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DISSOLUTION KINETICS OF CARBONATES IN SOIL

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1. INTRODUCTION

The dissolution kinetics of carbonates is important to many fields of applications, i.e., the maintenance of marble monuments, the uptake of calcium medicines, the dissolution of liming materials and apatite containing phosphate and carbonate crystals tightly held together, when it is introduced into the soil-plant system (ECONOMU et al., 1996) There are many sustainable carbonates modifications that appear as initial solid phases in many carbonate precipitation processes, and most probably as precursors in carbonate geological sediments. The kinetics of carbonates (CaCO₃) 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. In a subsequement experimental investigation with pure calcite and dolomite, (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-firstorder kinetic rates of dissolution of the two carbonate species (dolomite and calcite) when reacted with excess of 5M HCl. (GEHLEN et al 2005) carried out kinetic experiments with biogenic carbonates. They derived an average reaction rate order n = 2.3 ± 0.4 . The higher reaction order is explained in terms of multiphase system. The concomitant dissolution of carbonate fractions characterized by variable reaction rate constants.

The dissolution rates of calcite (limestone CaCO₃) in CO_3^{2-} containing aqueous solutions are determined by three rate-controlling processes: (i) the kinetics of dissolution at the mineral surface, which depends on the chemical composition of the solution at the liquid–rock boundary. (ii) Mass transport by diffusion away from this boundary for the dissolved material Ca²⁺, HCO₃⁻, and CO₃²⁻ and towards this boundary for the reactant CO₂. (iii) Conversion of CO₂ into H⁺ and HCO₃⁻. The dissolution of untreated is accompanied by intense breakdown of the particles, and the rate of extent of breakdown depends on the particles size. Adequate pretreatment with steam makes the carbonate partical resistant to breakdown, and the dissolution rate becomes very slow. The time dependent diffusion reaction equations are solved for free drift dissolution by a finite difference scheme, to obtain the dissolution rate of calcite as a function of the average calcium concentration in the water film.

(WANG TIANGUI & LI ZUOHU 2005) found that the concentration of calcium ions in solution does not affect the dissolution of carbonates, but increase of carbon dioxide partial pressure retards the dissolution of carbonate, and the observed dissolution fluxes are predicted by the model when k=5 and n=4.5. This range of k values has important implications regarding the type of carbonate dissolving and its location within the sediment column. At low values of k, organic carbon rain rates become the dominant driving force of carbonate dissolution. At higher values of k, dissolution of carbonate within equatorial Pacific sediments can be adequately described with k=20 \pm 10, a rate constant much lower than some previously used values. Limestone dissolution kinetics is important in understanding problems such as geochemical weathering

(BJERLE & ROCHELLE, 1982, PLUMMER et al., 1978, SJÖBERG & RICKARD, 1983, WALLIN & BJERLE, 1989a; SCHOTT et al., 1989, PLUMMER & WIGLEY, 1976). Found that the rate of CO_3^{2-} mineral dissolution is determined by the physical and chemical characteristics of the stone, including the type and amount of impurities as well as the mineral crystallography. The chemistry and temperature of the solution are also important.

(PLUMMER & WIGLEY, 1976, BERNER & MORSE, 1974, BERNER & MORSE, 1974, CHAN & ROCHELLE, 1982), found that the kinetics of calcite dissolution in acetic acid solutions was investigated over a wide range of pH using a rotating disk apparatus. The kinetics of the reversible surface reaction, and the rate of transport of products away from the surface. The dissolution is influenced by the transport of both reactants and products, while above about pH 3.7, the dissolution is influenced predominantly by the kinetics of the surface reaction. A general model was developed to account for the combined effects of transport and reaction on the rate of dissolution. The effect of acetate ions on the rate of dissolution was investigated in alkaline solutions (pH 8.2 to 14) to eliminate the effects of hydrogen ion attack. The presence of acetate ions was found to have no significant affect on the rate of dissolution when compared to potassium chloride and sodium chloride solutions. The rate of dissolution was observed to decrease over this pH range and could not be described by previous reaction mechanisms. Therefore, a surface dissociation mechanism involving water was introduced and was shown to describe the rate of dissolution over the pH range of 8 to 14. About 50 % of the CO_2 released by human activity since the beginning of the industrialization has accumulated in the atmosphere (FEELY et al., 2004 and SABINE et al., 2004) mentioned the other half of the total release was taken up by the terrestrial biosphere (20%) and the ocean (30%).

The objective of this study to investigate the acid dissolution kinetics of calcium carbonate (CaCO₃)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. LITERATURE SURVEY

Atmospheric CO₂ has steadily increased since about 1850 and is currently increasing at a rate of 0.5% / year (Lal, 2002), stimulating investigations into the numerous reservoirs and fluxes within the global C cycle. Soil carbonate is the major form of soil inorganic C. (Euvrard, 2000), is the third largest C reservoir, surpassed only by the soil organic C and ocean reservoirs. The pedogenic carbonates occurs and discern differences among (i) pedogenic carbonate formed in limestone parent material, (ii) pedogenic carbonate formed in igneous parent material, and (iii) soil carbonate in the form of detritus limestone. However, each of the three types of soil carbonate revealed significant differences in relative to those of the calcite reference. Figure (1) show the carbon dioxide is an atmospheric constituent that plays several vital roles in the environment. It is a greenhouse gas that traps infrared radiation heat in the atmosphere. It plays a crucial role in the weathering of rocks. It is the carbon source for plants. It is stored in biomass, organic matter in sediments, and in carbonate rocks like limestone.



Figure (1). The Carbon Cycle and carbonate

(MARLAND 1975) show that the carbon dioxide is removed from the atmosphere by dissolving in water and forming carbonic acid

 $CO_2 + H_2O \rightarrow H_2CO_3$ (carbonic acid) (1) Carbonic acid is used to weather rocks, yielding bicarbonate ions, other ions, and clays $H_2CO_3 + H_2O + silicate minerals \rightarrow HCO_3^- + cations (Ca^{2+}, Fe^{2+}, Na^+, etc.) + clays$ Calcium carbonate is precipitated from calcium and bicarbonate ions in seawater by marine organisms like coral $Ca^{2+} + 2HCO_3 \rightarrow CaCO_3 + CO_2 + H_2O$ (2)

However, not all types of soil carbonate have the potential to sequester C from the atmosphere in a remediation timeframe of decades to centuries. For example, limestone detritus from the Permian Hueco Formation sequestered C over 240 million years ago, and does not represent a sink for atmospheric C in a remediation timescale. On the other hand, delicate biotic features such as calcified fungal hyphen and root hairs found in Holocene soils of southern New Mexico may represent the process of C sequestration in a remediation timeframe. (KRAIMER, 2005). Further remediative evidence of carbonate pedogenesis was provided in a laboratory experiment when bacteria and fungi from a southern New Mexico soil precipitated carbonate crystals within a time span of days to months. (MONGER et al., 1991) Although pedogenic carbonate formed in limestone parent material and pedogenic carbonate formed in igneous parent material were likely formed in different chemical environments and influenced by different proportions of biotic and a biotic precipitation, and found no robust mineralogical distinctions between the two types of pedogenic carbonate. Detrital limestone, lacking any exposure to pedogenesis, also provided no basis for distinctions among the soil carbonates.

2.1. CHARACTERIZATION OF CALCAREOUS SOILS

Calcareous soils occur naturally in arid and semi-arid regions because of relatively little leaching (BRADY & WEIL, 1999). They also occur in humid and semiarid zones if their parent material is rich in carbonates, such as limestone, shells or calcareous glacial tills, and the parent material is relatively young and has undergone little weathering. Some soils that develop from calcareous parent materials can be calcareous throughout their profile. This will generally occur in the arid regions where precipitation is scarce. (BRADY & WEIL, 1999). In some soils, CaCO₃ has been leached from the upper horizons, and accumulated in B or C horizons. These lower CaCO₃ layers can be brought to the surface after deep soil cultivation and in other soils, the CaCO₃ deposits are concentrated into layers that may be very hard and impermeable to water. These caliche layers are formed by rainfall leaching the salts to a particular depth in the soil at which water content is so low that carbonates precipitate. (JACKSON & ERIE, 1973) mentioned the soils can also become calcareous through long period of irrigation with water containing dissolved CaCO₃.

(HAGIN & TUCKER, 1982) and (BRADY & WEIL, 1999) states that a major characteristic of calcareous soils is that they develop in regions of low rainfall and must be irrigated to be productive. Marginal desert soils, with low content of organic matter and high concentration of carbonates can be of high agricultural value by supplying the

nutrients in the soil solution through drip irrigation, for example, tomato grown on a virgin desert soil containing 85% CaCO₃. when providing N, P and K through the irrigation system, (KAFKAFI & BAR YOSEF, 1980). Calcareous soils cover more than 30% of the earth surface, and their CaCO₃ content varies from a few percent to 95% define calcareous soil as a soil that its extractable Ca^{2+} and Mg^{2+} levels exceed the cation exchange capacity (CEC).

(MARSCHNER, 1995, HAGIN & TUCKER 1982) show that the calcareous soils have free $CaCO_3$ in the profile. The carbonates, due to their relatively high solubility, reactivity and alkaline character, buffer the pH of most calcareous soils within the range of 7.5 to 8.5. These soils generally have 100% base saturation, and the exchange complex is dominated by Ca²⁺. Nutrient management in calcareous soils differs from that in non-calcareous soils because of the effect of soil pH on soil nutrient availability and chemical reactions that affect the loss or fixation of almost all nutrients. Both native and applied P is tied up in highly insoluble Ca²⁺ and Mg²⁺ phosphates, rendering the added P only sparingly available for plant uptake. Fe³⁺, Zn²⁺, Mn²⁺ and Cu²⁺ deficiencies are common in soils that have a high carbonate due to reduced solubility at alkaline pH values. Improved fertilizer management is required to grow crops successfully on calcareous soils. To avoid ammonia volatilization, fertilizers containing ammonium-N or urea should be moved into the root zone with rainfall or irrigation, or be incorporated into the soil. Band placement of P minimizes soil contact thus reducing or delaying the formation of insoluble Ca²⁺ and Mg²⁺ phosphates. Crops planted on calcareous soils may require above normal levels of K^+ and Mg^{2+} fertilizer for satisfactory nutrition.

(LOEPPERT & SUAREZ, 1996) and (BARDY & WEIL 1996) mentioned that the sources of $CO_3^{2^-}$ of lime include marl. Oyster shells basic slag and precipitated carbonates, but ground limestone is the most common end is by far the most widely used of all liming materials. The two important minerals carried by limestone are calcite, which is mostly (CaCO₃), and dolomite, which is primarily calcium-magnesium carbonate (CaMg(CO₃)₂). These minerals occur in varying proportion in limestone. When no dolomite is present, the limestone is referred to as calcite. As the magnesium increases, this grades into dolomite limestone. So, if the stone is almost entirely composed of CaMg(CO₃)₂, the term dolomite is used. Most of the crushed limestone on the market today is either calcitic and/or dolomitic.

Dolomitic limestone and the oxides or hydroxides made from them have one advantage over the calcitic stones. They provide both Ca^{2+} and Mg^{2+} to the soil/plant system. In situations where available Mg^{2+} is low, dolomite or dolomitic limestones

would be the products of choice. The nutrient-supplying ability of all liming materials should not be overlooked. Ground limestone is effective in increasing crop yields. It varies in the amount of Ca^{2+} and Mg^{2+} carbonates from approximately 75-99%. The total CO_3^{2-} level of the representative crushed limestone is about 94%.(FISCHBECK, 1972) estimated the losses of lime from Broadbalk field at Rothamsted, which has grown wheat for 130 years and where the surface soil contained 5% of CaCO₃ when the experiment began. Annual loss varied from 665 kg CaCO₃ ha⁻¹ on the unfertilized plot to 1054 kg CaCO₃ ha⁻¹ from the plot which had annually 63kg Nha⁻¹. (FISCHBECK, 1971) also gave the losses in experiments where acid soils had been limed shown in the following table(1):

Table (1) shows the Losses of CaCO ₃ from woburn and Rothanisted sons.					
	Limestone applied	Annual loss			
	(t CaCO ₃ / ha)	(kg CaCO ₃ / ha)			
Woburn	5	176			
	12	703			
Sandy loam	19	1343			
Rothamsted	5	88			
	10	138			
Clay loam	20	904			

Table (1) shows the Losses of CaCO₃ from Woburn and Rothamsted soils.

(INGLE et al. 1973) gave the annual losses from arable and grassland soils limed to pH = 6.5 and 6.0 respectively as 336 and 235 kg CaCO₃ ha⁻¹. For rough grazing on acid (pH = 5.0) soils, the loss was estimated to be 118 kg CaCO₃ ha⁻¹. The depth of CaCO₃ horizons is strongly dependent on soil water flow and increases with increasing mean annual precipitation. (KAMHI 1963, & JENNY 1980) through its effect on evapotranspiration, temperature in the soil. (KAMHI 1963, HONJO et al., 1978 & MCFADDEN 1985) found that the wind plays a critical role in the rate of formation of calcic horizons, because wind borne dust and dissolved constituents in precipitation are considered the dominant sources of Ca²⁺ for deposition as CaCO₃ in noncalcareous desert soils. Also, the biotic factor can influence CaCO₃ deposition through its effects on:

(1) Soil CO₂ concentrations, which is changed the soil pH and CaCO₃ solubility,

(2) Evapotranspiration.

(BROWN 1956, REEVES 1970, GARDNER 1972, GILE 1981, MCFADDEN 1985 & SCHLESINGER 1985) studied the soils formed on calcareous parent materials accumulate pedogenic CaCO₃ at higher rates than soils formed from noncalcareous parent material. (LATTMAN 1973, & SCHLESINGER 1985) mentioned that parent material also controls to

a large extent, the water-holding capacity (WHC) of soils the WHC in turn, controls the depth of wetting and $CaCO_3$ deposition. Practical consequences of CO_3^{2-} chemistry in soils are depending on two important consequences of the surface and precipitation chemistry of $CaCO_3$ in soil.

2.1.1. AVAILABILITY OF CARBONATES IN NATURE

About 50% of the CO_2 released by human activity since the beginning of the industrialization has accumulated in the atmosphere (FEELY et al., 2004). The other half of the total release was taken up by the terrestrial biosphere (20%) and the ocean (30%). (SABINE et al., 2004) studied the seawater carbonates; CO_2 behaves like a weak acid. The associated chemical reactions drive a decrease in pH (increase in acidity) and in carbonate ion concentration:

 $CO_2 + H_2O + CO_3^{2-} \quad \longleftarrow \quad 2HCO_3^{-}. \tag{3}$

This process known as acidification (CALDEIRA & WICKETT, 2003; FEELY et al., 2004; ORR et al., 2005) decreases the saturation state of seawater with respect to calcium carbonate (CaCO₃).

While calcification appears to be linearly related to the saturation state in corals, experimental results obtained for foraminifera and coccolithophores suggest the existence of a threshold value of saturation state below which the calcification will decrease drastically (GATTUSO et al., 1998; BIJMA et al, 2002; KLEYPAS et al., 1999; RIEBESELL et al., 2000; ZONDERVAN et al., 2001; ZONDERVAN et al., 2002; KLEYPAS et al., 2006). Unmitigated acidification of oceanic waters will ultimately threaten the existence of marine calcifies and cause major changes in marine ecosystems. In terms of feedback on rising atmospheric CO₂, three distinct yet interconnected groups of processes involving CaCO₃ can be identified:

1. *Calcification*: CaCO₃ precipitation leads to a pCO_2 (where P is the partial pressure of CO₂, usually assumed to be that of the atmosphere) increase according to Eq. (4):

$$Ca^{2^+} + 2HCO_3^- \longleftarrow CaCO_3 + CO_2 + H_2O$$
(4)

A decrease in calcification would thus favor the uptake of atmospheric CO_2 by the ocean and acts as a negative feedback on rising atmospheric pCO₂. (GRUBER et al., 2005; FRANKIGNOULLE et al., 1994; ZEEBE & WOLF-GLADROW, 2001) mentioned that the ratio of CO_2 released per mole of CaCO₃ precipitated is a function of the buffer capacity of the seawater acid-base CO_2 system. Under present conditions, roughly 0.6 moles of CO_2 are released per mole of CaCO₃ precipitated; this ratio will increase as the overall buffer capacity of seawater decreases in response to anthropogenic CO_2 uptake.

2. *Dissolution*: The effect of dissolution follows directly from the stoichiometry of Eq. (4) (backward reaction). Enhanced dissolution of $CaCO_3$ in response to acidification increases ocean alkalinity thereby favoring CO_2 uptake, which can be considered as a negative feedback on atmospheric pCO₂.

3. *CaCO₃ export and rain ratio effect*: A decrease in calcification will alter the ratio of organic C to inorganic C (the rain ratio): an increase in rain ratio will promote the dissolution of CaCO₃ in marine sediments resulting in a higher alkalinity (ARCHER & MAIER-REIMER, 1994), a negative feedback operating on timescales of 10000 years. Alternatively, if the ratio of organic C to inorganic C is closely bound by the process of ballasting (ITTEKOTT, 1993; ARMSTRONG et al., 2002; KLAAS & ARCHER, 2002), less CaCO₃ production would imply less ballasting of organic C fluxes and a shallower demineralization, which corresponds to a positive feedback on atmospheric CO₂. This model change in pelagic calcium carbonate production (CaCO₃, as calcite in the model) and dissolution in response to rising atmospheric CO₂. The model predicts values of CaCO₃ production and dissolution in line with recent estimates. The effect of rising pCO₂ on CaCO₃ production and dissolution was quantified by means of model simulations forced with atmospheric CO₂ increasing at a rate of 1% per year from 286 ppm to 1144 ppm over a 140 year time-period. The simulation predicts a decrease of CaCO₃ production by 27% (GEHLEN et al., 2007).

2.1.2. ROLE OF CARBONATES IN PLANT NUTRITION

(HIGGINS, et al., 2000, 2001; BRADY & WEIL, 1999). Plants take up calcium in the ionic form (Ca^{2^+}). Uptake is not as efficient as for other plant nutrients. It occurs just behind the root tip, in contrast with potassium where uptake occurs along most of the length of the root. Consequently, anything which affects new root growth may prevent calcium uptake and induce a deficiency. This includes adverse weather conditions such as drought, low temperatures, high humidity, poor soil aeration and water logging. For example, "blossom-end" rot in tomatoes, which is attributed to inadequate calcium, can be induced by a period of moisture stress, even though the soil may have adequate calcium levels.

(LINDSAY, 1979 AND PEARCE et al. 1999) Competition also occurs with other cations, e.g. ammonium (NH_4^+), potassium (K^+) and magnesium (Mg^{2+}) for root uptake. Within plants, calcium is not mobile. Once calcium is deposited in leaves, it cannot be remobilized from them to the growing tips. Calcium is required for cell elongation and cell division. Adequate calcium helps delay leaf senescence and slows down or prevents leaf and fruit fall (abscission). In assessing the need to apply calcium and the form in which it is best applied, the soil pH should be considered in addition to the soil's

calcium status. In very acid soils, calcium will need to be applied in a form which will raise the soil pH, e.g. lime, and at higher rates than are normally required to correct calcium deficiency alone. Calcareous soils are alkaline because of the presence of CaCO₃, which dominates their chemistries. The $CO_3^{2^-}$ is characterized by a relatively high solubility, reactivity and alkaline nature; their dissolution resulting in a high solution HCO₃⁻ concentration which buffers the soil in the pH range of 7.5 to 8.5.

 $CaCO_3 + H_2O \rightarrow Ca^{2+} + HCO_3^- + OH^-$

(5)

(KOVÁCS, B. et al., 2004; MARSCHNER, 1995, and OBREZA et al., 1993) The determination of particle size distribution (PSD) is one of the most important fundamental physical properties of soils, which determines both the physico-chemical, mechanical, geotechnical, moreover environmental behavior of the sediments. Although the measurement of PSD is frequently performed in soil labs using different techniques. There are two important problems to solve: automation and continuous PSD curve generation. To overcome the mentioned troubles the new, hydrostatic method of continuous particle size distribution measurement was introduced, and also a new evaluation method (the method of finite tangents) was developed. To prove the developed methods both for soil testing and measurement evaluation the pilot test equipment called ASTA was built. The measurements shows that the hydrostatic method is suitable for the measurement of PSD curves, the accuracy of measurements using ASTA device was adequate to the measurements with the traditional hydrometer method. Particle size distribution, surface area and reactivity are important properties of soil CO_3^{2-} which influence soil pedogenic, chemical and rhizosphere processes (LOEPPERT & SUAREZ, 1996). CaCO₃ provides a reactive surface for adsorption and precipitation reactions, for example, of P, trace metals and organic acids (TALIBUDEEN & ARAMBARRI, 1964, and AMER et al., 1985). CO_3^{2-} reactivity influences the rate of volatilization of ammonia (RYAN et al., 1981). CO₃²⁻ affects also rhizosphere processes, especially those processes in which acidification is an important factor. For example, the Fe-deficiency response of dicotyledons involves the exudation of H^+ and acidification of the rhizosphere. The effectiveness of Fe-deficiency stress response is therefore negatively influenced by the neutralization of plant-produced acidity, which is influenced by the reactivity of the CO_3^{2-} phase (LOEPPERT et al., 1988, and MORRIS et al., 1990).

2.1.3. CARBONATES IN SOIL

(HAMILTON, et al 2001). Lime carbonates are used on acidic soils to correct acidity and supply calcium. Typical application rates are in the range of 2.5 to 7.5 t/ha. Lime is insoluble, and takes time to react in the soil; picture (1) shows the calcit stage at 40 cm. In annual crops, it should be applied several months ahead of planting and be incorporated into the soil. The effectiveness of lime is therefore very dependent on its particle size. Lime that is coarser than 250 microns (0.25mm) has little value in raising soil pH, at least in the short term.



Picture (1)An excavated trench 1.1 meters deep with a moderately indurated calcit stage at 40 cm

Calcium plays an important role in determining soil physical and chemical characteristics, i.e. structure and pH. Calcium ions cause soil colloids (clay platelets) to bond or aggregate together, forming crumbs or peds. Soils dominated by calcium are friable and well-structured, have good internal drainage, and are easy to cultivate. They are often described as self-mulching. In contrast, sodium, and to a lesser extent magnesium, because clay platelets to disperse. Soils dominated by sodium and/or magnesium have low infiltration rates, crust after rain, are puggy when wet, set hard on drying and are difficult to cultivate. Exchangeable calcium levels and soil acidity are usually closely related. Calcium is most available in the pH range 7.0 to 8.5. Under low pH or acidic soil conditions, exchangeable calcium levels in the soil are usually low and the solubility of manganese and aluminum increase and may become toxic. (MICHÉLI E, et al 1999) The whole horizon is impregnated with calcium-carbonate including numerous hard and powdery concretions ranging in size from 1 mm to 10 mm.



Picture (2 and 3). Accumulation of less soluble salts or non-saline substances Calcium carbonates (Calcisols) World Reference Base for Soil Resources Principles and structure by Erika Michéli Szent István University, Hungary

In regions of limited rainfall, Picture (2 and 3).show that the accumulation of less soluble salts or non-saline substances Calcium carbonates. carbonates (particularly CaCO₃) accumulate in soils. Where evapotranspiration exceeds precipitation, the downward flow of water through the soil profile is sufficient only to remove the most soluble weathering products, such as Na⁺ salts. Intermittent rains can flush out soluble salts even when the amount of percolating water is 1% or less of the total rainfall. Less soluble compounds, on the other hand, accumulate because of limited water flow. The Mg²⁺ and K⁺ form secondary aluminosilicates. Secondary silicates containing Ca²⁺ as a structural ion are rare, but Ca²⁺ remains instead as an exchangeable cations and is precipitated as calcite, aragonite, or vaterite all CaCO₃ and occasionally as the more soluble gypsum (CaSO₄.2H₂O) calcite formed in soil allows little Mg²⁺ substitution into its structure, and dolomite (CaMg(CO₃)²) apparently forms only under marine conditions.

Calcite, aragonite and vaterite can also accumulate from groundwater when hydrostatic pressure or capillary actions move Ca^{2+} and CO_3^{2-} rich waters upward in the soil profile. The losses of CO_2 to the atmosphere, and evapotranspiration of the water, lead to precipitation of CaCO₃. This mechanism sometimes accounts for CaCO₃ accumulation in soils of more humid regions.

There are two important consequences of the surface and precipitation chemistry of CaCO₃ in soil. Firstly the surface adsorptive reactions with phosphate ions, (BOISCHOT

et al., 1950), (TALIBUDEEN & ARAMBARRI 1964, WHITE A. F. & BLUM, A. E. 1995) stated that with Fe^{2^+} and Fe^{3^+} ions and with Zn^{2^+} and Mn^{2^+} ions adversely affect the ready availability of such ionic constituents of soils to plant roots and decrease the reactivity of added and native limestone. (GILE 1965) mentioned that the carbonate ions also react with appetites in adsorption precipitation reactions to from carbonate apatite of indeterminate composition; however no evidence is available of their occurrence in soils.

Secondly, the dissolution and precipitation chemistry of soil carbonates is intimately involved. The deposition of calcium and magnesium carbonates occurs differentially in the upper and lower soil horizons or in various sizes and shapes of particles. (Sherman et al. 1962), (Gaikawad & Hole 1965), (Gile 1965) (Anderson, 1968, Rostad & Arnaud, 1970, Smalley, 1974) found that the long catena of calcareous and saline/alkaline soils, the living and dead plant and animal life also contribute to such processes in the development of carbonate rich horizons in soils by enriching the CO2 and calcium in microenvironments (Mathews, 1965, wells 1962) (Abedi & Talibudeen, 1974) found the involutions are associated with powdery calcite (both soft and hardened) that have much higher liquefaction potential than the surrounding clay or silty clay in the sequence. This indicates that the presence of this type of calcium-carbonate had an important role in the development of the involutions.

2.1.4. SOIL WATER AND CALCIUM CARBONATE (CaCO₃) FLUXES

(ZOLTÁN H. et al. 2005), (GILE et al. 1981) states that the all precipitation was assumed to enter the surface horizon. Only saturated flow through the soil profile was considered. If precipitation exceeded the water-holding capacity (WHC) of the first horizon, water moved into the second horizon. This procedure continued with deeper horizons until the soil absorbed all the precipitation or the bottom horizon was reached. Water flux past the soil profile base treated as leachate and was assumed lost from the system.

The rate of CaCO₃ deposition in soils is largely controlled by the influx of Ca²⁺. Ca²⁺ can enter soils through weathering from calcareous and noncalcareous parent materials and from atmospheric deposition in dust and precipitation. Most studies in southwestern deserts suggest that atmospheric Ca²⁺ influxes are sufficient to explain the rates of CaCO₃ deposition in noncalcareous parent materials (BROWN, 1956, REEVES, 1970, GARDNER, 1972, GILE et al., 1981, MCFADDEN, 1985, and SCHLESINGER, 1985). As currently structured, the CALDEP program does not consider weathering of noncalcareous rocks, but the program can handle initial carbonate in the soil profile and subsequent weathering material. (GILE et al. 1981) found the atmospheric dust

carbonate (CaCO₃) input was $0.51 \text{g/m}^2/\text{yr}$, and the precipitation Ca²⁺ concentration was 3.0 mg/L.

2.1.5. **REACTIONS OF LIME IN THE SOIL**

(BRADY et al. 1996): mentioned that the Ca^{2^+} and Mg^{2^+} compounds, when applied to an acid soil, react with CO_2 and with the acid colloidal complex.

Reaction with carbon dioxide

All liming materials-whether the O^{2^-} , OH^- , or the $CO_3^{2^-}$, when applied to an acid soil react with CO_2 and water to yield the HCO_3^- form. The CO_2 partial pressure in the soil, usually several hundred times greater than that in atmospheric air, is generally high enough to drive such reactions. For the purely Ca^{2^+} limes, the reactions are as follows.

 $CaO + H_2O + 2CO_2 \longrightarrow Ca(HCO_3)_2$ (6) $Ca(OH)_2 + 2CO_2 \longrightarrow Ca(HCO_3)_2$ (7)

$$CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2$$
(8)

Reaction with soil Colloids

These liming materials react directly with acidic soils, the Ca^{2^+} and Mg^{2^+} replacing H^+ and Al^{3^+} on the colloidal complex. The absorption with respect to Ca^{2^+} may be indicated as follows, assuming H^+ ions are replaced.

$$\underline{\text{Micelle}} + \text{Ca}(\text{OH})_2 \longrightarrow \underline{\text{Ca}} \underline{\text{Micelle}} + 2\text{H}_2\text{O}$$
(9)

$$\underline{\text{Micelle}} + \text{Ca}(\text{HCO}_3)_2 \longrightarrow \underline{\text{Ca}} \underline{\text{Micelle}} + 2\text{H}_2\text{O} + 2\text{CO}_2$$
(10)

$$\underline{\text{Micelle}} + \text{CaCO}_3 \qquad \longrightarrow \qquad \text{Ca} \underline{\text{Micelle}} + \text{H}_2\text{O} + \text{CO}_2 \qquad (11)$$

As these reactions proceed, CO_2 is freely evolved, pulling the reaction to the right. In addition, the absorption of the Ca^{2+} and Mg^{2+} ions raises the percentage base saturation of the colloidal complex, and the pH of the soil solution increases correspondingly.

2.2. MINERAL AND CARBONATES DISSOLUTION KINETICS

An understanding of the factors controlling calcite dissolution is important for modeling geochemical cycles and impacts of greenhouse gases on climate, diagenesis of sediments, and sedimentary rocks. It also has practical significance in the investigation of behavior of carbonates. Limestone dissolution kinetics is important in understanding problems such as geochemical weathering (PLUMMER & WIGLEY, 1976), (BERNER & MORSE, 1974), the distribution of CO_3^{2-} sediments in marine environments (BERNER & MORSE, 1974), (CHAN & ROCHELLE, 1982), (BJERLE & ROCHELLE, 1982) the liming of acidified natural waters and the design of limestone contactors. Limestone or calcite dissolution has been studied using rotating disks (PLUMMER et al., 1978), (SJÖBERG &

RICKARD, 1983), (WALLIN & BJERLE, 1989a; SCHOTT et al., 1989), rotating cylinders agitated batch reactors containing crushed limestone particles (PLUMMER & WIGLEY, 1976). The rate of CO_3^{2-} mineral dissolution is determined by the physical and chemical characteristics of the stone, including the type and amount of impurities as well as the mineral crystallography. The chemistry and temperature of the solution are also important.

2.2.1. DISSOLUTION OF CARBONATES.

Several independent studies have suggested that carbonate dissolves in waters that lie above the saturations horizons for carbonates (ANDERSON & SARMIENTO, 1994; LOHMANN, 1995; MILLIMAN & DROXLER, 1996; MILLIMAN et al., 1999; CHEN et al., 2002; SCHIEBEL, 2002). This shallow depth CaCO₃ dissolution (SDCCD) has implications for the understanding of the global carbon cycle. Because of the CO₂ uptake by marine and terrestrial systems, the current increase of atmospheric CO₂ is half that expected from anthropogenic releases (IPCC, 2001). Important for the marine system is that calcifying organisms at the sea surface (e.g. molluscs, corals, and calcifying plankton) have a reducing effect on the CO₂ uptake capacity by turning dissolved carbonates from rivers and upwelling into shells. Conventional wisdom is that the carbonates shells are dissolved when they reach the saturation horizon of aragonite or calcite during sinking, which provides the excess alkalinity that can be supplied to the surface ocean via upwelling/diapycnal mixing. The impact of the SDCCD finding is that it implies a shorter time scale for the cycling of carbonates within the ocean. This would have implications for feedbacks between climate, atmospheric CO₂, and the marine carbon cycle.

(MILLIMAN & DROXLER, 1996; MILLIMAN et al., 1999) found that the alkalinity distribution is thought to be a very important piece of evidence in support of SDCCD Like oxygen or nutrients, (WOLLAST 1994 & DITTMAR, 1884) studied the cycling of carbonates alkalinity has the advantage of being without much experimental or sampling error. In addition, spatial changes basically follow hydrographic changes and are otherwise continuous and gradual only. (FRIIS et al. 2003, 2007) investigated the significance of in situ dissolution of carbonates above its saturation horizons using observations from the open sub polar north Atlantic and to a lesser extent a 3-D biogeochemical model. (FEELY et al., 2002; SABINE et al., 2002; CHUNG et al., 2003; FEELY et al., 2004) (MORSE & ARVIDSON 2002) The dissolution kinetics of CaCO₃ in aqueous solutions has been widely studied for many years. However, the reaction mechanisms could not be clearly determined because of the complexity of the carbonic acid system. For example, the dissolution reaction can be written in the following ways:

$$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-}$$
(12)

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-, \tag{13}$$

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2CO_3, \tag{14}$$

$$CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^{-},$$
(15)

 $CaCO_3 + H_2O + CO_2 \rightarrow Ca^{2+} + 2HCO_3^{-}.$ (16)

(PLUMMER et al. 1978) extensively studied this problem and put forth a group of reactions and a complex rate equation:

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-, \tag{17}$$

$$CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^{-},$$
(18)

$$CaCO_3 + H_2O \rightarrow Ca^{2+} + HCO_3^- + OH^-,$$
(19)

(ARAKAKI & MUCCI 1995) obtained a general equation for dissolution and precipitation of calcite in simple solutions by combining the experimental data of their own with those of others and the surface complexation model of (VAN CAPPELLEN et al. 1993) (* denotes a surface complex):

$$*CO_3^- + 2H^+ \rightarrow *Ca^{2+} + H_2CO_3,$$
 (20)

$$*Ca^{+} + H_2CO_3 \rightarrow *CO_3H + CaHCO_3^{+},$$
(21)

$$*CO_3H + CaHCO_3^+ \rightarrow *Ca^{2+} + H_2CO_3 + CaCO_3,$$
(22)

$$CaCO_3 \text{ (solid)} \rightarrow CaCO_3,$$

(DREYBRODT et al. 1996) and (LIU & DREYBRODT 1997) investigated the dissolution of granular calcite in the H₂O–CO₂–CaCO₃ system, and concluded that the dissolution rate depends critically on the ratio of solution volume to the surface area of reacting minerals, the dissolution is controlled entirely by conversion of CO₂ into H⁺ and HCO₃⁻, whereas in the range from 10^{-3} cm to 10^{-1} cm both CO₂ conversion and molecular diffusion are rate-controlling factors.

Recently, new approaches for studying surface reaction processes, e.g., atomic force microscopy and optical interferometry, have also been applied to investigate calcite dissolution (HILLNER et al., 1992a,b; DOVE & PLATT, 1996; LIANG et al., 1996a,b; DAVIS et al., 2000; LEA et al., 2001; MACINNIS & BRANTLEY, 1992; SHIRAKI et al., 2000; and CHUNG, S. N.,et al., 2003). There remains a major challenge in integrating these new means into meaningful and practical methods. A general theory of surface dissolution mechanisms that is required to satisfactorily correlate observations of mineral surfaces with concentrations of dissolved components is currently lacking. As (MORSE & ARVIDSON 2002) pointed out, "there is no general equation that can be applied to all calcites and simply correlate surface area with solution composition." Moreover, little is known about the influences of temperature on calcite dissolution

(23)

kinetics in the surface-reaction-controlled near-equilibrium region that commonly exists in natural systems.

The dissolution of carbonate has been extensively studied over the past decades (GEHLEN et al., 2007; MORSE & BERNER, 1972; INGLE et al., 1973; BERNER & MORSE, 1974; BERNER, 1976; MORSE, 1978; HONJO & EREZ, 1978; PLUMMER et al., 1978; KEIR, 1980; WALTER & MORSE, 1985; CHOU et al., 1989; ARAKAKI & MUCCI, 1995; MORSE & ARVIDSON, 2002; GEHLEN et al., 2005 a,b). (KEIR 1980) derived a reaction rate from laboratory dissolution experiments with synthetic calcite. The higher order dependence was challenged by (HALES & EMERSON 1997a) and (HALES & EMERSON 1997a),. The authors re-evaluated experimental data and concluded that the rate of dissolution is linearly dependent on under saturation (n=1). According to the high reaction order derived by (KEIR, 1980) could be attributed to uncertainties in the saturation state of the experimental seawater. (GEHLEN et al., 2007) the first order calcite dissolution kinetics proved to be more consistent with the interpretation of in-situ pore water pH measurements (HALES & EMERSON, 1997a, b). As stressed by (GEHLEN et al. 1999), a satisfying reproduction of pore water profiles through diffusion-reaction models is, however, not a proof per se of the validity of a kinetic expression. (GEHLEN et al. 2005b) carried out kinetic experiments with biogenic carbonates. They derived an average reaction rate order of $n=2.3 \pm 0.4$ from 8 experiments with biogenic carbonates in artificial seawater. The higher reaction order is explained in terms of a multiphase system. It results from the concomitant dissolution of carbonate fractions characterized by variable reaction rate constants. While the in-depth discussion of carbonates dissolution kinetics is the preceding section highlights the need for further experimental studies of the dissolution behavior of biogenic carbonate phases. They adopted a linear dependency of carbonate dissolution on under saturation (n=1). Since the extrapolation of experimental results from controlled laboratory experiments which express reaction rate constants normalized to the specific surface area of carbonate (KEIR, 1980; GEHLEN et al., 2005b) to the global scale is not straightforward, and used the evolution with depth of carbonate fluxes recorded in sediment traps to derive the apparent reaction rate constant k (1/time). And also selected stations for which mean annual fluxes were reported from at least two different deployment depths from a comprehensive data set on particle fluxes (DITTERT et al., 2005). In order to derive dissolution rates from carbonate fluxes, the time it takes for settling particles to bridge the depth interval between trap deployments needs to be known.

(WANG TIANGUI & LI ZUOHU 2005) studied the dissolution kinetics of granular carbonate in concentrated aqueous sodium dichromate solutions at pH 6.0–7.0 and 110–

130°C. The results indicate that the dissolution reaction is mix-controlled and the surface reaction is the prevailing factor. The concentration of Ca^{2+} in solution does not affect the dissolution of carbonate, but increase of carbon dioxide partial pressure retards the dissolution of carbonate. (WANG TIANGUI & LI ZUOHU 2005) mentioned that understanding of the factors controlling calcite dissolution is important for modeling geochemical cycles and impacts of greenhouse gases on climate, digenesis of sediments, and sedimentary rocks. It also has practical significance in the investigation of behavior of carbonates in petroleum and natural gas reservoirs and in the preservation of buildings and monuments constructed from limestone and marble. A large number of papers have been published on dissolution kinetics of carbonate in aqueous solutions. (GEHLEN et al. 2007) carried out model experiments in order to quantify the evolution of carbonate production and dissolution under conditions of increasing atmospheric CO₂. (FRIIS et al. 2007) and (WILLIAM 1992): The observed pattern can instead be explained by (I) salinity dependent variations of alkalinity at the sea surface and subsurface and (II) transport of dissolved carbonate from below the saturation horizon into depths that are above the saturation horizon of carbonates.

2.2.2. KINETICS OF DISSOLUTION:

The kinetics of carbonate dissolution is very sensitive to the surface structure, composition, and physical properties of the crystals. (EVAGELOS et al.,1996). The dissolution rate of carbonates particles is decreased with the increase of the particle size and is affected dramatically by treatment. The dissolution of untreated is accompanied by intense breakdown of the particle, and the rate of extent of breakdown depends on the particle size. Adequate pretreatment with steam makes the carbonate particle resistant to breakdown, and the dissolution rate becomes very slow. (SDOUKOS & ECONOMOU, 1985 a,b) and (KRALJ & BRECEVIC 1994). Report that there are many metastable carbonate modifications that appear as initial soild phases in many carbonate precipitation processes, and most probably as precursors in carbonate geological sedimentations.

2.2.3. CARBONATE DISSOLUTION AND Ca REACTIONS

(Ross et al., 2007): the dissolution of carbonate was significantly increased ($p \le 0.05$) in all treatments when considering the original status of both soils. (LAL, 2002, KRAIMER et al. 2005). Further premeditative evidence of carbonate pedogenesis was provided in a laboratory experiment when bacteria and fungi from a southern New Mexico soil precipitated carbonate crystals within a time span of days to months (MONGER et al., 1991). The dissolution of carbonate has been extensively studied over

the past decades (LEBRON & SUAREZ 1998, VATER, 1897, 1899, MORSE & BERNER, 1972; INGLE et al., 1973; BERNER & MORSE, 1974; BERNER, 1976; MORSE, 1978; HONJO & EREZ, 1978; PLUMMER et al., 1978; KEIR, 1980; WALTER & MORSE, 1985; CHOU et al., 1989; ARAKAKI & MUCCI, 1995; MORSE & BENDER, 1990, MORSE & ARVIDSON, 2002; GEHLEN et al., 2005a, b, VAN DER WEIJDEN 1997). The fraction of carbonate lost to dissolution was calculated as the difference in carbonate concentrations between the respective upper and lower traps. (EVAGELOS et al. 1996) mentioned that a mechanism based on the adsorption of the phosphoric acid on the external surface of the carbonate solid phase followed by reaction of surface species with phosphoric acid and further transfer of the formed $Ca(H_2PO_4)^2$ in the solid-liquid interface for the dissolution of carbonate particles in a phosphoric acid solution is assumed. The reaction of surface species with phosphoric acid was found to be the ratedetermining step. The dissolution of untreated particles is accompanied by intense breakdown of the particles, and the rate and extent of breakdown depends on the particle size. Adequate pretreatment with steam makes the carbonate particle resistant to breakdown, and the dissolution rate becomes very slow. (WILLIAM et al. 1994) mentioned that the range of k values has important implications regarding the type of carbonate dissolving and its location within the sediment column. At low values of k, organic carbon rain rates to the seafloor become the dominant driving force of carbonate dissolution. At higher values of k, the degree of bottom water under saturation becomes more important. Dissolution of carbonate within equatorial Pacific sediments can be adequately described with $k = 20\pm10\%$, a rate constant much lower than some previously used values. (KAUFMANN & DREYBRODT 2007) stated that dissolution rates of limestone covered by a water film open to a CO₂ containing atmosphere are controlled by the chemical composition of the CaCO₃-H₂O-CO₂ solution at the watermineral interface. At low water-film thickness this reaction becomes rate limiting. The time dependent diffusion reaction equations are solved for free drift dissolution by a finite difference scheme, to obtain the dissolution rate of calcite as a function of the average calcium concentration in the water film. Dissolution rates are obtained for high under saturation.

2.2.4. MODELS FOR LIMESTONE DISSOLUTION

A number of models have been developed for predicting the rate of carbonate dissolution in aqueous systems. Some of these are entirely empirical and some have a partial basis in fundamental principles (SJÖBERG, 1976) and (PLUMMER et al., 1979; BJERLE & ROCHELLE, 1984): The potential for transport control of calcite dissolution has been recognized by many investigators (KING & LIU, 1933; TOMINAGA et al., 1939;

KAYE, 1957; WEYL, 1958; NIERODE & WILLIAMS, 1971; BERNER & MORSE, 1974; LUND et al., 1975; PLUMMER & WIGLEY, 1976; BJERLE & ROCHELLE, 1984; CHAN & ROCHELLE, 1982; WALLIN & BJERLE, 1989b; HADDAD, 1986, and LEE et al., 2003;). There is some agreement that in neutral to alkaline solutions the dissolution of calcite is controlled by mixed kinetics in which the rate depends on both a surface chemical reaction and the transport of reactants and/or products to or from the reaction sites (SJÖBERG & RICKARD, 1983, 1984a,b, 1985; BERNER & MORSE, 1974; PLUMMER et al., 1978; COMPTON & DALY, 1984).

(HADDAD 1986) concluded that predicting the rate of calcitic limestone dissolution in a packed-bed contactor requires knowledge of both the hydrodynamic mass transport properties of the mineral-water system and the kinetics of the heterogenous reaction at the calcite surface. Most existing models of calcite dissolution are based on results obtained using large crystals of essentially pure calcite. For example, a number of studies have been done with Iceland spar. The direct application of these results to the dissolution of calcite crystals in limestone is questionable. Differences between limestone and pure calcite that may affect dissolution kinetics include: (a) impurities in the limestone such as silica, Al and Fe, (b) crystal growth histories and defects, and (c) crystal grain sizes.

(SCHOTT 1999) and (TAYLOR et al. 2001): magnetite dissolution was treated with a surface speciation model and the dissolution rate formula described as a function of the concentration of the surface species. (WHITE & BRANTLEY 2003) also demonstrate a correlation between a decreasing weathering rate and increasing age of the substrate. The rate of carbonate mineral dissolution is determined by the physical and chemical characteristics of the stone (WALLIN & BJERLE, 1989b), including the type and amount of impurities and the mineral crystallography. The chemistry and temperature of the solution are also important. (WALLIN & BJERLE 1989b) used the film theory model for the dissolution of limestone compared with an empirical dissolution model based on the assumption of reaction rate control. Both dissolution models were developed for limestone-water systems. The film theory model consists only of well-known physical constants and bulk concentrations. The hydrodynamic parameter must be determined for both models. The dissolution experiments performed on a rotating limestone cylinder system were used to test the ability of these two models to predict the dissolution rate of limestone in aqueous systems, where the mass transfer of the dissolving species is the rate limiting step. Of specific significance was the ability of each model to predict the dissolution rate at different pH-values, CO₂ partial pressures and hydrodynamic conditions at constant temperature. The film theory model describes the rate of limestone dissolution quite satisfactorily within the conditions investigated. Due to the good model-experiment agreement, the dissolution process can be described by a mass transfer model such as the film theory model.

In a CO_2 free environment, the comparison reveals that the film theory model predicts the dissolution rate with higher accuracy, closely describing the dependence of pH on the dissolution rate. However, in a CO_2 environment, the models give a similar correlation to experimental data. The good correlation for the reaction control model in a CO_2 atmosphere is highly dependent on the three rate constants which must be experimentally determined. The film theory model contains. This makes the film theory model easier to apply when considering the dissolution rate of limestone in the mass transfer controlled region. The film theory model provides a reasonable mechanism for the dissolution process in the mass transfer controlled region, based only on theoretical considerations.

2.3. FACTORS AFFECTING CARBONATE DISSOLUTION

2.3.1. IMPURITIES IN LIMESTONE

Natural limestones contain varying amounts of impurities (BOYNTON, 1980). Impurities can be classified as either homogeneous or heterogeneous. Homogeneous impurities are usually silt, sand or clay (or other forms of silica such as quartz) that entered the stone when it was first deposited and are therefore uniformly distributed throughout the formation. Heterogeneous impurities are contaminants that have accumulated between the strata or are loosely embedded in the stone.

The most common impurities in limestone are Si and Al followed by Fe. Si is usually present as silica or with Al in alumino silicate minerals. Al may also be present as alumina. Fe may exist as an FeCO₃ or FeO, distributed heterogeneously from minerals such as pyrite or limonite. Other, usually much less significant, contaminants include Mn, Cu, Ti, Na and K (BOYNTON, 1980). (MURRAY et al. 1954) analyzed 45 high-Ca limestone samples and found measurable amounts of silica, alumina, and MgO in each of them. K, Na and S.

A spectrographic analysis indicated the Fe, Ba, Sr and Sn were also present. Relatively pure limestones tend to develop a thin, lightcovered crust when weathered. Impure varieties, especially those containing Fe, weather yellowish or brown, and if there is much clay or sand, an obvious crust is formed. According to (NORTH, F.J. 1930), weathering involves the removal to solution of the carbonate fraction of the stone and, if much insoluble material is present, it tends to remain behind, forming a superficial layer usually different in colour from the unweathered rock.

2.3.2. STONE COMPOSITION AND CRYSTALLOGRAPHY

Silicate weathering has revealed the existence of a surface leached layer (HOLDREN & BERNER, 1979; SCHOTT et al., 1981; BERNER & SCHOTT, 1982; SCHNOOR, 1989; CHOU & WOLLAST 1984). Studied the feldspar weathering by the formation of a residue layer consisting mainly of Al and silica at the mineral surface. The rate of weathering of feldspar was found to be controlled by the existence and properties of the residue layer. As the layer increased in thickness, the rate of dissolution decreased rapidly until it reached a quasi-steady state value. The quasi-steady state condition, it was suggested, is due to a balance between the rate of dissolution of the fresh feldspar (which depends on the diffusion of reactants and products through the residue layer) and the rate of dissolution of the residue layer. (SCHNOOR 1989) has called this phenomenon "initial incongruent dissolution". Weathering experiments by (SVERDRUP 1990; SVERDRUP 1990) indicated that the dissolution rate of minerals containing Al, like feldspar, biotite and anorthite, is affected by the presence of Al if the solution Al concentration is greater than some limiting value. When Al is produced by chemical reaction at the mineral surface this rate is determined by the Al concentration gradient from the particle surface to the bulk solution.

(SVERDRUP 1990) suggests that a similar mechanism could apply to cations such as Ca, Mg, K, Na, Fe, and Si that are released from the mineral surface during dissolution. Differences in surface defect density, kink and step density, and the number of edges and corners per unit volume of a mineral can all combine to bring about significant differences in dissolution kinetics (SCHOTT et al. 1989; BURTON et al., 1951). For calcite this problem were studied the dissolution of Iceland spar (high purity calcite) using rotating mcylinders strained to a high defect density. They proposed that dissolution occurs preferentially at active sites such as lattice defects. Minerals with greater defect densities dissolve faster since their effective surface areas are greater than more perfect specimens of the same compound. (COMPTON & DALY 1984) found the rate of dissolution of Iceland spar was sensitive to the method of surface preparation. Surfaces obtained by misorienting the crystal face provided more sites at which dissolution could occur and thus dissolved faster than surfaces with ordinary cleavage planes. (COMPTON & DALY 1986) have shown that the dissolution rate of Iceland spar is influenced by surface morphology and the method used to prepare the surface of the stone sample. Freshly cleaved crystals were essentially unreactive, but surfaces obtained by misorienting the crystal faces dissolved faster than the ordinary cleavage planes because, it was assumed, these provide more terrace sites at which dissolution can occur. The relationship between dissolution rate and particle grain size for alkali

feldspars was studied by (HOLDREN & SPEYER 1985, 1987). They observed that the dissolution rate increased linearly with decreasing grain size down to a critical range (approximately 50-100 μ m). In this range, they hypothesized, the grain size and distance between adjacent reactive sites become roughly equivalent. For grain sizes below the critical region, rate and reactant surface area were not related, however, the rates for larger grain size minerals were reported as rates per unit area, where rate and area had a linear relationship.

The dissolution of dolomitic limestones (CaMg(CO₃)₂) was studied by(PLUMMER & BUSENBERG 1982) in CO₂-H₂O-acid systems using a temperature range of 1.5 to 65°C. In the early stages of dissolution the carbonate component of calcite dissolves faster than the dolomite component, forming a Mg-enriched surface. After the initial period of enhanced carbonate dissolution, Ca²⁺ and Mg²⁺ ions were released stoichiometrically. Pure dolomite dissolves more slowly than pure calcite (RAUCH & WHITE, 1977; PALMER, 1991). In stones that are a mixture of calcite and dolomite, the dissolution rate has been shown to decrease in a regular way with increasing dolomite content of the rock (RAUCH & WHITE, 1977; HERMAN & WHITE 1985) studied the dissolution of dolomite samples and concluded that the dissolution rate increases with decreasing grain size.

2.3.3. EFFECT OF TEMPERATURE

The effect of temperature on the dissolution kinetics of limestones has received limited study. (RICKARD & SJÖBERG 1983) showed that the experimentally observed rate constant for the dissolution of calcite in aqueous solutions is controlled by a surface reaction and a mass transfer resistance that act in series. They therefore concluded that the overall dissolution rate constant is likely to be a complex function of the temperature. The temperature dependence of rate constants for heterogeneous reactions is usually quantified using the Arrhenius equation, i.e.,

$$\ln k = Ea/RT + \ln A \tag{24}$$

where Ea is the apparent activation energy, R is the gas constant (8.314 J mol⁻¹ k⁻¹), k is the dissolution rate constant at the absolute temperature, T, and A is a constant. The apparent activation energies for heterogeneous reactions have been used to discriminate between reactions showing transport control, surface chemical reaction control or mixed kinetics. The magnitude of Ea for reactions controlled by transport processes is typically much less than values for surface and homogeneous chemical reactions, e.g., 10 to 20 kJ/mol versus 30 to 100 kJ/mol.

(RICKARD & SJÖBERG 1983) concluded that at 25°C the rate of calcite dissolution in the H⁺-dependent regime is controlled by mass transfer, which they assumed to be the diffusion of H⁺ from the bulk solution through the mass transfer boundary layer to the stone surface. In the H⁺-independent regime the surface chemical reaction controls and in the transition region between these limits the kinetics is a function of both the surface reaction and mass transfer. Lower temperatures cause the surface chemical reaction rate constant to become smaller and the extent of the transition region expands into the H⁺dependent region. (LUND et al. 1975) used a rotating cylinder to study the rate of dissolution of calcite in hydrochloric acid. The dissolution rate was limited by mass transfer at 25°C, even at high cylinder rotational speeds. At -15.6°C both mass transfer and surface reaction resistances were important.

2.3.4. EFFECT OF TRACE SPECIES IONS IN SOLUTION

Another important factor that may affect the dissolution rate of calcite is the presence of trace species in solution that adsorb on the mineral surface. Inhibition can occur at very low levels of trace species as demonstrated by the strong retarding effect on calcite dissolution of micromolar concentrations of dissolved Sc⁴⁺ (TERJESEN et al., 1961) and orthophosphate (BERNER & MORSE, 1974). While modeling limestone dissolution in soils. (WARFVINGE & SVERDRUP 1989) found that the rate of deactivation due to adsorbed impurities on the limestone surface had a significant influence on the model calculations. Fresh calcite was coated with rust coloured precipitates when exposed to soil solutions or surface waters containing iron and dissolved organic C.

2.3.5. EFFECT OF pH

The kinetics of calcite dissolution in acetic acid solutions was investigated over a wide range of pH using a rotating disk apparatus (DOVE et al., 2001). The dissolution is influenced by the rate of transport of reactants to the surface, the kinetics of the reversible surface reaction, and the rate of transport of products away from the surface. Below about pH 2.9, the dissolution is influenced by the transport of both reactants and products, while above about pH 3.7, the dissolution is influenced predominantly by the kinetics of the surface reaction. (ALICE et al., 2005) Soil acidity and alkalinity determine soil reaction. Soil reaction is usually described in terms of soil pH, a measure of the amount of H⁺ in the soil. The pH scale goes from 1 to 14, 1 being very acid indicating very large amounts of H⁺. The midpoint, pH 7.0, is neutral, meaning that the soil is neither acid nor basic. All things considered, the most desirable pH for the growth of most plants if

about pH 6.5, very slightly acid. In Nebraska, soil pH values run from about pH 4.5 to pH 9.0.

(POKROVSKY et al., 1999) A general model was developed to account for the combined effects of transport and reaction on the rate of dissolution. The effect of acetate ions on the rate of dissolution was investigated in alkaline solutions (pH 8.2 to 14) to eliminate the effects of H^+ attack. The presence of acetate ions was found to have no significant affect on the rate of dissolution when compared to results in potassium chloride and sodium chloride solutions. The rate of dissolution was observed to decrease over this pH range and could not be described by previous reaction mechanisms. Therefore, a surface dissociation mechanism involving water was introduced and to describe the rate of dissolution over the pH range of 8 to 14. (BOUDREAU et al. 1993) show that the theoretical predictions of a closed and an open system model for the evolution of pH and calcite-saturation state during the sequential oxidation of organic matter by O_2 , NO_3^- , and SO_4^{2-} . The closed-system model is similar to previous thermodynamic models found in the geochemical literature. The open system model allows for differential diffusion of dissolved species, exchange with overlying waters, fast acid/base reactions, and a variety of spatially distributed sources and sinks. In particular, dissolution and precipitation of minerals are included either as local equilibrium processes as in the case of calcite dissolution, or as depth-dependent exponentials as for FeS and CaCO₃ precipitation. The model calculations reveal that closed and open systems have qualitatively similar behavior with respect to pH and CO_3^{2-} saturation. However, a quantitative comparison establishes that the closed-system model represents usually an upper limit on pH in the oxic zone of sediments, while it always sets a lower bound on pH in the zone of SO_4^{2-} reduction.

(SMITH, et al., 1994) The changes in closed and open systems during oxic decay are more complex than those of pH. The closed system will present an upper limit when the initial pH is high (8.0), but does not exhibit limiting behavior if the initial pH is low (i.e., 7.0). The closed-system model always places a lower limit during sulfate reduction. Both models predict that CaCO₃ dissolution can buffer the potential pH fall due to oxic CO₂ production; however, quantitative evaluation of this effect requires a diagenetic model with realistic dissolution kinetics. The precipitation of CaCO₃ has only a modest lowering effect on pH. The oxidation of total dissolved ammonia and sulfide by O₂ represents a potentially strong source of protons. Counter-intuitively, such oxidation reactions at the base of the oxic layer will raise the pH at a given O₂ concentration because of a concomitant decrease in the O₂ penetration depth. In addition, the O₂ demand of the sediments can switch almost entirely from organic matter decay to reduced byproduct oxidation as the amount of sulfate reduction increases. By products oxidation leads, however, to lower calcite-saturation states, and this can lead to more dissolution of fossil material near the sediment-water interface.

2.4. MODELING OF CARBONATE DISSOLUTION IN LIMESTONE CONTACTORS

(HADDAD 1986) described the dissolution of calcite in limestone contactors by adapting the rate model derived by (RICKARD & SJÖBERG 1983). RICKARD & SJÖBERG'S model assumes that the dissolution of carbonate in acidic solutions is controlled by a heterogenous reaction, the rate of which is determined by a mass transfer resistance and a surface reaction acting in series. According to this assumption, the rate of carbonate dissolution, (r), is given by:

$$\mathbf{r} = \mathbf{k}_{\mathrm{o}} \mathbf{a} \left(\mathbf{C}_{\mathrm{eq}} - \mathbf{C} \right) \tag{25}$$

where C_{eq} and C are the equilibrium and bulk fluid Ca^{2+} ion concentrations, respectively, and a is the interfacial area of CaCO₃ per unit volume of fluid. k_o is the overall dissolution rate constant and is given by:

$$k_{o} = [(1/k_{L}) + (1/k_{c})]^{-1}$$
(26)

where k_L is the mass transfer rate constant for the Ca²⁺ and k_c is the first order surface reaction rate constant. For a limestone contactor C_{eq} is a function of the chemistry and temperature of the untreated water. And calculated using the chemical equilibrium model. The quantity a is the interfacial area of carbonate per unit volume of interstitial water and, for a limestone contactor with stone that is essentially 100 % carbonate, is given by:

$$a = 6(1-e)/(de\Psi)$$
 (27)

where d and Ψ are the volume-mean diameter and sphericity of limestone particles and, is the bed porosity. According to (HADDAD, 1986; LETTERMAN et al., 1991), for a packed bed of crushed limestone, the magnitude of k_L can be determined using equations derived by (CHU et al. 1953). Equation (28) was used for values of the modified REYNOLD'S number (MRe) in the range $1 \le MRe \le 30$,

$$k_{\rm L} = 5.7 \ {\rm U_s} \ ({\rm MRe})^{-0.87} \ ({\rm S_c})^{-2/3},$$
 (28)

and Equation (29) was used for values in the range $30 \le MRe \le 10,000$,

$$k_{\rm L} = 1.8 \ {\rm U_s} \ ({\rm MRe})^{-0.44} \ ({\rm S_c})^{-2/3}$$
 (29)

The modified REYNOLD'S number is given by:

$$MRe = dU_s / (v(1-e))$$
(30)

and the SCHMIDT number, S_c, by:

$$S_{c} = v / D \tag{31}$$

where v is the kinematic viscosity, D is the Ca^{2+} ion diffusivity and U_s is the superficial velocity of the fluid. (HADDAD 1986) assumed that the magnitude of k_c is determined by

the chemistry of the solution at the CaCO₃ surface and used data from (SJÖBERG & RICKARD 1984) to derive the following empirical relationship:

 $k_c (cm/s) = 1.6 \times 10^{14} \{H_{eq}\}^{1.7}$ (32) where $\{H_{eq}\}$ is the interfacial (equilibrium) hydrogen ion activity. In this study the magnitude of $\{H_{eq}\}$ was calculated with the chemical equilibrium model and is related to the equilibrium Ca²⁺ ion concentration (C_{eq}). (HADDAD 1986) used the following version of the continuity equation to model the limestone dissolution process in a contactor operating at steady-state,

 $N_D d^2 C/dZ^2 - e dC/dZ + r\Theta = 0$ (33)

where N_D is the dimensionless axial dispersion number, C is the Ca²⁺ ion concentration, Z is the dimensionless depth, Θ is the mean fluid residence time and r is the Ca²⁺ dissolution rate expression. Equation (25) was substituted for r into Equation (33) and the resulting expression was integrated over the depth of the column to obtain,

 $(C_{eq}-C_{bL})/(C_{eq}-C_{bo}) = \exp\{-k_o a L \notin /U_s + (k_o a L \notin /U_s)^2 N_D\}$ (34) where C_{bo} and C_{bL} are the influent and effluent Ca^{2+} concentrations and L is the overall depth of the contactor. This equation assumes that the rate of dissolution at any point in the bed is constant with time and, therefore, factors such as residue layer formation and limestone particle shrinkage are insignificant. (HADDAD 1986) derived the following approximate equation for N_D using data from a tracer response study,

$$N_{\rm D} = 2(d/L) \tag{35}$$

Equations (26) through (32), (34) and (35) effectively predict the initial performance of a contactor filled with fresh limestone (LETTERMAN et al., 1991)., (HADDAD 1986) observed that the effluent pH and Ca²⁺ ion concentration decreased with time. The discrepancy between the values predicted by the steady-state model and the measured values increased with time. (HADDAD 1986) used the steady-state model (Equations 26-32 and 34-35) to develop a time-step simulation program for predicting the performance of contactors during the non-steady-state behavior of long term operation. In this program the operational period is divided into short time intervals and the contactor bed is divided into thin layers. The steady-state model predicts the amount of Ca²⁺ dissolved from each layer during each interval of time. After each interval, a new stone diameter is calculated for each of the layers using the amount of Ca^{2+} dissolved. (HADDAD 1986) used x-ray energy spectroscopy to analyze the Ca^{2+} concentration when it is plotted as a function of volume water treated, using data from (HADDAD 1986). surface of limestone particles from the contactor used in the long term experiment. He observed that the surface density of Al, silica and Fe had increased during the experiment and concluded that a "residue layer" had formed as the carbonate dissolved from the limestone matrix.

As the residue layer increased in thickness, he assumed, it limited the transport of Ca^{2+} ion away from the surface of the limestone and slowed the rate of dissolution. The transport of Ca^{2+} ions across the residue layer was modeled using,

$$k_{\rm f} = D \varepsilon_{\rm r} / (\delta J_{\rm r}) \tag{36}$$

where k_f is the residue layer mass transfer coefficient, C_r and δ are the porosity and thickness of the residue layer, D is the diffusivity of the Ca²⁺ in the bulk solution, and J_r is the pore length (tortuosity) factor. An expression for δ was derived by assuming that the thickness of the residue layer was much less than the diameter of the particle and that it increased as Ca²⁺ dissolved from the surface of the limestone, i.e.,

 $\delta = [M (1-\beta) (f)] / [0.4 \beta \rho_s (1-e_r)]$ (37)

where M is the cumulative mass of Ca^{2+} dissolved per unit area of stone, β is the mass fraction of carbonate in the stone, ρ_s is the mass density of the residue solids and f is the fraction of the total residue solids that remains on the stone surface. The following equation for k_f is obtained by substituting Equation (37) into Equation (33),

 $k_f = 0.4 \beta DK/[M(1-\beta)].$ (38)

The coefficient k in Equation (38) includes all the parameters that (HADDAD 1986) could not measure experimentally and is given by,

 $K = \rho_{s} (1-C_{r}) (Cr) / [(f) (J_{r})]$ (39)

The residue layer mass transfer coefficient, k_f , was included in the calculation of the overall dissolution rate constant by expanding Equation (26) as follows,

$$k_{o} = [(1/k_{L}) + (1/k_{c}) + (1/k_{f})]^{-1}$$
(40)

HADDAD calibrated the non-steady-state simulation program (with the residue layer resistance) by finding that k = 0.6 gave good agreement between the measured and model predicted effluent Ca²⁺ concentrations. This value of k was in reasonable agreement with a value of k calculated using rough estimates of the magnitudes of the parameters in Equation (38).

2.5. INFLUIENCE OF CHEMICAL COMPOSITION AND FINENESS OF LIMING MATERIALS

The chemical composition of liming materials affects the rate of reaction of these compounds with soil. For example, burned and hydrated limes reacts quickly with soils, bringing about significant changes in soil pH in only a few weeks. In contrast, limestone (particularly those high in dolomite) reacts much more slowly, taking a year and even longer too fully react with soil colloids. (TAO CHEN et al., 2006) The formation of carbonate mineral scale is a persistent and expensive problem in soil. The magnesium ion, present in formation and injection waters in downhole conditions, is a key determinant in carbonate scale formation. The kinetics of calcium carbonate scale formation is studied both in the bulk solution and on a metal surface. The Mg²⁺ ion

adsorbs into the deposited crystals and the ratio of Mg^{2+} in the deposit formed on the metal surface is proportional to the ratio of Mg^{2+}/Ca^{2+} in the scaling water. The distribution coefficient in surface deposition and in bulk solution is a constant and independent of the concentration of Mg^{2+} ions in the bulk solution. Simultaneously, the Mg^{2+} ion accelerates the crystal transformation from vaterite to calcite and adsorbs on the surface of vaterite and calcite causing an increase in surface roughness in addition to distortion of crystals.

2.5.1 CHEMICAL GUARANTEES OF LIME

There are several methods of expressing the relative chemical value of lime. The most common ones are the following:

- *Calcium Carbonate equivalent* (EL MAHI et al., 1987) Sometimes known as the neutralizing power. If a lime were chemically pure CaCO₃, the CaCO₃ equivalent would be 100. If all of the lime was in the CaCO₃ form, but it was only 95% pure, the CaCO₃ equivalent would be 95. Other forms of lime can be converted to the CaCO₃ equivalent by the use of atomic and molecular weights. For example, assume that it is desired to calculate the CaCO₃ equivalent of chemically pure CaO:

% CaCO₃ equivalent = (molecular weight of CaCO₃/ molecular weight of CaO) * 100

 $= (100/56) * 100 = 17806\% \text{ CaCO}_3 \text{ equivalent}$ (41) The pounds of equivalent CaCO₃ of any quantity of CaO can be obtained by multiplying the pounds of pure CaO by 178.6%

- *Calcium oxide equivalent* This form of chemical guarantee is obtained also by the use of molecular weight. For example, if pure $CaCO_3$ were converted to its CaO equivalent, the calculations would be:

% CaO equivalent = (molecular weight of CaO/ molecular weight of CaCO₃) * 100

= (56/100) * 100 = 56% CaO equivalent(42) To obtain the CaO equivalent of MgCO₃, the calculations are:

% CaO equivalent = (molecular weight of CaO/ molecular weight of MgCO₃) * 100

= (56/84) * 100 = 66.7 % CaO equivalent (43)

A conventional oxide, this form of lime guarantee consist of converting the Ca to CaO, the Mg to MgO, and adding the two. Elemental percentage, of Ca and/or Mg. This method of expressing lime guarantee is determined in a similar way. If pure $CaCO_3$ were to be reported as elemental Ca, the calculations would be:

% Ca = (atomic weight of Ca / molecular weight of CaCO₃) * 100

= (40/100) * 100 = 40% Ca equivalent (44)

2.5.2. CHEMICAL GUARANTEES AND CHEMICAL EQUIVALENCY

(LESLIE et al., 2000) The chemical composition of liming materials also determines their long-term effects on soil pH and how much of each material is needed to achieve these effects. Likewise, it informs the user about the chemical equivalency and nutrient contents of different materials, thereby preventing misinterpretations regarding their comparative chemical values. There are advantage and disadvantage to each of these means of expressing the liming effectiveness. However, it is relatively easy to convert one means of expression to another using the concept of chemical equivalency. In other words, one atom (or molecule) of Ca^{2+} , Mg^{2+} , CaO, MgO, CaCO₃, or MgCO₃ will neutralize the same amount of acidity as another. Consequently, to make comparisons among different liming materials it need merely multiply by the ratios of their molecular masses. For example, to calculate the CaCO₃ equivalent of a pure burned lime (CaO) will need simply multiply by the molecular ratio of CaCO₃ to CaO:

 $CaCO_3 / CaO = 100/56 = 1.786$

(45)

(ARVIDSON, R. S., et al., 2003, GEORG K., et al., 2007) Thus, 1mg (1000 kg) of this pure burned lime will neutralize as much acidity as 1786 kg of a pure limestone. Some adjustment will need to be made, of course, for the percentage purity of the respective liming materials. Using chemical equivalencies it is possible to compare a different means of expressing the liming abilities of four materials a burned lime (oxide) a hydrated lime (hydroxide), and two limestones (one dolomitic, the other calcitic). Each is considered to be 95% pure.

2.6. LIME REQUIREMENTS: QUANTITIES NEEDED

(FULLER, et al., 1999) Lime is any material that: contains calcium (Ca^{2^+}) or magnesium (Mg^{2^+}) and will neutralize soil acidity. For example, calcium carbonate (CaCO₃) is a liming material because it contains Ca^{2^+} and the carbonate portion of the material (CO_3^{-2}) will neutralize soil acidity. Liming materials include limestone, burned lime, slaked lime, marl, oyster shells, slag, cement plant flue dust, mine tailings, sugerbeet sludge, wood ashes, and paper mill lime sludge. Liming materials fall into the following four categories: carbonate, oxides, hydroxides, and byproduct materials.

Carbonates: carbonates are the most widely available and most widely used liming materials. Carbonates are generally less expensive and easier to handle than other lime materials. Ground high grade limestone or calcitic limestone is nearly pure calcium carbonate (CaCO₃). This material is the most commonly used lime source. The major advantage is its relative low cost. Dolomitic limestone, or dolomite (MgCO₃ +CaCO₃), is also a commonly used source. Dolomite usually costs a little more than calcitic limestone and changes the soil pH more slowly, but it has the advantage of containing

 Mg^{2^+} as well as Ca^{2^+} . Together, cacitic limestone and dolomitic limestone account for more than 90% of the lime used in the United States. Both materials are naturally occurring rocks that are mined in the Inland Pacific Northwest and ground for agricultural use. CaCO₃ and dolomite are both mined.

Marl and oyster shells are also carbonate materials. Marl is a naturally occurring mixture of clays, carbonates of Ca^{2^+} and Mg^{2^+} , and shell remnants. Oyster shells are pure calcium carbonate but are important only in some coastal regions. (MARTIN, et al., 1996) and (PRENCIPE, et al., 2004) Factors favoring carbonates over oxides and hydroxides include: (1) ease of handling. (2) Lower cost and (3) the availability of many more sources. Although smaller amounts of hydroxides and oxides are needed for raising soil pH, those two materials generally are used only when the grower requires a rapid pH change.

The amount of liming material required bringing about a desired pH change is determined by several factors, including (1) the change in pH required, (2) the buffer capacity of the soil, (3) the chemical composition of the liming materials to be used, and (4) the fineness of the liming materials. The relationship of buffering to limestone requirements of soil with different textures. Because of greater buffering capacity, the lime requirement for acid fine-texture clay is much higher than that for sand or a loam with the same pH value.

2.6.1. LIMING MATERIALS

(WARREN et al., 1992) More than 90% of the agriculture lime used is $CaCO_3$, some is $CaMg(CO_3)_2$ and a much smaller quantity is CaO or $Ca(OH)_2$. To a chemist, lime is CaO, but to a farmer, agronomists, and a soil scientist, lime means $CaCO_3$ equivalent. The common liming materials are:

- Calcic limestone (CaCO₃), which is ground limestone.
- > Dolomitic limestone (CaMg (CO_3)₂), from ground limestone high in magnesium.
- Quicklime (CaO), which is burned limestone.
- ➤ Hydrated (slaked) lime (Ca (OH)₂), from quicklime that has changed to the hydroxide.
- Marl (CaCO₃), from the bottom of small freshwater ponds in areas where the soils are high in lime. The lime has accumulated by precipitation from drainage waters high in lime.
- > marl contains many shell remains from ancient marine animals.
- Chalk (CaCO₃), from soft limestone deposited long age in oceans.
- Blast furnace slag (CaSiO₃ and Ca₂SiO₄), a by-product of the iron industry. Some slags contain phosphorus and mixture of CaO and Ca(OH)₂. This product is called basic slag and is used primarily for its phosphorus content.

Miscellaneous sources, such as ground oystershell, wood ashes, and byproduct lime resulting from papermills, and water-softening plants.

All the liming materials mentioned have value for supplying Ca^{2^+} or both Ca^{2^+} and Mg^{2^+} , raising the pH, and making Al^{3^+} , Mn^{2^+} , and Fe^{3^+} less toxic. The choice of a particular liming material is determined by the cost in relation to its purity, the ease of handling, and the speed with which the lime reacts in the soil.

2.6.2. MATERIALS AND MANUFACTURE

Naturally occurring minerals which are commonly used to raise soil pH are CaCO₃ (limestone) and (CaMg(CO₃)₂) (dolomite). Magnesite, MgCO₃, is sometimes used with CaCO₃ as a magnesium source in magnesium-deficient acid soils and crushed serpentine (Mg₃Si₂O₅(OH)₄) is also used as a magnesium supplement. Other less-commonly used liming materials are quick or burnt lime, CaO; hydrated or slaked lime, Ca (OH)₂ and magnesia, MgO.

Waste products from manufacturing processes using limestone can be used for neutralizing soil acidity. The production of CaO produces a dust composed of varying proportions of CaCO₃ and CaO, and precipitator dusts from cement manufacture additionally contain about 5% K₂O. Steel production also produces alkaline slags of variable composition (WILLIAM, 1994); an analysis of some New South Wales alkaline waste materials is provided by (SPACCINI R et al, 2001). Experiments in Southern New South Wales indicated that the slag materials are useful provided they are crushed finely. Human wastes can also be effective liming materials; sewage ash from Canberra has been evaluated, principally due to its higher phosphorus content (NIELSEN et al., 1984; WALTER et al., 1985). However, the restricted production and the conditions imposed on its handling have hindered its agricultural use.

(SMIDT E, et al, 2002). The most common liming material is CaCO₃. In eastern Australia it commonly occurs as calcite, which may be metamorphosed to marble. The process of calcite extraction includes quarrying, jaw crushing to 7-15 cm diameter, hammer milling and finally ball milling to fine particle sizes. Stone and particle size fractions are separated by mechanical screens and finally by air centrifugation. This can be contrasted with the situation in Western Australia where limestone sands, of variable purity, are simply excavated and sold unprocessed. Additional detail on liming materials and production technology can be found in (GONZÁLEZ-MUNOZ et al, 2000) and the distribution of limstones Australia is described by (BERNER et al, 1976).
2.6.3. **CALCULATING LIME NEEDS**

(SENESI, et al, 2003 and VAGENAS, et al, 2003) Assuming to provide a recommendation as to how much limestone should be applied for the production of a high-pH-requiring by crop (asparagus) to be grown in a loam soil that is currently quite acid (pH = 5.0). The action exchange capacity (CEC) is about 10 c_{mol}/kg and it should be raise up to the pH to about 6.8. The soil is now at 50% base saturation and will need to be brought to about 90% base saturation to reach the goal of pH = 6.8. By following the next steps, it can be easy to calculate how much of dolomite limestone with a CaCO₃ equivalent of 90 will need to apply to soil to bring about the desired pH changes:

1. The c_{mol} of Ca^{2+}/kg soil needed to bring about the change since the CEC is 10 c_{mol}/kg and we need a 40% change in base saturation (from 50 to 90%) the Ca^{2+} required.

$$10 c_{\rm mol}/kg * 40*100 = 4 c_{\rm mol} Ca^{2+}/kg \text{ soil}$$
(46)

2. Since each Ca^{2+} has two charges 4 c_{mol} can be expressed in grams at Ca^{2+} by multiplying by the molecular mass at Ca^{2+} (40) and then dividing by 2. The Ca^{2+} change and by 100 since we are dealing with a centimol:

 $4 c_{mol} Ca^{2+} * (40/2 * 1/100) g Ca / c_{mol} = 0.8 g Ca$ (47)

3. The amount of CaCO₃ needed to provide the $0.8g \text{ Ca}^{2+}$ by multiplying by the ration of the molecular masses of CaCO₃ and Ca²⁺ 0.

$$.8 \text{ g/kg soil} * 100(\text{CaCO}_3)/40(\text{Ca}^{+2}) = 2 \text{ g CaCO}_3/\text{kg soil}$$
(48)

- 4. To express the 2 g CaCO₃/kg soil in terms of mass needed to change the pH of hectare furrow slice (HFS) it must multiply by: 2.2 * 106 kg/HFS (49)
- 5. Since the $CaCO_3$ equivalency of the used limestone is only 90; some 100 kg would by required to match 90 kg of pure CaCO₃ consequently. The amount at limestone needed would be adjusted upward a factor of 100/90.

4.4 * 100/90 = 4.9 Mg/HFS, or about 2.2 tons per acre-furrow slice. (50)

2.7. KINETICS OF THE CO₂-H₂O-CaCO₃

(KACHANOSKI et al. 1992) showed in the following figure (2)



Gas-liquid Film

Solid-liquid interface

The CO₂-H₂O-CaCO₃ system, with particular attention to the gas-liquid and solidliquid interfaces. The figure (2) describes the three-phase under investigation. The CO₃²⁻ chemical reactions involving the ten solute species within the bulk aqueous phase are very fast, with reaction rates on the order of 10^{-6} to 10^{-9} reciprocal seconds. In contrast, physico-chemical reactions between the gaseous and liquid phases, as well as between the liquid and solid phases, are much slower and are considered rates limiting. For modeling purposes, a thin liquid film between the bulk gaseous and aqueous phases is envisioned, through which exchange of CO₂ occurs by diffusion. A second rate-limiting transport layer, the solid-liquid interface, is envisioned at the immediate surface of the bulk solid phase where surface reactions such as adsorption of Ca²⁺ and CO₃²⁻ occur leading to incorporation of these ions into the crystal lattice (precipitation).

The reverse processes involving desorption of Ca^{2^+} and $CO_3^{2^-}$ occurs during dissolution of the solid phase. Mineral dissolution and precipitation are significantly influenced by the transport of Ca^{2^+} and $CO_3^{2^-}$ toward and away from the mineral surface. This transport occurs in the bulk aqueous phase and is controlled either by chemical diffusion or by a combination of diffusive and hydrodynamic forces. The latter involves the hydrodynamic movement within the liquid phase due to convective forces and the formation bubbling and dissolution of soil gases. In laboratory studies the hydrodynamic forces are due primarily to stirring of the solution with magnetic bars. (EVANGELOU & WHITTIG 1984) found that the kinetic dissolution compares well with a standard titrimetric method for quantitative $CO_3^{2^-}$ determination in calcite-dolomite systems. For purposes of comparison, a number of weathered and partially-weathered Mancos Shale samples were analyzed by the two methods. For the titrimetric determinations, samples were digested for 48 h at room temperature in a known (excess) volume of 0.127 M HCl. The pH of all suspensions was between 1.6 and 2.0 at the end of the digestion period. Excess acid was then titrated to pH 4.2 with 0.226 M NaOH to determine CO_3^{2-} content of samples.

2.8. METHODS OF DETERMINATION OF CARBONATE:

(CHANEY et al. 1982) made a survey of laboratory methods for the determination of the carbonate content of soils. The survey looks at (1) the accuracy obtained, (2) operator skill required, and (3) relative equipment costs, in addition to other variables. The conclusion from this survey is that the pressure calcimeter method (Carbonate-Bombe) is the best method suited for geotechnical engineering applications. There are two simple ways to measure the amount of the released gas: (a) measure the volume of the gas under isoperimetric conditions such as the use of a Scheibler calcimeter, and (b) measure the pressure of the gas under isochors conditions. (WILLIAMS, 1948; MARTIN & REEVE, 1954; and WOODWARD, 1961). (EILER et al. 2002) and (THOMAS-KEPRTA et al. 2000, 2001) drew attention to the differences between these two types of carbonate occurrence in ALH84001. The studies of (MCKAY et al. 1996) focused on carbonates exposed on fracture surfaces. (GOLDEN et al. 2000, 2001) proposed a mildly hydrothermal origin at temperatures of ~150°C, with donation resulting from a change in solution composition due to the precipitation of kinetically favored carbonates, with magnetite forming by siderite decomposition during a brief heating at 470°C.

2.8.1. REACTION OF CALCITE WITH SURFACTANT HCl ACID

(AL-MOHAMMAD et al. 2006) Surfactant-based acids have been extensively used in matrix and acid fracturing treatments in CO_3^{2-} formations. As the acid spends and the pH rises, the surfactant molecules aggregate and form long entangled micelles, which enhance the apparent viscosity of the solution. The high viscosity is required for proper acid diversion, which is needed in horizontal and vertical wells with long target zones. Successful field data were obtained with surfactant-based acid, however the impact of the viscoelastic surfactant used on the reaction of the acid with the rock was not systematically examined before. The reaction between calcite and surfactant-based acids was thoroughly investigated using the rotating disk apparatus. The effects of disk rotational speed, surfactant concentration and temperature on the dissolution rate were determined. All experiments were conducted using 20 wt% HCl and various combinations of corrosion inhibitor and surfactant concentrations. The system pressure was maintained at 1,000 psi and the reaction was allowed to proceed for 20 minutes only. Samples from the reaction vessel were collected at various times and were analyzed for Ca^{2^+} using ICP. The apparent viscosity of surfactant-based acids was

measured as a function of shear rate, temperature, and surfactant concentration using a HTHP Brookfield viscometer. The viscoelastic surfactant significantly reduced the dissolution rate of calcite with HCl. This trend continued as the concentration of the surfactant was increased to 4 wt%. The effect of temperature on the dissolution rate was similar to that of temperature on the apparent viscosity of surfactant solutions where there was a maximum in viscosity at 50-60°C. The dissolution rate was controlled by mass transfer of H^+ to the surface of calcite.

(AL-MOHAMMAD et al. 2006) Carbonate reservoirs are heterogeneous, with large variations in rock permeability. Stimulation fluids will flow through the path of the least resistance where the permeability is high or the damage (skin) is low. Therefore, there is a need for a proper fluid diversion to enhance the outcome of matrix acid treatments. Effective diversion is the key for the success of carbonate matrix stimulation treatments, especially for long horizontal and multi-lateral wells. Conventional stimulation treatments include stages of regular acid with suitable diverters including: foam, gelled and/or in-situ gelled acids. However, several concerns have been expressed regarding the use of polymer-based fluids in matrix acidizing treatments. Hydrochloric acid reacts with carbonate materials very fast creating high conductivity flow paths in the formation (known as wormholes). Since the diversion using surfactant-based acid system is relatively new to the petroleum industry, many studies have been conducted in order to better understand this system and utilize it in various applications. The reaction kinetics of viscoelastic surfactant acid with carbonate rocks has not been studied in detail before.

2.8.2. Reaction of calcite with surfactant H_3PO_4 acid

(EVAGELOS et al. 1996) studied a mechanism based on the adsorption of the phosphoric acid on the external surface of the carbonate solid phase followed by reaction of surface species with phosphoric acid and further transfer of the formed $Ca(H_2PO_4)_2$ in the solid-liquid interface for the dissolution of carbonate particles in a phosphoric acid solution is assumed. The reaction of surface species with phosphoric acid was found to be the rate-determining step. The dissolution rate of carbonate particles is decreased with the increase of the particle size and is affected dramatically by treatment. The dissolution of untreated particles is accompanied by intense breakdown of the particles, and the rate and extent of breakdown depends on the particle size. Adequate pretreatment with steam makes the carbonate particle resistant to breakdown, and the dissolution rate becomes very slow.

2.9. DETERMINATION OF CARBONATES IN SOILS

(CALCIMETER BERNARD METHOD) Percentage of calcium carbonate, CaCO₃ (%), is defined as the total carbonates which is contained in 100 g of dry soil to express total carbonates, (CaCO₃, MgCO₃ etc) as CaCO₃.

Principle: The determination of $CaCO_3$ (%) is based on the volumetric analysis of the carbon dioxide CO_2 , which is liberated during the application of hydrochloric acid solution HCl 4N in soil's carbonates and is described with the following reaction:

 $(CaCO_3 + MgCO_3) + 2 HCl \rightarrow (CaCl_2 + MgCl_2) + H_2O + CO_2 \uparrow$ (51)

During the application of the acid into the soil sample a characteristically foaming is observed, evidence of carbon dioxide's liberation and the existence of carbonate salts consequently.

Reagents: Methylorange indicator: Dissolve 50mg methylorange sodium salt in 100 ml H₂O, which contain 15.2ml of HCL 0.01N solution. Mild heat the solution, and when it gets cold an infiltration follows. Calcimeter Bernard filling solution: Dissolve 200 g CaCl₂ .6H₂O in 100 ml distilled water, add 3 drops methylorange indicator and some drops of non-concentrated solution of hydrochloric acid till the solution becomes red-orange. Solution of HCL 4N: Dilute 340ml concentrated HCL with distilled water up to 1000 ml. Instrument: Calcimeter Bernard

Procedure:

- 1. Weigh 2.00 g of prepared soil sample and transfers it into the Bernard apparatus conical flask. Afterwards fill the glass of the apparatus till the ³/₄ of its height with HCL 4N solution and place it into the conical flask attentively. Pay attention, that the tubule stays upright with the acid (Solution of HCL 4N) inside. Cap the conical flask with its particular plug and then zero the level of the filling solution. With the left hand bring the pear shaped glass container next to the graduated column for the fluids both in the pear shaped container and in the graduated tube stand in the same level.
- 2. With the right hand, shake gently the conical flask, so, the HCL 4N solution comes in contact with the prepared soil sample. Then CO₂ liberated. The filling solution of graduated column descends due to the pressure of liberated CO₂. At the same time, we lower the pear shaped container for its fluid level to remain in the same level with the fluid of the column. This way the hydrostatic pressure equalizes.
- 3. When the liberation of the CO_2 is finished, stop the agitation and note the column's reading. In case the carbonate content is too high and the liberated gas displaces all the fluid from the graduated column repeat the process, decreasing the quantity of

the prepared soil sample into 1.00 gr. Although in this case the same happens, repeat the process with 0.50 g of prepared sample.

Calibration: The determination of the correction factor f of the instrument is as follow: Weigh about 0.10 g CaCO₃, which has been dried at 104 °C, transfer it into the Bernard apparatus conical flask and follow the same process as described above

$$V^*WfT^*22.1$$
 (52)

Where: V = ml produced CO₂, W = g weighted CaCO₃, T = temperature of measurement, in k.

2.9.1. DEFINITION OF CALCAREOUS SOILS

A calcareous soil is a soil that has free calcium carbonate (CaCO₃) in the profile, i.e. contains enough CaCO₃ so that it effervesces when treated with hydrochloric acid. When free carbonates are present, the acid will produce bubbling due to the evolving of CO₂ gas (LOEPPERT & SUAREZ, 1996):

 $CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O$ (53)

Calcareous soils cover more than 30% of the earth surface, and their CaCO₃ content varies from a few percent to 95% (MARSCHNER, 1995). (HAGIN & TUCKER 1982) define calcareous soil as a soil that its extractable Ca and Mg levels exceed the cation exchange capacity.

3. MATERIALS AND METHODS

3.1. MATERIALS

3.1.1. SOIL SAMPLES

The Hungarian soil samples were taken from the genetic horizons at different soil samples. Soil particles were fractionated into the next size fractions (BUZÁS, 1993)

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. The soil samples are:

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 the soil sample 15- Nagyhörcsök (0-32 cm), (32-60 cm), (60-104 cm) and (104-140 cm). 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. The pseudo-first-order kinetic equation (2 term + Q constant) was fitted to the data.

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 CO₂ released was measured in a Scheibter's calcimeter (BUZÁS et al. 1993). Pure calcite and dolomite were powered and

their carbonate content was also determined. The CO_2 development was read 27 times between 0-60 minutes.

	Soil comple	V	^H _U	ъH	CaCO ₃	Humus	AL-P ₂ O ₂	AL-K ₂ O
	Son sample	ΓA	$P H_2O$	P _{KCL}	%	%	mg/kg	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

Table (2): the general characterization of soil samples

Picture (4): the Hungarian map and show that the soil samples on the map.



3.1.2. REAGENTS:

Hydrochloric acid (HCl) was used at 10% ^w/_w concentration.

3.1.3. APPERATRES

The experiments were carried out to determine the dissolved carbonates in the soil samples using Scheibter's calcimeter. The apparatus designed for kinetic dissolution of carbonate as shown in (Fig.3)



Fig. (3) Schematic of Scheiber's calcimeter system for kinetic dissolution analysis of carbonate in soil samples.

As shown in the above mentioned schematic (Fig. 3):

- 1- U-shaped connecting tube, one of its arm is a calibrated with "cm³" degree (monometer).
- 2- Closed glass tube with a cubic capacity of 200 cm³, which is connected, to the upper part of the calibrated tube (1).
- 3- Top with three bore-holes.
- 4- Reaction plate.
- 5- Reaction vessel, in which the examined material will, placed inside.
- 6- Small tubes for holding the acid.
- 7- Graduated bottle, which collects the excess the liquid from U-shaped tube.

3.1.4. MECHANICAL ANALYSIS

The determination of soil texture is called particle size analysis or mechanical analysis. Determining the texture in the laboratory uses a basic principle of sedimentation called "Stokes Law". Stokes Law states that the speed or velocity with which particles settle out of a liquid medium is dependent on a constant factor (k) and the radius of the particles. Or, the bigger the particle, the faster it will fall out of suspension. k is composed of the factors:

 $V = kr^{2}, \qquad \text{and} \qquad k = 2g (d_{1}-d_{2}) \div \mu$ (54) Where: g =acceleration of gravity, d₁ =density of particle, d₂ =density of liquid

 μ =viscosity of liquid, v =velocity



Picture (5): Sieve analysis



Picture (6)Hydrometer analysis

(YOUNGBERG 1957) This procedure is used to determine the distribution of particle sizes in soils. The distribution of particle sizes larger than the No. 200 sieve {(shown in picture (5)} is determined by sieving and the distribution of particle sizes smaller than the No. 200 sieve is determined by a sedimentation process. A sample of soil, water, and a dispersing agent is thoroughly mixed and washed into a 1000 ml glass cylinder. The mixture is then left undisturbed for the settlement period. With a high concentration of soil particles in suspension, the mixture of water and soil will exhibit a high specific gravity. As soil particles begin to settle, the specific gravity of the mixture will gradually approach the specific gravity of water. The specific gravity is measured at fixed intervals with a hydrometer. The size and quantity of the various particles in a soil have a distinct influence on its behavior. Soils containing relatively high percentages of clay size particles may be expected to exhibit greater plasticity and volume change characteristics than soils containing predominantly sand and silt sizes.

The results obtained by this procedure are essential for the classification of the soil and the determination of the quantity of sand, silt, and clay size particles of which the soil is composed.

Materials and Equipment:

Test procedure: This procedure contains deviations. It is a short cut procedure designed to obtain approximate data. If more accurate data is required or if failure of material occurs, the material shall be tested again, this time in strict conformance.

- The sample used for this test procedure has been prepared in conformance it will be received in a pint jar with the necessary identification forms, and Remove the jar cover and place the material passing the No. 10 sieve in an oven maintained at a temperature not exceeding 25°C for 12 hr. At the end of the drying period, weigh a representative sample of approximately 50 g to the nearest 0.01 g. The drying period may be eliminated by weighing a representative sample of approximately 50 g and at the same time take a 20 g sample for hygroscopic moisture determination. The weight of the sample is later adjusted for the percent of hygroscopic moisture and the adjusted weight used in the calculations as the weight of the tested sample, as shown in Steps 1 and 2 of the calculations.
- Pour this sample into an evaporating dish, add 125ml of the stock solution of Calgon, mix thoroughly, and let soaks for not less than 12hours. A stock solution of Calgon is prepared by dissolving 45.7g of sodium hexameter phosphate (Calgon) in 1000ml of water. At the end of the soaking period, pour the contents of the evaporating dish into the baffle-rods type dispersion cup making certain that all the soil is transferred from the dish into the dispersion cup by carefully washing it with additional water. Fill the cup 3/4 full, place it in the stirrer, and mix for one minute.
- After dispersion, transfer the soil and water into the 1000 ml cylinder. Make certain that all material has been transferred from the dispersion cup into the cylinder by carefully washing with the aid of a wash bottle. Add water to the cylinder and bring the level of water to the 1000 ml mark on the cylinder. Using the palm of the hand or a rubber stopper, cover the open end of the cylinder, turn the cylinder upside down and back again approximately once each second for a period of one minute. After the one minute shaking, place the cylinder in the controlled temperature water bath and immediately start the timer.
- Without removing the cylinder from the bath at the end of 30 minutes, very carefully insert the soil hydrometer {(shown in picture (6)} into the cylinder. As soon as it has stabilized, read the hydrometer at the top of the meniscus to the nearest 0.5 division and record. Remove the hydrometer and place it in clean water. Introduce a

thermometer into the cylinder; read and record the temperature of the liquid. Repeat Steps 9 and 10 at the end of 60 minutes. After the 60 minute hydrometer and temperature readings, remove the cylinder from the water bath and pour the contents over a No. 200 sieve. Rinse the cylinder with water over the No. 200 sieve to make sure that all the material has been removed from the cylinder. Wash the material retained on the No. 200 sieve thoroughly until the wash water is clear.

Transfer all materials retained on the No. 200 sieve to an evaporating dish and dry to a constant weight in an oven maintained. Assemble a set of 3 in. diameter sieves containing the No. 40, No. 200 and the bottom pan, and pour the oven dry sample into the nested sieves. Place the assembly in the sieve shaker for 7 to 10 minutes. Additional sieves may be used when required. Weigh the material retained on each sieve to the nearest 0.01 g and record.

Calculations:

- Calculate the percent of hygroscopic moisture: Percent hygroscopic = (Wa - Ws)/ Ws x 100 (55) Where: Wa = weight of air dried hygroscopic sample (approximately 20 g), And Ws = weight of oven dried hygroscopic sample.
- Calculate the oven dry weight of test sample: Ws = Wa x 100 / (percent hygroscopic + 100) (56) Where: WA = weight of air dried test sample (approximately 50 g), Ws = weight of oven dried test sample.
- 3- Obtain the weight of material passing each sieve (Wp), by subtracting successively from the total weight of test sample (Ws) the weight retained on each sieve (WI).
- 4. Calculate the percent passing each sieve (Pp) by the following formula: Pp = (Wp / Ws) x 100 (57) Where: Pp = percent passing sieve, Wp = weight of material passing sieve, and Ws = total weight of test sample.
- 5- Calculate the percent total sample passing each sieve by the following formula: S Percent total sample passing = Pp x (S / 100) (58)
 Where: Pp = percent passing sieve, and S = percent total sample passing the No. 10 sieve.
- 6. Calculate the amount of coarse sand in the soil mortar by the following formula: Coarse sand = 100 - Pp 40 (59) Where: Pp40 = percent passing the No. 40 sieve.
- Calculate the amount of fine sand in the soil mortar by the following formula:
 Fine sand = Pp40 Pp 200 (60)

Where: Pp40 = as calculated in Step 6, and Pp200 = percent passing the No. 200 sieve.

- 8. Calculate the amount of clay and colloids in the soil mortar by the following formula: Clay and colloids = {(H + C) / Ws} x 100 (61)
 Where: H = hydrometer reading after 60 minutes, C = correction factor obtained from chart for corresponding temperature of liquid of the 60 minute readings, and Ws = total weight of test sample from Step 2 of procedure.
- 9. Calculate the amount of silt in the soil mortar by the following formula:
 Silt = 100 percent (percent coarse sand + percent fine sand + percent clay and colloids).
 (62)

Than Report the percent passing each sieve to the nearest whole number and the percentages of coarse sand, fine sand, silt and clay, and colloids in the soil mortar to the nearest whole number.

3.2. Methods

3.2.1 DETERMINATION OF DISSOLVED CARBONATE IN TERM OF CARBONATES USING SCHREIBER'S CALCIMETER.

The apparatus was standardized by analysis of known quantity of carbonate under the prescribed standard condition. Calcimeter apparatus was set-up by balancing the air gas inside, and the level of the liquid in both arms of U-shapes tube (water monometer) was upstanded and adjusted to zero. Soil sample (0.5-1.0 g) was added in the reaction vessel. Hydrochloric acid with concentration 10% $^{\rm w}$ /_w was filled in the small glass tube suspended in reaction vessel and the reaction vessel than tightly closed by rubber stopper. Keeping in mind that the valve of three-hole is kept in open position, and after checking the zero reading of U-shaped arms, the mechanical shaker is set in motion by converting the reaction vessel up-side-down, the acid reach the soil sample and the reaction immediately start. Carbon dioxide evolved from the reaction and pass through out the glass tube to the U-shaped tube, the level of liquid in U-shaped tube will flow down, as far the reaction is going on, the amount (volume) of CO₂ increased. By using plate shaker down the reaction vessel on mechanical shaking, the reaction was gone. At the end of the reaction the liquid in the U-shaped tube is stabilized and no more CO_2 was evolved. CO₂ volumes were measured at 0.0, 0.25, 0.50, 0.75, 1.00, 1.25, 1.50, 1.75, 2.00, 3.00, 4.00, 5.00, 6.00, 7.00, 8.00, 9.00, 10.0, 15.0, 20.0, 25.0, 30.0, 35.0, 40.0, 45.0, 50.0, 55.0 and 60.0 minutes as a reaction interval. Some samples the time until 120.0 minutes. The total carbonate expressed in terms of CaCO₃ %, calculated using the following formula;

 $CaCO_3 = M^*A^{100/G}$

Where: M = the growth of carbon dioxide "cm³" numbers. $A = CaCO_3$ quantity according to 1 cm³ carbon dioxide, at the observable temperature and airspace. G = the weight of the material. And the first order kinetic equation is fit to the measured data:

 $Y = Q + A_1 (1-e^{-k_1 t}) + A_2 (1-e^{-k_2 t})$ (64) Where: Y = is the amount of carbonate developed, % Q = is the amount of carbonate developed very faster, in the first 20 second, %. A₁ and A₂ = are the maximum amount of carbonate developed faster and slower respectively, %. k₁ and k₂ = 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.

(63)

4. **RESULTS AND DISCUSSION.**

Computer analysis was used to separate the very fast, fast and slow carbonate dissolution reactions in the genetic horizons of a Keszthely and Nagyhörcsök chernozem soil. In the genetic horizons of the soil the manometric and another thirteen soil samples (Agyagosszergény, Mosonmagyaróvár, Nagyszentjános, Orosháza, Mezőhegyes, Új-Szeged, Szeged-Öthalom, Iregszemcse, Kecskemét, Nagyhörcsök, Őrbottyán, Csávoly, and Ozsákpuszta) data were analyzed in the coarse sand and clay fractions. The fitted first order kinetic equations very well described the parallel reactions. At the same time calcite (Bakonycsernye 20 – calcite, 99%) C) and dolomite (Tinnye Zajnat-triászdolomit, 100%) were used to demonstrate the fast and slow dissolution reactions, respectively. (LOEPPERT & SUAREZ, 1996) found that the calcareous soil is a soil that has free CaCO₃ in the profile, contains enough CaCO₃ so that it effervesces when treated with hydrochloric acid. When free carbonates are present, the acid will produce bubbling due to the evolving of CO₂ gas. During the course of investigations of natural sources of dissolved minerals soil samples, the following results are obtained.

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

Table (3). Kinetic parameters of carbonate dissolution of Calcite and Dolomite

Table (3) and Figures (3 and 4) 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 ($k_1 = 14.4$) and the half-life-time is ($1t_{1/2}$ (min) = 0.05) minute. It is really fast one. In the case of dolomite the slow reaction with ($k_2 = 0.24$) and with a half-life-time ($2t_{1/2}$ (min) = 2.4) minute, not so slow. Carbonate content in the soil sample analyzed is used as differentiation criterion for classes at the family level of soil taxonomy. The calculated values of carbonate equivalent from the analysis of CO₂ evolved using the calcimeter method will theoretically overestimate the weight percent of carbonate in soil samples. Twenty seven reaction time intervals were used in the measurement of CO₂ evolution. Consequently, significant reactions with soil samples constituents take place. The used method is based on differential pseudo-first-order kinetic rate of dissolution of soil samples when reacted with excess of 10% ^w/_w HCl. Hydrochloric acid as strong acid as well as the nonselective reagent was used to attack soil constituents to liberate the carbonate in the form of CO₂. This happened in the

reaction vessel. The carbon dioxide which released from the soil sample was measured in the water monometer (one arm of U-shaped tube).



Figure (3).Carbonate dissolution kinetics of Dolomite

Figure (4). Carbonate dissolution kinetics. of Calcite

4.1. The genetic horizons of Keszthely and Nagyhörcsök soil samples

4.1.1. The genetic horizons of Keszthely

(HAMID, Y. S. & FULEKY, GY 2008). During soil development the fast dissolution process disappeared from the coarse sand fraction of the upper horizon, but this process significantly increased in the accumulation horizon both in the coarse sand and clay fractions of the Keszthely soil. Considering the rate constant values, the real slow process could be characterized with ($k_2 = 0.08$), the real fast process with ($k_1 > 1.0$). The upper soil horizon (0-25 cm) shows a distinguished property, e.g., in the coarse sand fraction there is no fast reaction ($k_1 = 0.0796$), only 1% very fast one. The genetic horizons of the Keszthely soil profile (Table 4 and Figures 5 to 12) show that the first two upper horizons (0-25 and 25-45 cm), the clay fraction contains faster carbonate dissolution reactions than the coarse sand fraction contains slower carbonate dissolution reactions than the coarse sand fraction.

The results demonstrated that the fast process in the clay fraction in the upper horizon (0–25 cm) is slow ($k_1 = 0.82$) and contained a small amount of carbonate (2.4). While in the B horizon (25–45 cm), the carbonate accumulation was at maximum mainly in the coarse sand fraction. Carbonate content of soil profile formed on Keszthely loess 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 %), and 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.

4.1.2. The genetic horizons of Nagyhörcsök

(Table 5 and Figures 13 to 20) show that, In the Nagyhörcsök soil the leaching removed mainly the well soluble calcite-like carbonates from the upper horizon. Considering downward the genetic horizons of the Nagyhörcsök soil profile (Table 5 and Figures 13 to 20), show the rate constant of the faster dissolution process increases and the half-life-time decreases. Comparing the rate constant values of the faster processes in the upper horizon (0-32 cm) 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 not so fast ($k_1 = 0.50$ and $k_1 = 0.43$). This relates to dolomite-like carbonate dissolution. The same fact can be concluded also from the half-life-time of these processes ($1t^{1/2}$ min = 1.4 and 1.6). The low carbonate content of the upper horizon (3.6) %) and its low carbonate content in the clay fraction are the result of a leaching process. All these facts prove that the leaching removed mainly the well soluble calcite-like carbonates from the upper horizon. At the same time the dolomite-like carbonates remained mainly in this horizon. Carbonate content of soil profile formed on loess on Nagyhörcsök was determined is 4 genetically levels. Layer (0-32 cm) contained carbonate of (6.0%). Fast processes were dominated in fraction coarse sand and clay in layer (32–60 cm) (20.9 % carbonate). Slow process appeared in every genetically layer and in both of the fractions, but missed in the upper 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. The faster reactions $(Q + A_1)$ in all horizons and fractions exceed the rate of slow reaction. However the fast reaction in the upper horizon is not as fast as in the deeper horizons (Figures 13 to 20).

(HAMID Y. S. et al. 2006 & 2008b). In all the genetic horizons of Keszthely and Nagyhörcsök soil samples, the slow process practically the same in the coarse sand and clay fractions (4–5% and 1–2%, respectively). 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 processes 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 show largest value in B horizon (32–60 cm) (accumulation horizon). These results are agreements with (GILE et al. 1981) have also shown the all precipitation was assumed to enter the surface horizon. Only saturated flow through the soil profile was considered. If precipitation exceeded the water-holding capacity (WHC) of the first horizon, water moved into the second horizon. This procedure continued with deeper horizons until the soil absorbed all the precipitation or the bottom horizon was reached. Water flux past the soil profile base treated as leachate and was assumed lost from the system.

depth/fraction	g/100g	1/min	g/100g	1/min	g/100g	min	min	g/100g	%	%	%	%
0-25 cm	A_1	\mathbf{k}_1	A ₂	k ₂	Q	$^{1} t_{1/2}$	² t _{1/2}	A ₁ +A ₂ +Q	A ₁	Q	A ₁ +Q	A ₂
original soil	2.5189	0.1740	0.4185	0.0128	1.4289	3.9836	54.1521	4.3662	57.6898	32.7252	90.4150	9.5850
coarse sand	8.7226	0.0796	0.0000	0.0019	1.5718	8.7079	0.0000	10.2944	84.7314	15.2686	100.0000	0.0000
clay	4.0564	0.8283	2.0107	0.0824	1.7111	0.8368	8.4120	7.7782	52.1513	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	6.7050	59.1058	65.8108	34.1892
coarse sand	8.0123	1.2154	7.8143	0.0913	0.0000	0.5703	7.5920	15.8266	50.6257	0.0000	50.6257	49.3743
clay	13.9946	2.1369	2.7699	0.2436	2.4115	0.3244	2.8454	19.1759	72.9800	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	20.5904	57.3139	77.9042	22.0958
coarse sand	31.0025	4.8565	9.1795	0.2692	3.0584	0.1427	2.5748	43.2405	71.6980	7.0731	78.7711	21.2289
clay	23.8247	1.7687	3.2117	0.2055	15.3453	0.3919	3.3730	42.3818	56.2146	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	18.3413	39.3333	57.6746	42.3254
coarse sand	19.7756	5.8659	7.1732	0.2773	15.3371	0.1182	2.4996	42.2859	46.7665	36.2700	83.0365	16.9635
clay	28.8265	1.5256	2.8271	0.0940	2.8283	0.4543	7.3739	34.4820	83.5988	8.2023	91.8011	8.1989

Table (4) Kinetic parameters of carbonate dissolution of Keszthely Particle size distribution



Figure (5). Carbonate dissolution kinetics of coarse sand fractions in the Keszthely soil in the depth 0-25 cm

Clay 0-25 cm



Figure (6). Carbonate dissolution kinetics of clay fractions in the Keszthely soil in the depth 0-25 cm



Figure (7). Carbonate dissolution kinetics of coarse sand fractions in the Keszthely soil in the depth 25-45 cm



Clay 25-45 cm

Figure (8). Carbonate dissolution kinetics of clay fractions in the Keszthely soil in the depth 25-45 cm



Figure (9). Carbonate dissolution kinetics of Coarse sand fractions in the Keszthely soil in the depth 45-64 cm



Figure (10). Carbonate dissolution kinetics of clay fractions in the Keszthely soil in the depth 45-64 cm



Figure (11). Carbonate dissolution kinetics of Coarse sand fractions in the Keszthely soil in the depth 64-115 cm

Clay 64-115 cm



Figure (12). Carbonate dissolution kinetics of clay fractions in the Keszthely soil in the depth 64-115 cm

depth/fraction	g/100g	1/min	g/100g	1/min	g/100g	min	min	g/100g	%	%	%	%		
0-32 cm	A_1	\mathbf{k}_1	A ₂	\mathbf{k}_2	Q	$^{1} t_{1/2}$	² t _{1/2}	A ₁ +A ₂ +Q	A ₁	Q	A ₁ +Q	A ₂		
original soil	2.4120	0.2784	2.1480	0.0691	1.4486	2.4898	10.0311	6.0085	40.1429	24.1085	64.2514	35.7486		
coarse sand	18.3809	0.5025	5.4607	0.1029	5.4482	1.3794	6.7361	29.2898	62.7551	18.6010	81.3562	18.6438		
Clay	6.6653	0.4283	0.0000	0.0069	3.0646	1.6184	100.4561	9.7299	68.5032	31.4968	100.0000	0.0000		
32-60 cm	32-60 cm													
original soil	3.3343	0.6573	5.8435	0.0836	11.7371	1.0545	8.2912	20.9149	15.9423	56.1183	72.0606	27.9394		
coarse sand	20.3292	0.8063	3.7934	0.1617	1.9145	0.8597	4.2866	26.0371	78.0779	7.3529	85.4308	14.5692		
Clay	15.3577	0.8983	4.4868	0.0493	10.0953	0.7716	14.0598	29.9398	51.2952	33.7188	85.0139	14.9861		
60-104 cm							•							
original soil	21.5851	4.8462	10.0881	0.1169	0.0000	0.1430	5.9294	31.6732	68.1493	0.0000	68.1493	31.8507		
coarse sand	16.3862	1.3324	11.8942	0.1385	5.3505	0.5202	5.0047	33.6310	48.7236	15.9095	64.6331	35.3669		
Clay	17.9158	0.9771	3.4647	0.1519	17.2339	0.7094	4.5632	38.6144	46.3966	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	7.9031	57.4089	65.3119	34.6881		
coarse sand	14.0353	1.5909	17.4296	0.1932	10.3597	0.4357	3.5877	41.8246	33.5576	24.7693	58.3269	41.6731		
Clay	12.0389	1.6109	11.4093	0.3955	14.0659	0.4303	1.7526	37.5140	32.0916	37.4950	69.5867	30.4133		

Table (5) Kinetic parameters of carbonate dissolution of Nagyhörcsök Particle size distribution



Figure (13). Carbonate dissolution kinetics of Coarse sand fractions in the Nagyhörcsök soil in the depth 0-32 cm



Figure (14). Carbonate dissolution kinetics of clay fractions in the Nagyhörcsök soil in the depth 0-32 cm



Figure (15). Carbonate dissolution kinetics of Coarse sand fractions in the Nagyhörcsök soil in the depth 32-60 cm



Figure (16). Carbonate dissolution kinetics of Clay fractions in the Nagyhörcsök soil in the depth 32-60 cm



Figure (17). Carbonate dissolution kinetics of Coarse sand fractions in the Nagyhörcsök soil in the depth 60-104 cm



Figure (18). Carbonate dissolution kinetics of Clay fractions in the Nagyhörcsök soil in the depth 60-104 cm



Figure (19). Carbonate dissolution kinetics of Coarse sand fractions in the Nagyhörcsök soil in the depth 104-140 cm



Figure (20). Carbonate dissolution kinetics of Clay fractions in the Nagyhörcsök soil in the depth 104-140 cm

The results are compatible with (KAMHI 1963, & JENNY 1980) Mentions that the depth of CaCO₃ horizons is strongly dependent on soil water flow and increases with increasing mean annual precipitation through the effects on transpiration, temperature in the soil. And also with (LOEPPERT & SUAREZ, 1996) Particle size distribution, surface area and reactivity are important properties of soil CO_3^{2-} which influence soil pedogenic, chemical and rhizosphere processes, and with (HAMILTON, et al 2001). introduced the lime CaCO₃ is used on acid soils to correct acidity and supply calcium. The effectiveness of lime is therefore very dependent on its particle size. Lime that is coarser than 250 microns (0.25mm) has little value in raising soil pH, at least in the short term. (SHERMAN et al. 1962), (GAIKAWAD & HOLE 1965), (GILE, 1965) described the dissolution and precipitation chemistry of soil carbonates is intimately involved. The deposition of calcium and magnesium carbonates occurs differentially in the upper and lower soil horizons in various sizes and shapes of particles. (EVAGELOS et al., 1996) and (HAMID, Y. S., & FULEKY GY. 2008). described The dissolution rate of CaCO₃ particles is decreased with the increase of the partical size and is affected dramatically by treatment. The dissolution of untreated is accompanied by intense breakdown of the partical, and the rate of extent of breakdown depends on the partical size. Adequate pretreatment with steam makes the CaCO₃ partical resistant to breakdown, and the

dissolution rate becomes very slow. The time dependent diffusion reaction equations are solved for free drift dissolution by a finite difference scheme, to obtain the dissolution rate of calcite as a function of the average calcium concentration in the water film. Dissolution rates are obtained for high under saturation

4.2. The Carbonate dissolution kinetics of coarse sand and clay fractions in soil samples.

(Tables 6 and 7) and (Figures 21 to 46) show that the kinetic parameters of carbonate dissolution. The used equations (63 and 64) 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 (A₁ = 0.2 and A₁ = 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 (k₁ = 0.9978 and k₁ = 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 (A₁ + Q) were interconnected the Ca²⁺ content of solution,

the slow processes were interconnected the Mg^{2+} content of solution. This is further evidence that calcite dissolution expected during fast processes and dolomite like carbonates dissolution expected during slow processes. (MORSE & ARVIDSON 2002) pointed out, "there is no general equation that can be applied to all calcites and simply correlate surface area with solution composition." Moreover, little is known about the influences of temperature on calcite dissolution kinetics in the surface-reactioncontrolled near-equilibrium region that commonly exists in natural systems. (GEHLEN et al., 2007) states that the first order calcite dissolution kinetics proved to be more consistent with the interpretation of in-situ pore water pH measurements. (WANG TIANGUI & LI ZUOHU 2005) found that the concentration of calcium ions in solution does not affect the dissolution of CaCO₃, but increase of carbon dioxide partial pressure retards the dissolution of CaCO₃, and the observed dissolution fluxes are predicted by the model when k=5 to 100%/d and n=4.5. This range of k values has important implications regarding the type of carbonate dissolving and its location within the sediment column. At low values of k, organic carbon rain rates to the seafloor become the dominant driving force of carbonate dissolution. At higher values of k, the degree of bottom water under saturation becomes more important. Dissolution of carbonate within equatorial Pacific sediments can be adequately described with $k=20\pm10\%/d$, a rate constant much lower than some previously used values.

(MORSE & ARVIDSON 2002) summarized some important findings. that in the case of extreme undersaturation the diffusion-controlled dissolution kinetics is prevailing. As equilibrium is approached, there is a region of transition toward surface-controlled dissolution kinetics, and a changing surface-reaction-controlled region exists until equilibrium is reached. However, the reaction mechanisms could not be clearly determined because of the complexity of the carbonic acid system.

~9)	ugosszor	gony											
depth/fraction	g/100g	1/min	g/100g	1/min	g/100g	min	min	g/100g	%	%	%	%	
0-20 cm	A_1	\mathbf{k}_1	A_2	k ₂	Q	$^{1} t_{1/2}$	$^{2} t_{1/2}$	$A_1 + A_2 + Q$	A_1	Q	$A_1 + Q$	A ₂	
original soil	1.4706	2.0575	0.7553	0.1187	0.0000	0.3369	5.8395	2.2259	66.0665	0.0000	66.0665	33.9335	
coarse sand	0.2006	0.9978	0.1989	0.1834	0.0028	0.6947	3.7794	0.4023	49.8547	0.7057	50.5604	49.4396	
clay	5.0614	1.0028	4.0663	0.0128	0.8963	0.6912	54.1521	10.0240	50.4931	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	22.0715	35.6303	57.7018	42.2982	
coarse sand	18.5338	1.0730	5.7164	0.1692	0.0000	0.6460	4.0966	24.2502	76.4274	0.0000	76.4274	23.5726	
clay	24.7197	1.2455	12.3882	0.1801	0.0000	0.5565	3.8487	37.1079	66.6157	0.0000	66.6157	33.3843	
Nag	yszentján	os											
original soil	3.1652	0.7600	1.6820	0.0954	2.6137	0.9120	7.2657	7.4609	42.4232	35.0322	77.4555	22.5445	
coarse sand	2.0511	1.0241	1.7622	0.1247	0.0000	0.6768	5.5585	3.8133	53.7882	0.0000	53.7882	46.2118	
clay	11.8502	1.6811	2.8358	0.2274	0.0000	0.4123	3.0481	14.6860	80.6902	0.0000	80.6902	19.3098	
Oro	sháza	-											
original soil	1.4451	2.4300	0.5483	0.1691	0.0663	0.2852	4.0990	2.0596	70.1614	3.2190	73.3804	26.6196	
coarse sand	0.9005	0.8845	0.2744	0.1879	0.0000	0.7837	3.6889	1.1748	76.6453	0.0000	76.6453	23.3547	
clay	3.0147	1.5883	2.0503	0.1802	0.0000	0.4364	3.8465	5.0649	59.5206	0.0000	59.5206	40.4794	
Mez	őhegyes												
original soil	2.5843	1.0886	2.6089	0.1368	0.8033	0.6367	5.0669	5.9965	43.0974	13.3957	56.4932	43.5068	
coarse sand	22.4974	1.7593	2.4481	0.0936	0.0000	0.3940	7.4054	24.9455	90.1864	0.0000	90.1864	9.8136	
clay	3.5573	2.0367	2.0314	0.2196	0.1179	0.3403	3.1564	5.7066	62.3365	2.0661	64.4026	35.5974	
Új-S	zeged	1	I	I	I	I	I	1			1	1	
original soil	2.4048	2.1628	0.8054	0.0940	0.0000	0.3205	7.3739	3.2102	74.9103	0.0000	74.9103	25.0897	
coarse sand	6.2199	1.5327	0.0000	0.0162	0.0000	0.4522	42.7869	6.2199	100.0000	0.0000	100.0000	0.0000	
clay	2.8781	1.7713	0.0000	0.3852	0.0000	0.3913	1.7994	2.8781	100.0000	0.0000	100.0000	0.0000	
Sze	ged-Öthal	om	n	1	n	1	1				T	-	
original soil	4.0997	1.9952	2.1082	0.0940	0.2467	0.3474	7.3739	6.4546	63.5162	3.8215	67.3376	32.6624	
coarse sand	9.3426	0.9271	0.0000	0.0000	0.8270	0.7477	-	10.1696	91.8681	8.1319	100.0000	0.0000	
clay	11.4173	0.7016	0.0000	0.0323	0.0000	0.9880	21.4597	11.4173	100.0000	0.0000	100.0000	0.0000	
Ireg	szemcse	1	n	1	n	1	1						
original soil	7.3892	0.1765	2.6281	0.0002	1.8647	3.9272	-	11.8821	62.1883	15.6936	77.8819	22.1181	
coarse sand	32.1834	0.7965	1.2219	0.0823	0.0000	0.8702	8.4222	33.4053	96.3421	0.0000	96.3421	3.6579	
clay	9.4302	0.4711	0.1129	0.0063	0.0000	1.4713	110.0234	9.5430	98.8170	0.0000	98.8170	1.1830	

 Table (6) Kinetic parameters of carbonate 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	\mathbf{k}_1	A ₂	k ₂	Q	$^{1} t_{1/2}$	² t _{1/2}	A ₁ +A ₂ +Q	A ₁	Q	A ₁ +Q	A ₂	
original soil	0.5468	1.9604	0.0000	0.0062	0.2597	0.3536	111.7979	0.8064	67.7987	32.2013	100.0000	0.0000	
coarse sand	4.9504	1.3742	5.5361	0.3044	0.6187	0.5044	2.2771	11.1052	44.5773	5.5716	50.1489	49.8511	
clay	4.5865	1.8651	0.0000	0.0003	0.0000	0.3716	-	4.5865	100.0000	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	44.7581	11.1326	55.8907	44.1093	
coarse sand	1.1085	1.7125	1.0326	0.1607	0.2265	0.4048	4.3133	2.3676	46.8223	9.5648	56.3871	43.6129	
clay	8.9477	2.0510	0.0000	0.0158	0.0000	0.3380	43.8701	8.9477	100.0000	0.0000	100.0000	0.0000	
Csá	voly												
original soil	1.6333	1.6198	2.0129	0.1030	0.2465	0.4279	6.7296	3.8926	41.9580	6.3323	48.2904	51.7096	
coarse sand	4.0913	0.5441	0.8086	0.1277	0.0000	1.2739	5.4279	4.8999	83.4975	0.0000	83.4975	16.5025	
clay	3.5436	3.0570	1.5217	0.6884	0.0000	0.2267	1.0069	5.0653	69.9581	0.0000	69.9581	30.0419	
Ozs	ákpuszta												
original soil	6.0890	1.4421	8.6733	0.2465	0.3649	0.4807	2.8124	15.1272	40.2519	2.4122	42.6641	57.3359	
coarse sand	11.9900	1.6767	8.6453	0.3141	0.0000	0.4134	2.2067	20.6353	58.1045	0.0000	58.1045	41.8955	
clay	7.3493	0.7676	0.0992	0.0141	0.0000	0.9030	49.1594	7.4485	98.6682	0.0000	98.6682	1.3318	
Kec	skemét	•								•	•		
original soil	6.5003	2.5612	5.7982	0.1536	1.0606	0.2706	4.5127	13.3592	48.6580	7.9392	56.5973	43.4027	
coarse sand	5.7673	5.1076	2.5643	0.1332	0.0000	0.1357	5.2038	8.3316	69.2223	0.0000	69.2223	30.7777	
clay	17.3625	1.2876	0.0000	0.0032	0.0000	0.5383	216.6085	17.3625	100.0000	0.0000	100.0000	0.0000	

Table (7) Kinetic parameters of carbonate dissolution in different soil samples Particle size distribution. Nagyhörcsök



Agyagosszergény coarse sand

Figure (21). Carbonate dissolution kinetics of Coarse sand fractions in the Agyagosszergény soil



Figure (22). Carbonate dissolution kinetics of Clay fractions in the Agyagosszergény soil



Figure (23). Carbonate dissolution kinetics of Coarse sand fractions in the Mosonmagyaróvár soil



Figure (24). Carbonate dissolution kinetics of Clay fractions in the Mosonmagyaróvár soil



Nagyszentjános coarse sand

Figure (25). Carbonate dissolution kinetics of Coarse sand fractions in the Nagyszentjános soil



Figure (26). Carbonate dissolution kinetics of Clay fractions in the Nagyszentjános soil


Figure (27). Carbonate dissolution kinetics of Coarse sand fractions in the Orosháza soil



Figure (28). Carbonate dissolution kinetics of Clay fractions in the Orosháza soil



Figure (29). Carbonate dissolution kinetics of Coarse sand fractions in the Mezőhegyes soil



Mezőhegyes coarse clay

Figure (30). Carbonate dissolution kinetics of Clay fractions in the Mezőhegyes soil



Figure (31). Carbonate dissolution kinetics of Coarse sand fractions in the Új-Szeged soil



Figure (32). Carbonate dissolution kinetics of Clay fractions in the Új-Szeged soil



Szeged-Öthalom coarse sand

Figure (33). Carbonate dissolution kinetics of Coarse sand fractions in the Szeged-Öthalom soil



Figure (34). Carbonate dissolution kinetics of Clay fractions in the Szeged-Öthalom soil



Figure (35). Carbonate dissolution kinetics of Coarse sand fractions in the Iregszemcse soil



Figure (36). Carbonate dissolution kinetics of Clay fractions in the Iregszemcse soil



Figure (37). Carbonate dissolution kinetics of Coarse sand fractions in the Kecskemét soil



Figure (38). Carbonate dissolution kinetics of Clay fractions in the Kecskemét soil



Figure (39). Carbonate dissolution kinetics of Coarse sand fractions in the Nagyhörcsök soil



Figure (40). Carbonate dissolution kinetics of Clay fractions in the Nagyhörcsök soil



Figure (41). Carbonate dissolution kinetics of Coarse sand fractions in the Örbottyán soil



Figure (42). Carbonate dissolution kinetics of Clay fractions in the Örbottyán soil



Figure (43). Carbonate dissolution kinetics of Coarse sand fractions in the Csávoly soil



Figure (44). Carbonate dissolution kinetics of Clay fractions in the Csávoly soil



Figure (45). Carbonate dissolution kinetics of Coarse sand fractions in the Ozsákpuszta soil



Figure (46). Carbonate dissolution kinetics of Clay fractions in the Ozsákpuszta soil

4.3 DETERMINATION OF CARBONATES IN THE ORJGINAL SOIL SAMPLES

(KRALJ & BRECEVIC 1994). introduced the kinetics of carbonate dissolution is very sensitive to the surface structure, composition, and physical properties of the crystals. and (HOLDREN & SPEYER 1985, 1987) studied the relationship between dissolution rate and particle grain size for alkali feldspars. They observed that the dissolution rate increased linearly with decreasing grain size down to a critical range. The rate of CO_2 evolved in the reaction is directly proportional with the amount of carbonate formed. On the basis of this idea, the observations of the differences in the behavior of the soil samples with respect to the rate of CO_2 evolution following acid treatment can be shown in Figures (5 - 46). The amounts of carbonate in soil samples were calculated using Eq. (64). Figures (5 - 46).shows that the maximum carbonate obtained was in the sample Iregszemcse (coarse sand), while the minimum carbonate from Keszthely in the depth (45-64 cm) (coarse sand), almost contain higher carbonate than the other samples except the sample Agyagosszergény (coarse sand), and soil sample Orosháza (coarse sand).

Tables (4,5,6, and 7) Shows that the time required for total carbonate dissolution is varying with the source of the sample. It should be noted that the {soil sample of Keszthely required the minimum time was (9.0 min in clay fraction in the depth 0-25 cm), while the maximum time in the same soil sample was (45 min in coarse sand fraction in the depth 0-25 cm)} {and the soil sample of Nagyhörcsök required the minimum time was (7.0 min in clay fraction in the depth 0-32 cm), while the maximum time in the same soil sample was (30 min in clay fraction in the depth 32-60 cm and coarse sand fraction in the depth 60-104 cm and the depth 104-140 cm)}. The decreasing order of the other samples according to the time used for total carbonate in the form of CO₂ show that the minimum time was (1.0 min in clay fraction in the soil sample of Nagyhörcsök and Új-Szeged. while the maximum time in the same soil sample was (45 min in coarse sand fraction in the same soil sample was (45 min in clay fraction in the soils of Nagyhörcsök and Új-Szeged. while the maximum time in the same soil sample was (45 min in coarse sand fraction in the soils Agyagosszergény, Kecskemét.

According to the application of the products of Eq. (63) and fitted in Eq. (64) with the time required for CO₂ evolution, the total carbonate in each sample is obtained as shown in tables (4,5,6, and 7). The results have been fitted to the first order of kinetic equation with constant (Q), where Q is the dissolved calcium carbonate content very quickly and applied in the following equation.

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

Where: \mathbf{Y} = is the amount of calcium carbonate %. \mathbf{A}_1 and \mathbf{A}_2 = are the maximum of calcium carbonate %. In faster and slower processes respectively. \mathbf{k}_1 and \mathbf{k}_2 = are the constant rate of the faster and slower processes respectively. \mathbf{Q} = calcium carbonate % in the very fast processes.

The calculated parameters of calcium carbonate % are listed in Tables (4,5,6 and 7) As shown in Tables (4, 5, 6 and 7) that the smallest value of the constant rate of the faster reaction (k_1) was found in the samples Keszthely (coarse sand), and Nagyhörcsök (clay), (0.0796 and 0.4283 respectively), While the highest value was in the samples Keszthely (coarse sand), and Kecskemét (coarse sand), (5.8659 and 5.1076 respectively). Meanwhile, the value of constant rate of slower reaction (k_2) was at maximum with the sample Kecskemét (clay), (0.6884), and the minimum K₂ value was found in the sample Szeged-Öthhalom (0.000). The highest percentage of maximum calcium carbonate in faster reaction (A_1) was found in the soil sample Iregszemcse (32.1834), while the lowest percentage of A_1 was obtained in the sample Agyagosszergény (0.2006). In the slower reaction, the highest value of the maximum calcium carbonate (A_2) was calculated in the sample Nagyhörcsök in the depth 104-140 cm of fraction coarse sand (17.4296). The values of A_1 give an ideal classification because the arrangement of the soil samples according to the maximum carbonate % categorized the soil samples according to the main origin places of collection.

The results are an agreement with (Brady & Weil, 1999). Mentioned the occur in humid and semiarid zones if their parent material is rich in carbonate, such as limestone, shells or calcareous glacial tills, and the parent material is relatively young and has undergone little weathering. Some soils that develop from calcareous parent materials can be calcareous throughout their profile. This will generally occur in the arid regions where precipitation is scarce. In other soils, carbonate has been leached from the upper horizons, and accumulated in B or C horizons. These lower carbonate layers can be brought to the surface after deep soil cultivation and an agreement with (Brady & Weil, 1999). In some soils, the carbonate deposits are concentrated into layers that may be very hard and impermeable to water.

The results are an agreement too with (ECONOMU et al. 1996), the kinetics of carbonate dissolution is very sensitive to the surface structure, composition, and physical properties of the crystals they determined, that the dissolution rate of carbonate particles is decreased with the increase of the particle size. Also we are in an agreement with (TURNER & SKINNER 1959) that the 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. And (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 dissolution curves obtained from Eq. (64) for soil samples are shown from. (Fig. 3 to 44) That represents the relationship between the amount of carbonate (%) dissolution and the time required in both processes (during 60 min). The aim of such relationship is to describe the dissolution kinetics quantitatively and simply. It is suggested that the time required for carbonate formation in the slower and faster processes is an important factor to distinguish between these two processes. Our results are an agreement with (RAUCH & WHITE, 1977; PALMER, 1991). The dissolution the calcite component dissolves faster than the dolomite component, forming an mg-enriched surface. After the initial period of enhanced carbonate dissolves more slowly than pure calcite. In stones that are a mixture of calcite and dolomite, the dissolution rate has been shown to decrease in a regular way with increasing dolomite content of the rock. And an agreement with (RAUCH & WHITE, 1977), and (HERMAN & WHITE 1985), the dissolution of carbonate in soil samples and concluded that the dissolution rate increases with decreasing grain size.

5. CONCLUSIONS

The dissolution reaction of soil carbonates could be well described with firstorder kinetic equations, with one, two, and three term one. The amount of the carbonate can be characterized with the maximum values (A and Q) of the reactions, the solubility and reactivity with the rate constant (k) values and half-life-time values. The distribution of carbonates between soil horizons and particle size fractions could be also well described with the first order kinetic reactions and their parameters. During soil development from the coarse sand fraction of upper horizon disappear the fast reaction, but in the accumulation horizons its amount increased significantly both in the coarse sand and clay fractions. 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 processes 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.

At the Nagyhörcsök soil in the upper horizon the rate of the faster processes both in the coarse sand and clay fractions are not so fast (k₁: 0.50 and 0.43 respectively). These values and the half-life-time of the reactions (1.4 and 1.6, respectively) suppose dolomite-like carbonate dissolution. The lower carbonate content of the upper horizon and its coarse sand and clay fractions confirms the effect of the leaching process. During leaching mainly the calcite-like carbonates disappeared from the upper soil horizon. 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 measurement 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 $\{k_1(1/\min) = 1.0\}$, what is lower than the slow process by a magnitude. $\{k_2 (1/\min) = 0.1 - 0.2\}$. Solubility kinetic of calcite and dolomite Crystals break to 0.5 mm size were examined. Calcite 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 (0.0), 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. To the question:"Where dissolving the carbonates faster: in the more fine distributed clay fraction or in the coarse sand fraction?" we established, that according to our actual knowledge's, in the most of the case, smaller carbonate particles dissolving during faster processes. Much more difficult to answer the question:"What kind of carbonate compounds dissolving in connection to certain fractions and its solubility speed." Computerized data analysis provides obvious information only in very few cases. It is very rarely, that the dissolution of carbonates was happened only by fast or only by slow processes. Mainly both of the two processes are occurred. It shows that both of the forms of carbonates, the calcite like and dolomite like, are in the soil. The fraction of 1.0-0.3 of speed constant shows transition between calcite 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 calcite character is dominant. If speed constant is much higher than 1.0 or value Q proportion is significant (super fast process), these phenomenon's 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 to different kind of solubility occurs in the soil. That carbonates are mostly calcite-like, 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' speed of dissolution. If concentrations of Ca²⁺ and Mg^{2+} in salt acid solution are compared to the amount of dissolved carbonates by fast processes, then Ca^{2+} (R₂ = 0.9485), and Mg²⁺ (R₂ = 0.6610) hang together. If slow process is seen, then Ca^{2+} (R₂ = 0.81353) correlate to an Mg²⁺ (R₂ = 0.9124), namely Ca²⁺ dominants in fast processes, while Mg²⁺ dominates 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 CO₂ formation can be described by a first-order kinetic equation. Computerized analysis can separate dissolution process to more than one process, from previously formed CO2 during dissolution. 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 calcite and calcite like minerals, while the slow dissolving processes can be considered to dolomite and dolomite like minerals.

6. **NEW SCIENTIFIC RESULTS**

According to objectives the new scientific results are:

- 1. The carbonate dissolution calculated by computer analysis from CO₂ 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 CO₂ during dissolution.
- 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.

7. SUMMARY

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. Plants take up calcium in the ionic form (Ca^{2^+}) . Uptake is not as efficient as for other plant nutrients. It occurs just behind the root tip, in contrast with potassium where uptake occurs along most of the length of the root. Lime is any material that: contains calcium (Ca^{2^+}) or magnesium (Mg^{2^+}) and will neutralize soil acidity. For example, calcium carbonate $(CaCO_3)$ is a liming material because it contains Ca^{2^+} and the carbonate portion of the material (CO_3) will neutralize soil acidity.

The amount of liming material required bringing about a desired pH change is determined by several factors, including (1) the change in pH required, (2) the buffer capacity of the soil, (3) the chemical composition of the liming materials to be used, and (4) the fineness of the liming materials. The acid dissolution kinetics of $CaCO_3$ is important to many fields of applications. Particle size distribution, surface area and reactivity are important properties of soil CO_3^{2-} which influence soil pedogenic, chemical and rhizosphere processes. CaCO₃ provides a reactive surface for adsorption and precipitation reactions the kinetics of CaCO₃ dissolution is very sensitive to the surface structure, composition, and physical properties of the crystals. The dissolution rate of CaCO₃ particles is decreased with the increase of the particle size. Limestone dissolution kinetics is important in understanding problems such as geochemical weathering, the distribution of CO_3^{2-} sediments in marine environments. The chemistry and temperature of the solution are also important. The calcimeter method is simple and convenient method has been to give reliable estimates of carbonate in a variety of soil samples. In evaluating limestone for agricultural purposes it is common practice to determine the calcium carbonate content of the soil. Determination of carbonate by the procedure described here should serve the same purpose. The total carbonate content of limestone or soils is required; estimation of calcite, dolomite, and total content in one operation is particularly convenient

The Hungarian soil samples were taken from the genetic horizons of a chernozem soil at different soil samples. Soil particles were fractionated into the next size fractions. 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 (0.002-0.05 mm) and 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. The soil samples are: (Agyagosszergény, Magyaróvár, Nagyszentjános, Orosháza, Mezőhegyes, Új-Szeged, Szeged-Öthalom, Iregszemcse, Kecskemét, Nagyhörcsök, Őrbottyán, Csávoly, and 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 Keszthely (0-25 cm), (25-45 cm), (45-64 cm) and (64-115 cm) and the soil sample Nagyhörcsök (0-32 cm), (32-60 cm), (60-104 cm) and (104-140 cm). The dissolution kinetics of carbonates in thirteen "soil bank" soils, and in the Keszthely and Nagyhörcsök soils profiles and their coarse sand and clay fractions and also in calcite and dolomite samples were determined. The pseudo-first-order kinetic equation (2 term + Q constant) was fitted to the data. These soil samples were selected from different locations depending on the variation of CaCO₃. 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 % was added in excess. Pure calcite and dolomite were powered and their carbonate content was also determined. The CO₂ development was read 27 times between 0-60 minutes. The experiments were carried out to determine the dissolved CaCO₃ in the soil samples using Scheibter's calcimeter. The determination of soil texture is called particle size analysis or mechanical analysis. Determining the texture in the laboratory uses a basic principle of sedimentation called "Stokes Law". Stokes Law states that the speed or velocity with which particles settle out of a liquid medium is dependent on a constant factor (k) and the radius of the particles. Or, the bigger the particle, the faster it will fall out of suspension.

The results obtained by this procedure are essential for the classification of the soil and the determination of the quantity of sand, silt, and clay size particles of which the soil is composed. The apparatus was standardized by analysis of known quantity of carbonate under the prescribed standard condition. Calcimeter apparatus was set-up by balancing the air gas inside, and the level of the liquid in both arms of U-shapes tube (water monometer) was upstanded and adjusted to zero. Soil sample (0.5-1.0 g) was added in the reaction vessel. Hydrochloric acid with concentration 10% was filled in the small glass tube suspended in reaction vessel and the reaction vessel than tightly closed by rubber stopper. At the end of the reaction the liquid in the U-shaped tube is stabilized and no more CO_2 was evolved. CO_2 volumes were measured at 0.0, 0.25, 0.50, 0.75, 1.00, 1.25, 1.50, 1.75, 2.00, 3.00, 4.00, 5.00, 6.00, 7.00, 8.00, 9.00, 10.0, 15.0, 20.0, 25.0, 30.0, 35.0, 40.0, 45.0, 50.0, 55.0.and 60.0 minutes as a reaction interval. Some

samples the time until 120.0 minutes. The total carbonate expressed in terms of $CaCO_3$ %, calculated using the following formula; $CaCO_3 = M*A*100/G$. And the first order kinetic equation is fit to the measured data:

$$Y = Q + A_1 (1 - e^{-k_1 t}) + A_2 (1 - e^{-k_2 t})$$

In the case of calcite and dolomite only one first order kinetic reaction was supposed. The greater buffering capacity, the lime requirement for acid fine-texture, clay is much higher than that for sand or silt with the same pH value. Computer analysis was used to separate the very fast, fast and slow carbonate dissolution reactions in the genetic horizons of a Keszthely and Nagyhörcsök chernozem soil. In the genetic horizons of the soil the manometric and another thirteen soil samples. Data were analyzed in the coarse sand and clay fractions. The fitted first order kinetic equations very well described the parallel reactions. At the same time calcite and dolomite were used to demonstrate the fast and slow dissolution reactions, respectively. When free carbonates are present, the acid will produce bubbling due to the evolving of CO₂ gas. During soil development the fast dissolution process disappeared from the coarse sand fraction of the upper horizon, but this process significantly increased in the accumulation horizon both in the coarse sand and clay fractions of the Keszthely soil. Considering the rate constant values, the real slow process could be characterized with (k_2) , the real fast process with (k_1) . The upper soil horizon (0-25 cm) shows a distinguished property, e.g., in the coarse sand fraction there is no fast reaction only 1% very fast one. The genetic horizons of the Keszthely soil profile (Table 4 and Figures 5 to 12) show that the first two upper horizons (0–25 and 25–45 cm), the clay fraction contains faster carbonate dissolution reactions than the coarse sand fractions. But in the lower two horizons (45–64 and 64– 115 cm), the clay fraction contains slower carbonate dissolution reactions than the coarse sand fraction.

The results demonstrated that the fast process in the clay fraction in the upper horizon (0–25 cm) is slow and contained a small amount of carbonate. While in the B horizon (25–45 cm), the carbonate accumulation was at maximum mainly in the coarse sand fraction. Carbonate content of soil profile formed on Keszthely loess was determined is 4 levels. Carbonate was in the (0–25 cm) level. The highest carbonate content was in coarse sand. Considerable amount of superfast dissolved carbonate (Q) was in the whole soil profile. And (Table 5 and Figures 13 to 20) show that, In the Nagyhörcsök soil the leaching removed mainly the well soluble calcite-like carbonates from the upper horizon. Considering downward the genetic horizons of the Nagyhörcsök soil profile the rate constant of the faster dissolution process increases and the half-life-time decreases. Comparing the rate constant values of the faster processes

in the upper horizon (0–32 cm) 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 not so fast $(k_1 = 0.50 \text{ and } k_1 = 0.43)$. This relates to dolomite-like carbonate dissolution. The same fact can be concluded also from the half-life-time of these processes. The low carbonate content of the upper horizon and its low carbonate content in the clay fraction are the result of a leaching process. All these facts prove that the leaching removed mainly the well soluble calcite-like carbonates from the upper horizon. At the same time the dolomite-like carbonates remained mainly in this horizon. Carbonate content of soil profile formed on loess on Nagyhörcsök was determined is 4 genetically levels. Layer (0-32 cm) contained carbonate of (6.0%). Fast processes were dominated in fraction coarse sand and clay in layer (32-60 cm) (20.9 % carbonate). Slow process appeared in every genetically layer and in both of the fractions, but missed in the upper 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. The faster reactions $(Q + A_1)$ in all horizons and fractions exceed the rate of slow reaction. However the fast reaction in the upper horizon is not as fast as in the deeper horizons (Figures 13 to 20) In all the genetic horizons of Keszthely and Nagyhörcsök soil samples, (e.g. figure 47) the slow process practically the same in the coarse sand and clay fractions (4-5% and 1-2%, respectively). 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 processes 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, fast dissolved carbonates in fraction of coarse sand show largest value in B horizon (32-60 cm) (accumulation horizon).



Figure (47): Carbonate dissolution kinetics of Coarse sand fractions in the Keszthely soil in the depth 64-115 cm

According to the application of the products of Eq. (63) and fitted in Eq. (64) with the time required for CO_2 evolution, the total carbonate in each sample is obtained as shown in tables (4,5,6, and 7). The results have been fitted to the first order of kinetic equation with constant (Q), where Q is the dissolved calcium carbonate content very quickly. As shown in Tables (3, 4, and 5) that the smallest value of the constant rate of the faster reaction (k₁) was found in the samples Keszthely (coarse sand), and Nagyhörcsök (clay), (0.0796 and 0.4283 respectively), While the highest value was in the samples Keszthely (coarse sand), and Kecskemét (coarse sand), (5.8659 and 5.1076 respectively). Meanwhile, the value of constant rate of slower reaction (k₂) was at maximum with the sample Kecskemét (clay), (0.6884), and the minimum k₂ value was found in the sample Szeged-Öthhalom (0.000). The highest percentage of maximum calcium carbonate in faster reaction (A_1) was found in the soil sample Iregszemcse (32.1834), while the lowest percentage of A₁ was obtained in the sample Agyagosszergény (0.2006). In the slower reaction, the highest value of the maximum calcium carbonate (A₂) was calculated in the sample Nagyhörcsök in the depth 104-140 cm of fraction coarse sand (17.4296). The values of A_1 give an ideal classification because the arrangement of the soil samples according to the maximum CaCO₃ % categorized the soil samples according to the main origin places of collection.

8. Összefogalás

A dolgozat célja a talaj karbonát tartalma oldódási kinetikájának vizsgálata a képződő CO₂ mérésével, egyúttal néhány mechanikai frakció (durva homok és agyag) karbonát-tartalmának kinetikai paraméterekkel történő jellemzése. A karbonátok oldódási kinetikáját 13 un. "Talajbank" talajmintában, valamint egy keszthelyi és egy nagyhörcsöki szelvény talajmintáiban és mindezek két mechanikai frakciójában, illetve egy-egy dolomit és kalcit mintában vizsgáltuk. A mérési adatokra 2 tagú elsőrendű + Q konstans kinetikai egyenletet illesztettünk. A számítógépes elemzés segítségével a karbonátok oldódása során képződő CO₂ mennyiségből több folyamatot sikerült elkülöníteni. Talajok esetében megállapítható, hogy általában az agyagfrakcióban lévő karbonátok gyorsabban oldódnak mint a durva homok frakcióban lévők. A gyors oldódási folyamatok kalcit jellegű ásványokhoz, míg a lassú folyamatok dolomit jellegű ásványokhoz köthetők.

A talajok, illetve a talajok durva homok- és agyagfrakciójában lévő karbonátok oldódási kinetikájának leírására első közelítésben a kéttagú kinetikai elsőrendű reakcióegyenletet illesztettük kiegészítve egy legelső, nagyon gyors folyamattal (Q), amely az első mérési időpontig (15 sec) lezajlik. Az első folyamatot gyorsnak, a második folyamatot lassúnak tekintettük. Az első folyamat sebességi állandója k_1 1,0 1/perc körüli érték, mely a lassú folyamatnál egy nagyságrenddel kisebb (0.1-0.2 1/perc). Megvizsgálva a 0.5 mm-re elporított kalcit és dolomit kristályok oldódási kinetikáját, a kalcit egy nagyon gyors és egy gyors folyamat során oldódik, ahol a sebességi állandó érétke $\mathbf{k} = 1,3617$. A dolomit ezzel szemben egy un. lassú folyamat során oldódik fel, melynek sebességi állandója k = 0.2923. Természetesen azokban az esetekben, ha a talajok esetében nem volt lassú folyamat, vagy annak sebességi állandója 0.01 nagyságrendű volt, akkor ezt a folyamatot 0-nak tekintettük, hiszen a mérési tartományban érdemi oldódás ezen folyamattal nem történt.

A másik oldódási sebességet jelző paraméter a folyamat felezési ideje $t_{1/2}$. A ténylegesen gyorsnak tekinthető folyamatok esetében ennek értéke általában 1 perc alatt van, míg az un. lassú folyamatok esetében 2-7 perc között van. Arra vonatkozóan, hogy a finomabb eloszlású agyagfrakciókban vagy a durva homok frakcióban lévő karbonátok oldódnak-e gyorsabban, megállapítottuk, hogy az eddigi ismeretekkel egyezően a kisebb karbonát részecskék gyorsabb folyamatok során oldódnak fel – az esetek többségében. Sokkal nehezebb arra választ adni, hogy milyen karbonát vegyületek oldódnak az egyes frakciókhoz és oldódási sebességéhez kapcsolódóan. A számítógépes elemzése az adatoknak ugyanis nagyon ritkán mutatott egyértelmű képet, ami feltehetően a tényleges helyzetre. Ritkán fordult ugyanis elő, hogy csak gyors vagy

csak lassú folyamtokkal oldódtak volna a karbonátok a talajokban. Az esetek zömében mindkét folyamattípus előfordult, ami azt jelzi, hogy mind a kalcitszerű, mind a dolomitszerű – karbonátok jelen vannak a talajokban. A sebességi állandók 1.0-0.3 közé eső része pedig átmenetet képez a kalcit és dolomit között. Nyilván, amely k érték közelebb esik a 0.3-hoz, ott a dolomit jelleg dominál, amely pedig 1.0-hez esik közelebb, ott a kalcit jelleg dominál. 1.0-nél jóval nagyobb sebességi állandó, illetve jelentős arányú Q érték (nagyon gyors folyamat) a kalcitnál is jobban oldódó alkálifém karbonátok jelenlétére is utalhat. Olyan eset is előfordult, hogy a kiszámított két sebességi állandó értéke 1.0 és 0.3 közé esett és meglehetősen hasonló volt. Ekkor elképzelhető, hogy csupán egy közepes sebességű folyamat történik. Megerősíti az eddigieket, hogy a legtöbb talajban különböző oldékonyságú karbonátok fordulnak elő, amelyek legtöbbször kalcitjellegűek, de nagyon sok esetben oldódásuk a dolomitéhoz hasonló, sokszor viszont az oldódás kinetikája a két ásvány közötti oldódási sebességet mutat. Ha összevetjük a sósavas oldatban mért Ca^{2+} , illetve Mg^{2+} koncentrációt a gyors folyamtokkal oldódott karbonát mennyiséggel, akkor a $Ca^{2+} R^2 = 0.9485$, a $Mg^{2+} R^2 =$ 0.6610 összefüggésben vannak egymással. Ha a lassú folyamatot nézzük, akkor a Ca²⁺ $R^2 = 0.81353$, a Mg^{2+} $R^2 = 0.9124$ összefüggést mutat, vagyis a gyors folyamatok esetében a Ca²⁺ dominancia míg a lassú folyamatoknál a Mg²⁺ dominancia érvényesül, de a másik elemmel is minden esetben szoros összefüggés van. Végső következtetésként megállapíthatjuk, hogy a CO₂ képződés alapján számított karbonát oldódás számítógépes elemzés segítségével kinetikailag elsőrendű reakcióegyenlettel leírható. A számítógépes elemzés az oldódás során képződő CO2 mennyiségből több folyamatra képes bontani az oldódás folyamatát. Talajok esetében megállapítható, hogy általában az agyagfrakciókban lévő karbonátok gyorsabban oldódnak, mint a durva homok frakcióban lévők. A gyors oldódású folyamatok kalcithoz, illetve kalcit-jellegű ásványokhoz köthetők, míg a lassú oldódású folyamatok dolomithoz, illetve dolomitjellegű ásványokhoz.

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10. 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), and also that of calcite and dolomite 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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