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

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). During this research, quartz reserves of around 600 million metric ton (MMT) in different parts of Pakistan have been studied first then in order to proceed mines of Jhangshahi, Sindh were selected where more than 150 MMT of proven quartz reserves are available. In this research samples of quartz stone from Jhangshahi, Sindh mines acquired for detail elemental analysis which proved presence of more than 95% Silicon Dioxide. This elemental analysis further strengthens the concept of MGS extraction from locally available quartz. During this research work, a comparatively less used technique of using magnesium element as reductant for MGS extraction is developed indigenously by using magnesium as reducing agent was developed. In order to validate the results of experiment, eight different experiments were performed around 950^{O}C. After performing eight all the eight experiments all extracted products were characterized by using Scanning Electron Microscope - Energy Dispersive X-Ray Spectroscopy (SEM-EDS) techniques. This technique validated the presence of around 95% of MGS in all the extracted products.

Key words

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 resources but also attributed to hazardous effects to the environment. Today a reasonable percentage of total energy produced worldwide is being produced from renewable resources among which Solar option 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 (available in abundant all over the world) is known as photon which is converted into electric energy through solar cells 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 used globally among which carbothermic process (using carbon as reductant) is the most common. This carbothermic process requires high temperature furnaces which is suitable for mass production of MGS [4, 5]. However certain other methods are in used for extraction/ purification of MGS which were studied during this research but not applied for this MGS extraction research [6-8]. After studying different MGS extraction process, the process of using magnesium as reductant with varying technique is selected for this research work. The element magnesium is basically used to improve the extraction process as it was applied by Liu et al who performed this process for the synthesis of nano-Si from silicon dioxide [9]. Similarly, Favours et al., prepared nano-Si from the magnesiothermic reduction of silicon dioxide in a different process which was utilized for Li-ion batteries [10].

Literature review revealed that this technique of using Magnesium as reductant 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 reduction at laboratory scale in order to confirm the process. The complete process adopted during this research is hghllighted below.

2.1. Pre processing phase

During this research work, 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 eliminate 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 [16].

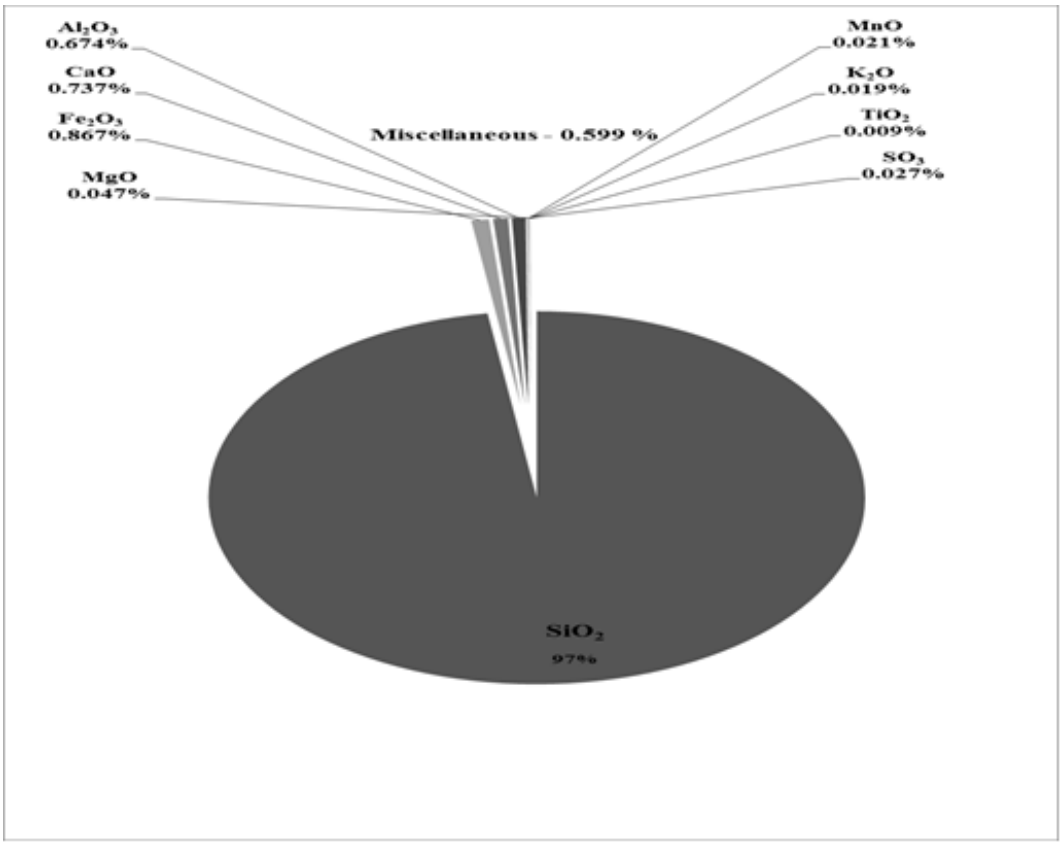

Figure-1: Elemental composition in Quartz samples of Jhangshahi, Sindh, Pakistan [16].

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
- 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. Conduct of experiment

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°C to get the homogeneous mixture. Figure-2 depicts powdered form of Quartz, Magnesium turning and homogenous mixture of quartz and magnesium.

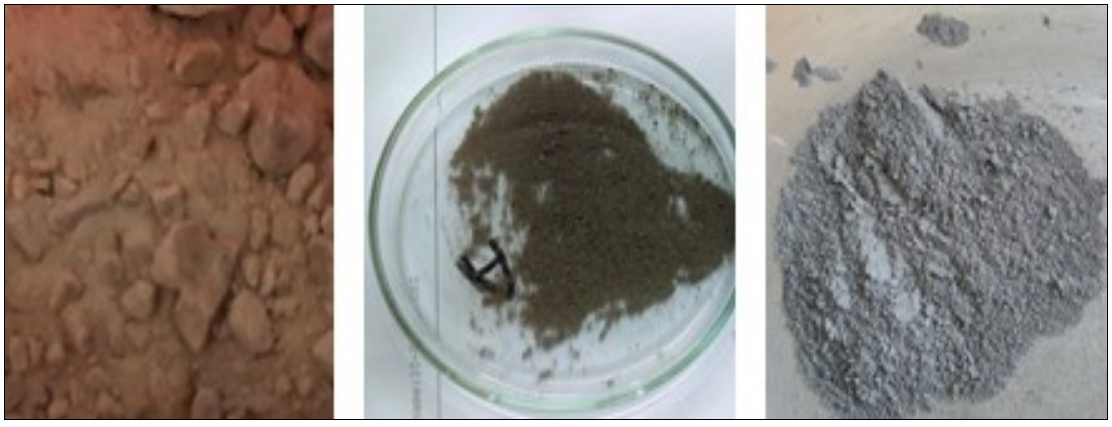

Figure-2: Powdered of Quartz, Magnesium and Homogenous Mixture

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. The next morning 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 Molar HCl Solution were prepared in eight different beakers and extracted products were left in that 2 Molar HCl for six hours.

At the end, these extracted silicon was filtered by using Whatman filter paper adjusted at the top of the funnel through pouring the samples in the funnel. Figure-3 illustrates the complete procedure adopted during experimentation phase.

Figure - 3: Step by step procedure for acquiring MGS

At the end, 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. 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 reductant 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 - 4a and 4b. The EDS results regarding elemental composition of different elements in all the eight samples are shown in figure - 5a and 5b. The results of all eight extracted products are summarized in table - 2 for comparative analysis which indicates presence of around 95% of MGS in all the samples which validates process used for extraction of MGS.

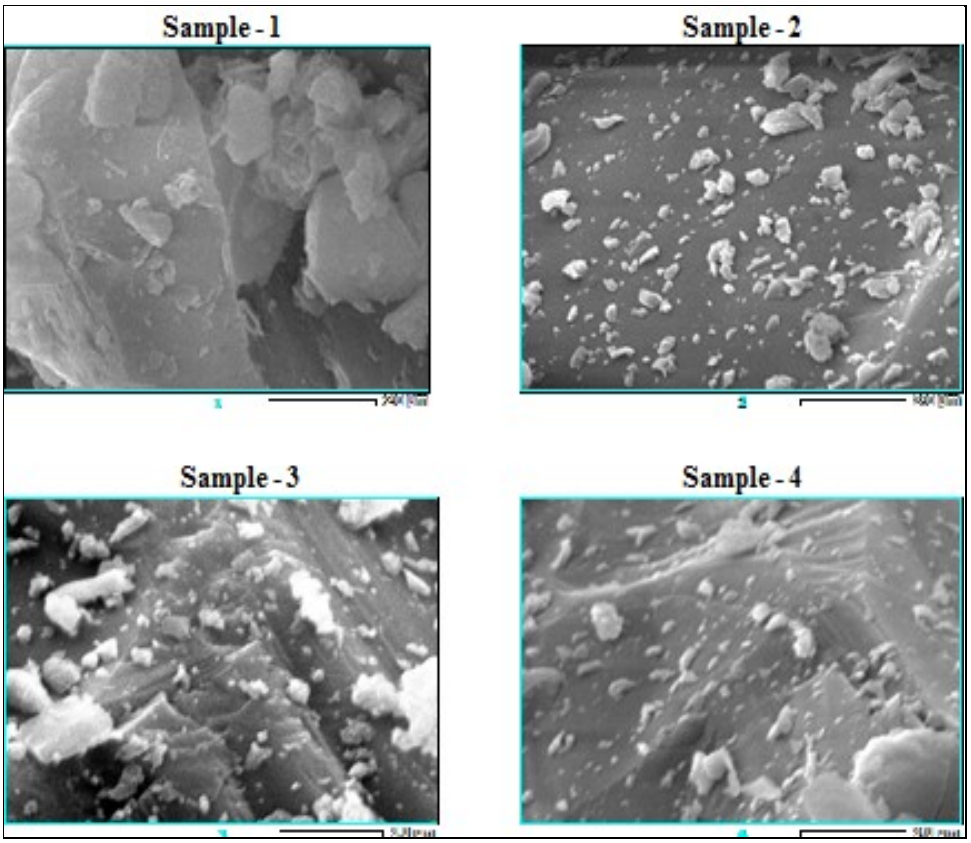

Figure - 4a: Images of samples 1-4 through SEM

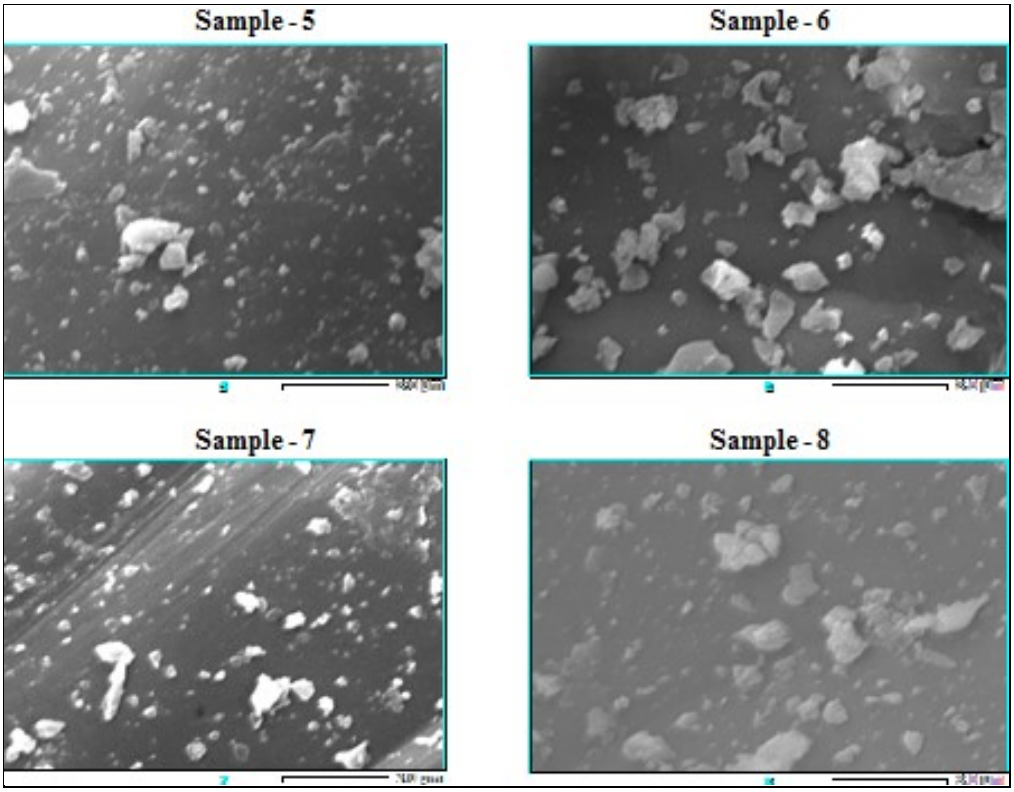

Figure - 4b: Images of samples 5-8 through SEM

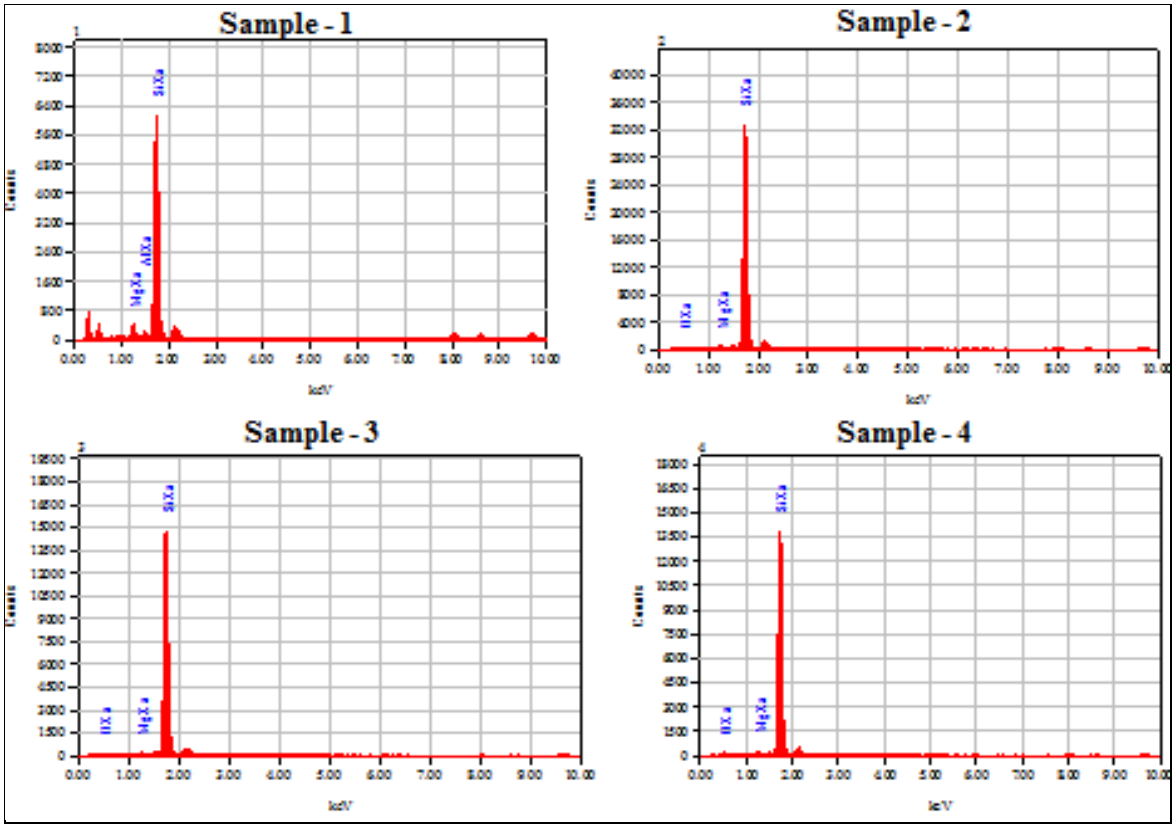

Figure - 5a: Graphical representation of different elements in samples 1-4

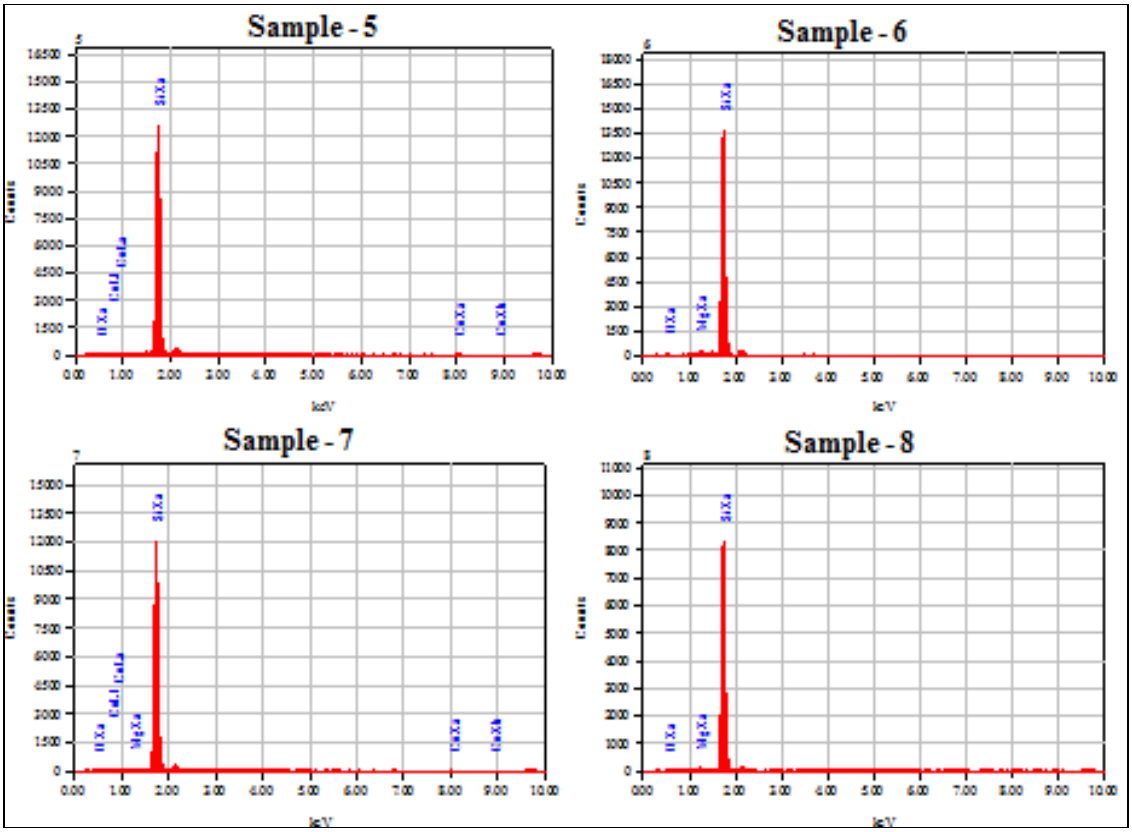

Figure - 5b: Graphical representation of different elements in samples 5-8

Table - 2: ZAF thod 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	

4. Conclusion

The mineral quartz available in different parts of Pakistan contain 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 used 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, a comparatively new process of utilizing Magnesium as reductant to extract MGS followed which resulted in extracting MGS on normal temperature of 950 ^{0}C. This temperature range is considerably lower temperature as compared to other conventionally employed processes like Carbothermic reduction process. This adopted procedure of utilizing magnesium as reductant proved best, economical and environmental friendly as it produced MGS of the range of 93-96%. The results are confirmed through SEM-EDS analytical technique thus further paved the way for new era of MGS in Pakistan.

Acknowledgement

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

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

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