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## Upgrading and Surface Coating of Egyptian White Sand with Polymers and Silanes

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Original scientific paper



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#### Abstract

Egypt is endowed with huge reserves of filler minerals, such as silica sand which form approximately 95% of the Earth's crust. The silica sand industry is used in many fields, such as pharmaceutical practices, chemicals, glass, ceramics, electronics, and photovoltaic industries. The aim of this study is to remove impurities from silica sand and apply surface modification processes to enhance its value for various industrial manufacturing applications. Various processing techniques, including classification, attrition scrubbing, magnetic separation, ultra-fine grinding and surface modification, were conducted throughout the study. The results indicated that attrition scrubbing to the classified size fraction of -0.6 + 0.1 mm was capable of reducing the iron concentration from 0.068% to 0.045%. Utilizing the Box-Behnken design, the optimal conditions for magnetic separation were identified, resulting in a decrease in iron content down to 0.012%. Simultaneously, the silica content increased from 99.05% to 99.76%. The results of ultrafine grinding using an attritor mill revealed that a grinding time of 2 hours is sufficient to reach a size suitable for the coating process. Surface modification of the produced ultrafine sand was conducted using polymers and silanes. The treated sand was characterized using SEM, zeta potential, adsorption density, and FTIR measurements. Notably, hydrophobicity increased, accompanied by an increase in particle size. Simultaneously, the surface becomes flatter, indicating the formation of a thin layer. Consequently, the coated sand proved to be a satisfactory material that met the criteria to be used as a filler in coating and paints.

#### **Keywords:**

white sand; RER magnetic separation; surface modifications; polymers; silane

### 1. Introduction

The demand for white sand resources has significantly increased, particularly in recent years, due to their widespread use as non-metallic minerals in numerous industrial applications. While silica sand deposits are present in almost every country globally, those with high purity are limited to a few specific locations (**Al-Abady**, **2022**).

Egypt is regarded to have some of the best white sands globally, a huge gold mine of white sand. Egypt has an estimated 20 billion tonnes of white sand strategically distributed along the Red Sea coast, South Sinai, and the Eastern Desert (**Hasanien et al., 2023**).

Silica sand serves as the main source of silicon, a naturally occurring material that forms the basis for an extensive variety of modern technologies. It plays a crucial role in the production of solar cells and electronic chips, essential components at the core of the substantial technological advancements that moved the world into the twenty-first century (Wahab et al., 2022; Vatalis et al., 2015). As a result, researchers should pay greater attention to white sand, which is a strategic gem that has not been fully utilized.

Coated silica sand plays a crucial role in enhancing the quality and durability of paints and coatings. Its utilization in paint manufacturing not only enhances the overall look and durability of the paint but also contributes to improvements in tint reduction and resistance against dirt. **Ibrahim et al (2016)** investigated the possibility of using high purity silica sand (99.8% SiO<sub>2</sub>) to produce high grade unique sodium silicate appropriate for use in a corrosion and abrasion resistant coating. When applied to steel surfaces, the excellent stability and hardness of the generated sodium silicate provided a good protective layer.

**Gaber et al (2012)** conducted a study utilizing pure silica sand sourced from the Eastern Desert of Egypt for the production of an anticorrosive primer paint. The re-

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search involved the production of ultrafine silica powder (less than 35 um) through the grinding of natural white sand deposits. Incorporating this powder as a filler at 7% in the paint resulted in excellent corrosion resistance, coupled with high hiding power and opacity.

Wei et al (2023) tested a new type of high-performance coated sand designed as a petroleum fracturing proppant material. Modified quartz sand, coated with a layer of low-density resin, was employed to reduce the overall density of the proppant. This strategic modification aimed to enhance the suspension of the proppant in fracturing fluid, also contributed to improved efficiency in hydraulic fracturing processes.

The application of coated silica sand is contingent upon its mineral composition, chemical and physical characteristics. It is primarily utilized in the production of glass and glass fibers, silicon carbide, sodium silicate, Portland cement, silicon alloys, and various metals. Additionally, it also used in water treatment, sandpaper, foundry sand, hydraulic fracturing, sandblasting, paint, and a variety of other applications (Vatalis et al., 2015; Ilyas, R. A., et al., 2022; Ramadan et al., 2023).

Egypt possesses substantial reserves of filler minerals, including high-grade materials such as calcium carbonate (limestone and calcite) and silica sand, as highlighted by Ibrahim et al. (2017). Various researchers have studied the characterization of these sand deposits, but limited work has been conducted on the purification and beneficiation process (Manel et al., 2016; Ibrahim et al., 2017; Sochea et al., 2020; Ibrahim et al., 2022). Magnetic separation is one of the most efficient physical methods for removing iron-bearing minerals from silica sand (Abdullah, 2023). During the mid-90s, significant advancements occurred in magnetic separation processes, utilizing neodymium-iron-boron rare earth magnet materials. This resulted in the development of the Rare Earth Roll Separator (RER), which focused on the dry processing of non-metallic minerals like feldspar and silica sands.

A novel polymeric system has been employed to modify sandy soils that are typically non-compactable. Soil reinforcement techniques are commonly used in geotechnical engineering. While traditional stabilizers like lime offer several advantages for enhancing soil strength, they often raise the pH level of the soil, potentially causing environmental issues, such as groundwater pollution or hindering vegetation growth (**Abbawi et al., 2015**). In recent years, non-traditional chemical additives like liquid polymers, enzymes, ions, and lignin derivatives have been investigated (**Hassan et al., 2020**; **Shrivastava et al., 2016**).

Polymeric materials, as non-traditional soil stabilizers, have been developed to enhance the physical and engineering properties of soil to meet the requirements of various engineering applications (**Wang et al., 2023**).

The current study aims to optimize the parameters of magnetic separators to improve the productivity of a

silica sand sample, particularly by enhancing the separation of iron-bearing contaminants. Statistical experimental design methodologies will be utilized. Additionally, the study will explore the ultrafine grinding of sand and the surface modification of sand using polymers and silanes to produce a product with specifications suitable for various industrial applications, such as a filler in coating and paints.

#### 2. Materials and methods

#### 2.1. Materials

A sample of white sand (99.0 %) was delivered from the Sinai area. The sample was ground dry in a porcelain mill and wet in an attritor mill to reach a size suitable for the coating process. Polyethylene oxide (PEO) and silane were purchased from Aldrich Co. Analytical-grade NaOH and HCl were used for pH regulation.

#### 2.2. Methods

#### 2.2.1. Sample preparation and attrition scrubbing:

The preparation process involved screening on 0.6and 0.1-mm screens. The size fractions larger than 0.6 mm and smaller than 0.1 mm were eliminated, and the remainder was cleaned using a "Denver" attrition scrubbing machine. The unit consists of two stainless steel opposed pitch turbine-type propellers, a stainless steel shaft and a shaft collar. The attrition was carried out to detach clay minerals and dust-coated silica particles that improve the chemical and physical characteristics of silica samples. Effective parameters, such as time, pulp density, and temperature, were studied. Then, wet screening was performed on a 0.1-mm sieve, where the size fraction less than 0.1 mm was rejected. The remainder was subjected to magnetic separation.

#### 2.2.2. Magnetic separation

The washed sand was fed to an Eriez Rare Earth roll (RER) magnetic separator to remove iron-bearing particles. Optimizing the magnetic separator parameters for better productivity of a silica sand sample, i.e. to separate iron-bearing contaminants, was carried out using the statistical Box-Behnken design of experiments under different conditions of splitter inclination angle, belt speed, and feed rate.

#### 2.2.3. Milling with an attritor mill

Milling with an attritor mill: A laboratory attrition mill "Union Process Attrition Mill Model 1S" was used for wet grinding of upgraded white sand. It contained a 9.5-liter stainless steel vessel with a unique rubber lining. Along with it was a stainless-steel shaft with five stainless steel arms. A 3 HP motor drove the shaft via a belt. The tank was jacketed for cooling and included a bottom discharge valve and a bar grid. Approximately 2.5 kg of a representative sample was mixed with 4 L of water containing 5 kg of 4 mm alumina balls, and it was then ground wet for various amounts of time. The preferred size for the process of surface modification of white sand is less than 10 microns (Guzzo et al., 2020; Hussain 2021; Blanc et al., 2020).

### 2.2.4. Surface coating of fine upgraded white sand

Surface coating of fine upgraded white sand: The rheological and physical properties of white sand particles were investigated using different concentrations of polymers, such as polyethylene oxide and silane.

## 2.3. Characterization of untreated and treated samples

### 2.3.1. Surface Characterization

The selected samples were observed on the fractured surface under a JSM6400 scanning electron microscope (SEM) to examine the morphology of the mineral before and after treatment with polymers and silane.

## 2.3.2. Particle Size Distribution

A laser particle size analyzer Fritsch model Analystte was used to determine the size of the samples before and after treatment.

### 2.3.3. FTIR Measurements

Infrared absorption spectra were recorded for white sand and polyethylene oxide (PEO) using a Fourier transform infrared spectrometer (Model FT/IR 6300). Samples were thoroughly washed with double-distilled water and vacuum dried. The KBr pellet technique was used to record the spectra. The difference spectrum was obtained by subtracting the spectrum of the untreated particles from that of the interacted minerals (**Mourad et al., 2022**).

### 2.3.4. Chemical Analysis

Routine chemical analysis was conducted using standard methods. L.O.I. was determined by the gravimetric method. Complete chemical analysis was conducted using Philips X-ray fluorescence (XRF), and XRD was conducted using Philips X-ray diffraction.

### 2.3.5. Adsorption Measurements

In adsorption experiments, 0.5 g of sample was added to 50 ml double distilled water at the required concentra-

tion of dispersing agent or polymer. After conditioning the pulp to equilibrium time, the samples were centrifuged at 15,000 rpm for 15 minutes to separate the supernatant from the settled fraction. The total organic carbon (TOC) content (residual concentration) in 40 ml of the supernatant was determined using a "Phoenix 8000" Total Carbon Analyzer (**Mourad et al., 2022**).

## 2.3.6. Surface Modification of white Sand using PEO

One gram of ultra-fine sand (less than 10  $\mu$ m in size) was added to 100 ml of a polyethylene oxide solution (500 mg/L). The latter was mixed using a magnetic stirrer at 2000 rpm and at pH » 3 for different time. The remainder of the polyethylene oxide in the supernatant after mixing was determined. So, the adsorption capacity of sand was calculated in mg polyethylene oxide per gram of sand.

## 2.3.7. Surface Modification of white Sand using Silane

Different concentrations of silane were prepared in an ethanol solution to hydrolyze it sufficiently. The volume proportion of alcohol and water was 2:1. Then, the sand sample was added into the silane solution. The system was mixed at 75°C using a water bath for 15 min. The product was immersed in deionized water for 24 h and then it is washed several times with deionized water to eliminate the influence of physical adsorbed silane. The modified sample was filtered and dried at 110°C.

## 3. Results and discussion

## 3.1. Characterization of the original sand sample

The representative sand sample is mainly composed of silica and this is confirmed by the chemical analysis (XRF), which indicated that the sample contains about 99.05 % SiO<sub>2</sub> with a small amount of iron (0.068% Fe<sub>2</sub>O<sub>3</sub>) (see **Table 1**).

## 3.2. Upgrading of the white sand sample

### 3.2.1. Attrition scrubbing

To remove the ferruginous clayey layer from the sand, attrition scrubbing was carried out in the fraction size (-0.6+0.1 mm) after separation of the coarse size (+0.6 mm) and fine size (-0.1 mm) fractions. Scrubbing causes scratching and rubbing of the particle surface and thus removes surface impurities.

Table 1: Chemica	l analysis of the	original white sand
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Item	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	V <sub>2</sub> O <sub>5</sub>	Cr <sub>2</sub> O <sub>3</sub>	L.O.I
Original Sand	99.05	0.185	0.24	0.068	0.045	0.04	0.024	0.033	0.089	0.084	0.140



**Figure 1:** Effect of pulp density on the cleaning of sand at 30 min and room temperature



**Figure 2:** Effect of time on the attrition scrubbing of white sand at pulp density 60% and room temperature



Figure 3: Effect of temperature on attrition scrubbing of white sand at pulp density 60% and time 60 min

Figure 1 depicts the effect of pulp density on sand cleaning. It was found that a high solid pulp density (60%) resulted in the highest removal of both aluminum and iron oxides. This is due to the efficient collisions between the particles and the paddles (Haghi et al., 2008; Ibrahim et al. 2013).

An increase in scrubbing time can provide a gradual improvement of sand grade (**Hickin and Huntley 2011**). **Figure 2** shows the results of iron and aluminium oxides content over time. These studies show the gradual decrease in iron and alumina oxides content with an increase in scrubbing time. Both aluminum oxide grade and recovery were reduced down to 0.125% and 66% respectively at 60 min. Also, the iron content was gradually reduced from 0.068 to about 0.050%, and then was almost constant after 60 min. However, it was noticed that there was no remarkable improvement by increasing the attrition time to 60 minutes. It is indicated that 60 min is sufficient for surface cleaning (**Ibrahim et al. 2013**).

**Figure 3** shows the effect of the scrubbing temperature on the sand cleaning at an attrition time of 60 min and 60% pulp density. Both the aluminum oxide grade and recovery were reduced down to 0.0.085% and 44.68% respectively with an increasing temperature up to 353 K, (80°C). Also, the iron content was reduced down to 0.045% with a recovery of 64.5% at 353 K. It is indicated that the efficient collision between the particles and the paddles is enhanced at a higher temperature (**Buttress et al., 2019**).

The white sand quality was improved during the attrition scrubbing process and a product containing 99.35% SiO<sub>2</sub> with a recovery of 97.97% was obtained at 60% pulp density, an attrition time of 60 min and a temperature of 353 K, (80°C) (see **Table 4**). The clay content (represented by Al<sub>2</sub>O<sub>3</sub>%) was reduced to 0.085%, which is acceptable for various sand applications (**Ibrahim et al. 2013**; **Othman et al., 2023**). However, the iron oxide content, which was reduced to 0.045%, needs further removal, to lower than 0.02%, to be accessible for advanced sand applications (**Ibrahim et al. 2013**). This could be achieved using the magnetic separation process.

#### 3.2.2. RER magnetic separation

The magnetic separation technique is applied on scrubbed white sand in order to reduce the iron content. The Box-Behnken design was used to optimize the magnetic separation using an RER magnetic separator and to estimate the interaction between different variables, as can be seen in **Table 2**.

The optimum conditions were evaluated with a second order polynomial function to conduct a correlation between studied variables, splitter inclination, belt speed and feed rate, and responses,  $SiO_2$  and  $Fe_2O_3$  grade and recovery.

ANOVA data for the beneficiation system implies the well convenience of the experimental results to the polynomial model equation and thus the accuracy of this model, as can be seen in **Table 3**. The model F-values indicate the model is significant. The Adequate Precision ratios prove an adequate signal (**Hassan et al., 2020**).

**Figures 4** to 7 show the assay and recovery of  $SiO_2$  and  $Fe_2O_3$  respectively as a function of RER separator parameters. It is displayed that high splitter inclination is recom-

Table 2: RER magnetic separator factor levels

Symbol	Parameter	Unit	(-)	(0)	(+)
А	Inclination angle	degree	80.00	85.00	90.00
В	Belt speed	rpm	60.00	80.00	100.00
С	Feed rate	kg/hr	5.00	32.50	60.00

The statistical parameters		SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>		
The statistical parameters	Assay%	Recovery %	Assay%	Recovery %	
Standard deviation	0.012	1.25	0.001	1.03	
R-Squared	0.979	0.954	0.994	0.981	
Adequate precision	18.22	10.39	36.16	19.20	
F-value	36.54	19.45	136.51	39.34	

Table 3: ANOVA for of RER magnetic separator



Figure 4: The response surface plots a and b of SiO2% resulting from the main effects of RER magnetic separation; inclination angle, belt speed, and feed rate.



Figure 5: The response surface plots a and b of SiO2 recovery % resulting from the main effects of RER magnetic separation; inclination angle, belt speed, and feed rate.

mended for the efficient separation of non-magnetic  $\text{SiO}_2$  from the paramagnetic  $\text{Fe}_2\text{O}_3$ . Therefore, increasing the splitter inclination up to 87.65 degrees increased both grade and recovery of  $\text{SiO}_2$  (see **Figures 4** and **5**) while decreased both grade and recovery of  $\text{Fe}_2\text{O}_3$  (see **Figures 6** and **7**). An additional increase in inclination angle to maximum values, from 88 to 90 degrees, is not recommended as it resulted in the highest  $\text{SiO}_2$  recovery values (see **Figure 4b**) but it had a reverse effect on the  $\text{SiO}_2$  grade values (see **Figure 4a**).

High  $SiO_2$  grade and recovery were obtained at low feed rate values. A monolayer of sand particles is preferred for efficient separation. Hence, increasing the feed rate affected the distribution of the magnetic and nonmagnetic particles and resulted in a multi-layer on the belt and hence reduced the separation efficiency.

Increasing belt speed up to moderate values (84 rpm) improved the separation of  $SiO_2$  from  $Fe_2O_3$ . However, at belt speeds higher than 84 rpm, the centrifugal forces may overcome the magnetic forces resulting in low beneficiation efficiency of both  $SiO_2$  grade and recovery values. **Figures 4b** and **5b** display the interaction between feed rate and belt speed variables. At low feed rates, a high belt speed is recommended for efficient separation while at high feed rate, moderate belt speed values showed more efficiency.



Figure 6: The response surface plots a and b of Fe2O3% resulting from the main effects of RER magnetic separation; inclination angle, belt speed, and feed rate.



Figure 7: The response surface plots a and b of Fe2O3 recovery % resulting from the main effects of RER magnetic separation; inclination angle, belt speed, and feed rate.

The best parameters of the Box-Behnken design of white sand beneficiation using an RER magnetic separator are: 87.65 degrees splitter inclination, 84.0 rpm belt speed and 5.0kg/hr feed rate. With these optimum parameters, a non-magnetic white sand concentrate containing 99.76% SiO<sub>2</sub> and 0.012% Fe<sub>2</sub>O<sub>3</sub> was obtained with an operational recovery of 88.26 and 25.65% respectively (see **Figure 8a-c** and **Table 4**).

#### 3.3. Ultrafine grinding of upgraded white sand

The nonmagnetic white sand concentrate of 99.76%  $SiO_2$ , 0.012%  $Fe_2O_3$  and 0.086%  $Al_2O_3$  was subjected to ultrafine grinding as a preparation step for the coating process. The ultrafine grinding of the upgraded white sand was achieved using an attritor mill. The process of grinding was carried out at 1000 rpm for different times ranging from (1 to 3hr) and it was noticed that at 2 hr, the particle size decreased sharply because sand has a high hardness, and so it needs more time to reach the required size. **Figure 9** and **Table 5** show the size distribution at different times (**El-Mofty et al., 2020; Agus et al., 2012; Danilov et al., 2021**). The ground product has a particle size of  $d_{90}$ . 7.8 µm and  $d_{50}$ . 2.90 µm, which is suitable for coating tests.

#### 3.4. Surface modifications

Surface modification tests were conducted on the ground product of the attritor mill. This product has a particle size of  $d_{90}$ . 7.8 µm and  $d_{50}$ . 2.90 µm, two surface modifiers were used: polyethylene oxide and silane.

## 3.4.1. Surface modification using Polyethylene oxide (PEO):

**Rubio, J. (1981)** found that polyethylene oxide is an effective flocculent in minerals such as quartz. The present work focuses on the adsorption behaviour of polyethylene oxide on sand. The parameters affecting the efficiency of the adsorption process as an effect of concentration of PEO, and the effect of conditioning time were studied. Also, the zeta potential, which is considered the most important factor for determining the success of the coating process, was measured before and after the treatment of white sand with PEO.

#### 3.4.1.1. Effect of the PEO concentration

Polyethylene oxide can be used as a selective flocculant for quartz. The adsorption density of PEO onto a



Figure 8: RER Optimization of the white sand; a) Desirability, b) Fe2O3%, and c) Fe2O3 recovery%.

Item	Original Sand	Scrubbed sand	Non-magnetic sand concentrate
SiO <sub>2</sub>	99.05	99.35	99.76
Al <sub>2</sub> O <sub>3</sub>	0.1855	0.085	0.086
CaO	0.24	0.023	0.01
Fe <sub>2</sub> O <sub>3</sub>	0.068	0.045	0.012
MgO	0.045	0.025	0.0035
Na <sub>2</sub> O	0.04	0.032	0.03
K <sub>2</sub> O	0.024	0.023	0.01
P <sub>2</sub> O <sub>5</sub>	0.033	0.035	0.005
V <sub>2</sub> O <sub>5</sub>	0.089	0.088	0.008
Cr <sub>2</sub> O <sub>3</sub>	0.084	0.085	0.008
L.O.I	0.14	0.138	0.075

**Table 4:** Chemical analysis of the original white sand, scrubbed sand and the non-magnetic sand concentrate

silica surface was increased gradually with an increase in the polymer concentration up to a certain concentration and after that, it almost reaches stability, as shown in **Figure 10**. Adsorption of a non-ionic polymer PEO



Figure 9: Effect of grinding time on size distribution

Time, hour	d <sub>50</sub> (μm)	d <sub>90</sub> (μm)
1.0	15.01	51.82
2.0	2.90	7.80
2.5	2.37	7.65
3.0	2.30	4.52



Figure 12: Zeta potential of white sand treated with PEO

onto silica usually occurs through hydrogen bonding between the ether oxygen of PEO and binding sites (surface hydroxyls) on the solid surface (**Rubio and Kitchener, 1976; Mathur, 1991**).

The high PEO concentration maintained a thick adsorption layer. At a low concentration of PEO, adsorption is expected to be uniform. This led to the formation of a thin adsorption layer, which was accompanied by a change in the zeta potential of sand ore where the charge surface of pure silica is negative at a pH range of 2-12, as shown in **Figure 11**. After treatment with the PEO polymer, the positivity increases with an increasing concentration at pH 3, as can be seen in Figure 12 (Liu et al., 2019).

#### 3.4.1.2. Effect of the coating time with PEO

The effect of time on the adsorption of polyethylene oxide on the sand surface was studied. It showed that the adsorption increases with an increase in time up to 60 min, as shown in **Figure 13**. The effect of stirring time showed that the highest rate of polymer adsorption takes place at 60 min. The experiments were performed using a concentration of 500 mg/l (**Liu et al., 2019**).



Figure 13: Effect of stirring time on the adsorption rate

## 3.4.1.3. Characteristics of the sand coated with PEO

Through the application of a PEO coating, the surface chemistry of the sand undergoes modification, imparting specific properties such as heightened durability, chemical resistance, and UV resistance. Furthermore, the coating renders the sand particles more hydrophobic, minimizing water absorption - an especially valuable feature in applications where water resistance is a priority.

The physical properties of sand were affected after coating with PEO as displayed by measuring the water and oil absorption rates (see **Table 6**). This result is achieved by using PEO at the surface of the sand. It is showed that the hydrophobicity of the sand is enhanced after treatment with PEO.

**Table 6:** Effect of PEO concentration on the physical properties of the sand sample

Dronorty	PEO %					
Toperty	0.00	3.00	6.00			
Oil absorption, %	25.00	10.50	0.90			
Water absorption, %	27.85	13.20	0.75			

The SEM images (see **Figure 14**) of the ground upgraded sand sample revealed its inherent features and surface characteristics. Before surface modification with



**Figure 14:** SEM micro-graphs of sand sample before (a) and after (b) surface modification with PEO

polyethylene oxide (PEO), the untreated sand exhibited a deformed structure. It is displayed that before treatment, the sand surface was distorted and heterogeneous (see Figure 15a).

Following the adsorption of PEO on the ground upgraded sand, the SEM images highlighted a distinct transformation in the sand's surface morphology. The presence of PEO was manifesting as a coating in the sand particle arrangement. After treatment with PEO, a layer of polyethylene oxide grafted on the surface of the sand and aggregated the particles which lead to a homogeneous and smooth surface (see **Figure 14b**). The surface modification with PEO may have enhanced its stability or altered the adhesion characteristics.

#### 3.4.2. Surface modification using silane

The molecular formula of the silane modifier and its chemical changes during hydrolysis are shown in **Figure 15**. During hydrolysis of the silane, the  $\text{SiOC}_2\text{H}_5$  group will transform into SiOH. The surface modification mechanism could be carried through in the mode given in **Figure 15**. In general, one SiOH of the silane coupling agent reacts with the hydroxyl groups of the quartz sand surface and forms a covalent bond, and two other SiOH molecules either have a condensation reaction with SiOH of another silane coupling agent or end up being free state (**Wei et al., 2013**), thus it is possible to form a hydrogen bond in the interface simultaneously.



Therefore, the group was grafted on the sand surface through a chemical bond (Li et al., 2008).

## 3.4.2.1. Effect of silane concentration

As shown in **Figures 16** and **17**, it was found that by increasing the concentration of silane, the particle size of sand increased, which indicated success of the coating of silane on the sand surface. This was confirmed by studying the adsorption density of the silane on the silica surface, which showed that by increasing the silane concentration, the adsorption density increased until it reached equilibrium at a concentration of 9%, with the experiments being carried out at 70°C for a conditioning time of 15 min (**Liu et al., 2019**).



Figure 16: Effect of silane concentration on the size distribution



Figure 17: Effect of different concentration of silane on the adsorption density of sand

#### 3.4.2.2. Effect of the coating time with silane

The effect of conditioning time was carried out up to 30 min. Figure 18 shows the results, which indicated that time is an important parameter for an efficient coating process and thus affects the particle size of the product (Liu et al., 2019).

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Figure 18: Effect of conditioning time on the size distribution

## 3.4.2.3. Characteristics of the sand coated with silane

The results proved that the physical properties of sand were affected after being treated with silane, as shown in **Table 7**. It was shown by measuring the water and oil absorption rates. This result is attributed to the presence of silane at the sand surface and more directly to the hydrophobic nature of the silane. From the above results, it could be concluded that the hydrophobicity of the sand is greatly improved by surface modification with silane.

 Table 7: Effect of silane concentration on the physical properties of the sand sample

Dronorty	Silane %				
Toperty	0.0	3.0	6.0		
Oil absorption, %	25.0	8.0	0.3		
Water absorption, %	27.85	9.0	0.4		

The FTIR spectra of the sand before and after modification with silane are shown in **Figure 19**. The spectrum of silane shows absorption peaks at 3459, 2958 and 1577 cm<sup>-1</sup> which correspond to an asymmetry stretching vibration, a symmetry stretching vibration and a deformation vibration of C-H, respectively. The spectrum of unmodified sand shows the peaks at 3755 and 1086 cm<sup>-1</sup> are characteristic of Si-OH. This indicates the presence of -OH functional groups on the surface of the sand. The spectrum of modified sand shows the absorption peaks at 3441, 2956 and 1081 cm<sup>-1</sup> represent the C-Si-O and Si-O-Si bonds. The asymmetry stretching vibration and deformation vibration of Si-O-Si were located at 777, 1081 and 693 cm<sup>-1</sup>, which demonstrates that silane exists in the sand surface.

Moreover, the physically adsorbed silane and reaction byproducts of the sand were washed with deionized water several times during the surface modification pro-



Figure 19: FTIR spectra of silane (a) and white sand before (b) and after (c) modification with silane

cess, so the physical adsorption between the sand and silane could be eliminated.

The SEM images of the ultrafine upgraded sand sample provided a detailed view of its natural morphology, revealing its structures and surface features, as can be seen in **Figure 20**. Before surface modification with silane, the unaltered sand exhibited a characteristic texture and composition. Specifically, **Figure 20a** shows the extremely rough, uneven, and heterogeneous nature of the unmodified sand surface.

In contrast, the SEM images after silane treatment showcased a visibly altered surface, indicating successful modification. The modified sand surface possessed a comparatively flatter surface (see **Figure 20b**) due to a thin layer of silane grafted on the surface of the sand. The silane coating is expected to introduce new properties, such as improved water repellence or enhanced adhesion, depending on the specific silane used. These comparative SEM images served as valuable visual evidence of the structural changes induced by the surface modification process, offering insight into the efficacy of the silane treatment on the sand particles.

The SEM images showed the strong adsorption of silane on the silica surface even rather than that of PEO and revealed the impact of silane on the sand's microstructure which provided valuable insight into the success of the surface modification process.



Figure 20: SEM micro-graphs of sand sample before (a) and after (b) surface modification with silane

	Original and		Specifications (%)				Possible	
No.	produced sand products	Upgrading processes	Particle size dist.	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO + MgO	industrial applications
1	Original sand	Classification	-6 +1 mm	99.05	0.068	0.185	0.285	Flat and container glass
2	Scrubbed sand	Classification and attrition scrubbing	-6 +1 mm	99.35	0.045	0.085	0.048	Domestic and decorative glassware
3	Nonmagnetic sand concentrate	Classification, attrition scrubbing and magnetic separation	6 +1 mm	99.76	0.012	0.086	0.0135	Optical glassware
4	Ultrafine upgraded sand	Classification, attrition scrubbing, magnetic separation and ultrafine grinding	d <sub>90:</sub> 7.8 μm, d <sub>50:</sub> 2.9 μm	99.76	0.012	0.086	0.0135	Plastics and rubber
5	Coated ultrafine upgraded sand	Classification, attrition scrubbing, magnetic separation, ultrafine grinding and coating (PEO / Silane)	d <sub>90:</sub> 7.8 μm, d <sub>50:</sub> 2.9 μm	99.76	0.012	0.086	0.0135	Filler in coating and paints

Table 8: The possible industrial applications for the original sand and the silica sand products obtained during this study

## 3.5. The possible industrial applications for the original sand and the obtained silica sand products

The original silica sand sample could be used in flat and container glass. However, after upgrading processes, it could be used in more advanced industrial applications based on their specifications, maximum  $\text{SiO}_2^{\,\%}$  and minimum Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO and MgO% with the particle size distribution, as shown in **Table 8** (**Wypych**, **2016; Ibrahim et al., 2016; Camara et al., 2020; Ilyas et al., 2022**).

The scrubbed silica sand product is suitable to be used in the manufacturing of domestic and decorative glassware while the nonmagnetic silica sand product is suitable to be used in the manufacturing of optical glassware (**Othman et al., 2023; Ezz El Din et al., 2016**).

The ultrafine upgraded silica sand of particle size distribution  $d_{90}$ :7.8 µm and  $d_{50}$ : 2.9 µm can be used in plastics and rubber (**Wypych**, **2016**). When coated with polyethylene oxide and silane, the ultrafine upgraded silica sand could be used as a filler in coating and paints (**Wypych**, **2016**).

#### 4. Conclusions

Throughout this study, many processing techniques, including classification, attrition scrubbing, magnetic separation, ultra-fine grinding, and surface modification, were conducted to upgrade a Sinai white sand sample of about 99.05 % SiO<sub>2</sub> and 0.068% Fe<sub>2</sub>O<sub>3</sub>. The attrition scrubbing of the sand sample with 60% pulp density for 60 min at 353 K reduced the aluminium and iron oxides content to 0.085 and 0.045% respectively. This product

is suitable to be used in the manufacturing of domestic and decorative glassware.

The RER magnetic separation of white sand was evaluated using the Box-Behnken design. The optimum parameters were a 87.65 degree splitter inclination, 84.0 rpm belt speed and 5.0kg/hr feed rate, with which a nonmagnetic concentrate containing 99.76% SiO<sub>2</sub> and 0.012% Fe<sub>2</sub>O<sub>3</sub> was obtained with an operational recovery of 88.26 and 25.65% respectively. The produced nonmagnetic silica sand concentrate is suitable to be used in the manufacturing of optical glassware.

The ultrafine grinding process of the upgraded sand was carried out by an attritor mill and it was found that 2 hours is enough time to obtain a size suitable for the coating process.

Polyethylene oxide (PEO) and silanes were used as selective modifying agents for silica. (PEO) adsorption onto silica occurs in an acidic medium through hydrogen bonding, and adsorption density increased with an increase in (PEO) concentration at a time up to 30 min.

Silane compound adhered to the sand surface through chemical bonds, and the adsorption density was increased by increasing the concentration until saturation which occurs at 9% of silane. Thus, the hydrophobicity of the sand is greatly improved. This was confirmed by SEM images, which showed that the modified sand surface possesses a flatter surface due to a thin layer of silane. The coated ultrafine white sand product could be used as a filler in coating and paints.

### 5. References

Abbawi, Z. W. and AL-Soudany, K. Y. (2015): Studying strength and stiffness characteristics of sand stabilized with cement and lime additives. Engineering and Technology Journal, 33(8),1857-1875. doi: 10.30684/etj.2015. 108828

- Abdullah, W. R. (2023): Improving Silica Sand Specifications for Making Colorless Glasses by Using Chemical and Physical Methods. Solid State Phenomena, 341, 77-85.
- Agus, W., Teguh, N. and Siti, R. (2012): Preparation Of Nanoparticle Silica From Silica Sand and Quartzite By Ultrafine Grinding. In Proceeding of Int. Conference, 28,1-7. https:// www.researchgate.net/publication/320805881
- Al-Abady, A. (2022): Characterization and potential upgrading of El-Zaafarana White Sand by Attrition scrubbing. J Univ Shanghai Sci Technol. 24(4), 79-90.
- Blanc, N., Mayer-Laigle, C., Frank, X., Radjai, F. and Delenne, J. Y. (2020): Evolution of grinding energy and particle size during dry ball-milling of silica sand. Powder Technology, 376,661-667. https://doi.org/10.1016/j.powtec.2020.08.048
- Buttress, A. J., Rodriguez, J. M., Ure, A., Ferrari, R. S., Dodds, C. and Kingman, S. W. (2019): Production of high purity silica by microfluidic-inclusion fracture using microwave pre-treatment. Minerals Engineering. 131, 407-419. https://doi.org/10.1016/j.mineng.2018.11.025
- Camara, A. S., Lütke, S. F., Pinheiro, C. P., Vieira, M. L. G., Sant'Anna Cadaval, T. R. and de Almeida Pinto, L. A. (2020): Chitosan-coated sand and its application in a fixedbed column to remove dyes in simple, binary, and real systems. Environmental Science and Pollution Research, 27, 37938-37945. https://doi.org/10.1007/s11356-020-09924-5
- Danilov, O. S., Taskin, A. V. and Elkin, O. I. (2021): Investigation of the Influence of Ultrafine Grinding and Ultrasonic Field on the Intensification of the Processes of Extraction of Iron Oxides from Ash and Slag Waste of Energy. In IOP Conference Series: Earth and Environmental Science. 666 (2), 022074. IOP Publishing. http://dx.doi.org/ 10.1088/ 1755-1315/666/2/022074
- Edem, C. A., Malu, S. P. and Ita, B. I. (2014): Characterization and beneficiation of the glass making potentials of silica sand deposit from River Benue North Central Nigeria. Journal of Natural Sciences Research, 4(19), 49-58.
- El-Mofty, S. E., Elbendari, A. M., Abuhasel, K. A. and El-Midany, A. A. (2020): Ultrafine dry grinding of talc by planetary mill: Effects of operating conditions. Obogashchenie Rud, (6), 21-25. https://doi.org/10.17580/or. 2020.06.04
- Ezz El Din, M., Abouzeid, A. M., El maadawy, Kh., Khalid, A.M. and El Sherif, R. E. (2016): Mineral Industry in Egypt– Part II Non Metallic Commodities – Silica Ores. Journal of Mining World Express (MWE), 5, 9-27. doi: 10.14355/mwe.2016.05.002
- Gaber, M. A. W. (2012): Evaluation of some natural ores from Egyptian eastern desert to be utilized in producing of paint materials. Journal of Petroleum and Gas Exploration Research, 2(1), 017-026.
- Guzzo, P. L., de Barros, F. B. M., Soares, B. R. and Santos, J. B. (2020). Evaluation of particle size reduction and agglomeration in dry grinding of natural quartz in a planetary ball mill. Powder Technology, 368, 149-159. http://dx.doi. org/10.1016/j.powtec.2020.04.052

- Haghi, H., Noaparast, M. and Ghorbani, A. (2008): Reduction of iron content from silica sand by scrubbing process. In Proceedings of the 11<sup>th</sup> Int. Mineral Processing Symposium, Belek-Antalya, Turkey, 2123, 259265. http://dx.doi. org/ 10.13140/2.1.4005.3447
- Hassan, El-Sayed R. E., Mutelet, F., Abdel-Khalek, N. A., Youssef, M. A., Abdallah, M. M. and El-Menshawy, A. H. (2020): Beneficiation and separation of Egyptian tantalite ore. In Key Engineering Materials, Trans Tech Publications Ltd. 835, 208-213. https://doi.org/10.4028/www.scientific.net/KEM.835.208.
- Hasanien, Y. A., Mosleh, M. A., Abdel-Razek, A. S., El-Sayyad, G. S., El-Hakim, E. H. and Borai, E. H. (2023): Green synthesis of SiO<sub>2</sub> nanoparticles from Egyptian white sand using submerged and solid-state culture of fungi. Biomass Conversion and Biorefinery, 1-14. http://doi:10.1007/ s13399-023-04586-y
- Hickin, A. S. and Huntley, D. H. (2011): Attrition experiments for the beneficiation of unconsolidated sand sources of potential hydraulic fracture sand, northeastern British Columbia; in Geoscience Reports, BC Ministry of Energy and Mines, 75-85.
- Hussain, Z. (2021): Comparative study on improving the ball mill process parameters influencing on the synthesis of ultrafine silica sand: a Taguchi coupled optimization technique. International Journal of Precision Engineering and Manufacturing, 22(4),679-688. http://dx.doi.org/10.1007/ s12541-021-00492-3
- Ibrahim, A. F., Seifelnassr, A. A., Al-Abady, A., El-Salmawy, M. S. and Abdelaal, A. M. (2022): Characterization and Iron Removal Enhancement of El-Zaafarana White Sand, Mining, Metallurgy & Exploration, 39(5), 2187-2198.
- Ibrahim, G. E. A., Mousa, A. S., El-Hariri, T. Y. M., Hassnien, I. M. and Zakzouk, N. I. (2016): New industrial use of Egyptian white sands from Wadi El-Dakhl Area, Eastern Desert, Egypt. Int J Innov Sci Eng Technol, 3(1), 216-525.
- Ibrahim S. S., Farahat M. M. and Boulos T. R. (2017): Optimizing the performance of the RER magnetic separator for upgrading silica sands. Particulate Science and Technology, 35(1), 21-28. http://dx.doi.org/10.1080/02726351.201 5.1121179.
- Ibrahim, S. S., Selim, A. Q. and Hagrass, A. (2013): Gravity separation of silica sands for value addition. Particulate Science and Technology, 31(6), 590-595. 10.1080/0272 6351.2013.800930.
- Ilyas, R. A., Izzat, M., Qusyairi, S. M., Sapuan, S. M., Atikah, M. S. N., Aisyah, H. A. and Ismail, H. (2022): Mineral-Filled Polymer Composites: Reliability, Challenges, Opportunities and Future Perspectives. Mineral-Filled Polymer Composites, 235-262.
- Li, H., Wang, R., Hu, H. and Liu, W. (2008): Surface modification of self-healing poly (urea-formaldehyde) microcapsules using silane-coupling agent. Applied Surface Science, 255(5),1894-1900. https://doi.org/10.1016/j.apsusc. 2008.06.170
- Liu, J., Cui, X., Santander, C., Tan, X., Liu, Q. and Zeng, H. (2019): Destabilization of fine solids suspended in oil media through wettability modification and water-assisted agglomeration. Fuel, 254,115623. https://doi.org/10.1016/j. fuel.2019.115623

- Manel, B. F., Gallala, W. and Saadi, A. (2016): Quartz sand beneficiation using magnetic and electrostatic separation to glass industries. Journal of New Technology and Materials, 6(1), 60-72.
- Mathur, V. K and Lasmarias, V. (1991): Supercalendered paper acid resistant calcium carbonate. In Proceedings from 1991 Papermakers Conference (pp. 331-339).
- Mourad, S. H., Abdel Rahman, M. K., AbdelL-Khalek, N. A., Sayed, S. A., Selim, K. A. and Salah, B. A. (2019): Upgrading of Egyptian talc ore for different industrial applications. Journal of Mineral, Metal and Material Engineering, 5, 38-50.
- Mourad, S. H., Khalil, M. M., Abdel-Khalek, N. A., Abdel-Khalek, M. A., Selim, K. A and Hassan, E. S. R. (2022): Influence of polymers on the grinding and rheology of ultrafine Egyptian calcium carbonate suspension. Physicochemical Problems of Mineral Processing, 58. https://doi. org/10.37190/ppmp/152163
- Othman, N., Mustaffar, M. I., Ismail, S. A., and Ibrahim, M. H. (2023): Upgrading silica rock quality by using attrition scrubbing and magnetic separation techniques. Materials Today: Proceedings. https://doi.org/10.1016/j.matpr.2023. 04.659.
- Ramadan, F., Essawy, M., Henaish, A. and El-Shafei, S. (2023): Evaluation of white sand deposits for industrial applications: a case study from Abu Zenima area, Sina, Egypt. Bulletin of Faculty of Science, Zagazig University, 2023(2), 42-57.
- Rubio, J. (1981). The flocculation properties of poly (ethylene oxide). Colloids and surfaces, 3(1), 79-95.
- Rubio, J. and Kitchener, J. A. (1976): The mechanism of adsorption of poly (ethylene oxide) flocculant on silica. Journal of Colloid and Interface Science, 57(1), 132-142 https://doi.org/10.1016/0021-9797(76)90182-X

- Shrivastava, A. K., Jain, D. and Vishwakarma, S. (2016): Frictional resistance of drilling fluids as a borehole stabilizer. International Journal of Geo-Engineering, 7, 1-15. http:// dx.doi.org/10.1186/s40703-016-0026-7
- Sochea, R., Somsak, S. and Numprasanthai, A. (2020): Study on beneficiation of silica sand by Wet High-Intensity Magnetic Separators (WHIMS) and reverse flotation technique for glass application: A case study from Sihanoukville, Cambodia. Warta Geologi. 46(3) 210-213.
- Vatalis, K. I., Charalambides, G. and Benetis, N. P. (2015): Market of high purity quartz innovative applications, Procedia Economics and Finance, 24, 734-742. https://doi. org/10.1016/S2212-5671(15)00688-7.
- Wahab, G. M., Ibrahim, G. E. D. A. and Wahab, A. A. A. (2022): Geological and engineering appraisal of hydraulic frac sand in some Egyptian localities as a proppant of oil well drilling. Heliyon, 8(8) e10233.
- Wang, T., Cao, W., Wang, Y., Qu, C., Xu, Y. and Li, H. (2023): Surface modification of quartz sand: A review of its progress and its effect on heavy metal adsorption. Ecotoxicology and Environmental Safety, 262,115179. https://doi. org/10.1016/j.ecoenv.2023.115179
- Wei, B., Chang, Q., Bao, C., Dai, L., Zhang, G. and Wu, F. (2013): Surface modification of filter medium particles with silane coupling agent KH550. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 434,276-280. https://doi.org/10.1016/j.colsurfa.2013.05.069.
- Wei, X., Wang, Y., Yang, T. and Song, Y. (2023): A Study on a new type of high-performance resin-coated sand for petroleum fracturing proppants. Coatings, 13(11), 1841.
- Wypych, G. (2016): Fillers Origin, Chemical Composition, Properties, and Morphology. Handbook of Fillers, 13–266 (page 209). doi:10.1016/b978-1-895198-91-1.50004-x

## SAŽETAK

# Nadogradnja i površinsko premazivanje egipatskoga bijelog pijeska polimerima i silanima

Egipat je obdaren golemim rezervama mineralnih punila kao što je silikatni pijesak koji čini približno 95 % Zemljine kore. Industrija silikatnoga pijeska koristi se u mnogim područjima kao što su farmaceutska industrija, kemijska industrija, industrija stakla, keramike, elektronike i fotonaponska industrija. Cilj je ovoga istraživanja ukloniti nečistoće iz silikatnoga pijeska i primijeniti procese površinske modifikacije kako bi se povećala njegova vrijednost za različite primjene u industrijskoj proizvodnji. U ovoj studiji provedene su različite tehnike obrade, uključujući klasifikaciju, struganje, magnetsku separaciju, ultrafino mljevenje i površinsku modifikaciju. Rezultati su pokazali da je struganje do klasificirane frakcije veličine od –0,6 + 0,1 mm moglo smanjiti koncentraciju željeza s 0,068 % na 0,045 %. Koristeći se tehnikom Box-Behnken, identificirani su optimalni uvjeti za magnetsku separaciju, što je rezultiralo smanjenjem sadržaj željeza do 0,012 %. Istodobno, sadržaj silicijeva dioksida povećao se s 99,05 % na 99,76 %. Rezultati ultrafinoga mljevenja pomoću mlina za mljevenje otkrili su da je vrijeme mljevenja od 2 sata dovoljno da se postigne veličina prikladna za postupak premazivanja. Površinska modifikacija proizvedenoga ultrafinog pijeska provedena je pomoću polimera i silana. Tretirani pijesak karakteriziran je pomoću SEM-a, zeta-potencijala, adsorpcijske gustoće i FTIR mjerenja. Posebno je povećana hidrofobnost, popraćena povećanjem veličine čestica. Istodobno, površina postaje ravnija, što upućuje na stvaranje tankoga sloja. Prema tome, premazani pijesak pokazao se kao zadovoljavajući materijal koji je zadovoljio kriterije za korištenje kao punilo u premazima i bojama.

#### Ključne riječi:

bijeli pijesak, RER magnetna separacija, površinske modifikacije, polimeri, silan

## Authors' contribution

K. E. Yassin (Associate professor of Mineral Processing at CMRDI) and A.M. Elbendari (Researcher of Mineral Processing at CMRDI) gathered rock samples and contributed in ultrafine grinding and characterization of samples. S.H. Mourad (Ph.D. Researcher) and El-Sayed R.E. Hassan (Associate professor of Mineral Processing at CMRDI) contributed in magnetic separation, ultrafine grinding and surface modifications, and evaluated the results. N.A. Abdel-Khalek (an Emeritus Professor of Mineral Processing at CMRDI), K.A. Selim (Professor of Mineral Processing and Dean of Minerals Technology Institute at CMRDI) and M.M.H. Khalil (Professor of Chemistry at University of Ain Shams) evaluated the results, reviewed the draft manuscript and provided technical suggestions. The entire work was written collaboratively by all of the authors.