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by

TURGUT GÜNDÜZ and MUSTAFA AKPOYRAZ

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A New Medhod In Reduction Of Silicon Tetrachloride

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ABSTRACT

In this study 99,9 % purity of silicon has been ebtained by reduction of silicon tetrachloride with sodium at about 310 ° C. Silicon tetrachloride needed for this reaction has been collected by passing dry and pure chlorine over the mixture of silicon dioxide and coke, heated to 900–1000 °C in a fused silica tubing.

INTRODUCTION

The importance of either pure silicon or its organic derivatives is increasing rapidly in present time. The reason for this, is the uses of silicon in modern electronics as semiconductor and the uses of its organic derivatives in the production of polimer products such as silicon rubbers, silicon lubricating oils and silicon greases [1], [2], [3], [4], [5], [6], [7].

Various methods have been developped to obtain pure silicon to meet the need of electronics industry. One of them is to reduce the molten silica by aluminum [8]. Another method is, to reduce silica by aluminothermic process [9], [10]. Because of the impurity of the products, both methods are far remote to meet the need of industry.

Today, common practice is to reduce silicon tetrachloride by various reductors, such as zinc, hydrogen etc. In addidion to these the thermal decompasition of silicon tetrahydride, silicon tetraiodide and silicon tetrabromide have been tried, but no satisfactory result has been obtained so far.

The zinc process is based upon the reduction of silicon tetrachloride by zinc vapor at about 950–1000 °C. There are numerous

studies on this process, [11], [12], [13], 1[14]. The yield of this process changes from 17 % to 50 %.

Because of the danger of explosion at 400–800 °C in the presence of water vapor and air, the thermal decomposition methods of silicon hydrides are not preferable [15], [16]. If temperature is reduced under given interval, no reaction takes place. A similar method, is the thermal decomposition of halosilicon hydrides at 1200–1300 °C [17], [18], [19], [20], [21].

In the present study, various ways of reduction of silicon tetrachloride to silicon have been planned and tried.

An electrical arc has been set up between platinum electrodes and the dry mixture of hydrogen and silicon tetrachloride has been passed through the electrodes at different temperatures. Unfortunately the yield reached by this way has been found to be round about 10 %. The reason for this, is the accumulation of silicon on the platinum electrodes at one place. High temperatures have increased the rate of reaction but not the yield of product.

Furthermore, other reductors namely magnesium, aluminum, iron, sulphur, phosphorous etc, have been tried at different temperatures and conditions but no satisfactory result has been obtained. Lastly molten sodium is tried at different temperatures in a pyrex glass flask. A very good and hopeful result has been attained. At about 310 °C a very dark blue (very nearly black) crystalline 99,9 % purity of silicon with a yield 52-53 % has been obtained. The detail of the method has been given below.

EXPERIMENTAL

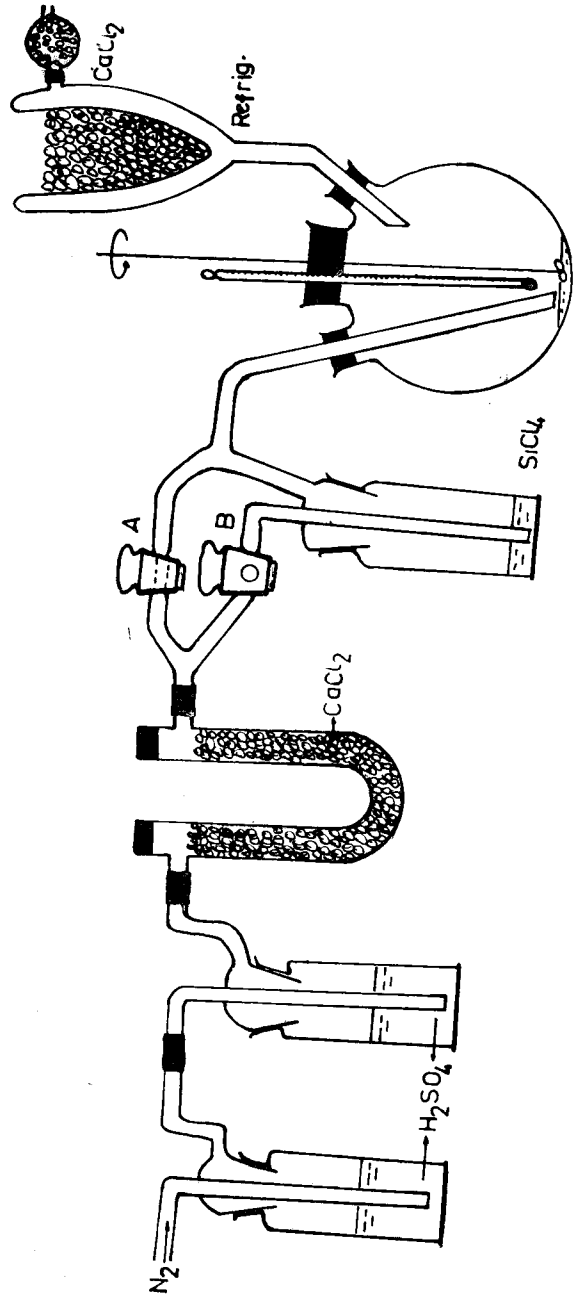
2 g of pure sodium is placed in pyrex glass flask, then a stream of dry nitrogen is passed through the flask for 5 minutes in order to expel the air from the apparatus (stopper A is open, stopper B is shut) Fig. 1. Then three necked Pyrex flask is heated by an electrical heater and sodium is melted. The vapor of silicon tetrachloride is passed over the molten sodium which is stirred at a proper speed by an electrical device (stopper A is shut, stopper B is open). A vigorous redox reaction takes place.

$$4Na + SiCl_4 \longrightarrow 4NaCl + Si$$

The temperature of flask is controlled by a thermometer. The excess of volatile silicon tetrachloride is refluxed by a special condenser containing ice-salt mixture or best cardise (solid CO_2) and acetone mixture. The reaction is completed in 15–20 minutes. The stream of nitrogen is stopped and flask is cooled and the reaction product is taken out. The product is powdered in a mortar and left for 2-3 hours in order to oxidize the excess of sodium in the air. To use other mean are not suitable to oxidize sodium. After this period of time the raw product, is introduced gradually into 10 % HCl acid solution. Product is filtered and washed by distilled water and then is put in a mixture of 1 ml 47 % HF and 0,5 ml of concentrated sulfuric acid in a nickel crucible. The product is mixed by a nickel spatula, for 30 minutes in order to remove trace amounts of silicon dioxide as silicon tetrafluoride. 2–3 ml of water is added to the mixture and then filtered off. Product is washed with distilled water and then dried at 110 °C in an oven A crystalin dark blue product is obtained. The temperature of the flask is kept roughly constant. Table–1 shows the results of the experiments at different temperatures. As observed from the table the yield increases by raising the temperature. But has a limit as 310 °C. Beyond this temperature flask is not resistable to the molten sodium. The stream of carrier nitrogen gas is kept constant by counting bubles per minute, through wash bottle.

When glass flask is replaced by a copper flask similar to those glass one, yield is increased by raising the temperature over 310 °C. But the products are contaminated by copper. The method seems to be stille more hopeful and fruitful, if a special flask, made of an appropriate metal or alloy, is used.

The purity of the products obtained at different temperatures has been determined by spectrophotometrically converting products to blue silicomolybdic acid (reduced forme). For this, first of all, accurately weighed (at a semimicro balance) silicon is fused with sodium hydroxide in a platinum crucible then converted to the yellow silicomolybdic acid. Yellow silicomolybdic acid is redu-

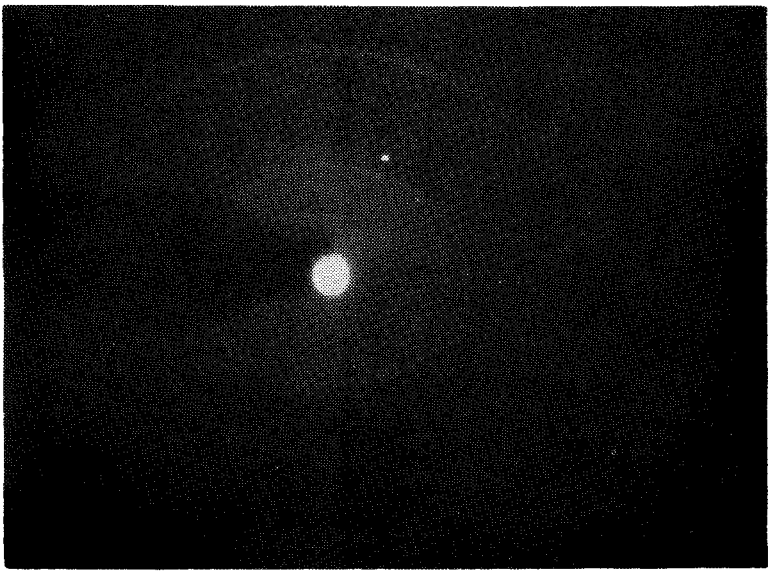

CaCl2
Refrig.
SiCl4
A
B
CaCl2
H2SO4
N2

ced by a solution of hydroquinone - bisulphite to blue water soluble silico - molybdic acid product. This product gives a strong absoprption band with a peak at 818 mμ wavelength [22]. For measurements, Beckman DU type UV and visible spectrophotometer was used.

TABLO: 1

Temperature of the flask (°C)	$SiCl_4$ (g)	Pure silicon (g)	Yield %
130	3,5	0,076	13
130	3,5	0,080	13
150	4	0,130	20
150	4	0,126	19
170	4	0,159	23
170	4	0,172	26
220	4	0,285	43
220	4	0,280	42
250	4	0,320	48
250	4	0,322	48
310	4	0,343	52
310	4	0,352	53

Examination of sample with x-ray (Dept. of physics. Faculty of science-Ankara) has shown that sample is crystalline, Fig 2.



Silicon tetrachloride has been obtained by passing dry chlorine over the mixture of coke and silica. If chlorine is passed over the mixture heated to 900–1000 °C, which is heated first 1600 °C and then cooled and ground, the yield is increased from 20 % to 40 % in respect to silica. Silicon tetrachloride is purified by refluxing liquid first with sodium, and then making fractional distillation (boiling point 57 °C).

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ÖZET

Bu çalışmayla, silisyum tetroklorürün yaklaşık 310 °C de sodyumla indirgeip % 99,9 saflıkta silisyum elde edilebileceği gösterilmiştir. İndirgeme için gerekli olan saf ve kuru silisyum tetraklorür silisten yapılmış bir boruda 900–1000 °C ye ısıtılmış kok ve silis karışımı üzerinden saf ve kuru klor gazı geçirmekle elde edilmiştir.

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