



Soviet-era science, translated into English

PHYSICAL CHEMISTRY

=====

1958

SovietRxiv

View the original and related papers at <https://sovietrxiv.org/items/ru-195801.17865>

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

Abstract

Full Text

PHYSICAL CHEMISTRY

G. S. KHODAKOV and E. R. PLUTSIS

ON THE SOLUBILITY OF FINELY GROUND QUARTZ IN WATER

(Presented by Academician P. A. Rebinder, 25 VII 1958)

The study of the physicochemical properties of finely ground quartz sand and, in particular, of its solubility at room temperature is of interest for understanding the mechanism of hardening of lime-sand binders ^(1,2) and the role of a finely ground sand filler in increasing the strength of concretes ⁽³⁾. Such investigations may also prove useful in studying the mechanism of grinding and in understanding those processes that occur with the material being ground in the grinding chamber. However, apart from the detailed investigation by Dempster and Ritchie ⁽⁴⁾, there are almost no works devoted to the study of the influence of the grinding process on the physicochemical properties of quartz, especially in the region of high dispersion. This is explained both by the novelty of the practical use of finely ground quartz sand in industry and by the difficulties of dispersion analysis in the range of particle sizes of fractions of a micron and less.

In the present work the solubility of quartz powders in distilled water was investigated. The powders needed for the study were prepared by dry grinding quartz sand from the Lyuberets quarry in a vibratory mill. The grinding times were taken as 2, 4, 8, and 16 min. The dispersion of the powders studied was assessed from the magnitude of their specific surface area, determined by the method of low-temperature adsorption of nitrogen ^(5,6), and for all the samples investigated it proved to be 7-9 m²/g, which corresponds to average particle sizes of approximately 0.3 μ .

The amount of quartz contained in solution was measured by a photocolometric method ⁽⁷⁾, the essence of which is that, upon interaction of acid solutions of silicic acid and ammonium molybdate, a yellow silicon-molybdenum complex is formed, corresponding to the composition $H_4[Si(Mo_3O_{10})_4] \cdot xH_2O$. The yellow complex is then reduced to form silicon-molybdenum blue. The sensitivity of this method reaches 1 mg/l.

The ground powders weighing 10 g were placed in glass cylinders, 300 ml of distilled water was poured over them, and they were shaken on a mechanical shaker for several hours. Subsequently the samples were stored without stirring. Control experiments showed that periodic stirring during long storage periods had no substantial effect on the rate of dissolution. Samples of up to 20 cm³ were

Fig. 1. Kinetics of dissolution of quartz sand in water at 20° for different grinding times

Figure 1: Fig. 1. Kinetics of dissolution of quartz sand in water at 20° for different grinding times

taken with a pipette from the upper part of the vessels and carefully centrifuged. Raising the temperature of the centrifuged solution to 100° did not increase its content of silicic acid, which indicates the absence of noticeable amounts of suspended particles.

The influence of the glass of the vessels and of silicon contained in the steel (entering the powders as a result of wear of the mill and balls) on the measured values of the silicic acid content in solution was allowed for in experiments in which

instead of quartz powder, corundum powder was used. The grinding of corundum and the measurements with it were carried out under conditions analogous to those for quartz, while the content of steel abraded in the corundum powder considerably exceeded the steel content in the quartz powders. These experiments showed that the amount of quartz passing into solution as a result of dissolution of the vessel glass and due to dissolution of silicon contained in the steel does not exceed 4 mg/l. Measurements carried out with unground quartz sand showed an insignificantly small value of its solubility, lying within the sensitivity limits of the method. It should be noted that in the present case the true solubility of quartz in water was determined, which is due to the method we chose for measuring the silica content in solution (8).

Fig. 1. Kinetics of dissolution of quartz sand in water at 20° for different grinding times

Figure 1 shows the kinetic curves for dissolution of finely ground quartz sand in water. The course of these curves confirms the formation of a true, rather than a colloidal, solution. Otherwise, one might expect a decrease in the measured solubility values with time after stirring had ended. The curves presented in Fig. 1 are well described by the kinetic equation

$$C = C_p(1 - e^{-k\tau}), \quad (1)$$

where C is the concentration of SiO_2 that has passed into solution during time τ , C_p is the solubility, and k is the dissolution-rate constant. The values of C_p can be determined from the data in Fig. 1, from which it is seen that, under the conditions of our experiments, saturation occurs after approximately 60–80 days of dissolution.

Fig. 2. Kinetics of dissolution of quartz sand in the coordinates $\tau - \ln \frac{C_p}{C_p - C}$

Fig. 2. Kinetics of dissolution of quartz sand in the coordinates tau $-\ln C_p/(C_p-C)$

Figure 2: Fig. 2. Kinetics of dissolution of quartz sand in the coordinates tau $-\ln C_p/(C_p-C)$

Fig. 3. Dependence of the equilibrium concentration of silicic acid in solution on the duration of grinding of quartz sand. 1 –equilibrium concentration, 2 – specific surface area

Figure 3: Fig. 3. Dependence of the equilibrium concentration of silicic acid in solution on the duration of grinding of quartz sand. 1 –equilibrium concentration, 2 –specific surface area

Equation (1) is conveniently written in the form

$$\ln \frac{C_p}{C_p - C} = k\tau,$$

which in semilogarithmic coordinates is represented by a straight line, whose slope tangent is equal to k . The experimental data shown in Fig. 2 confirm the validity of equation (1) as applied to the case under consideration and make it possible to calculate the constant k , the value of which, as is evident from Fig. 2, does not depend on the grinding time of quartz and, under the conditions of our experiments, is equal to 0.056 day^{-1} . At the same time, as shown in Fig. 3, increasing the duration of dry grinding of quartz leads to an increase in the solubility values C_p .

The data obtained are consistent with the fact that the powders of finely ground quartz sand under consideration possess practically identical surface areas, which, other conditions being equal, determine the dissolution rate. Along with this, the value of the solubility ...

solubility C_p at a given temperature is determined, evidently, by the physico-chemical properties of the powder, which change in the course of grinding. This is also confirmed by the fact that the process of dissolution of finely ground quartz in water, as follows from Table 1, is completely reversible: when the temperature is raised, the solubility of the quartz powder increases considerably, while lowering the temperature to room temperature causes a gradual decrease in the concentration of silicic acid.

Fig. 3. Dependence of the equilibrium concentration of silicic acid in solution on the duration of grinding of quartz sand. 1 –equilibrium concentration, 2 – specific surface area.

The solubility of finely ground quartz in water at room temperature, according to our data, reaches in some cases 120 mg/l, which is no less than 20 times greater than the solubility of coarse-crystalline quartz ⁽⁹⁾.

Table 1

Influence of temperature on the solubility of finely ground quartz in water (mg/l)

C_p	Duration of storage at 100°, hours	Duration of storage at 100°, hours	Duration of storage at 20°, days	Duration of storage at 20°, days
	1	3	11	25
33	60	109	—	—
60	82	169	—	—
73	176	222	109	87
89	160	210	128	115

Calculations by the Kelvin formula, carried out using the measured values of the specific surface area, show that for the investigated finely dispersed quartz powders the observed solubility values exceed the calculated ones by no less than 16 times. If one also takes into account the presence of unavoidable electric charges on the surface of the particles, this difference increases still more ⁽¹⁰⁾. Nor can the increase in solubility as a result of grinding be attributed to fractions of very finely dispersed particles in the powders studied. If the solubility were determined by such particles, one would expect a decrease in the concentration of silicic acid in solution in connection with the phenomenon of recrystallization of small particles into large ones ^(10, 11). The comparatively high solubility should have ensured a considerable rate of this process. However, no decrease in concentration was observed in our experiments even during very prolonged observations (more than a year). Moreover, as the experimental data show, the specific surface areas of powders that had stood for a long time in water also did not undergo any noticeable changes. On the other hand, the magnitude of the equilibrium concentration depends markedly on the time of grinding of the sand, although its specific surface area does not increase during the grinding process.*

The anomalously high solubility of finely ground quartz in water and its sharp increase with increasing grinding time are explained if one takes into account that in the mill not only does grinding of the quartz particles occur, but also disruption of their crystalline structure ⁽⁴⁾.

With a sufficiently long grinding time, dispersion as such ceases, while disordering of the crystal lattice

* This is connected with the very high energy intensity of the mill we used, in which the limit of grinding characteristic of quartz sand ⁽¹²⁾ is reached already after 2 min of grinding.

continues until the complete transformation of quartz into its amorphized variety. It is therefore natural to relate the observed solubility values of the powders not to their dispersity, but to the disordering of the crystal lattice of quartz and the

formation on the particle surface of amorphized layers (similar to Beilby layers), possessing increased free energy.

The data set forth above make it possible to explain the mechanism of formation of calcium and magnesium hydrosilicates when their hydroxides interact with finely ground sand in an aqueous medium at room temperature. As was shown ⁽¹⁾, in this process up to 7-8% of the quartz powder enters into combination with lime, which cannot be attributed solely to reactions on the surface of the grains ⁽²⁾. It is known that the solubility of $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ at 20° is, respectively, 1300 and 30 mg/l; the solubility of quartz, as we have observed, reaches 120 mg/l. Such values of the solubility of the initial components make possible the occurrence of a reaction in the liquid phase with the formation of calcium and magnesium hydrosilicates, whose solubility is extremely low. Therefore, in an aqueous medium conditions are created that ensure very high supersaturations for the new formations, which causes the crystallization of extremely fine nuclei of the new phase, their subsequent growth, and their coalescence with one another. As a result, the crystallization structure of limestone-sand stone is formed, whose strength reaches 240 kg/cm².

Thus, the hardening mechanism of lime-sand binders may be considered analogous to the mechanism of crystallization hardening through solution of such mineral binders as, for example, gypsum ^(13,14). In this case the strength of hardening lime-sand products increases as a result of the coalescence of crystals of new formations in supersaturated solutions of these same substances ^(15,16).

In the same way one may also explain the role of vibration-ground sand filler in increasing the strength of low-cement concretes. The free calcium hydroxide released when cement is mixed with water interacts in solution with quartz with the formation of calcium hydrosilicates, the crystallization of which leads to an increase in the strength of the cement stone.

In conclusion, the authors express their sincere gratitude to Academician P. A. Rebinder, D. S. Sominskii, V. B. Ratinov, and L. A. Feigin for discussion of the results and valuable comments, and to N. I. Gludina for assistance in the work.

All-Union Scientific Research Institute
of Fine Grinding

Academy of Construction and Architecture of the USSR

Received
23 VII 1958

CITED LITERATURE

1. D. S. Sominskii, G. G. Kornienko, V. V. Komonova, G. S. Khodakov, *Nauchn. soobshch. VNIITISM*, No. 28 (1957).

2. V. F. Abrosenkova, G. I. Loginov, P. A. Rebinder, *DAN*, 115, No. 3, 509 (1957).
3. P. A. Rebinder, N. V. Mikhailov, Reports at the conference on contemporary problems of concrete technology in the precast reinforced-concrete industry, 1956.
4. R. V. Dempster, P. D. Ritchie, *J. Appl. Chem.*, 3, No. 4, 182 (1953).
5. S. Brunauer, *Adsorption of Gases and Vapors*, 1, IL, 1948.
6. D. S. Sominskii, G. S. Khodakov, *Nauchn. soobshch. VNIITISM*, No. 29 (1957).
7. N. I. Gludina, M. A. Matveev, *Tr. Mosk. khim.-tekh. inst. im. D. I. Mendeleeva*, vol. 21, 49 (1956).
8. M. M. Piryutko, Yu. A. Shmidt, *Izv. AN SSSR, OKhN*, 1953, 607.
9. R. Iler, *The Colloid Chemistry of Silica and Silicates*, 1955.
10. M. Volmer, *Kinetik der Phasenbildung*, 1939.
11. G. Bakli, *Rost kristallov*, IL, 1954.
12. A. D. Lesin, *Nauchn. soobshch. VNIITISM*, No. 25 (1957).
13. Ya. L. Zabezhinskii, V. B. Ratinov, T. I. Rozenberg, *DAN*, 108, No. 6, 1137 (1955).
14. V. B. Ratinov, Ya. L. Zabezhinskii, T. I. Rozenberg, *DAN*, 109, No. 5, 979 (1956).
15. A. M. Smirnova, N. G. Zaitseva, P. A. Rebinder, *Koll. zhurn.*, 8, No. 1 (1956).
16. E. E. Segalova, V. N. Izmailova, P. A. Rebinder, *DAN*, 110, No. 5, 808 (1956).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.