in these sediments. When organic-rich sediments are exposed to oxygen, they undergo dramatic changes. Pyrite breaks down into iron oxyhydroxides upon weathering, releasing organic and inorganic acids to the environment. Organic matter combustion into carbon dioxide and/or released as dissolved or particulate organic matter. Redox-sensitive metals are mobilized as soluble higher oxidation state in the ground water, (sometimes at potentially toxic limits).



**Fig. 1:** Satellite image showing the location of the study area, NE Quseir, Red Sea

The reduction of these metals in the anoxic oil shale medium leads to their fixation at lower insoluble oxidation state. The study of heavy metals content in oil shales is of a great importance because they effectively act as a reservoir, which, after temporary storage of metals, can act as a source and a sink for metal contamination<sup>[3]</sup>. High levels of potentially toxic elements of concern to man and animals are present in natural geochemical materials, such as Cd and Mo in some oil shale<sup>[13,15,20]</sup>. Many workers have reported data concerning enriched values of trace elements in oil shales throughout the world<sup>[2,23,5,11,12,9,24,17]</sup>.

Oil shale in many places contains potential concentrations of heavy metals such as Zn, Mo, V, Cd, and Ni, besides U. This is the case of the oil shale in the Nakheil, NW Quseir area. As far as the authors are aware, the only published data on the potentiality of metals in the Egyptian oil shales are those of<sup>[7,1]</sup>. Moreover, the speciation of the heavy metals and uranium in the Egyptian oil shale is not yet studied.

Sequential extraction procedures are proposed to distinguish between different binding forms of elements, particularly metals in soils, sediments and solid matter. In the present study, extraction procedure has been used to evaluate the changes in the distribution and mobility of Cd, V, Ni, Mo, U and Zn. Based on these partitioning into specific fractions, an assessment of element's mobility and environmental influences becomes possible, which cannot be concluded from total element concentrations.

#### **Experimental Work:**

**A- Heavy Metals Potentiality:** Three technological samples representing oil shale, black chert and phosphate ore, about 100 kg weight each, were collected from the Nakheil mine, NW Quseir. The samples were crushed, quartered and pulverized to -100 mesh size. The samples were analyzed for trace and some major elements by the inductively coupled plasma-mass spectrometry (ICP-MS) in ACME laboratories of Vancouver, Canada (Table 1).

Representative proportion of the oil shale sample powder was considered for the sequential extraction experiments. Analysis of heavy metals in the different stages was performed using atomic absorption spectrometer model Unicam 969 supplied with acetylene and nitrous oxide burner heads. Regulators and integrated readings in absorbance and concentration were used.

**B- Heavy Mineral Identification:** The examination by SEM and analysis by EDX were conducted on heavy minerals fraction separated by bromoform for the washed silt size fraction of the oil shale. The disintegrated oil shale was soaked in water for several days, then the carbonate and organic matter contents were destructed by HCl and H<sub>2</sub>O<sub>2</sub> before sieving to recover the heavy fraction of the silt size. Petrographically, the heavy minerals are mostly occurring in the silt size<sup>[7]</sup>. These heavy minerals are the main carrier of trace elements; hence they have thoroughly been analyzed by EDX, especially for heavy metals and uranium.

**c- Sequential Extraction of Toxic Metals:** The leachability of heavy metals was done to have better understanding of the mode by which they are linked to the mineral constituents whether primary or weathered products. The sequential extraction scheme proposed in the present work is adopted after Tessier *et al.*,<sup>[19]</sup>. The bioavailable metals were determined as easily soluble phases, e.g. the exchangeable and sorbed ions. The most bioavailable metals are present in the easily soluble phases and as ion exchangeable or adsorbed sites. The least leached elements are in the residual or detrital silicate phases (Table 2).

#### **Procedure for the Sequential Chemical Extraction of Toxic Metals:**

1. Weigh 1g of each of the dried samples and place in glass beakers.
2. Shake each sample with 100ml of 1M MgCl<sub>2</sub> at a pH of 7.0 for one hour.
3. Filter and separate individually each of the precipitate and the filtrate.
4. The solid precipitate from the previous step of each sample will be shaken with 100ml of 1M sodium acetate for two hours at pH 5.0.
5. Filter and separate again each of the precipitate and the filtrate individually.
6. The solid precipitates, from the previous step, were shaken again with 0.04M hydroxylamine hydrochloride in 25% acetic acid at 95°C for about six hours.
7. Filter and separate the precipitate from the filtrate. In the filtrate, analyses of selected heavy metals were performed.

**Table 1:** Chemical analysis data of the studied oil shale, black chert and phosphorite from Nakheil mine, Quseir area

Oxides %	Oil shale	Black Chert	Phosphate
SiO <sub>2</sub>	16.92	72.71	4.75
TiO <sub>2</sub>	0.21	< 0.01	< 0.01
Al <sub>2</sub> O <sub>3</sub>	4.37	0.19	0.1
Fe <sub>2</sub> O <sub>3</sub>	1.61	0.71	1.55
MgO	0.68	0.07	0.22
CaO	14.72	13.6	47.92
Na <sub>2</sub> O	0.12	0.15	0.54
K <sub>2</sub> O	0.41	< 0.04	0.04
P <sub>2</sub> O <sub>5</sub>	3.38	5.83	27.67
MnO	0.02	< 0.01	0.02
Cr <sub>2</sub> O <sub>3</sub>	0.08	0.015	0.012
Total C	21.81	1.63	3.69
Total S	3.20	0.74	1.79
L.O.I.(950°C)	32.37	5.4	13.3
<b>Elements (ppm)</b>			
Cs	3.3	0.1	< 0.5
Rb	21.3	0.7	< 0.5
Sr	622.2	408.1	1908
Ba	66.6	28.6	130.9
Ga	7.9	0.5	0.7
V	2422	39	133
Cu	163	3.8	17.9
Zn	2314	74	177
Co	5.9	1.4	< 0.5
Ni	272	14.4	36.9
As	19.7	6.4	22.9
Cd	232.8	2.3	10.1
Sb	10.3	0.5	3
Mo	569.1	5.7	13
Pb	9.3	0.4	2.4
Ag ppb	1.9	< 0.01	0.3
Au ppb	1.7	1	4.9
W	0.8	5.6	0.7
Hg	0.15	0.02	0.12
Tl	5.9	1.3	2.5
Zr	63.6	3.3	11.5
Hf	1.6	< 0.50	< 0.50
Nb	4.4	0.5	< 0.50
Ta	0.3	0.1	0.1
Th	3.3	< 0.10	1.3
U	41	35.6	125.9

- The solid precipitate from the previous step was shaken with 30% H<sub>2</sub>O<sub>2</sub> for two hours in 0.02M HNO<sub>3</sub> at 95°C.
- After filtration, the precipitate is dried and a known weight was digested with a mixture of HF-HClO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> for the analysis of the selected heavy metals.

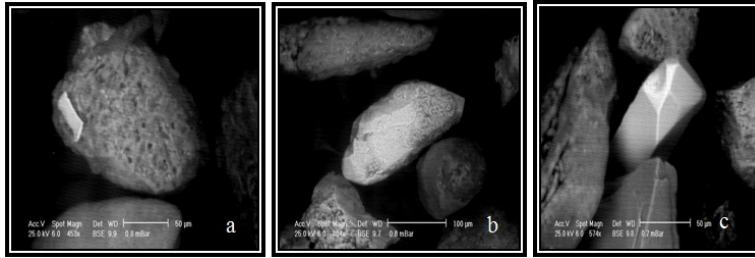
### RESULTS AND DISCUSSION

The studied oil shale of the Nakheil mines contains 41ppm U and can generally be described as uraniferous shale, but markedly poor in thorium. The phosphate ore and its capping black shale display even higher enrichment level of uranium over thorium. Such obvious enrichment of phosphorite by uranium can be attributed to diagenetic uptake, being permeable rock. In contrary, the uranium content of the non-permeable shale and chert reflects the syngenetic character of the depositional environments.

The SEM examination of the heavy minerals fraction suggests that part of the uranium content is confined to the rigid crystal structure of zircon (Fig 2a, b, c and Table 3). The poverty in thorium can be interpreted to the dominance of low concentration of thorium in monazite variety in the studied oil shale. The EDX data indicates that monazite is LREE carrier (Table 4) and diagnostically much depleted in thorium. These observations agree fairly well with the ICP-MS data where oil shale, chert and phosphate contain 3.3, <0.1 and 1.3 ppm Th, respectively. This almost non-radioactive variety of monazite is different than those known in the stream sediments of the Eastern Desert of Egypt or even in the black sands of the Mediterranean shoreline of Egypt (Figure 3). The Th-poor monazite is most probably derived from metamorphic terrain. Accordingly, it can be stated that total radioactivity of monazite and zircon is related to uranium and possibly potassium rather than to thorium.

**Table 2:** Sequential extraction data (ppm) of some heavy metals in oil shale of Nakheil mine, Quseir, Egypt

Elements	Head Sample ppm	MgDI,	Sodium Acetate	Hydroxyl Amine HCL	Hydrogen Peroxide	Residual	Recover ppm	Recovery %
Cd	232	0	0	73	135	0	207	89.4
Ni	272	0	19	53	105	80	257	94.5
Zn	2314	2	49	347	1157	283	1838	79.5
U	41	0	2	7	29	0	38	92.7
Mo	569	97	32	95	297	55	577	101.4
V	2400	71	45	288	333	1672	2409	100.4
Fe	20500	1	10	11827	4928	3942	20697	101.0
Mn	205	13	38	74	51	23	200	97.5



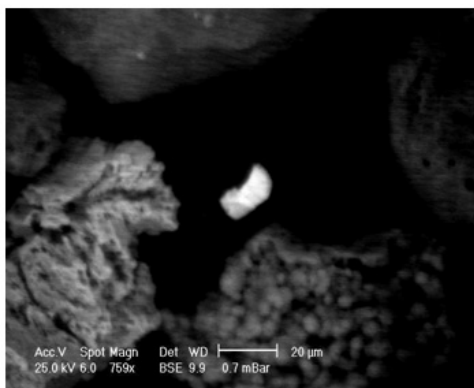
**Fig. 2:** Prismatic zircon inserted in phosphate grain (a), High hafnium- prismatic zircon with pitted surface (b) and, Prismatic zircon grain coated by calcium carbonate (c).

**Table 3:** Semi quantitative analysis data of different varieties of zircon grains separated from oil shale

Oxides	Weight %		
	Grain A	Grain B	Grain C
SiO <sub>2</sub>	24.12	22.99	28.09
Al <sub>2</sub> O <sub>3</sub>	< 0.2	3.40	0.88
ZrO <sub>2</sub>	54.87	49.04	58.05
HfO <sub>2</sub>	1.25	2.34	0.69
UO <sub>2</sub>	0.21	1.24	0.12
CaO	16.21	11.82	9.80
Fe <sub>2</sub> O <sub>3</sub>	3.33	8.80	1.85

**Table 4:** Semi quantitative analysis of the non-radioactive monazite picked from the studied oil shale

Oxides	Weight %
SiO <sub>2</sub>	2.93
Al <sub>2</sub> O <sub>3</sub>	0.98
P <sub>2</sub> O <sub>5</sub>	29.37
Fe <sub>2</sub> O <sub>3</sub>	3.45
ThO <sub>2</sub>	0.10
UO <sub>2</sub>	0.13
CaO	8.40
La <sub>2</sub> O <sub>3</sub>	17.48
Ce <sub>2</sub> O <sub>3</sub>	25.70
Pr <sub>2</sub> O <sub>3</sub>	2.14
Nd <sub>2</sub> O <sub>3</sub>	3.59
Eu <sub>2</sub> O <sub>3</sub>	1.11
Gd <sub>2</sub> O <sub>3</sub>	0.25
Yb <sub>2</sub> O <sub>3</sub>	0.56

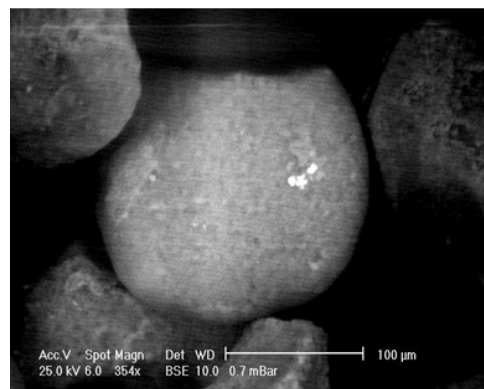


**Fig. 3:** Fine angular grain of monazite.

Cd, Ni, Zn, V, and Mo. The content of these metals is more than 10-fold the maximum permissible limit of soil as quoted by the World Health Organization (WHO) or the average of the earth's crust as given by Taylor and McLennan [18]. The SEM detects some of these potentially toxic metals in mineral form as cerussite (lead carbonate) and malachite (copper carbonate) and gypsum (Figs. 4 & 5 and Tables 5 & 6).

**Table 5:** Semi quantitative EDX data of cerussite picked from oil shale

Oxides	Weight %
SiO <sub>2</sub>	2.98
Al <sub>2</sub> O <sub>3</sub>	2.20
MgO	0.35
P <sub>2</sub> O <sub>5</sub>	21.02
SO <sub>3</sub>	3.11
SnO <sub>2</sub>	4.15
CaO	24.72
V <sub>2</sub> O <sub>5</sub>	0.29
Fe <sub>2</sub> O <sub>3</sub>	2.82
NiO	0.18
CuO	0.54
ZnO	0.25
PbO <sub>2</sub>	37.38



**Fig. 4:** Lead carbonate (cerussite) in rounded phosphate grain

**Heavy Metals:** The chemical analysis data (Table 1) suggest that the studied oil shale contains abnormally high concentrations of some heavy metals, especially;

**Table 6:** Semi quantitative EDX data of malachite picked from oil shale

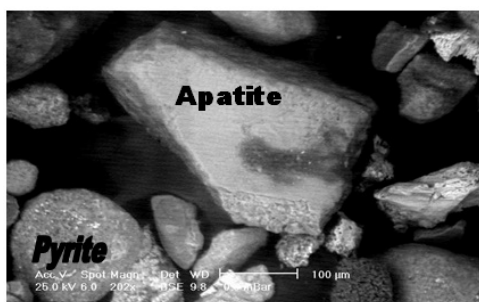
Oxides	Weight %
SiO <sub>2</sub>	36.07
Al <sub>2</sub> O <sub>3</sub>	32.11
P <sub>2</sub> O <sub>5</sub>	1.93
SO <sub>3</sub>	1.40
K <sub>2</sub> O	0.42
CaO	3.58
Fe <sub>2</sub> O <sub>3</sub>	1.38
CuO	8.63



**Fig. 5:** Copper carbonate mineral (malachite), very bright spot (up-right), near kaolinitic grain

**Table 7:** Semi quantitative EDX Analysis data of pyrite disseminated in apatite containing some heavy metals

Element	Weight %
Si	3.30
Al	1.49
P	11.97
Fe	46.53
S	13.14
K	0.34
Ca	20.28
Mg	0.64
Ti	0.26
V	0.09
Ni	0.33
Cu	0.56
Zn	1.06



**Fig. 6:** Pyrite (bright spots) disseminated in apatite containing some heavy metals

### Sequential Extraction of Heavy Metals and Uranium:

The studied oil shale contains some heavy metals (e.g., Cd, Ni, Zn, V and Mo) and uranium at concentrations levels higher than the maximum permissible concentration (MPC) limits in sediments. Hence fractionation of those heavy metals and uranium was done in the present work to find out the mode of occurrence and the speciation of each metal. A modified five stages sequential extraction procedure proposed by Tessier *et al.* [19], has been used to determine the speciation of the heavy metals and uranium. In other words, to define the bound between these metals and the different mineralogical phases also to detect the possible trend of metals mobilization under the different environmental conditions.

In fact, the reducing medium maintained by the high organic content of the oil shale favors the accumulation of some heavy metals as zinc, nickel, cadmium molybdenum and uranium. The anaerobic bacteria play an important role in the formation of sulfides in general, and framboidal pyrite in particular [14]. Most of the heavy metals can co-precipitate as sulfides or accumulate within the pyrite lattice. Upon weathering, these sulfides are oxidized to oxyhydroxides, carbonates or sulfates.

The basic assumption of sequential extraction is that the reagents used are able to dissolve one simple phase selectively without solubilization of others and to investigate the fractionation of the metals in solids where trace elements are either associated with organic matter, sorbed onto Fe/Mn oxides or complexed with hydroxides, sulfides and carbonates [8]. The sequential extraction of potentially heavy metals provides insight how the metals are incorporated in various component phases, and hence, their leaching (bioavailability).

Selective extraction generally follows a sequential procedure that is designed for each matrix. In the present work, a five-stage sequential extraction procedure was successfully applied to the organic-rich uraniferous oil shale from Nakheil mine. The partitioning of particulate metals was achieved for Cd, Ni, Zn, U, Mo, V, Fe and Mn into various fractions. The concentration of the metals in the leaching solutions and solid residue (after dissolution) were determined by atomic absorption spectrometry (AAS) providing information on the possible impact of particle-associated metals. The leaching abilities of metals proved to be different, so various distribution patterns have been achieved. It was found that the difference in partitioning depends considerably on the properties of the raw material and the operation conditions.

Zinc is one of the highly enriched elements in the study uraniferous oil shale, where its concentration is 0.23% in the head sample analyzed by ICP-MS (Table

1). According to the scanning electron microscope study, framboidal pyrite ( $\text{FeS}_2$ )<sup>[14]</sup>, which is product of anaerobic bacteria contains 1.06% Zn (Fig.6). This agrees with the sequential extraction data where 50% zinc is concentrated in the reduced form (0.115%, Table 2).

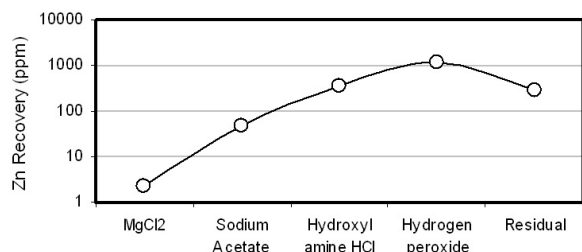


Fig. 7: Sequential extraction of zinc in Nakheil black shale

**Cadmium and Nickel:** According to the obtained data of the sequential extraction experiments, both metals are not bioavailable, as they have not been detected in the exchangeable phase. Their highest recovery is determined for the reduced stage (135ppm and 105ppm), which represents 58.1% and 38% of the total content, respectively. The Fe-Mn oxy-hydroxides play an important role as an accumulator for Cd and Ni (31 and 19%, respectively), but in case of Cd, the maximum recovery characterizes the reduced phase (135ppm).

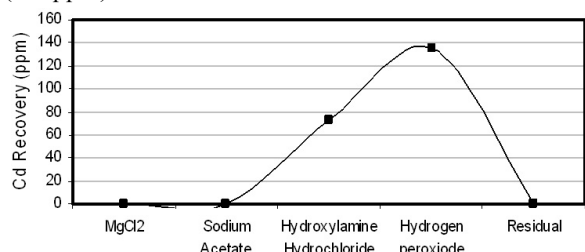


Fig. 8: Sequential extraction of cadmium in Nakheil black shale

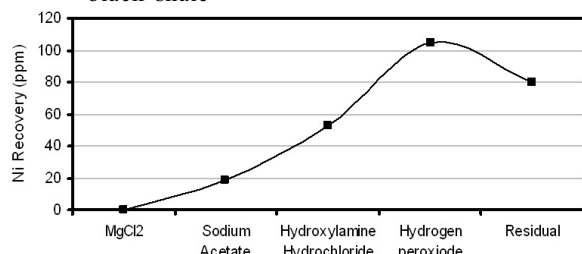


Fig. 9: Sequential extraction of nickel in Nakheil black shale

**Molybdenum:** similar to other heavy metals, the major quotient of Mo (52.2%) is recovered during the reduced stage where it is mostly bound to the sulfides

or organic matter. On the other hand, significant portions of Mo are recovered from the carbonate bound and Fe-Mn oxy-hydroxides bound fractions with an equal concentration of about 95ppm (13% in each phase).

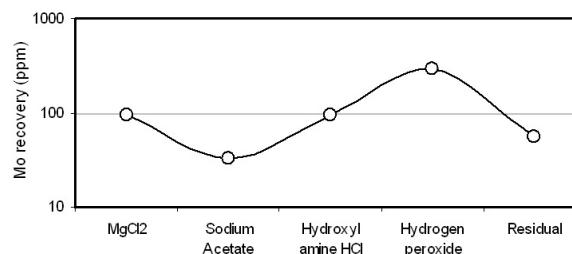


Fig. 10: Sequential extraction of molybdenum in Nakheil black shale.

**Vanadium:** has a concentration of 2400 ppm in the head black shale sample. This high V content is 40 fold the average earth's crust (60 ppm) as quoted by McLennan and Taylor<sup>[16]</sup>. From sequential extraction of vanadium dominants in the residual fraction, which means that vanadium mineral might be formed but it was not possible to detect by the used SEM technique.

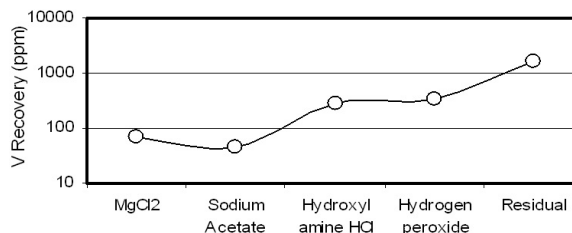
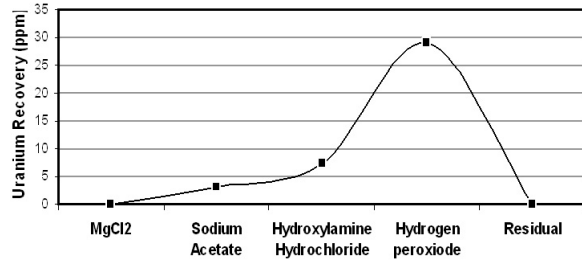


Fig. 11: Sequential extraction of vanadium in Nakheil black shale

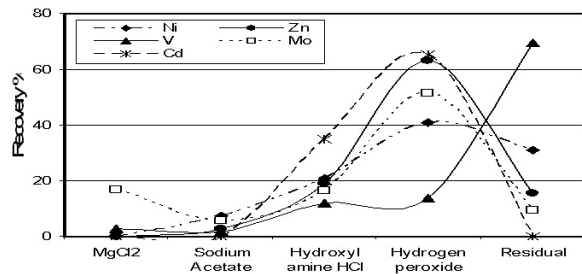
The exchangeable contents of molybdenum and vanadium are 97 and 71 ppm, respectively. This exchangeable content is ready to interact with surface (meteoric) water. The exchangeable quotient of these metals can easily be transferred to pollute the surface or the underground water. In arid region, like Egypt, inhabitants in the oases are entirely dependant on the underground water resources in their drinking and cultivation. The environmental hazards of transfer of the exchangeable Mo and V (97 and 71 ppm, respectively) to the groundwater should be considered seriously, since their maximum permissible limits (PML) in drinking water are <1 ppm for both elements.

**Uranium:** has concentration of 41ppm in the head sample, hence can be considered as uraniferous shale. The sequential extraction experiments showed that uranium is mostly concentrated in the organic matter and sulfide-bound fraction, which suggests that the U

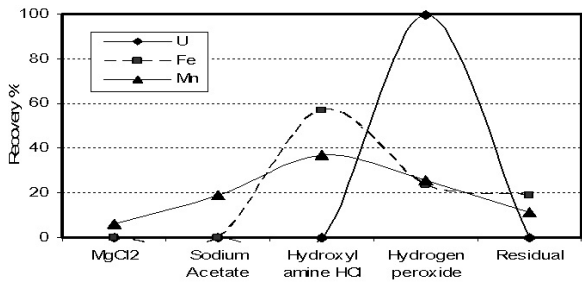
is occurring in the tetravalent state. This concludes that uranium can be recovered through oxidizing acid extraction.



**Fig. 12:** Sequential extraction of uranium in Nakheil black shale



**Fig. 13a:** Integrative sequential extraction of some heavy metals



**Fig. 13b:** Integrative sequential extraction of some heavy metals

**Conclusions:** The studied organic rich uraniferous black shale from phosphate Nakheil mine, Quseir area, contains high potentially toxic heavy metals and uranium exceeding the maximum permissible concentration (MPL) limits in sediments and in the average continental crust. As in most organic-rich sediments, uranium is enriched in the oil shale where its concentration reaches 41ppm, which can be categorized as uraniferous shale. The reduction potential maintained by the organic matter of the oil shale reduces the soluble hexavalent uranium into the insoluble tetravalent one. Five stages sequential extraction procedure was used to fractionate uranium and the heavy metals; Cd, Zn, Ni, V and Mo. This distinguishes between the different binding forms of elements in oil shale. Conceptually; the solid material

can be partitioned into specific fractions, which can be extracted selectively by using appropriate reagents. Sequential extraction procedures (SEP) are operationally defined methods proposed for speciation in solid samples. The basic assumption of sequential extraction is that the reagents used are able to dissolve one simple phase selectively without solubilization of others and to investigate the fractionation of the metals in solids where trace elements are either associated with organic matter, sorbed onto Fe/Mn oxides or complexed with hydroxides, sulfides and carbonates. Most of the heavy metals (Ni, Cd, Mo, and Zn) and uranium have their highest recovery values in the reducing stage where the high organic content in the shale favors the accumulation of those elements. Detailed scanning electron microscope (SEM) study was carried out on the separated heavy mineral fractions occurring in the silt size of the oil shale. This study highlighted the mode of occurrence of the studied metals. Assembly of minerals as zircon of different varieties, monazite, apatite, pyrite, cerusite and gypsum, were also found and manifested by the SEM. Compatibility of results between sequential extraction and the scanning electron microscope was observed in most of the results obtained.

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#### REFERENCES

1. Amer, A.M., 1994. Hydrometallurgical processing of Egyptian black shale of the Quseir-Safaga region. *Hydrometallurgy*, 36: 95-107.
2. Atkinson, W.J., 1967. Regional geochemical studies in county Limerick, Ireland with particular reference to selenium and molybdenum. Ph.D Thesis, University of London.
3. Bopeng, Shurong Xie, Meilian Xiao and Zi Song, 2006. Geochemistry of soils derived from black shale, Central Hunan, *Chinese Journal of Geochemistry*, 25(1).
4. Cornell, R.M. and U. Schwertmann, 1996. *The Iron Oxides Rock Coatings*. Weinheim, VCH, pp: 573.
5. Coveney, R.M. Jr and M.D. Glascock, 1989. A review of the origins of metal-rich Pennsylvanian black shales, *Applied Geochemistry*, 4: 347-367.

6. Dyni, J.R., 2006. Geology and resources of some world oil-shale deposits: USGS Scientific Investigations Report, 2005-5294: 42.
7. El-Kammar, A.M., M. Darwish, G. Philips and M.M. El-Kammar, 1990. Composition and origin of black shales from Quseir area, Red Sea Coast, Egypt, *Journal of University of Kuwait (Science)*, 17: 177-190.
8. Forstner, U. and G.T.W. Wittmann, 1983. *Metal Pollution in the Aquatic Environment*, 2nd edn, Springer, Berlin, 486.
9. Jin-Soo Lee, Hyo-Taek Chon, Jong-Shin Kim, Kyoung-Woong Kim and Hi-Soo Moon, 1998. Enrichment of potentially toxic elements in areas underlain by black shales and slates in Korea, *Environmental Geochemistry and Health*, 20: 135-147.
10. Jones, B. and D.A. Manning, 1994. Comparison of geochemical indices used for the interpretation of paleoredox conditions in ancient mudstones. *Chemical Geology*, 111: 111-129.
11. Kim, J.H., 1989. Geochemistry and genesis of the Guryongsan (Ogcheon) uraniferous black slates. *Journal of the Korean Institute of Mining Geology*, 22: 35-63
12. Kyoung-Woong Kim and Iain Thornton, 1993. Influence of uraniferous black shales on cadmium, molybdenum and selenium in soils and crop plants in the Deog-Pyoung area of Korea, *Environmental Geochemistry and Health*, 15(2/3): 119-133.
13. Lakin, H.K., 1972. Selenium accumulation in soils and its absorption by plants and animals, *Geological Society of American Bulletin*, 83(181).
14. Love, L.G., 2006. Early diagenetic iron sulphides in recent sediments of wash (England), *Sedimentology*, 9(4): 327-352.
15. Lund, L.J., E.E. Betty, A.L. Page and R.A. Elliott, 1981. Occurrence of naturally high cadmium levels in soils and its accumulation by vegetation, *Journal of Environmental Quality*, 10: 551.
16. McLennan, S.M. and S.R. Taylor, 1999. Earth's continental crust. In (C.P. Marshall and R.W. Fairbridge, Eds.) *Encyclopedia of Geochemistry*. Kluwer Academic Publishers, Dordrecht, the Netherlands, 145-151.
17. Pasava, J., P. Sulovsky and M. Kovalova, 2003. Geochemistry and mineralogy of Proterozoic metal rich black shales from the Bohemian Massif, Czech Republic, with a description of possible new molybdenum selenide and telluride phases. *Canadian Mineralogist*, 31: 745-754
18. Taylor, S.R. and S.M. McLennan, 1995. The geochemical evolution of the continental crust. *Rev. Geophys.*, 33: 241-265.
19. Tessier, A., P.G.C. Campbell, M. Bisson, 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Analitica Chimica Acta*, 51: 844-85.
20. Thornton, I., 1983. *Geochemistry applied to agriculture*. In: I. Thornton (ed.), *Applied Environmental Geochemistry*, pp. 231-266. Academic Press, London.
21. Troger, U., 1984. Upper Cretaceous rocks in Quseir area: *Bull. Inst. Desert Egypt*, 2: 35-53.
22. Twenhofel, W.H., 1939. Environments of origin of black shales AAPG, 23: 1178-1198.
23. Vine, J.D., 1969. Element distribution in some Paleozoic black shales and associated rocks. *United States Geological Survey Bulletin*, 1214: 1-32.
24. Vine, J.D. and E.B. Yourtelot, 1970. *Geochemistry of black shale deposit, a summary report*. *Economic Geology*, 65: 253-272.