

## DISSOLUTION KINETICS OF SOIL CALCIUM CARBONATE CONTENT

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### Abstract

The carbonate content in the agricultural soils is very important, and sometimes causes a critical problems regarding to the plant nutrition. So, the information about the soil carbonate content should be noted. The calcimeter method is simple and convenient method has been to give reliable estimates of carbonate in a variety of soil samples.

Thus, the objective of this work is to investigate a procedure based an estimation of carbonate, using long and short reaction time. Calcimeter apparatus was used to determine the dissolution kinetics of calcium carbonate in twelve different Hungarian soil types using nonselective acid reagent HCl of 10%. Three processes of carbonate dissolution were investigated under laboratory conditions, and the processes were examined by a computer program, given the followings: one very fast reaction (Q a constant parameter), another faster ( $k_1, A_1$ ) and a slower ( $k_2, A_2$ ) first order kinetic reactions.

### Introduction

Bardy and Weil (1996) mentioned the sources of carbonate of lime include marl. Oyster shells basic slag and precipitated carbonates, but ground limestone is the most common and is by far the most widely used of all liming materials. The two important minerals carried by limestone are calcite, which is mostly calcium carbonate ( $\text{CaCO}_3$ ), and dolomite, which is primarily calcium-magnesium carbonate  $\text{CaMg}(\text{CO}_3)_2$ .

Always and Zetterberg (1935) are also subject to errors, since strong acids (e.g., HCl) may dissolve Ca and Mg from noncarbonate sources such as clay minerals, amphiboles, pyroxenes, and feldspars. This could occur when soils containing dolomite are subjected to prolonged treatments with relatively high concentration of HCl.

In evaluating limestone for agricultural purposes it is common practice to determine the calcium carbonate content of the soil. Calcite and dolomite contents in several samples of Mancos Shale, as determined by the kinetic dissolution method. Evangelou et al. (1984) concluded that the kinetic dissolution method for differentiation and quantitative determination of calcite and dolomite singly or mixtures, is discriminatory, highly sensitive, and rapid. Experimentation to date has involved only calcite and dolomite. The method's applicability for other carbonate species and for mixtures of more than two species has not been tested. Here, we can distinguish our samples in the point of carbonate dissolution according to Evangelou (1984). Holford and Mattingly (1975) found that the specific surface area of  $\text{CaCO}_3$  was an inverse hyperbolic function of the percentage of  $\text{CaCO}_3$  and ranged from 16 to 500  $\text{m}^2 \text{g}^{-1}$ . Skinner (1959) mention that the determination of calcite and dolomite in soil of limestones is based on the difference in the rates of solution of calcite and dolomite. The  $\text{CO}_2$  evolved from reaction of a mixture of calcite and dolomite in excess HCl is measured at frequent intervals until the reaction is completed. The amounts of carbonate found in the four soil samples by this intercept method using 26 time intervals were in a good agreement with amounts known to be present.

The theoretical and experimental studies have shown that grinding and passing the samples through a 0.5 mm sieve allowed partial mixtures of calcite and dolomite to be quantitatively differentiated by kinetic dissolution. He stated that the difference in rate of solution of calcite and dolomite in acid or HCl has been used for many years to differentiate the two minerals qualitatively.

Kachanoski, (1992) mentioned that the carbonate chemical reactions involving the solute species within the bulk aqueous phase are very fast, with reaction rates on the order of  $10^9$  to  $10^6$  reciprocal seconds. Evangelou, (1984) concluded that the kinetic dissolution method for differentiation and quantitative determination of calcite and dolomite singly or mixtures, is

discriminatory, highly sensitive, and rapid. Experimentation to date has involved only calcite and dolomite. The method's applicability for other carbonate species and for mixtures of more than two species has not been tested.

Determination of carbonate by the procedure described here should serve the same purpose. Where total carbonate content of limestone or soils is required, estimation of calcite, dolomite, and total content in one operation is particularly convenient. The results in which the reaction proceeds the release of CO<sub>2</sub> with time become somewhat irregular and varies within the samples. Evangelou et al. (1984), and also with Turner and Skinner (1959) in a subsequent experimental investigation with pure calcite and dolomite, showed that acid dissolution did indeed follow pseudo-first-order kinetics, with some deviations after 50% of samples had reacted with acid. They also demonstrated that different rate constants are obtained for dolomite by varying the effective diameter of dolomite crystals. Even though different rate of constant may be yielded by dolomite, depending upon crystal size, rates are sufficiently different from rates of dissolution of calcite of equivalent size as to be readily separable from calcite. Evangelou (1984) mentioned that there is some deviation in dissolution rates near the end of the reaction, but not before rate constants have been established for the slower reacting dolomite in the two phase systems under investigation.

The main aims of the present study are: Determination of the rate of soil calcim carbonate dissolution. Deriving the calcim carbonate dissolution into three processes. Conclusion about the reachivity of soil's calcim carbonate content. Thus, the objective of this work is to investigate a procedure based an estimation of carbonate, using long and short reaction time.

#### Materials and Methods.

Twelve soil samples were used in this study. Samples were collected, each by the following: A 25 cm soil sample in column form was collected from six different soils in Hungary after removing the first 2 cm top layer. These soil samples were selected from different locations depending on the variation of CaCO<sub>3</sub>. The soil samples were air-dried and mixed well ground with blender and passed through 2mm sieve plate. Table 1 shows the some properties of each soil. Hydrochloric acid (HCl) was used at 10% concentration.

Table 1. Characterization of soil samples.

Soil Code	Soil Origin			CaCO <sub>3</sub>	Humus	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O
		KA	PH	%	%	mg/kg	mg/kg
AK10	TÁRKÁNY	48	7.49	20.53	4.49	217.29	231.3
AK11	TÁRKÁNY	50	7.47	16.95	5.43	143.4	130.41
AK12	TÁRKÁNY	50	7.43	13.2	3.1	266.61	165.03
AK14	TÁRKÁNY	50	7.31	10.19	4.23	223.23	185.41
AK20	TÁRKÁNY	40	7.47	11.34	4.61	213.27	118.4
DK17	ESZTERGOM	41	7.44	10.01	2.52	241	161.91
DK18	ESZTERGOM	46	7.25	8.39	2.98	247.81	155.97
BG13	SZÁKSZEND	35	7.61	12.07	1.82	283	233.7
TZ19	BANA	40	7.42	5.63	2.89	538.1	405.7
VD24	TÁRKÁUY	36	7.54	6.07	3.51	282.03	194.45
NY15	NAGYIGMAND	37	7.56	6.44	3.07	193.2	323.1
4	KOMLO4	150	7.87	46.15	0.57	#	#

#### Determination of dissolved carbonate in term of CaCO<sub>3</sub> using Scheibler's calcimeter

CO<sub>2</sub> volumes of developed were measured at 0.0, 0.25, 0.50, 0.75, 1.0, 1.25, 1.50, 1.75, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 15.0, 20.0, 25.0, 30.0, 35.0, 40.0, 45.0, 50.0, 55.0, 60.0 minutes. The total carbonate expressed in terms of CaCO<sub>3</sub>%, calculated using the following formula

$$\text{CaCO}_3 \% = \frac{MA}{100} \times 100/g \quad (1)$$

Where:

$M$  = developed carbon dioxide  $\text{cm}^3$ .

$A$  =  $\text{CaCO}_3$  quantity % according  $1 \text{ cm}^3$  carbon dioxide, at the observable temperature

$g$  = the weight of the material.

According to the application of the products of Eq. (1) and fitted in the Eq. (2)

$$Y = A_1 \{1 - \exp(-k_1 t)\} + A_2 \{1 - \exp(-k_2 t)\} + Q \quad (2)$$

Where:

$Y$  = is the amount of calcium carbonate %.

$A_1$  and  $A_2$  = are the maximum of calcium carbonate % in faster and slower processes, respectively.

$k_1$  and  $k_2$  = are the rate constants of the faster and slower processes respectively.

$Q$  = calcium carbonate % in the very fast process.

The calculated parameters of calcium carbonate % dissolution are listed in Table 2.

### Results and Discussion

As it is shown in Table (2) below that the smallest value of the constant rate of the faster reaction ( $K_1$ ) was found in the sample TZ19 ( $K_1 = 1.8381$ ), while the highest value was in the samples AK12 and VD24 (8.4954 and 8.3197 respectively). Meanwhile, the value of constant rate of slower reaction ( $K_2$ ) was at maximum with the sample VD24 (0.40288), and the minimum  $K_2$  value was found in the sample BG13 (0.08481). The highest percentage of maximum calcium carbonate in faster reaction ( $A_1$ ) was found in the soil sample KOMLO4 (44.60415), while the lowest percentage of  $A_1$  was obtained in the sample VD24 (3.17416). In the slower reaction, the lowest value of the maximum calcium carbonate ( $A_2$ ) was calculated in the sample AK20 (1.07611), and the highest value was obtained in the sample AK12 (4.93977).

Table (2) Estimation of  $K_1$ ,  $K_2$ ,  $A_1$ ,  $A_2$  and  $Q$  from first order of kinetics equation (Eq. 16)

Soil Samples	$K_1$	$K_2$	$A_1$ mg/kg	$A_2$ mg/kg	$Q$ mg/kg
TÁRKÁNY (AK10)	4.9633	0.19379	18.0895	3.54	0.007754
TÁRKÁNY (AK11)	7.6155	0.21262	13.33114	3.22887	0.00651
TÁRKÁNY (AK12)	8.4954	0.1296	10.29053	4.93977	0.000481
TÁRKÁNY (AK14)	6.4367	0.24378	8.082672	2.29413	0
TÁRKÁNY (AK20)	6.6477	0.31643	10.74302	1.07611	0.022198
ESZTERGOM (DK17)	3.8084	0.13468	7.547694	4.04299	0
ESZTERGOM (DK18)	3.8404	0.13559	5.924029	3.93016	0
SZÁKSZEND (BG13)	4.5149	0.08481	9.031306	4.41591	0
BANA (TZ19)	1.8381	0.130208	4.50138	3.014178	0.1169
SZAKSZEND (VD24)	8.3197	0.40288	3.17416	3.39924	0.004
NAGYIGMAND(NY15)	6.5883	0.22662	3.34568	3.60308	0.01
KOMLO4	5.5608	0.23261	44.60415	2.94401	0

The classification of soil samples according to the parameters calculated in Table (2) will be:

According to  $K_1$ : AK12 > VD24 > AK11 > AK20 > NY15 > AK14 > KOMLO4 > AK10 > BG13 > DK18 > DK17 > TZ19.

According to  $K_2$ : VD24 > AK20 > AK14 > KOMLO4 > NY15 > AK11 > AK10 > DK18 > DK17 > TZ19 > AK12 > BG13.

According to  $A_1$ : KOMLO4 > AK10 > AK11 > AK20 > AK12 > BG13 > AK14 > DK17 > DK18 > TZ19 > NY15 > VD24.

According to  $A_2$ : AK12 > BG13 > DK17 > DK18 > NY15 > AK10 > VD24 > AK11 > TZ19 > KOMLO4 > AK14 > AK20

From this, the type of artificial classification indicated, it seems that the values of A1 give an ideal classification because the arrangement of the soil samples according to the maximum  $\text{CaCO}_3$  % categorized the soil samples according to the main origin places of collection.

*Relationship between (K) and value of (A):* The results show that K1/K2 was 70 in the sample AK12, and 45 in case of the sample BG13 and in AK11, it was 36.1, while it was 29.5 in the sample NY15 and 29.2 in the samples of DK17 and DK18. The lowest value of K1/K2 was in the sample TZ19. Regarding to the ratios of A1/A2, the highest values were in the cases of KOMLO4 and AK20, and the lowest value was in the samples of VD24 and NY15.

*Distinguish between the amounts of carbonates in faster and slower reactions:* Sixty minutes were the time required for dissolution kinetics (Fig. 1, 2, 3, and 4) of slower and faster processes for carbonate formation. The time requirement is an important factor to distinguish between these two processes. Depending on the represented materials, the soil samples can be grouped into the followings:

- Group (A): contains the sample of NY15 which indicates that the difference in the amounts of carbonates between the two processes is very limited.
- Group (B): contains the samples of VD24, TZ19, and DK18 which indicate a low difference in the amounts of carbonates between the two processes.
- Group (C): contains the samples of AK12, BG13 and DK17 which indicate a medium difference in the amounts of carbonates between the two processes.
- Group (D): contains the samples of AK10, AK11 and AK14 which indicate a high difference in the amounts of carbonates between the two processes.
- Group (E): contains the samples of AK20 and KOMLO4 which indicate a very high difference in the amounts of carbonates between the two processes.

The results demonstrate the model of carbonate dissolution, and it should be noted that the experimental kinetic studies on the carbonate dissolution were carried out under conditions far removal from field conditions. It may be concluded that the method described is simple, can reasonably estimate the carbonate content of soil samples, and does not require special equipment. This technique can be readily adapted to routine soil analysis without the need for preparation of additional chemicals.

On the basis of the above mentioned results, it is easy to make a schematic research work point for the future as the following: (1) Calcium carbonate deposition model for modeling the processes and easily parameterized for sites and useful for long-term simulations. (2) Validate to model with field observations. (3) Consider the roles of state factors in controlling calcium carbonate, and (4) Role of some environmental factors (biotic and abiotic) affecting the carbonate dissolution in soil samples.

Dissolution kinetics of soil calcium carbonate content

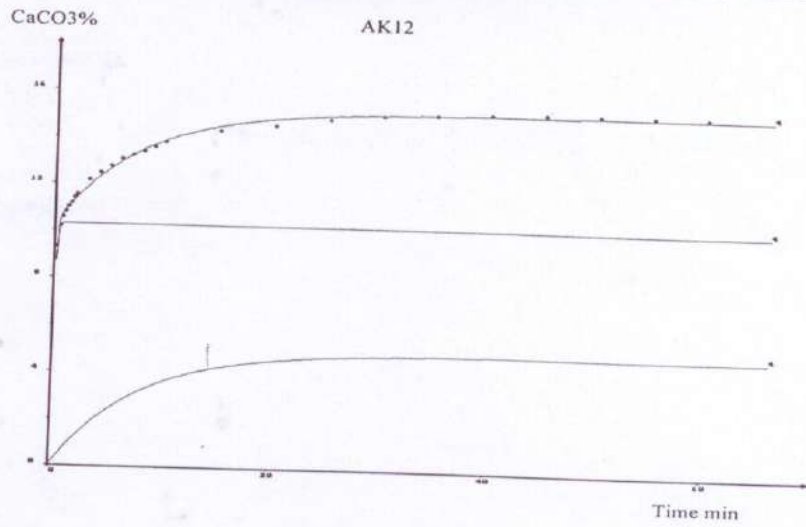


Fig. 1. The relationship between the faster and slower processes of carbonate dissolution in soil sample (AK12)

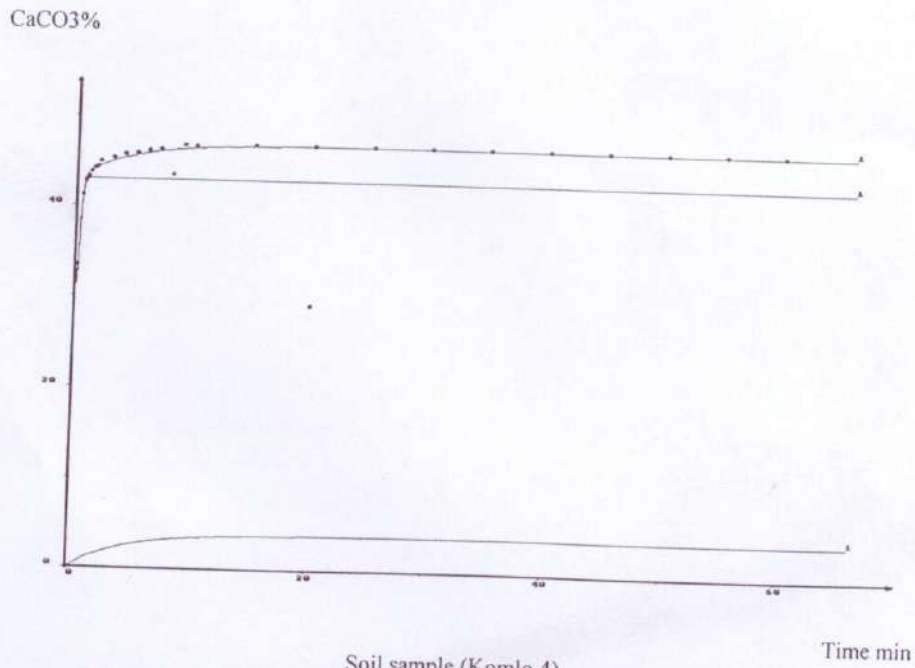
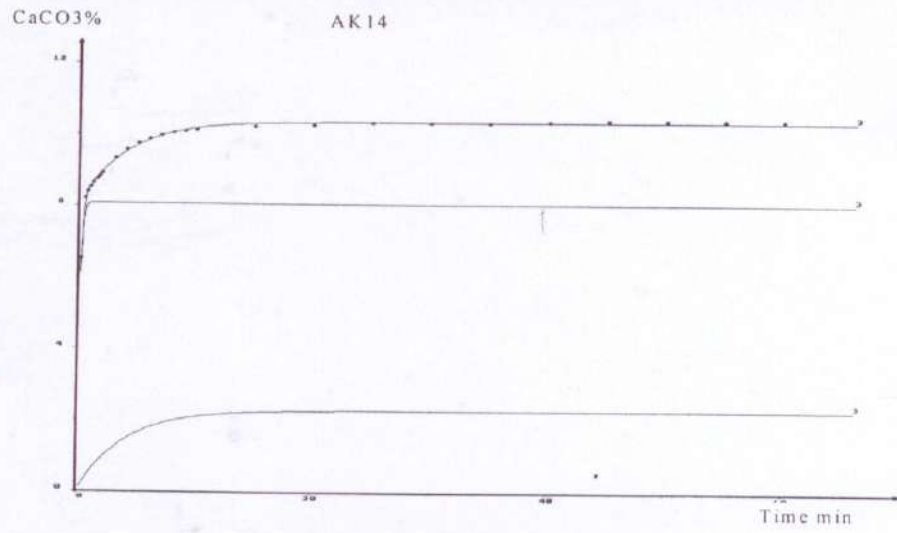
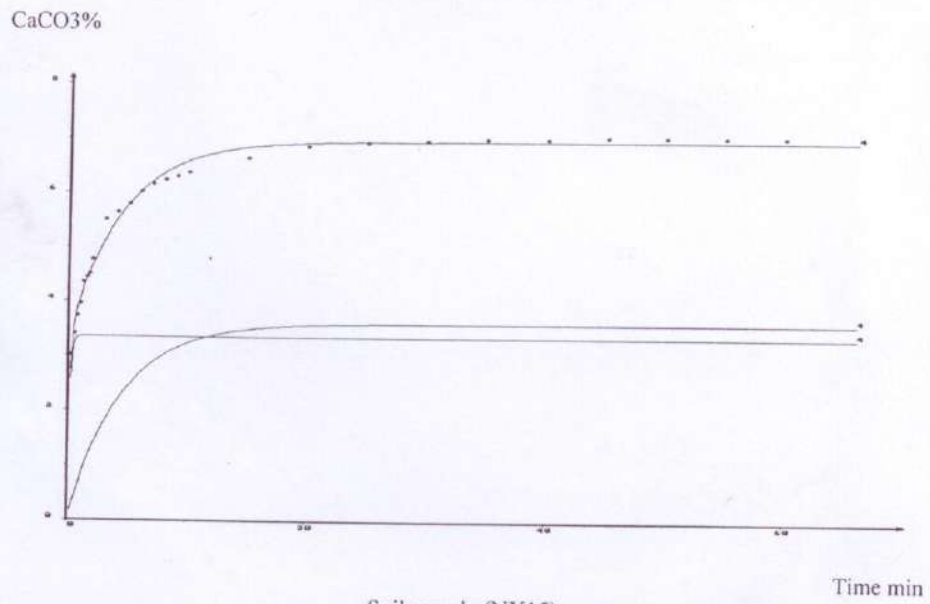


Fig. 2. The relationship between the faster and slower processes of carbonate dissolution in soil sample (Komlo 4)



Soil sample (AK14)  
Fig. 3. The relationship between the faster and slower processes of carbonate dissolution in soil sample (AK14)



Soil sample (NY15)  
Fig. 4. The relationship between the faster and slower processes of carbonate dissolution in soil sample (NY15)

### Conclusion

On the basis of the technique used, and depending on the volume of carbon dioxide and time require for dissolution, the following informations can be pointed out: The amounts of carbonate present in the twelve soil samples by this intercept method using 26 time intervals (during 60 min) were determined. The time required to complete the reaction in reactor vessel was varied from 15 to 55 minutes throughtout the four samples. three of the samples required a time between 30 to 55 minutes, and one sample needed 15 and 25 minutes respectively. Soil sample of Komlo4 is the highest soil carbonate contained while NY15 is the lowest soil sample carbonate contained.

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