1001. *The Chemistry of Silicon Carbide Surfaces.*

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A layer exists on silicon carbide particles which dissolves more readily than the interior. The material of the layer exchanges with [^{31}Si]silicic acid. The surface of a silicon carbide particle appears to resemble that of a quartz particle.

SEVERAL methods have indicated that a layer exists on the surface of quartz particles which has a different composition from that of the interior, and was shown by Holt and King[1] to be silicic acid. Silicon carbide crystals normally have a surface layer which is not silicon carbide; Finch and Wilman,[2] by electron diffraction, estimated that its thickness was less than 43 Å. They believed it to be silica, formed by oxidation of the crystal surface in the furnace during manufacture. They could remove it by abrasion or hydrofluoric acid or aqueous alkali, and re-form it by heating the crystals in a Bunsen flame.

We have applied Holt and King's method[1] to the surface of a silicon carbide powder, prepared by grinding large crystals in a rubber-lined tumbling box through which air was drawn and separating the dust by elutriation. Particles of approximately 10 μ diameter were separated from this powder by sedimentation in water. The powders were prepared at room temperature and received no heat treatment except oven-drying at 120°. The specific area of the powder was measured both optically and by nitrogen adsorption (B.E.T. method), the latter giving the value 0·5 m.^{2}/g. and the former 0·14 m.^{2}/g. That the specific area of a quartz powder was determined by the B.E.T. method to be about four times the value obtained optically indicates that the surface roughness of the quartz and the silicon carbide were similar.

The silicon carbide powder was studied by following its rate of dissolution in dilute sodium hydroxide and by measuring the exchange of silicon when the particles were in contact with a solution of labelled orthosilicic acid.

Dissolution of Silicon Carbide in 0·1N-*Sodium Hydroxide.*—Silicon carbide powder (1 g.) and 0·1N-sodium hydroxide (15 ml.) were shaken gently in Polythene tubes at 25°. At measured intervals the tubes were opened and the suspensions centrifuged. A slight permanent turbidity was present in the supernatant liquid which increased with the time of extraction. The dissolved silica in the supernatant liquid was estimated colorimetrically;[3] under these conditions this silicomolybdate method gives a measurable change in colour intensity with a change in silica concentration of 0·015 mg. of SiO_2/100 ml.

The amount of dissolved silica increases rapidly during the first hour, then much more

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[1] Holt and King, *J.*, 1955, 773.

[2] Finch and Wilman, *Trans. Faraday Soc.*, 1937, **23**, 337.

[3] King and Stantial, *Biochem. J.*, 1933, **27**, 990.

slowly (Fig. 1). After 10 hr. a linear plot is given, which, extrapolated to zero time, shows that 0·37 mg. of SiO_2 dissolves per g. of powder during the phase of rapid solution. The initial rapid dissolution indicates that there was a surface layer on the particles more readily soluble than the bulk.

Exchange between Dissolved [^{31}Si]*Silicic Acid and a Silicon Carbide Surface.*—Holt and King [1] showed that silicic acid exchanges between the surface layer on quartz and a solution in contact with it. Evidence for a similar exchange between the layer on silicon carbide and dissolved silicic acid was sought.

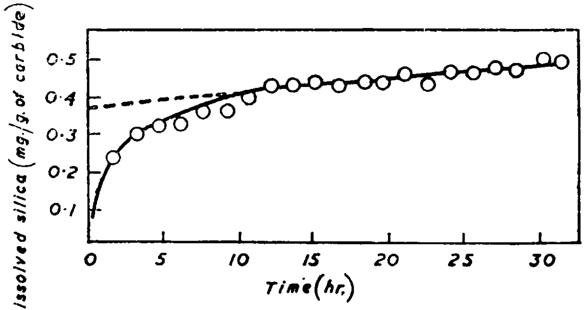

FIG. 1. *Rate of dissolution of silicon carbide powder in* 0·01N-*sodium hydroxide at* 25°.

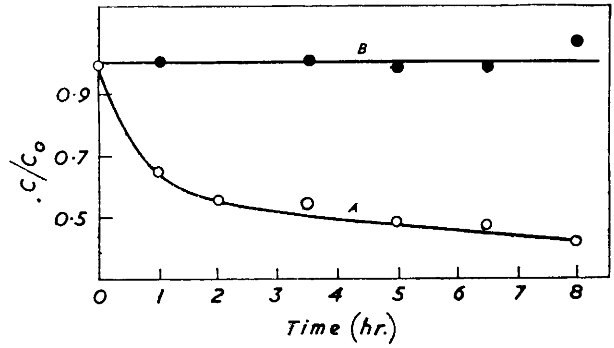

FIG. 2. *Alteration in the concentration of* [^{31}Si]*silicic acid (curve A) and total silicic acid (curve B) on adding silicon carbide powder to a silicic acid solution at* pH 2·8. *The change in the concentration of the solute is denoted as the ratio of the concentration (C) after a measured time to the initial concentration* (C_0).

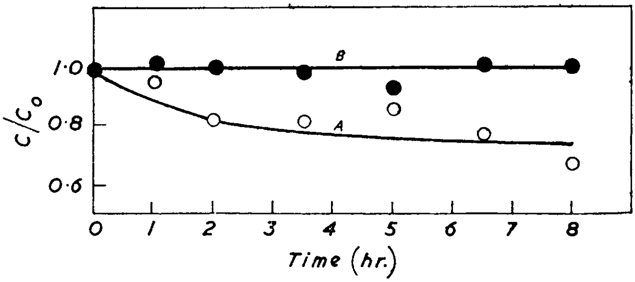

FIG. 3. *Alteration in the concentration of* [^{31}Si]*silicic acid (curve A) and total silicic acid (curve B) on adding silicon carbide powder to a silicic acid solution at* pH 8·7. *For C and* C_0 *see Fig.* 2.

Powdered fused silica (" Vitreosil ") was irradiated in the Harwell pile for 12 hr., then fused with sodium carbonate. A solution of the melt in water was brought to the required pH and diluted to 10 mg. of SiO_2 per 100 ml., whereat the solution is just below saturation with respect to orthosilicic acid and no polymerisation occurs.[4] Silicon carbide powder (1 g.) was gently shaken with this silicic acid solution (20 ml.) in Polythene tubes at 20°. Tubes were opened at intervals of up to 8 hr. and the contents filtered off. The total silica in the liquid was determined by the silicomolybdate colorimetric method and the labelled silica by a Geiger counter. Experiments were carried out in both acid and alkaline solutions. The solutions became increasingly turbid, particularly at alkaline pH, and more so if the silicon carbide had been pre-treated with sodium hydroxide

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[4] Richardson and Waddams, *Research*, 1954, **7**, 542.

The results of the silica determinations are plotted in Figs. 2 and 3. The total mass of dissolved silica did not vary during the experiments but the mass of labelled dissolved silica fell rapidly at first, then more slowly until equilibrium was approached after 5—6 hr. Apparently, there is an exchange of silica between the surface of the silicon carbide powder and the solution. The constant value for the total dissolved silica precludes the possibility of the results' being due to adsorption.

Although Holt and King removed the layer from quartz by extraction with sodium hydroxide, after which treatment the dissolved silicic acid exchanged with surface silica at a diminished rate, we could not obtain a silicon carbide powder free from the rapidly-soluble layer by extraction with sodium hydroxide, washing with water, and air- or oven-drying. Possibly the rapidly-soluble layer is re-formed too quickly for the silicon carbide surface to be detected.

These results suggest that the surface of a silicon carbide particle is normally coated with a layer which resembles that on powdered quartz, whose formation does not require high temperatures. The extent of the layer on the powder can be estimated from the weight of silica which dissolves rapidly and the surface area of the powder, if it is assumed that the layer is silica. The volume, V, of a crystallographic unit cell is $M/\boldsymbol{N}\rho$ (M, molecular weight; ρ, bulk density of the solid). The unit cell being assumed to be a cube, the area occupied by a cell in the surface is $V^{\frac{2}{3}}$. The weight of a monolayer covering 1 m.^{2} is $MV^{\frac{2}{3}}\boldsymbol{N}^{-1} = 0{\cdot}89$ mg./m.^{2} ($M = 60$; $\rho = 2{\cdot}56$). The observed weight of the layer is 0·74 mg./m.^{2}. If the layer is hydrated, as is assumed, the area occupied would be somewhat larger, but data are not available for a calculation to be made. The readily soluble layer represents, approximately, a monolayer on the surface of the silicon carbide. (From the sensitivity of the silicomolybdate it is calculated that a change in silica concentration equivalent to one-hundredth of a monolayer could be detected.)

The rate of dissolution of the silicon carbide in dilute sodium hydroxide, calculated from the *linear* part of the curve, can be compared with the rates for quartz powders measured by King.[5] Two quartz powders gave the values 19 and 16 μg. of SiO_2/(m.^{2} hr.). After the powders had received prolonged treatment with sodium hydroxide to remove the outer layer, the rates were reduced to 8·8 and 10 μg. SiO_2/(m.^{2} hr.) respectively. The silicon carbide powder dissolved more rapidly [8 μg. of SiO_2/(m.^{2} hr.). The rate of dissolution of silicon carbide particles when the outer layer of silicic acid has been removed is, then, similar to that of the core of the quartz particles.

The fracture of silicon carbide crystals leaves in the newly-formed surfaces equal numbers of silicon and carbon atoms with unsatisfied valencies, and it must be supposed that reaction immediately occurs with either atmospheric oxygen or water vapour. If the silicon atoms react with oxygen, the surface must contain SiO ions; if, as is more likely, they react with water, the surface will consist of $Si(OH)_2$ ions. The outer layer of a silicon carbide particle will then resemble that of a quartz particle. In each case there is, apparently, adsorbed on this surface a layer of silicic acid. Dissolution of silicon carbide in dilute sodium hydroxide entails first the removal (rapid) of the adsorbed silicic acid and then the break-up of the main lattice, with the production of very small insoluble particles, possibly carbon, giving a turbid solution.

Elton and Mitchell[6] found that the ionic adsorption energies of various ions adsorbed on silicon carbide surfaces were remarkably similar to those when the ions were adsorbed on silica surfaces,[7] confirming our findings that the two surfaces are similar.

We thank the British Steel Castings Research Association for financial assistance and the Carborundum Company for gifts of crystalline silicon carbide.

THE UNIVERSITY, READING. [*Received, June 4th,* 1957.]

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[5] King, M.Sc. Thesis, Reading, 1955.

[6] Elton and Mitchell, *J.*, 1947, 741.

[7] Benton and Elton, *Trans. Faraday Soc.*, 1953, **49**, 1213.