

Structural and Mineralogical Imperfections of Some High Grade Quartz Ores Diagnose Their Chemical Reactivity

Mervat S. Hassan* and T.R. Boulos

Central Metallurgical Research & Development Institute, P.O. Box 87, Helwan-Cairo, Egypt

Abstract: The grade of a quartz ore is not a measure of its chemical reactivity. A high grade quartz sample (B) showed low reactivity in sodium silicate production. Structural imperfection usually occurs due to lattice defects in the quartz tetrahedron as a result of several substitutions that happen during mineralization. The random distortion of the quartz tetrahedron that could be affected by various mechanical and thermal stresses is accompanied by similar distortion in the crystallinity index which could be the reason for better chemical reactivity. The imperfect crystallinity of quartz sample (A) accompanied by highly shear petrography with micro-veinlets and fissures in its matrix has a direct impact on its fineness as revealed by its low grindability index (17.9 kwh/t) and highly surface area (13.07 m²/g) measurements. Both properties enhance chemical reactivity of quartz sample (A). Both structural and physical imperfection of quartz affect its chemical reactivity not only its grade.

Keywords: Quartz, sodium silicates, crystallinity index, grindability index, surface area

INTRODUCTION

Quartz is one of the most abundant minerals found in the Earth's crust (12% of its weight) [1]. It is a major component of numerous igneous and sedimentary rocks and is present in an impure state in many siliceous rocks. Cristobalite and tridymite are the other most common forms of what is commonly known as crystalline silica.

Alkali-silica reaction is largely controlled by three constituents: alkalis and silica as reagents and moisture both as a reagent and a transport medium. The mechanism of silica dissolution is not so much controlled by alkalis, but rather by dissolved OH-ions breaking silica bonds which then recombine with alkali-ions present [2-4]. The reaction of finely dispersed microsilica is generally not regarded as an alkali-silica reaction since it is not deleterious. The silica present in aggregate can be of very different nature, affecting its degree of alkali-reactivity or inertia. Many publications have been dedicated to the relationship between the nature and reactivity of aggregate [2-4].

Already in 1955 [5], the first edition of "The Colloid Chemistry of Silica and Silicates" was published, a standard work that over the years became famous. It provided an excellent introduction to the chemistry of silica dissolution. However, since its first publication much research had been conducted. The recent review volume edited by Heaney *et al.* [6] contains an exhaustive compilation of contributions dealing with silica and its behavior under various geological

conditions. Silica dissolution under weathering Conditions are reviewed in Dove [7].

This work aimed at finding relationship between structural imperfection, physical properties and chemical reactivity of two Egyptian quartz ores employed in local production of sodium silicate. Quartz (A) is known to be the highly reactive sample in sodium silicate production than quartz (B)

MATERIALS AND EXPERIMENTAL TECHNIQUES

Five kilograms of batches of two quartz samples quarried from Marwit El-Sweiqat (A) and Marwit Rod El-Leqah (B) quarries along Marsa Alam – Idfu road, Eastern Desert, of Egypt were delivered by El Nile Mining Co. to CMRDI. The secondary crushed samples were homogenized and then quartered by a Jones sampler to get 0.5 kg representative batches; one of which was finely ground to less than 200 meshes for complete chemical analysis. This was carried out by XRF method using Phillips PW 2400 X-ray spectrometer. Meanwhile, hand-picked rock pieces were collected from every sample for petrographic and mineralogical analysis. This latter was conducted by XRD method using a PW 1170 Phillips diffractometer with CoK α radiation. Powder scanned from 2° to 65° 2 θ . Bulk crystallinity of the quartz samples carried out using the 2 θ interval of 66° to 69° according to Murata and Norman [8]. Scanning was conducted at 1/4°/min with Ni filter CoK α radiation.

The morphology of quartz samples was measured using Zeiss polarizing microscope attached with computer program analysis (Olympus analysis digital image solution, 5 programs). The morphology of quartz mineral and their grains aggregates boundaries were studied by means of a Phillips S-2400 s SEM. On the other hand, surface area (BET) was measured using Nova 2000 analyzer after degassing the samples at 100°C for 2hrs.

*Address correspondence to this author at the Central Metallurgical Research & Development Institute, P.O. Box 87, Helwan-Cairo, Egypt; E-mail: mervathassan@hotmail.com

RESULTS

Chemical Composition of Quartz Samples and their Structural Imperfections

From the chemical point of view, both quartz samples look identical, high in grade with 99.9% SiO₂ (Table 1). But, the two samples show some dissimilarity in trace elements (Table 2). Sample (A) contains more Cu, Zr, Ba, Sb and Nd than sample (B), which on the other hand, contains relatively more Cr, Pr, Hf, Ta and Th than the latter. It is known that, the quartz deposit is formed generally as a result of precipitation of SiO₂ from hydrothermal solutions and its subsequent crystallization under conditions of low temperature, pressure and chemical reaction with the country rocks. However, in most minerals, there is a crude positive correlation between temperature and the concentration of structural impurities. These relationships can also be applied to the structural impurities in quartz. Therefore, high temperature igneous rocks produce poor quality quartz (β-quartz) in terms of structural impurities, whereas, many pegmatite and some hydrothermal vein deposits (α-quartz), in general, produce better qualities. Both quartz samples are of igneous origin but, nevertheless, it seems that the hydrothermal formation of each sample and the subsequent transformation from β- quartz to α-quartz are not the same. This might lead to differences in their structural impurities. Therefore, regardless of their identical high grade chemical composition, they portray different chemical imperfection in the SiO₄ tetrahedron structure. The type and frequency of lattice defects in quartz are influenced by the thermodynamic conditions during mineralization.

Mineralogical Composition of the Quartz Samples and their Chemical Reactivity

X-ray diffraction patterns of quartz were compared with the data of Murata and Norman [8]. It was found that in the two localities, the samples are composed essentially of quartz. Traces of clay minerals, mica, carbonate and gypsum were recorded in XRD patterns of the both samples. Quartz (SiO₂) is indicated by its characteristic X-ray diffraction peaks at 0.33 and 0.425nm, a minor amount of smectite

Table 1. Major Oxide of Quartz Samples

Oxides	A wt%	B wt.%
SiO ₂	99.90	99.95
Al ₂ O ₃	0.039	0.011
Fe ₂ O ₃	0.037	0.028
TiO ₂	0.0004	0.0007
CaO	0.003	0.002
K ₂ O	0.002	0.0006
MgO	0.001	0.001
P ₂ O ₅	0.001	0.001
Na ₂ O	0.009	0.006
LOI	0.08	0.08

Table 2. Trace Elements Distribution in Quartz Samples

Elements	A (ppm)	B (ppm)
Cr	4.68	5.83
Cu	11.37	7.58
Zn	4.1	3.19
As	0.15	0.1
Rb	1.97	1.89
Sr	18.74	18.27
Y	2.35	2.
Zr	4.16	3.92
Mo	1.87	1.87
Sn	1.9	1.09
Sb	1.99	1.21
Ba	24.29	23.68
Pr	0.75	1.52
Nd	10.56	---
Yb	3.75	3.71
Hf	0.69	2.76
Ta	0.42	0.94
Pb	11.45	11.81
Th	0.79	3.98

((Na,Ca) (Al,Mg)₆(Si₄O₁₀)₃(OH)₆.nH₂O) at 1.5nm, mica at ~ 1.0nm and calcite (CaCO₃) at ~0.3nm. The crystallinity indexes of quartz samples were measured according to the equation of Murata and Norman (1976); Crystallization index= 10aF/b, where F is 1.67

The method of computing the crystallinity index from the intensity of the (212) peak at 67.74° was shown by means of XRD patterns of the samples, (Fig. 1). The highly reactive sample (A) posses a very low index (1.2) compared with 10 for sample (B), the lower reactive sample.

Apparently the big difference in the X-ray index of crystallinity of quartz from two different regions is mostly a reflection of the different geological events. The imperfect crystallization of sample (A) which might be a reason for its better chemical reactivity could be due to random distortions of the quartz lattice induced by various mechanical and thermal stresses inherent in crystallizing granitic magma or brought to bear on a solidified pluton. However, the much better crystallinity of sample (B) may be due to intense metamorphism.

Sample Petrography

Petrography of the quartz samples showed that, sample (A), with the imperfect crystallinity, consists essentially of coarse grains, anhedral crystals of quartz that show undulose

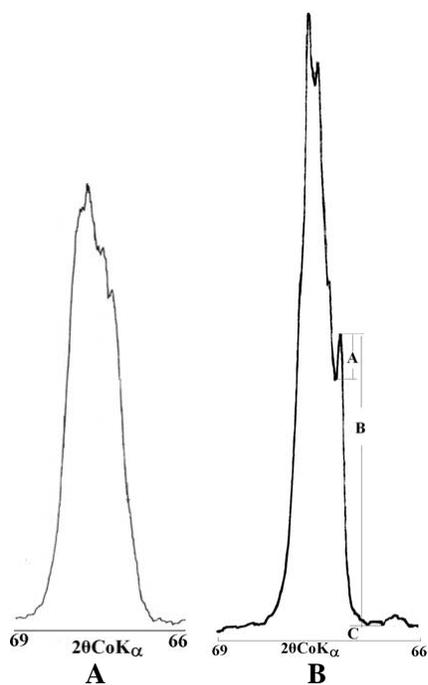


Fig. (1). Crystallinity index of quartz A and B.

extinction. Quartz crystals are highly sheared and mylonitized due to strain. Based on grain size and fabric, the quartz grains are deforming by dislocation creep [9]. The most interesting feature is the micro-veinlets which are nearly of parallel orientation due to shearing. These veinlets are filled with secondary minerals including carbonates, gypsum and sericite (fine-grained aggregate of mica-like phases) admixed with microcrystalline quartz. The microfractures are stained by brownish-grey substance that may be carbonaceous material/ admixed with iron oxides, (Fig. 2). SEM image and EDX of quartz (A) are shown in Fig. (3). Hans-Rudolf *et al.* [10] have examined thin sections of quartz bearing aggregate and they confirmed that quartz grains that exhibiting undulatory extinction (strain shadow in which band sweeps across a quartz grain due to bending of the crystal lattice by stress) are highly reactive because of its high dislocation density. Sample (B), on the other hand, consists of coarse to very coarse, anhedral and interlocked crystals of quartz. These crystals are characterized by wavy extinction and sutured edges. Quartz forms a sugary texture, and some quartz crystals have fluid inclusions (vacuoles) which are nearly concentrated in lines, (Figs. 4 and 5). This texture could be the reason of its low alkali reactivity.

Physical Properties of Quartz Samples

The highly sheared quartz (A) crystals supported with micro-veinlets and microstructure might affect its grindability. Work index measurements of both quartz samples showed that sample (A), showing the imperfect crystallinity has 17.9 Kwh/t as compared with 24.03 Kwh/t for sample (B). Figs. (6) and (7) depict the size distribution of both ground samples illustrating the fineness of sample (A).

In the mean time, BET surface area values of both samples are 13.07 m²/g for sample (A) as compared with 9.55 m²/g for sample (B).



Fig. (2). Photograph of quartz (A) X-25, C.N.

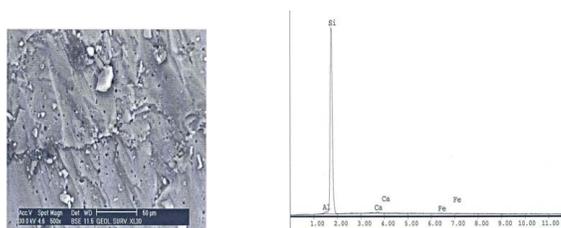


Fig. (3). SEM and EDX of quartz (A).

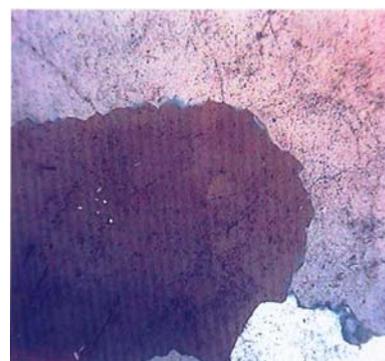


Fig. (4). Photomicrograph of quartz B.

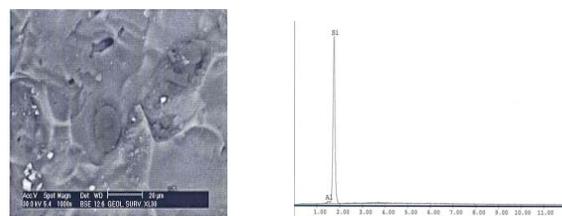


Fig. (5). SEM and EDX of quartz (B)

The imperfect crystallinity of sample (A), as demonstrated by the microveinlets and fissures in its matrix, might have affected its grindability and the resulting surface area and consequently enhanced its chemical reactivity. The fineness of this sample with the relatively high surface area will, no doubt, enhance its chemical reactivity.

DISCUSSION

The key point in the alkali-silica reaction is the hydrous dissolution of silica in the presence of dissolved Na and/or K

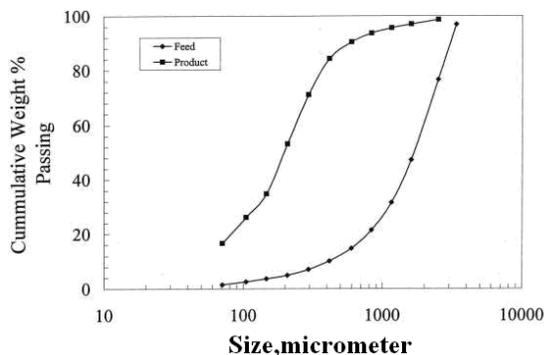


Fig. (6). Grindability index of quartz (A).

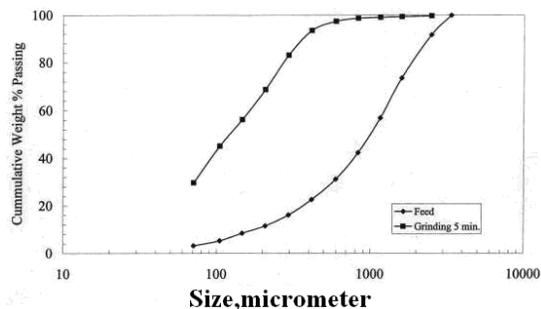


Fig. (7). Grindability index of quartz (B).

at high $\text{pH} > 13$, commonly obtaining in OPC concrete, sodium silicates product. The properties and qualities of the silica and its environment may affect its solubility under the given conditions. The exact definition of a grain boundary differs with the boundary type. In general terms, a grain boundary is defined as a two-dimensional lattice defect that introduces a misorientation with no long-range stress field... In this respect, a high-angle misorientation is in fact a plane between two individual grains, in contrast to a low-angle misorientation that is to be regarded as a defect in one single crystal [11]. Thus, a grain boundary formally represents a planar array of dislocations. Within a dislocation, and in a small volume embedding the dislocation, the crystal lattice is distorted and deviates significantly from the proper quartz structure. Interatomic bonds may be dangling loose and incompatible foreign ions tend to concentrate at dislocations and their direct vicinity since lattice stress can be released easier. As a result, aggressive media have an easier job breaking the stressed bonds in and next to structural defects than elsewhere. Thus, the solubility of a solid at dislocation arrays including grain boundaries is increased relative to immaculate material. A corollary to this is that quartz solubility would in fact reflect the quality of its crystal lattice.

CONCLUSIONS

- 1) The grade of quartz ore is not a measure of its chemical reactivity. Lattice defects that are influenced by thermodynamic conditions during mineralization lead to several substitution in the SiO_2 tetrahedron causing structural imperfection.
- 2) The random distribution of the quartz tetrahedron that could be affected by various mechanical and thermal stresses resulted in distortion in its crystallinity index which might be the reason for better chemical reactivity of sample (A).
- 3) The imperfect crystallinity of sample (A) accompanied by its loose petrography with microveinlets and fissures along the quartz grains has a direct impact on its finesses in terms of its low grindability index and high surface area parameters that enhance its alkali-reactivity

REFERENCES

- [1] Kauffer, E.; Moulut, J.C.; Masson, A.; Protois, J.C.; Grzebyk, M. Comparison by X-ray diffraction and Infrared spectroscopy of two samples of α quartz with the NIST SRM 1878a α quartz. *Ann. Occup. Hyg.*, **2002**, *46*(4), 409-421.
- [2] Fookes, P.G. An introduction to the influence of natural aggregates on the performance and durability of concrete. *Q. J. Eng. Geol.*, **1980**, *13*, 207-229.
- [3] Dolar-Mantuani, L. Handbook of concrete aggregates - a petrographic and technological evaluation. Noyes Publications: New York, **1983**.
- [4] French, W.J. *The Characterization of Potentially Reactive Aggregates*. Proceedings of the 9th International Conference on alkali-aggregate reaction in concrete, Poole, A.B., Ed. London, UK, **1992**, *1*, p. 338-346.
- [5] Ilready, R.K. *The Colloid Chemistry of Silica and Silicates*, 1st ed.; Cornell University Press: Ithaca, New York, **1955**, p.324.
- [6] Heaney, P.J.; Prewitt, C.T.; Gibbs, G.V., Eds : Silica: physical behavior, geochemistry and materials applications. *Rev. Mineral.*, **1994**, *29*, 606.
- [7] Dove, P.M. Kinetic and thermodynamic controls on silica reactivity in weathering environments. In: White, A.F.; Brantley, S.L., Eds.; Chemical weathering rates of silicate minerals: *Rev. Mineral.*, **1995**, *31*, 235-290.
- [8] Murata, K.J.; Norman, M.B. An index of crystallinity for quartz. *Am. J. Sci.*, **1976**, *276*, 1120-1130.
- [9] Fissler, D.A. *Quantitative Analysis of Strain in the Seine River Metaconglomerates*, Rainy Lake Region, Northwestern Ontario, Canada. M.S. Thesis, University of Wisconsin-Milwaukee, **2006**.
- [10] Hans-Rudolf, W.; Monteiro, P.J.M.; Shomglin, K. Relationship between aggregate microstructure and mortar expansion: A case study of deformed granitic rocks from the Santa Rosa mylonite zone. *J. Mater. Sci.*, **2008**, *43*, 278-1285.
- [11] Poirier, J.P. Creep of Crystals: *High-Temperature Deformation Processes in Metals Ceramics and Minerals*. Cambridge University Press: Cambridge, **1985**, p.260.