

Ashraf M. AMER^{*}, Kadry. N. SEDIEK^{**}

COMPOSITIONAL AND TECHNOLOGICAL CHARACTERISTICS OF SELECTED GLUACONY DEPOSITS OF NORTH AFRICA

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The studied gluacony deposits were collected from the Egyptian and Libyan outcrops. The Egyptian gluacony deposits are widely recorded in the Upper Cretaceous, while Libyan gluacony lies within the Oligocene succession. The collected gluacony rocks were subjected to petrographic and infrastructure investigation. Also chemical investigations using microprobe analysis were carried out on some pellet-like gluacony grains. The results of chemical analysis showed that the studied gluacony grains in both areas did not have identical K₂O content. Egyptian gluacony had from 5.30 to 10.07% K₂O while the Libyan type had relatively higher content of K₂O, which vary from 8.9 to 12.67%. The studied gluacony samples had similar contents of Fe, Al, Cu, and Zn with different contents of Ca, Mg and V oxides. Direct acid leaching laboratory studies were conducted as an alternative route of the roast-leach treatment for the extraction of potassium from studied gluacony. The effects of leaching temperature, acid concentration, leaching time, and particle size were investigated.

Key word: gluacony deposits, petrography, extraction, potassium, leaching

INTRODUCTION

Gluacony deposits are known and represented in many sedimentary formations, especially those of Cretaceous, Eocene and Oligocene ages. Green Sand, Green Marl and Green Earth were the names given to the sediments rich in the yellowish, bluish to greenish black minerals which contain gluaconite. The term gluacony has been used after such eminent workers as Odin and Matter (1981) as well as Van Hauten and Purucker (1984). In spite of numerous works on gluacony all over the world, a few studies have been carried out on the Egyptian gluacony rocks (El Sharkawi and Khalil, 1977; Glenn and Arther, 1990; Ahmed, 1995; and Sediek, 1999). Previously the gluacony deposits were used as fertilizers (Tedrow, 1957).

^{*} Alexandria University, Faculty of Science, Environmental Science Department, Alexandria, Egypt

^{**} Alexandria University, Faculty of Science, Geology Department, Alexandria, Egypt

Many crops improve with the use of glaucony, especially the forage type. On the other hand some crops are poisoned or burned with the use of glaucony due to the presence of sulfur and sulfides. There is a great need in Egypt for the development of a new process for extraction of potassium from secondary sources to meet the demand of the potassium fertilizer industry (Choudhury et al., 1973; Soni, 1990; Yedav and Sharma, 1992 and Mazumder and Sharma, 1993). Roast-leach method is considered as a traditional technique used for potassium extraction from the glauconitic sandstone. This investigation aim is to gather data on the mineralogical, petrographic and chemical composition of studied glaucony, kinetic of direct acid leaching of glaucony samples as well as the reaction mechanism.

GEOLOGIC SETTING

The studied glaucony samples were collected from the Libyan and Egyptian outcrops. The Libyan glaucony deposits were taken from the area located in the Northeastern side of Al Jabal al Akhdar, which lies in the northeastern part of Libya about 65 km from Benghazi City. Geologically the Libyan glaucony deposits were created during the late middle Oligocene of Abraqe Formation, which occur in the Northwestern side of the Jabal Akhdar anticlinorium, Northern Cyrenaica platform, NE Libya (EL Hawat and Shelmani, 1993). The thickness of these deposits is about 4 meters that is underlain by calcarenitic limestone and overlain by marl limestone. The Egyptian glaucony samples were collected from three main localities, two of them lie in the Western Desert (Abu Tartur Plateau and Gebel Teneda). The third locality lies in the Eastern Desert (Abu Syndyk) close to Wadi Qasseib. The stratigraphic position of the studied glaucony deposits in the Western Desert lies within the upper member of the Phosphatic Formation of Campanian-Maastrichtian (Youssef, 1957; Awad and Ghobrial, 1965), while glaucony of the Eastern Desert lies in the Raha Formation of Cenomanian Age. The Abu Tarture and Teneda glaucony deposits occur in an alternating position with black and gray claystone, siltstone and sandstone beds. On the other hand the Abu Syndyk glaucony alternates with pale yellow to gray skale, marl and limestone bands.

MATERIALS AND METHODS

Thirty glaucony samples were taken from the glaucony beds of the described localities. Thin sections of the collected samples have been examined petrographically under polarized microscope. The glaucony grains or pellets were picked and concentrated after treatment with diluted acetic acid to remove the carbonate material. The picked glaucony grains were examined under binocular microscope to investigate the morphology of the particles. Some of the separated grains were mineralogically investigated by X-ray diffraction (XRD). Others were chemically analyzed with X-ray fluorescence (XRF) and/or microprobe analyses at the Technical University of Berlin (Germany) or Central Laboratory of the Faculty of Science of Alexandria University.

The grains and pellets of six different selected samples have been examined by scanning electron microscopy (SEM) also in the Central Laboratory to define their characteristic nano-structure.

The pressure leaching experiments were carried out in 2 dm³ capacity vertical autoclave. The experimental procedures and leaching system were similar to that described before (Sharma and Roy, 1979). Before leaching a representative sample of glaucony deposits was ground in a ball mill and sieved into the following fractions (300-180 µm), (180-150 µm), (150-106 µm), (106-75 µm), and (<75 µm). The following parameters regarding potassium extraction were studied: temperature (125-225 °C), hydrochloric acid concentration (20 wt.%), grain size (300-75 µm), leaching time (15-90 minutes).

PETROGRAPHIC INVESTIGATION

LIBYAN GLUACONY DEPOSITS (LG)

The Libyan glaucony rocks are of granular facies. The rock groundmass consists of sand-sized green pellet-like grains. Their sizes vary from coarse sand to coarse silt. The morphological forms of glaucony pelletal grains vary from ovoid, globular, oblate, sphenoid to capsule and are given in order of their decreasing in abundance. These pellet-shaped grains occur as admixture with the carbonate constituents, which are commonly expressed by foraminiferal tests and detritus of nummulites. The components of the admixture here are cemented by micro-sparry calcite. The rock ground mass is free from any detrital quartz grains.

EGYPTIAN WESTERN DESERT GLUACONY ROCKS (WDG)

Sedik (1999) has studied the petrography of the glaucony rock. Two main types have been described. The first was the Abu Tarture dark green structure-less glauconic sandstone, and the second was Teneda light green laminated glauconic sandstone. For both types the pellet-type grain forms dominate and vary from 59 to 68% for the first type and from 58 to 63% for the second one.

EGYPTIAN EASTERN DESERT GLUACONY ROCKS (EDG)

This type of glaucony deposits differs from the above mentioned types, where the rock framework is composed of two main types of grains. The less common grains (about 15%) are represented by quartz and feldspar detritus grains, which show a wide degree of roundness and vary from sub-rounded to angular and display normal to wavy extinction under the crossed nicol. The more common grains (about 60%) are represented by the grass green glaucony grains, their sizes vary from silt to medium sand size and display various forms, which vary from well rounded to irregular elongate grains. Both types of grains are cemented by argillaceous material of brownish staining.

SCANNING ELECTRON MICROSCOPY (SEM)

Gluaucony minerals are easily interpreted with the aid of scanning electron microscopy based on the shape and position of the mineral laminae. In the case of Libyan gluaucony the SEM microphotograph shows predominantly, closely packed platy and lamellar structure, which commonly characterizes illitic gluaucony, interfered with laminae of a swollen lamina creating a box work-like structure of smectite, forming about 20% of the lamellar structure (Fig. 1).

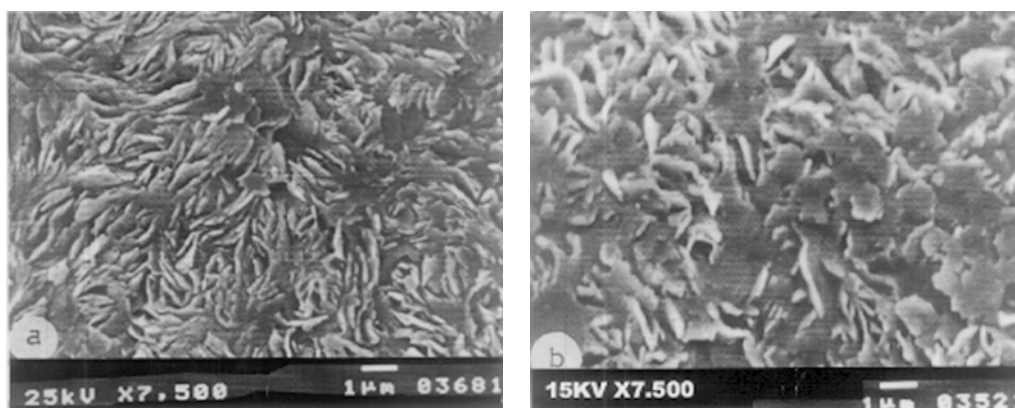


Fig.1 SEM microphotographs of a North Africa gluaucony samples (a) Libyan gluaucony, (b) Egyptian gluaucony

In the Egyptian gluaucony (EDG), the SEM microphotograph shows a relatively larger, less closely platy structure, in comparison to the Libyan type. These plates include a swollen lamellar structure of gluaucony smectite, forming < 15% of the lamellar structure (Fig.1). The infra-structure of the WDG shows similar characters to the Libyan type (Sediek, 1999).

CHEMICAL COMPOSITION

In order to discuss the chemistry of the gluaucony minerals, study the relationship between cation contents one must take in consideration the genesis of these gluaucony materials. The results of the microprobe analysis of the representative samples are given in Table 1. The obtained data show that the SiO_2 content remains fairly constant at certain level and lies between 49.66 and 54.25%. There is no a great difference of silica contents in different gluaucony samples. The silica content resembles the data of Smulikowski (1954) and Odin and Matter (1981). The contents of Al_2O_3 lie between 5.09 and 13.22%. The highest value is observed for gluaucony of the Eastern Desert while the lowest for the Libyan gluaucony. Generally, the EDG shows high contents

relatively to the other studied areas either on local or wide scale as in the works of Foster (1969) and Odin and Matter (1981). The content is high but does not reach the alumina content of Paleozoic glaucony. It means that the alumina content in glaucony deposits more or less depends on the geologic age or at least on the degree of post depositional evolution.

The results of the chemical analysis show more or less wide variation of MgO content, which is between 1.31 and 5.28%, with a relatively higher values for the Libyan type than for the Egyptian one (Table 1). Generally, the obtained results of MgO correspond well with the data given by Odin and Morton (1988). The Fe₂O₃ contents of the studied samples lie between 16.21 and 28.78%. The lowest values were detected in the WDG samples, while the highest content of Fe₂O₃ was recorded in the LG type. The obtained data for Fe₂O₃ agree well with the results of Foster (1969) and Odin (1975). Potassium is a common element in the studied glaucony sediments, and is considered as the main indicator of the behavior and evolution of glaucony. The Libyan glaucony shows high content of potassium (8.90-13.74%) while the Egyptian glaucony contains 5.06-7.40%. The presence of potassium is related to the marine origin.

Table 1. Chemical analysis of some glaucony deposits of North Africa

Sample	SiO ₂	Al ₂ O ₃	MgO	K ₂ O	CaO	TiO ₂	V ₂ O ₃	Fe ₂ O ₃	CuO	ZnO
Libyan glaucony										
L.G.1	51.01	5.09	3.49	8.90	0.00	0.00	0.00	28.78	1.35	1.39
L.G.3	49.66	5.48	4.58	13.74	0.00	0.00	0.00	24.45	1.02	1.08
L.G.5	52.00	6.36	4.99	12.00	0.00	0.00	0.00	25.24	1.04	1.04
L.G.7	52.16	6.44	5.28	12.76	0.00	0.00	0.00	20.62	1.04	1.04
Western Desert Egyptian glaucony										
Ab.1	50.04	5.18	2.03	6.24	2.13	0.09	0.00	22.39	0.00	0.00
Ab.4	44.00	6.02	3.08	5.71	2.54	0.18	0.00	25.43	0.00	0.00
T.4	54.25	6.08	2.17	5.55	1.58	0.19	0.00	16.21	0.00	0.00
T.7	51.84	5.67	2.24	5.06	1.53	0.17	0.00	18.33	0.00	0.00
Eastern Desert Egyptian glaucony										
As.1	53.02	7.97	2.51	7.40	0.71	0.09	0.02	22.34	1.13	1.78
As.2	51.63	13.22	1.31	6.78	0.66	0.19	0.00	19.85	2.16	2.00

The results of microprobe analysis shows that the CaO content varies from zero, as in Libyan glaucony to about 2.54 %, as in WDG (Table 1). There is a relationship between the CaO and K₂O content, which occur in the interlayer structure. There is an increasing content of K₂O on the expense of CaO as in Libyan glaucony and vice versa in the Egyptian one (Table 1). Other oxide such as TiO₂, V₂O₃, CuO and ZnO are invariably present in the studied glaucony. The first two oxides are present in trace content (EDG and WDG samples) or are completely absent, as in LG (Table.1). The second two oxides are also invariably present, but in a minor amounts as in LG and EDG, or are completely absent, as in WDG.

TECHNOLOGICAL STUDY

The glaucony deposits were leached for 2 hours at 125-225°C with 20 wt. % HCl and the results are plotted in Figure 2, where the potassium extraction increases with the increasing temperature and acid stoichiometry. More than 90% is extracted within 2 hours at > 150°C. Potassium extraction was 60 and 65% at 175°C and 225°C, respectively. Increasing the acid concentration to 100% of the theoretical acid requirement extracted only 70% of the potassium at 150°C. Increasing the acid available to 120% of the theoretical amount increased the extraction to 85%. Leaching time was investigated to define the minimum retention time for maximum extraction of potassium at a minimum effective temperature.

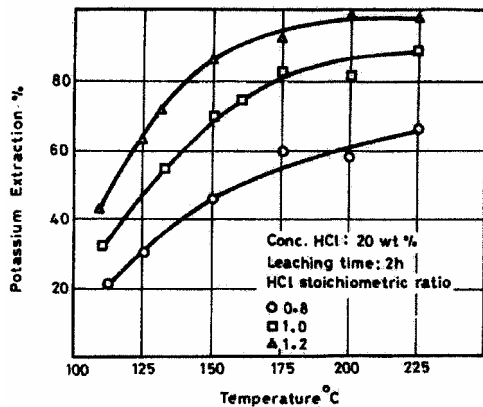


Fig. 2 Effect of temperature on potassium extraction

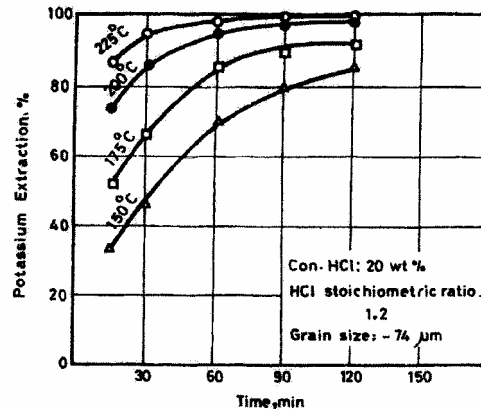


Fig. 3 Effect of leaching time on potassium extraction

The studied glaucony deposits were leached with 20% HCl at 175°C and 200°C for periods of 15 min to 2h. Experimental data are plotted in Figure 3, where more than 90% of potassium was extracted in most experiments that have leaching times of 90 min at temperature 175 to 225°C and all curves showed an increase in potassium extraction with increase in time of leaching. In experiments, which have a stoichiometric ratio equal to 1.2 or greater, about 98 to 99% of potassium was extracted within 60 min for experiments conducted with a stoichiometric ratio of 1:2. Analysis of the experimental data indicates that increasing of HCl stoichiometry from 1.00 to 1.20 is more effective in improving potassium extraction than increasing leaching temperature from 150°C to 200°C, or leaching time from 30 to 90 min (Fig. 3).

Most of the hydrochloric leaching research reported by many authors (Surana and Warren, 1969; Amer, 1994) were made with a 20 wt. % excess of 27% HCl solution. This choice was based on calculations to provide the maximum concentration of potassium chloride. Higher HCl concentrations would cause the precipitation of

KCl · 6H₂O in the leaching slurry, which would lead to blinding the filter. Lower acid concentrations, which would require evaporation using a double extraction, did not improve the filtration characteristics of the residue. From Figure 4, it can be observed that the percent of potassium extraction increases with decreasing particle size of glauconitic particles. This may be due to a better liberation of potassium in the finer sizes of glaucony as indicated in Table 2. The behavior of aluminum, silicon and iron during the hydrochloric acid leaching of glauconite is given in Table 3.

Table 2. Size –wise chemical analysis of glaucony samples

Size (µm)	Weight %	K ₂ O %
+ 180	9.66	1.99
- 180 + 150	31.37	5.31
-150 + 106	7.80	5.42
-106 + 75	15.16	5.66
-75	6.01	5.71

Table 3. Behavior of alumina, iron and silicon during HCl pressure leaching of the glaucony samples

Experiment No.	Stoichiometry	Temp. C°	Analyses						
			Pregnant liquor				Residue		
			Al ₂ O ₃	Fe ₂ O ₃	HCl	Density	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂
1	0.8	125	5.0	0.11	4.88	1.139	24.4	0.63	59.0
2	0.8	150	7.3	0.15	N.d	1.164	13.5	0.45	66.6
3	0.8	175	7.5	0.16	N.d	1.162	11.2	0.35	70.8
4	0.8	200	7.1	0.15	N.d	1.170	10.9	0.62	75.2
5	0.8	225	5.8	0.15	0.09	1.154	9.91	0.57	76.4
6	1.0	125	7.5	0.16	N.d	1.195	8.55	0.31	69.5
7	1.0	125	8.2	0.17	N.d	1.212	6.80	0.28	81.8
8	1.0	125	8.5	0.19	0.46	1.217	3.28	0.19	83.5
9	1.0	125	8.6	0.19	N.d	1.217	1.65	0.15	85.5
10	1.2	125	3.4	0.07	N.d	N.d	27.2	0.68	55.0
11	1.2	135	6.1	0.13	N.d	1.177	13.5	0.49	73.4
12	1.2	150	6.5	0.14	3.93	1.193	2.92	0.17	77.8
13	1.2	175	7.3	0.16	N.d	1.197	0.86	0.14	85.3
14	1.2	200	7.3	0.16	3.38	1.197	0.81	0.12	85.3
15	1.2	225	6.5	0.14	N.d	1.190	0.61	0.12	87.4

N.d = Not determined

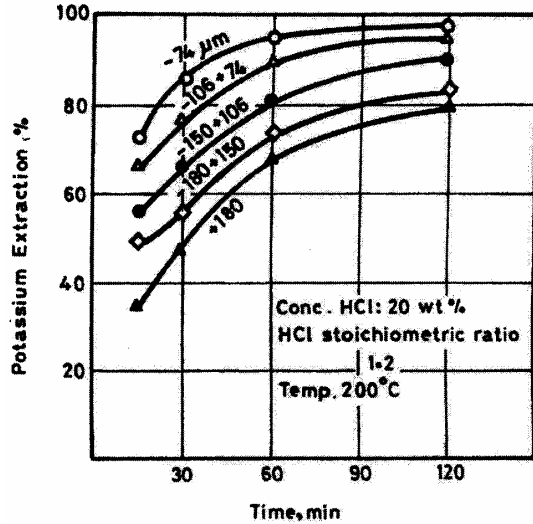
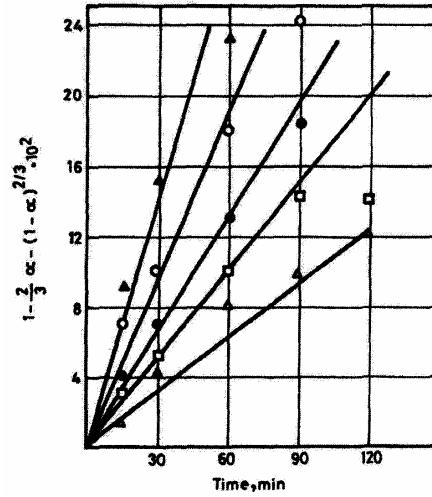


Fig. 4. Effect of particle size on potassium extraction

Fig. 5. Relation between $1 - \frac{2}{3} \alpha - (1 - \alpha)^{2/3}$ and t

KINETIC ASPECTS

The identification of the reaction mechanism constitutes an important step in the analysis of the high temperature kinetic data. For this purpose the Ginstling-Brunshstein equation has been used:

$$1 - \frac{2}{3} \alpha - (1 - \alpha)^{2/3} = Kt$$

where α is the fraction of potassium converted to potassium chloride, K the rate constant and t is the leaching time. The values of $1 - \frac{2}{3} \alpha - (1 - \alpha)^{2/3}$ have been plotted against time t as shown in Figure 5. For further confirmation of the rate-controlling step, the data presented in Figure 3 are represented using the Ginstling-Brunshstein equation, the plots are shown in Figure 5. As these plots also yielded straight lines, it is confirmed that the present process is diffusion controlled. For determination of the apparent activation lines, as shown in Figure 6, K values were plotted against $1/t$ as shown in the Arrhenius plot (Fig. 7), where the value of the calculated activation energy equals to 16.6 kJ/mol. This value agrees with the diffusion controlled mechanisms of Levenspiel (1972).

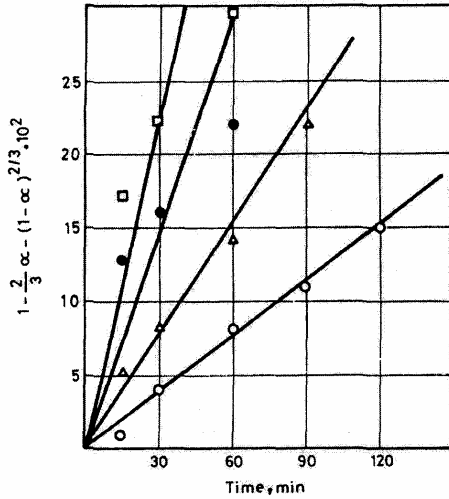


Fig.6. Ginstling- Brunshstein plot for different particle size

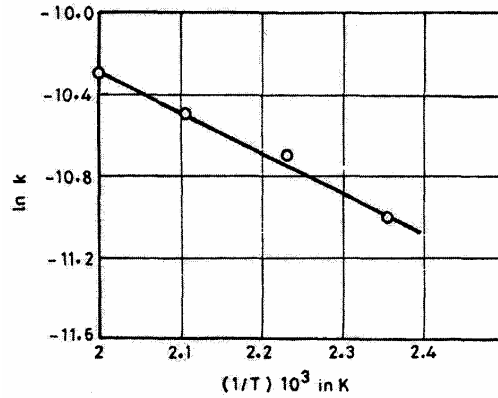


Fig.7. Arrhenius plot for determination of apparent activation energy

CONCLUSION

The studied glaucony rocks contain grains with granular faces. They form a considerable percent of the rock framework and vary from 60 to 68%. The remaining percent is represented either by detrital quartz or by carbonate grains. The results of chemical analysis proves that the glaucony pellets have high silicon, aluminum, iron oxides and considerable percent of potassium, while low percent of calcium and magnesium oxides. Other oxides as TiO_2 , V_2O_3 , CuO and ZnO are also present but in trace amounts. A direct hydrochloric acid processing of the Egyptian and Libyan glaucony deposits was carried out to produce chlorides of potassium and aluminum by a autoclave leaching as an alternative route to the roast-leach processing technique. The most favorable conditions for extraction of 95% of the potassium present in the glaucony deposits of both Egyptian and Libyan types are: temperature $200^\circ C$, acid concentration 20% by weight, grain size $-75 \mu m$, and leaching time 90 min. Calculation of the temperature dependence of the rate constant gives the activation energy of 16.6 kJ/mol, which is consistent with the values of the activation energies reported for diffusion controlled reactions.

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Badaniom poddano złoża glaukonitu znajdujące się w Egipcie i Libanie. Złoże egipskie pochodzi z okresu Dolnej Kredy, podczas gdy złoża libańskie pochodzą z Oligocenu. Skały glaukonitowe badano petrograficznie oraz analizowano ich strukturę wewnętrzną. Dodatkowo przeprowadzono badania za pomocą mikrosondy wybranych próbek glaukonitu z dwóch złóż, nie mających identycznych zawartości K₂O. Glaukonit pochodzący z Egiptu zawierał od 3,9 do 12,6% K₂O. Badane próbki glaukonitu z Libanu zawierały od 3,9 do 12,6%. Badane próbki glaukonitu zawierały taką samą ilość Fe, Al, Cu i Zn. Różnice wystąpiły w przypadku tlenków Ca, Mg i V. Bezpośrednie kwasne ługowanie było przeprowadzone w warunkach laboratoryjnych. Badania nad ługowaniem zostały przeprowadzone jako alternatywna metoda ekstrakcji potasu. Badano wpływ temperatury, stężenia kwasu, czasu ługowania oraz wielkość ziaren na parametry procesu.