AN EFFECTIVE RAPID TECHNIQUE FOR EVALUATING AND QUANTIFYING ALKALINITY IN COAL SPOILS AND CRUSHED LIMESTONE [+]

by

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ABSTRACT.

A rapid, automated procedure was employed to differentiate and quantify siderite, calcite and dolomite in geologic strata. The technique is based on the different rates of dissolution of the three carbonate species when reacted with excess 5 mol/litre HC1. It has been shown that the pseudo-first order rate constants for the three minerals are 27.64, 6.75 and 0.23 (hr)- 1 respectively. The above data point out that the effectiveness of calcite and dolomite in neutralizing acid drainages, considering that kinetic factors are involved, are vastly different. Furthermore, siderite is virtually indestructible in even very strong acid. Data from geologic samples revealed that the rates of dissolution of residual carbonates by a strong acid vary from that of calcite to siderite, even though x-ray diffraction revealed that the carbonates are mainly calcite and ankerite. This has some very important implications in evaluating effectiveness of these carbonates in neutralizing acid drainages. It appears that armoring and weak crystalinity of the carbonate particles play a very important role in controlling their reactivity. The technique presented effectively demonstrates carbonate reactivity. Furthermore, the technique was due to other minerals and colloidal phases. The technique can be used as means of quantifying the reactivity of residual spoil carbonates and therefore allow one to predict the effectiveness of such carbonates in neutralizing and/or controlling acid mine drainage. This has eluded us to the present.

INTRODUCTION

Different quantification of carbonates in disturbed geologic systems and in pure limestone strata is necessary in order to be able to predict processes and degree of influence on the natural environment. Carbonate minerals in the natural environment may have different effects due to their different solubility and rate of reactivity. For example, the rate of reactivity of calcite with acid is much greater than that of dolomite with acid (Petersen and

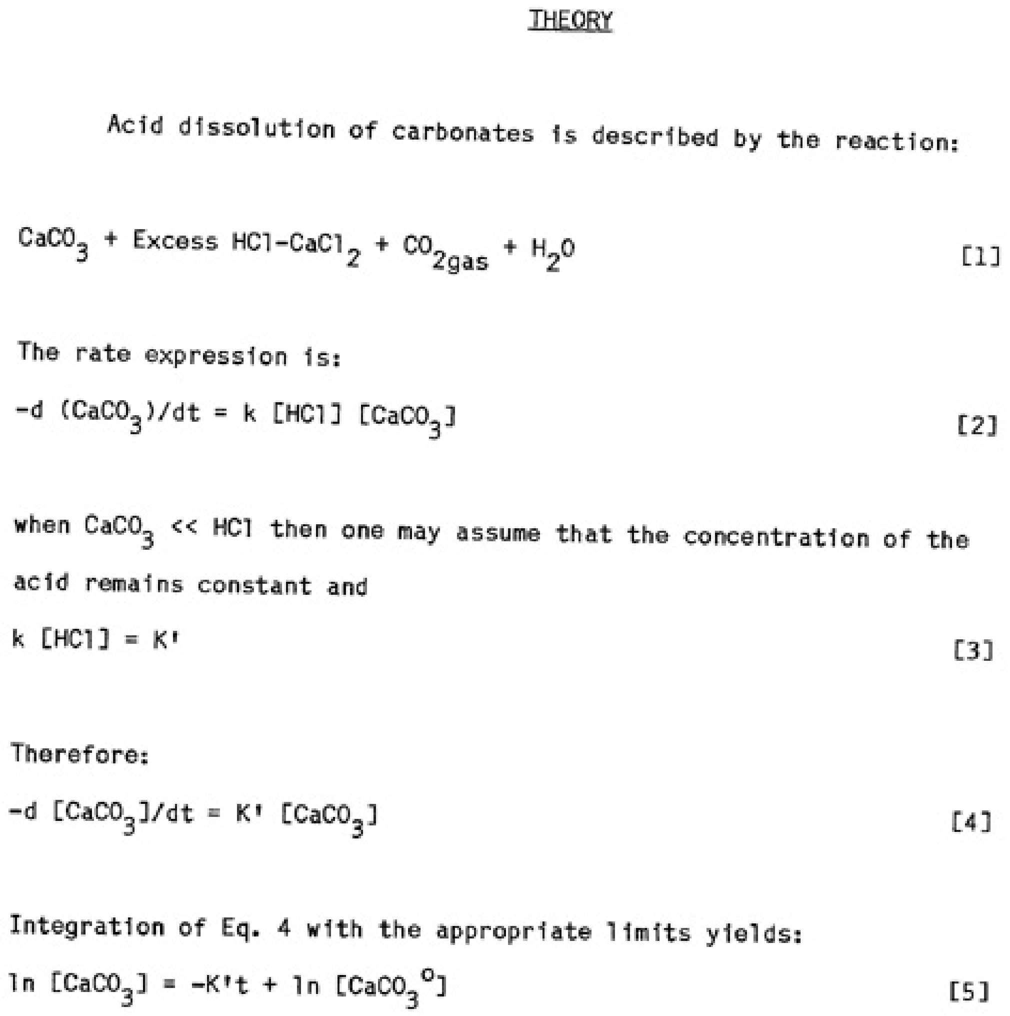
Chesters, 1966). Another carbonate mineral that is encountered in coal spoils is siderite. Its rate of reaction with strong acid is negligible in relationship to the rate of reaction of calcite and dolomite (Roberts et al., 1984).

The presence of carbonates in pyritic coal spoils does not necessarily mean that these carbonates will be available to neutralize acidity generated from the oxidation of pyrite (Caruccio and Geidel, 1985). The type of carbonates present and the degree of armoring play a very important role in determining neutralization effectiveness. Techniques that are currently used to determine alkalinity in coal spoils (Sobek et al., 1978) are erroneous simply because they are based on acid consumption. However, because spoils are enriched with amorphous minerals ($FeOH_x$, $MnOH_x$).- these minerals dissolve by the added acid and, during back filtration of the solution or slurry, the dissolved metals behave as if they are not present. This is because they often precipitate at above neutral pH. This result causes failure of the recommended techniques listed by Sobek et al. (1978) to estimate reactivity of residual spoil carbonates.

The purpose of this study is to demonstrate that carbonates have different rates of acid reactivity. These different rates of carbonate acid reactivity are based on type and degree of armoring. Furthermore, the manometric technique can be used to determine quantity and quality of spoil residual alkalinity without interferences from the dissolution of primary and secondary mineral spoil components.

THEORY

Acid dissolution of carbonates is described by the reaction:



THEORY

Acid dissolution of carbonates is described by the reaction:

$$CaCO_3 + \text{Excess } HCl - CaCl_2 + CO_{2gas} + H_2O \qquad [1]$$

The rate expression is:

$$-d\ (CaCO_3)/dt = k\ [HCl]\ [CaCO_3] \qquad [2]$$

when $CaCO_3 << HCl$ then one may assume that the concentration of the acid remains constant and

$$k\ [HCl] = K' \qquad [3]$$

Therefore:

$$-d\ [CaCO_3]/dt = K'\ [CaCO_3] \qquad [4]$$

Integration of Eq. 4 with the appropriate limits yields:

$$\ln\ [CaCO_3] = -K't + \ln\ [CaCO_3^{o}] \qquad [5]$$

where $CaCO_3^{O}$ represents the original amount of solid phase carbonate added to the reaction vessel and $CaCO_3$ represents amount of solid carbonate species that remains in the reaction vessel at any time during the reaction. The K' value is the reaction constant and its value will be dependent upon the carbonate species (Evangelou et al. P 1984).

A plot of in ($CaCO_3$) against time should provide a straight-line relationship in the case of a single carbonate species. For polycarbonates several slopes are expected with each carbonate species having a characteristic K' value. Extrapolation of the slope(s) against the Y-axis should identify and quantify the specific carbonate species associated with the particular slope.

MATERIALS AND METHODS

Apparatus. -- The apparatus used for kinetic dissolution of carbonates is described by Roberts et al. (1984). A 250-ml Erlenmeyer flask is connected by a pressure-resistant 6.25 mm Poly-Flo tubing to a differential-pressure Viatran transducer (Model 219-12). The pressure hose is connected to a ground-glass joint that fits air-tight in the Erlenmeyer flask. It is secured in position with rubberbands on specially made glass hooks attached to the flask. The pressure transducer is connected to a strip-chart recorder via an Arista D.C. power supply (Model 46-476) for continuous monitoring of pressure generated in the vessel due to acid carbonate dissolution. For a detailed schematic see Evangelou et al., (1984) and Roberts et al., (1984).

Geologic strata and pure mineral samples were ground to pass through a 0.5 mm sieve (Evangelou et al., 1984; Turner and Skinner, 1959). Samples representative of the geologic strata and pure minerals were weighed into polypropolene cups for each determination and the cup was floated on 100 ml 5 mol L^{-1} HC1. The flask with the acid and the floating sample was secured on a rotational 60 cycle shaker. The motion caused by the shaker, set at a maximum speeds forced the floating cup to sinks causing the dissolution reaction to proceed. Completion of the reaction is considered the point at which pressure in the reaction vessel, as shown by the strip-chart recorders remained constant.

RESULTS AND DISCUSSION

The relationship between grams of $CaCO_3$ and pressure is shown in Fig. 1. Kinetic dissolution data of pure carbonate minerals (Fig. 2) demonstrates that the decomposition of carbonates in strong excess HCl acid is a pseudo-first-order reaction. The difference in the proportionality constant W) between the three minerals is large enough so that it can serve as means of differentiating quantitatively the minerals in mixtures of the three. This is demonstrated in Fig. 3. The sharp bend on the lines are indicative of the presence of two minerals. Extrapolation of the line of the lesser negative slope against the y-axis would allow one to quantify the two mineral species (the testing and use of the procedure is discussed in Evangelou et al. (1984), and Roberts et al., (1984)).

The data in Figures 4, 5 and 6 demonstrate differences in reactivity of the carbonates present in geologic strata. The data

when compared to x-ray diffraction reveal important information concerning neutralization of acid mine drainage. Fig. 4 shows a proportionality constant of 35 hr^{-1} as opposed to a minimum 27 hr^{-1} for 0.5 mm diameter calcite particles. The K' value of the sample suggests that the geologic stratum contains calcite. X-ray diffraction shows that the carbonates present are dolomite ($CaMg(CO_3)_2$) and ankerite ($Ca(Mg, Fe, Mn)(CO_3)_2$). The fact that ankerite may have an acid dissolution rate much higher than well crystalized dolomite (Evangelou et al., 1984; Roberts et al., 1984) suggests that using the most common laboratory test in determining alkalinity in geologic strata (Sobek et al., 1978) may lead to erroneous interpretation of the results. In other words, the destruction of ankerite due to acidic conditions in the spoil will leave the water enriched in dissolved manganese. The data in Fig. 5 show that the acid kinetic dissolution of the particular sample resembles that of dolomite. X-ray diffraction does not point out that the sample contains dolomite. The data in Fig. 6 represents carbonate kinetics similar to those of siderite ($FeCO_3$). However, x-ray diffraction does not collaborate the finding. Perhaps the carbonate mineral present in the sample is amorphous. The data in Table 1 show a good agreement for most samples between neutralization potential and carbonates determined manometrically. However, for some samples inconsistencies are apparent. These inconsistencies involve samples of low neutralization potential. The apparent inconsistencies are not unexpected since the manometric technique measures actual carbonates while neutralization potential measures carbonates and pH buffering minerals, such as manganese oxides, iron oxides and clay minerals. However, the neutralization potential exhibited by the latter minerals is only of use in neutralizing acidity if these minerals are buffered at high pH (i.e. iron hydroxides but not manganese oxides and clays (Stumm and Morgan, 1970)). The manometric technique is more functional when compared to other techniques since it identifies and quantifies carbonate reactivity.

Another possible use of the manometric technique is that it helps to identify possible discrepancies in determining acidity in samples. This is accomplished by pointing out the presence of acid metal carbonates, whose role is acid mine drainage formation is poorly understood.

Table 1. Amounts and species of carbonates reacted and relative recovery of each species by acid dissolution. Table taken from Roberts et al. (1984).

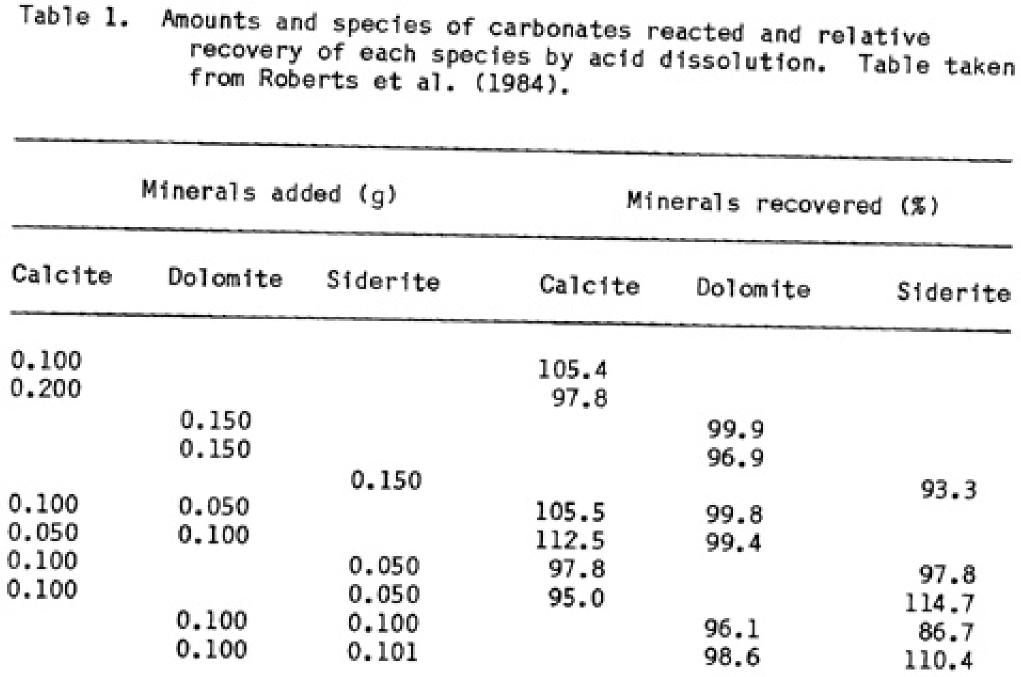


Table 1. Amounts and species of carbonates reacted and relative recovery of each species by acid dissolution. Table taken from Roberts et al. (1984).

Minerals added (g)			Minerals recovered (%)		
Calcite	Dolomite	Siderite	Calcite	Dolomite	Siderite
0.100			105.4		
0.200			97.8		
	0.150			99.9	
	0.150			96.9	
		0.150			93.3
0.100	0.050		105.5	99.8	
0.050	0.100		112.5	99.4	
0.100		0.050	97.8		97.8
0.100		0.050	95.0		114.7
	0.100	0.100		96.1	86.7
	0.100	0.101		98.6	110.4

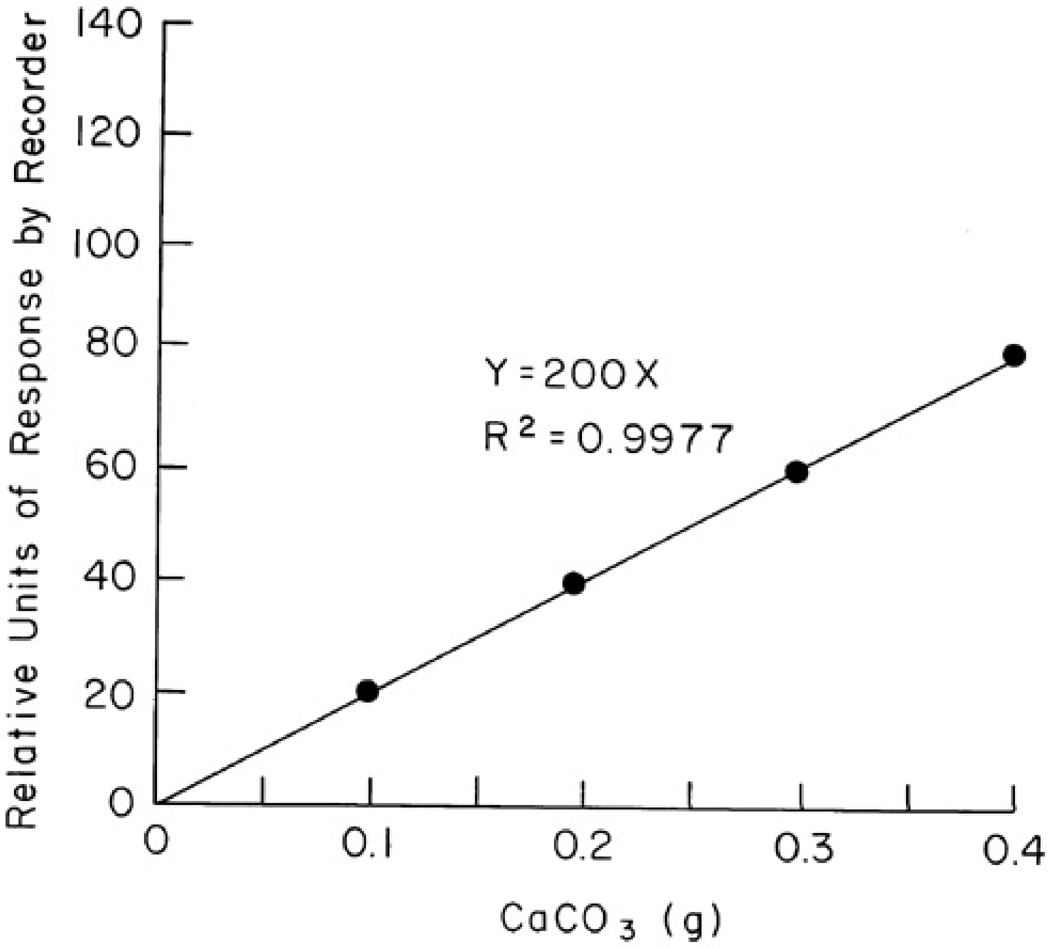


Fig. 1. Relationship between pressure transducer output and grams of calcium carbonate (Evangelou et al. 1984).

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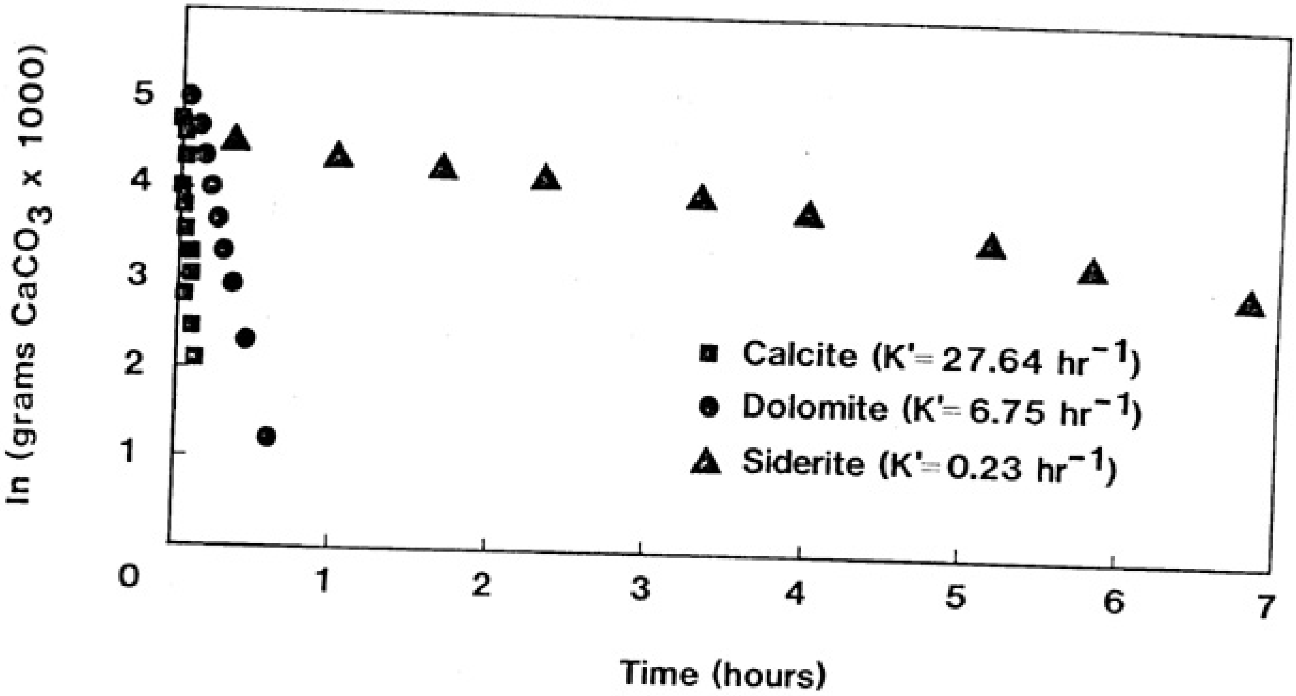

Fig. 2. Kinetic dissolution of carbonate minerals in strong hydrochloric acid (Roberts et al. 1984).

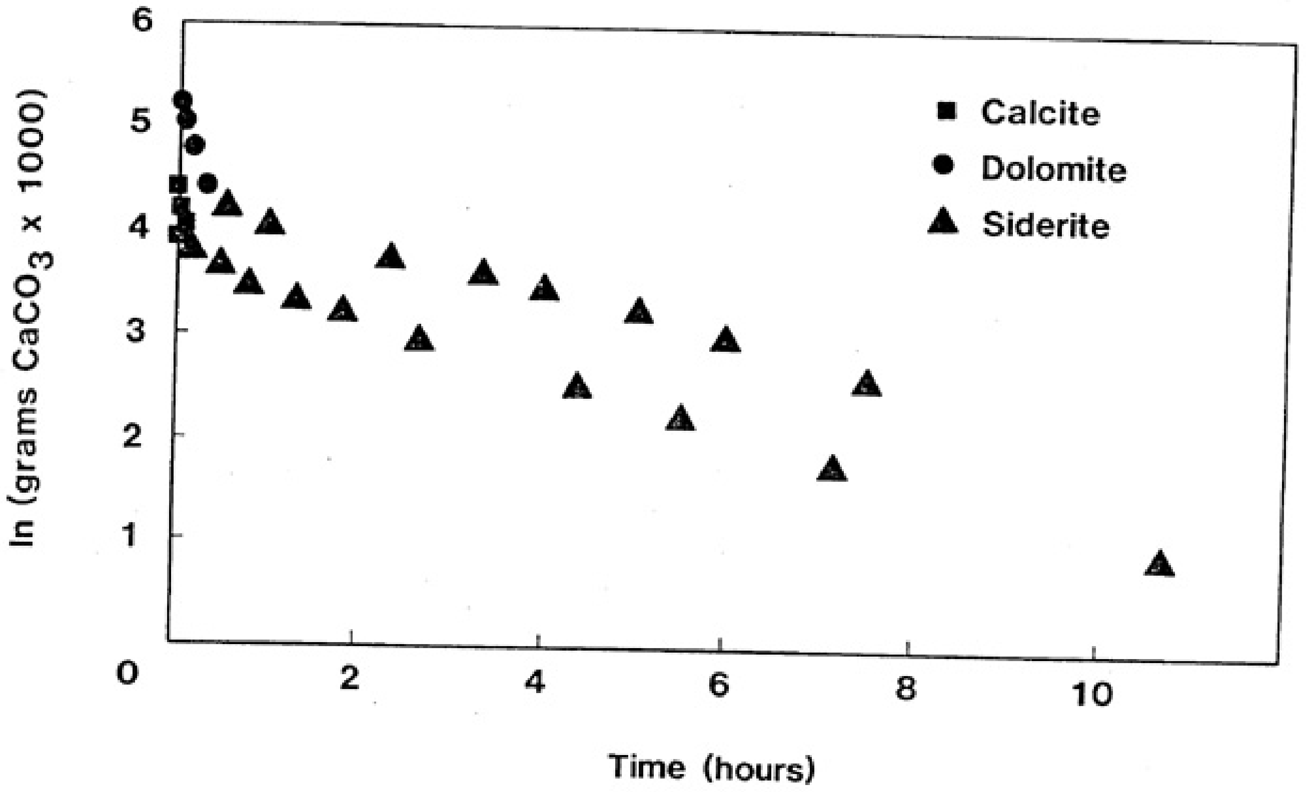

Fig. 3. Kinetic dissolution of mixtures of pure carbonate minerals in strong hydrochloric acid (Roberts et al. 1984).

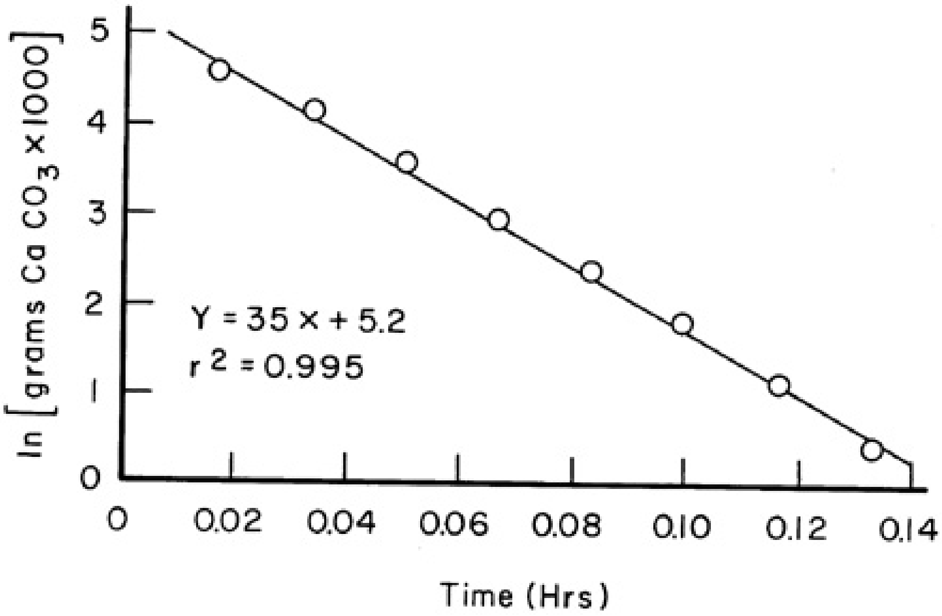

Fig. 4. Kinetic dissolution of geologic stratum carbonates in strong hydrochloric acid.

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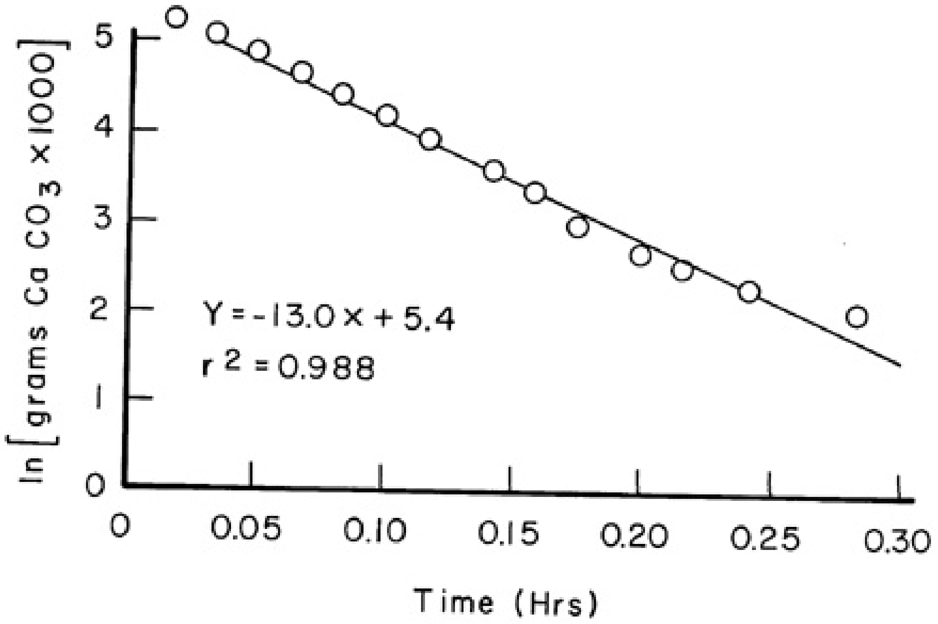

Fig. 5. Kinetic dissolution of geologic stratum residual carbonates in strong hydrochloric acid.

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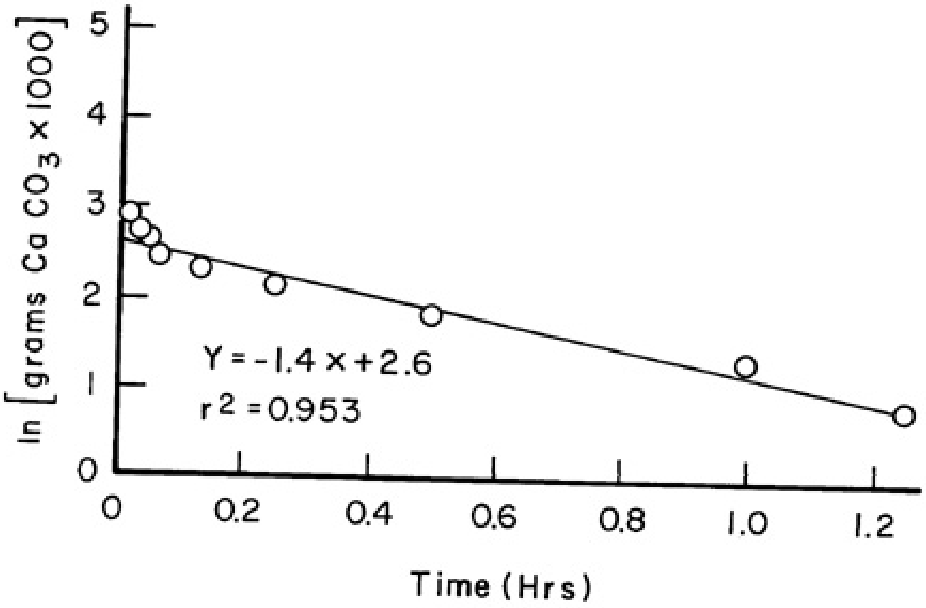

Fig. 6. Kinetic dissolution of geologic stratum residual carbonates in strong hydrochloric acid.

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