Preparation of MGS by using Magnesium as reducing agent from Quartz deposits of Pakistan

Zaib Ullah Khan[1], Nasim Akhtar Khan[2], Ahmed Yar[3]

1. Faculty of Engineering Science and Technology (FEST), Hamdard University, Karachi, Pakistan.
2. Osmani & Company (Consultant Engineers-Architects-Planners), Karachi, Pakistan.
3. Institute of Chemical Sciences, Bahauddin Zakariya University, Multan, Pakistan.

Email: rajazaibkhan@yahoo.com[1]

Abstract

The quartz stone available in different parts of Pakistan has never been studied before as precious mineral resource for acquiring Metallurgical Grade Silicon (MGS). In this work, the quartz available at Jhangshahi, Sindh was selected to extract silicon where more than 150 MMT of proven quartz reserves are available. A detailed elemental analysis of the acquired quartz was performed which proved presence of more than 95% Silicon dioxide. This elemental analysis further strengthens the concept of MGS extraction from locally available quartz. The study involves the extraction of silica from quartz ore using magnesium element as a reducing agent. In order to validate the results of experiment, eight different experiments were performed around 950 ^{O}C and all the extracted products were characterized by using Scanning Electron Microscope-Energy Dispersive X-Ray Spectroscopy (SEM-EDS) techniques. This technique validated the presence of approximately 95% of MGS in the extracted products.

Keywords: Quartz, Silicon dioxide, Extraction process, Magnesiothermic process

1. Introduction

Due to the increasing demand of energy worldwide, a shift of energy production from conventional resources to renewable resources is seen. This shift is evident not only due to the exhaustion of conventional fuels but also attributed to hazardous effects to the environment. Today a reasonable percentage of total energy worldwide is being produced from renewable resources among which Solar energy is prominent. The increasing use of solar option for energy production is mainly because it utilizes sun radiation reaching to the earth. This sun radiation (abundantly available all over the world) is in the form of photon which is converted into electric energy through solar cell scientifically known as Photovoltaic (PV) cell [1, 2]. Today the most common material used for manufacturing of Solar cells is Silicon which is obtained by applying different extraction processes to abundantly available reserves of Quartz, Silica or Silica sand. These reserves are available in excess as hard crystalline stone in varieties of shapes in many parts of the world [3]. Moreover, this element Silicon is also being used in various high technical stuffs and electronic items as well as energy storage and conversion devices.

Today, various extractive procedures/ techniques for acquiring MGS are in use globally among which carbothermic process (using carbon as reductant) is the most common. This carbothermic process requires high temperature furnace which is suitable for mass production of MGS [4, 5]. Various methods are in use for extraction/ purification of MGS and reported in literature [6-8]. The process of using magnesium as reducing agent with modifications was selected for this research work. The element magnesium is basically used to improve the extraction process as it was applied by Liu et al. [9] who performed this process for the synthesis of nano-Si from silicon dioxide. Similarly, Favours et al., [10] prepared nano-Si from the magnesiothermic reduction of silicon dioxide in a different process which was utilized for Li-ion batteries.

Literature review revealed that this technique of using magnesium is not common for MGS extraction despite economical (consume less energy) as compared to other processes due to following main advantages [11, 12]:

- Less resources requirement (can be performed easily at laboratory scale).
- Less energy consumption
- No production of hazardous gases during the process (more environmental friendly) [13, 14].

2. Experimental detail

The process for MGS extraction from locally available Quartz (Jhangshahi, Sindh) was performed previously through carbon reduction process in high temperature furnace with high energy cost. This process adopted during the research involved another new process using magnesium as reducing agent at laboratory scale in order to confirm the process. The complete process adopted during this research is hghlighted below.

2.1. Pre processing phase

Quartz ore from Jhangshahi, Sindh was selected as a source for obtaining Metallurgical Grade Silicon (MGS) by using Magnesium powder as reducing agent. This method can be considered more useful as compared to carbon reduction process for developing countries which are already suffering from energy crisis as it eliminates requirement of high temperature furnace as the temperature requirement during this setup is around 950 ^{o}C.

As a first step, the elemental analysis of quartz stones verified presence of 96 % of Silicon dioxide making it suitable for further processing. Figure-1 illustrates composition of different elements in Quartz stones acquired from Jhangshahi, Sindh [15-16].

2.2. Equipment and Reagents used

Following different types of equipment and reagents have been used in order to perform this extraction experiment.

- Resistance Furnace (Model - ELF11/6 B) with following specifications
    - Maximum temperature range – 1350^{O}C
    - Chamber Dimensions (H x W x D in mm) - 165 x 180 x 210
- High Strength Al clay Crucible
- Pistil and mortar

DOI: http://dx.doi.org/10.24949njes.v10i2.317

- Petri dishes, funnel, beakers, tong and Spatula
- 100 Micron Strainer (Sieve)
- Whatman Quantitative Filter Paper (Ashless, Grade - 42, Diameter-185mm) from Sigma Aldrich
- Hydrochloric Acid (36.5 - 38% Reagent Grade) from Sigma Aldrich
- Deionized Water from MilliQ
- Magnesium Turnings (Reagent Grade - 98%) from Sigma Aldrich

2.3. Procedure

The Quartz sample obtained was in the shape of hard stone which was crushed by using pistil and mortar for obtaining Quartz in powdered form. Similarly, Mg turnings obtained from local market were crushed into powder form. After that both these substances were mixed together in a ratio of 1:2 (1 part Mg and 2 parts Quartz) and dried for few hours in an oven at 100 ºC to get the homogeneous mixture. Figure-2 depicts powdered form of Quartz, Magnesium powder and homogenous mixture of quartz and magnesium.

Now, eight samples with varying quantities were taken from this homogeneous mixture to perform eight sets of experiments. All these samples were prepared carefully to ensure exact ratio by using high accuracy laboratory weight balancing machine. These eight samples were further placed into eight different Al clay crucibles which can withstand temperature range up to 2500 ºC in order to validate / authenticate the percentage of MGS in the extracted product. In first operation, two crucibles were placed inside the furnace main inner firing chamber. In this way furnace is operated four times in order to achieve eight set of end products in the shape of MGS.

After placing crucibles inside the furnace inner main operating chamber, the furnace temperature is set at 950 ºC which is the expected temperature ranges for this type of experiment. The furnace is then operated for 6 hours continuously and at the end of the experiment crucibles were removed from the furnace and placed into desiccator to bring it to the room temperature. Similar procedure is repeated for four times, thus furnace is operated four times in order to achieve eight sets of end product. At the culmination of each furnace operation, all crucibles were removed and placed into the desiccator. In the next step, all these crucibles were removed from desiccator and the extracted products were sieved one by one separately through 200 micron size sieve. In order to purify extracted products, 2 M HCl solution were prepared in eight different beakers and extracted products were left in that 2 M HCl for six hours.

At the end, these extracted silicon were filtered by using Whatman filter paper.

The element received after filtration is washed many times with deionized water to get the pure form of MGS.

2.4. Characterization

After obtaining eight samples of MGS extracted through above experiments all samples were characterized one by one by using SEM-EDS techniques at Centralized Science Laboratory, Karachi University, Pakistan. This technique renders composition of different elements in the extracted product.

3. Results and discussion

During this work, we were able to investigate a new source for obtaining MGS from specific type of quartz stone available in various parts of Pakistan. During this research work, a comparatively different technique by using magnesium as reducing agent is used which lower down high temperature requirement. Due to normal temperature requirement, the process of extracting MGS can be performed in simple electric furnace at laboratory scale. The experiment followed simple method involving reduction of silicon dioxide with magnesium (A highly reactive metal) through the exothermic process. During this exothermic process, a large amount of energy was released which is sufficient to reduce the homogenous mixture of quartz and magnesium into MGS with desired percentage of Silicon. However this e process resulted in the formation of Magnesium Oxide, small amount of Magnesium silicide and unreacted Magnesium which need to be purified. As a first step unreacted Quartz was separated from the extracted product through sieving process with 200 mesh size sieve. The hydrochloric acid solution (prepared specially with deionized water) was used to further purify the extracted MGS as HCl solution reacted with Magnesium oxide, Magnesium Silicide and left over magnesium to form Magnesium Chloride. This magnesium chloride is soluble in water along with volatile silane while hydrogen gas is evolved during the process thus left behind MGS. The eight extracted samples of MGS are then prepared to perform SEM-EDS tests in Centralize Science Laboratory, Karachi University. The magnified images through SEM results of all the eight samples are shown in figure-3. The EDS results regarding elemental composition of different elements in all the eight samples are shown in figure-4. The results of all eight extracted products are summarized in table-1 for comparative analysis which indicates presence of around 95% of MGS in all the samples which validates process used for extraction of MGS

According to the results, the Silicon presented the prominent peak however, some other minor peaks also appeared suggesting the presence of other elements like Fe, Ca, Mg, Mn, Al etc. along with silicon. However, they are in very minute percentage. Therefore, the extraction process is selective for Si which resulted in a high percentage of metal in the extracted product. EDS in this case was performed to determine the amount of silicon extracted from the quartz ore in order to calculate its percentage purity.

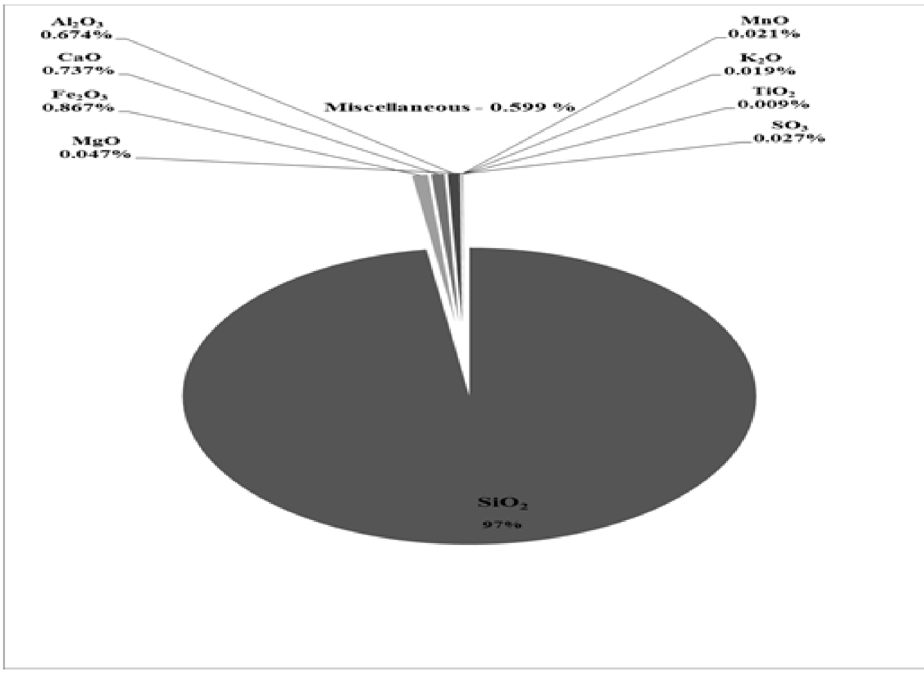


Figure-1: Elemental composition in Quartz samples of Jhangshahi, Sindh, Pakistan [16]

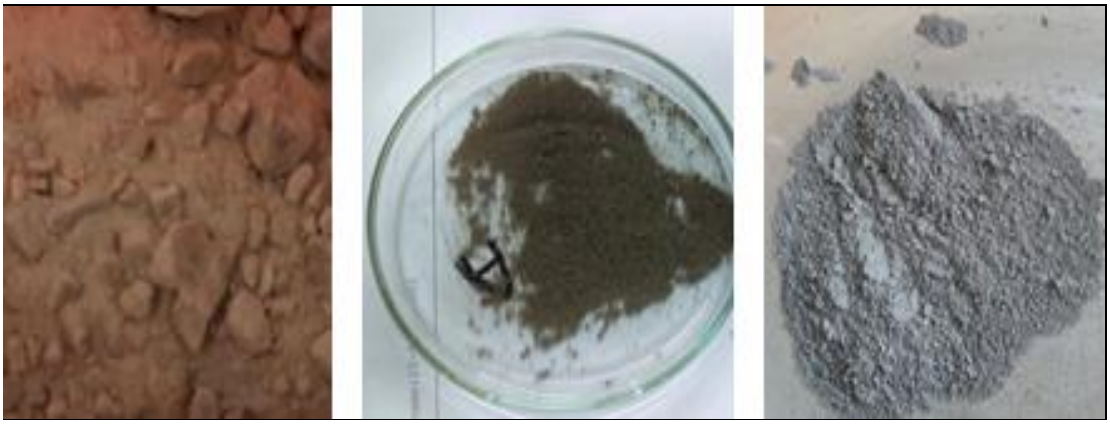
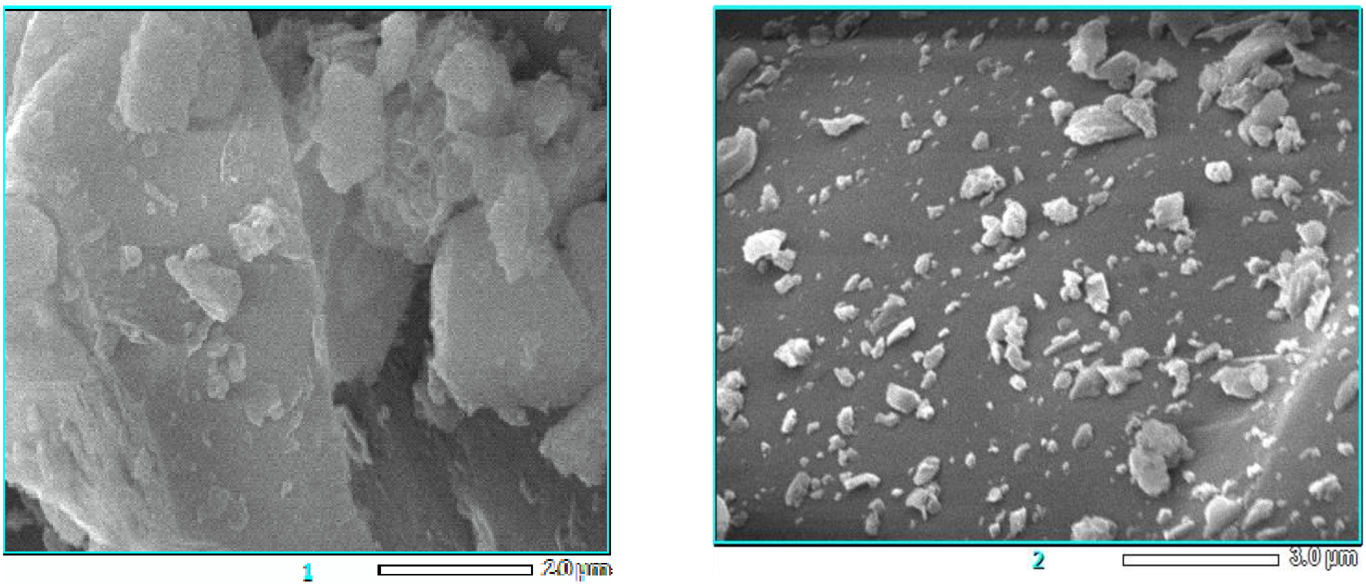


Figure-2: Powdered Quartz, Magnesium and Homogenous Mixture



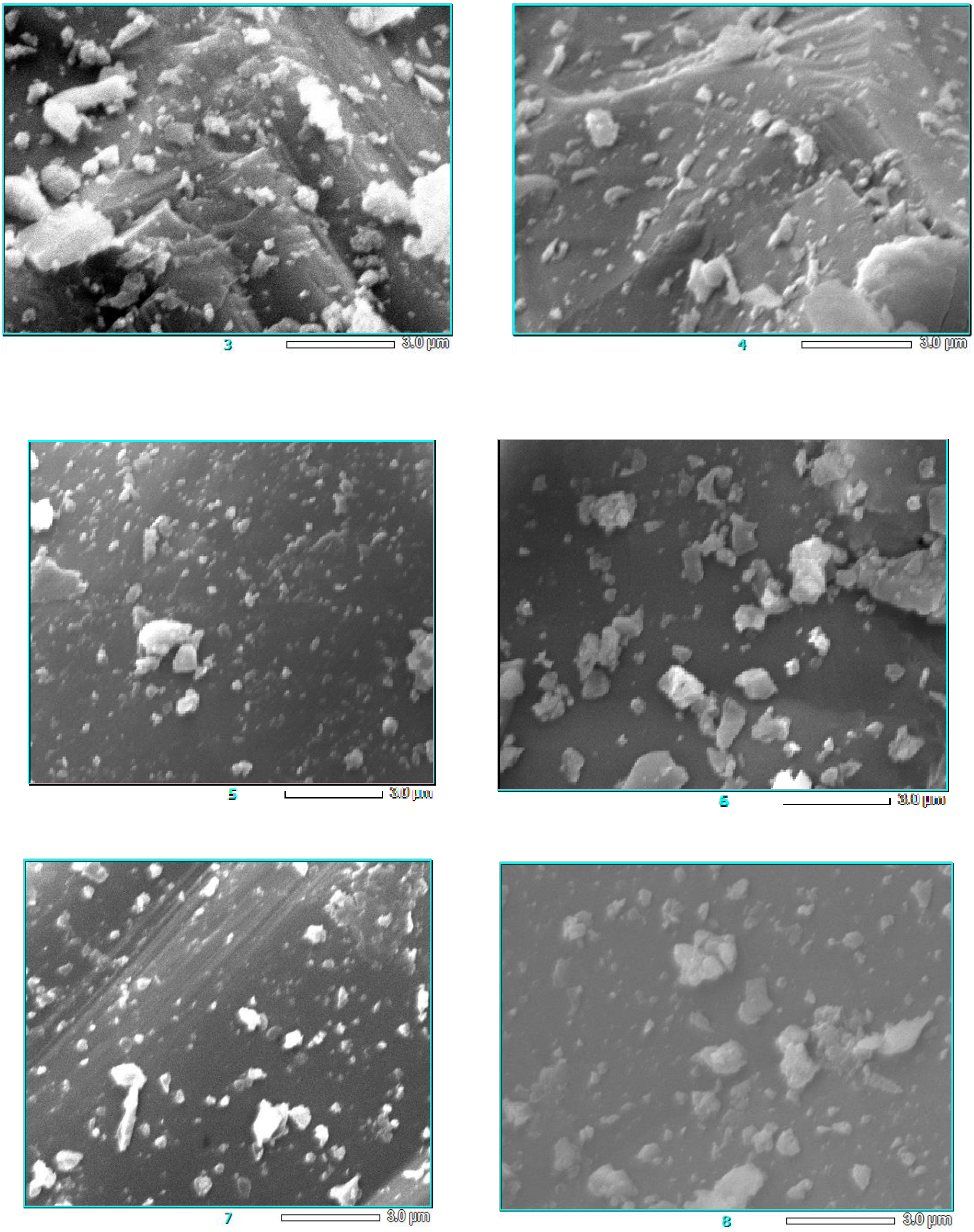
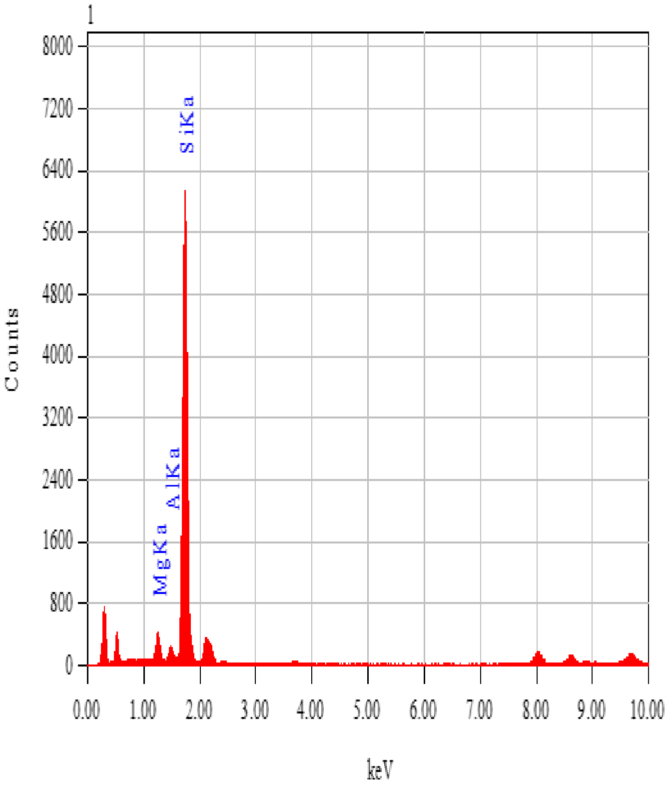
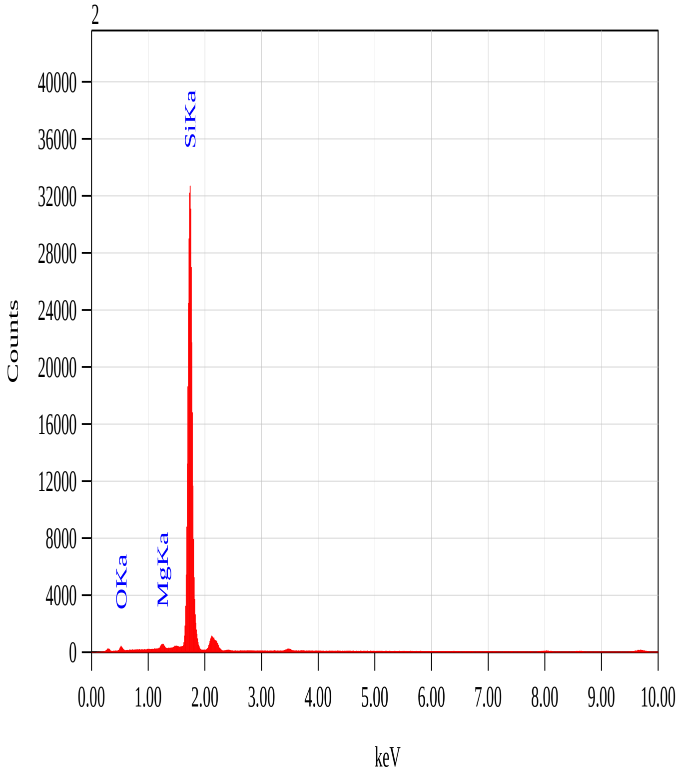
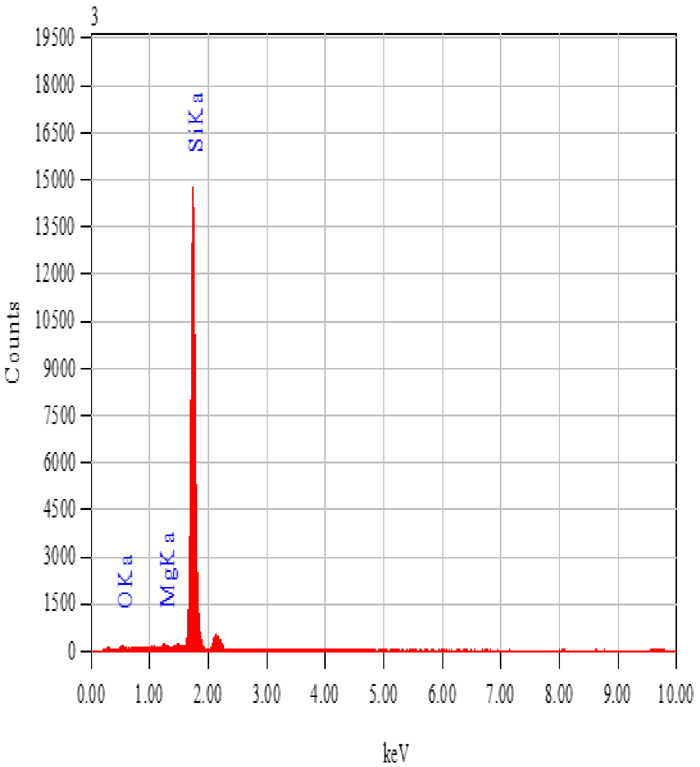
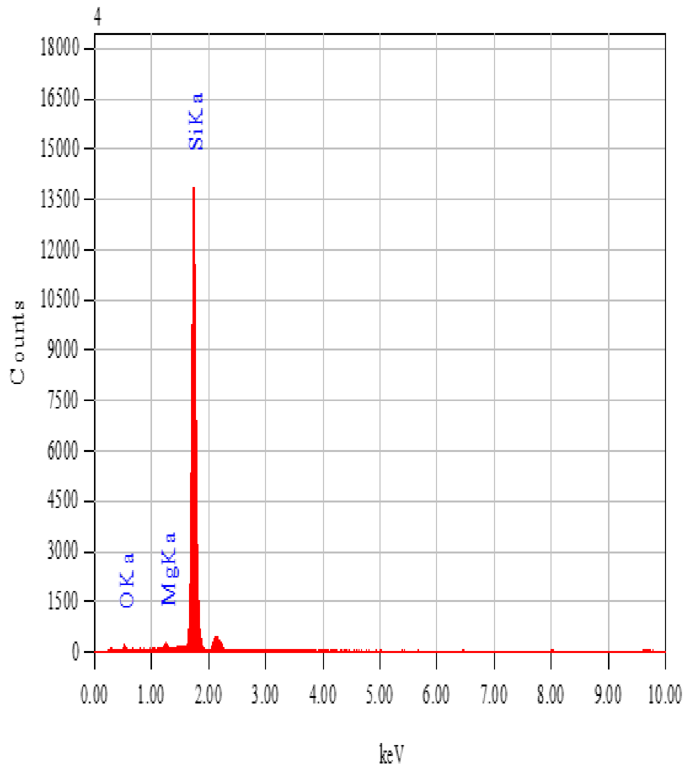


Figure-3: SEM images of extracted Si samples (1-8).


1
SiKa
AlKa
MgKa
Counts
8000
7200
6400
5600
4800
4000
3200
2400
1600
800
0
0.00 1.00 2.00 3.00 4.00 5.00 6.00 7.00 8.00 9.00 10.00
keV


2
SiKa
OKa
MgKa
Counts
40000
36000
32000
28000
24000
20000
16000
12000
8000
4000
0
0.00 1.00 2.00 3.00 4.00 5.00 6.00 7.00 8.00 9.00 10.00
keV


3
SiKa
OKa
MgKa
Counts
19500
18000
16500
15000
13500
12000
10500
9000
7500
6000
4500
3000
1500
0
0.00 1.00 2.00 3.00 4.00 5.00 6.00 7.00 8.00 9.00 10.00
keV


4
SiKa
OKa
MgKa
Counts
18000
16500
15000
13500
12000
10500
9000
7500
6000
4500
3000
1500
0
0.00 1.00 2.00 3.00 4.00 5.00 6.00 7.00 8.00 9.00 10.00
keV

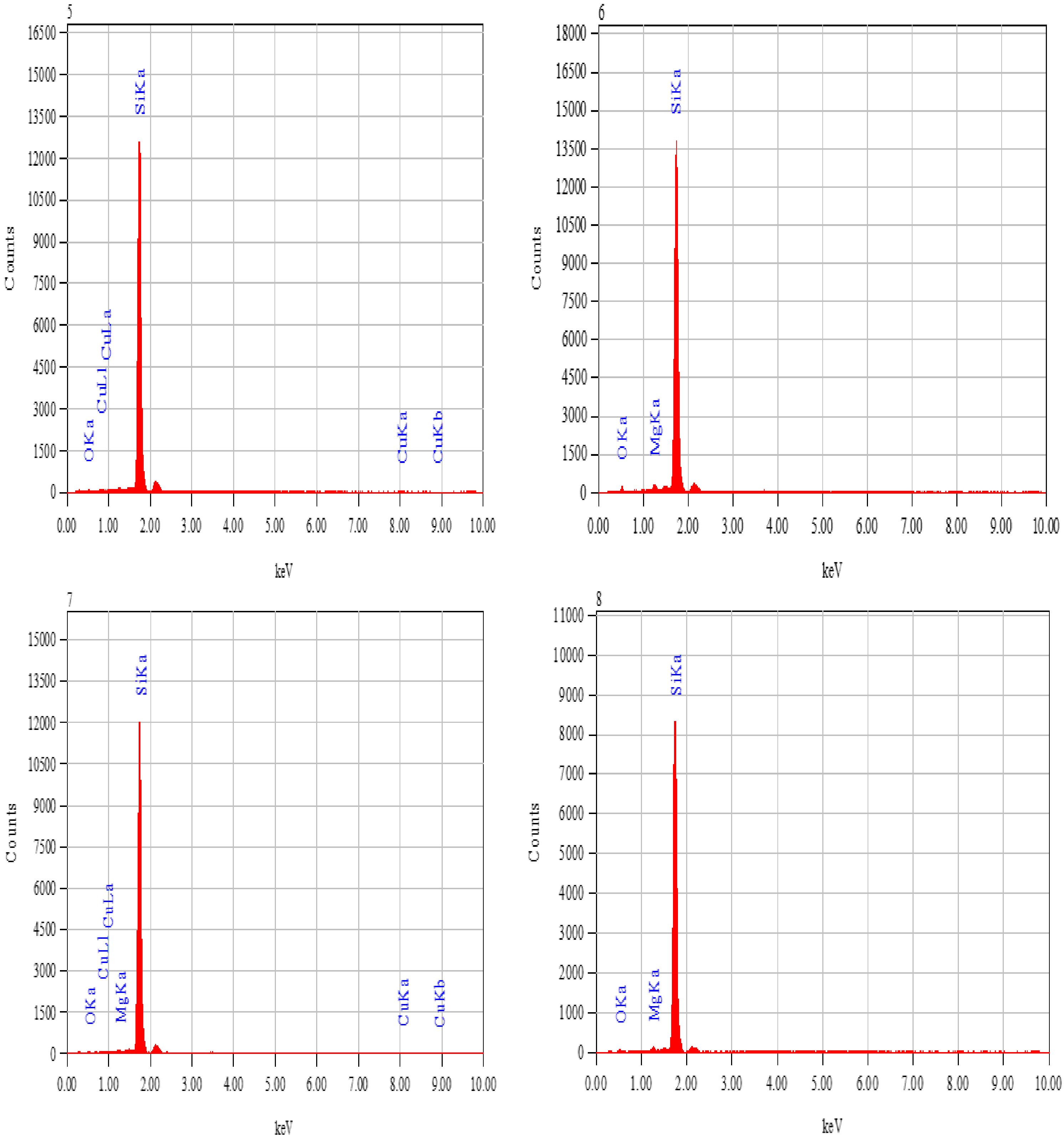


Figure-4: Graphical representation of different elements in extracted Si samples (1-8).

Table - 1: ZAF Method of Standard less Quantitative Analysis through JED - 2300 Analysis Station by JEOL, Japan

Element/ Sample	Mg	Al	*Si*	O	Cu	Others	Remarks
1	4.51	2.15	***92.91***	-	-	0.43	

2	1.04	-	***93.66***	4.88	-	0.42	
3	0.74	-	***94.44***	4.44	-	0.38	
4	1.07	-	***92.76***	6.015	-	0.57	
5	-	-	***96.48***	2.21	1.04	0.27	
6	1.55	-	***92.22***	5.61	-	0.63	
7	0.43	-	***96.06***	2.15	0.96	0.4	
8	0.90	-	***95.06***	3.7	-	0.35	

Conclusion

The mineral quartz available in different parts of Pakistan contains high amount of silicon dioxide and hence considered to be a strong potential source for obtaining MGS. Presently, there are many extraction procedures which are under use by different renowned companies for extracting MGS. However, in Pakistan still no progress is seen to obtain MGS from this precious mineral which is available abundantly. In this research work, Magnesium is selected as a reducing agent to extract MGS which resulted in extracting MGS at temperature of 950 ºC. This temperature range is considerably lower temperature as compared to other conventionally employed processes like Carbothermic reduction process. This adopted procedure of utilizing magnesium proved best, economic and environmental friendly as it produced MGS in the range of 93-96%. The results are confirmed through SEM-EDS analytical technique, thus further paving the way for new era of MGS in Pakistan.

Acknowledgements

We are immensely thankful to following dignitaries for their great support in performing this unique experiment.

1. Prof. Dr. Tariq Mahmood Ansari, Dean Faculty of Science / Director Institute of Chemical Sciences, Bahauddin Zakaria University, Multan, Pakistan.
2. Assistant Professor Dr. Suryyia Manzoor, Institute of Chemical Sciences, Bahauddin Zakariya University, Multan, Pakistan.
3. Mr. Muhammad Altaf Shahid, C.E.O Solex Chemical Industries, Multan, Pakistan.

References

[1] M. A. Green, K. Emery, Y. Hishikawa, W. Warta, E. D. Dunlop, "Solar cell efficiency tables (Version 45), Progress in Photovoltaics Research and Applications", Vol. 23 No. 1, 2015, pp. 1-9.

[2] N.D. Kaushika, A. K. Rai, "An investigation of mismatch losses in solar photovoltaic cell networks", Energy Journal, Vol. 32, No. 5, 2007, pp. 755-759.

[3] "New Brunswick mineral occurrence database", URL "http://dnre-mrne.gnb.ca/MineralOccurrence/", Accessed on Jul 2015.

[4] B.G. Gribov, K.V. Zinov'ev, "Preparation of high purity silicon for solar cells", Inorganic materials, Vol. 39, No. 7, 2003, pp. 653-662.

[5] L.P. Hunt, V.D. Dosaj, J.R. McCormick, L.D. Crossman, "Purification of Metallurgical grade Silicon to Solar grade Quality", International Symposium on Solar Energy Vol. 1, 1976, pp. 200-215.

[6] J.M. Juneja, T.K. Mukherjee, "A study of the purification of metallurgical grade silicon", Hydrometallurgy, Vol. 16 No. 1, 1986, pp. 69-75.

[7] Z. Jing, L. Tingju, M. Xianodong, Dawie, L., Dehua, L., "Optimization of the acid leaching process by using an ultrasonic field for metallurgical grade silicon:, Journal of Semiconductors, Vol. 30, No. 5, 2009, pp. 053002-6.

[8] T.L. Chu, S.S. Chu, "Partial purification of metallurgical silicon by acid extraction", Journal of Electrochemical Society, Vol. 130, No. 2, 1993, pp. 455-457.

[9] N. Liu, K. Huo, M. T. McDowell, J. Zhao, & Y. Cui, "Rice husks as a sustainable source of nanostructured silicon for high performance Li-ion battery anodes", Scientific Reports 3, doi:10.1038/srep 01919, 2013.

[10] Z. Favors, W. Wang, H. H. Bay, Z. Mutlu, K. Ahmed, C. Liu, M. Ozkan, C. S. Ozkan, "Scalable Synthesis of Nano-Silicon from Beach Sand for Long Cycle Life Li-ion Batteries", Scientific reports, Vol. 4, 2014, pp. 5623.

[11] W. Luo, X. Wang, C. Meyers, N. Wannenmacher, W. Sirisaksoontorn, M. M. Lerner, X. Ji, "Efficient Fabrication of Nano porous Si and Si/Ge Enabled by a Heat Scavenger in Magnesiothermic Reactions", Scientific Reports, Vol. 3, 2013, pp. 2222.

[12] I. Wazamtu, N. A. Sani, "Extraction and quantification of silicon from silica sand obtained from Zauma River, Zamfara state, Nigeria", European scientific journal, Vol. 9, 2013, pp. 160-168.

[13] P. M. Cox, R.A. Betts, C.D. Jones, S.A. Spall, I.J. Totterdel, "Acceleration of global

warming due to carbon cycle feedbacks in a coupled climate mode", Letters to Nature, Vol. 408, 2000, pp. 184-187.

[14] S. Solomona, G. K. Plattnerb, R. Knuttic, P. Friedlingstein, "Irreversible climate change due to carbon dioxide emissions", Proceedings of the National Academy of the United States of America, Vol. 106, 2009, pp.1704-1709.

[15] Zaib Ullah Khan, Nasim A. Khan, J. Askari, I. Amin, "Design and Development of Low Scale, High Temperature, Hybrid Furnace for the Extraction of Metallurgical Grade Silicon from Raw Mineral Quartz", Life Science Journal, Vol. 10, No. 2, 2013, pp.375-383.

[16] Technical Analysis Report by Dr. M. Yaqoob, Chief Scientific Officer (C.S.O.), "XRD and XRF Studies / Analysis Report of Mineral Quartz Sample of Jhangshahi, Sindh, Pakistan", Pakistan Council of Scientific & Industrial Research (PCSIR) Laboratory, Karachi Complex, Karachi, Pakistan, 2011.

[17] O. P. Khanna, A Textbook of Material Science and Metallurgy (for Engineering Students)". Vol 1, Dhanpat Rai Publications Ltd, New Delhi, India, 1981.

[18] L. Louise, C.T. Prewitt, D.J. Weidner, Structure and Elastic Properties of Quartz at Pressure, American Mineralogy Journal, Vol. 65, 1980, pp. 920-930.

[19] J-S. Li, X-X. Li, Q. Shen, Z-Z. Zhang, Du, F-H., 2010. Further purification of industrial quartz by much milder conditions and a harmless method. Environmental Science and Technology, Vol. 44, pp. 7673-7677.

[20] D. Eliezer, D. E. Aghion, E. Froes, Magnesium Science, Technology and Applications. Journal of the Minerals, Metals and Materials Society Vol. 5, 1998, pp. 201-212.