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Acid Leaching of Uranium from Weathered Uraniferous Black Shale

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Abstract: This paper describes the chemical leaching of uranium from weathered black shale by using sulfuric acid (H_2SO_4) and acidic ferric sulfate ($Fe_2 (SO_4)_3$ solutions as lixiviants. The black shale sample was radioactive in nature due to the presence of uranium and its decay radio-isotope products like ^{226}Ra, ^{214}Pb and ^{214}Bi. The γ-activity of natural ^{235}U was 97.6 ± 1.34 Bq Kg^{-1}. The shale sample showed 48±1% porosity with bulk density of 1.38 ± 0.015 g/ cm^3. The main minerals identified in the weathered shale sample were quartz, illite, microcline (K-feldspar), anorthite (Ca-feldspar), gypsum and hematite. A mixed layer illite-smectite phase at 10.8Å was also detected indicating the weathering of clay minerals present in the shale sample. The shale sample was polymetallic in nature and contained 0.005% U_3O_8, 0.24% V_2O_5, 0.038% NiO, 0.012% CuO, 0.037% CeO_2 and 0.019% ZnO on dry matter basis. The shale sample was organic carbon rich and contained 19.60% C, 1.25% N and 2.50% H, which indicated the presence of nitrogenous hydrocarbon compound(s). Uranium was present in the tetravalent oxidation state (U^{4+}) in the shale matrix. A series of leaching experiments were conducted in shake flasks and percolation column for uranium dissolution from black shale with and without acidic ferric sulfate solutions of pH 1.5 and pH 2.0 at 30±2 °C. Uranium leaching efficiency was mainly attributed to the concentrations of H_2SO_4 and Fe^{3+} ions in the leaching solutions. Uranium dissolution from the weathered black shale mainly attributed to redox reaction of U^{4+} to U^{6+} with Fe^{3+} as an oxidant in acidic leaching environment.

Keywords: Weathered black shale, Illite-smectite mixed interlayer phase, kerogen, ferric sulfate, sulfuric acid, uranium leaching

Introduction

Black shales are fine-grained sedimentary rocks formed by the sedimentation of mud, clay or silt and contain organic carbon rich compound (kerogen) and some graphite content (inorganic carbon). They are polymetallic in nature with variable portions of sulfide and silicate minerals. Black shales host U, Cu, Ni, Co, Mn, Mo, V, Re, Zn and Pt-group metals among others. The metal-bearing minerals are dispersed as tiny particles and trapped in the organic matter of black shale-matrix. Uranium in black shales is usually associated with the organic phase and minor fractions in clay minerals. Black shales contain minor amounts of pyrite (FeS_2), marcasite (FeS_2), and other sulfide minerals like pyrrhotite ($Fe_{1-x}S$), $CuFeS_2$, and ZnS. Some black shale deposits contain nodules or layers of calcite ($CaCO_3$) and magnesite ($MgCO_3$) and some deposits are enriched in base, strategic, rare-earth and precious metals (Mossman et al., 2005; Loukola-Ruskeeniemi and Heino 1996; Vine and Tourtelot 1970). Black shales exist in all parts of the world and the organic rich mud became a reservoir of trace metals (Tourtelot, 1979). Many black shale deposits have been explored, but their commercialization remains uncertain due to low metal concentrations and international price fluctuations. Recovering multiple metals and possibly rare earths may lower the economic threshold for commercial processing

The bio-weathering of black shale releases heavy metals and organic-carbon compounds as acid mine drainage (AMD) and therefore, impacts the environment and health of aquatic ecosystems (Jin et al., 2013; Mathur et al., 2012). The weathering phenomenon of black shales leads to elevated metal concentrations in the surface water and stream sediments due to bacterial oxidation of pyrite and sulfide minerals to form soluble metal sulfates at acidic pH (Evangelou, 1995; Ogendi et al., 2004). The oxidation process of pyrite and sulfide minerals is mainly mediated by the indigenous acidophilic iron- and S-oxidizing bacteria.

Chemical leaching of uranium ores with sulfuric acid (H_2SO_4) solution as lixiviant is a predominant process (Lottering et al., 2008; Guettaf et al., 2009; Kim et al., 2014; Tasa et al., 1995). The recovery of uranium from Polish Peribaltic sandstone ore was obtained with leaching efficiency of 85-95% using sulfuric acid as lixiviant (Gajda et al., 2015). Uranium was extracted from Abu-Tartur Plateau black shale containing 0.0052% U using 750 kg/t H_2SO_4 with 75 kg/t HNO_3 and 10 kg/t NH_4NO_3 at 110ºC (Guirguis et al., 2014). An average uranium leaching efficiency in the range of 81% U was achieved from Poland dictyonemic black shale using H_2SO_4 as lixiviant (Kiegiel et al., 2015; Frąckiewicz et al., 2012). The leaching efficiency of 90% U was obtained from Korean Okcheon black shale containing 0.057% U using 2M H_2SO_4 as lixiviant at 80 °C during 24 hr leaching (Kim 2013).

Chamiari black shale deposit is located in the Maanki Formation, Gandghar Range, Hazara district (Khyber Pakhtunkhawa Province), Pakistan (Arif et al., 2005).

The top surface of shale formation is sheared and contains incoherent pebbles and at some places look like alluvium deposited on the flat lying areas along the slope. The thickness of weathered/ oxidized zone of black shale formation is 15-17 meters. Pyrite (7-10% FeS_2) was originally present in the weathered zone of black shale formation but it was oxidized by the indigenous acidophilic Fe- and S-oxidizing bacteria to generate H_2SO_4 and $Fe_2(SO_4)_3$ (Bhatti and Butt 2007). This bacterial oxidation phenomenon has resulted partially leached out U and other associated metals downward direction or washed out with infiltration of rain water from the shale bed. Uranium concentration in this zone is 50 ppm U_3O_8 as compared to the uranium contents present in the anomalous zone and primary zones. The anomalous zone is 8-10 meters thick shale bed lying at the depth of 15-17 to 25 meters depth which contains 100-150 ppm U_3O_8 with fresh pyrite (7-10% FeS_2) and calcite ($CaCO_3$). In the present study, chemical leaching experiments were performed to characterize the dissolve uranium from weathered black shale sample using H_2SO_4 and $Fe_2(SO_4)_3$ solutions in shake flasks and column at 30±2°C.

Materials and Methods

Black shale sample

A representative black shale sample was collected from the surface of weathered/ oxidized zone of the Chamiari black shale deposit, Ghazi-Tarbela (Pakistan) by digging a pit of one-meter cube ($1M^3$). The shale sample was thoroughly mixed, homogenized, dried and ground to pass through 200 mesh sieve particle size for mineral and chemical analyses and acid leaching studies.

X-ray diffraction analysis

X-ray diffraction (XRD) analysis of topfill powder mount was conducted using CuKα-radiation (Bruker D8 Advance, Germany). The sample was scanned from 3 to 70 °2Θ in increments of 0.05 °2Θ with a 2 second step time. Minerals were identified in the automatic mode using powder diffraction library of International Centre for Diffraction Data (ICDD) by matching diffractogram and, then manually to confirm the phases.

Ferric sulfate solutions

Chemical leaching solutions (lixiviants) of sulfuric acid and ferric sulfate of various concentrations (0, 2, 4, 6, 8 and 10 mM Fe^{3+}) of pH 1.5 and pH 2.0 were prepared by dissolving appropriate amounts of the reagent in distilled water. The pH of the solutions was adjusted with 5M H_2SO_4.

Shake flasks leaching experiments

The leaching experiments were performed in 500 ml shake flasks (150 rev/ min) which contained 50 g of shale sample in 100 ml ferric sulfate solutions of various concentrations (0, 2, 4, 6, 8 and 10 mM Fe^{3+}) of pH 2.0 and pH 1.50 at 30 °C. At intervals, leach slurry samples were removed for pH monitoring and the chemical analysis of dissolved uranium in the leach solutions.

Column leaching experiments

A PVC column of 15-cm diameter and 1.0 meter height was used in percolation column leaching studies of the black shale. The column had flat acrylic bottom which was fitted with 1.0 cm diameter outlet in the centre. A bed of 15-cm glass beads of 5 mm diameter was prepared at the bottom of column and the shale (30-kg) was manually charged in the column. The column was fed from a reservoir containing 10-ltr water of pH 1.70 adjusted with H_2SO_4 at a flow rate of 0.5 liter/ hr. Column effluent was collected after each complete passing of 10-ltr solution through the column. The pH of column effluent was monitored and re-adjusted to 1.70 with H_2SO_4 for next recycling.

Analytical techniques

Uranium contents in the weathered black shale sample and process leach solutions was determined by a standard spectrophotometric method (Johnson and Florence 1971). The concentrations of ferrous iron (Fe^{2+}) and total dissolved iron (Fe_{total}) in leach solution were determined by a standard spectrophotometric method using 1,10-orthophenanthroline as chromogenic reagent (Herrera et al., 1989). The concentration of ferric iron (Fe^{3+}) in solution was derived by calculation ($Fe_{total} – Fe^{2+}$). The pH of leach solution was measured with a pH meter (Jenway 3520, UK).

Results and Discussion

Weathered black shale sample

The weathered black shale sample was radioactive due to the presence of uranium and its decay products such as ^{232}Th, ^{226}Ra and ^{40}K. The γ-activity of natural ^{235}U present in the shale sample was found 97.6 ± 1.34 Bq Kg^{-1} which was associated from ^{226}Ra and its decay radio-isotope products (^{214}Pb and ^{214}Bi). The γ-activity of ^{226}Ra, ^{228}Ra and ^{40}K were 920.31±0.31, 178.90±2.58 and 518.10±15.10 Bq Kg^{-1}, respectively (Ogendi et al., 2004).

The pH of the leachate of shale sample was measured after shaken for 1 hr. The pH-value depends upon the relative abundance of H^+ and OH^- ions produced by hydrolization of compounds leachable from the sample. The pH 6.80±0.20 of slurry was observed which indicated that the shale sample was near to neutral pH-value. The bulk density of the shale sample was 1.37±0.02 g/cm^3 with maximum dry density (MDD) of 1.864±0.062 g/ cm^3. The porosity of the sample was 48±1% indicating the mineral grains are loosely packed in the shale matrix. The shale sample showed liquid limit of 28±1% and plastic limit of 19±1%. The presence of clay minerals, mixed-layer clays and montmorillonite (especially Na-saturated montmorillonite) have a significant influence on liquid limit and plasticity index, whereas only the amount of montmorillonite and mixed-layer clay appreciably affects the plastic limit (Chan et al., 1984).

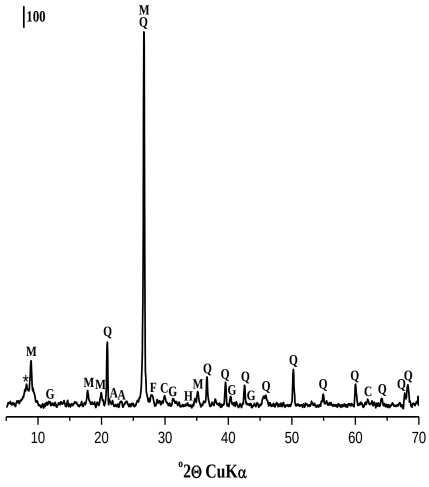

Fig. 1 Powder XRD pattern of weathered black shale sample. A = Anorthite, C = Calcite, G = Gypsum, H = Hematite, M = Illite, Q = Quartz, * = Illite-smectite interlayer phase.

X-ray diffraction analysis

Fig. 1 shows the X-ray diffractogram of weathered black shale sample and the main minerals identified are reported in Table 1. The minerals identified are quartz, illite, microcline, anorthite, hematite and gypsum. A mixed layer illite-smectite phase at 10.8Å was also detected indicating the weathering of shale sample (Fig. 1). Weathering has affects the mineralogy of the shale exposed to surface by oxidation of pyrite (FeS_2) to produce sulfuric acid which has resulted partial dissolution of clay minerals and metals present in the shale-matrix. The sulfuric acid has also neutralized calcite ($CaCO_3$) mineral present in the shale to form gypsum ($CaSO_4 \cdot 2H_2O$). Quartz (SiO_2) mineral was present in major abundance as silicate mineral in the sample.

Table 1 Mineral analysis of weathered black shale sample.

Mineral identified	**Mineral Formula**
Quartz	SiO_2
Illite	$(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$
Montmorillonite	$(Na,Ca)_{0.33}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot nH_2O$
Microcline	$KAlSi_3O_8$
Hematite	Fe_2O_3
Gypsum	$CaSO_4 \cdot 2H_2O$

Chemical analysis

The chemical analysis of the shale sample is reported in Table 2. The shale sample contained 0.005% U_3O_8 on dry matter basis which indicated that the sample contained very low concentration of uranium. The presence of other valuable metals like Ni (0.03%), Cu (0.01%), Ce (0.03%) and V (0.135%) was also detected in the sample. The shale sample contained 36.98% SiO_2, 12.35% Al_2O_3 and 14.17% Fe_2O_3 as the major constituents of the sample. The presence of kerogen (nitrogenous hydrocarbon compound) in the shale sample was reported by Bhatti and Butt (2007). The shale sample contained average contents of 20.5% C_{total}, 1.25% N and 2.5% H. The shale sample was organic carbon rich polymetallic in nature.

Table 2 Chemical analysis of black shale sample.

Constituents	**%**	**Constituents**	**%**
SiO_2	36.98	NiO	0.038
Al_2O_3	12.35	CuO	0.012
Fe_2O_3	14.17	MnO	0.010
FeO	<0.10	As_2O_3	0.012
CaO	0.45	B_2O_3	0.262
MgO	0.19	BaO	0.090
Na_2O	0.71	Cr_2O_3	0.013
K_2O	1.69	CoO	0.004
V_2O_5	0.24	WO_3	0.017
TiO_2	0.67	Ce_2O_3	0.037
PbO	0.063	La_2O_3	0.010
ZnO	0.019	U_3O_8	0.005

Shake Flasks Leaching Experiments

During leaching studies, the pH-values of leach solutions of all the treatments increased gradually throughout the experimental studies (Fig. 2). This increase in initial pH 2.0 was due to the presence of acid-consuming mineral(s) in the black shale sample. It was obvious from the leaching data that during first 24 hr leaching time, the pH of the leaching solutions of all the treatments was found in the pH range of 2.40-3.01. As the pH increased, the ferric ion underwent precipitation to form insoluble iron hydroxide or jarosite formation. After 7-days of leaching, the pH of all the solutions was found above pH 3.0 except the solution containing 10 mM $Fe_2(SO_4)_3$. It was observed that with an increase of ferric iron (Fe^{3+}) content in the lixiviant, there was an increase in U dissolution from black shale during first 24 hr leaching (Fig. 3), but the soluble U content in the leach solution was precipitated as the pH of the solution increased. Uranium dissolution from black shale was found higher in the lixiviant of initial pH 1.50.

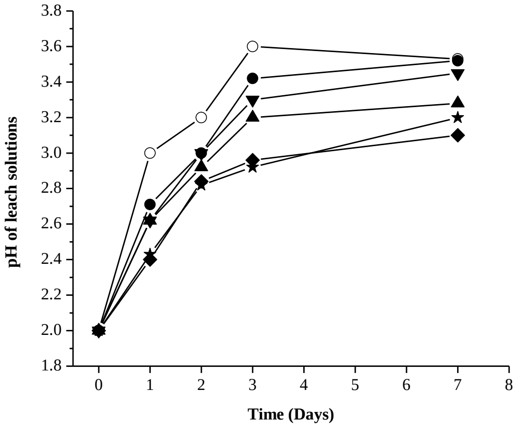

Fig. 2 pH profiles of uranium leach liquors of weathered black shale of shake flask leaching studies with different concentrations of $Fe_2(SO_4)_3$ at 30 ˚C. (○) 0 mM $Fe_2(SO_4)_3$ solution (●) 2 mM $Fe_2(SO_4)_3$ solution (▼) 4 mM $Fe_2(SO_4)_3$ solution (▲) 6 mM $Fe_2(SO_4)_3$ solution (◆) 8 mM $Fe_2(SO_4)_3$ solution (★) 10 mM $Fe_2(SO_4)_3$ solution.

The soluble uranium concentration in the leach solution of initial pH 1.5 containing 10 mM $Fe_2(SO_4)_3$ was 17.2 ppm U_3O_8 during 7-days leaching (Table 3). But, the uranium content of the leach solution without $Fe_2(SO_4)_3$ was 13.0 ppm U_3O_8. The pH of the leach solution obtained from the black shale without ferric sulfate was found pH 1.82 after 7-days of leaching, whereas the pH of leach solution containing ferric sulfate was pH 1.64 under similar leaching conditions.

Table 3 Uranium dissolution from black shale with and without $Fe_2(SO_4)_3$ solution of pH 1.5 under shaking condition at 30±2˚C for 7-days

Leaching solution	pH of leaching solution	pH of leached solution	Dissolved metals in leach solution (mg/L)				U_3O_8
			Fe_{Total}	Fe^{3+}	Fe^{2+}	U_3O_8	(%)
Acidified water	1.50	1.82	1213	1084	129	13.0	52.0
10 mM $Fe_2(SO_4)_3$ solution	1.50	1.62	1388	1263	125	17.2	68.8

During this leaching process, hematite (Fe_2O_3) mineral present in the shale matrix was dissolved by a chemical reaction with H_2SO_4 at pH 1.5 and produced $Fe_2(SO_4)_3$ during leaching process according to following reaction:

$$Fe_2O_3 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 3H_2O \qquad (1)$$

$$UO_2 + ½\,O_2 + H_2SO_4 \rightarrow UO_2SO_4 + H_2O \qquad (2)$$

$$UO_2 + Fe_2(SO_4)_3 \rightarrow UO_2SO_4 + FeSO_4 \qquad (3)$$

$$UO_2SO_4 + SO_4^{2-} \rightarrow UO_2(SO_4)_2^{2-} \qquad (4)$$

$$UO_2(SO_4)_2^{2-} + SO_4^{2-} \rightarrow UO_2(SO_4)_2^{4-} \qquad (5)$$

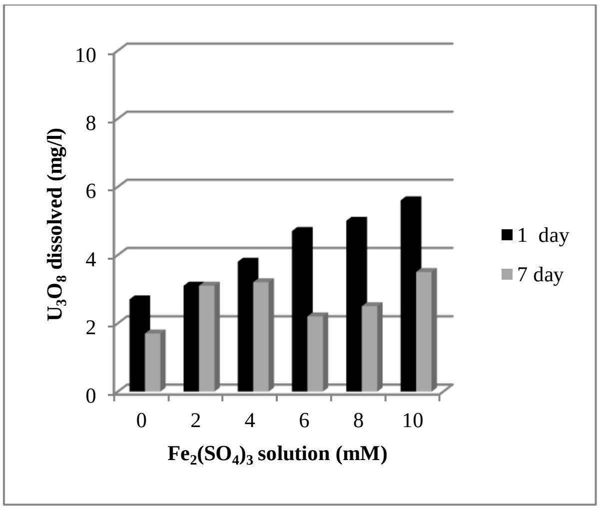

Fig. 3 Uranium dissolution from weathered black shale with and without $Fe_2(SO_4)_3$ solutions of initial pH 2.0 during 1 and 7-day leaching time at 30 ˚C.

It is clear from the leaching data that the acid leach solution containing large amount of soluble ferric iron (1084 ppm Fe^{3+}) favored the dissolution of uranium from black shale (Table 3). It is concluded that uranium dissolution from black shale was dependent on pH and Fe^{3+} concentration in the leaching solution. During uranium leaching process from ores, tetravalent state uranium (U^{4+}) involved a redox reaction to hexavalent state (U^{6+}) upon dissolution. The redox reaction of uranium oxidation between reduced uranium (UO_2) as the electron donor and Fe^{3+} as the electron acceptor (Bhatti and Tuovinen 2023; Tuovinen and Bhatti 1999; Tuovinen 1986). In acid leaching systems, the primary oxidant is ferric iron (Fe^{3+}), which is reduced to ferrous iron (Fe^{2+}) by its chemical reaction with U^{4+} (reaction 3). Uranium oxidation with O_2 as the electron acceptor is relatively slow as compared with Fe^{3+}-mediated oxidation. Ferric iron (Fe^{3+}) is the most common species used to oxidize insoluble U^{4+} to soluble U^{6+} in uranium hydrometallurgy (Mahmoud et al., 2011; Tebo 2011). In sulfuric acid leaching process, the presence of sufficient concentration of free acid is necessary to keep soluble uranium and Fe^{3+} ions in the leach solution. The re-precipitation of soluble U does not occur in the presence of sufficient amount of free acid in acid sulfate leaching process. The rate of uranium dissolution from ores also increases at pH 1.7-1.9 which attributes an increase in free acid concentration during sulfuric acid leaching process. The dissolution of uranium from uraninite (UO_2) varies in the pH range of pH 2.0-5.0 of the lixiviant, but independent of pH for more acidic leaching environment. Casas et al. (1998) attributed to a change in surface coverage by protonated uranium complex ($UO_2(OH)^+$). The dissolution rate of uranium from UO_2 was not significant change below pH 2.0, but at above pH 2.0 there was a rapid drop in the dissolution rate due to the hydrolysis of Fe^{3+} ions to the formation of insoluble iron compounds (Celeda and Lara 1965). Uranium dissolution from black shale was dependent on

H^+ and Fe^{3+} concentrations in the leaching solution. Uranium dissolution from shale was mainly attributed to the concentrations of H_2SO_4 and $Fe_2(SO_4)_3$ in the leaching process.

Column Leaching Studies

Soluble uranium content in the leach solutions of column leaching studies are reported in Table 4. It is obvious that from the technical data that uranium was leached out from shale during percolation with acidified water pH 1.70. Uranium recovery of 16.4% U_3O_8 was achieved in 5-cycles during 30 days leaching.

Table 4 Percolation column leaching studies of weathered black shale with acidified water (pH 1.70)

No. of Cycle	pH of feeding solution	pH of leached solution	Physical appearance of leached solution	U_3O_8 in leached solution (mg/l)	Total U_3O_8 in leached solution (mg)	U_3O_8 Recovery (%)
1	1.70	2.95	Colorless	13.4	134	8.93
2	1.72	2.85	Colorless	15.2	152	10.13
3	1.72	2.50	Colorless	17.2	172	11.47
4	1.70	2.15	Colorless	19.6	196	13.07
5	1.70	1.95	Pale yellow	24.6	246	16.40

The physical appearance of the leach solution was pale yellow indicating the presence of Fe^{3+} ion. In this leaching system, sulfuric acid reacted with hematite (Fe_2O_3) and illite minerals present in the shale matrix produced $Fe_2(SO_4)_3$ which oxidized U^{4+} present in the shale matrix. So, uranium was dissolved from shale during the experimental leaching conditions. The leaching data simulate the heap leaching process.

Conclusion

The leaching results demonstrate that uranium dissolution from weathered black shale depends on the concentration of $Fe_2(SO_4)_3$ and H_2SO_4 in the leaching solution (lixiviant). Sulfuric acid acts as a leaching agent while ferric sulfate as an oxidizing agent during leaching process The leaching data of uranium leaching from the shale sample mainly attributed to the H_2SO_4 and $Fe_2(SO_4)_3$ concentrations in the leaching solutions during leaching process.

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References

Arif, A. Z., Khan, T. M., Shah, M. S., Qadir, A., Shah, S. Z., Shah, Z. (2005). Subsurface uranium exploration in graphitic metapelites, Chamiari Area–Tarbela, District Haripur. Technical Report, Regional Exploration Office, PAEC, Peshawar, Pakistan.

Bhatti, T. M., Tuovinen, O. H. (2023). Some historical briefs and outlooks of the chemical and biological acid leaching of uranium ores. *The Nucleus* **60** (1-2), 28-34.

Bhatti, T. M., Butt, K. A. (2007). Bioleaching of uranium from Chamiari low-grade black shale. Technical Report No. DGNFC-AEMC-1/2007. PAEC, Islamabad, Pakistan.

Bhargava, S. K., Ram, R., Pownceby, M., Grocott, S., Ring, B., Tardioa, J., Jones, L. (2015). A review of acid leaching of uraninite. *Hydrometallurgy* **151**, 10-24.

Casas, I., de Pablo, J., Gimenez, J., Torrero, M.E., Cara, E., Finch, R.J., Ewing, R.C. (1998). The role pe, pH and carbonate on the solubility of UO_2 and uraninite under nominally reducing conditions. *Geochimica Cosmochimica Acta* **52** (13), 2223-2231.

Celeda, J., Lara, J. G. (1965). The kinetics and mechanism of the dissolution of uranous-uranic oxide in sulfuric acid in presence of ferric ion. *J. Inorg. Nucl. Chem.*, **27**, 2561-2572.

Chan, D. Y. C., Pashley, R. M., Quirk, J. P. (1984). Surface potentials derived from co-ion exclusion measurements on homoionic montmorillonite and illite. *Clays Clay Miner.*, **32**, 131-138.

Evangelou, V. P. (1995). Pyrite Oxidation and its Control: Solution Chemistry, Surface Chemistry, Acid Mine Drainage (AMD), Molecular Oxidation Mechanisms, Microbial Role, Kinetics, Control, Ameliorates and Limitations, Microencapsulation, - CRC Press, Boca Raton, Florida, USA.

Frąckiewicz, K., Kiegiel, K., Herdzik-Koniecko, I., Chajduk, E., Zakrzewska-Trznadel, G., Wołkowicz, S., Chwastowska, J., Bartosiewicz, I. (2012). Extraction of uranium from low-grade Polish ores: dictyonemic shales and sandstones. *Nukleonika*, **58** (4), 451-459.

Gajda, D., Kiegiel, K., Zakrzewska-Koltuniewicz, G., Chajduk, E., Bartosiewicz, I., Wolkowicz, S. (2015). Mineralogy and uranium leaching of ores from Triassic Peribaltic sandstones. *J. Radioanal. Nucl. Chem.*, **303** (1), 521-529.

Guettaf, H., Becis, A., Ferhat, K., Hanou, K., Bouchiha, D., Yakoubi, K., Ferrad, F. (2009). Concentration-purification of uranium from an acid leaching solution. *Phys. Procedia,* **2**, 765-771.

Guirguis, L. A., Farag, N. M., El-Sayed, M. A., Hagag, M. S. (2014). Solvent leaching of uranium from Abu-Tartur Plateau black shale. In 4th International Conference on Radiation Research and Applied Sciences, Taba, Egypt. 111-119.

Herrera, L., Ruiz, P., Aguillon, J.C., Fehrmann, A., 1989. A new spectrophotometric method for the determination of ferrous iron in the presence of ferric iron. *J. Chem. Technol. Biotechnol.*, **44**, 171-181.

Jin, L., Mathur, R., Rother, G., Cole, D., Bazilevskaya, E., Williams, J., Carone, A., Brantley, S. (2013). Evolution of porosity and geochemistry in Marcellus Formation black shale during weathering. *Chem. Geol.,* **365**, 50-63.

Johnson, D. A., Florence, T. M. (1971). Spectrophotometric determination of uranium (VI) with 2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol. *Analytica Chimica Acta,* **53**, 73-79.

Kiegiel, K., Zakrzewska-Kołtuniewicz, G., Gajda, D., Miśkiewicz, A., Abramowska, A., Biełuszka, P., Danko, B., Chajduk, E., Wołkowicz, S. (2015). Dictyonema black shale and Triassic sandstones as potential sources of uranium. *Nukleonika,* **60** (3), 515-522.

Kim, JS, Chung KW, Lee HI, Yoon HS, Kumar JR. (2014). Leaching behaviour of uranium and vanadium using strong sulphuric acid from Korean black shale ore. *J. Radioanal. Nucl. Chem.,* **299**, 81-87.

Kim, J.S. (2013). Research and development for the recovery of uranium and vanadium from Korean black shale ore. *J. Korean Inst. Res. Recycl.,* **22** (1), 3-10.

Lottering, M. J., Lorenzen, L., Phala, N. S., Smit, J. T., Schalkwyk, G. A. C. (2008). Mineralogy and uranium leaching response of low grade South African ores. *Miner. Eng.,* **21**, 16–22.

Loukola-Ruskeeniemi, K., Heino, T. (1996). Geochemistry and genesis of black shale—hosted Ni-Cu-Zn deposit at Talvivaara, Finland. *Econ. Geol.,* **91**, 80-110.

Mahmoud, A., Abbas, S. S., Hasan, Z. T., Ali, V. (2011). Bioleaching of low grade uranium ore of Saghand Mine. *Iran. J. Chem. Chem. Eng*., **30** (4), 72-79.

Mathur, R., Jin, L., Prush, V., Paul, J., Ebersole, C., Fornadel, A., Williams, J. Z., Brantley, S. L. (2012). Insights into the weathering of black shale: Cu isotopes and concentrations in the Marcellus Formation shale, Huntingdon County, Pennsylvania (U.S.A.). *Chem. Geol.,* 304-305, 175-184.

Mossman, D. J., Gautheir-Lafaye, F., Jackson, S.E. (2005). Black shales, organic matter, ore genesis and hydrocarbon generation in the Paleoproterozoic Franceville Series, Gabon. *Precambrian Res.,* **137** (3-4), 253-272.

Ogendi, G. M., Hannigan, R. E., Farris, J. L., Smith, D. (2004). The impact of black shale weathering on sediment quality. *J. Arkansas Acad. Sci.,* **58**, 84-90.

Swanson, V. E. (1961). Geology and geochemistry of uranium in marine black shales—a review: *U.S. Geol. Surv. Prof. Pap.,* 356-C, 67-112.

Tasa, A, Garcia, O. Jr., Bigham, J., Vuorinen, A., Tuovinen, O. H. (1995). Acid and biological leaching of black shale from Toolse, Estonia. In *Biohydrometallurgical Processing,* Vol. I. T. Varga, C. A. Jerez, J. V. Wiertz, and H. Toledo (eds.), University of Chile, Santiago, Chile. pp. 229-238.

Tebo, B. M. (2011). Direct and indirect processes leading to uranium(IV) oxidation. In Microbial Metal and Metalloid Metabolism: Advances and Applications. J. F. Stolz and R. S. Oremland (eds.), Wiley ASM Press, New Jersy, 139-156.

Tourtelot, H. A. (1979). Black shale – Its deposition and diagenesis. *Clays Clay Miner*., **27** (5), 313-321.

Tuovinen, O. H. (1986). Acid leaching of uranium ore mediated with microbial catalysis. *Biotechnol. Bioeng. Symp.,* **16**, 65-72.

Tuovinen, O. H., Bhatti, T. M. (1999). Microbiological leaching of uranium ores. *Miner. Metall. Proc.,* **16**, 51-60.

Vine, J. D., Tourtelot, E. B. (1970). Geochemistry of black shale deposits-a summary report: *Econ. Geol.,* **65**, 253-272.