



XXII CONGRESSO
BRASILEIRO DE
ENGENHARIA QUÍMICA
23 a 26 de Setembro de 2018
Hotel Maksoud Plaza
São Paulo – SP



XVII ENCONTRO BRASILEIRO
SOBRE O ENSINO DE
ENGENHARIA QUÍMICA
27 a 28 de Setembro de 2018
USP
São Paulo – SP

STUDY ON PHOSPHORUS REMOVAL FROM METALLURGICAL GRADE SILICON BY ACID LEACHING FOR SOLAR APPLICATION

FREDERICCI C¹, POCO JGR², FERREIRA NETO JB¹, NEIRA JBV³

¹ Instituto de Pesquisas Tecnológicas do Estado de São Paulo, Centro de Tecnologia em Metalurgia e Materiais, Laboratório de Processos Metalúrgicos

² Centro Universitário FEI, Departamento de Engenharia Química

³ Universidade Federal do Sul e Sudeste do Pará, Faculdade de Engenharia de Materiais
E-mail para contato: catiaf@ipt.br

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/SiO₂ ratio of 6 and 5 wt% of CaF₂ 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 99.9999%) 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



XXII CONGRESSO
BRASILEIRO DE
ENGENHARIA QUÍMICA
23 a 26 de Setembro de 2018
Hotel Maksoud Plaza
São Paulo – SP



XVII ENCONTRO BRASILEIRO
SOBRE O ENSINO DE
ENGENHARIA QUÍMICA
27 a 28 de Setembro de 2018
USP
São Paulo – SP

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

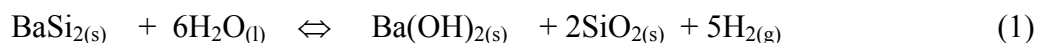
A synthetic slag of the $\text{BaO-SiO}_2\text{-CaF}_2$ system was prepared using BaCO_3 (Aldrich), SiO_2 (Jundu) and CaF_2 (Aldrich) with BaO/SiO_2 molar rate of 6 and 5 wt% of CaF_2 . All compounds were mixed and then heat treated in a zirconia crucible at 800 °C for 16 h. After cooling, the material 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 ($-500 \mu\text{m} + 44 \mu\text{m}$). The crystalline phases were determined by X-ray diffraction (Shimadzu XRD 6000 using Co K_α).

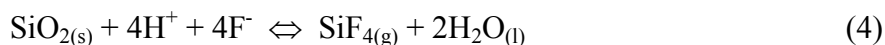
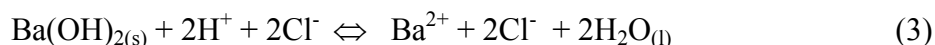
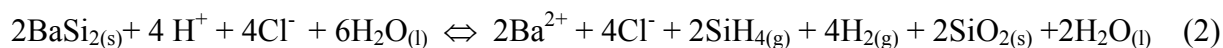
The powders were leached in three steps. In the first one, 20 g of the powdered silicon were leached with 100 mL distilled water for 2 h. The powder was filtered and dried. In the second step the powder, resulted from the first step, was mixed with a 100 mL solution 10 wt% HCl (37 %) and was leached 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:



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:



The $\text{Ba}(\text{OH})_2$ 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.

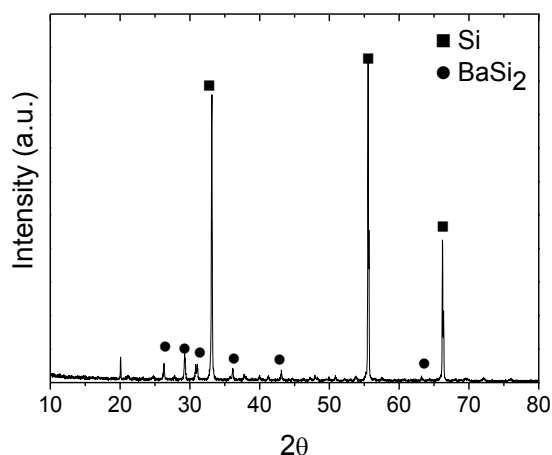


Figure 1 – X-ray diffractogram of the sample MG-S treated with barium slag.

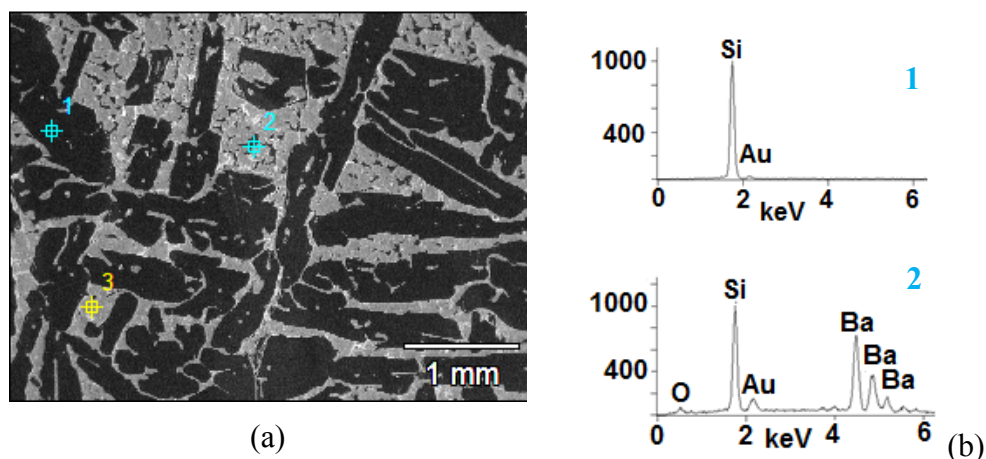


Figure 2 – (a) SEM micrograph and (b) EDS spectra of points 1 and 2 shown in (a) of the sample of MG-Si with barium slag.

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.

Table 1 – Content of P in the Si samples before and after leaching

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



XXII CONGRESSO
BRASILEIRO DE
ENGENHARIA QUÍMICA
23 a 26 de Setembro de 2018
Hotel Maksoud Plaza
São Paulo – SP



XVII ENCONTRO BRASILEIRO
SOBRE O ENSINO DE
ENGENHARIA QUÍMICA
27 a 28 de Setembro de 2018
USP
São Paulo – SP

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 BaSi_2 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.

5. REFERENCES

- FERRREIRA NETO JB, RIBEIRO TR, LIMA ML, LOTTO AA, VILCA JB - Obtenção de silício grau solar por rota metalúrgica. *Revista Brasileira de Energia Solar*, 6, 1, p. 37-46, 2015.
- FONTANETO LP, NOVARA AP, et al. Process for purifying silicon, US PATENT 4,241,037, p. 1-3, 1980.
- HERRMANN RFW, TANIGAKI K, KUROSHIMA S, SUEMATSU H - Superconductivity in silicon-based barium-inclusion clathrates – *Chem. Phys. Lett.*, 283, p. 29–32, 1998.
- ISTRATOV AA, BUONASSISI T, PICKETT MD, HEUER M, WEBER ER - Control of metal impurities in “dirty” multi-crystalline silicon for solar cells. *Mater. Sci. Eng. B*, 134, p. 282–286, 2006.
- LAI H, HUANG I, GAN C, XING P, LI J, LUO X - Enhanced acid leaching of metallurgical grade silicon in hydrofluoric acid containing hydrogen peroxide as oxidizing agent, *Hydrometallurgy*, 164, p. 103–110, 2016.
- METELEVA-FISCHER YV, YANG Y, BOOM R, KRAAIJVELD B, KUNTZEL H - Microstructure of metallurgical grade silicon during alloying refining with calcium. *Intermetallics*, 25, p. 9-17, 2012.
- SHIMPO T, YOSHIKAWA T, MORITA K - Thermodynamic study of the effect of calcium on removal of phosphorus from silicon by acid leaching treatment, *Metallurg. Mater Trans B*, p. 277-284, 2004.

ACKNOWLEDGMENTS

This work was supported by BNDES-FUNTEC and MINASLIGAS.