SZENT ISTVÁN UNIVERSITY
DOCTORAL SCHOOL OF ENVIRONMENTAL SCIENCES

Dissolution kinetics of carbonates in soil

Ph.D. Thesis

Yosof Salih Ali Hamid

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1. INTRODUCTION

The distribution and amount of carbonates influence soil fertility. The increase of calcium carbonate in soil usually leads to many problems related to fertilization. The extent and rate are affected by the amount of carbonates in the soil, the chemical and physical nature of the carbonates (e.g., particle size and mineralogy). Lime $CaCO_3$ is used on acidic soils to correct acidity and supply calcium. Lime is insoluble, and takes time to react in the soil. The activity of lime is therefore very dependent on its particle size. Lime that is coarse has little value in raising soil pH, at least in the short term.

The kinetics of carbonates ($CaCO_3$) dissolution is very sensitive to the surface structure, composition, and physical properties of the crystals (ECONOMU et al. 1996). They determined, that the dissolution rate of carbonates particles are decreased with the increase of the particle size. It was concluded that effective diameter of carbonate crystals and activation energies of calcite and dolomite are two important parameters affecting acid dissolution rates. (TURNER & SKINNER 1959) showed that acid dissolutions did indeed follow pseudo-first-order kinetics. Even though different rate constants may be yielded by dolomite, depending upon crystal size, rates are sufficiently different from rates of dissolution of calcite of equivalent size. (EVANGELU et al. 1984) used a method which based on differential pseudo-first-order kinetic rates of dissolution of the two carbonate species (dolomite and calcite) when reacted with excess of 5M HCl.

The objectives of this work were to investigate the acid dissolution kinetics of calcium carbonate representative Hungarian agricultural soils. The purposes of the experiments involved in thesis:

1. Separate the different particle size fractions and determine the dissolution kinetics of carbonates. Is the activity in the relation with particle sizes?
2. Determination of dissolution kinetics of carbonate content in soils and in their particle size fractions (coarse sand and clay), and also that of calcite and dolomite with the measurement of CO_2 development in time. How can explain the activity of carbonates in soil? We try to explain the activity of carbonates with the rate of dissolution.
3. Determine the effect of limestone composition, especially the calcite and impurity content of the carbonate, on the kinetics of carbonate mineral dissolution. Is the activity in relation to mineralogy?

2. Materials and methods

2.1. Soil samples:

1- Agyagosszergény,	2- Mosonmagyaróvár,	3- Nagyszentjános,
4- Orosháza,	5- Mezőhegyes,	6- Új-Szeged,
7- Szeged-Öthalom,	8- Iregszemcse,	9- Kecskemét,
10- Nagyhörcsök,	11- Őrbottyán,	12- Csávoly,
13- Ozsákpuszta.		

And another two horizons soil samples were used too in this study. The Two soil samples were collected, each by the following: soil sample:

14- Keszthely (0-25 cm), (25-45 cm), (45-64 cm) and (64-115 cm) and soil sample
15- Nagyhörcsök (0-32 cm), (32-60 cm), (60-104 cm) and (104-140 cm).

2.2 Fractionation:

Table (1): the general characterization of soil samples

	Soil sample	K_A	$P^{H}{}_{H_2O}$	$P^{H}{}_{KCL}$	$CaCO_3$ %	Humus %	AL-P_2O_2 mg/kg	AL-K_2O mg/kg
1.	**Agyagosszergény**	38	7.5	7.1	2.22	6.6	213	197
2.	**Mosonmagyaróvár**	47	7.6	7.2	30.4	2.7	224	133
3.	**Nagyszentjános**	40	7.7	7.3	7.46	2.6	569	512
4.	**Orosháza**	42	7.6	7.1	2.06	3.5	109	222
5.	**Mezőhegyes**	46	7.7	7.1	5.99	4.2	200	216
6.	**Új-Szeged**	43	7.8	7.1	3.21	1.2	133	124
7.	**Szeged-Öthalom**	38	7.7	7.3	6.45	2.5	298	216
8.	**Iregszemcse**	37	7.6	7.1	11.88	2.4	184	139
9.	**Kecskemét**	24	8.1	7.8	13.36	0.3	101	34
10.	**Nagyhörcsök**	38	7.6	7.0	0.81	3.1	117	151
11.	**Őrbottyán**	28	7.7	7.4	3.88	1.0	62	56
12.	**Csávoly**	41	7.3	7.3	3.89	3.3	390	276
13.	**Ozsákpuszta**	60	7.4	7.0	15.13	3.0	106	118
14.	**Keszthely**	33	7.0	6.6	4.36	1.6	38	98

The samples were taken from the genetic horizons of a chernozem soil at Keszthely. Soil particles were fractionated into the next size fractions are:

coarse sand	0.25-2.00 mm
fine sand	0.05-0.25 mm
coarse silt	0.02-0.05 mm
silt	0.01-0.02 mm
semi fine silt	0.005-0.01 mm
fine silt	0.002-0.005 mm
clay	< 0,002 mm

Thirteen surface 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 thirteen different soils in Hungary after removing the first 2 cm top layer.

2.3. Carbonates Detemination and Method:

In this work we discuss the carbonate dissolution processes only in the coarse sand and clay fractions. Pure calcite and dolomite were powered and their carbonate content was also determinal. The CO_2 development was read 27 times between 0-60 minutes. The dissolution kinetics of carbonates in thirteen "soil bank" soils, in the Keszthely and Nagyhörcsök soil profiles and their coarse sand and clay fractions and also in calcite (Bakonycsernye 20 – calcite, 99%) C) and dolomite (Tinnye Zajnat-triászdolomit, 100%) samples were determined. These soil samples were selected from different locations depending on the variation of carbonates. The soil samples were air-dried (~ 25 °C) until constant weight through and mixed well ground with blender and passed through 2 mm sieve plate. In this work I discuss the carbonate dissolution processes only in the coarse sand and clay fractions. The measured amount of particle size fraction was put into a glass. Hydrochloric acid, 10 % $^{w}/_{w}$ was added in excess. The volume of CO_2 released was measured in a Scheibter's calcimeter. Pure calcite and dolomite were powered and their carbonate content was also determined.

2.4 Calculation:

The pseudo-first-order kinetic equation (2 term + Q constant) was fitted to the data. 3 term first order kinetic equation was fitted to the measured data:

$$\mathbf{Y = Q + A_1(1\text{-}e^{-k1t}) + A_2(1\text{-}e^{-k2t})} \qquad (1)$$

Where: Y = is the amount of carbonate developed, %
Q = is the amount of carbonate developed very fastly, in the first 20 second, %
A_1 and A_2 = are the maximum amount of carbonate developed faster and slower respectively, %
k_1 and k_1 = are the rate constants of the faster and slower processes, respectively, 1/min

In the case of calcite and dolomite only one first order kinetic reaction was supposed.

3. Results and discussion

3.1 The Carbonate dissolution kinetics of Calcite and dolomite

Table (2). Kinetic parameters of carbonate dissolution of Calcite and Dolomite

Sample/fraction	A_1 (%)	k_1 (1/min)	A_2 (%)	k_2 (1/min)	Q (%)	$^1t_{1/2}$ (min)	$^2t_{1/2}$ (min)
Calcite	58.6	14.4	0	0	0	0.05	-
Dolomite	-	-	62.6	0.24	0		2.4

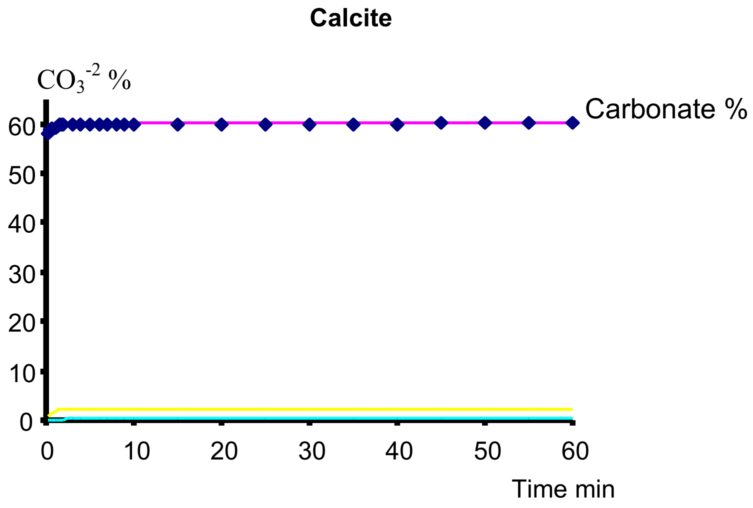

Figure (1) Carbonate dissolution kinetics. of Calcite

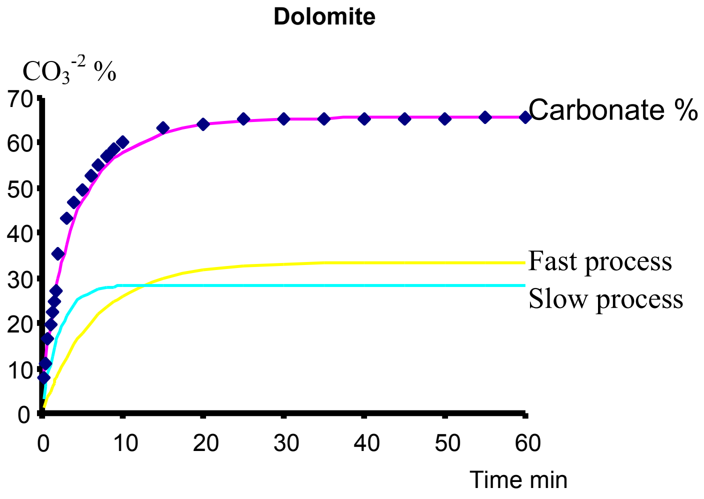

Figure (2) Carbonate dissolution kinetics of Dolomite

(Table 2., and Figures 1 & 2). show the kinetic parameters of carbonate dissolution. The used equations in all cases very well fit to the measured data. Calcite and dolomite dissolution can be characterized with one first order reaction. Calcite with one fast reaction, where k_1 is very big (14.4) and the half-life-time is 0.05 minute. It is really fast one. In the case of dolomite the slow reaction with k_2 (0.29) and with a half-life-time 2.4 minute, not so slow.

3.2 The genetic horizons of Keszthely and Nagyhörcsök soil samples

3.2.1 The Soil sample of Keszthely

Table (3) Kinetic parameters of carbonate ($CaCO_3$ %) dissolution of Keszthely Particle size distribution

depth/fraction	g/100g	1/min	g/100g	1/min	g/100g	min	min	g/100g	%	%	%
0-25 cm	A_1	k_1	A_2	k_2	Q	$^1t_{1/2}$	$^2t_{1/2}$	A_1+A_2+Q	Q	A_1+Q	A_2
original soil	2.5189	0.1740	0.4185	0.0128	1.4289	3.9836	54.1521	4.3662	32.7252	90.4150	9.5850
coarse sand	8.7226	0.0796	0.0000	0.0019	1.5718	8.7079	0.0000	10.2944	15.2686	100.0000	0.0000
clay	4.0564	0.8283	2.0107	0.0824	1.7111	0.8368	8.4120	7.7782	21.9985	74.1498	25.8502
25-45 cm											
original soil	0.7859	1.0505	4.0073	0.1639	6.9278	0.6598	4.2291	11.7211	59.1058	65.8108	34.1892
coarse sand	8.0123	1.2154	7.8143	0.0913	0.0000	0.5703	7.5920	15.8266	0.0000	50.6257	49.3743
clay	13.9946	2.1369	2.7699	0.2436	2.4115	0.3244	2.8454	19.1759	12.5755	85.5555	14.4445
45-64 cm											
original soil	7.4739	4.2322	8.0203	0.1460	20.8039	0.1638	4.7476	36.2981	57.3139	77.9042	22.0958
coarse sand	31.0025	4.8565	9.1795	0.2692	3.0584	0.1427	2.5748	43.2405	7.0731	78.7711	21.2289
clay	23.8247	1.7687	3.2117	0.2055	15.3453	0.3919	3.3730	42.3818	36.2073	92.4219	7.5781
64-115cm											
original soil	6.1441	4.7003	14.1785	0.1769	13.1761	0.1475	3.9183	33.4987	39.3333	57.6746	42.3254
coarse sand	19.7756	5.8659	7.1732	0.2773	15.3371	0.1182	2.4996	42.2859	36.2700	83.0365	16.9635
clay	28.8265	1.5256	2.8271	0.0940	2.8283	0.4543	7.3739	34.4820	8.2023	91.8011	8.1989

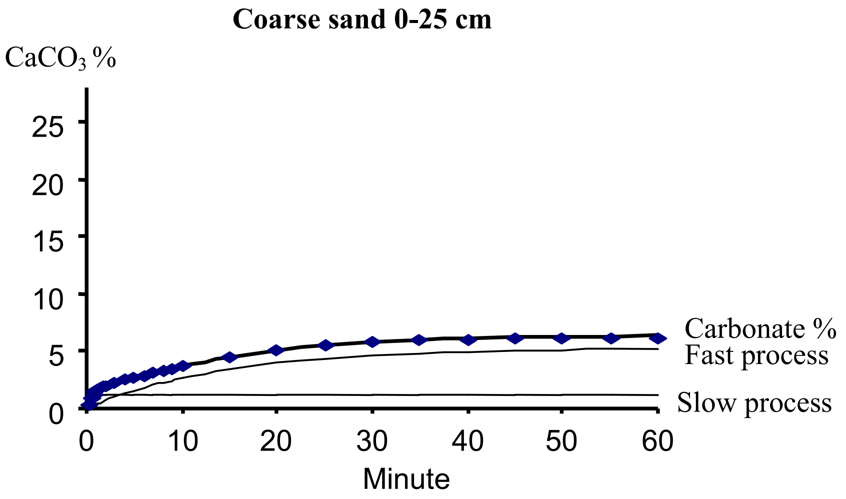

Figure (3) Carbonate dissolution kinetics of coarse sand fractions in the Keszthely soil in the depth 0-25 cm

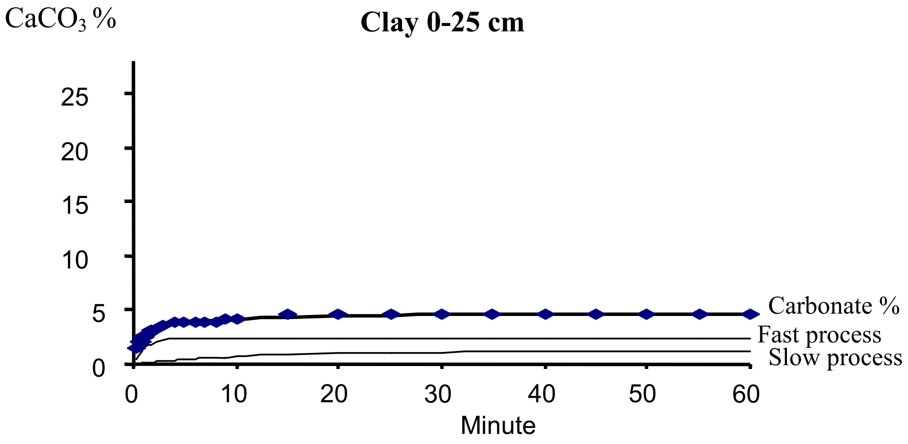

Figure (4) Carbonate dissolution kinetics of clay fractions in the Keszthely soil in the depth 0-25 cm

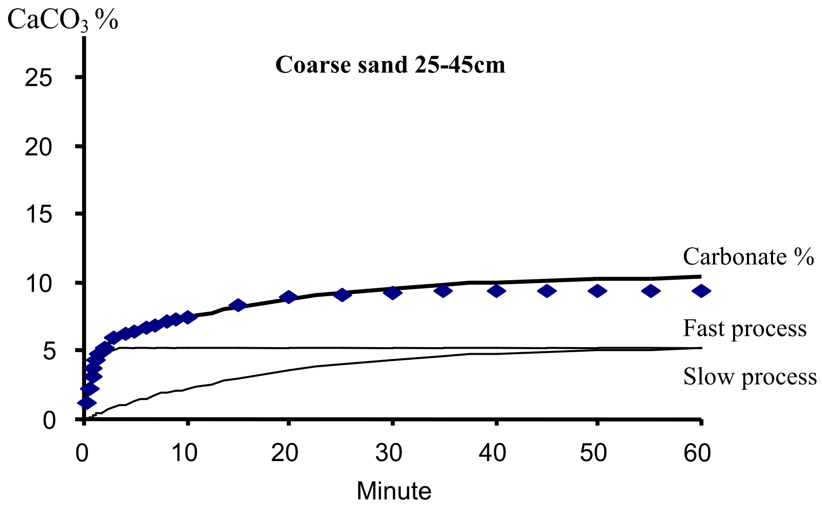

Figure (5) Carbonate dissolution kinetics of coarse sand fractions in the Keszthely soil in the depth 25-45 cm

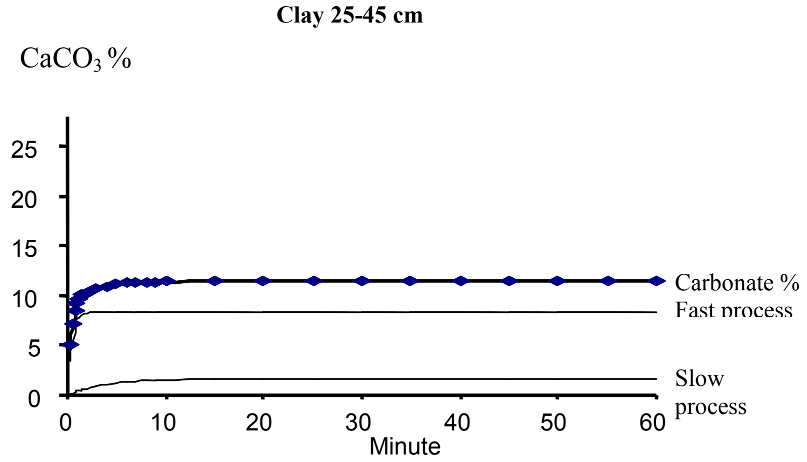

Figure (6) Carbonate dissolution kinetics of clay fractions in the Keszthely soil in the depth 25-45 cm

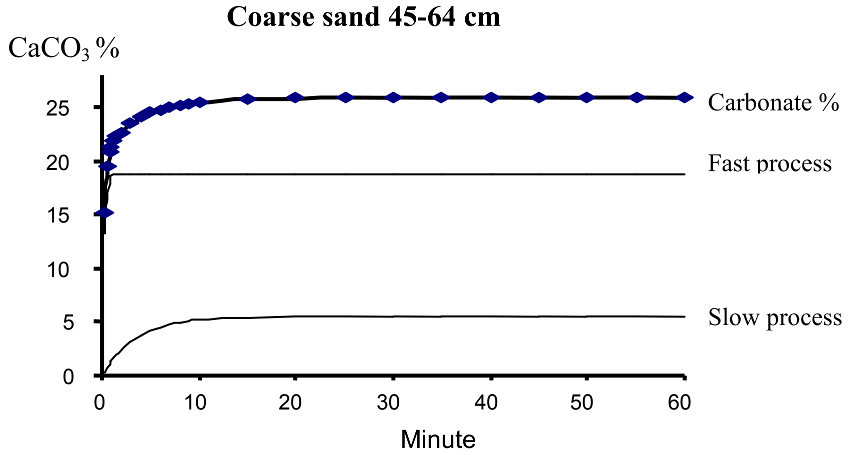

Figure (7) Carbonate dissolution kinetics of Coarse sand fractions in the Keszthely soil in the depth 45-64 cm

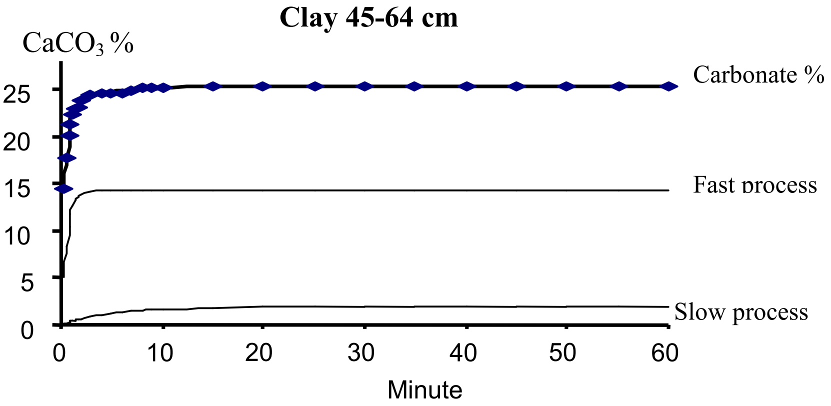

Figure (8) Carbonate dissolution kinetics of clay fractions in the Keszthely soil in the depth 45-64 cm

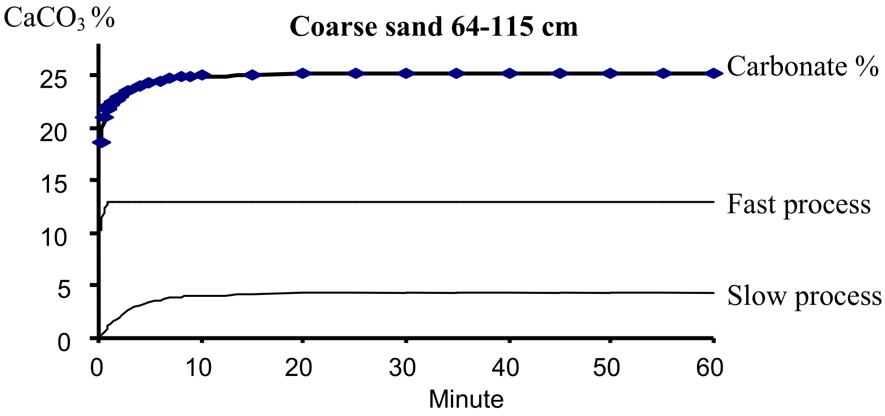

Figure (9) Carbonate dissolution kinetics of Coarse sand fractions in the Keszthely soil in the depth 64-115 cm

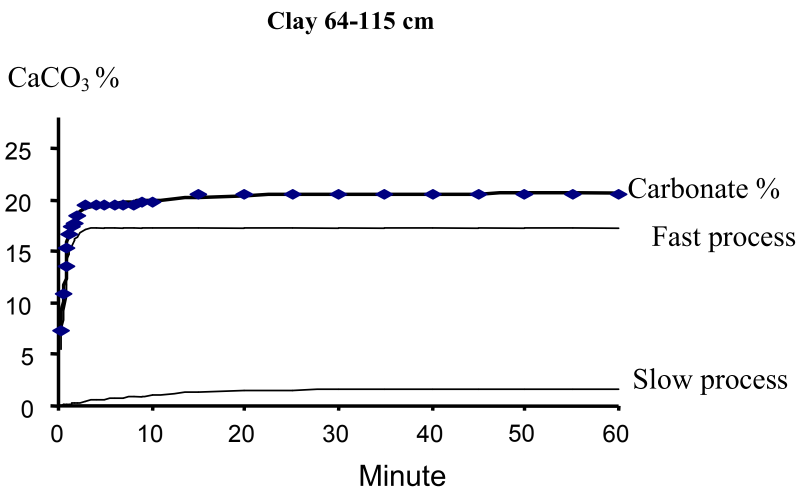

Figure (10) Carbonate dissolution kinetics of clay fractions in the Keszthely soil in the depth 64-115 cm

Table (3) and figures (3 to 10) show that the carbonate content of soil profile formed on Keszthely loes was determined is 4 levels. 4.3% carbonate was in the 0-25 cm level. The highest carbonate content was 10.1% in coarse sand. The most part of carbonate dissolved slowly in coarse sand fraction. 74.1 % of carbonate content of clay fraction dissolved by fast process. Considerable amount of superfast dissolved carbonate(Q) was in the whole soil profile. The 25-45 cm soil layer contained 11.7% carbonate. The rate slow and fast processes in coarse sand fraction were almost the same. In the clay fraction the fast processes were dominated. We experienced the same case in layer 45-64 cm also, and the same in layer 64-115 cm. It means the fast process was dominated in clay fraction, but the proportion of it was large in coarse sand too. In all the genetic horizons the slow process practically the same in the coarse sand and clay fractions, 4-5 % and1-2 %, respectively. The upper soil horizon shows a characteristic picture, in the coarse sand fraction there is no fast reaction, only 1 % very fast one. The clay fraction almost, in all horizons contains more fast dissolution reaction carbonate than the coarse sand fraction. In the upper horizon in the clay fraction the fast process is rather slow ($k_1 = 0.82$) and small (2.4). The carbonate accumulation well follows the soil development, its maximum mainly is in the coarse sand fraction, of the B horizon. Interesting to recognize the rather high Q values in the course sand fractions (1 and 9 %). Considering the rate constant values, the real slow process could be characterized with $k_2 = 0.08$, the real fast process with $k_1 > 1.0$.

3.2.2 The Soil sample of Nagyhörcsök

Table (4) Kinetic parameters of carbonate ($CaCO_3$ %) dissolution of Nagyhörcsök Particle size distribution

depth/fraction	g/100g	1/min	g/100g	1/min	g/100g	min	min	g/100g	%	%	%
0-32 cm	A_1	k_1	A_2	k_2	Q	${}^1t_{1/2}$	${}^2t_{1/2}$	A_1+A_2+Q	Q	A_1+Q	A_2
original soil	2.4120	0.2784	2.1480	0.0691	1.4486	2.4898	10.0311	6.0085	24.1085	64.2514	35.748
coarse sand	18.3809	0.5025	5.4607	0.1029	5.4482	1.3794	6.7361	29.2898	18.6010	81.3562	18.643
Clay	6.6653	0.4283	0.0000	0.0069	3.0646	1.6184	100.4561	9.7299	31.4968	100.0000	0.000
32-60 cm											
original soil	3.3343	0.6573	5.8435	0.0836	11.7371	1.0545	8.2912	20.9149	56.1183	72.0606	27.939
coarse sand	20.3292	0.8063	3.7934	0.1617	1.9145	0.8597	4.2866	26.0371	7.3529	85.4308	14.569
Clay	15.3577	0.8983	4.4868	0.0493	10.0953	0.7716	14.0598	29.9398	33.7188	85.0139	14.986
60-104 cm											
original soil	21.5851	4.8462	10.0881	0.1169	0.0000	0.1430	5.9294	31.6732	0.0000	68.1493	31.8507
coarse sand	16.3862	1.3324	11.8942	0.1385	5.3505	0.5202	5.0047	33.6310	15.9095	64.6331	35.3669
Clay	17.9158	0.9771	3.4647	0.1519	17.2339	0.7094	4.5632	38.6144	44.6307	91.0273	8.9727
104-140 cm											
original soil	2.5758	1.9345	11.3057	0.1205	18.7110	0.3583	5.7523	32.5926	57.4089	65.3119	34.6881
coarse sand	14.0353	1.5909	17.4296	0.1932	10.3597	0.4357	3.5877	41.8246	24.7693	58.3269	41.6731
Clay	12.0389	1.6109	11.4093	0.3955	14.0659	0.4303	1.7526	37.5140	37.4950	69.5867	30.4133

Table (4) show that the carbonate content of soil profile formed on loes on Nagyhörcsök was determined is 4 genetical levels. Layer 0-32 cm contained carbonate of 6.0%. Fast processes were dominated in fraction coarse sand and clay. Fast processes were dominated in fraction coarse sand and clay in layer 32-60 cm (20,9 % carbonate). Slow process appeared in every genetical layer and in both of the fractions, but missed in the uppest layer of clay fraction. Fast processes dominated in two fractions of both of the lower layers (60-104 and 104-140 cm). Proportion of slow process increased gradually by stepping lower and lower. Considering the genetic horiyons of the Nagyhörcsök soil profile (Table 4) the rate constant of the faster dissolution process increases and the half-life-time decreases.

Proportion of slow process is continuously decreased with the depth in soil profile of Keszthely, in coarse sand fraction. But unlike this, proportion of fast proceses gradually increased from upper layers to lower layers in soil profile Nagyhörcsök. The carbonate distribution of both of the fraction of Keszthely's soil can be explained by the ion mobility of water activity, what is the typical process of forest soils. Different trend occurred in Nagyhörcsök's soil. That is chernozem, where water fluctuation is typical. Fast dissolved carbonates in fraction of coarse sand shows largest value in B (accumulation) horizon.

3.2.3 The Carbonate ($CaCO_3$ %) dissolution kinetics of coarse sand and clay fractions in the different soil samples.

Table (5) Kinetic parameters of carbonate ($CaCO_3$ %) dissolution in different soil samples Particle size distribution.

Agyagosszergény

depth/fraction	g/100g	1/min	g/100g	1/min	g/100g	min	min	g/100g	%	%	%
0-20 cm	A_1	k_1	A_2	k_2	Q	$^1t_{1/2}$	$^2t_{1/2}$	A_1+A_2+Q	Q	A_1+Q	A_2
original soil	1.4706	2.0575	0.7553	0.1187	0.0000	0.3369	5.8395	2.2259	0.0000	66.0665	33.9335
coarse sand	0.2006	0.9978	0.1989	0.1834	0.0028	0.6947	3.7794	0.4023	0.7057	50.5604	49.4396
clay	5.0614	1.0028	4.0663	0.0128	0.8963	0.6912	54.1521	10.0240	8.9414	59.4346	40.5654

Mosonmagyaróvár

original soil	6.7097	0.6559	12.8587	0.1366	10.8316	1.0568	5.0743	30.4000	35.6303	57.7018	42.2982
coarse sand	18.5338	1.0730	5.7164	0.1692	0.0000	0.6460	4.0966	24.2502	0.0000	76.4274	23.5726
clay	24.7197	1.2455	12.3882	0.1801	0.0000	0.5565	3.8487	37.1079	0.0000	66.6157	33.3843

Nagyszentjános

original soil	3.1652	0.7600	1.6820	0.0954	2.6137	0.9120	7.2657	7.4609	35.0322	77.4555	22.5445
coarse sand	2.0511	1.0241	1.7622	0.1247	0.0000	0.6768	5.5585	3.8133	0.0000	53.7882	46.2118
clay	11.8502	1.6811	2.8358	0.2274	0.0000	0.4123	3.0481	14.6860	0.0000	80.6902	19.3098

Orosháza

original soil	1.4451	2.4300	0.5483	0.1691	0.0663	0.2852	4.0990	2.0596	3.2190	73.3804	26.6196
coarse sand	0.9005	0.8845	0.2744	0.1879	0.0000	0.7837	3.6889	1.1748	0.0000	76.6453	23.3547
clay	3.0147	1.5883	2.0503	0.1802	0.0000	0.4364	3.8465	5.0649	0.0000	59.5206	40.4794

Mezőhegyes

original soil	2.5843	1.0886	2.6089	0.1368	0.8033	0.6367	5.0669	5.9965	13.3957	56.4932	43.5068
coarse sand	22.4974	1.7593	2.4481	0.0936	0.0000	0.3940	7.4054	24.9455	0.0000	90.1864	9.8136
clay	3.5573	2.0367	2.0314	0.2196	0.1179	0.3403	3.1564	5.7066	2.0661	64.4026	35.5974

Új-Szeged

original soil	2.4048	2.1628	0.8054	0.0940	0.0000	0.3205	7.3739	3.2102	0.0000	74.9103	25.0897
coarse sand	6.2199	1.5327	0.0000	0.0162	0.0000	0.4522	42.7869	6.2199	0.0000	100.0000	0.0000
clay	2.8781	1.7713	0.0000	0.3852	0.0000	0.3913	1.7994	2.8781	0.0000	100.0000	0.0000

Szeged-Öthalom

original soil	4.0997	1.9952	2.1082	0.0940	0.2467	0.3474	7.3739	6.4546	3.8215	67.3376	32.6624
coarse sand	9.3426	0.9271	0.0000	0.0000	0.8270	0.7477	-	10.1696	8.1319	100.0000	0.0000
clay	11.4173	0.7016	0.0000	0.0323	0.0000	0.9880	21.4597	11.4173	0.0000	100.0000	0.0000

Iregszemcse

original soil	7.3892	0.1765	2.6281	0.0002	1.8647	3.9272	-	11.8821	15.6936	77.8819	22.118
coarse sand	32.1834	0.7965	1.2219	0.0823	0.0000	0.8702	8.4222	33.4053	0.0000	96.3421	3.657
clay	9.4302	0.4711	0.1129	0.0063	0.0000	1.4713	110.0234	9.5430	0.0000	98.8170	1.1830

Table (6) Kinetic parameters of carbonate ($CaCO_3$ %) dissolution in different soil samples Particle size distribution.

Nagyhörcsök

depth/fraction	g/100g	1/min	g/100g	1/min	g/100g	min	min	g/100g	%	%	%
0-20 cm	A_1	k_1	A_2	k_2	Q	$^{1}t_{1/2}$	$^{2}t_{1/2}$	A_1+A_2+Q	Q	A_1+Q	A_2
original soil	0.5468	1.9604	0.0000	0.0062	0.2597	0.3536	111.7979	0.8064	32.2013	100.0000	0.0000
coarse sand	4.9504	1.3742	5.5361	0.3044	0.6187	0.5044	2.2771	11.1052	5.5716	50.1489	49.8511
clay	4.5865	1.8651	0.0000	0.0003	0.0000	0.3716	-	4.5865	0.0000	100.0000	0.0000
Örbottyán											
original soil	1.7396	2.1721	1.7144	0.1436	0.4327	0.3191	4.8269	3.8868	11.1326	55.8907	44.1093
coarse sand	1.1085	1.7125	1.0326	0.1607	0.2265	0.4048	4.3133	2.3676	9.5648	56.3871	43.6129
clay	8.9477	2.0510	0.0000	0.0158	0.0000	0.3380	43.8701	8.9477	0.0000	100.0000	0.0000
Csávoly											
original soil	1.6333	1.6198	2.0129	0.1030	0.2465	0.4279	6.7296	3.8926	6.3323	48.2904	51.7096
coarse sand	4.0913	0.5441	0.8086	0.1277	0.0000	1.2739	5.4279	4.8999	0.0000	83.4975	16.5025
clay	3.5436	3.0570	1.5217	0.6884	0.0000	0.2267	1.0069	5.0653	0.0000	69.9581	30.0419
Ozsákpuszta											
original soil	6.0890	1.4421	8.6733	0.2465	0.3649	0.4807	2.8124	15.1272	2.4122	42.6641	57.3359
coarse sand	11.9900	1.6767	8.6453	0.3141	0.0000	0.4134	2.2067	20.6353	0.0000	58.1045	41.8955
clay	7.3493	0.7676	0.0992	0.0141	0.0000	0.9030	49.1594	7.4485	0.0000	98.6682	1.3318
Kecskemét											
original soil	6.5003	2.5612	5.7982	0.1536	1.0606	0.2706	4.5127	13.3592	7.9392	56.5973	43.4027
coarse sand	5.7673	5.1076	2.5643	0.1332	0.0000	0.1357	5.2038	8.3316	0.0000	69.2223	30.7777
clay	17.3625	1.2876	0.0000	0.0032	0.0000	0.5383	216.6085	17.3625	0.0000	100.0000	0.0000

Tables 5 and 6 show that the kinetic parameters of carbonate dissolution. The used equations (1) in all cases very well fit to the measured data.

Agyagosszergény fluvisol soil of river Raba from ”Soil Bank’s” the amount of carbonate in the original soil sample (2.2 %) and the amount of carbonate in the both of coarse sand (0.4 %) and clay (10 %) fractions. It also contains super fast dissolved carbonate in clay fraction, its amount is less than error margin (Q = 0.1). Carbonates both of the slow and fast dissolved, enriched in fraction clay, clearly separated fast and slow process. Comparing the rate constant values of the faster reactions in the coarse sand and clay ($A_1 = 0.2$ and $A_1 = 5.061$) with the rate constant of calcite and dolomite dissolution the rate constant of the faster processes both in the case of coarse sand and clay are ($k_1 = 0.9978$ and $k_1 = 1.0028$). The same fact can be concluded also from the half-life-time of these processes ($1t^{1/2}$ min = 0.6947 and $1t^{1/2}$ min = 0.6912).

Mosonmagyaróvár Fluvisol soil the amount of carbonate in the original soil sample (30 %) and it's contain large amount of carbonate both in coarse sand (24 %) and clay (37 %) fractions. None of the fractions contains super fast dissolved carbonate (Q = 0). Slow and fast processes are separated fine and its quantity is substantial. The faster processes both in the case of coarse sand and clay are (k_1 = 1.0730 and k_1 = 1.2455). The same fact can be concluded also from the half-life-time of these processes ($1t^{1/2}$ min = 0.6460 and $1t^{1/2}$ min = 0.5565).

Nagyszentjános soil from Danube terrace content Carbonate is lower significantly (7 %), none of the examined fraction contained super fast process. The clay fraction contains the most carbonate (14.2 %). Slow and fast processes are separated fine. The faster processes both in the case of coarse sand and clay are (k_1 = 1.0241 and k_1 = 1.6811). The same fact can be concluded also from the half-life-time of these processes ($1t^{1/2}$ min = 0.6768 and $1t^{1/2}$ min = 0.4123).

Orosháza soil contains carbonate of (2%). The most of carbonate is in clay fraction (5 %). None of the fractions contains super fast dissolved carbonate. Slow and fast processes are separated fine in clay fraction. The speed constant of fast process of coarse sand is quite low (k_1 = 0.8845) and A_1 is also low (0.9005).

Mezőhegyes soil the amount of carbonate in the original soil sample (6%) Carbonate content is significantly high in clay (24.9 %) in the very low content of coarse sand (5.7%). Only the clay fraction contains super fast dissolved carbonate, (0.1g) carbonate in (100 g soil). The fast process is the largest in coarse sand fraction, amount is almost (k_1 = 1.7593) and (A_1 = 22.4974). Slow and fast processes are separated fine in coarse sand and clay fractions.

Új-Szeged soil, fluvisol of Tisza, the amount of carbonate in the original soil sample (3 %) and it's contain low amount of carbonate in both of coarse sand (6.2 %) and clay (2.87 %) fractions. None of the fractions contains super fast dissolved carbonate (Q = 0). The faster processes both in the case of coarse sand and clay are (k_1 = 1.5327 and k_1 = 1.7713). The same fact can be concluded also from the half-life-time of these processes ($1t^{1/2}$ min = 0.4522 and $1t^{1/2}$ min = 0.3913). its mean there is none of the fast and slow processes are in the coarse sand and clay fractions. The former process is also missing in the original sample. Coarse sand fraction contains larger amount of fast dissolved carbonate (6%).

Szeged-Öthalom sample contains carbonate of (6.5%). Carbonate content of coarse sand and clay fractions are almost the same (10% and 11%). Coarse sand fraction contains small amount of super fast dissolved carbonate (0.1g carbonate in 100 g soil). (Q = 0.8 %). Carbonate content dissolved by the fast process in both of the case (k_1 = 0.9271 and k_1 = 0.7016). In case of coarse sand the process is somewhat faster. Slow process is missing in every fraction.

Iregszemcse soil is developed in loess. The amount of carbonate in the original soil sample (11.9%) Carbonate content is significantly high in coarse sand (33.4 %) in the low content of clay it contains carbonate of (9.5%), super fast process is missing in every fraction. Large amount of fast process and small amount of slow process are in the coarse sand fraction and the fast process is not too fast ($k_1 = 0.7965$). Dissolution speed of carbonate in clay fraction is slow low that it should be seen as slow process ($k_1 = 0.4711$). This is one of the”Soli Bank’s” soil, in which the speed of dissolution not really indicates calcite, even more indicates deformed calcite crystalline lattice.

Kecskemét soil from Danube-Tisza Interval the amount of carbonate in the original soil sample is (13.4 %) and the amount of carbonate in the both of coarse sand (8.3 %) and clay (17.4 %) fractions. It also contains super fast dissolved carbonate in clay fraction, its amount is less than error margin ($Q = 0.0$). Carbonates both of the slow and fast dissolved. Comparing the rate constant values of the faster reactions in the coarse sand and clay ($A_1 = 5.7673$ and $A_1 = 17.3625$) with the rate constant of the faster processes both in the case of coarse sand and clay are ($k_1 = 5.1076$ and $k_1 = 1.2876$). The same fact can be concluded also from the half-life-time of these processes ($1t^{1/2}$ min = 0.1357 and $1t^{1/2}$ min = 0.5383). A fast and a slow process work in case coarse sand fraction, super fast process is missing. Carbonate of clay fraction is dissolved by fast process. Slow and super fast processes are missing.

Nagyhörcsök soil the amount of carbonate in the original soil sample is (0.8%). Coarse sand fraction contains (11 %) two times more carbonate than clay fraction (4.6%). carbonates are dissolved in both fast and slow processes ($k_1 = 1.9604$ and $k_1 = 1.8651$) and ($k_2 = 0.3044$ and $k_2 = 0.0003$). The super fast process is far too few in coarse sand fraction. The half-life-time of these processes ($1t^{1/2}$ min = 0.5044 and $1t^{1/2}$ min = 0.3716). Carbonate content of clay fraction is dissolved by a fast process.

Örbottyán soil the amount of carbonate in the original soil sample is (4%). All of the three solubility process are working in coarse sand fraction (super fast: 0.2%, fast: 1.1%, slow: 1.0%). The carbonate content of clay fraction is (9%) and the amount of carbonate in the coarse sand fraction (2.4 %). Carbonate content of this fraction are dissolved by a fast process.

Csávoly soil of Bácskai Löszhát the amount of carbonate in the original soil sample is contains almost (4%). Coarse sand and clay fractions are contain carbonate in almost same quantity (4.9% and 5.1%). Super fast dissolution is missing in all fractions, but carbonate is dissolved in a slow and a fast process both of fractions. However fast process in coarse sand fraction should be also seen as slow process ($k_1 = 0.5441$). But slow process in clay fraction should be seen as fast process ($k_2 = 0.6884$).

Ózsákpuszta soil from Duna floodplain the amount of carbonate in the original soil sample is (15 %) and the large amount of carbonate in the coarse sand fraction (20.6 %) than the clay fraction (17.4 %). Super fast process is missing in every fraction. Carbonate content of coarse sand fraction is dissolved by a fast and a slow process ($k_1 = 1.4421$, $k_2 = 0.2465$). Carbonate is dissolved from clay fraction by a process, that the speed constant is ($k_1 = 0.7676$, $k_2 =$

0.0141). None of the fractions contains super fast dissolved carbonate (Q = 0). The half-life-time of these processes ($1t^{1/2}$ min = 0.4134 and $1t^{1/2}$ min = 0.9030).

Ca^{2+} and Mg^{2+} content determined by salt acid extract of original samples were correlated by the quantity of carbonate dissolved during fast and slow processes. As we expected, the fast processes (A_1 + Q) were interconnected the Ca^{2+} content of solution, the slow processes were interconnected the Mg^{2+} content of solution.

4. CONCLUSIONS

For the description of solubility kinetic of carbonates in coarse sand and clay fractions of soil and soil samples, the dual first-order kinetic equation was fit complemented by the very first super fast process(Q), what undergone till the first measurment timing(15 sec). The first process was seen as fast, the second process was seen as slow. Speed constant of the first process is around value k_1 1.0 1/min, what is lower than the slow process by a magnitude. (0.1-0.2 1/min. Solubility kinetic of calcit and dolomite cristals breaked to 0.5 mm size were examined. Calcit is dissolved by a super fast and a fast processes, where the kinetic constant is k = 1.3617. On the contrary dolomite dissolved by a slow process, where the kinetic constant is k = 0.2923.

Certainly, in that cases when slow process was missing or speed constant was in scale of 0.01, then this process was seen as 0, because substantive dissolution did not happen by this process. The half-life value $t_{1/2}$ is the other parameter, which indicates the speed of dissolution. Usually the value of this is under 1 minute in the case of considerable really fast processes, while in the case of so-called slow processes its value is between 2-7 minutes. we established, that according to our actual knowledges, in the most of the case, smaller carbonate particles dissolving during faster processes. Computerized data analysis provides obvious information only in very few cases. It is very rarely, that the dissolution of carbonates were happened only by fast or only ba slow processes. Mainly both of the two processes are ocurred. It shows, that both of the forms of carbonates, the calcit like and dolomite like, are in the soil. The fraction of 1.0-0.3 of speed constant shows transition between calcit and dolomite. It is obvious, that where value k closer to 0.3, the dolomite character is dominant, where k closer to 1.0, the calcit character is dominant. If speed constant is much higher than 1.0 or value Q proportion is significant (super fast process), these phenomenons can refer the presence of alkaline carbonates. On some occasions, the values of two calculated speed constants were between 1.0 and 0.3, and looked like quite similar. In that case it is possible, that this were caused by a medium speed process. This conform it, that carbonates with different kind of solubility occures int he soil. That carbonates are mostly calcitlike, but in so much case its dissolution very similar to the dolomite’s one. However many times, the kinetics of dissolution shows speed what is somewhere between the two minerals’s speed of dissolution. If concentrations of Ca^{+2} and Mg^{+2} in salt acide solution are compared to the amount of dissolved carbonates by fast processess, then Ca^{+2} $R^2 = 0.9485$, a Mg^{+2} $R^2 = 0.6610$

hang together. If slow process is seen, then Ca^{+2} $R^2 = 0.81353$ correlate to a Mg^{+2} $R^2 = 0.9124$, namely Ca^{+2} dominants in fast processes, while Mg dominats in slow processes, but there is also a close relationship to the other element.

We can establish a final conclusion: carbonate dissolution calculated by computer analysis from CO_2 formation can be described by a first-order kinetic equation. Computerized analysis can separate dissolution process to more than one processes, from previously formed CO_2 during dissoluion. In the case of soils, it can be determined that usually carbonates in clay fraction are dissolving faster than carbonates in coarse sand fraction. The fast dissolving processes can be considered to calcit and calcit like minerals, while the slow dissolving processes can be considered to dolomite and dolomite like minerals.

4. NEW SCIENTIFIC RESULTS:

According to objectives the new scientific results are:

1. The carbonate dissolution calculated by computer analysis from CO_2 formation can be described by a first-order kinetic equations.
2. Computerized analysis can separate dissolution process to more than one processes, from the formed of CO_2 during dissoluion.
3. In the case of soils, it can be determined that usually carbonates in clay fraction are dissolving faster than carbonates in coarse sand fraction.
4. The fast dissolving processes can be considered to calcit and calcit like minerals, while the slow dissolving processes can be considered to dolomite and dolomite like minerals.

5. FUTURE PROPOSITION

Large areas of calcisols and gypsisols are found in Libya, especially in the Eastern Desert, in the north-eastern and south-eastern parts of the Eastern Desert, Calcisols are dominated by a calcium carbonate-rich horizon within 1.25 m of the soil surface. Their subsoil properties are variable, ranging from those with subsoil clay accumulation to those with no B-horizon development at all. The organic matter contents vary but they are never saline and neither do they exhibit evidence of gleying in the upper meter.

Gypsisols are similar to calcisols in terms of most diagnostic properties with the very important exception of the type of calcium accumulation in the upper 1.25 m . In gypsisols this zone is dominated by gypsum (calcium sulphate). The clay in many calcisols and gypsisols combined with the low amounts of organic matter means that most of these soils are characterized by inherently low fertility and poor water- holding capacity. Nevertheless, with irrigation and manuring or fertilizer application, they are being reclaimed on the desert land and in some of the Eastern Desert. The high calcium carbonate and calcium sulphate content of some calcisols and gypsisols can create further soil management problems. In many calcisols and gypsisols the calcium carbonate and sulphate has aggregated and hardened to from calcium or gypsum, respectively. These are rock-like materials which create severe problems for root penetration and ploughing, especially as they are usually found in the upper 1.25m of the soil. A further physical problem, which is particularly prevalent when these soils have high silt content and are irrigated, is surface crusting which dramatically reduces the infiltration rate. Other management problems are concerned with soil chemistry. The levels of available phosphorus are low due to the high pH, and the micronutrients such as copper, iron, manganese, and zinc also have low availabilities. There is often potassium and magnesium supply problems due to the calcium imbalance and the soils have very low levels of microorganisms. On the basis of these parameters, we made some sets of further propositions:

1. Determination of dissolution kinetics of carbonate content in soils and in their particle size fractions (coarse sand and clay), with the measurement of CO_2 development in time.
2. Description of solubility kinetic of carbonates in coarse sand and clay fractions in soil samples.
3. Computerized analysis can separate dissolution processes to more than one process, during dissolution in the soils.

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