CHANGES IN SURFACE OF DRY ACTIVATED QUARTZ AND MAGNESITE POWDERS DURING DYNAMIC AND STATIC CONTACTS WITH LIQUID ENVIRONMENTS OF VARIOUS POLARITY

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The influence of liquid environments of various polarity on the metastable states formed during dry grinding of quartz and magnesite have been investigated. The X-ray amorphous phase content and the excess enthalpy accumulated during energy intensive dry grinding remain unaffected during short-termed dispergation regrinding as well as during long-termed stirring and static storage of the activated powders in liquid environment. The changes in specific surface area depend upon: the permitivity of liquid environment, crystallochemical properties of the activated powder and conditions of their mutual contact.

INTRODUCTION

Grinding in a liquid environment belongs to conventional methods of preparing ultrafine powders.

Experimental studies of the action of various grinding environments have in most cases been concentrated on the determination of the newly created surfaces which have thus been considered as the required property. Experimental studies and industrial practice have provided substantial proof of the fact that the efficiency of the size reduction increases in a surface active environment. According to literature data [1], the effect of grinding environment during grinding of minerals with polar surfaces increases with increasing permitivity. The influence of the surface tension of liquid is also considered [2].

The fineness is although a required but not the only one effect of grinding. During energy-intensive grinding various metastable states are formed, differing in time and thermal stability. As to the source of structural metastability the disturbance of the short- and long range order of atoms may be considered. The compositional metastability may be taken as a consequence of a partial mechanochemical conversion of the ground substance. The morphological metastability originates from the fresh surface activity causing e.g. aggregation of ground particles into secondary formations (agglomerates at dry grinding, flocules in liquid environment).

The metastable states formation and stability may be influenced by many factors. Amongst the most important ones the specific energy of grinding, the grinding environment, and the temperature should be mentioned.

The influence of the grinding environment quality and the energy consumption on the granularity structure and thermodynamic state of carbonates and quartz was studied in our previous papers [3, 4]. It was found that mechanically induced bulk defect concentration and the excess enthalpy content in the ground powders depend upon the specific grinding energy consumed for activation. The adsorption – active environment plays the most significant role by preventing agglomeration. It was also proved that agglomerates formed during dry grinding may be destroyed by a short-termed peptization regrinding in a adsorption-active environment.

In the present paper results of a complex study are presented including the influence of crystallochemical properties of activated solids and physical properties of the environment on the peptization regrinding as well as on the time stability of metastable states formed in dry activated powders of magnesite and quartz.

EXPERIMENTAL

Mechanically activated powders of magnesite and quartz were prepared by dry grinding to a specific surface area $S = 4.7 \pm 0.2\ \mathrm{m^2g^{-1}}$. The above samples were subjected to a peptization regrinding in various polarity liquid environments. The conditions of grinding and regrinding are summarized in Table I. In Table II the physical properties of the liquids are characterized.

The dry activated samples were also exposed to a long-termed contact with the above mentioned liquids in a suspension with a solid to liquid ratio 1:20. A duplicate series of experiments were carried out under dynamic and static conditions of contact.

In the first case the suspension was stirred for 24 hours with a magnetic stirrer ($n = 19.25\ \mathrm{s^{-1}}$). The static contact of powders with liquid environment was followed for 26 days. The changes proceeding at exposition of a thin layer of powder to air atmosphere were also followed.

The specific surface area was determined from the adsorption isothermes of benzene vapour. The determination sensitivity was of the order $0.1\ \mathrm{m^2g^{-1}}$ and the relative reproducibility $R = \pm 1$ to 2%.

The particle size distribution data were measured on a sedimentation balance (Sartorius 184610, Vi-

Table II

Physical properties of liquid environments

Environment	Relative permitivity ($F.m^{-1}$)	Dipole moment (Debye)	Surface tension ($N.m^{-1}$)	Density $\times 10^3$ ($kg.m^{-3}$)	Viscosity (cP)
Water	80.36	1.853	72.75	1.00	1.010
Methanol	33.50	1.700	22.60	0.793	0.611
Toluene	2.38	-	28.40	0.866	0.367

Table I

Conditions of dry activation grinding (I) and peptisation regrinding (II)

Conditions of grinding	Mineral	
	Magnesite	Quartz
I.		
mill	vibration (selfconstructed)	planetary Pulverisette 4 (Fritsch)
grinding-drum	steel	tungsten-carbide
media	steel balls 10–30mm	WC 10–20mm
acceleration	8.1 g	9.2 g
filling	75 %	30 %
charge	0.1 kg	0.05 kg
II.	magnesite	quartz
mill	vibration	planetary
solid to liquid ratio	1.0	

enna). The measurements were carried out in aqueous environment with a small addition of natrium phosphate dispergator.

X-ray diffraction phase analysis was carried out using the method of standard addition. The crystalline phase content, x, was determined from the ratio of relative intensities for the relevant mineral to fluorite (Table III). The relative intensity was measured on the X-ray diffraction apparatus Dron 2.0 with a GUR 5.0 goniometer (Tekhsnabexport, Moscow) under following conditions: Fe K_α radiation ($U = 24$ kV, $I = 10$ mA), time constant 1, limit of measurement 10^3 imp. s^{-1}.

The decrease in the degree of structural arrangement in activated solids brings about an increase in their enthalpy content. The "excess" enthalpy of magnesite was determined from the difference of heats released at dissolution of activated and non-activated samples in 5M HCl solution [5]. Heat evolved during dissolution were determined by means of an adiabatic micro-calorimeter constructed at our Institute [6]. The accuracy of measurements was 5.10^2 J, and the reproducibility of results $R = \pm 2$ to 3%.

RESULTS AND DISCUSSION

According to Table III the relative reproducibility of the X-ray amorphous phase content determination is 5.42 and 3.11% for magnesite and quartz, respectively. The relative standard deviation of the X-ray amorphous phase content calculated from values in Table IV for magnesite is 6.95%, in Table V for quartz is 3.2%. Considering the above fact it may be assumed that under investigated conditions of contact no relaxation of mechanically induced bulk defects occur.

The effect of environment is represented mainly by the modification of the surface of dry activated particles.

Table III

Interplanar spacing d of selected planes {h k l} and relative reproducibility value R of investigated minerals and standard addition component (fluorite)

Sample	{h k l}	d nm	R (%)
Magnesite	104	27.42	5.42
Quartz	101	33.43	3.11
Fluorite	111	31.43	-

Table IV

Undersize fraction d_{10}, specific surface area S, X-ray amorphous phase content A, excess enthalpy ΔH_{ex} measured for dry ground sample of magnesite as well as for samples exposed to contact with mobile phases under following conditions: I – peptization regrinding, II – stirring, III – storage under static conditions.

Environment		t	d_{10} (%)	S (m^2g^{-1})	A	ΔH_{ex} ($kJkg^{-1}$)
t (h)	air	8	53.86	4.93	0.557	194.70
I t (h)	water	0.25	85.71	30.03	0.552	206.44
	methanol	0.25	70.82	11.96	0.563	206.90
	toluene	0.25	48.20	4.00	0.561	206.80
II t (h)	water	1	58.00	20.31	0.499	179.30
		3	62.50	21.62	0.524	198.90
		24	–	20.14	0.453	196.80
	methanol	1	57.90	9.04	0.454	187.80
		3	61.10	8.29	0.527	198.50
		24	–	8.60	0.501	186.40
	toluene	1	–	4.96	0.557	224.30
		24	51.90	5.00	0.478	187.20
III t (days)	air	7	–	5.90	0.535	191.80
		20	52.00	6.01	0.488	184.50
	water	3	–	22.71	0.550	181.40
		8	–	23.00	0.481	215.90
		21	56.80	22.00	0.543	188.80
	methanol	1	-	8.20	0.557	201.90
		21	55.60	8.65	0.536	195.20
	toluene	8	–	5.18	0.495	196.70
		20	52.90	4.96	0.519	207.20

During short-termed regrinding of dry activated samples in adsorption-active environment of methanol and water a 2 and 5 fold increase in specific surface area occur, respectively. Considering a simultaneous increase in the representation of the d_{10} undersize particles it can be assumed that the increase in specific surface area is mainly due to the peptization of agglomerates. Regrinding of the investigated samples in non-polar toluene results in a slight decrease in the specific surface are. The specific surface area and the content of d_{10} undersize particles remain unchanged during long-termed stirring and static contact of magnesite and quartz powders with toluene (Figs. 1 to 3 and Table IV and V).

Changes in specific surface area brought by stirring and static contact of the investigated samples with methanol and water molecules can not be explained by destroying of agglomerates.

During long-termed stirring and static storage of quartz in liquid methanol and water as well as at the contact with atmospheric humidity a decrease in specific surface area occur. The above results are in a good agreement with the data obtained by Khodakov [7] and may be explained by an interactions of active surface centers with the molecules of water and methanol.

From the viewpoint of traditional knowledge about surface passivation occurring during "ageing" of powders the increase of specific surface area during stirring and storage of magnesite (Figs. 1 and 2) is surprising. For explanation of the obtained results the influence of surface decomposition of carbonates proceeding during energy intensive grinding should be considered. According to data published in [7] the measured values of specific surface area and the changes which have taken place within a constant

Table V

Undersize fraction d_{10}, specific surface area S, X-ray amorphous phase content A measured for dry ground sample of quartz as well as for samples exposed to contact with mobile phases under following conditions: I – peptization regrinding, II – stirring, III – storage under static conditions:

Environment		t	d_{10} (%)	S (m^2g^{-1})	A
t (h)	air	8	79.05	4.96	0.332
I t (h)	water	0.25	84.60	8.58	0.335
	methanol	0.25	80.50	5.67	0.312
	toluene	0.25	67.50	3.65	0.309
II t (h)	water	1	76.00	2.67	0.319
		3	–	2.82	0.321
		24	81.00	2.76	0.306
	methanol	1	81.00	2.98	0.337
		3	81.50	3.15	–
		24	79.80	3.38	0.310
	toluene	1	82.70	4.93	0.324
		24	81.10	5.02	0.309
III t (days)	air	7	–	3.73	0.325
		20	79.50	3.44	0.295
	water	3	–	2.74	–
		8	–	2.71	0.313
		21	79.50	2.40	0.317
	methanol	1	–	3.65	–
		21	77.80	3.20	0.311
	toluene	8	–	–	0.340
		20	80.00	4.58	0.337

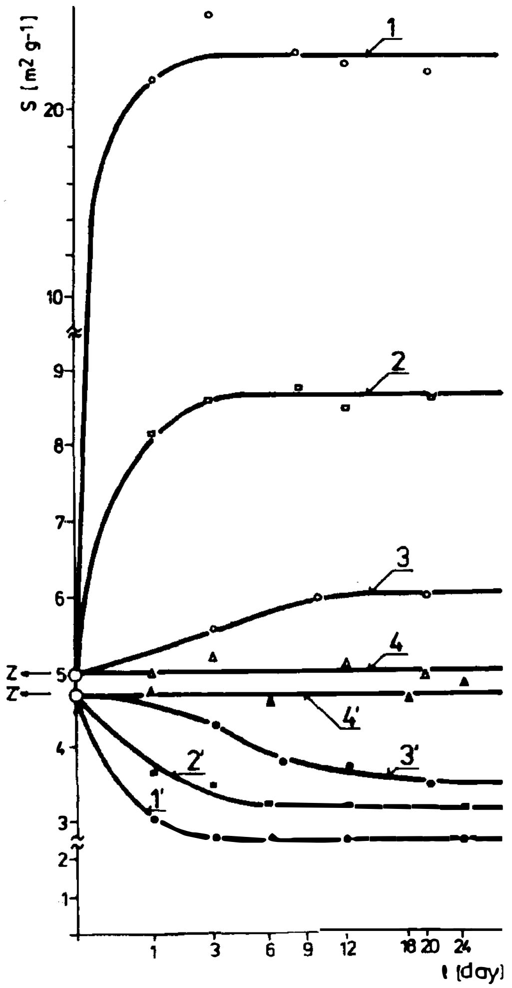

Fig. 1. Specific surface area S vs. time t of storage the dry ground samples of magnesite (empty points) and quartz (full points) in water (1, 1') methanol (2, 2') air (3, 3') and toluene (4, 4').

time lapse after grinding increase with decreasing chemical stability of carbonates and are directly proportional to the degree of their mechanochemical decomposition. Based on the above results it may be assumed that in addition of the granulometric composition of investigated magnesite samples, the measured values of specific surfae are strongly influenced by formation of a porous MgO surface layer reacting with atmosphere humidity and oxygen containing polar liquids by formation of highly dispersed surface compounds.

CONCLUSIONS

The changes in surface of dry activated powders during a contact with mobile phases depend upon the crystallochemical properties of solids, permitivity of the liquid environment and upon the conditions of their mutual contact.

During short termed regrinding of dry activated samples in polar liquids peptization of agglomerates occur, resulting in a 2 to 5 fold increase in specific surface area. The polar surfaces of fine magnesite and quartz particles interact with water and methanol molecules during long-termed stirring and storage. The formation of surface centers in these interations effects the adsorptively determined specific surface area. Comparison between "ageing" of oxides an insoluble salts type minerals has showed that changes in the surface area can be affected by the presence of the product of mechanochemical reaction.

The effect of non-polar toluene on surface changes will manifest itselt only during intensive strain. Mechanosorption of toluene molecules supports flocu-

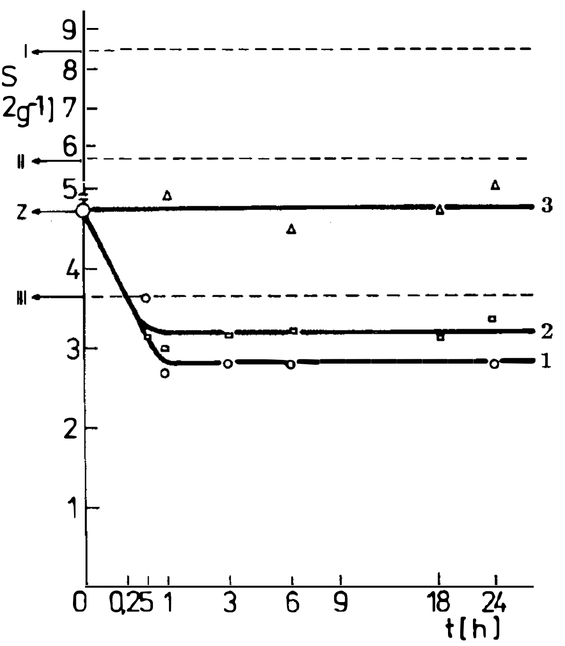

Fig. 2. Specific surface area S vs. time t of stirring the dry ground magnesite in liquid water (1), methanol (2) and toluene (3). (The effect of a 0.25 h peptization regrinding in water (I), methanol (II) and toluene (III) is indicated by interrupted horizontal lines).

lation during regrinding and causes a slight in specific surface area. During long-termed stirring and storage the effect of toluene is protective, the specific surface area and granularity of dry activated powders remain unaffected.

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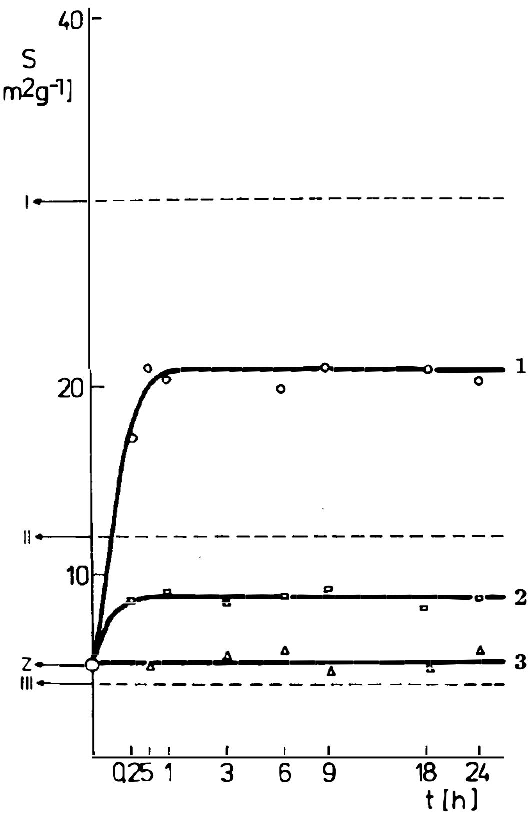

Fig. 3. Specific surface area S vs. time t of stirring the dry ground quartz in liquid water (1), methanol (2) and toluene (3). (The effect of a 0.25 h peptization regrinding in water (I), methanol (II) and toluene (III) is indicated by interrupted horizontal lines).

ZMENY POVRCHU KREMEŇA A MAGNEZITU PRI DISPERGAČNOM PREMLETÍ A STÁRNUTÍ V PROSTREDIACH RÔZNEJ POLARITY

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Skúmali sa zmeny povrchu a štruktúry jemnodisperzných práškov kremeňa a magnezitu pri krátkodobom premletí, premiešavaní a pri dlhodobom odležaní v kvapalnom prostredí rôznej polarity a vo voľnej atmosfére. Zatiaľ čo štruktúra a obsah zvyškovej entalpie práškov ostáva nezmenený, veľkosť povrchu sa mení v závislosti od povahy prostredia a minerálu. Krátkodobé premletie spôsobuje dezagregáciu charakterizovanú vzrastom špecifického povrchu a zastúpenia jemných častíc u kremeňa a magnezitu. V procese premiešavania a odležania sa zrnitosť prášku nemení. Pokles špecifického povrchu u kremeňa je spôsobený kompenzáciou povrchových valencií a aktívnych centier adsorbovanými molekulami prostredia. U magnezitu sa naopak zistil vzrast hodnôt špecifického povrchu, ktorý je pravdepodobne spôsobený vznikom vysokodisperznej povrchovej vrstvy MgO, poťažne produktami reakcie MgO s molekulami prostredia.

Obr. 1. Zmeny špecifického povrchu S magnezitu (prázdne body) a kremeňa (plné body) v závislosti od času statického kontaktu t s prostredím vody (krivka 1 a 1'), metanolu (krivka 2 a 2'), toluénu (krivka 4 a 4') a s voľnou atmosférou (krivka 3 a 3').

Obr. 2. Špecifický povrch S magnezitu v závislosti od času premiešavania t v prostredí vody (1), metanolu (2) a toluénu (3). (Efekt 0,25 hodinového dezagregačného premletia vo vode (I), v metanole (II) a v toluéne (III) je vyznačený prerušovanými vodorovnými čiarami).

Obr. 3. Špecifický povrch S kremeňa v závislosti od času premiešavania t v prostredí vody (1), metanolu (II) a toluénu (III). (Efekt 0,25 hodinového dezagregačného premletia vo vode (I), v metanole (II) a toluéne (III) je vyznačený prerušovanými vodorovnými čiarami).