

ADSORPTION OF SOME METAL IONS ON THE SURFACE OF CALCITE CRYSTALS

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ABSTRACT

The adsorption of nickel, copper, manganese and cobalt ions on the surface of calcite crystals was measured as a function of the concentration of metal ions. It was found that at equilibrium concentration of calcium carbonate the adsorption of metal ions on the surface of calcium carbonate crystals in order: Ni > Cu > Mn > Co. The adsorption of these metal ions on the crystal surfaces may be interpreted in terms of the Langmuir adsorption isotherm.

INTRODUCTION

The precipitation and dissolution of calcium carbonate are of considerable importance in wide variety of fields such as oceanography, sedimentology, water purification and energy production technology¹⁻⁴. One of the most common forms of mineral scale is the formation of calcium carbonate, which causes serious problems in a number of instances from household appliances to boilers, cooling towers and oil-recovery processes⁵⁻⁷. Whenever crystals grow or dissolve, the rate of growth or dissolution may be strongly affected by the presence of the non-constituent ions or molecules. The reduction in the growth and

dissolution rates may be interpreted by the adsorption of the non-constituent ions or molecules at active sites on the crystal surfaces⁸⁻¹⁰. Metal ions have been widely used in preventing crystal growth of alkaline earth fluorides, sulphates, oxalates and carbonates¹¹⁻¹⁴.

EXPERIMENTAL

Adsorbates: Solutions of metal ions were prepared using either Reagent Grade (Fisher Scientific Co., and J.T. Baker Co.) or Ultrapure (Alfa Chemical Co.) chemicals and triply distilled, deionized water. The concentration of nickel, copper, manganese and cobalt ions ($\pm 0.2\%$) were determined by atomic absorption (Perkin Elmer Model 2380) or by exchanging the metal ion for hydrogen ion on a Dowex-50 ion exchange resin and titrating the liberated acid with standardized carbon dioxide-free potassium hydroxide standard solution (Dilutit, J.T. Baker Co.).

Adsorbent: Calcite seed crystals were prepared by a method similar to that used by Reddy and Nancollas¹⁵ by adding 0.20 M calcium chloride to 0.20 M sodium carbonate solution at 25°C. The crystals were aged for at least 3 weeks before use. The seed crystals were confirmed as calcite crystals by X-ray powder diffraction (Shimadzu XD-3 diffractometer). The specific surface area (SSA) of the crystals, measured using a single point nitrogen adsorption apparatus (30% nitrogen, 70% helium, Quantasorb II, Quantachrome, Greenvale, NY), was 0.63 m²g⁻¹.

Adsorption Experiments: Accurately weighted samples of the calcites crystals were placed in tightly stoppered bottles containing a given volume of saturated calcium carbonate solution. The suspensions were

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dispersed, by magnetic stirrers for 10 minutes before a measured volume of the adsorbate solution was added. The time allowed for adsorption varied between 5 min and 24 h., but it was confirmed that adsorption was effectively completed within 1 h. The calcite weights varied from 50 to 100 mg; the initial adsorbate concentration in the equilibrating systems was from 1 to $12 \times 10^{-6} \text{ mol l}^{-1}$. The amounts adsorbed were taken as the differences between the initial and final concentrations. With each batch of equilibrating samples, controls without adsorbent were included; in no case was adsorption onto the bottle detected.

Analytical Methods: The solutions were filtered through $0.22 \mu\text{m}$ Milipore filters, which had been prewashed in order to remove any residual wetting agents or surfactants. Then they were analysed by atomic absorption (Perkin Elmer Model 2380).

RESULTS AND DISCUSSION

Experiments to study the adsorption of some metal ions such as nickel, copper, manganese and cobalt on the surface of calcite crystals suspended in saturated calcium carbonate solution have been performed at 25°C . In all cases the experimental isotherms correspond to the Langmuir-type model. The Langmuir isotherm can be derived from either kinetic or equilibrium arguments^{15,16} and is most commonly applied to the chemisorption of gases. The appropriate form of the isotherm as applied to solutions may be given by:

$$\theta = \frac{kC}{1 + kC} \quad (1)$$

where θ is the fraction of the solid surface covered by adsorbed molecules and k is a constant at constant temperature. Now $\theta = N/N_m$

where N is the number of moles adsorbed per gram of solid at an equilibrium solute concentration C and N_m is the number of moles per gram required to form a monolayer. Making this substitution and rearranging Eq. (1), we obtain.

$$\frac{C}{N} = \frac{C}{N_m} + \frac{1}{kN_m} \quad (2)$$

plot of C/N versus C will yield a straight line from which k and N_m can be obtained from the slope and intercept respectively. Experimental adsorption isotherm for nickel, copper, manganese and cobalt cations on the surface of calcite crystals are given in Fig. 1. It is immediately apparent that the isotherms of Ni onto CaCO_3 have a steeper "knee" than those for Cu, Mn and Co. This feature indicates a higher adsorption affinity for the metal ions in the following order: Ni > Cu > Mn > Co.

Typical plots of experimental data according to Equation are shown in Fig. 2. The linearity of all of the plots in this figure indicates, therefore, that the adsorption model is quite adequate for the treatment of adsorption data with the present metal ions and the experimental adsorbent. The adsorption parameters of the metal ions under study were obtained from linear regressions of data such as shown in Fig. 2, the numerical values of these parameters are given in Table 1. It is seen that the affinity constant k increases in the following order Ni > Cu > Mn > Co, which reflect the higher adsorption in the same order.

Due to our interest in the kinetics of crystal growth and dissolution of sparingly soluble salts it was reported recently that the presence of these metal ions, even at relatively low concentration ($5 \times 10^{-5} \text{ mol l}^{-1}$), markedly retards the rate of dissolution of calcite

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crystals¹⁷. The numerical values of the kinetic equilibrium constants (k) for the adsorption of the copper ions on the calcite crystals surface has been calculated at the different relative undersaturations (σ).

The relative undersaturation, σ , is defined by:

$$\sigma = \frac{\{([Ca^{2+}]_o[CO_3^{2-}]_o) - ([Ca^{2+}][CO_3^{2-}])\}}{([Ca^{2+}]_o[CO_3^{2-}]_o)} \quad (3)$$

where $[Ca^{2+}]$, $[CO_3^{2-}]$ and $[Ca^{2+}]_o$, $[CO_3^{2-}]_o$ are the undersaturation and saturation molar concentrations of free lattice ions, respectively. Plots of these values against σ in Fig. 3. show the striking increase in the kinetically derived adsorption affinity for the copper ions near equilibrium¹⁷. In Fig. 3 a measured value for the equilibrium adsorption affinity for copper ions (at $\sigma = 0$) is included for comparison. Fig. 3 shows that a good agreement between the kinetic adsorption affinity constants and the equilibrium adsorption affinity constant for the adsorption of copper ions on the surface of calcite crystals.

Table 1. Adsorption parameters for some metal ions onto calcite crystals at 25°C.

Metal ions	N_m 10^7 mol gm^{-1}	k $10^{-6} \text{ l mol}^{-1}$
nickel	4.90	4.53
copper	5.00	3.63
manganese	4.80	2.56
cobalt	4.60	2.33

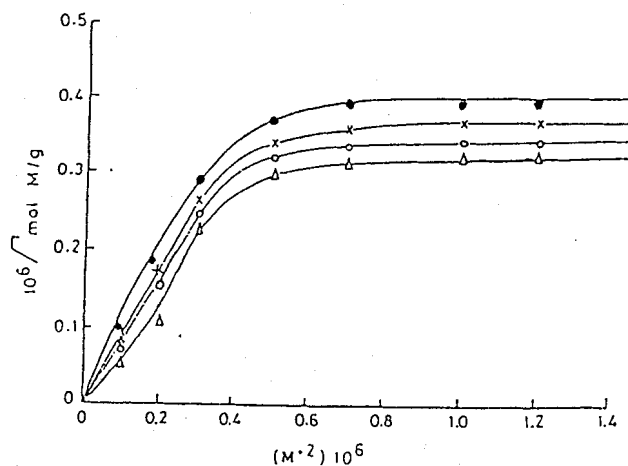


Fig. 1. Adsorption isotherm of Ni(●), Cu(x), Mn(o) and Co(Δ) onto calcite crystals at equilibrium. Plots Γ against $[M^{+2}]$.

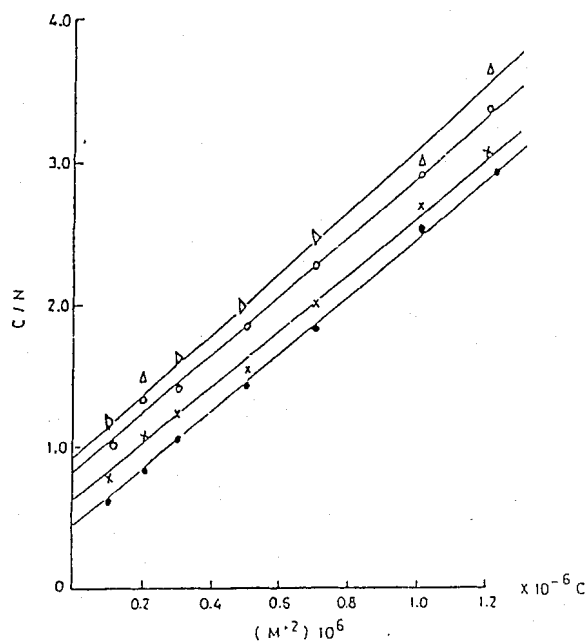


Fig. 2. Adsorption isotherm of Ni(●), Cu(x), Mn(o) and Co(Δ) onto calcite crystals at equilibrium. Plots C/N against $[M^{+2}]$ according to equation 2.

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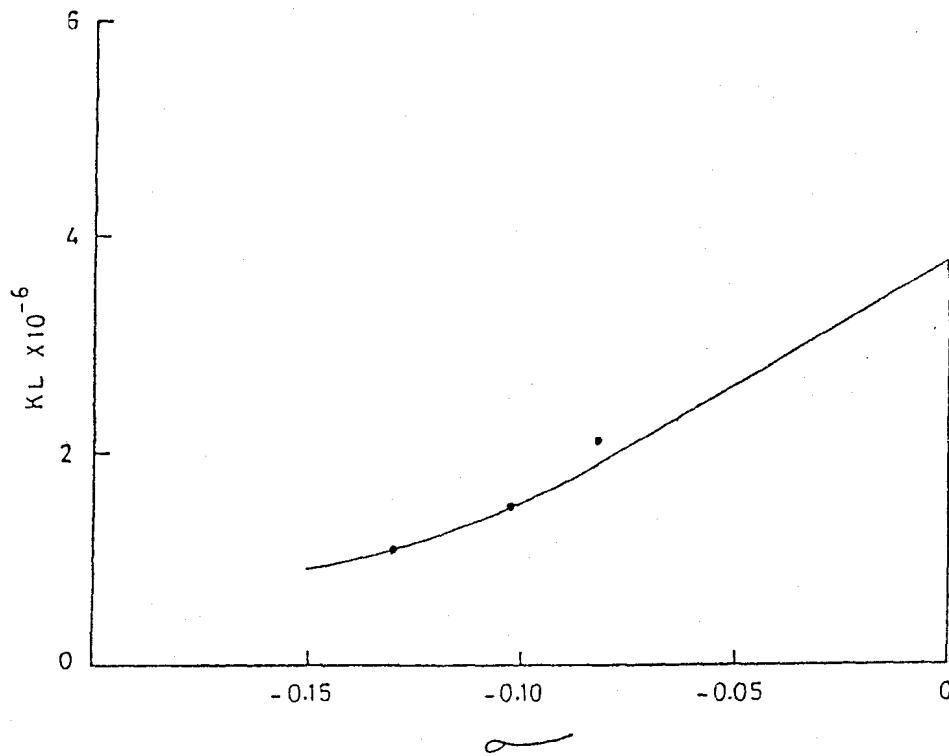


Fig. 3. Plots of equilibrium constants $k(\bullet)$ against σ . An equilibrium value of $k(\blacksquare)$ at saturation ($\sigma = 0$) is included for comparison.

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إدمصاص أيونات بعض العناصر على السطح البللورى للكالسيت

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ملخص البحث :

قيس إدمصاص أيونات النيكل ، النحاس ، المنجنيز والكوبالت على السطح البللورى للكالسيت مع تغير تركيز أيونات هذه العناصر .

ولقد وجد أنه عند حد التشبع لتركيز كربونات الكالسيوم فإن إدمصاص هذه الأيونات على السطح البللورى لكربونات الكالسيوم يتبع هذا الترتيب النيكل < النحاس < المنجنيز < الكوبالت .

ولقد فسرت نتائج إدمصاص هذه العناصر على هذا السطح البللورى فى ضوء منحنى لانجمير للإدمصاص .