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Reduction of Iraqi Sand to Produce Silicon with High Purity

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Abstract

This study deals with extraction of silicon from Iraqi sand. The sand was supplied by State Company for Mining Industries from Um-Erdhuma Formation in Anbar Province. It is found that Iraqi sand has 98% of silica (SiO_2).Pyrometallurgy and hydrometallurgy processes were applied for extraction of silicon by reduction and leaching respectively. Reduction was carried out in an alumina crucible by using magnesium powder with particle size of 75µm as reducing agent under argon gas. Several parameters were studied to determine the best results that affected the extraction of silicon. These parameters involved the reduction temperatures (750,850,950)℃ and ratio of Mg/SiO_2 (2:1, 2.5:1, 3:1).The best conditions for the reduction of Iraqi sand to produce silicon were, at 850℃, 2:1 Mg/SiO_2 with 99.3% purity and at 950℃, 3:1 Mg/SiO_2 with 99.2 %purity. Leaching processes were done for purification of produced silicon by using 4:1 volume ratio of 4M HCl and 4M CH_3COOH respectively for one hour at 70℃. Additional purification step was done by using H_2SO_4 acid, which was diluted by 1:4 ratio for three hours at 100℃.

Keywords: Iraqi sand, magnesiothermic reduction, silicon, acid leaching.

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1-Introduction

The Iraqi sand is characterized by a high percentage of SiO_2 and other elements exist in [1]. 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 [6][7]. jehad &jasim[2]study the extraction of silicon with high purity of 99% by using Iraqi starting materials

(Quartzite rock, plant coal) in electric arc furnace at 1500℃ . Mishra et al. [3] produced Polycrystalline silicon from amorphous silica obtained from rice-husk white ash by using calcium, the reduction temperature 720℃. The final purity of silicon was 99.9% after acid leaching with concentrated HNO3 and HF. Sadique [4] extracted high purity silicon (99.1% purity) from waste of silica fume (SF). He reached to 99.1% Si by using Pyrometallurgical process .The best temperature for reduction were (750-850) °C at 2:1 mixing ratio of Mg/SF. Al Mubarok et al.[5] produced Silicon from high purity silica obtained from Lapindo mud . It was found that the Pyrometallurgical process at 650 °C for 3 hours get high purity of silicon (98%) when the ratio of Mg/SiO_2 was 5/6.2. The product was treated with HCl: CH3COOH solutions followed with HF:CH3COOH solutions. Reduction by magnesium is more suitable due to [8]:

(a) Its simplicity and low temperature conditions.

(b)The supply of reasonably pure magnesium is assured, since it is the eighth most abundant material in the Earth's crust.

(c)Reaction products other than silicon can easily be removed by acid leaching.

The aim of this work is to produce high purity silicon from Iraqi sand by using Pyrometallurgy and hydrometallurgy processes.

2-Materials and methods

2-1The silica sand sample was supplied by state company for mining industry from Um-Erdhuma Formation in Anbar Province / Western Iraq. The chemical analysis of the elements was carried out by using X-ray fluorescence-XRF as shown on Table (1).

2-2Magnesium powder the powder of Mg was bought from Iraqi market (Thomas baker) with minimum assay 98.5% with particle size 75um is used as reducing agent.

2-3Mixing and pressing processes different ratios of Mg/SiO_2 (2:1, 2.5:1, 3:1) were mixed for 1 minute manually. The specimens were poured into the compression die having a bore diameter of 3 cm in predetermined amounts and pressed under20 tons for 1 minute.

Table (1): Chemical composition of the silica sand.

SiO2	98%
Al2O3	0.6
Fe2O3	0.05
SO3	0.04
TiO2	0.09
CaO	0.3
P2O5	0.6

2-4 Reduction Process the reduction process was carried out in Carbolite furnace (type CWF12/13, England, max.

temp 1200℃) under inert gas argon with different temperatures (750,850,950)℃ for 2 hours. The specimen put in steel crucible (11cm diameter, 15 cm length) which covers tightly. The cover was open from the middle to insert the tube of steel for argon gas flow. After that the products were taken for XRD analysis.

2-5 Leaching Processes the leaching processes were done to remove impurities in the reduction product. The first leaching step was done by using 4M HCl and 25% CH_3COOH at 70℃ for 1 hour using magnetic stirrer. The insoluble residue separated from solution by vacuum pump using filter paper. After completion of the filtration, the filter cake was washed with distilled water for several times and then dried in an electric drying Oven at 100 °C for two hour. The filtrate ($MgCl_2$) can be used as liquid for its benefits or can be recycled to recover magnesium again. Additional purification step was done with H2SO4 for 3 h at 100℃, acid dilution ratio 1:4.

2-6 X-ray diffraction analysis

It was done for the identification of the compounds of the reduction product was made by X-ray diffraction (XRD) analysis type (BRUKER), voltage 30kv, current 10MA, χ Cu 1.540A˚, Scan rate (speed) 5-10˚ Min. The test was done at Geological Department, College of Sciences, University of Baghdad.

2-7 X-Ray fluorescence analysis

The purity of silicon powder was carried out by using X-ray fluorescence-XRF (AMETEK 2010, Germany). The analysis was conducted at Geological Department, College of Sciences, University of Baghdad.

3- Results and discussion

3-1 Reduction Reaction

The reduction reaction was carried out in closed steel crucible. Atypical product is shown in Fig (1) and The corresponding X-ray diffractogram in Fig (2) . There are several compounds appear in the reduction products, at (750,850)°C the product have following compounds: silicon, MgO and Mg_2Si whereas at 950°C are silicon ,MgO and $MgSiO_3$ **.**The sharp and high intensity of MgO and Si peaks indicate that those two are the major phases under the experimental conditions. The following solid/gas reactions might have occurred [9]:

$$SiO_2(s) + 4Mg(g) = 2MgO(s) + Mg_2Si(s) \quad (1)$$

$$Mg_2Si(s) + SiO_2(s) = 2MgO(s) + 2Si(s) \quad (2)$$

Banerjee et al.[8] and Kondoh et al.[10] reported in Differential temperature analysis that onset temperature containing Mg and silica powder was approximately 493-540°C well below the melting point of Mg. These results suggested that the reactions take place in solid state.

Figure (1) Example of reduced product

3-2 Effect of Addition Magnesium Powder

Table (2) shows the Mg powder added to silica in different ratios as 2:1, 2.5:1, 3:1. As seen from table (2) the amount of Mg addition have large effect on the reduction of silica. It had been shown that at 750℃ using ratio of 3:1 Mg/SiO_2, Mg2Si appears with very high amount (26%), whereas at 2:1 ratio, appears with small amount (12.7%). At 850℃ when the ratio is 3:1 Mg/SiO_2 the amount of Mg2Si is (9%) whereas at 2:1 Mg/SiO_2 decrease to about (0.1%).As a result of XRD the intensity of Si peaks increases as the ratio decreases to about 2:1 . Kalem [9] explain that by increasing Mg

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content in the batch excess Mg reacts with Si to produce Mg2Si according to following equation.

Si(s) + 2Mg (g) = Mg2Si(s) (3)

Dvorina at el. [11] found that Mg2Si causes violent reactions upon contact with HCl. So the product of Mg2Si at high amount is undesirable because it react to form silane gas (SiH_4) which cause losses in Si element. The $MgSiO_3$ compound appears with minimum amount (4.2 %) at 3:1 ratio while it is increased to about (6.5%) at 2:1 ratio.

Figure (3) and (4) show the relationship between formations of Mg2Si and $MgSiO_3$ with Mg/SiO_2 ratios, Indicates that at ratio of 2:1 produced Mg2Si with least amount and 3:1 ratio produced $MgSiO_3$ with least amount.

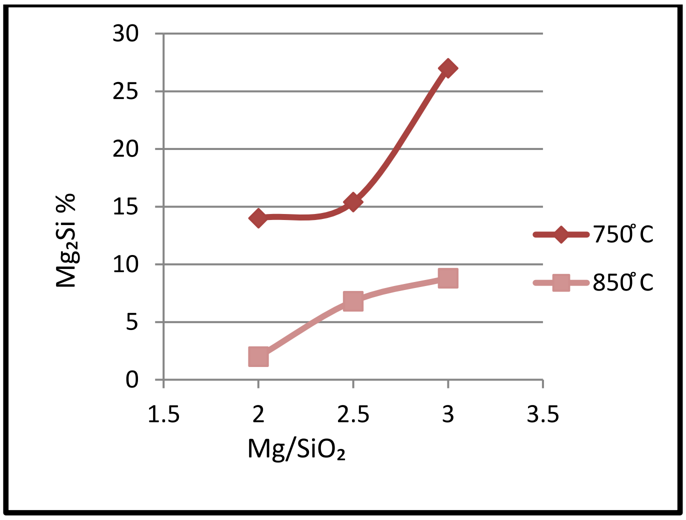

Figure (3) effect of Mg/SiO_2 ratio on Mg2Si.

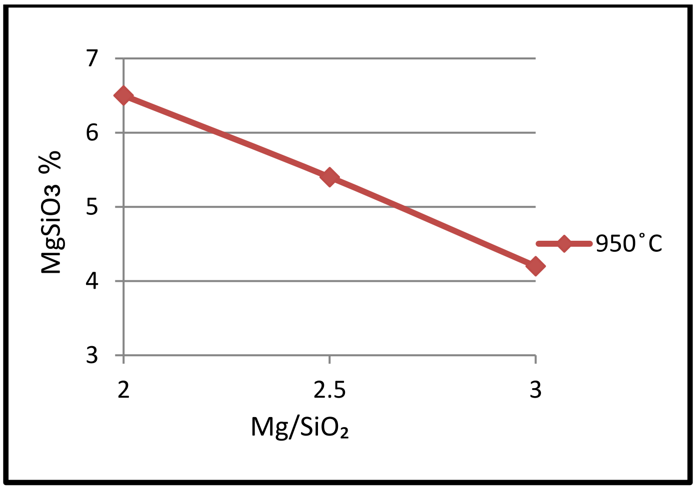

Figure (4) effect of Mg/SiO2 ratio on MgSiO3.

3-3 Effect of Temperatures

Table (2) shows the effect of reduction temperature on the reduction reaction of SiO_2 at constant ratio of Mg/SiO_2. According to XRD at higher temperatures of 850°C and 950°C, peak of Mg2Si decreased. Sadique [4] explain that at high temperature Mg2Si content will decrease. However, at temperature of 950°C $MgSiO_3$ produced. Banerjee at el. [8] explained that When temperature increase the formation of $MgSiO_3$ increase according to reaction (4). Figure (5) represents the effect of temperature on Mg2Si compound at different ratios. As described previously, the formation of Mg2Si at 750°C significantly increased at higher Mg/SiO_2 ratio. Comparing the results of 750°C with that of 850°C and 950°C (Table2). At 3:1 ratio of Mg/SiO_2 the amount of Mg2Si decreased from 26% at 750°C to 0% at 950°C. While at 2.5:1 ratio of Mg/SiO_2 the amount of Mg2Si decreased from 17 % at 750°C to 4% at 850°C.

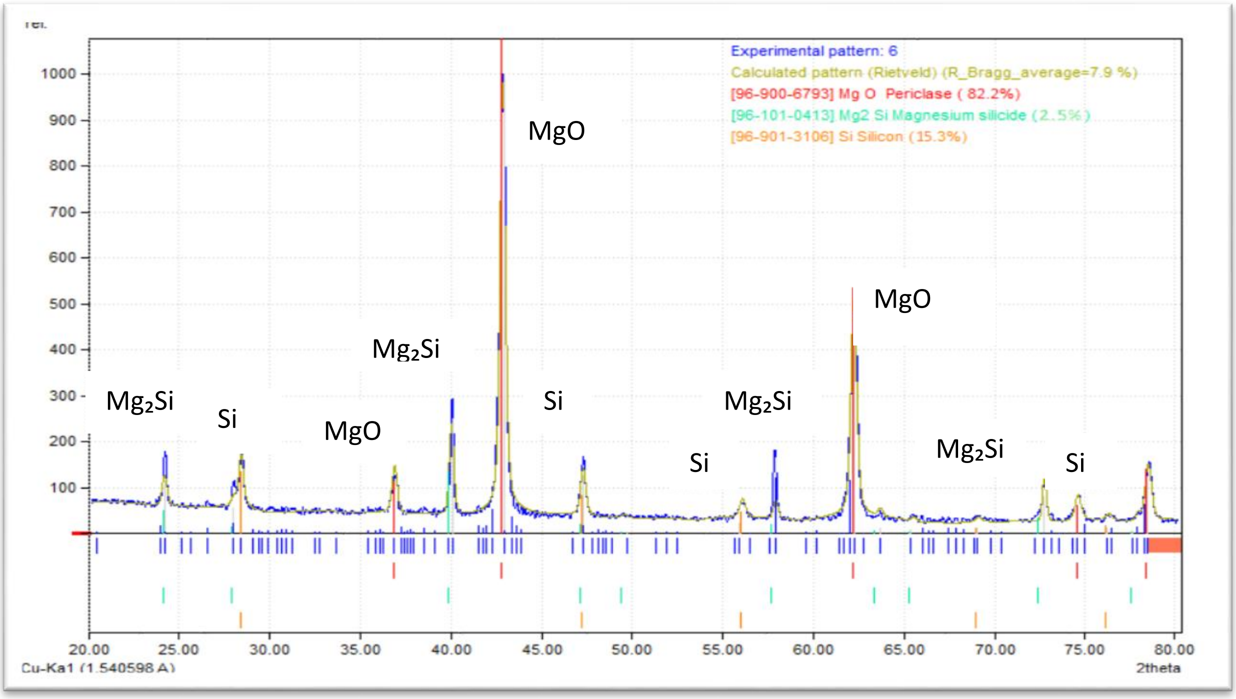

Figure (2) XRD pattern of reduction products at 850°C and ratio of Mg/SiO_2 = 2:1.

Table (2) quantification of XRD for experimental variables for reduction.

Mg/SiO_2	Temp, ̊C	Si % average	MgO%	SiO_2%	Mg_2Si%	$MgSiO_3$
2:1	750	9.6	72.3	5.2	12.7	-
	850	16.2	79.7	4.9	0.1	-
	950	14.9	74.8	3.6	-	6.5
2.5:1	750	6.4	75.9	0.6	17	-
	850	15.8	75.8	3.4	4.9	-
	950	15.3	77.4	0.7	-	5.4
3:1	750	6	65.8	1.1	26.9	-
	850	13.1	75.8	2.1	8.8	-
	950	16.3	78.3	1.1	-	4.2

3-4 Evaluation of Silicon Amount Production

The silicon was evaluated, since the main purpose of the reduction experiments is to achieve the highest amount of Si with high purity. Figures (6) and (7) show Si average as a function of Mg/SiO_2 ratio and temperature respectively. As seen, the maximum amount of Si is achieved at Mg/SiO_2 ratio of 2:1 at 850℃ because the less amount of Mg2Si was produced .As well at Mg/SiO_2 ratio of 3:1 at 950℃ because the less amount of MgSiO3 was produced .

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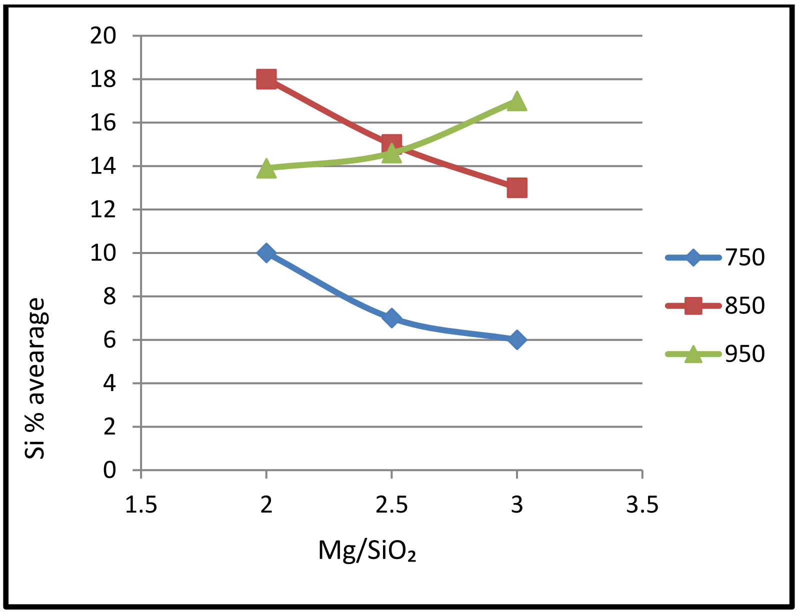

Figure (6) Effect of Mg/SiO_2 ratio on silicon average with different temperatures.

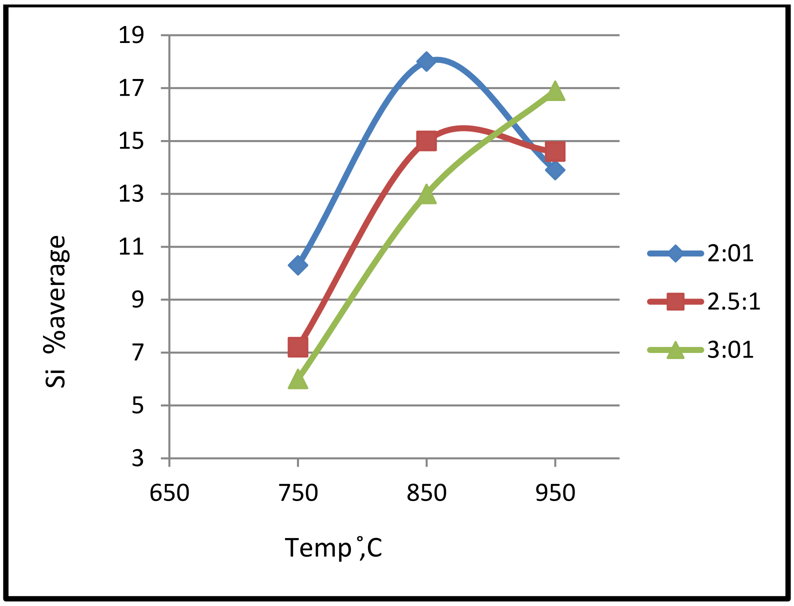

Figure (7) effect of temperatures on silicon average with different Mg/SiO_2 ratio.

3-5 Leaching of Mg Compounds

The leaching process of MgO, $MgSiO_3$ and Mg_2Si was done by treatment with 4MHCl and 25% acetic acid solutions at 70℃ for 1 hour. Nandi et.al [12] proved that Magnesium silicide (Mg_2Si) reacts with HCl solution and produces silane gas as shown in equation (5). Raschman [13] had been proved that MgO is readily dissolved in HCl and remains in the solution as MgCl2 as shown in equation (6). From figure (8) found that MgO and Mg_2Si peaks were not observed these results proved that the complete dissolution of Mg compounds.

$$Mg_2Si(s) + 4HCl\ (aq) = SiH_{4\,(g)} + 2MgCl_2\ (aq) \quad (5)$$

$$Mg^{2+}\ (aq) + 2Cl^- = MgCl2\ (aq) \quad (6)$$

$$MgSiO3(s) + HCl\ (aq) = MgCl2\ (aq) + HSiO3\ (aq) \quad (7)$$

Additional purification step was done with sulphuric acid. The leaching conditions were a leaching time of 3 h, acid dilution ratio of 1:4, leaching temperature of about 100℃ and solid to liquid ratio of 1:6. The Chemical composition of pure silicon was done using the X-ray florescence spectrophotometer (XRF) table (3) and table (4).

Table (3) Chemical Composition of pure silicon (950℃, 3:1).

Si%	99.21
Al2O3%	0.718
Fe2O3%	0.065
CaO%	0.001
SO3%	0.005

Table (4) Chemical Composition of pure silicon (850℃, 2:1).

Si%	99.34
Al2O3%	0.591
Fe2O3%	0.051
CaO%	0.003
SO3%	0.015

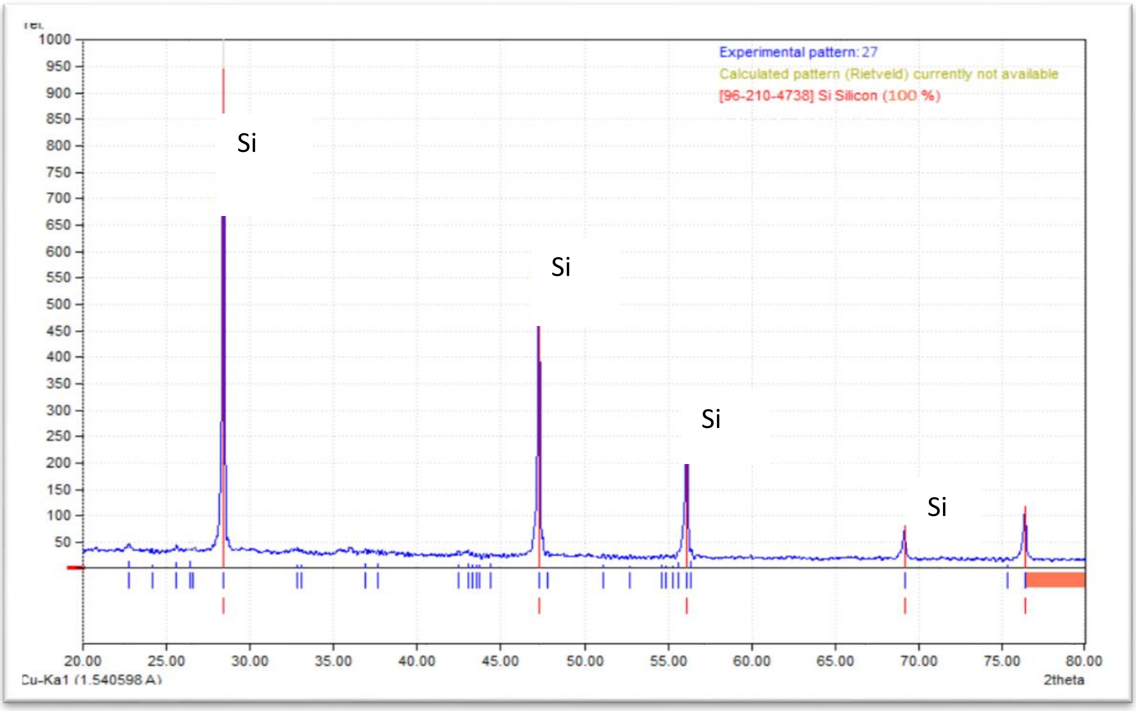

Figure (8) XRD pattern after initial leaching at 70°C for 1 hr (Mg/SiO_2 = 3:1 at 950℃).

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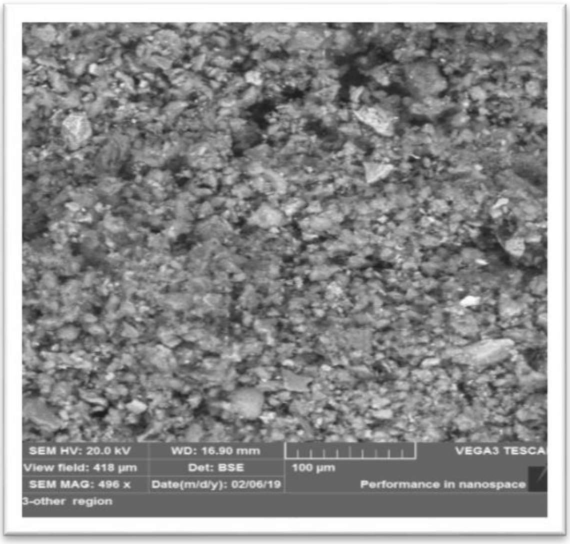

Figure (9) SEM of as produced silicon (950 , 3:1).

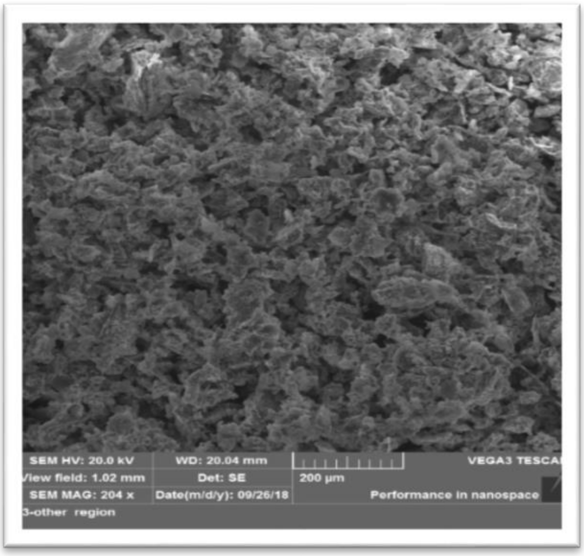

Figure (10) SEM of as produced silicon (850 , 2:1)

Figure (10) as produced silicon powder

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4- Conclusions

1- Pure Silicon has been successfully produced from Iraqi sand by using Pyrometallurgical and hydrometallurgical processes.
2- The reduction process was carried out with magnesium powder (75um particle size) as the reducing agent to decrease the reduction temperature of Iraqi sand.
3- The first leaching step 4MHCl, 25% CH3COOH carried out to remove Mg compounds.
4- Additional purification step was done with sulphuric acid to remove other impurities.
5- The best reduction conditions were found to be 2:1, 3:1 ratios of Mg/SiO_2 at (850,950)℃ with 99.3 % and 99.2% purity respectively.

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