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Technical Note

Chemical upgrading and aluminothermic reduction of Egyptian sand

M. Radwan*, M. M. Rashad, S. Z. El-Tawil

Central Metallurgical Research and Development Institute, P.O.Box: 87 Helwan, Cairo, Egypt

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ABSTRACT

Al-Si alloys produced by aluminothermic reduction of Egyptian sand were leached with hydrochloric acid to produce metallurgical-grade silicon (MG-Si) powder and aluminium chloride solution. Metallurgical-grade silicon containing ~99.3% Si was obtained at the following conditions: particle size 100% -0.1mm, temperature of the reaction was 50°C, time of reaction 20.0 minutes, solid/liquid ratio 1:9g/ml and acid concentration 6.24M. The iron content in aluminium-silicon alloy is almost dissolved into the solution (besides aluminium) and non-significant iron content (~0.2%) is detected in the upgraded silicon metal.

Keywords: Leaching; Metallurgical-grade silicon; Al-Si alloys

1. INTRODUCTION

Upgrading of elemental silicon from the aluminium-silicon alloys produced by aluminothermic reduction of silica can be achieved by three methods:

i-Acid leaching process by dissolving aluminium content in mineral acids. For example, Cordoba *et al.* (1986) treated their aluminium-silicon alloys (containing ~ 30-50% Si) with hot concentrated hydrochloric acid and obtained pure silicon metal practically iron-free, with traces aluminium and 0.6-1.5% carbon and oxygen. Yasuornai (1973) prepared fine powder of silicon by treating Al-Si alloys with hydrochloric acid solution. Santos *et al.* (1990) showed that the leaching behavior of MG-silicon is dependent strongly on the composition of major impurities. An additional acid leaching refining step can be performed effectively when the major impurities present in the silicon sample are aluminium, iron and alkalis. Dietl *et al.* (1983) made a soaking for a MG-Silicon in aqueous solution of 2.5% hydrochloric acid and 5% hydrofluoric acid for 2h to remove iron, aluminium and calcium, the predominant impurities.

ii-Molten-Salt electrolysis process in which the electrolytic extraction of Al from the aluminium-silicon alloy charged as anode feed is performed as follows (Sharma and Mukherjee, 1991):

At the anode : $Si_xAl_y \rightarrow y\ Al^{+3} + x\ Si + 3y\ e^-$ (1)

At the cathode: $Y\ Al^{+3} + 3\ ye^- \rightarrow y\ Al$ (2)

Where x and y represents the contents of silicon and aluminium in the alloy.

iii-Fractional crystallization followed by acid leaching where the alloy is transferred to the crystallizer kept at the temperature above the liquids and then the temperature reduced to near the eutectic temperature (about 577°C) and consequently silicon platelets are precipitated from solution (Kotval and Strock, 1980; Dawless, 1981).

The present study aims to upgrading of metallurgical-grade silicon from the aluminum-silicon alloys produced by aluminothermic reduction of Egyptian sand using direct leaching with hydrochloric acid. All the parameters affecting the efficiency of leaching were systematically studied and the optimum conditions were determined.

* Corresponding author. E-mail: radwan72001@yahoo.com

2. EXPERIMENTAL

2.1. Raw materials and apparatus

The aluminium-silicon alloy samples were prepared by aluminothermic reduction of Egyptian white sand from Abu-Zenima locality, Sinai (Radwan, 1997). Pure hydrochloric acid 32% from the El-Nasr Company for Pharmaceutical and Chemical Industries, Egypt was used as the leaching agent. The reaction between the alloy and hydrochloric acid was performed in a 500ml round bottom flask placed in a thermostatically controlled water bath. The slurry was mechanically agitated at a rate of 500rpm. The aluminium chloride solution was filtered under vacuum in a Buchner–type filter using polypropylene filter cloth of 74μm size.

2.2. Procedure

The reaction vessel was inserted in a thermostatically controlled water bath. The amount of Al-Si alloy was added gradually with constant agitation to the hydrochloric acid solution in the reaction vessel. Addition of the sample should be carried out with care to avoid escaping of the sample out the flask by the gaseous reaction products. After the elapse of the reaction time, filtration was carried out to separate the unreacted portion of the sample from aluminium chloride solution. The solid residue which is mainly elemental silicon was washed by distilled water three times and then dried at 150°C. The aluminium in filtrate was determined by titration with EDTA using xylenol–orange indicator at pH 5-6. At optimum leaching parameters, silicon metal was subjected to complete chemical analysis by using atomic absorption spectroscopy (AAS).

3. RESULTS AND DISCUSSION

3.1. Characterization of aluminium-silicon alloys

Radwan (1997) prepared Al-Si alloys from Abu-Zenima white sand, Egypt by the thermite process using aluminum as a reductant. The optimum conditions of this stage for maximum silicon recovery (88%) are: aluminium quantity in charge 70 wt% over stoichiometry, mean particle size of aluminium -430+150μm, grain size of sand sample -105μm, weight ratio of energizer/sand 1.35 and ratio of charge weight/volume of vessel 0.4g/cm^3. The chemical analysis of the produced metallic aluminium-silicon alloys is given in Table 1. The results showed that the alloys contains mainly 50.96% Al, 47.6% Si and 1.32% Fe.

Table 1
Chemical analysis of starting aluminium-silicon alloy

Constituent	Wt.%
Si	47.6
Al	50.96
Fe	1.32
Ca	0.0024
Mg	0.0035
Mn	0.047
S	0.003

3.2. Production of metallurgical-grade silicon

Metallurgical-grade silicon is recovered from Al-Si alloys by leaching with hydrochloric acid according to the following reaction:

$$(Al\text{-}Si)_{(s)} + 3\ HCl_{(l)} \rightarrow Si_{(S)} + AlCl_{3(l)} + 3/2\ H_{2(g)} \quad (3)$$

The main advantages of this route are that being based on a low temperatures process and it has low energy requirements. The acid used must be capable of dissolving aluminium without attacking silicon itself. Hydrochloric acid which is available in cheap prices is chosen as leachant for removal of aluminium, the principal constituent present in the produced alloy. The Al-Si alloy samples were crushed to -100μm size in a porcelain ball mill. The optimum conditions affecting on the hydrochloric acid leaching such as temperature, time, acid concentration and liquid/solid ratio were studied. The percentage of dissolved aluminium in the leachant solutions is considered as the effective parameter for the upgrading process.

3.2.1. Effect of temperature

To study the effect of temperature on aluminium removal from aluminium-silicon alloy, a series of experiments is carried out in the temperature range of 25-80°C at constant time 30 minutes and liquid/solid ratio of 10:1 using 6.24M hydrochloric acid concentration. In general, lower temperatures increase viscosity and hence decrease reactant ion mobility, and thus low reaction efficiencies are expected. While, higher temperatures lead to the increase of the corrosivity of hydrochloric acid and consequently higher corrosion rate of the industrial units is encountered (Abdel-Aal, 1995). The leaching results obtained are given in Figure 1. They reveal that the percentage of dissolved aluminium increases from about 88% to a maximum constant values (~ 100%) by increasing the leaching temperature from 25°C to 50°C, respectively.

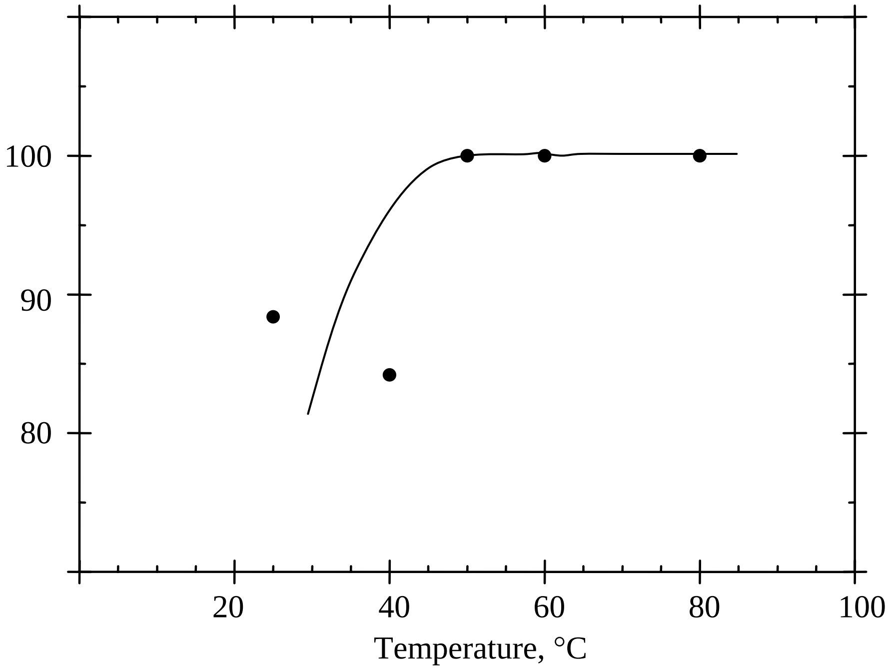

Figure 1. Effect of leaching temperature on removal of aluminium from the Al–Si alloy by HCl treatment

3.2.2. Effect of reaction time

The leaching experiments were carried out at constant liquid/solid weight ratio of 10:1 and HCl concentration of 6.24M and constant leaching temperature of 50°C for different times ranges from 5 to 30 minutes. The results obtained are given in Figure 2. About 98% aluminum removal from the treated aluminium–silicon alloy is achieved after five minutes. Nearly complete aluminium is removed after 20 minutes. The high removal rate of aluminium from the alloy after only five minutes hydrochloric acid leaching at this low temperature can be regarded to the structure of the alloy which consists of primary silicon and simple eutectic aluminium–silicon mixture. The eutectic mixture is a mechanical mixture and not a compound therefore aluminium can be easily dissolved by the acid.

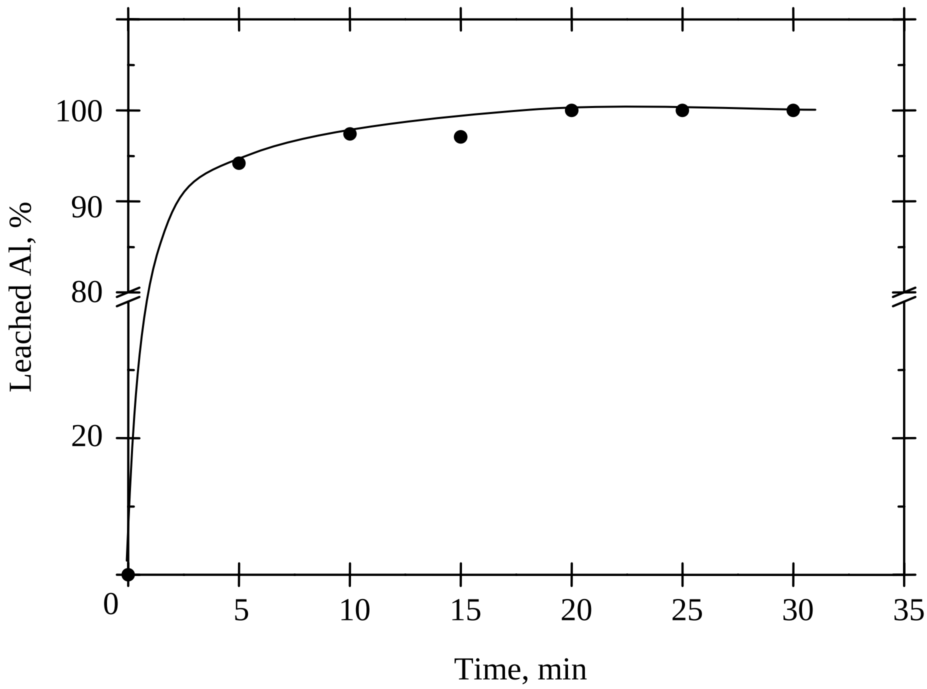

Figure 2. Effect of leaching time on removal of aluminium from the Al–Si alloy by HCl treatment.

3.2.3. Effect of HCl concentration

A series of experiments is performed using various hydrochloric acid concentrations from 4.37M to 6.24M at constant liquid/solid weight ratio of 10:1 and constant temperature of 50 °C and leaching time of 20 minutes. The results reveal that the molarity of hydrochloric acid has a significant effect on the aluminium removal from the treated alloy, Figure 3. About 80 % aluminium is removed at 4.37M hydrochloric acid and complete removal is achieved using 6.24 M concentration which is the stoichiometric amount of hydrochloric acid necessary to remove all aluminium content from the starting aluminium-silicon alloy according to Equation (3).

3.2.4. Effect of liquid/solid ratio

A set of experiments was conducted using various liquid/solid weight ratios ranging from 7 to 10g/g. The experiments were carried out under the following conditions:

Temperature :	50°C
Reaction time:	20min
Hydrochloric acid concentration:	6.24M

The results given in Table 2 show that the liquid/solid weight ratio slightly affects the aluminium removal efficiency. The optimum liquid/solid weight ratio is equal to 9 which leads to complete leaching of aluminium from the alloy.

Table 2
Effect of liquid/solid wt. ratio on aluminium removal from Al–Si alloy

Liquid/solid wt. ratio	Leached Al, %
7	98.1
8	99.4
9	100
10	100

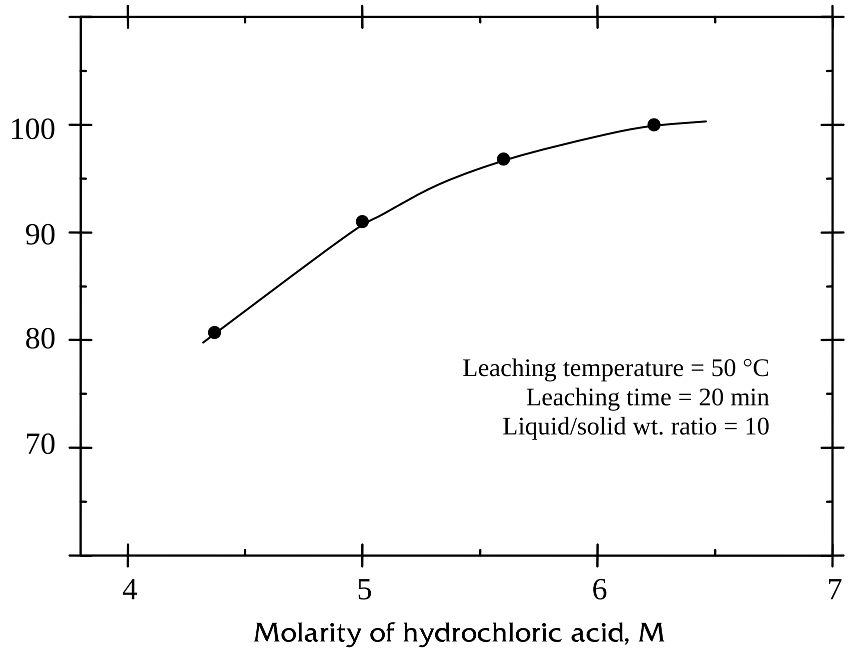

Figure 3. Effect of hydrochloric acid concentration on removal of aluminium from the Al–Si alloy

3.2.5. Optimum leaching parameters

The optimum conditions of acid leaching of thermite-derived aluminium-silicon alloy to recover elemental silicon can be summarized in the following Table 3. At these conditions, near complete removal of aluminium from the treated alloy is accomplished. This means that aluminium is present in this alloy in a structure form which is easily removed by acids.

Table 3
Optimum conditions of HCl-leaching of thermite-derived Al-Si alloy

Parameter	Optimum value
Leaching temperature, °C	50
Leaching time, min	20
Acid concentration, M	6.24
Liquid/solid weight ratio	9

3.2.6. Quality of the produced metallurgical-grade silicon

Chemical analysis of the produced silicon powder is given in Table 4. Pure metallurgical-grade silicon (~ 99.3% Si) is obtained. It is known that the metallurgical-grade silicon quality ranges from 93-98%. This means that the produced silicon metal by this route is beyond the metallurgical-grade quality.

Table 4
Chemical analysis of produced silicon powder

Constituent	%
Al	0.48
Fe	0.18
Ca	0.0044
Mg	0.0062
Mn	0.016
S	0.002

It can be seen that most of iron content present in the aluminum-silicon alloy is dissolved into the solution besides aluminium under the operating conditions. The filtrate, aluminum chloride solution, can be concentrated and then crystallized as $AlCl_3.6H_2O$.

4. CONCLUSIONS

Metallurgical-grade silicon of 99.3% purity was produced from Egyptian sand after reduction by aluminothermic process and subsequent acid leaching. The acid leaching process is proved to be an easy way to upgrade the silicon from the thermite-derived aluminium-silicon alloys. The formed aluminum-silicon alloy was leached with hydrochloric acid and the optimum conditions for near complete removal of aluminium were: temperature of the reaction 50°C, time of reaction 20 minutes, liquid/solid weight ratio 9:1 and hydrochloric acid concentration 6.24M. The produced silicon is suitable for both metallurgical and chemical applications and may be considered as potential starting material for post-purification processes for photovoltaic and electronic applications because Egyptian sand contains no boron and phosphorous. The filtrated aluminum chloride solution was concentrated and crystallized as aluminium chloride hexahydrate.

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