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Up-grading of Locally Produced Metallurgical Grade Silicon (MG-Si)

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LOCALLY produced metallurgical grade silicon (MG-Si ~ 97%) was upgraded by using wet-milling process. This is including milling of MG-Si in presence of 2M HCl solution for different time periods up to 60 min. The effect of milling time in HCl solution was studied. Soaking of the milled products (at optimum milling time 15 min.) with continuous stirring in the same solution of 2M HCl for interval time up to 240 min. also were investigated. Finally, the effect of addition of 2M HF to the milled product was discussed. The leached samples were investigated by X-ray fluorescence (XRF), and scanning electron microscope (SEM). It was found that, 99.92% purity of MG-Si was achieved after 15 min milling time with 2M HCl followed by addition 2M HF for 240 min with continuous stirring. About 97 % removal efficiency of the impurities was obtained.

Keywords: MG-Si, up-grading of MG-silicon, purification of silicon, acid leaching.

Introduction

In recent years, solar grade silicon (SOG-Si), purified from metallurgical grade silicon (MG-Si) as the feedstock of the PV industry, has been in great demand, with a rapid development of more than 30% annual growth rate [1-4]. The dominant method for purification of silicon is Siemens process. But it is a highly complicated and considered as of high cost process. The development of a cheap process for the production of solar grade silicon (SOG-Si) of 99.9999 % purity is a challenging task and the subject of recent world's wide research. These developed methods involve separation of impurities from silicon by acid leaching, slag refining, vacuum distillation, directional solidification [5-7]. Among the proposed alternative purification methods is the acid leaching of pulverized MG-Si. The principle of the acid leaching process is that most of the metallic elements present as impurities in MG-Si have a high segregation coefficient in silicon. Thus, in spite of the high solubilities of the impurities in the molten silicon, they have small solubilities in the solid and remain concentrated at the grain boundaries. Upon grinding the MG-Si, fracture occurs mainly at grain boundaries exposing the impurities to the action of the acids [8]. The acid leaching enables purification of silicon, with the advantages of simple equipment, low cost, low energy consumption and dealing with a large quantity [9]. The past studies are almost focused on the effect of impurity removal of a variety of specific methods and the optimum process parameters. Due to the use of different materials, the results of different studies are quite different [9-12]. Recently, Sahu and Asselin [13] investigated the effects of using two different oxidizing agents, such as ferric chloride and ammonium persulfate, on the purification of MG-Si by leaching with hydrochloric acid. The addition of an oxidizing agent improved the extraction of impurities from the MG-Si. Also, the pretreatment of MG-Si to remove certain metallic impurities has a significant effect on the refining process. The purification of MG-Si can be achieved also by calcination and quenching before leaching, in addition to complexation with glycerin as a ligand [14].

The aim of this paper is the utilization of MG-Si produced by reduction smelting technique in EAF at Central Metallurgical Research& Development Institute (CMRDI) to obtain upgrading of the purity value of MG-Si. This is applied through studying the factors affecting the wet milling in presence of hydrochloric acid solution, and the effect of hydrofluoric acid addition.

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Experimental

The chemical analysis of the starting MG-silicon (~97%) is shown in Table 1, the main impurities are Fe, Ca, Al, Ti, and Cu with the presence of minor amounts of P, Na, and S. The silicon lumps were crushed by a jaw crusher, and subjected to sieve analysis. The milling process was carried out using planetary ball mill (P400 Germany) and ball powder ratio (BPR) of 10:1. The leaching process was initiated during the milling process by milling -0.5mm+2.5mm fraction with 100 ml of 2M HCl solution which called wet-milling process. Also, all experiments were carried out with liquid-solid weight ratio of 10: 1. After each experiment, the sample was filtered and washed with de-ionized water before drying. The metallic impurities were chemically analyzed by XRF. The flow sheet of the wet milling process of MG-Si is shown in Fig.1.

The removal efficiency of impurities (R_M) can be calculated according to the following equation:

$$R_M=\left[\frac{M_{Raw\ Si}-M_{Purified\ Si}}{M_{Raw\ Si}}\right]\times 100$$

Where,
$M_{Raw\ Si}$ = Content of total impurities in raw MG-Si
$M_{Purified\ Si}$ = Content of total impurities in purified Si

TABLE 1. Chemical analysis of MG-Si.

Elements	Al	Fe	Ca	Na	Ni	P	Mn	Cu	S	Ti
Concentration/ ppmw	3930	11530	10850	130	350	280	280	1020	120	1860

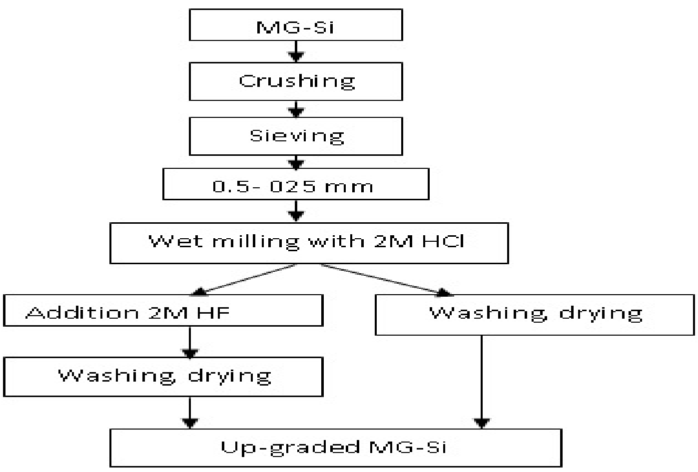

Fig. 1. Flow sheet of the wet milling of MG-Si

Results and Discussion

Effect of milling time

To study the effect of milling periods, about 10 g of MG-Si sample was subjected to milling with 100 ml of 2 M HCl solution in planetary vertical ball mill for different periods 15, 30, and 60 min. Figure 2 shows the effect of milling period with 2M HCl solution on the concentrations of the impurities which present in MG-Si as Al, Fe, and Ca. It is noticed that, the concentrations of the metallic impurities decreased up to milling time 15 min. and no significant result was obtained after this period. It is also observed that the removal of impurities was better for calcium, aluminum and worst for iron. This result may be due to: by increasing the milling time, the particle size of MG-Si was reduced to less than 45µm after milling time 60 min., where some impurities tend to segregate to grain boundaries or to interstitial positions. These impurities are very friable so can be removed more effectively [9]. Moreover, some impurity phases (as Fe) adsorbed at the silicon surface which became more difficult to be removed from this finer fraction by further washing during the leaching process.

Figure 3 illustrates the morphologies of the silicon samples examined by SEM after milling for 15 min. in 2 M HCl solution. The images show that the surface of MG-Si has many grooves

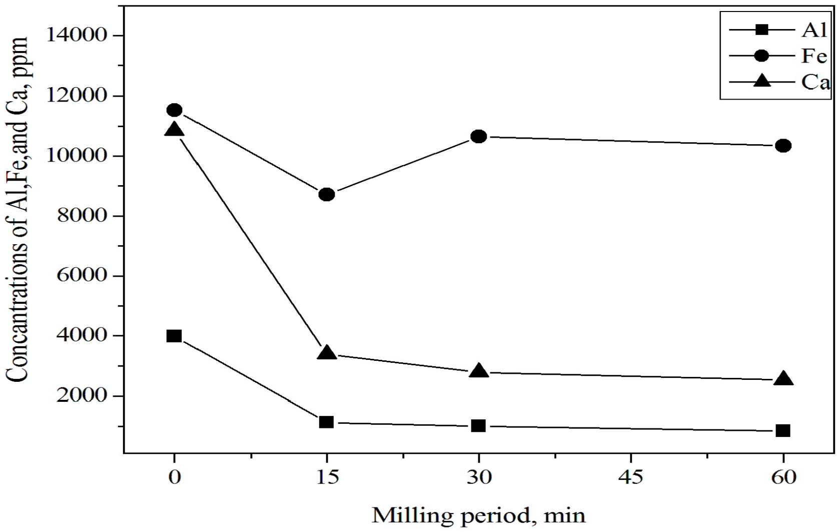

Fig. 2. The concentrations of Al, Fe, and Ca impurities for the MG-Si after milling for different periods with 2M HCl solution.

and scrapes after milling process. So, the milling process causing a large material stress, which lead to make many cracks and defects along the crystal boundaries. Therefore, impurities are exposed on the surface of the silicon and dissolved in acids, which is beneficial for their removal by acid leaching process.

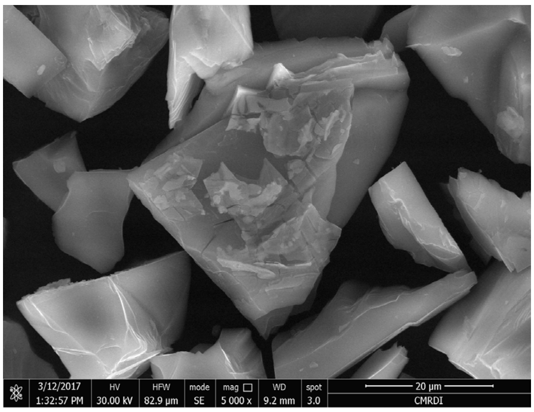

Fig. 3. SEM analysis for MG-Si samples after milling with 2M HCl for 15 min.

Effect of soaking time in HCl solution after milling step

The MG-Si samples which milled in 2 M HCl solution for 15 min. (wet milling step) were soaked in the same solution for different periods up to 240 min. with continues stirring at room temperature. Figure 4 shows the effect of soaking time in 2M HCl for different periods on the metallic impurities concentrations as Al, Fe, and Ca which present in the milled MG-Si. It was observed that the impurities concentrations decreased by increasing the soaking period in HCl solution. Also, the removal efficiency for Fe, Al, and Ca was increased.

The SEM analysis of the milled MG-Si after soaking in 2M HCl for 240 min. was shown in Fig. 5. From SEM analysis there are many grooves, scrapes and agglomeration of the impurities at the surface of silicon after milling and soaking processes. These agglomerations of impurities in separated forms are caused during the milling process. From XRF analysis, the purity of obtained silicon was increased from 98.3% to 99.0% after soaking in the same solution for 240 min. it is concluded that the milling assisted leaching process with further soaking in the same solution is better for calcium and aluminum than iron. This phenomenon may be due to less solubility intermetallics of iron phases [15]. It was mentioned that aluminum-containing intermetallic compounds often contain calcium, so consistency of the removing trend between aluminum and calcium is better than between aluminum and iron. Therefore the removal of impurities by HCl is better for aluminum, calcium and worst for iron [8, 9, 15].

Effect of HF addition on the milled MG-Si

The wet milled samples by 2M HCl at optimum milling time (15 min.) were subjected to leaching process with 2M HF solution. HF was added directly to the samples after milling step. The effect of HF addition directly to the milled samples for different periods 60, 120, and 240 min. at room temperature was investigated. Figure 6 shows the impurities concentration of Al, Fe and Ca in MG-Si samples after milling step followed by adding HF for different periods up to 240 min. A sharp decrease in the impurities concentration can be seen after adding HF to the solution, also the removal efficiency increased to about 97% for iron, aluminum and calcium respectively at room temperature. It is worthy to notice that, 99.92% purity of the silicon was achieved after addition of 2M HF and this is in agreement with many authors [9,15]. The addition of HF directly to the sample after milling accelerates the removal of the metallic impurities of MG-Si than using HCl only.

Figure 7 illustrates the morphologies of the MG-Si after milling with 2M HCL for 15 min. then adding 2M HF for 240 min. It was clear that the surface of the MG-Si appears smooth and

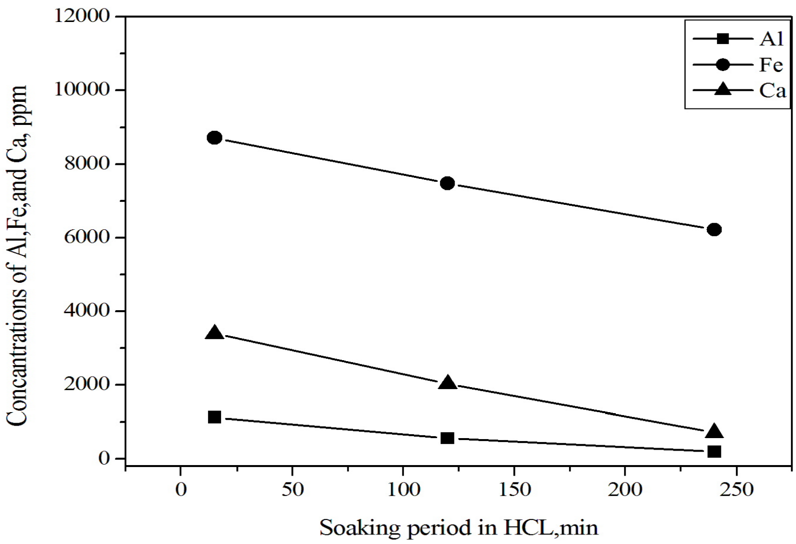

Fig. 4. The impurities concentrations of Al, Fe, and Ca after milled MG-Si with 2M HCl for 15 min. then soaked in the same solution for different periods

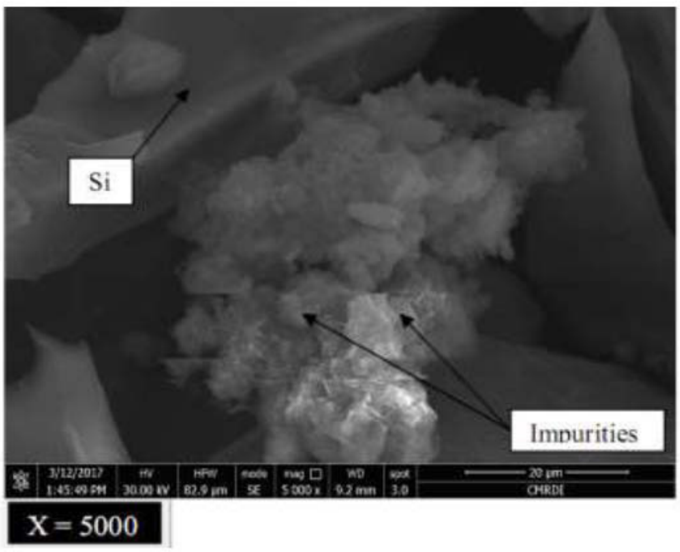

Fig. 5. SEM analysis for MG-Si after milling 15 min. then soaking in the same solution of 2M HCl for 240 min.

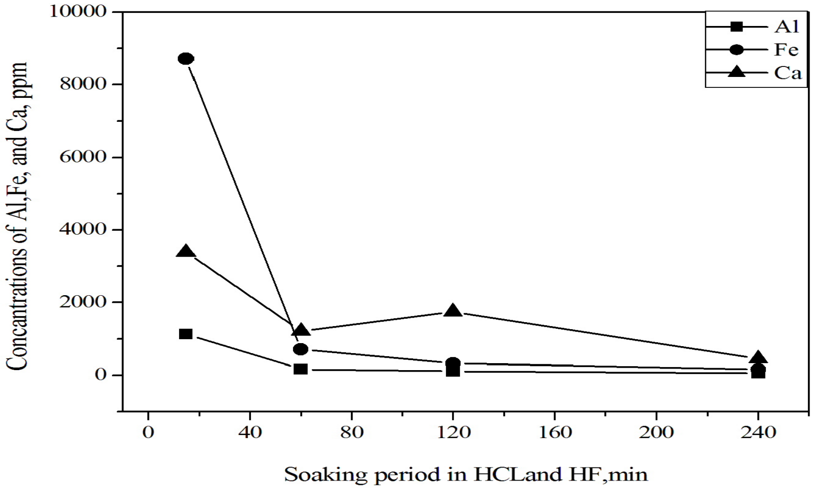

Fig. 6. The impurities concentrations of Al, Fe, and Ca in MG-Si after milling 15 min. with 2M HCl followed by addition 2M HF for different periods.

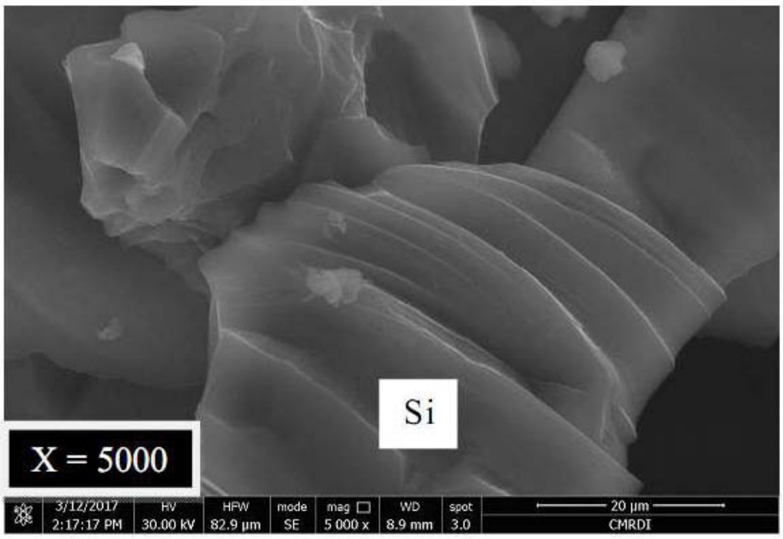

Fig. 7. SEM analysis for MG-Si powders after milling with 2M HCL for 15 min. followed by adding 2M HF for 240 min.

clean and there are many grooves and scrapes on the surface of the silicon so the crystal boundary was not obvious. This change may be attributed to the milling process which enhances the removal of metallic impurities by acid leaching process.

Conclusions

1. The wet milling with 2M HCl is a pretreatment step and a novel method for up-grading of MG-Si and used to increase the efficiency of the leaching process
2. This method proved that the optimum liberation size of silicon is ranged from +90 µm to +45 µm.
3. This study concluded that the wet milling with acid improves the leaching and up-grading process of MG-Si. This is because the wet milling causes groves, scraps, and micro inclusions. Also the phases of unstable impurities are dissociated and exposed at the surface of silicon particle which enhances its removal by acid leaching.
4. The addition of HF improves the effect of HCl

on the removal of the impurities.

5. The addition of hydrofluoric acid (2M HF) to hydrochloric acid (2M HCl) resulted in refining of MG-Si (99.92 %) at room temperature for 240 min. after milled with 2M HCl solution for 15 min as a pretreatment step for the leaching process. The removal efficiency of impurities also enhanced to about 97%.

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رفع جودة السيليكون التجاري المتنج محليا

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تتضمن هذه الدراسة رفع جودة السيليكون التجاري المنتج محليا والذي تم تحضيره بدرجة نقاوة حوالي ٩٧ ٪ وذلك عن طريق عملية الطحن الرطب وتتضمن هذه العملية طحن السيليكون التجاري في وجود حمض الهيدروكلوريك (بتركيز ٢ مول) اثناء عملية الطحن . وتم دراسة العوامل المؤثرة علي رفع جودة السيليكون بهذه الطريقة وتشمل تأثير كلا من زمن الطحن , نقع السيليكون الناتج بعد الطحن في نفس المحلول من حمض الهيدروكلوريك لفترات زمنية مختلفة , وايضا اضافة حمض الهيدروفلوريك الي السيليكون بعد طحنه مع محلول حمض الهيدروكلوريك .

وكانت النتائج التي تم الوصول اليها من هذه الطريقة كالاتي ان السيليكون التجاري تم تنقيته الي ٩٩,٩٢ ٪ بكفاءة ازالة للشوائب تصل الي ٩٧ ٪وذلك بعد طحنه مع حمض الهيدروكلوريك (بتركيز ٢ مول) لمدة ١٥ دقيقة ثم اضافة حمض الهيدروفلوريك (بتركيز ٢ مول) لمدة ٢٤٠ دقيقة عند درجة حرارة الغرفة.