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CHEMISORPTION CAPABILITIES OF ANATASE SURFACE

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With methods of computer techniques and on basis of crystallographic and XRS data the surface concentration of the active centres in water chemisorption were calculated for the characteristic planes of the anatese. Calculated was also the size of graines whose stage of hydration is equal to the experimentally determined quantity of chemisorbed water.

The hydrated titanium dioxide (HTD) having the structure as that of the anatase when it is exposed to heat treatment loses water gradually. This process was studied widely and interpreted in various, often controversial ways [1]. The aim of this paper was to find out if the anatase surface reacting with water particles can form different chemical entities or the same ones and which is the relationship between the grain sizes of anatase and the amount of active chemisorption centres on its surface. The final solution was to be found theoretically with the use of a computer.

Calculation procedures

There was an algorithm defining coordinates x, y, z of the lattice points of anatase in a similar way as for alunite [2]. Next the programme "ANATASE" was prepared and that programme used crystallographic parameters of anatase [3, 4] - shown in Table 1 - and allows to calculate and accumulate numeric values of coordinates x, y, z in the computer memory for all the lattice points in any selected section of the crystal. This programme allows also to calculate distances of such points in any determined combination, to arrange these distances and to select the smallest distances. The list of distances between a titanium ion and its nearest environment is given in Table 2. The correctness of those values is an evidence that the programme "ANATASE' is correct.

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Table 1 Coordinates of the lattice points of anatase [3, 4] $a = 3.73$ Å; $c = 9.37$ Å; $u = 1.95$ Å/c

Kind of ion	Coordinates x/a	y/a	z/c	Kind of ion	Coordinates x/a	y/a	z/c
Ti^{4+}	0	0	0	O^{2-}	0	0	u
					0	0	$-u$
	0	1/2	1/2		0	1/2	$(1/4)+u$
	1/2	1/2	1/4		0	1/2	$(1/4)-u$
	1/4	0	3/4		1/2	1/2	$(1/2)+u$
					1/2	1/2	$(1/2)-u$
					1/2	0	$u-(1/4)$
					1/2	0	$(3/4)-u$

Table 2 Distances in coordinating polyhedrons of anatase calculated according to "ANATASE" programme

Central ion, its index*	Distance	Neighb. ion, its index*
O^{2-}	1.9059Å	Ti^{4+} T4211
O1222	1.9059Å	T4221
	1.9500Å	T1222
Ti^{4+}	1.9059Å	O^{2-} O8211
T1222	1.9059Å	O8221
	1.9059Å	O3122
	1.9059Å	O3222
	1.9500Å	O1222
	1.9500Å	O2222

* - letter and four digits identify the point of lattice in computer memory

The programme "SURFACE" was prepared in order to collect - among ions being on the selected surface limiting the solid - ions of the same type having defects of same kind in their coordinating polyhedrons. In Fig. 1 is shown, as an example, planes 101, 001 and 100 of the anatase crystal. The criteria of the selection were: occurence of these planes in typical mineralogical forms [5] and coming from the significant signals on the powder XRS spectrum. On these planes there are marked ions with incomplete coordination. Ions of this type represent possible points of chemisorption. Besides the above concept treated as the main one, there was also considered the possibility of ending grains of the solid with anions. According to Boehm [6], presence of anions - not cations - on boundary surfaces of the grain is more probable because of the polarizing properties. In order to keep the grain electro-inertness totally, the excess of a negative charge must be compensated with ions H^+ "taken" from the liquid in which the crystal is

formed. Such a state is the same as the state which result from chemisorption of a water particle on the surface ion Ti^{4+} (the main version). Results of calculations carried out with the programme "SURFACE" are given in Table 3.

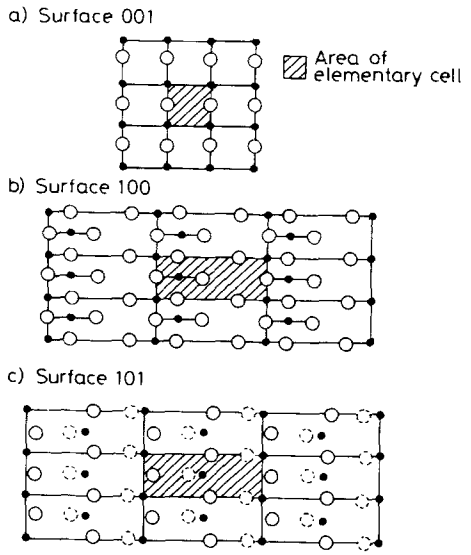


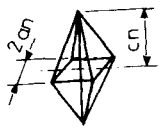
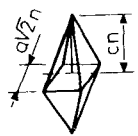
Fig. 1 Surfaces 001, 101 of anatase as a boundary surface of grain • - Ti^{4+} ions, ° - O^{2-} ions

Results and discussion

The presumed shape of the grain (Table 3, column 1) decided which planes (column 2) with the specific concentration of the surface chemisorption centres (column 3) are to be studied. It was introduced parameter "n" while describing the grain shape. This was standard of the grain size. Next the grain volume was determined and its surface as the function of this parameter (column 4 and 5). It allowed to calculate the quantity of moles of chemisorption centres occurring in one mole of TiO_2 included in the grain (column 6) knowing that one elementary cell of anatase with volume "a^2c" includes 4 particles of TiO_2.

The state of the anatase hydration (x) characteristic for the chemisorption capacity (TiO_2) appeared to be dependent on the grain shape and its size (n). It was proved experimentally [7] that studied HTD contains

Table 3 Chemisorptive properties of anatase calculated according to "ANATASE" program

Grain shape	Kind of surface	Surface concentration $H_2O/(nm)^2$	Grain volume	Grain surface	x	$n_{0.34}$	$d_{z0.34}$
	001	7.2	$v = a^2cn^3$	$S = (4ac + 2a^2)n^2$			
	010	5.7			$\frac{6}{n}$	17.65	90Å
	100	5.7					
	101	10.63	$v = \frac{8}{3}a^2cn^3$	$S = 8a\sqrt{a^2 + c^2}n^2$			
	011	10.63			$\frac{3}{n}$	8.82	62Å
	111	7.79	$v = \frac{4}{3}a^2cn^3$	$S = 4a\sqrt{2c^2 + a^2}n^2$			
					$\frac{3}{n}$	8.82	50Å
	112	7.05	$v = \frac{2}{3}a^2cn^3$	$S = a\sqrt{16a^2 + 8c^2}n^2$			
					$\frac{3}{n}$	8.82	39Å

a,c - lattice constants of anatase,

n - standard of grain size,

x - state of the anatase hydration $TiO_2 \cdot xH_2O$,

$n_{0.34}$ - size of grain having $0.34 \cdot 6.02 \cdot 10^{23}$ places for H_2O, $d_{z0.34}$ - substitute diameter of grain having this number of surface centres

0.34 mole of H_2O in each 1 mole of TiO_2 and this water cannot be desorbed in temperature 295 K.
Results of this paper allow to assume that it may be the water chemisorbed on the surface of grains with sizes within some limited figures. In order to compare these sizes, the substitute diameter (d_z), or the cube edge with a proper volume, was calculated. A little bit different diameters of grains with different shapes were obtained and, in these grains, the amount of centres reacting with water is exactly 0.34 mole H_2O in 1 mole of TiO_2 (column 9 in Table 3). The diameter calculated theoretically agree exactly with the real one occurring during the production of pigments.

Conclusions

1. Prepared was the programme "ANATASE" by means of which could be calculated the location of each lattice point of anatase and usefulness of the programme was proved when calculations of inter-lattice point distances of coordinating polyhedrons of titanium and oxygen were conducted.
2. Prepared was the programme "SURFACE" by means of which can be calculated surface ions of one type having the same defects in their coordinating polyhedrons.
3. The correctness of the programme "SURFACE" was verified by comparison of chemisorption capabilities of anatase calculated according to this programme with the experimentally determined amount of water chemisorbed by anatase. The complete agreement was found for the grain sizes ca 10 nm.
4. Minimum surface concentration of chemisorption centres was obtained for the plane 100: it amounts to 5.7 particle of H_2O in 1 nm^2.

References

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Zusammenfassung — Mittels Computerverfahren und auf der Basis kristallographischer und röntgenographischer Daten wurde für die charakteristischen Ebenen von Anatas die Oberflächenkonzentration aktiver Zentren der Chemisorption von Wasser berechnet. Berechnet wurde auch die Größe von Gebieten, deren Hydratationsgrad gleich der experimentell ermittelten Menge chemisch absorbierten Wassers ist.