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# RECYCLING OF SILICA DUST – BYPRODUCTS FOR SI-SEMICONDUCTOR INDUSTRY

Beneficiation process has been developed to provide selective separation of silica dust material. This material is produced from the furnaces of silicon metal and ferrosilicon and considered to be of little or even of no value material. Cyclone classification of original sample,  $90\% - 15 \mu m$  in size, followed by froth flotation using cheap local collectors was carried out to remove the unburned and the iron contaminants. Dewatering tests were also carried out for the diluted pulp concentrate. A simple flowsheet has been suggested to produce bright silica fine product exceeded 99.5% SiO<sub>2</sub>, from starting material with 95.5%.

### INTRODUCTION

For the past twenty years, silicon has been the central core material sustaining the semiconductor industry worldwide. It is expected to continue in that role into the next century (Cunningham 1993). Silicon metal and ferrosilicon are produced by the reduction of silica (SiO<sub>2</sub>) to silicon (Si) in a submerged arc electric furnace. A typical charge consists of silica as beneficiated quartz or quartzite; coal, coke or charcoal as a reductant; wood ships for porosity and when producing ferrosilicon, iron in the form of steel scrap or iron ore.

Silicon metal and ferrosilicon furnaces produce a material that is referred to as silica dust, silica fume or microsilica. Originally, this material was considered as a byproduct of little or no value. However, as a matter of fact, the byproduct is not only a waste of a source but is also costly in terms of paying for dumping in landfill sites. Silica dust is now used as an additive in a number of different products, including high-strength concrete.

The Egyptian Ferrosilicon Company used silica deposit, in the Eastern Desert, and iron scrap in the production of ferrosilicon. Output (byproduct) is around  $20 \cdot 10^6$  kg of silica dust annually. The target of this research is to recycle waste silica dust into commercially valuable product. This will reduce the dependence on mining and lead to a new generation of material supply.

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#### EXPERIMENTAL

### Materials

Silica dust waste sample, weighing about 50 kg, was kindly supplied from the Egyptian Ferroalloys Company in Edfu. The sample was very fine in size and grey in colour. Commercial kerosene and analar grade pine oil 'Cynamid' as frothing agents. Locally produced dodecyl benzene-sulphonic acid and quaternary ammonium salt produced from Misr Petroleum Company as petroleum byproduct. Rice bran oil was supplied by the Egyptian Extractive Oil Company. Commercial grade  $H_2SO_4$  and NaOH were used as pH regulators. Commercial grade sodium silicate was also used.

#### **Experimental techniques**

Chemical as well as particle size analyses were carried out for the silica dust sample. Cyclosizer of 'Warman' type was used for the particle size analyses. Microscopic investigation of the thin sections and XRD of the original sample were also conducted.

The original sample was prepared for beneficiation processes via size degradation and classification stages. The sample was vigorously attritioned in 'Denver' attritioner of  $50 \cdot 10^{-3}$  m<sup>-3</sup> capacity, 0.28 m·0.28 m 2-cell, with two motors each of 11 W. The sample was attritioned at 50% solid for 30 min at speed of 700 rpm. No dispersing agent was required, where it showed complete dispersion at natural pH (7.5–8). The attritioned slurry was delivered after dilution to 20% solids, to 'Mozley' 2" hydrocyclone (C107X4). The cyclone was adjusted at inlet pressure of 14.63 · 10<sup>-3</sup> kg·m<sup>-2</sup> and vortex finder of 14 mm to obtain the required  $d_{50}$  cut point. The classification was repeated twice to obtain clean overflow –10 µm product. The cyclone underflow +10 µm, rejected fraction, was collected, dried, weighed and analysed. The classified –10 µm product was transferred at the same pulp density (20% solids ) to 5 · 10<sup>-3</sup> m<sup>3</sup> 'Denver' flotation cell.

For the sedimentation tests, the sample was homogenized by a mechanical blender. The pulp sample was placed in a standard 100 cm<sup>3</sup> graduated glass cylinder with a stopper (Kuskin and Nebera 1966). The pH was adjusted and the contents of the cylinder were mixed by inversion (5 times) for 15 seconds, and then were allowed to settle. The height of the interface of the settled pulp was recorded against the settling time in minutes (Kuskin and Nebera 1966). Brightness measures (GE Meter-% MgO) was determined using brightness meter (Tappi 1973).

### **RESULTS AND DISCUSSION**

### Sample characterization

Table 1 shows the size analysis of the original sample which reveals its fineness, where about 81% by weight is less than 5  $\mu$ m and 0.82% by weight only is higher than

44  $\mu$ m. Sample chemical analysis is depicted in Table 2. It has a relatively low silica content (95.5% SiO<sub>2</sub>) as filler compound. It is contaminated with traces amounts of Fe<sub>2</sub>O<sub>3</sub>, CaO, MgO, and Al<sub>2</sub>O<sub>3</sub> reaching 0.5%, 0.21%, 0.33%, and 1.16%, respectively. The loss of ignition is measured indicating the unburned carbon content is of 1.8%.

Size, µm	Yield, %	Cummulative, wt. %
+44 -44+33 -33+25 -25+15 -15+10 -10+5	0.82 0.47 0.59 0.82 6.66 9.96	0.82 1.29 1.88 2.70 9.36 18.98
-5	81.02	100

Table 1. Size analysis of the otiginal silica dust sample

Table 2. Comlete chemical analysis of the original silica dust sample

Constituent	wt.%
SiO <sub>2</sub>	95.5
Fe <sub>2</sub> O <sub>3</sub>	0.5
$Al_2O_3$	1.16
CaO	0.21
MgO	0.33
Na <sub>2</sub> O	0.30
K <sub>2</sub> O	0.60
С	1.80

### **Flotation feed preparation**

The sample was cycloned to remove the  $+10 \mu m$  fraction which was found to contain most of the iron content and little amount of carbon contaminants as is shown from its chemical analysis, Table 3. The  $-10 \mu m$  fraction was subjected to flotation cell to remove the remained carbon and iron.

### Silica dust beneficiation

A double circuit flotation process was suggested for the separation of both carbon and iron contaminants from the classified silica dust sample. The first circuit was a reverse flotation circuit for carbon separation, (Sablik and Pawlik 1986, Vanangam et al. 1989). For iron removal two options were tested. These include direct flotation, using local cationic reagent for silica separation. The other option is the reverse anionic flotation for iron removal. The results of both techniques were about comparable. This technology will allow us to transform the silica dust from a waste by-product into a Si-semiconductor source.

### A. Carbon separation circuit

The unburned carbon is separated from the classified  $-10 \ \mu m$  silica dust slurry by adding a frothing agent (pine oil,  $0.5 \ \text{kg} \cdot 10^{-3} \ \text{kg}$ ) and an effective amount of kerosene oil,  $2 \ \text{kg}/10^3 \ \text{kg}$  (Tondu et al. 1996, Groppo et al. 1996). The pH of the slurry was between 8.5–9. The kerosene coats the unburned carbon grains forming a hydrophobic film. Controlled air is introduced into the system for frothing the pulp mixture. The hydrophobic unburned carbon froths to the surface and is removed by skimming off the frothing layer. The flotation retention time was relatively long (20 min).

A concentrate product with 0.89% C was obtained which was directed to the second flotation circuit, Table 3.

Fraction	Yield, %	SiO <sub>2</sub> ,%	Fe <sub>2</sub> O <sub>3</sub> , %	С, %
Hydrocyclone under flow	6.16	86.46	5.75	2.39
Hydrocyclone over flow				
Carbon flotation circuit tail	3.28	85.10	1.97	25.73
Carbon flotation circuit concentrate	90.56	96.49	0.087	0.89
Original	100	95.50	0.50	1.80

Table 3. Chemical analysis of classified and carbon flotation circuit products

#### **B.** Iron separation circuit

For the direct flotation of silica, a local quaternary ammonium salt  $(0.2 \text{ kg/}10^3 \text{ kg})$  was used, (Abdel Khalek et al. 1994). The pH of the pulp was maintained at the same pH of the first circuit, pH (8.5–9) which is a privilege for the process.

On the other hand, the reverse flotation of iron contaminants was treated using local anionic sulphonate reagent. It is a locally produced dodecyl benzenesulphonic acid blended with rice bran oil/kerosene suspension in the ratio 1 : 0.5 : 0.5, (Abdel Khalek et al. 1994). The oil acts as a foam regulator as well as a collector due to its fatty acid content, (Abdel Khalek et al. 1994). The consumed dose of the reagent mixture was 2 kg/10<sup>3</sup>kg. Sodium silicate (2 kg/10<sup>3</sup> kg) was added as bulk depressant to the fine silica. The pH of the pulp was adjusted at pH 2–3. This was a drawback if compared to the cationic circuit where the pH was unchanged.

Table 4 depicts the chemical analysis of the final concentrates of two processes. The cationic circuit concentrate assays 99.52% SiO<sub>2</sub>, 0.002% Fe<sub>2</sub>O<sub>3</sub>, and 0.031% C

with a recovery 75.09%, was obtained from a feed sample contains 95.50% SiO<sub>2</sub>, 0.50% Fe<sub>2</sub>O<sub>3</sub>, and 1.80% C. The final step involves collecting concentrated fraction of the silica which was subjected to dewatering process.

Process	Yield	$SiO_2$	Fe <sub>2</sub> O <sub>3</sub>		С	
	[%]	[%]	[%]	Dist. [%]	[%]	Dist. [%]
Cationic flotation						
Concentrate	75.09	99.52	0.002	1.91	0.031	0.87
Tail	15.47	81.54	0.500	98.09	5.10	99.13
Calculated Head	90.56	96.45	0.087	100	0.90	100
Feed	90.56	96.49	0.087	100	0.89	100
Anionic flotation						
Concentrate	80.2	99.32	0.0017	1.73	0.03	3.37
Tail	10.36	74.58	0.750	98.27	7.50	96.63
Calculated Head	90.56	96.52	0.087	100	0.88	100
Feed	90.56	96.49	0.087	100	0.89	100

Table 4. Iron removal from classified silica dust sample

### Dewatering and product handling

The prospects of dealing with large quantities of diluted slurries containing very fine particles seem at first to be daunting. However, it was found that the dewatering characteristics of silica fines concentrate were not what was expected for material in this size range. Thickening tests were conducted on the beneficiated pulp. This product was found as a very stable dispersed pulp (20% solids) of pH 8.5–9. Gravitational free settling technique at various solution pH and solid/liquid ratio was used in these tests.

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pH	Settling time to obtain 40% solids
1.4	stable dispersed pulp
4	stable dispersed pulp
6	stable dispersed pulp
10	20 hours

5 hours

> 12.5

Table 5. The effect of pH on the settling behaviour of 5% solids silica fines

Table 5 presents the effect of pH on the settling behaviour of silica fines slurry. It is appeared that the settling behaviour of silica fines is obviously affected by pH variation. It was noticed that a stable aqueous suspension of silica fines was attained at pH < 10 where the solid particles acquire a negatively charged hydration film. This was due to the presence of charged cationic surfactant species adsorbed on silica particles. In addition, it is seen that the silica particles fines settled from 2% solid by weight to 40% solids after about 20 hr at pH = 10. The settling time decreases sharply to



Fig.1. Settling rates of silica fines at different solid, %

only 5 minutes as the pH was raised to 12.5–13. At these high pH's value (12.5–13), the OH<sup>-</sup> ions neutralize the positive charge of the nitrogen atom of the amine collector adsorbed on the surface of the silica particles, forming a neutral adsorbed molecules. The presence of such neutral molecules lower the critical hemi-micelle concentration, (Kuzkin et al. 1965). However, the principal function of these neutral molecules is to lower the electrostatic energy of repulsion between adjacent charged ionic polar groups of the collector enhancing hemi-micelle formation within the stern plane. This will result in gathering the hydrocarbon chain present on the silica particles surfaces. The silica particles will then tend to flocculate (Kuzkin et al. 1965).

The pulp solid content affects the rate of settling since it determines the number of interparticle collisions (Rabah, Ahmed Yehia 1992). In addition, the rate at which aggregates form is proportional to the square of the concentration of the particles. Figure 1 shows that the increasing in the solid percentage from 5% to 20% solids leads to decreasing the settling rate linearly. This behaviour can partially be related to the change in the pulp viscosity. The settling velocity decreases with increasing the viscosity of a pulp raising its density. However, the silica fines concentrate of about 20% solids reached 88% solid after about 20 hour when the pH of the medium was adjusted above 12.5. The product is then dried for shipment to its respective markets.

#### Evaluation and uses of the end product

Figure 2 illustrates the tentative beneficiation flowsheet to recycle the silica dust wastes. The final concentrate assays 99.52% SiO<sub>2</sub>, 0.002% Fe<sub>2</sub>O<sub>3</sub>, and 0.031% C with a recovery of 75.09% weight percentage. This was obtained from a feed sample content 95.5% SiO<sub>2</sub>, 0.50% Fe<sub>2</sub>O<sub>3</sub>, and 1.8% C. Calcination of this product was carried out at 873 K and 1273 K for 2 hours to improve the particle size distribution, besides its brightness. Table 6 illustrates the whiteness measures of the products.





Table 6. The whiteness measures of the silica fines

Product	Whiteness degree
Original	41.0
Concentrate	86.0
Concentrate (873 K)	94.0

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The purity as well as the highly inertness character of the bright silica fines could elect it as a light weight component in a wide variety of product. Modified silica ingradient offer superior resistance to corrosion, they are often used in corrosion protection systems, such as the lining of pumps used in the chemical industry. When the application involve contact with moisture, for instance, when it is exposed to the elements, silica commonly treated with a silane coupling agent (Hanson 1995). Silica treated in such a fashion is commonly employed in cycloaliphatic epoxy resins which is used as a high voltage insulation material. In electrical application, silane coated silica flour offers an improvement in flexural strength, surface smoothness, resistance to ultraviolet radiation and better tracking resistance as a result of less smoothing after flashover (Hanson 1995).

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**Yehia A., Ibrahim S. S.,** Odzysk py<sup>3</sup>u krzemionkowego – pó<sup>3</sup>produktu dla przemys<sup>3</sup>u pó<sup>3</sup>przewodników krzemowych. *Fizykochemiczne Problemy Mineralurgii*, 31, 267–274 (w jêz. angielskim)

Opisano proces oczyszczania pyłu krzemionkowego powstającego w piecach łukowych podczas produkcji krzemu i żelazokrzemu, który uważany jest za bezwartościowy materiał odpadowy. W celu wydzielenia 90% materiału w klasie –15 mikrometrów zastosowano klasyfikację w cyklonach. Następnie, aby usunąć z krzemionki składniki nie spalone oraz zanieczyszczenia żelazem, zastosowano flotację pianową, wykorzystując tanie lokalne kolektory flotacyjne. Przeprowadzono również testy odwadniania rozcieńczonej zawiesiny koncentratu flotacyjnego. Podano schemat wzbogacania badanej

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odpadowej krzemionki, w wyniku którego otrzymuje się wybielony pył krzemionkowy, zawierający powyżej 99,5% SiO<sub>2</sub> (wobec 95,5% SiO<sub>2</sub> w materiale wyjściowym).