Materials Research Proceedings **8** (2018) 105-114 doi: http://dx.doi.org/10.21741/9781945291999-12

Fe_2O_3 hematite quantity increase in quartz sand by heat treatments

Ana COTAI, Traian Florin MARINCA, Florin POPA*

Materials Science and Engineering Department, Technical University of Cluj-Napoca, 103-105, Muncii Avenue, 400641 Cluj-Napoca, Romania

ana.cotai@yahoo.com, Florin.POPA@stm.utcluj.ro, Traian.MARINCA@stm.utcluj.ro

Keywords: Quartz sand, Milled sand, Heat treatments, Hematite (Fe_2O_3)

Abstract. Heat treatments were performed on the quartz sand to increase the quantity of Fe_2O_3 hematite phase. The heat treatments were performed on the as-received sand samples. The heating temperatures were chosen in the range of 120-600 °C and the time durations in the range of 1-24 h. The sand phases evolution on the temperature was followed by differential scanning calorimetry (DSC). Identification of the phases was realized by X-ray diffraction. The modifications of the iron quantity and distribution in the sand particles were identified by Energy Dispersive X-ray Spectroscopy **(**EDX**)** analyses. An optimum temperature/time for the annealing was identified, leading to highest Fe_2O_3 content. Testes for magnetic separation were performed to validate the method.

Introduction

At present, there is a steady increase in demand for high purity quartz worldwide [1]. Quartz is used frequently in glass, ceramic and even in nano-industries [2]. Quartz sand is the most common type of sand in the nature [3]. It is used all over the world in different applications because of distinct physical characteristics, like hardness, chemical and heat resistance, also low cost [4]. Depending on the training mode and where it is found, it appears in different shapes and colors [1].

The silicon dioxide that is used to manufacture glass is extracted almost all from quartz sand, which must have over 97 % SiO_2 [5]. Usually, the quartz is colorless or white, but the presence of the impurities can change the color. The iron oxide – hematite phase (Fe_2O_3) is one of the most frequent impurity and depending of the composition concentration, the quartz can alter the color up to yellow [3]. The quality of the sand is as better as the quantity of the iron oxide is smaller.

Despite the importance of the sand, the utilization is limited by the quality of the material which contains harmful mineral inclusions. The presence of the impurities, especially iron oxide, limit the sand utilization for high quality glass manufacturing [5]. A big part of the impurities released can be reduced or eliminated by physical operations, such as size separation, spiral concentration, magnetic separation, etc. [6]. The iron oxide from the sand can be reduced also by physicochemical method [4].

The most ecological method to improve the quality of the sand is the magnetic separation method. The magnetic separation is used to decrease and stabilize the iron content [7]. If the method is not effective enough, efficiency can be increased by a thermic treatment, mechanical milling or a specific granulometric class removal. The experiments presented in reference [5], shows that magnetic separation method removes about 80,49 % of iron oxide from sand and decrease the Fe_2O_3 content from 0,41 % down to 0,08%.

Materials Research Proceedings **8** (2018) 105-114 doi: http://dx.doi.org/10.21741/9781945291999-12

A big part of the impurities presents in the quartz sand contain iron and they are finely dispersed and low magnetic. The special magnetic separators, characterized by high magnetic induction (> 0,6 T), are used to eliminate such impurities. Lately, there where fundamental changes on the separators, especially at the level of magnetic parts. The old magnetic separator systems where replaced by systems that are based on permanent magnets of iron-neodymium-boron type. Thus, this change improved the quantity of the sand and decreased the manufacture cost [8].

The present study is focused on the quartz sand evaluation regarding the iron content and its influence on the color and Fe_2O_3 phase content. Changes induced by annealing are considered and their effects on the Fe_2O_3 phase presence. Finally, a basic magnetic experiment is performed for evaluation of the proposed method efficiency.

Materials and Methods

The quartz sand (Cluj County, Romania) was used for all the experiments. Samples of quartz sands were heat treated at different annealing times from 1h up to 24h. For each test the required amount of samples were placed in a ceramic crucible heated in the furnace. Maximum temperatures of 120, 200, 300, 400, 500 and 600°C were considered. For the thermal treatments was used a programmable INDUSTRY furnace, in oxygen atmosphere.

The structural evolution of the samples was highlighted by X-ray diffraction (XRD) using the Cobalt Kα radiation (1.79026 Å) in an Inel Equinox 3000 powder diffractometer in the 2theta = 20-110° range. The occurring of transformation during the heating process were investigated by differential calorimetrical analysis (DSC) using Setaram Labsys equipment. The heating rate was 10 °C/min and the used atmosphere was argon gas. The morphology of the samples was investigated by the JEOL-JSM 5600 LV scanning electronic microscope (SEM) equipped with an EDX spectrometer (Oxford Instruments - INCA 200 software). The optical images were recorded using the optical microscope VisiScope TL384M (VWR) type at 40x magnification. The magnetic separation experiments were performed with a commercial NdFeB magnet.

Results and Discussions

The first effect of sand annealing was the sand colour change. The color of annealed samples for 24 h at various temperatures ranging from 120 °C up to 600 °C is presented in Fig. 1.

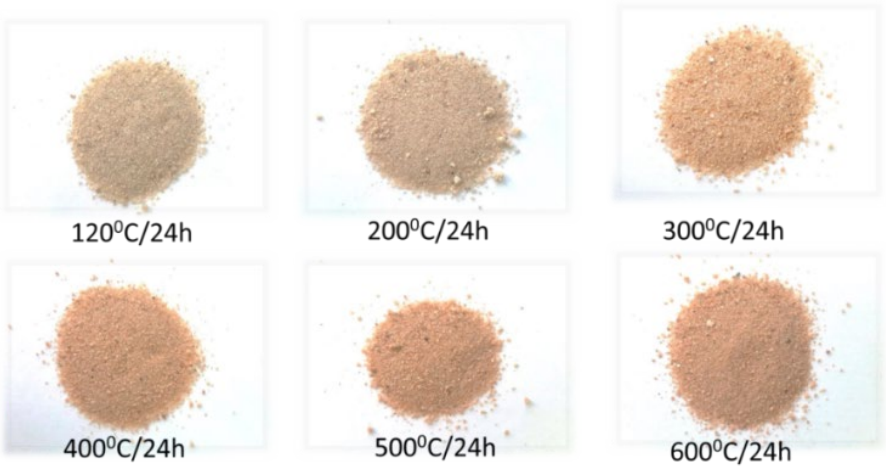
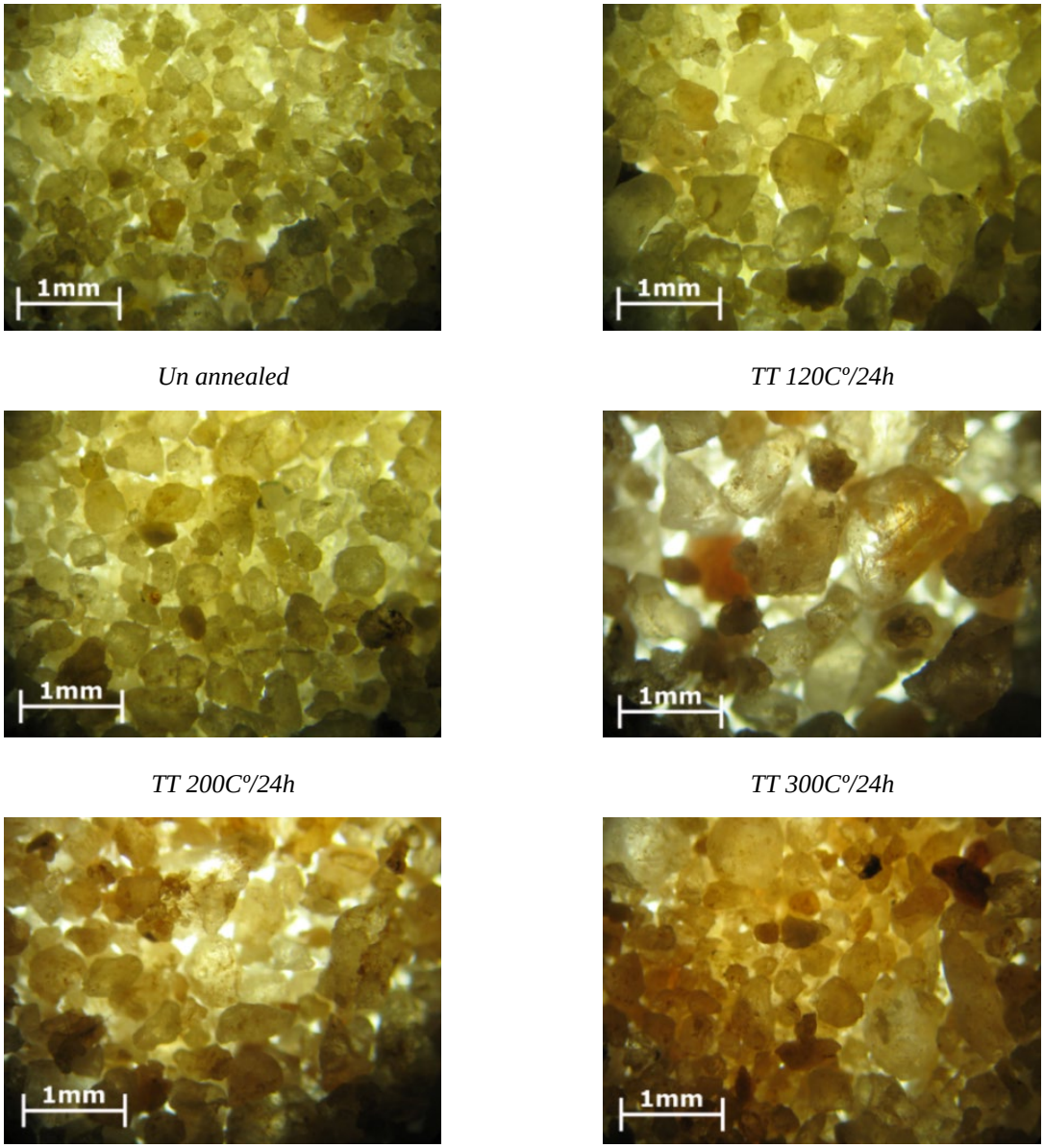


Fig.1. Color change observed in silica sand grains after heat treatment.

Materials Research Proceedings **8** (2018) 105-114 doi: http://dx.doi.org/10.21741/9781945291999-12

Fig. 1 shows a color change of the sand with the increase of the temperature from yellow to pink-orange. Similar color change upon annealing was observed in [9].

Color change with temperature rise suggests that changes occur in the crystalline structure or impurity phase of sand beyond loss of pores moisture content and dehydration of iron deposits [9]. At temperatures above 250-300 °C, the color changes correspond to the dehydration of the iron compounds as indicated in [10]. The samples observed by eye, were analyzed by optical microscopy, and the recorded images at a magnification of 40X are presented in Fig. 2 for the samples annealed for 24h at different temperatures and in Fig. 3 for samples annealed at 600 °C at different durations.



Un annealed *TT 120Cº/24h*

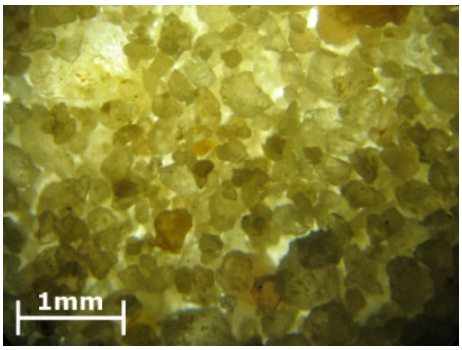
TT 200Cº/24h *TT 300Cº/24h*

TT 400Cº/24h *TT 600Cº/24h*

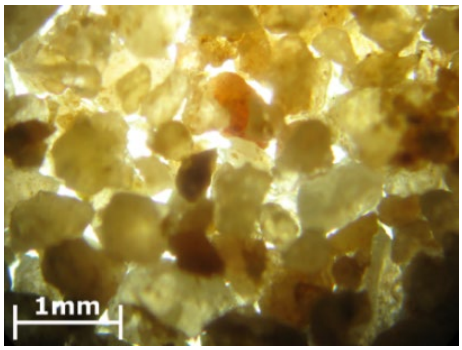
Fig. 2. Color change of grain sand with temperature rise during heat treatment (24h annealing time). Optical microscopy images, x40.

Materials Research Proceedings **8** (2018) 105-114 doi: http://dx.doi.org/10.21741/9781945291999-12

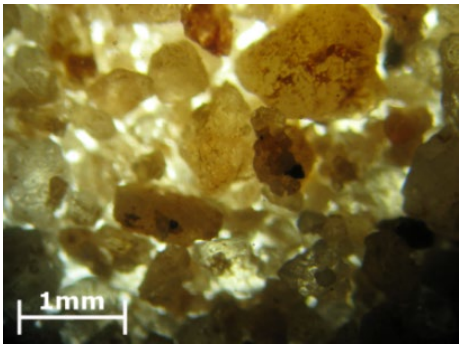
In the images presented in Figs. 2 and 3, it is observed a change in the color of the sand grains upon increasing temperature and annealing time. For samples treated at 600 ˚C is observed the most intense pink-orange color. The change of sand color to red suggests the formation of Fe_2O_3 in sand from additional iron phases. X-ray diffraction (Fig.4) confirm the appearance of the Fe_2O_3 phase. The color change is observed for samples heated more than 300 °C. For temperatures smaller than 300 °C no color change is recorded. Later in our discussion the occurrence of this color change for high temperature relates to calorimetric measurements and some structural changes upon heating.



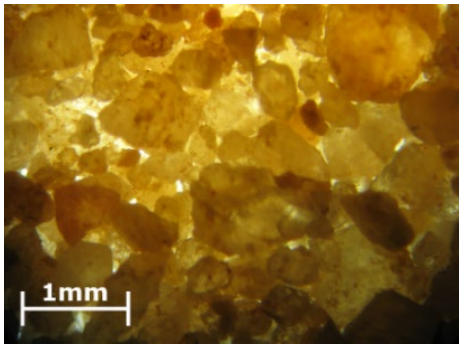
Un annealed



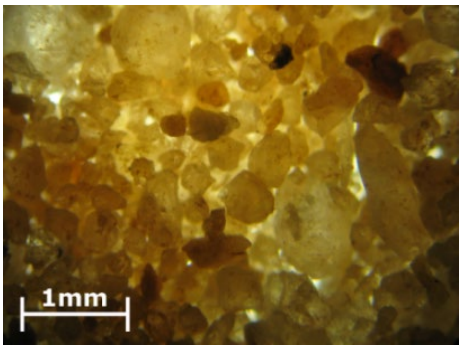
TT 600Cº/3h



TT 600Cº/6h



TT 600Cº/12h



TT 600Cº/24h

Fig. 3. Change in the color of sand grains depending on the annealing time at TT of 600 ˚C.

Materials Research Proceedings **8** (2018) 105-114 doi: http://dx.doi.org/10.21741/9781945291999-12

As concerning the annealing time, the color change is more visible after 12 h of heating as can be seen for the heat treatment at 600 °C (Fig. 3). Such behavior can be connected with the time needed for iron phase to transform under the temperature influence.

For confirming the possible structural changes in the quartz sand, X-ray diffraction studies were performed for samples annealed 24h at different temperatures, Fig. 4.

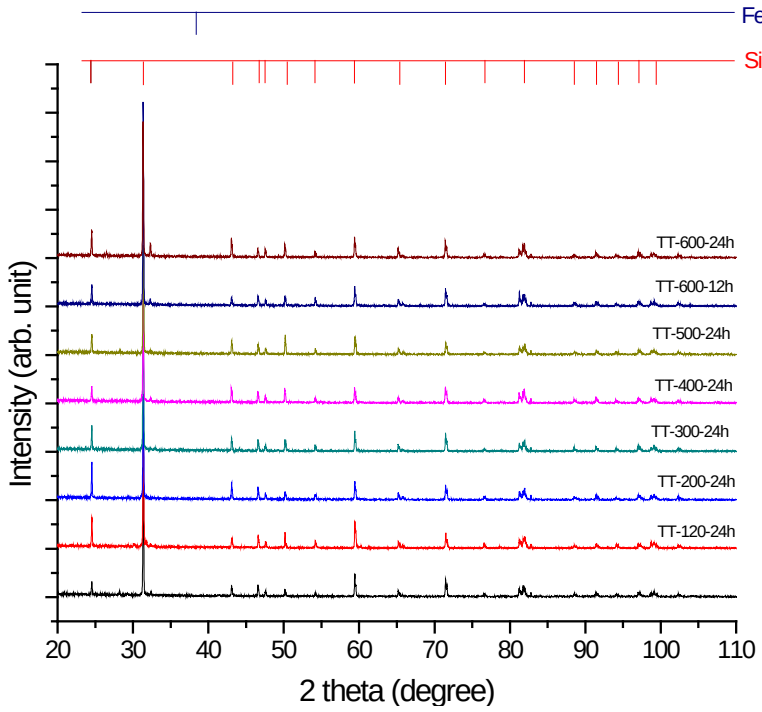


Fig.4. *X-ray diffraction of sand after heat treatments at different annealing temperatures for 24h.*

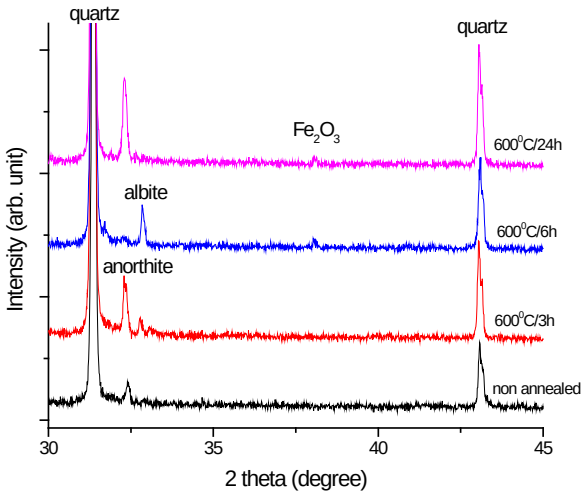


Fig.5a. *Detailed view of the Fe_2O_3 peaks*

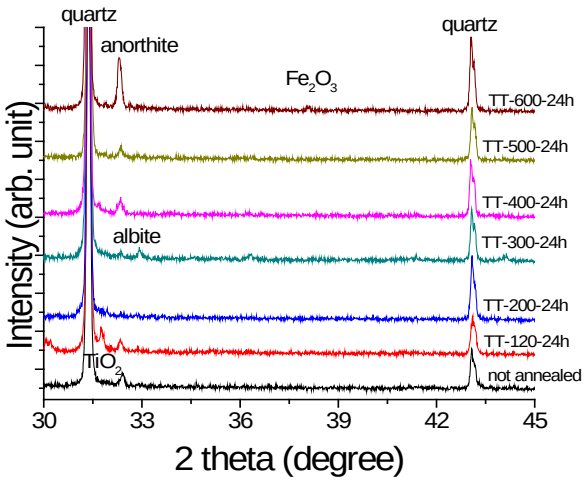


Fig.5b. *Detailed view of the Fe_2O_3 peaks*

Materials Research Proceedings **8** (2018) 105-114 doi: http://dx.doi.org/10.21741/9781945291999-12

The Fig. 4 shows that the main phase present in all diffractograms is quartz. X-ray diffraction patterns on sand heat treated at different temperatures show that both iron oxides and other silicon minerals phases changes when temperature rise. This affirmation is sustained by the pattern study in the angular range 30 – 45 ° (Fig. 5 a and b). Due to the presence of a small amount of iron (about 0.6%), the iron oxide signal is weak, but visible for samples annealed more than 6 h at 600 °C. The occurrence of the Fe_2O_3 peak is an indication of this phase quantity increase upon annealing in air.

The formation of iron oxide (Fe_2O_3) is highlighted in the samples treated at 600ºC (Fig. 5a) with a hold time longer than 6h at the 2theta diffraction angle of 38º. However, an analysis at smaller angles indicates the presence of other phases, as shown in Fig.5b. Concerning the annealing temperature, the Fe_2O_3 phase is visible only for the samples annealed at 600 °C. It is believed that at lower temperatures the iron phases receive less energy and is difficult to form Fe_2O_3 in large quantity. Other minor phases are, albite, and other complex phases containing Al, Si, K, Ca and O. To clarify the behavior in temperature, DSC experiments were carried out, and the results are shown in Fig. 6. In Fig. 6 are presented the DSC curves for the non-annealed sample and for a sample firstly annealed at 600 °C for 24h.

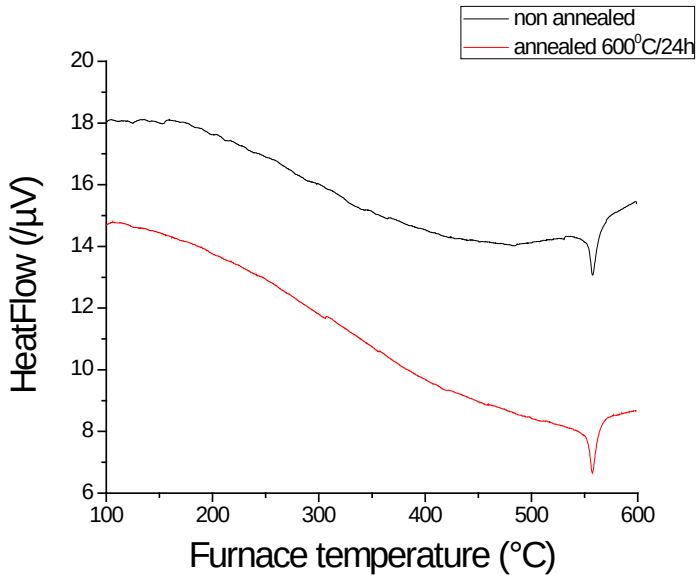


Fig. 6. DSC analysis of sand treated thermally for 24 hours. The heating was done at 600 °C.

In the DSC experiments an endothermic transformation peak is recorded at 575 °C. In order to explain this thermal event two hypothesis can be considered: (a) the presence of ferrimagnetic phase Fe_3O_4 magnetite which has the ferrimagnetic to paramagnetic transition at about this temperature; (b) the formation of FeO wüstite type phase by the reaction of the magnetite with the iron contained in the other phases in the sand or hematite Fe_2O_3 successive reduction. The reaction possibility is argued by the iron – oxygen phase diagram [11].

Materials Research Proceedings **8** (2018) 105-114 doi: http://dx.doi.org/10.21741/9781945291999-12

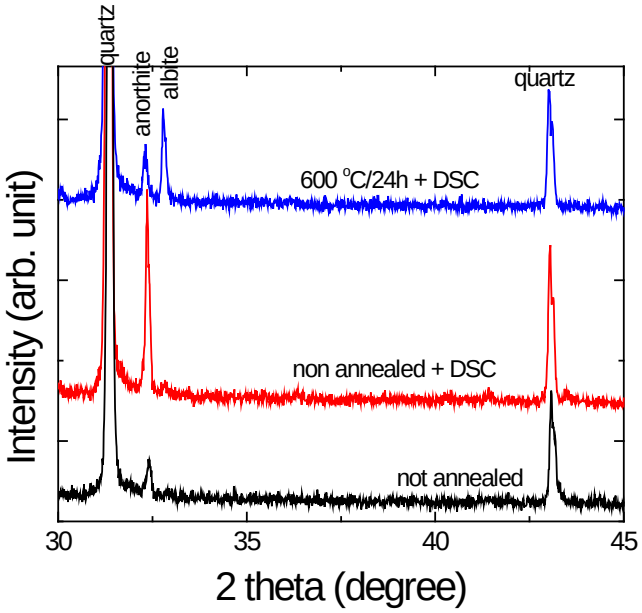
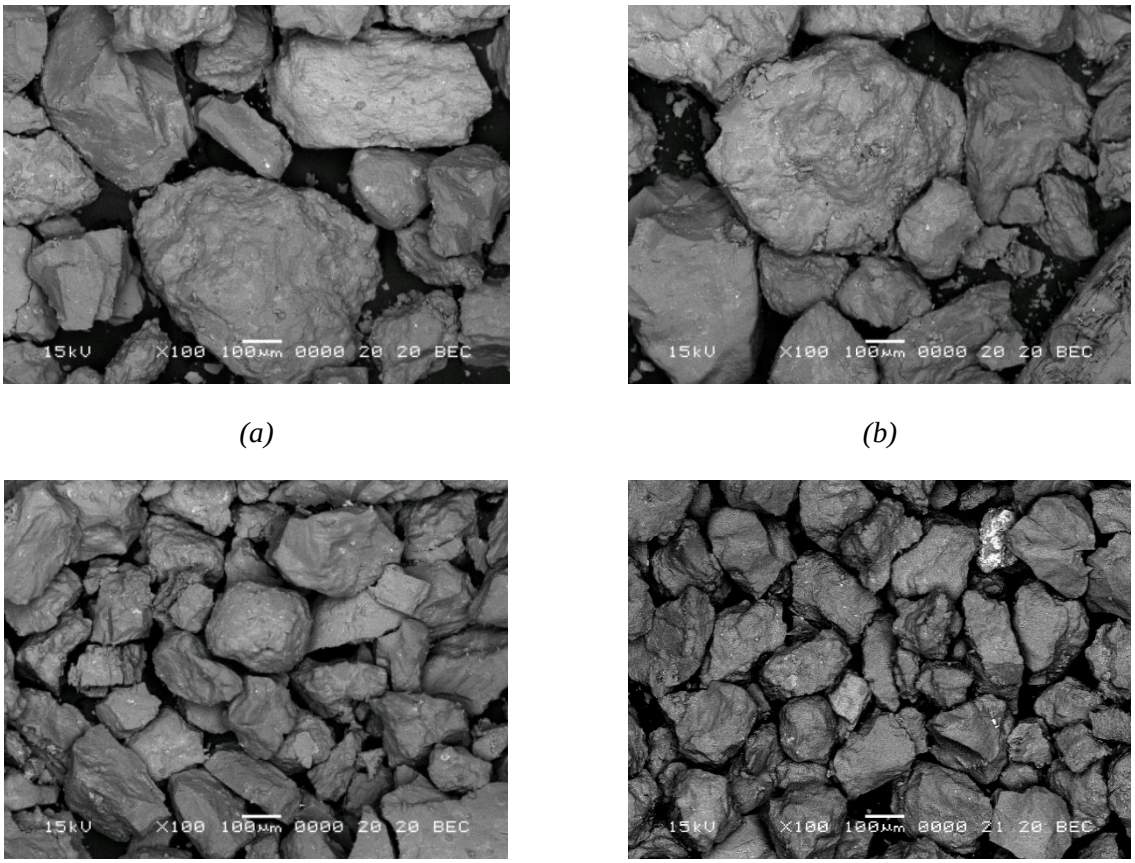


Fig. 7. X-ray diffraction patterns recorded after DSC experiments.

The formation of the FeO phase and the modification of the Fe-O phases ratio is sustained by the presence of different phases containing iron in the sand. However, the X-ray diffraction patterns recorded after DSC experiments shows no Fe_2O_3 peak or other iron-oxide phases (Fig. 7). This behavior is understandable if we consider the fact that the FeO phase formed at high temperature is not stable upon cooling in normal condition, but it can be encountered alongside other iron oxides. In the DSC experiment, the cooling take place in inert atmosphere and the FeO phase does not further oxidize, and the remains in the samples alongside of Fe_2O_3 and Fe_3O_4. Since the iron quantity is very small, the formation of the phases in DSC is smallest than the XRD experiment resolution. Another aspect than must be taken into account the non-stoichiometry of the FeO phase. This phase can occur in a large variety of $Fe_{1-x}O$. This hypothesis does not explain the occurrence of the Fe_2O_3 peak for the annealed samples. But a notable difference is between the two experiments the annealing is performed in air and the DSC is performed in argon gas. In air the FeO phase is further oxidized at cooling and forms in the presence of oxygen the Fe_2O_3 phase. Similar can happen with Fe_3O_4. In air cooling, the formed quantity of Fe_2O_3 exceeds the minimum quantity required for phase peak to be observable in the diffraction patterns.

To check the morphological changes induced by annealing, the SEM images were recorded for samples heated at 600 °C for different durations. The images are shown in Fig. 8.

Materials Research Proceedings **8** (2018) 105-114 doi: http://dx.doi.org/10.21741/9781945291999-12



(a) *(b)*

(c) *(d)*

Fig. 8. Scanning electron images of the sand annealed at different temperatures up to 24 h. SEM images of sand treated at: (a)- 600 ^{0}C/ 3h, (b)- 600 ^{0}C / 12h, (c)- 600 ^{0}C / 24h. In (d) is presented an image of the un-annealed sample.

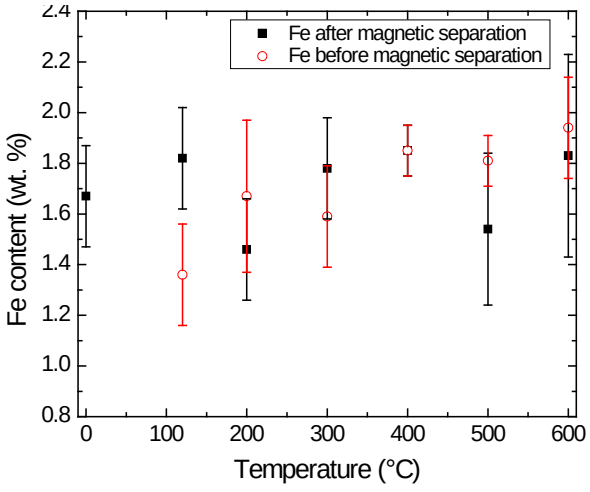


Fig. 9a. Modification of Fe concentration of sand upon temperature increase (annealing for

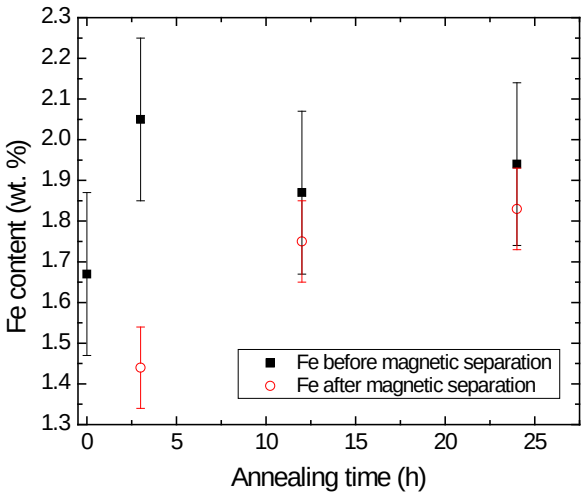


Fig. 9b. Modification of Fe concentration of

24h). sand with annealing time (TT 600 °C).

As the annealing time increase, the surface of the particles became smoother. The surface change can be an indication of the phase modification inside the particles.

Performing an EDX analysis on multiple samples from the same annealing conditions, the quantity of iron was extracted and plotted in Fig. 9 versus annealing time (a) and versus annealing temperatures (b). In the same time, a magnetic separation was performed on the samples, and the iron quantity after separation is also shown for both experiments.

As expected during the annealing, the quantity of iron atoms remains almost constant in the samples. But a basic magnetic separation induces modifications. If we consider first the annealing temperature (Fig. 9a), the iron quantity removed variation is in connection with the color of the samples: up to 300 °C the removed quantity is either higher, either lower than before magnetic separation. Such variation can be the effect of sampling and low magnetic fraction of the iron oxide. Once the color of the sample is changed, for temperatures larger than 400 °C, the quantity of iron after magnetic separation is lower than before. Such modification is the effect of iron-oxygen phase change in this temperature range, as discussed for DSC measurements.

If we look at the annealing duration, at 600 °C, for all the annealing times, the iron quantity in the samples after magnetic separation is lower than before separation. The maximum difference occurs at low annealing times (3 h). Once again, the origin of this effect is connected with the Fe-O changes observed in the DSC measurements.

Summary

The quartz sand was studied from the point of view of phase and phase relation versus annealing at various temperatures and durations. The sand annealed at 600 ^{0}C is enriched in Fe_2O_3; annealed at lower temperatures the quantity of Fe_2O_3 is not visible by X-ray diffraction. The Fe_2O_3 phase is visible at annealing times larger than 6 h (at 600 ^{0}C). For lower temperatures, the Fe_2O_3 phase is not visible in the X-ray patterns. The DSC measurements indicates the occurring of an endothermic transition at 575 °C, with two possible cause: Curie temperature of Fe_3O_4 and FeO wustite phase formation. At cooling, in the DSC sample Fe_2O_3 phase is not visible in the X-ray diffraction patterns. The sample enrichment in Fe_2O_3 phase in air annealing is favored by oxygen presence and the reduction of high temperature Fe-O phases. This phenomenon does not occur in DSC experiments, performed in inert gas. The removal of iron is more efficient upon heating above 400 °C and for low annealing times.

References

[1] M. F. M. dos Santos, E. Fujiwara, E. A. Schenkel, J. Enzweile, C. K. Suzuki, Quartz resources in the Serra de Santa Helena formation, Brazil: A geochemical and technological study, J. South Am. Earth Sci. 56 (2014) 328-338. https://doi.org/10.1016/j.jsames.2014.09.017

[2] S. Beddiaf, S. Chihi, Y. Leghrieb, The determination of some crystallographic parameters of quartz, in the sand dunes of Ouargla, Algeria, J. Afr. Earth. Sci. 106 (2015) 129–133. https://doi.org/10.1016/j.jafrearsci.2015.03.014

[3] Information on https://owlcation.com/stem/Beaches-Unusual-Colour/

[4] T. R. Boulos, A. Yehia, M. B. Morsi, S. S. Ibrahim, High quality fused silica from egyptian silica sand, Int. J Sci. Eng. Investigation. 6 (2017) 160-166.

[5] M. Bounouala, A. S. Chaib, Removal of iron from sandstone by magnetic separation and leaching: case of el-aouana deposit (Algeria), Mining Sci. 22 (2015) 33−44.

[6] F. Du, J. S. Li, X. X. Li, Z. Z. Zhang, Improvement of iron removal from silica sand using ultra-assisted oxalic acid, Ultrason. Sonochem, 18 (2011) 389–393. https://doi.org/10.1016/j.ultsonch.2010.07.006

[7] N. N. Konev, Magnetic Enrichment of quartz sands. Analysis of separator operation, Glass Ceram. 67 (2010) 132-137. https://doi.org/10.1007/s10717-010-9246-z

[8] N. N. Konev and I. P. Salo, Removal of iron-containing impurities by magnetic separation, Glass Ceram. 56 (1999) 32 – 33. https://doi.org/10.1007/BF02681401

[9] S.G.Zihms, C.Switzer, J. Irvine, M. Karstunen, Effects of high temperature processes on physical properties of silica sand, Eng. Geology 164 (2013) 139-145. https://doi.org/10.1016/j.enggeo.2013.06.004

[10] V. Brotons , R. Tomas, S. Ivorra, J.C. Alarcon, Temperature influence on the physical and mechanical properties of a porous rock: San Julian's calcarenite, Eng. Geology 167 (2013) 117–127. https://doi.org/10.1016/j.enggeo.2013.10.012

[11] ASM diagrams (CD).