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INFLUENCE OF FINE GRINDING ON THE PHYSICOCHEMICAL PROPERTIES OF SOLIDS

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1. INTRODUCTION

An increase in the degree of dispersion of solids produces an increase in the rate of heterogeneous chemical processes which is proportional to the specific surface of the species involved, and it also results in activation and the more effective utilisation of many materials. Dispersion raises the activity of several catalysts, improves the covering power of pigments and the quality of fillers for rubbers and plastics, lowers the temperature for sintering articles in powder metallurgy, etc. One of the most universal and widely used methods for the dispersion of solids is their mechanical disintegration — grinding — which is applied to very many materials employed in various branches of industry. Among them are cements, ores, metals, fuels, and paints, the total annual production of which is counted in hundreds of millions of tons. The degree of dispersion of solids which have undergone grinding is continually being raised, and the corresponding range of production extended.

With the modern level of development in grinding and mixing techniques the velocity of heterogeneous processes can be increased tens of thousands of times by grinding. However, this is not the sole result of the mechanical disintegration of solids. At the present time a considerable body of experimental data has accumulated showing that fine grinding produces also a considerable increase in the specific reactivity (calculated per unit surface) of substances in the solid state. Several other of their physical and physicochemical properties are also changed, such as density, phase transformation points, and adsorption capacity.

The study of the physicochemical properties of disperse systems forms part of a new field of science, physicochemical mechanics, developed by P. A. Rebinder and his

school. The aim of this branch of science is to obtain materials having a specific structure and strength[1], and also to find a basis for optimum methods of mechanical working by the application of physicochemical factors. The active medium used has been found to exert a considerable influence on the disintegration of solids. The mechanism of this effect involves penetration of molecules from the medium into the structure of the solid, which substantially changes the character of the breakdown[2]. It is therefore not surprising that the conditions of grinding and especially the participation of the active medium in this process will appreciably influence also the accompanying changes in the physicochemical properties of the ground solids.

The causes of the increased specific reactivity and of the change in other physicochemical properties of solids resulting from mechanical dispersion can be summarised as follows:

1. Decrease in particle size, increase in curvature of the surface, and growth in the contribution of the surface layers[3-11]. This phenomenon, which is common to all disperse systems, independently of their mode of preparation, is complicated with ground materials, however, by formation of considerable numbers of flats and edges, aggregation of particles, and surface damage by "amorphisation"[12].
2. Mechanical distortion of the crystal lattice in the surface layers of solids, their transformation as a result of plastic deformation into a quasi-amorphous state, metastable at ordinary temperatures, with an increase in free energy[12-46]. Mechanical dispersion causes even substances which are amorphous in the usual sense to become considerably more active than their unground analogues[21,32].
3. Exposure of fresh surfaces, accompanied by the formation on them of unbalanced valencies, free radicals[3,37,38,47-50]. Such surfaces react vigorously with various media, and this explains, for example, the pyrophoric properties of metals, the oxidising power of quartz, and the spontaneous combustion of graphite[3,12,38]. The formation of free radicals during the mechanical working of polymers in the process of mechanochemical synthesis[50-59] is especially valuable.

In several cases grinding distorts the secondary aggregation structure of highly disperse materials: carbon blacks, sols, Tripoli earths, clays, etc. This process may not be accompanied by appreciable increase in the primary dispersion, but the redistribution or breakdown of bonds between particles and the formation of unsaturated radicals substantially change the behaviour of such substances as fillers in rubbers and plastics and in the production from them of articles which are subjected to extrusion and baking[60-62].

The widespread industrial application of fine grinding has made necessary research of direct practical value. The most complete and systematic study has been made of the effect of grinding on such physicochemical properties of solids as adsorptive power[27,33-35,63-65] and solubility[31-33,66]. These properties are quite general, and in several cases may characterise adequately the activity of the materials. A considerable number of papers are also known in which the effect of grinding has been assessed directly from technological parameters[66-97].

It is difficult to generalise the extremely varied experimental work on the effect of grinding on the physicochemical properties of solids. This is due firstly to insufficiently clear definitions for disperse systems of such basic concepts as interface, particle size, and surface energy; and secondly to the complexity of measurements in disperse systems, for example, of particle size. Methods for the quantitative assessment of change in structure and activity of the surface layers in the grinding of solids are also insufficiently developed. For these reasons careful analysis of the method of measurement and of the experimental conditions is also required in order to compare results of investigations on the same problems. However, by no means all papers give a detailed account of experimental techniques, and it is not yet possible to establish a more or less rigorous relation between degree of dispersion, structural changes, and the activity of solids.

2. DECREASE IN PARTICLE SIZE

The influence of a decrease in particle size on the activity of solids has been examined by the methods of thermodynamics[3-10]. This leads to the well-known Kelvin formula for the equilibrium saturated vapour pressure or solubility of small spherical particles or drops

$$\ln\frac{C}{C_\infty} = \ln\frac{P}{P_\infty} = \frac{2\sigma M}{RT\rho r}, \qquad (1)$$

where C and P are respectively the solubility of and the saturated vapour pressure over drops or particles of radius r, C_∞ and P_∞ are their values over a plane surface or at sufficiently large r, R is the gas constant per mole, T the absolute temperature, σ the specific interfacial energy, ρ the density of the particles, and M their molecular weight. It follows from the Kelvin formula that, as the particles become smaller, their solubility and vapour pressure rise. Phase transformation temperatures fall with decrease in particle size. For spherical particles of small dimensions the variation in phase transformation temperature at constant pressure is governed by the expression[7]:

$$\frac{T_\infty - T}{T_\infty} = \frac{2\sigma M}{rQd}, \qquad (2)$$

where T_∞ and T are the temperatures corresponding to massive systems and to small particles of radius r respectively, and Q is the molar heat of phase transformation. Formula (2) makes it possible to determine $T(r)$ at constant pressure.

The thermodynamics of disperse systems has been developed in connection with problems involved in the formation and growth of condensed phases (drops, crystals) in the works of Gibbs[4], Curie[5], Vul'f[6], Volmer[7], and other writers[8-10]. Recently Poltorak has made attempts to generalise the thermodynamics of disperse systems by taking into account the change in density of the substance in a thin layer adjacent to the surface[10]. When this factor and also the edge energy are allowed for, the expression for the excess chemical potential of one component in the small particles, relative to its value in large particles, becomes

$$\Delta\mu_j = \frac{\overline{V}_j}{v}\left\{\frac{2}{3}\sum_i S_i\sigma_i + \frac{1}{3}\sum\tau_k l_k\right\}, \qquad (3)$$

where v is the volume of the particle, $\overline{V}_j(r)$ the partial molar volume of the j-th component in the disperse phase, the mean of the internal volume and the volume of a surface layer of thickness δ, S_i the surface area of the crystal face, l_k the length of the edge, σ_i the specific surface energy corresponding to the faces, and τ_k the specific

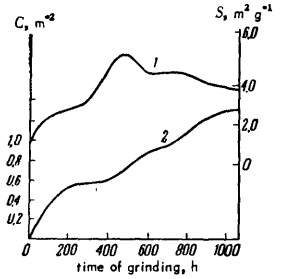


Fig. 1. Effect of grinding of kaolin on: 1) specific surface (determined from the adsorption of nitrogen at -90° K); 2) extent of dissolution (per unit surface area in wt.% of kaolin dissolved in 0.75 *N* HCl at room temperature during 48 h)[12].

linear energy corresponding to the edges. Summation is carried out over all edges and faces of the particle. If $\overline{V}_j(r)$ is expressed in terms of the thickness of the surface layer, the size of the particle, and the concentration of the j-th component, an expression is obtained for the excess chemical potential, which can be written in approximate form

$$\Delta\mu_j = \left\{\frac{2}{3}\sum_i \sigma_i S_i + \frac{1}{3}\sum_k \tau_k l_k\right\} \frac{2\overline{V}}{\overline{V}^\delta + \overline{V}}, \qquad (4)$$

where $\overline{V}^\delta$ is the mean partial molar volume in the surface layers.

If the density were greater in the surface layers, $2\overline{V}/(\overline{V}^\delta + \overline{V}) > 1$, and the total chemical potential of the substance at the given degree of dispersion would be higher than that calculated from the Gibbs equation[10].

However, the postulate of increased density in the surface layers of highly disperse phases is hardly applicable to systems obtained by mechanical grinding. A series of papers will be examined below, in which it has been shown experimentally that the density of the surface layers of pulverised solids has decreased[14,15]. Tolman and Kirkwood consider that a layer 2–5 molecular diameters thick, with a continuous decrease in density, is present at the interface between a condensed phase and a vapour or a solution. Several experimental facts can be explained on this assumption[98].

Determining the density of the surface layers is not the only difficulty in the thermodynamics of disperse systems. The problem of the change in specific surface energy has not been clarified at all. This parameter is usually regarded as independent of particle size, but there are indications that it does vary[98,99]. Another difficulty is, as has been mentioned, the uncertainty in measurements of the interfacial area and the particle dimensions.

For many solids $M = 30-80$, $\rho = 2-3$ at 300°K, and $\sigma = 100-1000$ ergs cm^{-2}. On the basis of the classical formula (1), ignoring later corrections, we have

$$\ln\frac{C}{C_\infty} = \ln\frac{P}{P_\infty} \simeq \frac{A}{r},$$

where $A = 10^{-6}-10^{-7}$ cm. Consequently an appreciable change in activity can be expected only with extremely low particle sizes, of the order of 10^{-6} cm and below. Experiment, however, shows an increase in reactivity with considerably larger particles[13,16-31].

The absence of a direct relation between degree of dispersion and reactivity in solids is shown especially clearly with very prolonged grinding. In this case, after a considerable increase in degree of dispersion, a limit to the degree of pulverisation is reached or even some decrease ensues, as a result of the very dense aggregation of highly disperse particles[12,33]. At the same time, the specific reactivity steadily grows as grinding is prolonged, as Gregg showed in the case of kaolin (Fig. 1). After 1000 h of grinding the extent of dissolution of the kaolin in 0.75 *N* hydrochloric acid had reached 58% after 48 h, whereas the dissolution of unground kaolin under the same conditions was insignificant. Similarly, the temperature at which removal of constitutional water effectively begins is lowered (from ~550° to 250° after 1000 h). The latent heat involved in the elimination of water is also diminished. All this also points to profound changes in the structure of solids occurring in the course of grinding[12].

3. CHANGE IN STRUCTURE OF SOLIDS

The mechanical processing of solids changes substantially several physicochemical properties of their surfaces[3]. Thus when metals are polished, an amorphous layer is formed on their surface which is termed the Beilby layer, and is chemically more reactive than the unpolished metal. A similar increase in activity occurs in the polishing of the surfaces of glass and other non-metallic materials. X-Ray examination of the surface layers shows that their crystal lattice has been strongly distorted, in many cases with the disappearance of any long-range order in the arrangement of the atoms. Amorphisation and other changes in crystal structure are produced also in the course of mechanical subdivision[37]. Much work has been done on the properties of the deformed surface layers of disperse solids, most of it, however, without regard to the conditions of grinding, in particular without taking account of adsorption of the medium. Yet it follows from the basic assumptions of physicochemical mechanics that these factors should have a considerable influence on the thickness and properties of the deformed surface layers[1,2].

The most extensive group of investigations on the physicochemical properties of highly disperse solids have been devoted to the silicates. In 1921 Lencher first showed that quartz is partly converted into an amorphous form by prolonged grinding[13]. Subsequent work on the physicochemical properties of silicate dusts developed in connection with the problem of silicosis[100,101]. It was then assumed that silicosis results from poisoning of the organism by products of the interaction of quartz with proteins in living tissues (pH 7.4 at 37°)[6]. An investigation was therefore made of the dissolution of powdered quartz and natural dusts in buffer solutions of various pH values, and also of the influence of both chemical and thermal treatments of the powders on the dissolution of foreign impurities. The most systematic and complete work was done by Ritchie and coworkers[20-28] during 1952–1954. Although it was subsequently discovered that silicic acid, formed in the dissolution of silicates, is very rapidly eliminated from the organism, and is consequently unable to cause silicosis[29], the above work exerted a great influence on the evolution of ideas both on the nature of silicosis and on the properties of powdered quartz.

It was shown that the high solubility of ground quartz is due to the formation, on the surface of its particles, of a thin layer analogous to the Beilby layer[21]. Removal of the surface layers by dissolution in hydrofluoric acid results in a sharp drop in solubility to the normal value typical of the corresponding crystalline and amorphous modifications (Table 1). The degree of dispersion of the specimens was the same before and after treatment with acid.

Similar results are obtained also on the dissolution of the surface layers from particles of quartz, quartz sand, and vitreous quartz in a borate buffer (pH 7.5, 37°). Mechanical treatment (polishing) of particles from which the surface layer has first been removed by dissolution restores their original high activity. X-Ray examination of powders before and after removal of the active surface layers[17-19] showed them to have an amorphous structure. However, the substantially higher activity of such layers compared with vitreous quartz suggests that the structures differ.

The density of the surface layers on the quartz particles is rather lower than that of crystalline quartz, which appreciably diminishes the mean density of the finely ground powder[14,15]. Pulverising vitreous quartz, however, results in the formation, on the surface of its particles, of a layer which has a rather higher density than has fused quartz (Table 2). No denser crystalline forms of silica were then detected in the products obtained by grinding vitreous quartz. The increase in density is probably due to the exposure of microscopic cavities on the breakdown of the particles[15].

Various methods, including differential thermal analysis[24,25], electron diffraction[25], and X-ray diffraction[18], have been used to measure the thickness of the active amorphous layers formed by grinding on the surface of crystalline particles of quartz. Data on the change in density[17] and solubility measurements[17,18] have been utilised. When it was necessary in this work to measure particle size in order to calculate the thickness of the amorphous layer, the mean values were determined from the specific surfaces measured by the air-permeability method.

The results obtained in this work (Table 3) show considerable discrepancies in the thickness of the amorphous layer. This may be explained by the quartz powder undergoing strong molecular aggregation on dry grinding[33-35]. Moreover, with very fine powders ($r < 1\ \mu$) the air-permeability method gives results which are not very reliable and which

TABLE 1. Extent of dissolution (mg per 100 ml after 40 days) of silica in borate buffer (pH 6.5, 37°).

Rock crystal*		Quartz sand		Vitreous quartz	
irreversible	reversible	irreversible	reversible	irreversible	reversible
2.30	0.15	0.99	0.44	6.70	1.14

* A form of colourless quartz (Ed. of Translation).

TABLE 2. Effect of grinding on the density of quartz and vitreous quartz, g cm^{-3}.

Test substance	Time of grinding	Mean particle size, μ	Density of powder at 18°	Density of amorphous layer
Rock crystal	initial	250	2.664	—
	5 min	70	2.647	—
	2 h	2.4	2.640	2.590
	17 h	1.3	2.606	2.551
Vitreous quartz	initial	450	2.201	—
	17 h		2.230	—

TABLE 3. Estimated thickness of amorphised surface layer quartz.

Method of determination	Thickness of layer, μ
Solubility	0.02—0.03
X-Ray diffraction	0.03
Density measurements	0.03—0.05
Electron diffraction	0.03—0.06
Chemical analysis	0.04—0.07
Differential thermal analysis	0.11—0.15

are in any case too low by factors of 2–3. Therefore the data quoted, which were obtained without regard to the specific features of the grinding, are to be considered only as comparative results.

A study has been made[33,34] of the effect on the amorphisation of quartz of the conditions of grinding, including the influence of the medium and also the relation between degree of dispersion and degree of amorphisation. The amorphised phase in pulverised quartz sand, originally containing not less than 98% of crystalline quartz in the low-temperature α-modification, was estimated quantitatively by differential thermal analysis, from the size of the temperature peak corresponding to the $\alpha \rightleftharpoons \beta$ transformation at 574°. The degree of dispersion was determined from the specific surface of the deaggregated powders measured by the B.E.T. method.

Since the surface layers of the particles become amorphous on grinding[21], a comparison of the content of amorphous phase in the powders Q with their specific surface S enables us to determine the mean thickness of the amorphous layer on the crystal nuclei, which for not too fine particles is $l = Q/\rho S$ (when $r \gg l$).

As follows from the experimental data plotted in Fig. 2, the thickness of the amorphous layer on quartz particles ground in dry air changes very sharply on sufficiently prolonged grinding, from ~20 Å when the dispersion is coarse to a few hundred ångström units. In contrast to this, on grinding in an active medium (with water) the thickness of the amorphous layer remains constant at 20 Å over a considerable range of specific surfaces, up to 50–60 m^2 g^{-1}, and increases slightly only on further rise in the degree of

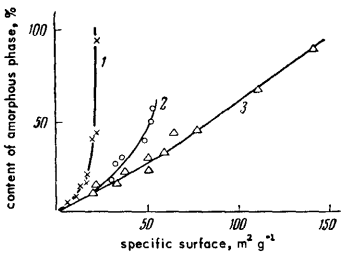


Fig. 2. Comparison of degree of dispersion and amorphisation of quartz on grinding: 1) in dry air; 2) with 1.2% of water; 3) with 80% of water.

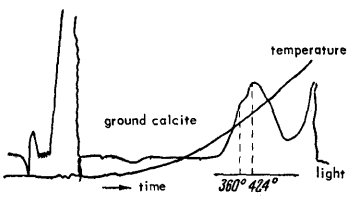


Fig. 3. Thermoluminescence of ground calcite[46].

dispersion. The depth of amorphisation of the coarse particles obtained by grinding with 1.2% of water is the same as for particles which have been ground with 80% of water, but it increases quite rapidly with growth in the specific surface to 30–50 $m^2 g^{-1}$. This sharp transition corresponds to a decrease in the surface concentration of liquid to 1–0.5 of a saturated monolayer. Thus the thickness of the amorphous layer on the crystalline grains of ground quartz does not remain constant, as had been supposed earlier, but depends both on the duration of grinding and especially on the medium in which the grinding is effected.

X-Ray examination of powders ground to different extents shows[33,37] that, with increasing duration of grinding, the background blackening of the X-ray photographs gradually becomes greater, while the diffraction maxima characteristic of the quartz lattice remain quite distinct, without appreciable broadening. Consequently the amorphisation of quartz cannot be attributed to a gradual decrease in size of the individual crystals, as can occur, for example, in the grinding of graphite[36]. In view of the fact that the high temperatures necessary for the fusion of quartz (1700°) do not arise in the mill, plastic deformation of the particles must be regarded as the most probable cause of amorphisation. Such deformation may arise in thin layers adjacent to cleavage surfaces, where the greatest shearing stresses are concentrated at the instant of rupture. Such layers are very shallow, in any case not deeper than the thickness of the amorphous layer, 20 Å for coarse grinding, as previously mentioned. In this connection, the role of plastic deformation in the breakdown of coarse particles is just as small, but it increases with fine subdivision, when the particle size becomes comparable with the depth of the amorphised layer.

Comparison of the density curves for the X-ray photographs of vitreous quartz and of quartz which has been amorphised in a vibratory mill to almost complete destruction of the crystalline phase indicates a certain similarity in their structures in the sense that there is a complete absence of long-range order in the arrangement of the atoms. On this basis it may be supposed that the energy consumed in the irreversible deformation is not less than the specific heat of amorphisation of quartz, 4.4×10^9 ergs cm^{-3}.[32] The same value for the energy of the limiting irreversible deformations can be obtained from theoretical models if the limiting shearing stress is taken to be about 0.1 E, where E is the modulus of elasticity. If appreciable scale strengthening is assumed to be absent, the limiting density of elastic energy for quartz is considerably less than $\sim 2 \times \times 10^6$ ergs cm^{-3}.

Subdivision has a substantial effect on the structure not only of quartz but also of several other solids. A change in crystalline structure has been observed on grinding graphite and metals[41]. In nickel powders unstable crystalline modifications have been found which pass spontaneously at room temperature into the normal state. Graphite is enriched with the rhombic modification, and in the absence of adsorbed layers of moisture it is actively amorphised on prolonged grinding. Its structure becomes similar to that of amorphous charcoals and carbon blacks[36]. In contrast to quartz, graphite is amorphised with an appreciable gradual decrease in size of the crystallites and with enrichment in two-dimensional networks, as is discovered on analysis of the density curves for the diffraction maxima on the X-ray photographs. As has been shown by X-ray diffraction, prolonged grinding of organic substances such as sugar and cellulose[43] also results in their amorphisation. An investigation has been made of the effect of water on the amorphisation and the degree of dispersion of particles during the grinding of mica[44]. After identical times a considerably greater change in the structure of mica is observed with dry grinding than with grinding in water. This is consistent with the above data on quartz and graphite.

Thus amorphisation or other changes in structure resulting from mechanical working occur quite generally with all solids. This conclusion is supported also by experiments done by Pucheger[45], who showed that even such a brittle and hard material as diamond is subject to plastic deformation under mechanical stress. The interesting phenomenon of the triboluminescence of calcite[46] is probably also a consequence of such plastic deformation, leading to the formation of a quasi-amorphous structure. Ground calcite shows several thermoluminescence peaks, in contrast to the unground material (Fig. 3).

4. EXPOSURE OF CLEAN SURFACES AND FORMATION OF FREE RADICALS

Apart from amorphisation, one of the main causes of the high chemical activity of pulverised solids, which is not directly due to the decrease in particle size, is the exposure of clean surfaces and the formation of free radicals. This probably explains the pyrophoric properties of the usually extremely inert graphite, observed by Veselovskii and Ormanskaya after dispersing it in liquid argon[102]. Considerable evolution of heat was noted also by Feigin[103] when finely ground graphite was brought into contact with

air. Carbon black which has been ground in a ball mill or a roller mill ignites spontaneously on contact with air. Its ignition temperature falls to 425°–538°.[60] Zarif'yants *et al.*[47] investigated the chemisorption of oxygen on graphite which had been ground in an atmosphere of argon in a vibratory mill. According to their results, the surface becomes saturated with oxygen at a pressure close to atmospheric, and 80% of the oxygen chemisorbed at saturation is already irreversibly sorbed at ~100 mm Hg. Subsequent sorption of oxygen on the oxidised specimens is negligible. The specific values of the chemisorption do not depend on the degree of dispersion. The density of the saturated layer of oxygen on the graphite surface is ~2 μmoles m^{-2}, which is close to the values of ~ 5 μmoles m^{-2} obtained for milled carbon blacks[60]. This allows the density of active centres to be estimated as 2–5 per 10 surface atoms of the graphite or carbon black.

Free radicals were detected on vibratory-milled quartz by electron paramagnetic resonance[48]. Their presence is also indicated by the electron emission found when the surface of crushed quartz is examined with Geiger counters[49]. In agreement with the views of Weyl[37], this phenomenon can probably be explained as a result of the rotation of the silica tetrahedra emerging at the surface under the influence of polarisation forces. Storage in argon for up to 30 days does not appreciably lower the chemisorbing activity of vibro-milled graphite[47]. Similar data were obtained by Bentur[38], who studied the oxidation of a graphite surface and the evolution of free oxygen by quartz and by olivine. Thus the active state of the surface of finely ground solids is well maintained at normal temperatures in an inert atmosphere. When the temperature is raised to 300° the activity of solids resulting from grinding is appreciably diminished.

Extremely interesting results have been obtained on the interaction of the highly active surfaces of finely ground solids with organic substances. Free radicals effect, for example, the mechanochemical synthesis of polymers — graft polymerisation. Thus Kargin and Plate[51,52] observed the polymerisation of styrene, methyl acrylate, and methyl methacrylate on vibro-milling them with quartz, graphite, or common salt at room temperature.

The interaction of ground metal particles with polymer layers causes several peculiarities in the semiconductor properties of such compositions[53]. Systems obtained by adding ready-made polyisoprene (natural rubber) to form films on particles of powdered iron differ from those obtained by the polymerisation of isoprene in a vibro-mill. In the first case n-type conductivity is observed, and in the second p-type. The Seebeck coefficient of 5 $\mu V\ deg^{-1}$ in the first case had increased to 12–14 $\mu V\ deg^{-1}$ in the second. The resistivity was also greater in the second than in the first case. These differences perhaps indicate that stronger bonding between metal and organic substances and a more uniform distribution of polymer result from using the vibration procedure for shearing and activating surfaces.

It has been shown comparatively recently that free macroradicals react chemically with the surface of the filler, thereby forming stable compounds[54]. Therefore the physicochemical surface properties and the structure of the filler have a considerable influence on the strength of filled high polymers. An investigation of the effect of grinding carbon blacks in a ball mill on the properties of butyl rubber[60] showed that on prolonged grinding the carbon blacks undergo considerable changes in their physical and chemical properties. The particle shape changes from spherical to irregular, with rough edges, the degree of dispersion increases, the structural factor — reticulation of the structure — diminishes, aggregations break down, the oil-absorption decreases, and the density of packing of the carbon black particles increases. Similar changes are observed also in the vibro-milling of carbon blacks[61,62]. On interaction of the ground carbon blacks with butyl rubber the amount of "combined rubber–carbon black gel" is increased 2–3 times compared with unmilled carbon blacks, which appreciably improves the strength and technological properties of the vulcanised rubbers.

Fig. 4 shows how the strength and the elongation of a vulcanised butyl rubber filled with the processed carbon black are increased compared with a vulcanised rubber filled with ordinary carbon black. Used of processed blacks produces a considerable improvement also in the dynamic properties of butyl rubber: the flexibility is increased, the energy lost as heat on periodic loading is diminished, and elastic fatigue is decreased. Since, with sufficiently prolonged milling of the carbon blacks, the strength parameters of the vulcanised rubbers cease to depend on the duration of vulcanisation (Fig. 5), the technical processing of the butyl rubber is simplified. The shortening of the minimum time of vulcanisation at 149° from 92 to 26 min allows goods with improved properties to be obtained. Thus the life of the vulcanised rubbers is increased by 25–30%, and the electrical resistivity by more than two orders of magnitude.

The dispersion of carbon blacks and other constituents has a favourable effect on graphitic carbon used in electrical engineering (brushes, electrodes). The strength is doubled, the hardness trebled, and the resistivity halved[62].

All these effects can be explained in terms of the above ideas on the change in aggregation structure accompanying mechanical dispersion and the high reactivity of freshly formed solid surfaces. The increased activity of the carbon blacks probably results from the rupture of surface bonds and the increased number of unpaired electrons produced by breakdown of the particles[54]. This view is consistent with the investigations of Weyl[37] and of Bentur[38], and is supported by measurements of the chemisorption of oxygen on finely ground graphite[47].

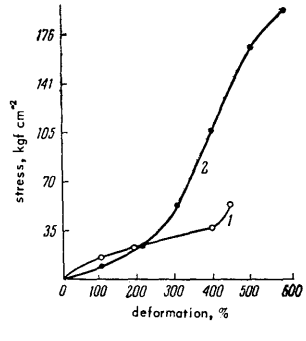


Fig. 4. Dependence of deformation on stress with vulcanised butyl rubber and: 1) ordinary carbon black; 2) carbon black processed in a ball mill[60].

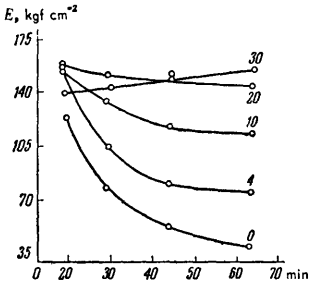


Fig. 5. Effect of time of valcanisation (min at 153°) on limiting tensile strength. (E, kgf cm^{-2}) for vulcanised butyl rubber with milled carbon black. The numbers on the curves indicate the time of grinding (in h) in a ball mill[60].

As in the case of minerals, mechanical working of the polymer results in the formation of unsaturated radicals. However, the life of such macroradicals in the free state is comparatively short at ordinary temperatures, as has been shown by electron paramagnetic resonance. At low temperatures, however, free macroradicals remain for quite a long time[48].

The breakdown of high-polymer molecules takes place also under the influence of high pressures. In this case the polymers undergo "chemical flow", the essence of which is that, at sufficiently high pressures, the polymers flow not only by displacement but also by mechanical rupture of the molecules and displacement of the fragments relative to one another. In contrast to ordinary viscous flow, chemical flow occurs also in systems having three-dimensional structures[55].

Free macroradicals are formed also by other mechanical processes, such as wear, rolling, mixing, freezing, and melting. This interesting phenomenon, which plays an important part in the chemistry of polymers, has been described in several special reviews (for example, see Refs. 56–58). However, the mechanism by which freshly formed surfaces and free radicals influence the synthesis of polymers and the formation of linear structures still remains obscure. The low density of active centres compared with the number of polymerisation acts indicates this to be a chain process, in which free radicals play the part of initiators of chain reactions[50]. The effect of different types of free radical acceptor on the mechanical degradation of polymers can be explained on this basis[59].

5. INCREASE IN ADSORPTION CAPACITY

Surface activation of finely pulverised solids on grinding is accompanied by an appreciable increase in their adsorptive power. Gibb and Ritchie[27] showed that the adsorption of dyes on pulverised quartz of particle size 125–200 μ is appreciably diminished after heat-treatment of the powder above 300°. The dimensions of the particles, and hence their specific surface, did not change in the course of such treatment. Removal of the active surface layer by washing with acid produces a similar effect. In this case, too, the decrease in particle size is negligible. In this way it was shown that adsorptive power is directly linked with the activity of the surface layers.

The adsorption of water vapour is especially sensitive to the condition of the surface. Zhdanov[63] found, by comparing the isotherms for the adsorption of water on vacuum-ground quartz, on silica gel, and on porous glass, that the first has considerably the higher specific adsorption capacity. It follows from his results that even repeat isotherms for water vapour on ground quartz with a surface of practically maximum hydration lie considerably higher than the isotherms on other forms of silica. It must be noted that the hydration of ground quartz is slow[63], probably owing to migration of water molecules from the surface layer to deeper layers and into narrow pores. In all the above cases either the surface layers of the particles were amorphous as a result of the grinding or the specimens themselves had been obtained in an amorphous form.

The difference in specific adsorptive capacity of different specimens of quartz depends on the conditions under which they have been obtained. The medium in which subdivision occurs has the greatest effect on the shape of the adsorption isotherms. Thus the specific adsorptive power is appreciably increased by grinding with small additions of water. The mode of mechanical subdivision and the size of the surface also influence adsorptive power[64].

Another factor having a considerable influence on the adsorption characteristics of finely divided solids is the molecularly compact aggregation of highly disperse particles[33]: as a result of mechanical working during grinding, the particles collect into dense aggregates, the internal surface of which is not available for the adsorption of nitrogen molecules at low temperatures. All known methods of dispersion analysis record such aggregates as single particles — diffraction methods cannot be used because of the amorphisation of the particles. However, when such aggregated powders are ground in water for such a short period that the increase in degree of dispersion resulting from breakdown of the primary particles can be neglected, their specific surface measured by the B.E.T. method is sharply increased severalfold. Such dense aggregation has been shown to occur on grinding the powder not only dry but also in benzene, acetone, and alcohol and with small additions of water and other liquids. Only large amounts of water, exceeding 40 wt.% based on the powder, possess a deaggregating power[33,34].

The effect of the molecular aggregation of highly disperse particles on adsorption characteristics can be assessed from determinations[35] of the adsorption isotherms of water and nitrogen on samples of quartz obtained by wet grinding completed by dry grinding. With such final grinding the adsorption of nitrogen vapour and the B.E.T. specific surface diminish, whereas the adsorption of water increases (Fig. 6). It can be assumed from these experiments that the ability of water molecules to penetrate into very narrow pores is greater than that of nitrogen molecules at low temperatures. Particle aggregation during grinding occurs also with corundum, calcite, etc.[33,34] The surface of quartz is equally accessible to the adsorption of water and to hydration.

Thus amorphisation of the surface layers of solids, depending on the conditions of grinding, and molecular aggregation exert a considerable effect on their specific adsorptive power. These factors, and also the differing abilities of molecules of different vapours to penetrate the

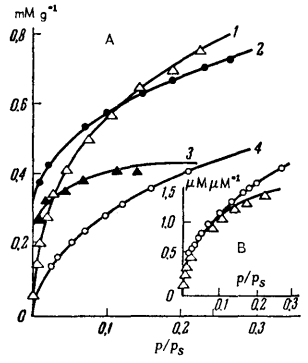


Fig. 6. A) Adsorption isotherms of water vapour (1 and 4) and nitrogen (2 and 3) on samples of quartz ground in water ($S = 53$ m^2 g^{-1}) (2 and 4) and of the same quartz but with grinding completed dry (1 and 3); B) adsorption isotherms of water vapour on the same specimens based on their content of structural water.

very narrow pores of the aggregates formed on grinding, cast doubt both on the values of the specific adsorption and hydration parameters calculated earlier from crystal-chemical considerations and on the correctness of measurements of the specific surface of ground materials. Unfortunately, these problems, which are of scientific and practical interest, have not yet been adequately studied.

6. INCREASE IN SOLUBILITY

As noted above, several investigations have established that solids acquire enhanced chemical reactivity as a result of decrease in particle size and surface degradation during grinding. This phenomenon has been studied in the greatest detail in the case of the solubility of quartz[31,33]. This substance was chosen for observation of the effects of grinding primarily because it is a typical brittle and hard crystalline material possessing great chemical stability. In this connection, the conversion of quartz into an extremely active form of silica on grinding is very significant. Furthermore, various methods of determining particle size, amorphous phase content, and degree of dissolution from the quantity of silicic acid in solution have been comparatively well developed for quartz, which facilitates experiments.

We have studied[31] the effect of grinding on the kinetics of the dissolution of quartz in water at room temperature. The concentration of silicic acid in solution was determined photocolorimetrically by the molybdate method. It can be assumed, on the basis of several investigations, that the molybdate method records only the silicic acid which is in true solution[20,21]. This is confirmed by the fact that boiling centrifuged solutions for several hours did not increase their content of "molybdate-active" silicic acid. The equilibrium solubility in water of carefully washed unground quartz sand at 20° did not exceed 1 mg litre^{-1}.

The dissolution of quartz in water is thermodynamically reversible. Raising the temperature to 100° increases the concentration of silica in solution (see Table 4), and prolonged storage of supersaturated solutions at room temperature lowers the concentration to close to the equilibrium value. Such comparatively rapid change in concentration takes place only in the presence of finely pulverised quartz. The silica content of a supersaturated solution, prepared by boiling finely divided quartz in water and then centrifuging to remove the highly disperse particles, falls considerably more slowly at 20°, even in the presence of the unground sand.

The rapid increase in solubility with rise in temperature is peculiar to amorphous silica. With crystalline quartz, however, raising the temperature even to 150° produces only an insignificant increase in its solubility[32]. The data in Table 4 indicate that the surface layer of particles of ground quartz does not consist of a conglomerate of intergrown submicroscopic crystals but, as has been shown above, represents a quasi-amorphous structure. In the case of extremely fine particles (of the order of a few intermolecular distances) these structures cannot be distinguished by either X-ray or electron diffraction.

The kinetics of the dissolution, in water at room temperature, of quartz of different degrees of subdivision is well represented by a first-order kinetic equation. The plot of $\ln[C_{eq}/(C_{eq} - C)]$ against t, the time of dissolution, where C is the quantity of silica in solution and C_{eq} the equilibrium concentration, is a straight line, the slope of which gives the rate constant k of dissolution. The value of k is independent of the duration of grinding or the specific surface of the powders, but differs with different pulverisers, depending on the intensity of their action.

Neither the equilibrium concentrations nor the rate constants for the dissolution of quartz in water are directly linked with the specific surface of the powders measured by the B.E.T. method. Experimental results show that the values of C_{eq} are higher for quartz ground dry in a vibro-mill for 8 h to a B.E.T. specific surface of 6 m^2 g^{-1} than for quartz after wet grinding for 11 h and having a B.E.T. specific surface of 74 m^2 g^{-1}.

Thus the physicochemical properties of ground quartz, which govern its dissolution in water at room temperature, are determined not by its degree of dispersion, its particle size, but by the state of the amorphised surface layers. This conclusion is also confirmed by a simple calculation of the solubility from the Kelvin formula. The equilibrium solubilities of quartz obtained by extrapolation of the kinetic curves increase with increasing duration of grinding, in several cases reaching 120–140 mg litre^{-1}. This exceeds by a factor of at least 15 the solubility of crystalline quartz with the same degree of dispersion calculated from data on the specific surface (B.E.T. method) and the normal solubility

TABLE 4. Reversibility of the dissolution of quartz in water (mg litre^{-1}).

C_{eq}	Boiling for		Storage at 20° for	
	1 h	3 h	11 days	25 days
60	82	169	—	77
73	116	222	109	87
89	160	210	125	115

of crystalline quartz[32]. In view of the absence of any recrystallisation effect, the high solubilities of ground quartz cannot be attributed to the fraction comprising the finest particles. Prolonged storage of the solutions (for more than a year) produces no appreciable decrease in the equilibrium concentration of silicic acid[31].

In experiments on the kinetics of the dissolution of quartz in water at room temperature, 0.1–0.25% of the solid passed into solution. The content of the amorphous phase was between 7–8% and 33% respectively. Consequently the values of the solubility and the rate constant for the dissolution of quartz in water represent the activity of only a very thin outer portion of the amorphised layers. In order to study the effect of grinding on the deeper-lying layers, measurements were made of the kinetics of dissolution of the powders in 20% alkali, with which silicic acid reacts in aqueous solution to form readily soluble salts. The amount of alkali taken was intentionally greater than that able to combine with all the silica passing into solution. As a result of this, the rate of dissolution of the quartz is limited mainly by the physicochemical properties of the test powder, not by saturation phenomena as in the case of dissolution in water. The absence of any appreciable decrease in the concentration of silica in the alkaline solutions when the temperature was lowered from 100° to room temperature can be regarded as supporting this assumption.

When powdered quartz is dissolved in alkaline medium at room temperature, depending on the duration of grinding, 5–15 wt.% passes into solution during a period of about two months, and this constitutes ~30% of the amorphised phase. After removal of the very thin surface layers (~2–5% of the amorphous phase) the rate of dissolution does not change further, which indicates a certain constancy of activity inside the amorphised layer. In these experiments, as in those on dissolution in water, the kinetic curves for quartz powders having the same content of amorphous phase but differing substantially in specific surface were identical.

Raising the temperature of the alkaline medium to 100° increases the rate of dissolution many times. The data illustrated in Fig. 7 show that in this case too, when almost all the amorphised phase passes into solution, the kinetics of dissolution of quartz under otherwise identical conditions depends only on the conditions (in this case the duration) of dispersion, not on the specific surface. Such a result cannot be due to an incorrect method of measuring the silicic acid concentration. That the method chosen was sufficiently sensitive to the effective surface area is confirmed by the fact that halving the weight taken in the same volume of liquid results in practically the same decrease in rate of dissolution.

Thus the chemical activity of ground quartz, which makes possible its use in several technological processes, such as the preparation of lime–sand binder, the manufacture of water-glass, etc., is due mainly, not to its disperse character, but to its degree of amorphisation, represented by the thickness and the physical state of the active layer. Nevertheless, this property is not taken into account in the majority of papers on the fine grinding of quartz and its technological application.

The solubility of the amorphised layer is diminished after heat-treatment of the powders. Raising the temperature and increasing the duration of heating result in a corresponding decrease in solubility. This and other

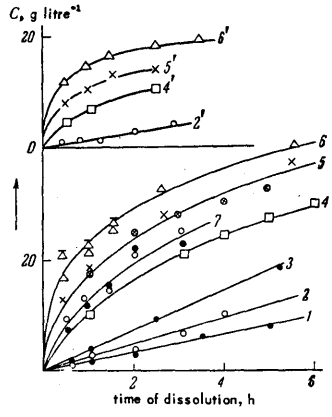


Fig. 7. Kinetic curves for the dissolution of quartz in 20% NaOH at 100° (5 g powder per 250 cm³ solution). Particle fractions: 1) 60–88 μ; 2) 25–30 μ; 3) 10–15 μ; 4) ground dry for 2 min (S = 11 m² g⁻¹); 5) 8 min dry (17 m² g⁻¹) and with 80% of water (50 m² g⁻¹); 6) 16 min dry (20 m² g⁻¹) and 32 min dry (22 m² g⁻¹); 7) 4 min grinding dry (14 m² g⁻¹) and with 80% of water (20 m² g⁻¹); 2′), 4′), 5′), and 6′) kinetic curves for the dissolution of 2.5 g powder in 250 cm³ solution, corresponding to curves 2, 4, 5, and 6.

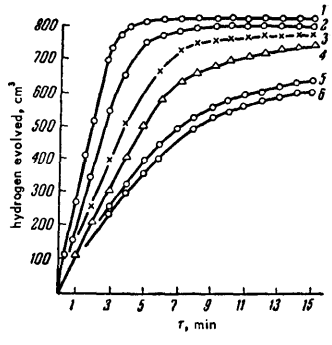


Fig. 8. Effect, on rate of dissolution of ground iron powders in 1 *N* HCl (τ = time of dissolution), of heating at 950° for different periods: 1) 0 (not heated); 2) 2 min; 3) 15 h; 4) 30 h; 5) 50 h; 6) 100 h.[66]

effects associated with the increased activity accompanying mechanical disintegration of solids are explained by the peculiar quasi-amorphous state of their surface layers, the molecules of which can, on heating, occupy sites of lower free energy[26]. However, insufficient work has yet been done on many physicochemical properties of the amorphised layers resulting from mechanical degradation, and especially their molecular structure. Experiments on the alkaline

etching[39] of pulverised quartz powders show merely the considerable non-uniformity of their structure. Such etching increases the specific surface from ~6 to ~200 $m^2 g^{-1}$. In this case, in contrast to silica gels of equally high dispersion, the cores of the nuclei remain crystalline, while the amorphised sheath is to a considerable extent removed. This may be of interest in several cases of adsorption and catalysis, for example, for the separation of optically active substances by successive adsorption on dextrorotatory and laevorotatory quartz[40].

Mechanical working considerably increases also the chemical activity of powdered iron, which is of great value in its use as a reducing agent[66]. The activity was determined by dissolving the powders in 1 *N* hydrochloric acid at 94° and measuring the rate of evolution of hydrogen. Iron powders of particle size 0.1–0.2 mm were ground and heated at 950° for different times to remove the structural distortions. The results plotted in Fig. 8 show that the chemical activity of mechanically deformed iron is several times greater than that of the undeformed metal. The effect of the mechanical processing then disappears only after heating at 950° for 100–120 h.

7. SOME ASPECTS OF THE PRACTICAL APPLICATION OF FINELY GROUND MATERIALS; RATIONAL DEGREE OF GRINDING

The increase in the rate of heterogeneous processes involving highly disperse solids, the considerable rise in their specific reactivity (per unit surface), and the lowering of phase transformation temperatures are responsible for the wide application of fine grinding in various branches of industry: chemical technology, the production of building materials, metallurgy, powder metallurgy, etc.[66-90]

The milling of solids has an especially strong effect on those technological processes involving them which go very slowly with ordinary materials. Thus practically no reaction occurs between unground quartz sand and lime in a moist medium at room temperature and atmospheric pressure. The use of vibro-ground sand, however, so activates its reaction with lime that lime–sand mixtures are used as binding materials. The rate of bonding by quartz of lime from aqueous solution rises rapidly with increase in its degree of dispersion[71,76,77]. The ratio of bonding rate to the specific surface then increases with growth in the latter, in agreement with views on the decisive role of the solubility of the sand grains, which increases with decrease in particle size and with increasing imperfection of structure of the surface layers. The strength of specimens made from a mixture of lime and unground sand is extremely low. However, the use of finely ground sand under ordinary conditions enables considerable strengths to be obtained, reaching 240 kg cm^{-2}.[71,72,74,76,78-81] The longer period of grinding the quartz corresponds to a high rate of interaction with lime, with the formation of monocalcium hydrosilicate. Since hydrosilicates govern the hardening process, the strength of the specimens and the rate of hardening increase with the degree of dispersion[78,79]. The strength of lime–sand products on hydrothermal processing is also appreciably increased by increase in the degree of dispersion of the sand. The setting time is thereby shortened, and the optimum temperature and pressure are lowered[83].

Fine grinding accelerates chemical processes also in the setting of cement, and increase in degree of dispersion improving its reaction with gypsum[82]. The use of finely ground cement in the production of reinforced concrete allows a smaller amount to be used, shortens the period of setting, and increases the strength of the concrete[75,88].

Treatment of powdered dolomite in a vibro-mill makes it possible to lower the sintering temperature by 100°–300° in the making of refractories and to obtain particles having improved mechanical properties[66,86-88]. With the relatively high firing temperatures of refractories, such a reduction in the temperature is of great practical value. The fine grinding of quartz and of feldspar shortens the time required for the sintering of glazes. The strength is thereby increased from 251 to 492 kg cm^{-1}, and the firing temperature lowered by 80°. Similar technological results are obtained by the vibro-milling of porcelain paste[89]. The use of finely ground materials improves the tendency of specimens to sinter, lowers the water absorption from 5.6% to 0.9%, and increases the quantity of cristobalite from 4% to 15%.[90]

The fine subdivision of oxides considerably improves the quality of parts made from them by powder metallurgy, and enables the temperature and duration of their firing to be diminished. Thus grinding allows Fe_2O_3 and SiO_2 powders to yield, on sintering at 1150° for 4 h, parts which are about ten times as strong as those obtained from the unground powders. In other cases grinding allows the sintering temperature, required to achieve a given strength, to be lowered from 1500° to 1300°.[66]

The temperature at which oxides are reduced is also considerably lowered as a result of fine grinding. The strength of this factor is shown by the reduction of Fe_2O_3 to Fe_3O_4 when Fe_2O_3 is ground in a vibro-mill at room temperature. The temperature at which Fe_2O_3 is reduced to Fe_3O_4 in a current of hydrogen is lowered by ~80° as a result of grinding. The effect of grinding disappears only when the oxides are heated to 900°. A similar lowering of the reduction temperature is observed also with NiO, MoO_3, and WO_3. Ground chromic oxide is completely reduced in a current of hydrogen at 1250°, whereas the unground powder is not reduced under these conditions[66].

In all cases of the industrial production and use of highly disperse materials, the question arises of the rational degree of grinding, which is governed primarily by the fact that the expense of grinding should be paid for by the technological improvement achieved. In view of the considerable energy consumption of grinding, in which only a small fraction of the energy consumed is usefully expended on the dispersion and degradation of the materials, this question is of great practical importance.

The fraction of the energy which is usefully consumed changes in the course of grinding, and rapidly decreases at sufficiently high degrees of dispersion. From the data plotted in Fig. 9 it is seen that grinding increases the heat of dissolution of sugar in water at room temperature[43], its value changing from negative to positive. However, with increased duration of grinding, the rate of change in the heat of dissolution rapidly decreases, and then becomes practically zero.

A similar retardation of the growth of activity occurs in the case of quartz[65]. The rate of increase in the solubility of quartz in water falls with increase in time of vibro-milling. Furthermore, as is shown by the data plotted in Fig. 7, when the grinding of quartz is prolonged, the increase in its solubility in alkaline medium almost ceases, the kinetic curves for 16 and 32 min coinciding. A

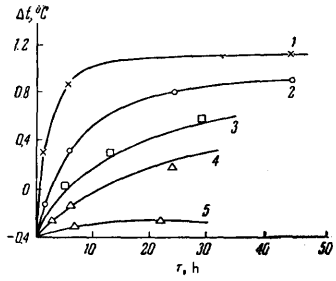


Fig. 9. Effect of duration of grinding of sugar on its heat of dissolution in water at 20° (11 g sugar in 200 cm^3 water). Curves 1–5 relate to various conditions of grinding [43].

slowing down of the yield of polymer with increasing duration of grinding is observed also in the mechanochemical polymerisation of methacrylamide in the solid state [93].

These phenomena probably result from the mechanical working producing not only increased dispersion, formation of free radicals, and destruction of the lattice, but also the reverse effects, as in the case of molecular aggregation. With a sufficient density of structural defects in the surface layers formed on dispersion, and with a given energy density produced by the ground material, a statistical balance is probably established between the formation and removal of defects. Increase in the energy intensity of the mechanical operations shifts the equilibrium towards an increased density of defects, and hence an increase in reactivity. As a result, the activity of the ground materials becomes greater, as has been shown in the cases of quartz [31] and sugar [43] (Fig. 9).

The growth in dispersion with time of grinding also slows down sharply. Sometimes this is due to dense aggregation of the particles, with their partial or complete reformation. However, this effect is observed also under conditions when aggregation is practically excluded: on grinding with water [34,94]. The decrease in the rate of dispersion is a consequence of the increasing specific consumption of energy in the limiting plastic deformation, which at a constant depth is proportional to the specific surface of the material. Therefore with the energy concentration, which the material can acquire in a single act of disintegration, limited for each mill, there is a limiting value of the dispersion, determined by the design of the grinder and the way in which it operates. The degree of dispersion increases, for example, with increasing amplitude of vibration in the vibro-mill. Hence the maximum dispersion which can be achieved also increases [94]. Similarly, the heat of dissolution of sugar in water and the solubility of quartz become greater as the action becomes more vigorous. It is characteristic that the increase in solubility ceases considerably earlier than the growth in dispersion or degree of amorphisation [65]. As has been mentioned, this is associated with the fact that the activity is determined by the state of extremely thin surface layers, which are constantly subject to mechanical constraints. In most cases the forces arising in the numerous contacts of particles and their rubbing against one another cannot cause disintegration, but are sufficient for deformation of the surface layers.

Another factor governing a rational degree of dispersion is the industrial desirability of speeding up the reactions. In several cases the use of highly disperse materials in ordinary technological layouts adapted for operation with comparatively coarse products leads to undesirable consequences. Thus, for example, very fine grinding of cement considerably shortens the time of hardening of concrete and could result in an increase in its strength. However, the cement solution then sets rapidly, becoming difficult to pack and transport. A rapidly hardening cement paste is therefore difficult to mix and set well, and the hardening process does not take place uniformly. The high water requirements of finely ground cement diminish the strength and density of the concrete. In production, therefore, a rational degree of grinding of cement is chosen experimentally on the basis of the optimum technological conditions for making it and utilising the equipment [92]. The optimum degree of grinding of quartz sand in the autoclave production of silicalcite is determined similarly [95].

Thus the use of highly disperse cement and sand proves inadvisable with the usual technological arrangements. However, the high activity of finely ground binders finds successful practical application in the technology of concrete development by Mikhailov and Rebinder [96,97] from the principles of physicochemical mechanics. The basis of this technology is the use of highly disperse cement and sands with a filler (readily available fine sand) with different frequencies of limiting vibration of the mixture at all stages of preparation of concrete from mixing to pouring and setting. This ensures a fuller utilisation of the bonding properties of cement, diminishes the consumption of the scarce coarse filler, and enables concrete of high strength, density, and durability to be obtained. Similarly, it would be useful to review the technological arrangements for other manufactures in which highly disperse materials are used.

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