

Determination of Specific Surface of Marble Powder by Isotopic Ion Exchange

By

B. V. ENÜSTÜN

(Department of Physical Chemistry, University of Ankara)

Özet: Ca^{45} kullanarak, katı yüzeyindeki iyon alış verişine dayanan radyometri metodu ile mermer tozunun özgül yüzeyi tayin edilmiş ve neticenin adsorpsiyonla bulunan değere uyduğu görülmüştür.

Yüzey dengesi uzun bir zaman aldığından, iyon alış verişinin katının iç tabakalarına intikali ve tekrar kristallenme gibi tali olaylardan dolayı, radyometrik ölçüleri sıfır zamanına ekstrapole ederek neticeye varılması lüzumu ve ilk anlardaki hızlı iyon alış verişini takip eden yavaş alış verişe uğrayan yüzeylerin de, adsorpsiyon gibi yüzey olaylarına katıldığı belirtilmektedir.

1. Introduction

Investigations of surface phenomena require accurate data on the specific surface of solids. The determination of the specific surface with accuracy involves laborious experimental techniques such as vapour adsorption. In the case of ionic crystals, however, the isotopic ion exchange provides an easy method which was first applied by Paneth et al. [1] using a natural radio-isotope. Owing to the great variety and abundant supply of artificial radio-isotopes, the field of application of this method has become much wider at the present time.

The method comprises shaking the powder specimen with a solution of known activity containing a radio-isotope of one of the ions of the solid and measuring the residual solution activity. Assuming that the ion exchange takes place at the solid surface only and that the ratio of the number of active isotope ions to the number of non-active isotope ions on the surface is the

same as that in the solution at the equilibrium, it can be shown that the specific surface Σ is given by

$$\Sigma = \frac{n s a - b}{m v b} \quad (1),$$

where n is the total number of gram-ions of the ions involved in the exchange in the solution, s is the surface area occupied by one mole of the solid concerned in the form of a monomolecular layer, v is the number of ions involved in the exchange in one formula unit of the solid, m is the mass of the powder specimen taken, a is the initial and b is the equilibrium activity (or counting rate) of the same amount of solution. s is calculable from the formula weight, density and the crystal geometry of the solid.

Experiments of this kind have shown in general that a rapid decrease in the solution activity at the beginning is followed by a gradual fall apparently due to self diffusion or recrystallization of the solid. Therefore, there exists an uncertainty in deciding on the time of equilibration. According to Paneth the surface equilibrium is attained in a few minutes^[2] and the surfaces which do not contribute to ion exchange in such a short period are not active, therefore, have no importance in surface phenomena^[3]. Kolthoff et al.^{[4], [5]}, on the other hand, are of the opinion that the surface equilibration takes much longer time, therefore, the activity should be observed over several hours and the effect of self diffusion or recrystallization be corrected by an extrapolation to zero time. Stow and Spinks^[6] have observed that the specific surface of SrSO_4 calculated from Sr^{++} exchange is significantly bigger than that calculated from SO_4^{--} exchange. This is probably due to either incomplete SO_4^{--} exchange at the surface or self diffusion of Sr^{++} . The fact that the rate of exchange of Sr^{++} is greater than that of SO_4^{--} as shown by Krehbiel and Spinks^[7] by elution experiments appears to support this point of view. The results of Miyazaki et al.^[8] who have found that the specific surfaces of iron oxides estimated by Fe^{+++} exchange are smaller than those obtained by the B.E.T. method can perhaps be explained also by the lack of surface equilibria.

In some cases a serious limitation of the method is a very rapid self diffusion or recrystallization. Langer^[9] and Zimens^[10]

have observed that especially freshly prepared silver halides undergo with a rapid homogeneous exchange of Ag^+ . Similar results have been obtained with AgBr in Br^- exchange by Kolthoff et al.[¹¹]. According to Murin[¹²] the self diffusion of Ag^+ and the exchange of Br^- through recrystallization are responsible for these phenomena.

The other extreme is the case of very slow surface exchange as reported for galena [²], [¹³].

Another possible complication is the ordinary adsorption of the radioactive substance by the solid[⁵]

These uncertainties on one hand, and our interest in the free energies of wetting of minerals[¹⁴] on the other, lead us to use this method for the determination of specific surface of marble powder and to compare the result with that obtained by a conventional method.

2. Experimental Results

A neutral 7.7×10^{-3} molar solution of CaSO_4 containing Ca^{45} was prepared. 10 ml. of this solution gave ($a \approx$) 1888 counts per minute in a liquid counter type M6H of «20 th Century Electronics Ltd». 5 grams of marble powder prepared from «May & Baker» marble chips were then dispersed in 50 ml. of this solution in a conical flask and shaken at room temperature. At the end of various time intervals about 12 ml. of the suspension was centrifuged and 10 ml. of the supernatant was counted in the same counter. The contents of the counter and the centrifuge tube were subsequently returned to the flask.

The results are shown in Fig. 1 plotting the counting rates against time (The half life of Ca^{45} is long enough not to necessitate any decay correction). The rapid fall in the activity at the beginning corresponds to the ion exchange at the surface. Although the slope of the curve becomes much smaller later, the residual activity does not remain constant even after 24 hours due to self diffusion or recrystallization as mentioned in Section 1. The straight portion of the curve was, therefore, extrapolated to the zero time as shown in Fig. 1 and 1330 c.p.m. was obtained for correct b .

Treating marble as calcite, it can be shown that the quantity s in eqn. (1) is given by

$$s = \left(\frac{M}{d}\right)^{2/3} \cdot \left(\frac{N_0 \sin \alpha}{1 - \cos^2 \alpha / \sin^2 \frac{1}{2} \alpha}\right)^{1/3} \quad (2),$$

where M is the formula weight of CaCO_3 , d is the density of calcite, N_0 is the Avogadro's number and α is the acute angle of a rhomboedral face of a calcite crystal. Using a value of $78^\circ, 5'$ for α [15], we found $s = 9.67 \times 10^8 \text{ cm}^2 \text{ mol}^{-1}$.

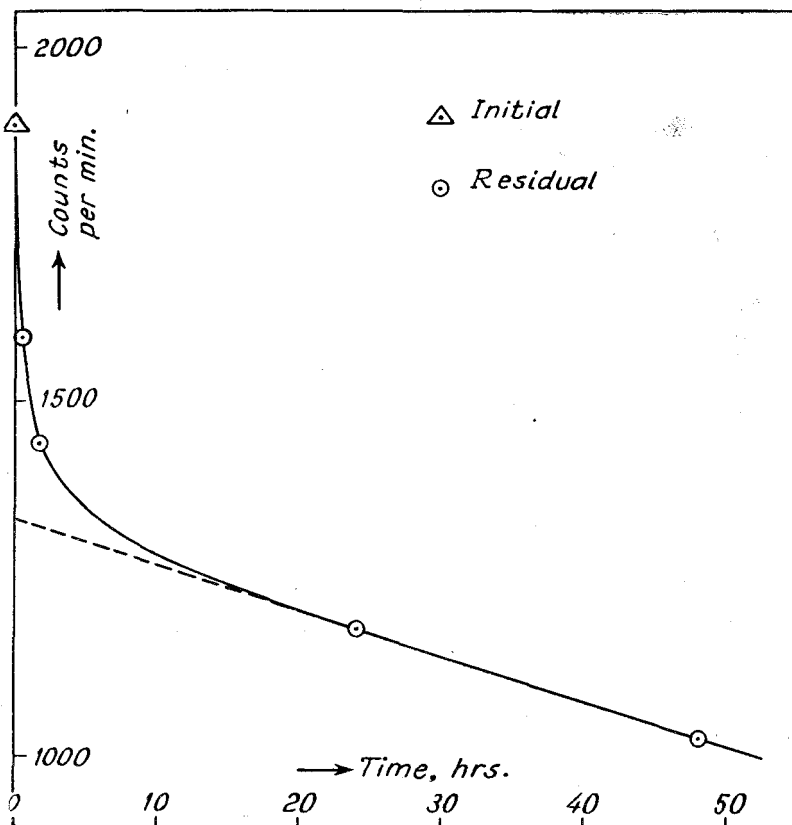


Fig. 1. Solution Activity Plotted vs. Time

The concentration of the CaSO_4 solution used was large enough to suppress the solubility of CaCO_3 effectively even in the presence of atmospheric CO_2 . Therefore, we calculated n directly from the concentration of CaSO_4 .

Substituting the values of $s, n, m, \nu = 1, a$ and corrected b given above into eqn. (1) we obtained $2.1 \times 10^4 \text{ cm}^2. \text{g}^{-1}$. for the specific surface of the marble powder.

As an independent check, we determined the specific surface of another portion of the same powder by the following method:

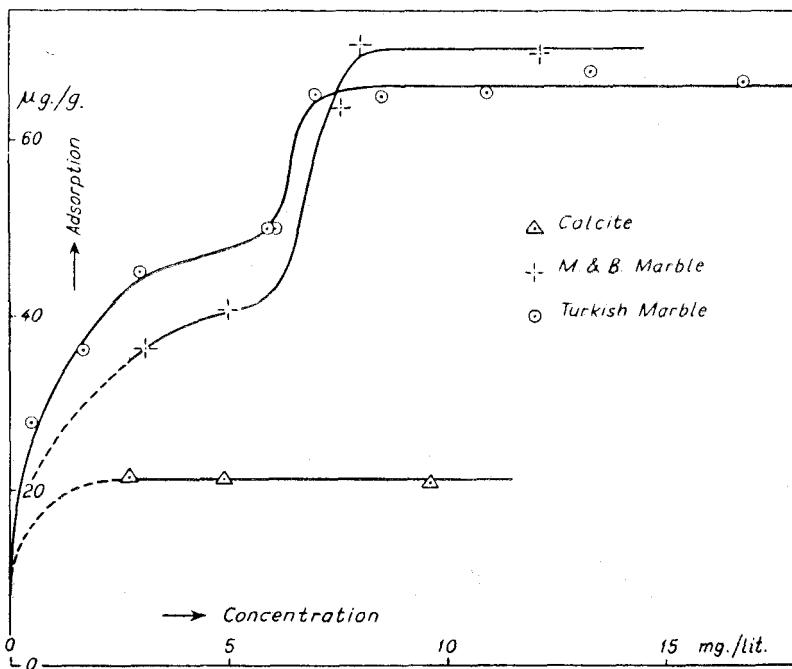


Fig. 2. Methylene Blue Adsorption Isotherms

The methylene blue adsorption of the specimen was determined colorimetrically at various concentrations at room temperature using a «Fisher» electrophotometer. Instead of calculating the specific surface directly from the maximum dye adsorption, as suggested by Paneth et al. [16], [17] which involves the uncertain assumption of monomolecular layer adsorption, we made a different approach. Namely, we also investigated similarly the methylene blue adsorption of a powdered calcite specimen of known specific surface ($9.9 \times 10^3 \pm 10^2 \text{ cm}^2. \text{g}^{-1}$.) determined by vapour adsorption [14] by the B.E.T. method. Both adsorp-

tion isotherms are shown in Fig. 2. It will be seen that the saturation has been reached in both cases. But, the isotherm for marble contains an *S* shaped portion in contrast to that for calcite. (An adsorption isotherm of the same shape was also obtained with another sample of marble of entirely different origin as shown also in Fig. 2).

The specific surface of the marble powder was calculated on the basis of proportionality of the limiting adsorption to the surface of the adsorbent and found as $3.3 \times 10^4 \text{ cm}^2 \cdot \text{g}^{-1}$.

3. Discussion

The agreement between the results of the two methods appears to be as good as can be expected. It follows from Fig. 1 that the complete surface exchange takes not less than 10 hours. We can conclude, therefore, that the surfaces which do not contribute to rapid ion exchange do in fact contribute to other surface phenomena such as vapour adsorption and that an extrapolation is essential to compute the residual activity for specific surface determinations.

The slow surface exchange observed in this particular case can be explained partly by the fact that the amount of total Ca^{++} present in the solution was rather large. Namely, considering the kinetic equilibrium at the solid surface and assuming that the ion exchange takes place at the surface only, it can be shown that

$$\ln \frac{a-b}{x-b} = \left(\frac{m\Sigma}{n} + \frac{s}{v} \right) kt \quad (3),$$

where x is the counting rate at the time t and k is the rate of dissolution of the particular ions concerned at the solid surface in water per unit surface area. The other symbols in eqn.(3) have already been defined in Section 1. It follows from this equation that the time factor $(m\Sigma/n + s/v)k$ determines the rate of ion exchange. In other words, the rate depends on the ratio m/n as well as on the nature of the solid and the ion. The time required for 50 percent surface exchange $t_{1/2}$ can be obtained from eqn.(3), viz.

$$t_{1/2} = \frac{0.693}{(m\Sigma/n + s/v)k} \quad (4).$$

According to the experimental results shown in Fig. 1, $t_{1/2}$ is about 30 minutes. Substituting this and the values of the other quantities in eqn. (4) we find $k \cong 1.7 \times 10^{-11}$ gram ion Ca^{++} per minute per cm^2 for CaCO_3 at room temperature. With this value, it can be calculated that by using a 50 ml. saturated solution of CaCO_3 containing Ca^{45} instead of 7.7×10^{-3} molar CaSO_4 solution and keeping the other variables same the time factor can be increased about 20 times, provided that the atmospheric CO_2 is carefully excluded from the system. Even then, the completion of the surface exchange would take not less than 1/2 hour.

The formation of monomolecular adsorption layer of methylene blue on 10^4 cm^2 adsorbent surface requires 1 mg. of dye^[17]. According to the results shown in Fig. 2, 10^4 cm^2 calcite surface is saturated only by 0.0215 mg. of methylene blue. It follows that either a monomolecular layer is not attained at the saturation or only a small fraction of calcite surface contributes to dye adsorption. This justifies the use of the comparative adsorption method described in Section 2.

The author wishes to thank Mr. W. J. Whitehouse and Mr. W. T. Spragg for their permission to use the facilities at the Baghdad Pact Nuclear Centre where this work was partly carried out, Miss Basima R. Al-Sa'ad and Mr. N. Kaşka for providing the samples and Mr. Y. Türkmen for his assistance in the adsorption experiments.

Bibliography

- [1] Paneth, F. A. and Vorwerk, W., *Z. Phys. Chem.*, (1922), **101**, 445, 480.
- [2] Paneth, F. A., «Radioelements as Indicators», McGraw Hill, New York, (1928).
- [3] Paneth, F. A., *J. Chim. Phys.*, (1948), **45**, 205.
- [4] Kolthoff, I. M. and Rosenblum, C., *J. Am. Chem. Soc.*, (1933), **55**, 2656.
- [5] Kolthoff, I. M. and Eggertsen, F., -*ibid.*, (1940), **62**, 2125.
- [6] Stow, R. and Spinks, J. W. T., *J. Chem. Phys.*, (1949), **17**, 744 ; *Can. J. Chem.*, (1955), **33**, 958.
- [7] Krehbiel, R. E. and Spinks, J. W. T., *Science*, (1956), **124**, 487.
- [8] Miyazaki, K., Seiyama, T. and Sakai, W., *Kôgyô Kagaku Zasshi*, (1956), **59**, 146.
- [9] Langer, A., *J. Chem. Phys.*, (1942), **10**, 821; -*ibid.*, (1943), **11**, 11.
- [10] Zimens, K., *Arkiv Kemi, Mineral. Geol.*, (1946), **A**, **21**, No. 17.
- [11] Kolthoff, I. M. and O'Brien, A., *J. Am. Chem. Soc.*, (1939), **61**, 3409, 3414; Kolthoff, I. M. and Bowers, R. C., -*ibid.*, (1954), **76**, 1503, 1510.
- [12] Muria, A. N., *Doklady Akad. Nauk S. S. S. R.*, (1950), **74**, 85.
- [13] Imre, L., *Kolloid Z.*, (1944), **106**, 89.
- [14] Demirel, T. and Enüstün, B. V., *Com. Fac. Sci. Univ. Ankara*, (1956), **B7**, 1.
- [15] Wyckoff, R. W. G., «Crystal Structures», Vol. I, Table VII, A, 2 Interscience, New York, (1948).
- [16] Paneth, F. A. and Thiman, W., *Ber.*, (1924), **57**, 1215.
- [17] Paneth, F. A. and Radu, A., -*ibid.*, (1924), **57**, 1221.

(Received 27 th Sept. 1957).