ABSTRACT – Metallurgical grade silicon (MG-S) contains a series of metal (Fe, Al, Mn, Cu, Ni) and non-metal (P, B) impurities which make it unsuitable for use in solar cells. It is known that various metallic impurities are rejected by the silicon during its solidification process, and those crystallize at grain boundaries as intermetallic compounds. However, P is difficult to segregate in silicon, unlike most other impurities, since their partition coefficient ($k_p$) is high (about 0.35). There are reports in the literature indicating the possibility of phosphorus removal by the introduction of elements that decrease the $k_p$ of P in silicon, such as calcium and barium. In this work, it was used barium, which was introduced in MG-S as a synthesized slag with BaO/SiO$_2$ ratio of 6 and 5 wt% of CaF$_2$ using a treatment of 1550 °C for 2 h. After melting, the ingot was milled obtaining particle in the range -35+400 mesh. The particles were leached in three steps by using water, HCl, and HF. The results showed that about 80 wt% of phosphorus was removed from the silicon after leaching treatment.

1. INTRODUCTION

Commercial silicon is obtained from high purity silica in electric arc furnaces by reducing the silicon oxide with a carbonaceous reductant comprising charcoal or mineral coal at a temperature of about 1900 °C. The silicon produced by this process is called metallurgical grade (MG-Si), having a degree of purity in the order of 99 wt% [ISTRATOV et al., 2006]. Higher purity silicon is required for the construction of semiconductor devices. Solar-grade silicon (SG-Si - purity 99.99999%) is used for the production of photovoltaic cells, while silicon above 99.999999 wt% (EG-Si) is necessary for electronic industry [LAI et al., 2016]. Until approximately the end of the 1990s, SG-S was obtained as a by-product generated during the production of electronic grade silicon. With the strong growth in demand for SG-Si, due to the expansion of the photovoltaic solar energy market as an alternative and renewable source of energy, there is a need to develop silicon dedicated to the photovoltaic solar independent of the EG-Si manufacturing industry. There are two possible routes to obtain this silicon: the chemical and the metallurgical [METELEVA, 2012]. This second one allows SG-Si to be obtained at a lower cost, directly from metallurgical
grade silicon, which contains a high level of impurities (Fe, Al, Mn, Cu, Ni, P and B) [FERREIRA NETO et al., 2015]. SHIMPO et al. [2004] studied the introduction of a calcium source in MG-Si and observed the formation of CaSi$_2$ with P in the grain boundary between silicon and the silicide phase, which can be leached in acidic solution. The objective of this work was to study the effect of water, HCl, and HF on the leaching process for P removal on a MG-Si reacted with barium slag.

2. MATERIALS AND METHODS

A synthetic slag of the BaO-SiO$_2$-CaF$_2$ system was prepared using BaCO$_3$ (Aldrich), SiO$_2$ (Jundu) and CaF$_2$ (Aldrich) with BaO/SiO$_2$ molar rate of 6 and 5 wt% of CaF$_2$. All compounds were mixed and then heat treated in a zirconia crucible at 800 °C for 16 h. After cooling, the material was milled and passed through 200 mesh sieve. It was used MG-Si from MINASLIGAS-Brazil, which presented about 14.3 ± 1.0 ppm of P. The weight ratio of slag/MG-Si was 1/1. They were mixed and melted in a graphite crucible at 1550 °C for 2 h under inert atmosphere (Argon) and cooled down at 0.5 °C/min. After solidification, the silicon was separated from the slag obtaining an ingot of about 8 cm in diameter by 20 cm high.

Samples of the ingot were analyzed by scanning electron microscopy (JEOL JSM 6300), and energy dispersive spectroscopy (EDS, Noran System). The ingot was milled and separated in particle size between 35 and 400 mesh (-500 μm + 44 μm). The crystalline phases were determined by X-ray diffraction (Shimadzu XRD 6000 using Co K$_\alpha$).

The powders were leached in three steps. In the first one, 20 g of the powdered silicon were leached with 100 mL distilled water for 2 h. The powder was filtered and dried. In the second step the powder, resulted from the first step, was mixed with a 100 mL solution 10 wt% HCl (37 %) and was leached for 5 h and then filtered and dried. Finally, the powder resulted from the leaching with HCl was mixed with a 100 mL solution of 10 wt% HF (38 %) and leached for 5 h. Every step was carried out at 80 °C through magnetic agitation. The amount of P was determined by ICP-OES (Varian) and was measured in triplicate.

3. RESULTS AND DISCUSSION

As can be shown in Figure 1 and 2, the phase formed at grain boundary is BaSi$_2$. According to literature [HERRMANN, 1998] BaSi$_2$ disintegrates through reaction with water:

$$\text{BaSi}_2(s) + 6\text{H}_2\text{O}(l) \iff \text{Ba(OH)}_2(s) + 2\text{SiO}_2(s) + 5\text{H}_2\text{O}(g) \quad (1)$$

The first step using water is important to remove the major quantity of BaSi$_2$. The reactions using HCl and HF are represented as following:

$$2\text{BaSi}_2(s) + 4\text{H}^+ + 4\text{Cl}^- + 6\text{H}_2\text{O}(l) \iff 2\text{Ba}^{2+} + 4\text{Cl}^- + 2\text{SiH}_4(g) + 4\text{H}_2(g) + 2\text{SiO}_2(s) + 2\text{H}_2\text{O}(l) \quad (2)$$

$$\text{Ba(OH)}_2(s) + 2\text{H}^+ + 2\text{Cl}^- \iff \text{Ba}^{2+} + 2\text{Cl}^- + 2\text{H}_2\text{O}(l) \quad (3)$$

$$\text{SiO}_2(s) + 4\text{H}^+ + 4\text{F}^- \iff \text{SiF}_4(g) + 2\text{H}_2\text{O}(l) \quad (4)$$

The Ba(OH)$_2$ and SiO$_2$ that are formed in the first step are scarcely soluble in water, but the first one is relatively soluble in HCl solution forming BaCl$_2$. The SiO$_2$ forms SiF$_4$ gaseous in HF solution, removing the precipitate in the silicon, showing that three steps are important to purify
the metallurgical grade silicon.

![X-ray diffractogram](image1.png)

**Figure 1** – X-ray diffractogram of the sample MG-S treated with barium slag.

![SEM micrograph and EDS spectra](image2.png)

**Figure 2** – (a) SEM micrograph and (b) EDS spectra of points 1 and 2 shown in (a) of the sample of MG-Si with barium slag.

In Table 1 the results of the chemical composition of the leached silicon powder after the three steps are presented. The leaching process used in this study resulted in a decrease from 14.3 ppm to about 3.3 ppm of P. Although for solar energy application the amount of P in the silicon should be below 1 ppm [FONTANETO, 1980 and LAI, 2016] the treatment with barium slag and further leaching show a potential successful route for MG-Si purification.

| Sample               | P (ppm)     |
|----------------------|-------------|
| Before Leaching      | 14.3 ± 1.0  |
| After Leaching       | 3.3 ± 0.5   |

**Table 1** – Content of P in the Si samples before and after leaching
4. CONCLUSIONS

It can be observed that about 80 wt% of P was removed from the MG-Si using the route by introducing in it BaO slag, which promotes the P segregation to the grain boundary, forming BaSi₂ that is leached by water, HCl, and HF. However, it is necessary to study the effect of reducing particle size, since coarse particle (about 500 µm) could contain grain boundaries that are not exposed to the contact with water and acid. This effect should be explored.

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