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SEDIMENTOLOGICAL AND TECHNOLOGICAL STUDIES OF ABU TARTUR BLACK SHALES, WESTERN DESERT, EGYPT

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Newly conventional combination of sedimentological and technological studies aid in estimation of the resource potential of the Upper Cretaceous clays of Duwi Formation Abu Tartur plateau Western Desert, Egypt. This formation consists of interbedded black to Grey shale, phosphatic and glauconitic sandstones.

The granulometric, mineralogical, and geochemical analyses were carried out on the black clays, which provided detailed information about textural parameters, composition and paleoenvironment of deposition

The technological studies of black shale is new for its interesting enrichments in various rare metals as nickel , chromium and vanadium . This investigation is a laboratory study for extraction of vanadium from black shales by hydrochloric acid processing to produce leach solutions of vanadium, aluminum and magnesium chlorides. The effects of various factors affecting the leaching process such as temperature, acid concentration, particle size and stirring speed as well as the kinetics of the leaching process were studied.

The most favorable conditions for the extraction of the vanadium present in the black shale are temperature 100° C, acid concentration 6 M by weight, grain size 17 μm and leaching time 90 min.

Key words: black shale, paleoenvironment, vanadium, leaching.

INTRODUCTION

The black shale sample were collected from Abu Tartur plateau, Kharga oasis which is located at the intersection of longitude 30 05 E. and latitude 25 32 N. This area had attracted attention of many geologists since the discovery of great phosphate deposits in 1967. The stratigraphic position of the investigated deposits lies within upper and lower member of the Phosphate Formation (Said 1990). This formation underlies the Dakhla shale and overlies the Quseir Formation; lithologically it consists of phosphate beds interbedded with black and gray claystone, sandstone, siltstone and glaucony beds.

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At the late time the government of the New Valley (El Kharga oasis) pay attention to exploit the wide extended clay deposits which exposed allover the oasis and extended even to El Dakhla oasis (El Kharga El Dakhla stretch). Among the clay deposits is the black shale, which have a considerable economic importance due to their special composition.

Black shales in Egypt are now known for their interesting enrichments in various metals especially rare vanadium (Melik 1971) and nickel (Amer 1994). No attempts havebeen made to process these black shales or to find a profitable use for them. The manufacture of vanadium alloys in Egypt depends mainly on imported vanadium. It is therefore claimed that the development of an indigenous source of vanadium to sustain self- sufficiency in vanadium. Attempts to utilize vanadiferous shales are mainly restricted to the leaching of vanadium by the stander roast-leach process (Sastry and Raju 1968, Bing and Thome 1978). A hydrometallurgical route has recently been proposed for the treatment and processing of vanadiferous shales. In this investigation black shale is leached with hydrochloric acid under mild condition whereby vanadium and iron dissolve. Separation of vanadium and iron can be achieved in economic scale using ion exchange (Martins at el. 1973 and Amer 1996).

MATERIAL AND METHODS

Twelve black shale samples were collected from the repeated black shale beds at Abu Tartur mine. Five-selected Sample were attained granulometric analysis, wet sieving was achieved by the use of pipette method (Lewis and McConchie 1993). Sand, silt, clay contents, sample nomenclature and four main statistical textural parameters Mz, бI, SkI and KG (Folk and Word 1957) were estimated (Tab. 1).

Table 1. Granulometric results, nomenclature and statistical textural parameters of the studied black shale

Samp. No.	Rock Constituents			Nomen clature	Statistical Textural Parameters			
	Sand	Silt	Clay		Mz	σ I	Sk I	KG
b.c.9	0.60	76.40	23.00	Silt	5.46	1.30	0.06	0.59
b.c.7	0.50	59.66	39.84	Clay –silt	5.64	1.62	0.17	0.61
b.c.5	0.40	84.09	15.51	Silt	5.33	1.30	0.45	1.78
b.c.3	0.60	87.70	11.70	Silt	4.67	1.76	1.10	1.63
b.c.1	0.98	76.82	22.19	Silt	5.51	1.71	0.56	0.69

Clay mineral analysis had carried out by XRD method on six selected samples. A qualitative and quantitative estimation for clay mineral were made to the whole sample and to the separated clay fraction after various treatment (air dried, glycol solvated and heating to 550 °C) in order to isolate the clay components. The resulted X-ray diffractograms were interpreted using Krotova and Kazakova method (1984).

Eight of the black shale samples were chemically analyzed at the Technical University of Berlin, Germany. Major elements were determined using energy dispersive X-ray florescence technique on fused pellets. Trace elements were also determined using pressed pellets and polyvinyl alchol as binding agents. Analytical results for selected and representative samples are listed in Table 2.

Table 2. Frequency distribution of the different minerals in the studied black shale

Samp. No.	Mineralogical composition							
	Q	Sm	I	S	K	F	J	Py
b.c.6	7.70	74.50	–	–	2.00	2.00	–	–
b.c.3	8.00	82.70	0.10	–	–	–	–	–
b.c.1	17.00	72.00	0.60	0.60	–	2.60	3.70	1.70

Q – Quartz Sm – Smectite I – Illite S – Sederite
F – Feldspar Py – Pyrite J – Jarosite K – Kaolinite

All leaching experiments were performed in 600-ml capacity glass beaker held in water bath controlled to ±1 °C using a thermostat/circulating pump. Using an impeller driven by a variable speed motor did the stirring of the liquid. The technique used in the present investigation has been described elsewhere (Amer 1996).

GRANULOMETRIC ANALYSIS

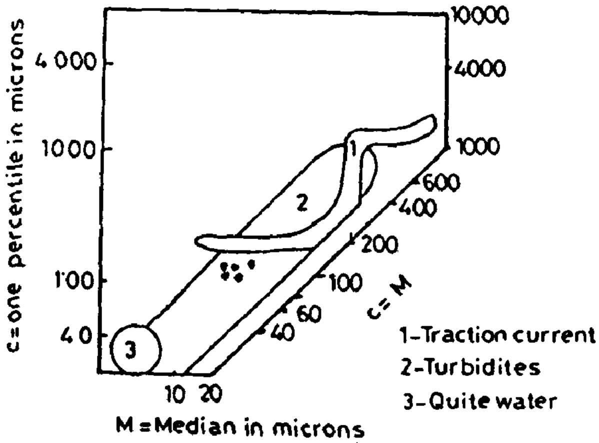
Wet sieving was used to analyze the black shales for define their textural composition. The obtained data and the resulted textural parameters are recorded in Table (1). It is appeared that the studied black shale lie belong silt and clay – silt according to (Picard 1971) .

Based on the illustrated data (Tab. 1) the studied sediments could be descriped as medium grained, poorly sorted, fine to strongly fine skewed silt.

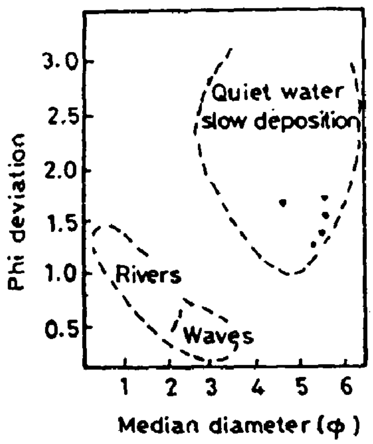
Generally the fine clay fraction is very sensitive to depositional process, so the auther tried to use the obtained Statistical Textural Parameters (STP) and their binary relations to give an idea about the ancient environment and transportation mechanism.

Plotting the estimated values of C (the one percentile) and M (the Median 50 percentile) on C-M pattern proposed by (Passega 1964), illustrate that the studied black shale was deposited under turbidity current (Fig. 1). Moreover the binary plots (Stewart 1958), had cleared that, these samples lie in quiet water (slow suspension) condition.

Therfore the authers assumed that the studied black shale resemble the third main type of suspension which occur when turbid flows enter bodies of waters with no significant density difference, such this situation the flow named hypopycal flow (Bates 1953, Tucker 1988). The fine material of black shale was settled out of suspension from admixture of water bodies most probably fluvio-marine environment.



(a) C – M. pattern (fter passega, 1957)



(b) Inclusive graphic standard deviation versus diameter

Fig. 1. Binary realationship of statistical textural parameter of Abu Tartur black shale

MINERALOGY

The results of X-ray diffraction analysis of Abu Tartur black shale are discussed below.

X-RAY ANALYSIS OF BULK SAMPLE

The bulk sample diffractograms revealed the presence of certain association as shown in Table 1. Quartz is present in moderate amount (7.7 to 17 %). Smectite is the dominant mineral (72 to 82.7 %), while feldspare forms small content (2.6 to 5.7), consequently kaolinite and illite as well as jarosite and pyrite occur as minor constituents (Tab. 2)

X- RAY ANALYSIS OF CLAY FRACTION

The X- ray diffractograms of the oriented clay fraction reveal the presence of high sharp peak 14.1 A and very weak 7.16 A peak on the untreated diffractogram. On the glycolated run the peak 14.1 shifts to larger spacing peak 17.9 A, while with heating to 550 C it collapsed and sharpened at 9.8 A peak (Fig. 2)

Using flow sheet for clay mineral identification (Starkey et.al. 1984, Krotova and Kazakova 1984) method, the clay fractions are composed of dominant smectite (montmorillonite) mineral with small amount of kaolinite-smectite interstratified layers.

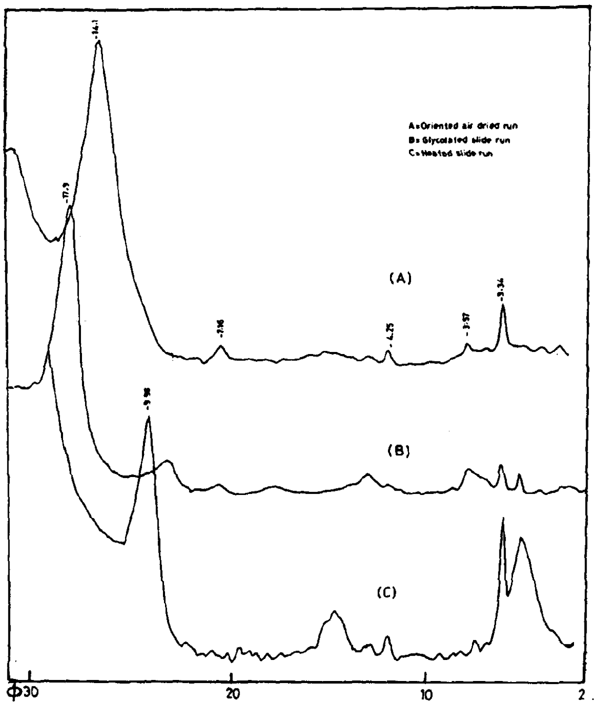


Fig. 2. Representative diffractogram of the clay fraction Abu Tartur black shale

The resulted clay mineralogy of the studied samples is taken as an indicator for paleoenvironmental interpretation where the abundance of smectite and low content of illite and kaolinite refer to deposition under fluvio-marine environments and the prevailed condition was of alkaline chemical affinity, at the same time the source rock had not attained intensive weathering.

GEOCHEMISTRY

The chemical analysis of eight selected samples is carried out in order to shed light on the chemical composition and their position relative to world types of black shale.

Table 3 A. Average content of the major elements of Abu Tartur black shale

Samp No.	Chemical Analysis									
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	P_2O_5	TiO	SO_3^{2-}
9,10	58.09	19.80	5.92	1.50	2.11	0.72	0.90	1.69	1.07	2.37
5,6	58.32	16.66	8.45	1.02	1.20	0.35	0.79	2.48	1.25	1.99
3,4	59.40	18.19	4.93	0.57	2.18	0.32	0.78	1.38	1.30	2.54
1,2	59.09	16.48	3.38	2.47	1.46	1.19	0.59	1.16	0.81	1.86

Table 3 B. Average content of the trace elements of Abu Tartur black shale

SampNo.	Content in PPM									
	V	Sr	Cr	Ni	Co	Cu	Zn	Ba	Pb	Zr
9,10	425	180	300	89	60	35	88	150	219	230
5,6	490	190	190	80	48	35	79	140	190	220
3,4	430	170	185	43	49	30	72	149	185	200
1,2	260	199	180	33	40	32	62	113	113	180

Twenty major and trace elements were determined. Tables (3 A, 3 B) show the average content of these elements, it is obviously clear that the analyzed black shale samples are poor in Fe_2O_3, CaO, MgO, K_2O, Na_2O, while rich in Al_2O_3, P_2O_5, TiO and nearly with the same content of SiO_2 relative to the published contents of the world shales. On the other hand, they are rich in V, Cr, Co, and Pb, while poor in Sr, Ba and with similar values of Ni, Cu, and Zn comparatively to the Turkian and Wedepohl, 1961 and the data compiled from (Cullers and Stone 1991, Cullers, 1995).

The chemical analysis agreed with the results of clay mineralogy investigation where the low percent of K_2O reflects the absence or low content of illite mineral.

According to the geochemical classification which based on the log values of the ratios SiO_2/Al_2O_3 and Fe_2O_3/K_2O (Herron 1988), the Abu Tartur black shale are classified into iron–shale

Two main recommended ratios were used, which have intimate relation to environment (Roaldest 1978). These ratios are K_2O/Al_2O_3 and MgO/Al_2O_3, plotting their values on Roaldest diagram has cleared that the studied black shale lied in the area between marine and non-marine environment.

TECHNOLOGICAL STUDY

LEACHING ASPECTS

Temperature:	40 – 100 °C
Hydrochloric acid conc.	2 – 8 M
Grain size	17 – 80 μm
Stirring speed	250 – 1000 rpm/min.
Time of leaching	20 – 100 min.
Solide/liquid ratio	0.1

The dissolution of vanadium and iron using hydrochloric acid can be expressed by the following :

$$V_2O_3 + 6HCl \rightarrow 2VCl_3 + 3H_2O \tag{1}$$

$$FeO(OH) + 3HCl \rightarrow FeCl_3 + 2H_2O \tag{2}$$

$$Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O \tag{3}$$

BEHAVIOUR OF VANADIUM

Effect of leaching time and temperature:

Results using 6 M HCl with grain size (17 µm) at 90 °C, stirring speed of 800 rpm/min are shown in figure 3. Vanadium extraction is highest ≥ 90%. The vanadium extraction increases with temperature. The activation energy for the leaching process is determined by an Arrhenius plot as shown in figure 4. The activation energy is calculated to be 18 kJ/mol which is indicative of a boundary layer diffusion control.

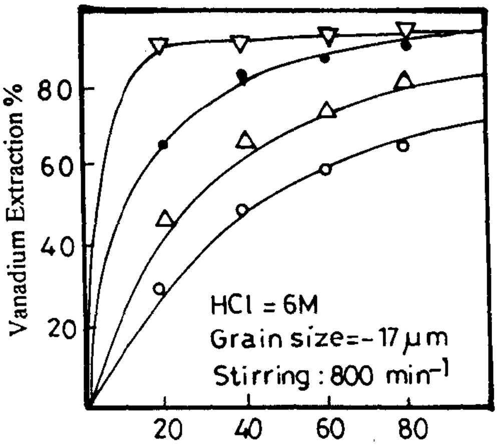


Fig. 3. Relation betwenn vanadium extraction and time at different temperatures

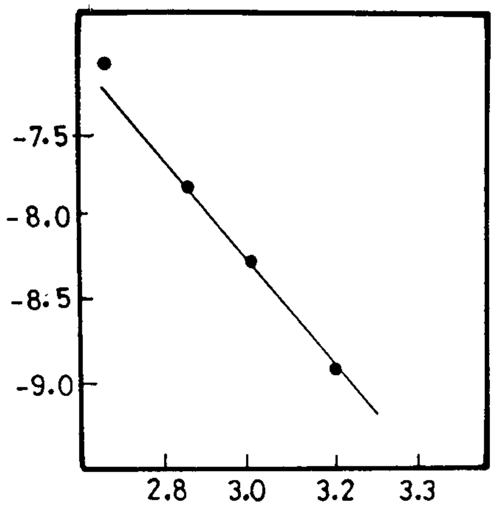


Fig. 4. Arrhenius plot for determining the activation energy

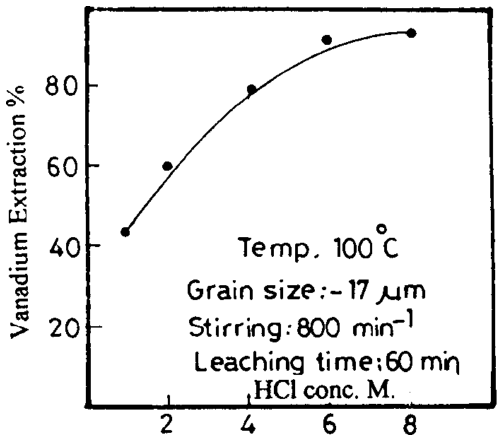
Effect of acid concentration:

Figure 5 shows the effect of HCl concentration in the range of 2-8 M. on leaching 17 µm. black shale deposits at rpm/800 min. agitation speed at 100 °C. It can be seen that the vanadium extraction increases with increasing acid concentration from 2-6 M.

Further increase of acid concentration has practically no effect on vanadium extraction. Chemical weathering affects the stability of silicate structures and probably accounts for enhanced extraction of vanadium. Increasing the temperature of acid results in a greater release of vanadium from its lattice position.

Effect of speed of agitation:

Figure 6 shows the effect of speed of agitation in the range of 250 – 1000 rpm/min using 6 M. HCl at 100 °C. It can be seen that, the rate of the reaction depends on the speed of agitation. As seen from figure 8, a plot of ln (1 - ά) versus time of the expremint at different agitation speeds yields a straight lines indicating that the leaching of black shale is a diffusion controlled process.



5. Effect of acid concentration on vanadium extraction

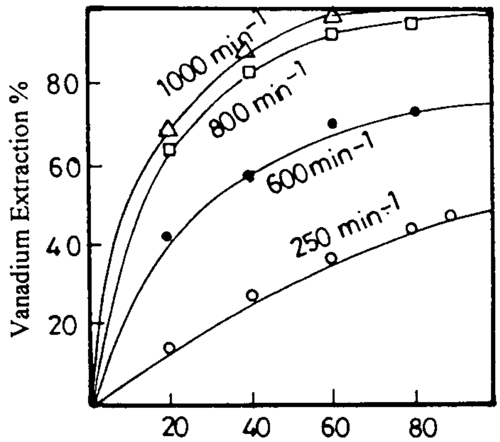


Fig. 6. Effect of speed agitation on vanadium extraction

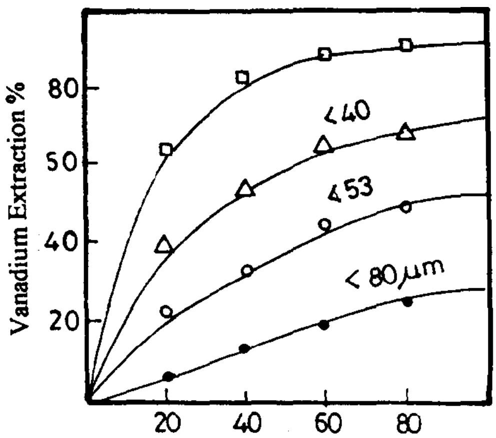


Fig. 7. Effect of particle size on vanadium extraction

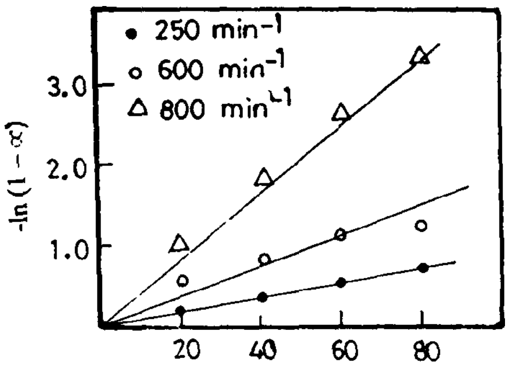


Fig. 8. Test of applicability of film diffusion model to the experimental data

Effect of particle size:

Figure 7 shows the results obtained when particle size fraction with mean diameter of 17, 40, 53, and 82 μm were used. The apparent rate constants k were calculated according to the following equation (Fig. 8).

$$\ln(1 - \alpha) = kt$$

where: α – fraction reacted of vanadium from Abu Tartur black shale
k – reaction constant min.
t – leaching time min.

The external surface areas were calculated for different particle size using the following equation assuming spherical particles :

$$S = \frac{2m}{3pd}$$

where S – external surface area for the particle – m²,
m. –- the mass of the sample being leached – kg,
p – the density of the sample – kg/m³,
d – the particle mean diameter – µm.

The specific apparent constant k/s were calculated and are given in Table 4. It is clear that the smaller the particle size, the larger the specific apparent rate constant .It is known that the smaller the particle size , the thicker the boundary layer surrounding the particle. This further confirms that the controlling step is diffusion through the boundary layer.

Table 4. Rate constants for various particle sizes

D [µm]	S [m²]	k [min^{-1}]	k/S [(m² · min)$^{-1}$]
17	0.7	0.044	0.0629
40	0.33	0.017	0.0515
53	0.29	0.009	0.0310
80	0.25	0.004	0.0169

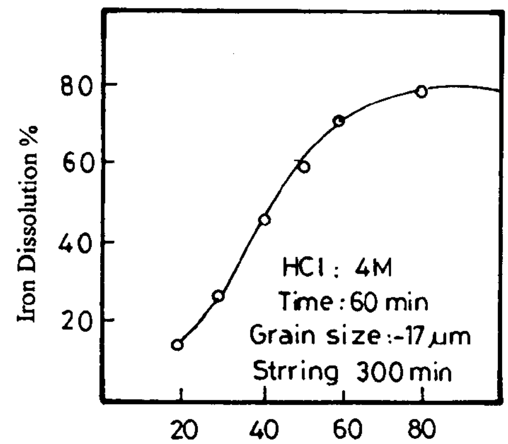


Fig. 9. Effect of temperature on iron dissolution

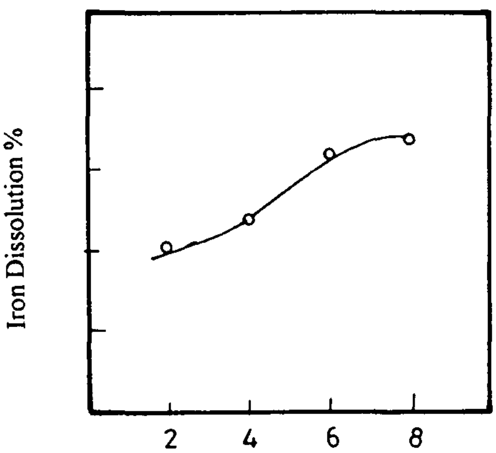


Fig. 10. Effect of hydrochloric acid concentration on iron dissolution

BEHAVIOUR OF IRON DURING HYDROCHLORIC ACID PROCESSING

Figures (9, 10) show the behaviour of iron as a function of temperature and acid concentration. At low temperature 40 °C acid concentration is the dominating factor in deciding the percentage of metal extraction.

SEPARATION OF VANADIUM AND IRON BY ION EXCHANGE

Recovery of vanadium from acid leach solution by ion exchange is economically feasible. Pilot scale tests were made. The leach solution was heated to 50 °C and sodium chlorate was added to oxidize vanadium (V_2O_3) to vanadium (V_2O_5), which was then sorbed by the resin, changing its color to bright red. After washing with water, vanadium was eluted by sulfurous acid solutions, the elute was deep blue due to vanadium (VCl), and the resin turned lemon yellow. The strongly sorbed HSO_3^- was removed by 2 % solution of $NaClO_3$ acidified at pH 1.5 with H_2SO_4. The resin again turned golden brown color.

CONCLUSIONS

Generally the Abu Tartur black shale represented granulometrically as silt and clay –silt. Mineralogical data showed that the black were composed of non-clay mineral association as quartz, feldspare, jarosite and pyrite and clay mineral represented by frequent smectite and traces of illite and kaolinite-smectite interstratified layer.

Geochemical data suggested that the black shale classified as iron-shale. These shales were rich in major oxides as Al_2O_3, P_2O_5,TiO and poor in CaO, MgO, K_2O and Na_2O with similar SiO_2 content comparatively to the known world shale.

Based on the combined sedimentological data, the main characters of the paleoevironments could be interpreted; the source area of black shale had not attained intensive weathering and the resulted materials had carried by fluvial action, which finally interfered and admixed with marine environment to create alkaline, quiet and reduced conditions.

The technological work done indicates that a promising process might be devised for hydrochloric acid leaching of Abu Tartur black shales.

Vanadium extraction from shales is a function of temperature, acid concentration and a stirring speed as well as particle size of used black shale. The reaction rate is controlled by the diffusion of vanadium from silicate structure of black shale. The calculated activation energy is found to be 18 K/mol.

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Badania sedymentologiczne i technologiczne miały za cel oszacowanie potencjalnych możliwości wykorzystania czarnych iłów ze złoża Abu Tartur leżącego na pustyni zachodniej w Egipcie. Złoże to zawiera czarny przechodzący w szary łupek, glaukonitowy i fosforanowy piaskowiec. Zostały przeprowadzone analizy granulometryczne, mineralogiczne i geochemiczne czarnych iłów. Wyniki analiz dostarczyły dokładne informacje o teksturze, składzie i paleosrodowisku złoża. Badania technologiczne czarnego łupka zostały przeprowadzone z uwagi na bogatą zawartość w nich metali rzadkich takich jak nikiel, chrom i wanad. Badano w skali laboratoryjnej, proces ekstrakcji wanadu kwasem solnym, otrzymując roztwór zawierający chlorki wanadu, glinu i magnezu. Wpływ różnych parametrów takich jak temperatura, stężenie kwasu solnego, uziarnienie nadawy, prędkość mieszania, na kinetykę procesu ługowania został przebadany. Najlepsze warunki ekstrakcji wanadu z czarnego łupka uzyskano stosując temperaturę 100^{o}C, stężenie kwasu solnego 6M, granulację nadawy 17 μm i czas ługowania 90 minut