Contents lists available at http://qu.edu.iq

Al-Qadisiyah Journal for Engineering Sciences

Journal homepage: http://qu.edu.iq/journaleng/index.php/JQES

Effect of pure Aluminum in Reduction of Silica from Sediments in Iraqi-Tigris

Bariq A.H. Al-Qaisi [a]* and Sami. I.J. Al-Rubaiey [a]

Dept. Production Eng. & Metallurgy, University of Technology , Baghdad, Iraq

A R T I C L E I N F O

Article history:
Received 03 April 2019
Received in revised form 15 May 2019
Accepted 19 May 2019

Keywords:
Tigris River
Sediments
Pyrometallurgy
Hydrometallurgy
Silic, and silicon

A B S T R A C T

This work was carried out on sediments in the Iraqi- Tigris river within the city of Baghdad. Three locations were taken from the Tigris river. The first is at the entrance to Baghdad City (Al-Muthanna Bridge), the second is in central Baghdad (Adhamiya) and the third is at the end of Baghdad (Diyala Jisr). The specimens were taken from the banks of the Tigris river at 1.5 meters from the edge of the water and a depth of 2 meters. Sediments formed mainly from silica, with concentrations between 59 - 66%. Therefore, the study focused on extracting the pure silicon element from these sediments. The extraction process of silicon from the sediments was performed in two stages. The first is pyrometallurgy stage, in which the reduction of silica was done by mixing pure aluminum powder with sediments at different mixing ratio (1:1, 1.5:1 and 2:1) sediments/aluminum and at temperatures (900, 950 and 1000)° C. The second stage was hydrometallurgy (leaching process), this process was carried out by using different concentrations (3,4 and 5)M of sulfuric acid to obtain silicon element with purity 98. 9%. The results show that the efficiency of extraction silicon from sediments of the Tigris river is greater than (88%).

1. Introduction

The sediments are formed on the banks of the rivers and at riverbed as a result of drift of the soil with the movement of water, in addition to the effect of streams and small rivers flowing into the main river [1].
The sediments are taken from the banks of Tigris river which contain various compounds such as (SiO2, CaO, MgO, Fe2O3, TiO2, Al2O3, P2O5, and K2O) at different concentrations. The source of sediments in Tigris River come from several areas, The most important one as Anatolia Plateau in Turkey: Also Tigris tributaries continue as the source of sediments in the Tigris river in Iraqi territory such Khabur, Great zab, Little zab ,Diyala river and Adhaim River [1].

The Sediments vary in Tigris river depending on the quality of the water and affected by different pollutants and type of soil and effect of Dayala river on these sediments [2, 3, 4].
The synthesis of high purity silicon from natural substances has been performed by several researchers, using metals like Mg, Ca, Al or C as reducing agents [5,6]. Sadique [7] extracted high purity silicon (99.1% purity) from the waste of silica fume (SF). He reached to 99.1% Si by using Pyrometallurgical process .The best temperature for reduction was (750-850)°C at 2:1 mixing ratio of Mg/SF. Jehad & Jasim [8] studied the extraction of silicon with a high purity of 99% by using Iraqi starting

* *Corresponding author.*
E-mail address: kaka2013331@gmail.com (*Bariq A.H. Al-Qaisi*)

https://doi.org/10.30772/qjes.v12i1576

materials (quartzite rock, plant coal) via electric arc furnace at 1500℃ . Mishra et al. [9] produced Polycrystalline silicon from amorphous silica obtained from rice-husk white ash by using calcium at the reduction temperature equaled to 720℃ .The final purity of silicon was 99.9% after acid leaching with concentrated HNO3 and HF . Onojah, A. [10] studied the extraction of silicon from rice husk ash and natural quartz by using magnesium powder however the two sources of silica gave silicon purities in the range of 97-98%. This study focuses on extracting pure silicon element from Sediments in Iraqi-Tigris River which contain silica for percentage (59 – 66)%

2. Experimental work

2.1. Sampling preparations

The specimens were taken from three locations at Tigris river in Baghdad City. The first is at the entrance to Baghdad City (Al-Muthanna Bridge), the second is in central Baghdad (Adhamiya) and the third is at the end of Baghdad (Diyala Jisr).
The specimens were taken from the banks of the Tigris river at 1.5 m from the edge of the water and a depth of 2 m at three different locations along the Tigris River within Baghdad city. which are;

- Al Muthanna Bridge
- Al-Adhamiyah
- Jisr Diyala

The samples were taken by 10 kg from each mentioned location, in depth of 2 m. These samples were taken using steel- mold, The samples then dried at 100˚C for 4hrs. This process was achieved by using a bender oven.

2.2. Chemical analysis

Chemical analysis of the river-sediments was carried out by using X-Ray Fluorescence (XRF) at the University of Baghdad / Iraqi- German laboratory as shown in **Tables 1,2 and 3**.

Table 1. X-Ray Fluorescence (XRF) at the Al-Muthanna Bridge

Compounds	Concentration %
SiO_2	59.974
CaO	20.421
Al_2O_3	8.035
Fe_2O_3	4.94
K_2O	1.447
P_2O_5	0.702
MgO	3.255
TiO_2	0.739

Table 2. X-Ray Fluorescence (XRF) at Al-Adhamiya Location

Compounds	Concentration %
SiO_2	59.29
CaO	18.17
Al_2O_3	8.739
Fe_2O_3	5,848
K_2O	1.523
P_2O_5	0.688
MgO	3.835
TiO_2	0.752
Others	0.165

Table 3. X-Ray fluorescence (XRF) at Jisr Diyala Location

Compounds	Concentration%
SiO_2	**66.007**
CaO	**16.26**
Al_2O_3	**7.70**
Fe_2O_3	**4.24**
K_2O	**1.400**
P_2O_5	**0.702**
MgO	**2.54**
TiO_2	**0.662**
Other	**0.078**

2.3. Grinding and Sieving Processes

These processes were accomplished to obtain particles with a size equal to 63 µm by using Ball mill machine for grinding time of 1hr.The speed of the ball milling was 300 rpm. Auto sieve shaker device at a specified range 53-710 µm was used for grinding process.

2.4. Washing process (primary leaching)

The samples are washing by using hydrochloric acid at 10% concentration for removal some metal oxides such as (MgO, CaO) and increases the silica ratio [11,12]. This process was done by a magnetic stirrer device for 80 ˚C at 2 hrs with a rotation speed of 500rpm and solid-liquid ratios (1-4). After each experience, the sample was filtered and dried in an oven at 100 ˚C for 2 hr. The following equations illustrate the process of dissolving some of the impurities [13,14].

$$CaO + 2HCl = CaCl_2 + H_2O \quad (1)$$

$$MgO + 2HCl = MgCl_2 + H_2O \quad (2)$$

2.5. Mixing and Pressing Processes

Different ratio of Al/Sediments were used. These ratios are (1:1, 1.5:1 , 2:1) the specimens were compressed using compression a die with a diameter of 3 cm, the applied load was 20 ton for 1 min.

2.6. Reduction Process

The reduction process was carried out in carbolite furnace (type cwf12/13, England) at temperatures 900, 950 ,1000 °C for 2 hrs, The specimens were tightly covered in steel crucible for dimensions (11 cm diameter, and 15 cm length) to full the crucible. The cover was supplied with value allow for following for argon gas flow. All specimens were tested by atomic absorption spectrometry, X-ray Diffraction Analysis test was done onetime for each reduction temperature.

2.7. Leaching process

The leaching process was done to remove impurities in the reduction process by using sulfuric acid at 3, 4 and 5 M and leaching temperature 100 °C for 4 hrs and solid to liquid ratio of 1:6 via using Heating mantle device. The insoluble residue was separated from the solution by vacuum pump using filtration paper. Then the filtered cake was washed with distilled water several times and then dried in an oven at 100 °C for 1hr.

2.8. X-ray Diffraction Analysis

To identify the formed compounds after reduction X-ray test was done on machine BRUKER. The test was accomplished under the following parameters: voltage 40 kV , current 30 mA ,1.540 A˚ and scan rate 5-10 ˚deg/min. The test was done at geological department , college of sciences, University of Baghdad.

2.9. X-ray fluorescence analysis

The purity of extracted silicon powder was tested by using X-ray fluorescence-XRF a type (AMETEK 2010 Germany). The analysis was conducted at the place mentioned above.

3. Results and discussion

3.1. Washing process (Primary leaching)

Tables 4, 5 and 6 show the increase of silica percentage in samples and decrease the percentage of other compounds after Primary leaching process according to X-ray fluorescence analysis compared with **Tables 1, 2 and 3.**

Table 4. X-Ray Fluorescence (XRF) at the Al-Muthanna Bridge location

Compounds	Concentration %
SiO_2	70.132
CaO	13.251
Al_2O_3	9.522
Fe_2O_3	2.651
K_2O	0.923
P_2O_5	0.632
MgO	1.554
TiO_2	0.519
Other	0.816

Table 5. X-Ray Fluorescence (XRF) at the Al-Adhamiyah Location

Compounds	Concentration %
SiO_2	68.241
CaO	11.216
Al_2O_3	11.631
Fe_2O_3	3.642
K_2O	0.989
P_2O_5	0.423
MgO	2.415
TiO_2	0.514
Others	0.929

Table 6. X-Ray Fluorescence (XRF) at the Jisr Diyala Location

Compounds	Concentration %
SiO_2	76.500
CaO	8.800
Al_2O_3	10.415
Fe_2O_3	2.145
K_2O	0.478
P_2O_5	0.315
MgO	0.918
TiO_2	0.211
Other	0.218

3.2. Reduction Process

The reduction process by mixing aluminum powder with sediments was carried out to obtain the silicon element from sediments in the Tigris river. The compounds present in the products at different temperature were Si and some traces like Al2O3, and Al non-react. In addition to the small amount of non-reacted silica as shown in **Tables 7, 8 and 9**.The mixing aluminum powder with silica in the reduction process, Al reacts with silica to produce directly Si element and alumina (Al2O3),because the aluminum element is more active metal than silicon, according to the following reaction(3)[12,13]. The corresponding X-Ray diffraction analysis (XRD) was shown in **Fig. 1**.

$$3SiO_2 + 4Al = 2Al_2O_3 + 3Si \qquad (3)$$

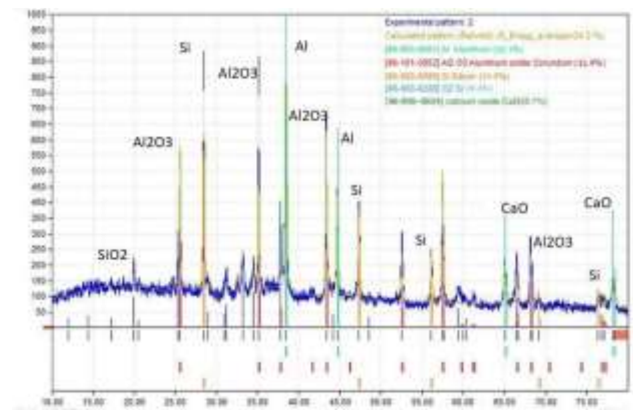

Figure 1. XRD pattern of reduction products at 1000˚C and ratio of Al/sediments 1:1

Table 7. Effect of Al/sediments ratio in reduction process at different temperature at the Al Muthanna Bridge location

Al/Sediments	Temperature C˚	Si %	SiO_2%	Al %	Al_2O_3 %	CaO %	Others %
1:1	900	18.2	0.9	32.5	42.2	5.3	0.9
1:1	950	20.9	0.7	31.5	40.2	6.1	0.6
1:1	1000	24.8	0.4	38.1	32.9	3.1	0.7
1.5:1	900	13.5	2.7	32.05	43.5	7.3	0.9
1.5:1	950	14.9	1.5	35.9	44.1	7.1	1.1
1.5:1	1000	16.1	1.2	30.6	43.1	6.8	2.2
2:1	900	11.2	3.2	34.4	40.2	9.2	1.8
2:1	950	13.4	2.7	33.1	41.8	7.8	1.2
2:1	1000	13.7	1.7	40.5	38.1	5.4	0.6

Table 8. Effect of Al/sediments ratio in reduction process at different temperature at the Al-Adhamiyah Location

Al/Sediments	Temperatue C˚	Si %	SiO %	Al %	Al_2O_3 %	CaO %	Other%
1:1	900	20.7	1.2	31.2	41.9	4.1	0.9
1:1	950	22.1	0.8	35.6	38.5	2.4	0.6
1:1	1000	25.3	1.9	29.1	38.9	3.8	1
1.5:1	900	16.4	1.6	38.3	39.6	3.2	0.9
1.5:1	950	14.8	1.5	32.6	46.8	2.7	1.6
1.5:1	1000	18.2	0.9	35.1	40.3	4.1	1.4
2:1	900	14.1	2.7	35.3	37.6	7.9	2.4
2:1	950	15.3	2.9	38.1	40.1	3.1	0.5
2:1	1000	15.6	2.4	37.4	38.2	4.9	1.5

Table 9. Effect of Al/sediments ratio in reduction process at different temperature at the Jisr Diyala Location

Al/Sediment	Temperature C˚	Si %	SiO_2 %	Al %	Al_2O_3 %	CaO %	Other %
1:1	900	19.6	1.6	35.3	36.1	5.5	1.9
1:1	950	23.4	1.2	33.4	32.6	6.8	2.6
1:1	1000	26.1	2.4	26.9	36.8	6.1	1.7
1.5:1	900	15.1	2.1	31.2	40.6	8.2	2.9
1.5:1	950	16.8	1.5	35.7	37.8	6.5	1.7
1.5:1	1000	17.2	1.1	30.3	43.7	6.4	1.3
2:1	900	12.5	1.8	31.1	43.5	8.3	2.8
2:1	950	13.7	0.8	35.9	46.9	9.2	1.8
2:1	1000	13.5	1.3	36.4	39.5	7.9	1.4

A. Effect of Al/sediments ratio in the reduction process at different temperature:

Tables 7 , 8 and 9 show the amount of Al powder added to sediments at referent mixing ratio 2:1 , 1.5:1 and 1:1 and different temperature 900, 950, 1000 ˚C. **The Tables sh**ow that the amount of Al addition have a large effect on the reduction of silica Located in sediments. It had been shown that at 1000 ˚C using ratio 1:1 Al/Sediments, Si appears very high amount in three locations (24.8, 25.3, and 26.1) %, whereas at 1000 ˚C ratio with a 2:1 appears small amount in three locations (13.7, 15.6, and 13.5)%. As a result of atomic absorption spectrometry and XRD analysis the percentage of extracted Silicon increase when mixing ratio decrease into 1:1 at constant temperature 1000 ˚C [7, 15].

Sadique[7]:explain when mixing aluminum or magnesium powder with silica in the reduction process , Al or Mg can react with Silica to produce Si element and alumina compound (Al2O3), because these elements are more active metal than silicon in ellingham diagram (ΔG of aluminum or magnesium ≥ ΔG of silicon). Sadique extracted high purity silicon (99.1% purity) from the waste of silica fume (SF) by using magnesium element to reduction of silica (SiO2).

Figure (2) shows Si content as a function of Al/sediments. The maximum amount of Si is achieved at mixing ratio1:1. While the Si yield decreases at mixing ratio 2:1 because of non-reaction all silica (SiO2) with Al powder.

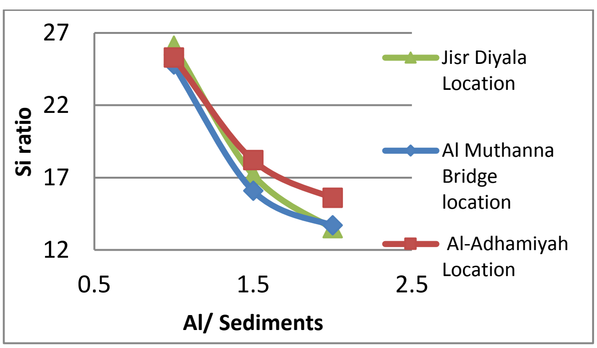

Figure 2. Shows the effect of Al/sediments ratio on the silicon yield at three different locations.

B. Effect of temperature in the reduction process:

As shown in **Tables 7, 8, and 9** that the effect of the temperature on the reduction process of SiO2 at a constant ratio of Al/SiO2 (1:1). According to atomic absorption spectrometry and XRD analysis at 900˚C appears silicon amount in three locations (19.6, 20.7, and 19.6). Whereas at high temperature of 1000˚C the silicon amount increases (24.8, 25.3, and 26.1). As a result of atomic absorption spectrometer, the amount of Si increases when the temperature increases into 1000˚C at constant mixing ratio (1:1)[7].

Figure 3. shows Si content as a function of temperature. The maximum amount of Si is achieved 1000 ˚C .While the Si yield decrease at 900 ˚C

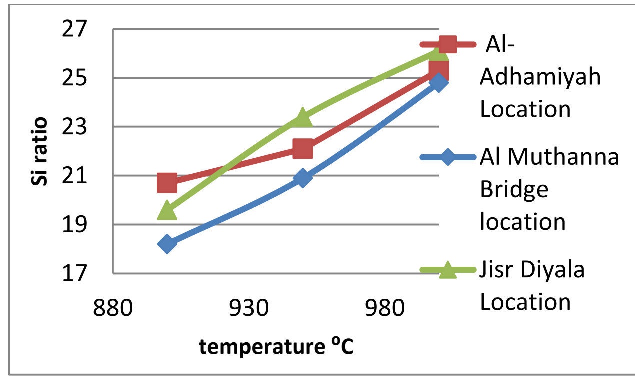

Figure 3. Shows the effect of temperature on silicon percentage at three different locations.

3.3. Evaluation of silicon amount production

The extraction of silicon process was evaluated since the main purpose of the reduction experiments is to achieve the highest amount of Si with high purity. The best condition for this process to obtain the maximum amount of Si 26.1 % with high purity 98.9% is achieved at the Al/sediments ratio of 1:1 at 1000℃.

3.4. Hydrometallurgical Process

Hydrometallurgy (leaching process) is a method for obtaining metals from their ores via using different solutions. the Pyrometallurgical process for extraction of silicon which was made at different conditions led to the production of various compounds in the reduction process such Al2O3. For the purification of the Produced silicon, the leaching processes were used. Table (10) shows the purification of silicon produced an effect of sulfuric acid on dissolving impurities in the samples and figure (4) shows the EDX spectra of the silicon powder. Angus L. Daniels [16] and Paween Numluk [17] explained that the aluminum oxide (alumina) react with sulfuric acid at different concentration (3–5)M and forming aluminum sulfate according to following equation(5) at 100 ˚C for 4 hrs, The efficiency of silicon extracted from sediments of Tigris river is greater than (88%).

$$Al_2\, O_3H_2O + 3H_2SO_4 = Al_2(SO_4)_3 + 6H_2O \qquad (4)$$

Table 10. XRF analysis of purification of silicon when temperature =100°C, and time=4hHr

Samples	Concentration M	Si%	SiO_2%	Al_2O_3%
Al-Muthanna Bridge	3	95.98	0.3	3.72
	4	98.9	0.3	0.8
	5	93.24	0.4	6.36
Adhamiyah	3	96.43	1.4	2.17
	4	98.4	1.5	0.1
	5	92.76	1.8	5.44
Jisr Diyala	3	96.92	2	1.08
	4	97.3	1.9	0.8
	5	93.65	2.1	4.25

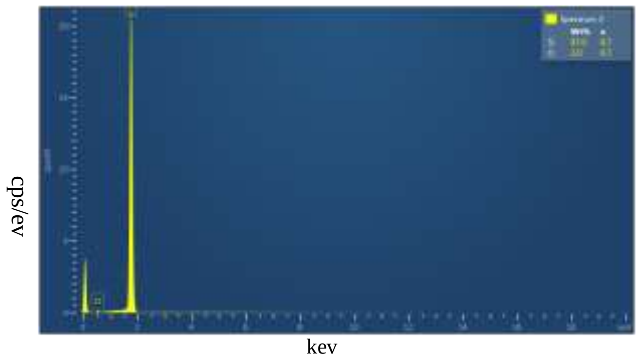

Figure 4. EDX spectra of the as-produced silicon

The SEM micrograph of the silicon powder as shown in **Fig. 5**. and it can be seen that the shape of particles is random and different size for 4 hrs of leaching time, 100 °C of temperature and (4M) concentration of sulfuric acid.

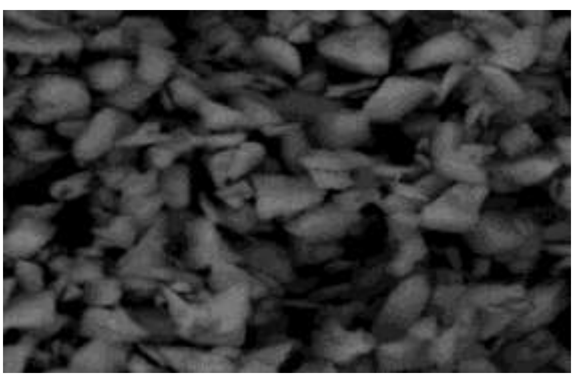

Figure 5. The SEM micrograph of as-produced silicon

The particle size distributions of silicon powder can be seen in **Fig. 6.** shows that approximately 90 %volume of the produced silicon is ≤ 66 µm, 50% of the produced silicon volume ≤ 22µm and 10% volume of the produced silicon is ≤ 5µm.

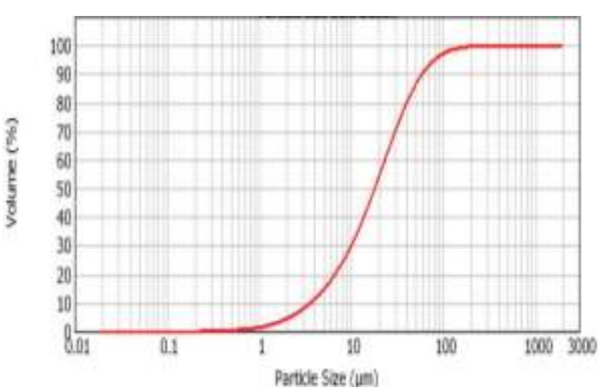

Figure 6. The particle size distribution of as-produced silicon

4. Conclusions

- Pure silicon (98,9%) has been successfully produced from sediments of Tigris river by pyrometallurgy and hydrometallurgy processes
- The reduction process was carried out with attrition of aluminum powder (63 µm particle size) at different ratio (2;1, 1.5;1 and 1;1) the best results obtained at ratio 1;1. The effect of Al powder is to decrease the reduction temperature of silica
- The leaching process carried out by using 4M H2SO4 to remove impurities such (Al2O3).
- The best reduction temperature was found at (1:1) mixing ratio of Al/Sediments was 1000˚C .
- The efficiency of silicon extracted from sediments of Tigris river is greater than (88%)

References

[1] Al-Bassam, K.S. and Al-Mukhtar, L.E.,. Heavy minerals in sediments of the Euphrates River. Iraqi Bulletin of geology and mining, 4(1) (2008) p. 29 – 41.

[2] Abdul-Hameed M. J. Al-Obaidy, Zahraa Zahraw Al-Janabi, Abdul-Rahman Al- Kubaisi, Distribution of Some Heavy Metals in Tigris River middle of Iraq, 11(2) (2014).

[3] Luma abdalalah skben Al-abadi, The relative distribution of mica minerals in sand fractions and different soil depths, Al-Qadisiyah Journal for Engineering Sciences, 14(4) (2008) p1-9.

[4] Philip, G., Mineralogy of Recent sediments of Tigris and Euphrates River and some older detrital deposits Jour. Sed. Pet. 38 (1968) p. 35 – 44.

[5] Nazma and M. Akhter, X–Ray diffraction analysis of silicon prepared from rice husk ash, J. Mater. Sci. 23, 23792381 (1998).

[6] L. P. Hunt, J. P. Dismukes, J. A. Amick, A. Schei and K. Larsen, Rice hulls as a raw material for producing silicon, Journal of the Electrochemical Society, 131 (1984) P.1683-1686.

[7] S. Elius Sadique , Production and Purification of Silicon by Magnesiothermic Reduction of Silica Fume, Copyright by Sarder Elius Sadique, (2010).

[8] Jehad. Abed Taies & Jasim H. Hassen, Production of Silicon Metal From Iraqi Sand ,journal of Baghdad for science , 11(1) (2014).

[9] Mishra P., Chakraverty A. and Banerjee H.D. Production and purification of silicon by calcium reduction of rice-husk white ash. Journal of Materials Science, 20 (1985) P.4387-4391.

[10] Onojah, A., Amah, A. N. and Ayomanor, B. O, Comparative studies of silicon from rice husk ash and natural quartz, American Journal of Scientific and Industrial Research, 3(3) (2012) p.146 -149.

[11] Daroon H. Khorsheed , Abbas R. Ali , Heavy Minerals Distribution in the Recent Stream Sediments of Diyala River Basin/ Northeastern IRAQ, Kirkuk University Journal /Scientific Studies, 10(4) (2015) p.415-438

[12] Abdul Salam Mehdi Salih, Study of morphological aspects and variation of clay minerals in the recent alluvial sediments of Tigres River in Sharqat area, Tikrit Journal of Pure Science, 15(1) (2009).

[13] Lide ،David. CRC Handbook of Chemistry and Physics, (2000).

[14] Perry ،R.؛ Green D.؛ Maloney J. Perry's Chemical Engineers' Handbook, (1984).

[15] Takeshi Okutami., Utilization of Silica in Rice Hulls as Raw Materials for Silicon Semiconductors , Journal of Metals, Materials and Minerals, 19 (2) (2009) pp.51-59.

[16] Angus L. Daniels, Edison Muzenda, Recovery of Aluminium Oxide from Flint Clay through H2SO4 Leaching, Proceedings of the World Congress on Engineering, 3 (2012) p1-3, 3p.

[17] Paweena Numluk and Aphiruk Chaisena, Sulfuric Acid and Ammonium Sulfate Leaching of Alumina from Lampang Clay, E-Journal of Chemistry, 9(3) (2012) p. 1364-1372