

REACTIONS OF Fe^{2+} AND Fe^{3+} WITH CALCITE¹

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Abstract—Ferrous or ferric perchlorate, 0.01 M, was reacted with calcite in stirred aqueous suspensions which were bubbled vigorously with an oxidizing purge gas. Two and three equivalents of CaCO_3 were dissolved per mole of Fe^{2+} and Fe^{3+} neutralized, respectively. With $\text{Fe}(\text{ClO}_4)_2$, the crystalline Fe oxide products partially coated the calcite surface. The dominant products were lepidocrocite and goethite when the purge gas was air or 20% CO_2 (balance air), respectively. After reaction with Fe^{2+} the edges and corners of the calcite crystals were generally rounded and the faces were non-uniformly pitted; however, after reaction with Fe^{3+} , a mosaic pattern with distinct ridges and channels was evident on the calcite. These ridges were somewhat pitted, but distinct stepped dislocations were present leading to a featureless and generally flat channel floor. When the calcite was separated from the Fe solution by a semi-permeable membrane, precipitation occurred predominantly on the calcite side and on the Fe side of the membrane in the Fe^{2+} and Fe^{3+} systems, respectively.

Fe oxyhydroxides precipitated from the $\text{Fe}(\text{ClO}_4)_3$ and $\text{Fe}(\text{ClO}_4)_2$ solutions by different mechanisms. In the $\text{Fe}(\text{ClO}_4)_3$ system, although the initial reaction may have been at the calcite surface, the bulk of the poorly crystalline ferrihydrite was formed by hydrolysis of Fe polymers in suspension. Neutralization occurred by the reaction with basic products of a surface-controlled dissolution of calcite, rather than by a direct reaction of acidic polymers with the calcite surface. In the $\text{Fe}(\text{ClO}_4)_2$ system, lepidocrocite or goethite formed by the partial hydrolysis of Fe^{2+} or Fe^{3+} by reaction with calcite or the basic products of calcite dissolution and subsequent precipitation of simple Fe species on existing FeOOH nuclei.

Key Words—Calcite, Dissolution, Goethite, Hydrolysis, Iron, Lepidocrocite, Precipitation.

INTRODUCTION

Reactions of Fe^{2+} and Fe^{3+} with calcium carbonate are important pedogenic processes. These reactions have a special significance in agriculture because Fe salts are rapidly immobilized as Fe oxides in calcareous soils and because Fe is commonly a limiting nutrient in plant growth.

Loeppert *et al.* (1984) found that the rate of reaction between calcite and solution phase $\text{Fe}(\text{ClO}_4)_2$ in a rapidly stirred and aerated system was linearly related to surface area of the calcite, with the linear regression line passing close to the origin. The reaction rate decreased with increased P_{CO_2} . In all experiments the dominant Fe oxide phases formed from the ferrous salt were lepidocrocite and goethite when the purge gas was air and 20% CO_2 (balance air), respectively. A reaction was suggested in which solution phase Fe^{2+} and/or Fe^{3+} reacted with CaCO_3 or its solution-phase dissolution products to form crystalline FeOOH . It was not determined whether the proposed reaction occurred on the surface of the calcite or in true solution. With $\text{Fe}(\text{ClO}_4)_3$, the rate of reaction was also linearly related to the surface area of the CaCO_3 ; here, ferrihydrite was the dominant solid product.

The objective of the present study is to clarify the nature of the reaction between solution phase $\text{Fe}(\text{ClO}_4)_2$ and $\text{Fe}(\text{ClO}_4)_3$ and calcite, especially with regard to the

stoichiometry of the reaction, the loci of precipitation, and the morphology of the precipitated phases.

MATERIALS AND METHODS

Sample preparation

Iron oxides were prepared by reacting $\text{Fe}(\text{ClO}_4)_2$ or $\text{Fe}(\text{ClO}_4)_3$ in aqueous calcite suspension as summarized by Loeppert *et al.* (1984). The sample was agitated vigorously with a paddle stirrer while an appropriate purge gas was bubbled through the suspension at a rate of 0.1 liter/min. The reactions were performed using a Radiometer automatic titrator equipped with a PHM 84 pH meter. Redox potential and/or pH were monitored continuously during the reaction. Unless otherwise noted, 500 μl of a 0.4 M solution of Fe salt was added to a suspension of 200 mg of sand-size calcite in 20 ml of deionized H_2O . These ratios represent the addition of 0.2 mmole of Fe salt to 2.0 mmole of calcite. Reactions involving $\text{Fe}(\text{ClO}_4)_2$ were allowed to proceed for approximately 30 min past the endpoint (Loeppert *et al.*, 1984); reactions involving $\text{Fe}(\text{ClO}_4)_3$ were allowed to proceed for the same time as the corresponding $\text{Fe}(\text{ClO}_4)_2$ samples.

Particle size separates of calcite were obtained by screening and were washed thoroughly with deionized H_2O to remove surface absorbed crystallites.

Separation and identification of phases

The Fe oxide product was separated from the sand-size calcite by gentle agitation and decantation and was

¹ Contribution from the Texas Agricultural Experiment Station.

concentrated onto a 0.45- μm membrane-filter disc. The products were air dried for 24 hr and examined by X-ray powder diffraction (XRD) using $\text{CuK}\alpha$ radiation which was monochromatized with a graphite crystal. Samples for analysis were spread uniformly on glass slides with the aid of acetone and scanned from 2° to $60^\circ 2\theta$ at a rate of $2^\circ 2\theta/\text{min}$. The crystallinities of the Fe oxide products were estimated from the half-height peak widths of the 3.29- \AA (120) lepidocrocite and 4.18- \AA (110) goethite reflections from scans obtained at goniometer speeds of $0.25^\circ 2\theta/\text{min}$. Corrections for instrument line broadening were made by subtracting the half-height peak width for the nearest peak of 5–20 μm quartz.

Scanning electron microscopy

Sand-size calcite or Fe-coated calcite was separated from the solution phase or suspended Fe oxide phase by gentle agitation and decantation of the latter, washed twice with deionized H_2O , and air dried for 24 hr. The samples were attached to aluminum stubs with double-stick cellophane tape rimmed with silver conductive paint, coated with approximately 100 nm of Au-Pd in a Hummer I sputtering unit, and examined with a JEOL JSM 25 SII microscope operating at 15 kV.

Dialysis studies

The $\text{Fe}(\text{ClO}_4)_2$ or $\text{Fe}(\text{ClO}_4)_3$ solution phases were separated from the aqueous calcite suspensions by a cellulose membrane with a 12,000 to 14,000 molecular weight cutoff. An appropriate purge gas was bubbled on each side of the membrane at a rate of 0.1 liter/min. The pH was monitored during the reaction. The iron oxide products on each side of the membrane were isolated and identified by XRD procedures.

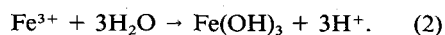
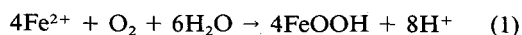
Steady-state (pH-stat) dissolution

Two hundred milligrams of calcite or Fe oxide-coated calcite was suspended in 20 ml of water and titrated with 0.5 N HCl at the desired pH using the Radiometer automatic titrator. Reaction rates were determined from the rate of consumption of HCl.

RESULTS AND DISCUSSION

Stoichiometry of the reaction

During the hydrolysis of Fe^{2+} and Fe^{3+} , H^+ is released as summarized in the following equations:



According to the stoichiometry of these reactions, 2 and 3 equivalents of H^+ are produced per mole of Fe^{2+} and Fe^{3+} hydrolyzed, respectively. If calcite is the proton sink for the above reactions, 2 and 3 equivalents of CaCO_3 must be consumed, respectively.

The amount of calcium carbonate consumed during

Table 1. Consumption of calcite during reaction with Fe salts and air as the purge gas.

Fe salt added	Calcite consumed	
	Actual (meq $\text{CaCO}_3/\text{mole Fe}$)	Theoretical
$\text{Fe}(\text{ClO}_4)_2$	2.07	2.00
$\text{Fe}(\text{ClO}_4)_3$	2.88	3.00

the reaction between $\text{Fe}(\text{ClO}_4)_2$ or $\text{Fe}(\text{ClO}_4)_3$ and calcite was determined from the difference between the amounts of initial and final calcite (Table 1). The final amount of calcite was determined by the pH-stat dissolution procedure. In each case the theoretical consumption of calcite from Eqs. (1) and (2) corresponded closely to the actual consumption of calcite, indicating that the quantity of calcite consumed was equivalent to the quantity of H^+ produced during hydrolysis of the Fe species. Therefore, the calcite appeared to be the proton sink during the neutralization reaction. The neutralization of acidic species may have occurred either by direct reaction with the calcite or by reaction with the products of calcite dissolution.

Morphology of precipitated Fe oxide phases

Scanning electron micrographs of sand-size calcite following direct reaction with $\text{Fe}(\text{ClO}_4)_2$ are shown in Figures 1 and 2. On samples for which the Fe oxide product was identified principally as lepidocrocite, a partial coating of Fe oxide was evident on the surface (Figure 1A). Exposed patches of calcite were noted which were probably due to mechanical abrasion and chipping of lepidocrocite flakes from the surface. The smaller particles of calcite were more completely coated. In contrast, the calcite surface was largely unstained following direct reaction with $\text{Fe}(\text{ClO}_4)_3$.

As shown in Figure 1A, the Fe oxide coating was not always in direct contact with the calcite surface. Voids between the two phases suggest that precipitation may have occurred at a finite distance from the calcite surface rather than directly at the calcite/solution interface. Also, the morphology of the lepidocrocite flakes at the calcite surface indicate that growth probably occurred on existing nuclei rather than directly at the calcite surface.

On samples for which the Fe oxide product was identified principally as goethite (Figure 2), the coating was primarily in the cracks and crevices of the calcite crystal, indicating that during the formation of goethite, the Fe oxide mineral was either less strongly attached or more readily abraded from the calcite surface. Goethite was the dominant phase formed at $P_{\text{CO}_2} \geq 0.20$. At these higher partial pressures of CO_2 the solubility of CaCO_3 is greater than for systems in equilibrium with air (Garrels and Christ, 1965). In addition, the kinetics of the dissolution of calcite is faster at higher

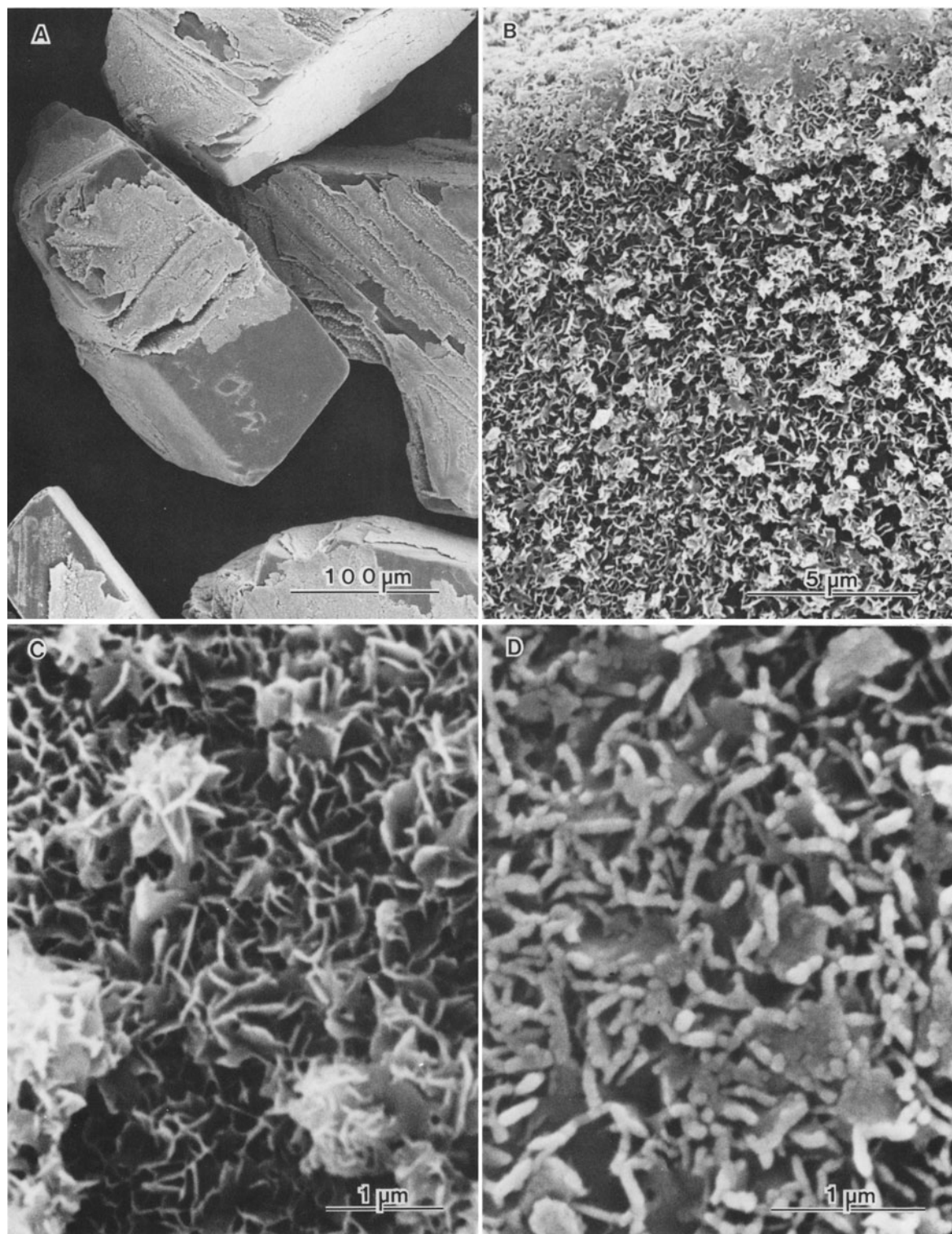


Figure 1. Scanning electron micrographs of coated calcite following the reaction of $\text{Fe}(\text{ClO}_4)_2$ with Iceland spar calcite when using air as the purge gas. D = coated calcite aged for two months over silica gel.

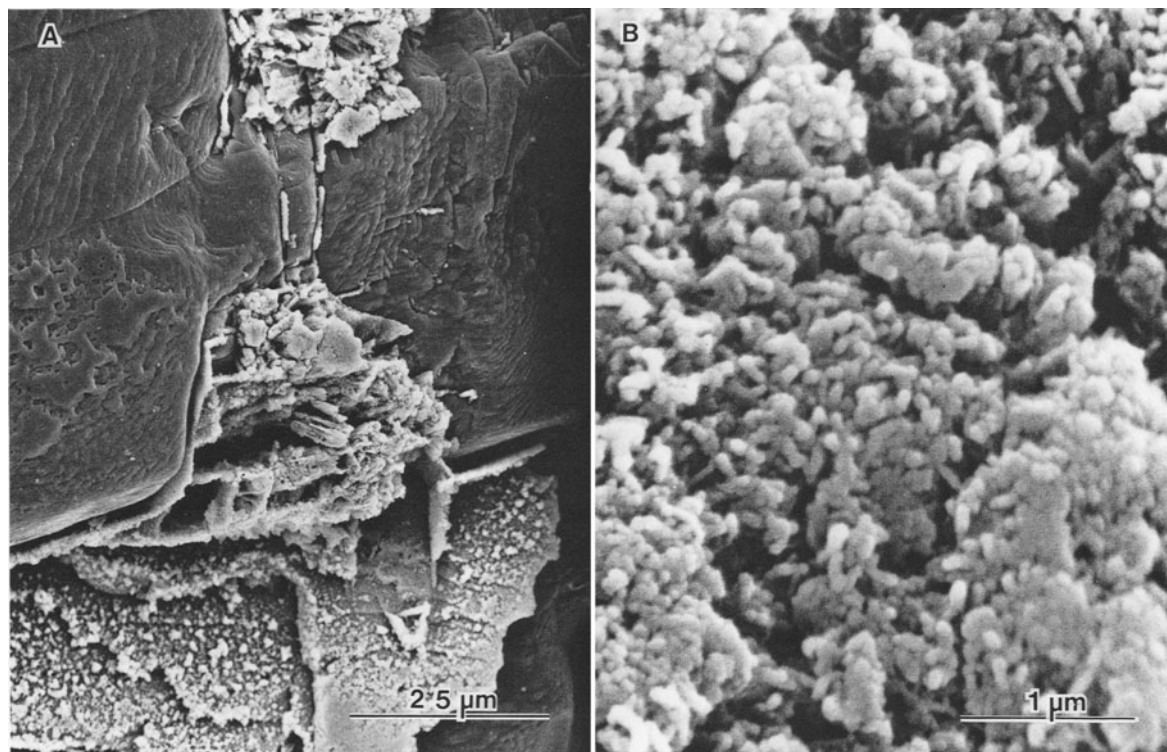


Figure 2. Scanning electron micrographs of coated calcite following the reaction of $\text{Fe}(\text{ClO}_4)_2$ with 40–60 mesh Iceland spar calcite when using 20% CO_2 (balance air) as the purge gas.

P_{CO_2} than in air (Plummer *et al.*, 1978), resulting in a higher HCO_3^- activity at a given distance from the CaCO_3 surface under the disequilibrium conditions of this experiment. The rate of oxidation of Fe^{2+} to Fe^{3+} was found in this laboratory to be less at higher P_{CO_2} , giving rise to lower disequilibrium concentrations of Fe^{3+} which, along with the higher concentration of solution phase HCO_3^- , created a situation in which reaction was more likely to occur at a greater distance from the surface at the higher partial pressure of CO_2 and to result in a less tightly bound surface coating.

High-magnification scanning electron micrographs of the coated calcites show different particle morphologies for the precipitated lepidocrocite and goethite precipitates (Figures 1 and 2, respectively). The lepidocrocite phase has the appearance of an irregular honeycomb of sharply folded sheets with interspersed “flowers” (Figures 1B and 1C). After aging for two months over silica gel, the edges of the sheets became more globular and rounded. The morphology of the aged material is more indicative of that commonly observed for goethite; however, increases in goethite concentration were not apparent from the XRD patterns of fresh and aged materials. Therefore, these effects of aging may be attributed to changes in aggregate morphology resulting from prolonged dehydration.

Iron oxides on the calcite surface which were iden-

tified primarily as goethite show a globular and lumpy morphology suggesting that they are poorly crystalline (Figure 3); however, the average half-height peak width of the 4.18-Å (110) reflection of goethite, corrected for instrument line broadening, was $1.0^\circ 2\theta$, comparable to that observed for lepidocrocite.

Surface reactivity of solid phase CaCO_3 following reaction with $\text{Fe}(\text{ClO}_4)_2$

Following the reaction of an Fe salt with calcite, the reaction mixture was titrated under steady-state conditions at pH 5.0. Berner and Morse (1974) showed that rate of dissolution of calcite under steady-state conditions is directly related to the reactive surface area of the solid phase. The rates of dissolution of the coated calcite samples are summarized in Table 2. The Fe oxide coating did not suppress the rate of dissolution of calcite at pH 5.0, and, in most experiments, the rate of dissolution was actually increased. These results suggest that the Fe oxide coating deposited under vigorously stirred conditions did not effectively block the reactive surface of the calcite from reaction with H^+ at pH 5.0. The increased rate of reaction may be attributed to the increase in actual reactive surface area due to etching of the calcite crystal during reaction with Fe salt.

Table 2. Steady-state (pH-stat) titration of 100–120 mesh calcite at pH 5.0 following reaction with Fe(ClO₄)₂.

Fe ²⁺ added (mmole/mg calcite)	pH-stat dissolution rate (meq/min)
0	0.0021
0.0001	0.0029
0.001	0.0033
0.01	0.0037
0.10	0.0037
1.00	0.0024

Dialysis studies

The results of experiments in which the calcite was separated from the Fe(ClO₄)₃ or Fe(ClO₄)₂ by a semi-permeable membrane are summarized in Table 3. The only Fe oxide product observed following the reaction of Fe(ClO₄)₃ with calcite was a poorly crystalline ferrihydrite with a broad XRD reflection centered at approximately 35°2θ. The half-height peak width of this reflection was approximately 5°2θ. Rapid hydrolysis of Fe³⁺ under conditions in which the solubility product of ferrihydrite is exceeded commonly yields ferrihydrite as the only product (Schwertmann and Taylor, 1977). Iron oxide phases were observed on both sides of the dialysis membrane but were most prevalent on the Fe side, indicating that direct contact with the calcite surface was not essential for polymerization and precipitation of the Fe oxide. The calcite surface remained largely unstained. The loci of precipitation suggest that neutralization was achieved predominantly by the reaction of H⁺ and Fe³⁺ species with the products of calcite dissolution, i.e., HCO₃⁻, CO₃²⁻, and OH⁻, rather than by direct interaction between Fe³⁺ and calcite. Apparently HCO₃⁻, OH⁻, and H⁺ moved more readily through the semi-permeable membrane than the much larger, partially neutralized Fe³⁺ polymer.

The above results are in sharp contrast to those obtained from the reaction of Fe(ClO₄)₂ with calcite, in which precipitation occurred predominantly on the calcite side of the membrane and staining of the calcite was appreciable. The red (Munsell 10 R 3/6) phase observed on the Fe side of the membrane was a poorly crystalline ferrihydrite with a broad, shallow band centered at approximately 35°2θ. Crystalline lepidocrocite and goethite were identified on the calcite side of the membrane. The predominant phase was largely dependent on the purge gas employed on the calcite side of the membrane, i.e., lepidocrocite and goethite were the dominant phases when air and 20% CO₂ (balance air) were used, respectively. The corrected half-height peak widths of lepidocrocite and goethite were approximately 0.9 and 1.2°2θ, respectively. These results agree with results of batch studies in which the dominant products were also lepidocrocite and goethite in

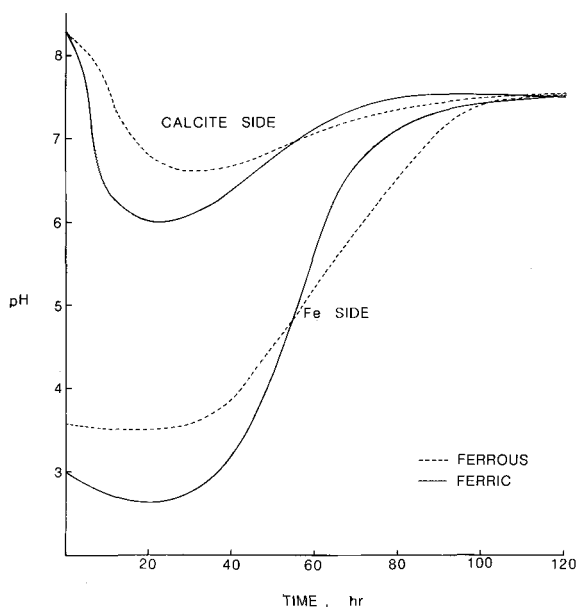


Figure 3. Plots of pH vs. time for reaction in which the 0.01 M Fe(ClO₄)₃ or Fe(ClO₄)₂ phase was initially separated from the calcite phase by a semi-permeable membrane.

air and 20% CO₂ (balance air), respectively (Loeppert *et al.*, 1984). Rapid oxidation and hydrolysis of Fe²⁺ results in formation of lepidocrocite (Schwertmann and Taylor, 1977); however, the presence of high partial pressure of CO₂ leads to formation of goethite rather than lepidocrocite (Schwertmann, 1959).

Plots of pH vs. time on both sides of the dialysis membrane are shown in Figure 3 for reactions in aerated suspensions involving Fe(ClO₄)₃ and Fe(ClO₄)₂. In both experiments the suspension pH on the calcite side of the membrane remained at about 6.0–8.0 during the course of reaction, indicating that the acidic species, H⁺ and/or Fe³⁺, rapidly neutralized after they crossed the membrane. The pH of the Fe(ClO₄)₃ phase decreased from 3.0 to 2.6 and then gradually increased

Table 3. Fe phases formed during the reaction of Fe(ClO₄)₃ or Fe(ClO₄)₂ with calcite in which the Fe solution and aqueous calcite suspension are separated by a semi-permeable membrane.

Purge gas		Fe(ClO ₄) ₃ system		Fe(ClO ₄) ₂ system	
Fe ²⁺ solution	Calcite suspension	Fe solution	Calcite suspension	Fe solution	Calcite suspension
Air	Air	F ¹	N ¹	F	L ¹
20% CO ₂	Air	F	F	F	L, G ¹
Air	20% CO ₂	F	N	F	G, L
20% CO ₂	20% CO ₂	F	F	F	G, L

¹ F = ferrihydrite; N = no visible phase; L = lepidocrocite; G = goethite.

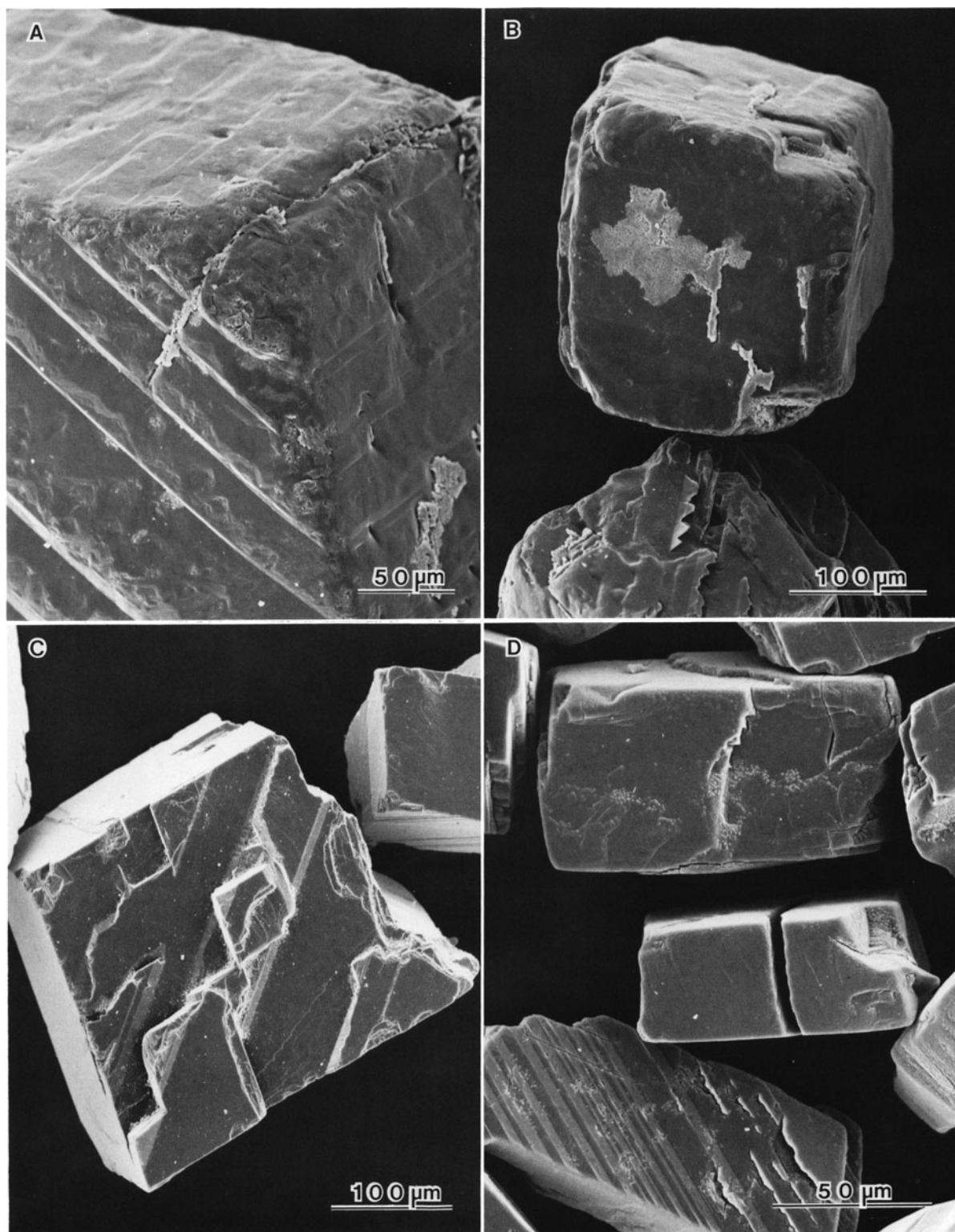


Figure 4. Scanning electron micrographs of calcite following the reaction of $\text{Fe}(\text{ClO}_4)_2$ with Iceland spar calcite when using air as the purge gas. C = water-washed calcite. D = Calcite treated under steady-state conditions with aqueous HCl at pH 5.5.

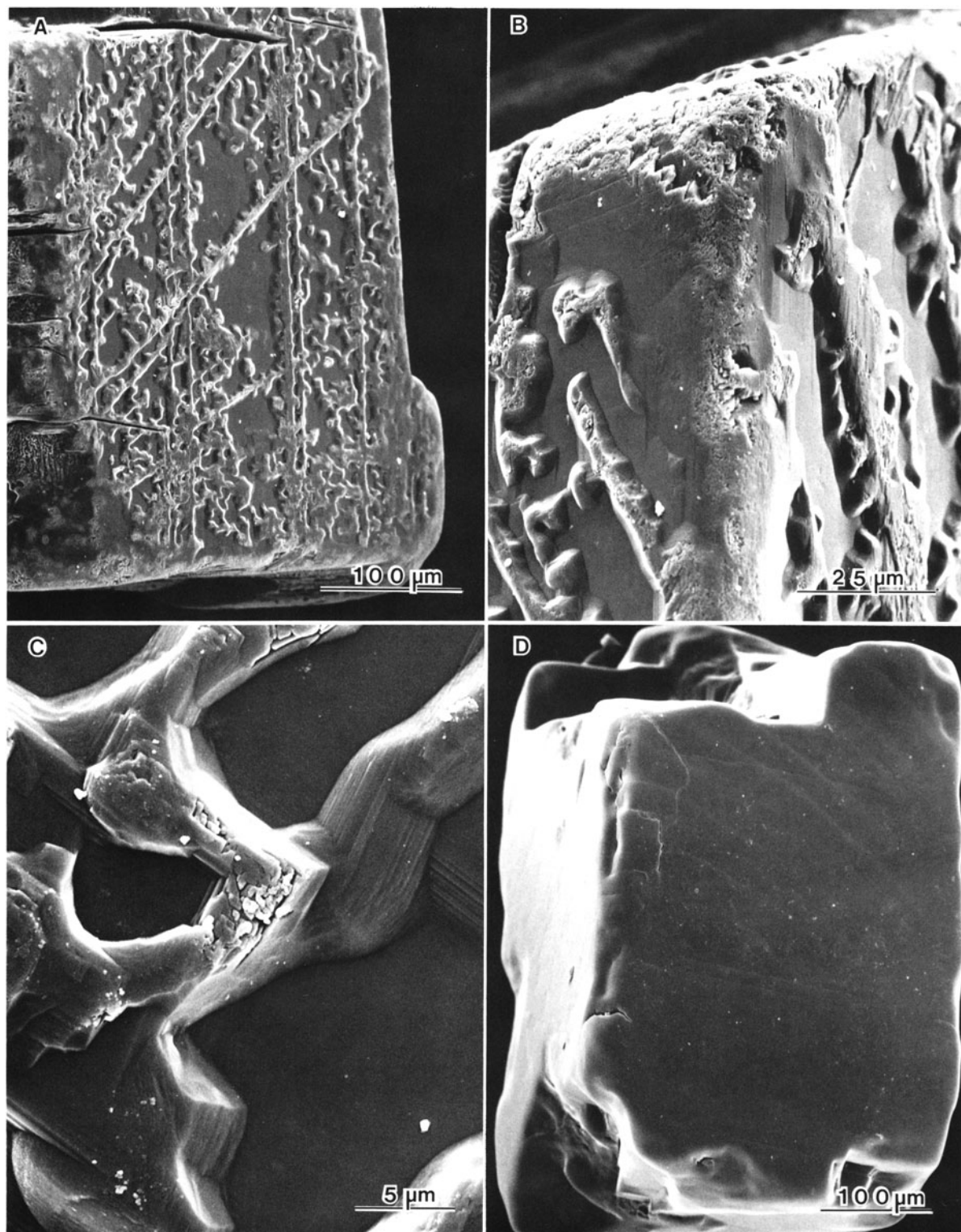


Figure 5. Scanning electron micrographs of calcite following the reaction of $\text{Fe}(\text{ClO}_4)_3$ with 40–60 mesh Iceland spar calcite when using air as the purge gas. D = calcite treated under steady-state conditions with aqueous HCl at pH 3.0.

to 7.5 as the Fe^{3+} was completely neutralized. The initial decrease in pH may have been due to the release of H^+ during the hydrolysis of Fe^{3+} species and indicates that on the Fe side of the membrane auto-hydrolysis occurred at a faster rate than neutralization. In contrast, the pH of the $\text{Fe}(\text{ClO}_4)_2$ phase did not decrease appreciably from an initial value of 3.5, indicating that rate of auto-hydrolysis did not exceed the rate of neutralization on the Fe side of the membrane. Prior to complete neutralization and equilibration, the Fe and calcite phases predominantly controlled the pH on their respective sides of the membrane.

The concentration of Fe^{3+} on the Fe side of the membrane in the $\text{Fe}(\text{ClO}_4)_2$ system should have been low compared to that expected for the $\text{Fe}(\text{ClO}_4)_3$ system due to the slow rates of oxidation expected in the observed pH range of 3.5 to 4.5 for the former (Stumm and Morgan, 1971). In the $\text{Fe}(\text{ClO}_4)_2$ system, polymerization of Fe^{3+} species on the Fe side of the membrane was much less likely. In actual fact, however, only traces of Fe oxide were observed. On the other hand, the oxidation of Fe^{2+} should have been much more rapid at pH 6.0 to 7.0 such as was observed on the calcite side of the membrane. Therefore, the Fe-oxide precipitation was more likely on the calcite side of the membrane than on the Fe side.

Morphology of the calcite phase as influenced by reaction with Fe perchlorates

Scanning electron micrographs of treated calcite corroborate the suggestion that the reactive surface area may have increased as a result of the reaction of the calcite with solution phase Fe. The surface of the 40–60-mesh calcite treated with $\text{Fe}(\text{ClO}_4)_2$ and air as the purge gas (Figure 4A, 4B) was rougher and more pitted than the surface of the water-washed sample (Figure 4C). Also, corners and edges were noticeably rounded. The treated sample remained partially coated with patches of Fe oxide, which were identified by XRD as lepidocrocite with a trace of goethite. A calcite sample treated with HCl under steady-state conditions at pH 5.5 to dissolve 10% of the crystal mass (Figure 4D) had a comparatively smooth surface and slightly rounded corners. This pH was selected because it was comparable to the reaction pH of the $\text{Fe}(\text{ClO}_4)_2$ /calcite system (Loeppert *et al.*, 1983a). The relatively rougher and more uneven surface of the Fe-treated sample may have been due to the irregular FeOOH coating (Figures 1 and 2) which may have retarded the movement of the products of carbonate dissolution, i.e., Ca^{2+} , HCO_3^- , CO_3^{2-} , and OH^- , from the surface and Fe monomers and H^+ toward the surface.

Calcite treated with $\text{Fe}(\text{ClO}_4)_3$ showed a distinct mosaic pattern with pronounced channels (Figures 5A, 5B). Crystal edges and corners were slightly rounded following treatment; however, distinct stepped dislocations (Burton *et al.*, 1951) were present in the walls

of the channels, and a featureless and generally flat channel floor (Figure 5C) was noted.

The ridges were significantly more pitted than the flat channel surface (Figure 5B, 5C). Iron oxide was readily dispersed from the calcite surface during the agitation process; however, the traces of oxide that remained were primarily on the ridges of the mosaic surface. From the above observations and from the general appearance of the crystal surface, on which the ridges of the mosaic pattern are commonly along cleavage planes of the calcite, the initial precipitation of X-ray-amorphous Fe oxide occurred along crystal defects and crystal edges and corners, thus protecting these surfaces from rapid dissolution and resulting in comparatively more rapid dissolution of the uncoated areas. Continued hydrolysis and polymerization to form poorly crystalline ferrihydrite probably occurred at these regions of Fe oxide accumulation, thereby blocking the surface and retarding dissolution of the calcite.

Dissolution in the channels took place predominantly by a surface-controlled, stepped-dislocation process rather than by a diffusion-controlled mechanism (see Burton *et al.*, 1951; Berner and Morse, 1974), although both processes were probably involved in dissolution of the crystal. The probability of a surface-controlled dissolution process is corroborated by the distinct stepped dislocations in the walls of the channels. In contrast, a typical diffusion-controlled dissolution pattern, in which 10% of the calcite crystal was dissolved under steady-state conditions at pH 3.5, is shown in Figure 5D. Diffusion-controlled dissolution resulted in pronounced rounding of corners and edges.

CONCLUSIONS

The reaction between the Fe salt and the calcite was stoichiometric, i.e., 2 and 3 equivalents of CaCO_3 were consumed per mole of Fe^{2+} and Fe^{3+} , respectively. Calcite served as a sink for the protons produced during the reaction; however, it is likely that the precipitation of Fe oxides originating from Fe^{2+} and Fe^{3+} in calcite suspensions occurred by different mechanisms. In the $\text{Fe}(\text{ClO}_4)_3$ system, following initial reaction at the calcite surface, continued hydrolysis and polymerization of the poorly crystalline ferrihydrite occurred at a finite distance from the surface.

Hydrolysis of Fe^{3+} probably occurred by auto-hydrolysis and polymerization with a resulting release of H^+ . This mechanism is corroborated by the reduction in pH during reaction in both the bulk studies (Loeppert *et al.*, 1984) and the dialysis results. Also, the neutralization of acidic Fe species most probably occurred by a reaction with the basic products of calcite dissolution rather than by a direct reaction with the calcite surface. This hypothesis is supported by the distinct step-dislocations on the surface of calcite, which are indicative of a surface-controlled dissolution rather than an attack by an acidic species. Also, in experi-

ments in which the calcite and Fe salt were separated by a semi-permeable membrane, precipitation occurred predominantly on the Fe side of the membrane. The partially hydrolyzed polymeric Fe species have a large diameter and slow mobility which would retard both the rate of attack of the calcite surface and the rate of movement through the semi-permeable membrane.

In the Fe(ClO₄)₂ system, crystalline iron oxides were formed by hydrolysis of Fe species at the calcite surface or in the solution, followed by attachment to existing FeOOH nuclei. The possibility that Fe species may have reacted directly with the calcite surface is supported by the rounded surface which is indicative of a diffusion-controlled reaction rather than a surface-controlled dissolution of calcite. Polymerization did not play as important a role in the crystallization process as it did in the Fe(ClO₄)₃ system. In the Fe(ClO₄)₂ system, growth most likely occurred by the addition of Fe²⁺ and/or Fe³⁺ or partially hydrolyzed monomers or oligomers to existing nuclei. Specific Fe-oxide phases were largely determined by the partial pressure of CO₂ of the purge gas.

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REFERENCES

- Berner, R. A. and Morse, J. W. (1974) Dissolution kinetics of calcium carbonate in sea water. IV. Theory of calcite dissolution: *Amer. J. Sci.* **274**, 108–134.
- Burton, W. K., Cabrera, N., and Frank, F. C. (1951) The growth of crystals and the equilibrium structure of their surfaces: *Royal Soc. London Philos. Trans. A-243*, 299–358.
- Garrels, M. and Christ, C. L. (1965) *Solutions, Minerals and Equilibria*: Freeman, Cooper and Company, San Francisco, 450 pp.
- Loeppert, R. H., Jackman, J. M., and Melton, J. R. (1983b) Dissolution of calcite under steady-state conditions: *Soil Sci. Soc. J.* (in press).
- Loeppert, R. H., Hossner, L. R., and Amin, P. K. (1984) Formation of ferric oxyhydroxides from ferrous perchlorate in stirred calcareous systems: *Soil Sci. Soc. Amer. J.* **48**, 677–683.
- Plummer, L. N., Wigley, T. M. L., and Parkhurst, D. L. (1978) The kinetics of calcite dissolution in CO₂-water systems at 5° to 60°C and 0.0 to 1.0 atm CO₂: *Amer. J. Sci.* **278**, 179–216.
- Schwertmann, U. (1959) Über die Synthese definierter Eisenoxyde unter verschiedenen Bedingungen: *Z. Anorg. Allg. Chem.* **298**, 337–348.
- Schwertmann, U. and Taylor, R. M. (1977) Iron oxides: in *Minerals in Soil Environments*, J. B. Dixon and S. B. Weed, eds., Soil Science Society of America, Madison, Wisconsin, 145–180.
- Stumm, W. and Morgan, J. J. (1970) *Aquatic Chemistry*: Wiley-Interscience, New York, 583 pp.

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Резюме— Железный или железистый перхлорат, 0,01 М, реагировал с кальцитом в мешаемых водных суспензиях, которые сильно пузырились при помощи окисляющего продувального газа. Два и три эквиваленты CaCO₃ растворялись на моль Fe²⁺ и Fe³⁺, соответственно. При использовании Fe(ClO₄)₂, кристаллические продукты окиси Fe частично покрывали поверхность кальцита. При использовании воздуха или 20% CO₂ (балансированный воздух) как продувального газа главными продуктами являлись лепидокрокит и гетит. После реакции с Fe²⁺ края и ребра кристаллов кальцита являлись в общем закругленными, а грани были неоднородно изрыты; однако после реакции с Fe³⁺ на поверхности кальцита была очевидна мозаичная структура с отчетливыми гребнями и бороздами. Эти гребни были до некоторой степени изрыты, но отчетливые ступенчатые дислокации присутствовали, ведя к борозде, лишенной характерных черт и в общем с плоской поверхностью. Когда кальцит сепарировался из раствора Fe через полупропускаемую мембрану, осаждение происходило в основном на кальцитовой стороне и Fe стороне мембраны в системе Fe²⁺ и Fe³⁺, соответственно.

Fe оксигидроксиды осаждались из растворов Fe(ClO₄)₃ и Fe(ClO₄)₂ путем различных механизмов. В системе Fe(ClO₄)₃, хотя начально реакция могла происходить на поверхности кальцита, большая часть слабо выкристаллизованного ферригидрита формировалась путем гидролиза полимеров Fe в суспензии. Нейтрализация, более вероятно, случалась путем реакции с основными продуктами поверхностно-контролируемого растворения кальцита, чем путем прямой реакции кислотных полимеров с поверхностью кальцита. В системе Fe(ClO₄)₂, лепидокрокит и гетит формировались путем частичного гидролиза Fe²⁺ или Fe³⁺ в реакции с кальцитом или с основными продуктами растворения кальцита и последующего осаждения простых веществ Fe на существующим ядре FeOOH. [E.G.]

Resümee—0,01 m Fe(II)- oder Fe(III)-Perchlorat wurde mit Calcit in gerührten, wässrigen Suspensionen, die heftig mit einem oxidierenden Spülgas durchperlt wurden, zur Reaktion gebracht. Zwei bzw. drei Äquivalente CaCO_3 wurden pro Mol Fe^{2+} gelöst bzw. Fe^{3+} neutralisiert. Im Fall von $\text{Fe}(\text{ClO}_4)_2$ überzogen die kristallinen Eisenoxid-Produkte z.T. die Calcitoberfläche. Die vorherrschenden Produkte waren Lepidokrokit bzw. Goethit, je nachdem, ob das Spülgas Luft war oder 20% CO_2 (Rest=Luft). Nach der Reaktion mit Fe^{2+} waren die Kanten und Ecken der Calcitkristalle im allgemeinen gerundet und die Flächen ungleichmäßig mit Löchern überzogen; nach der Reaktion mit Fe^{3+} zeigte sich jedoch ein Mosaikartiges Muster mit deutlichen Graten und Kanälen. Die Grate waren löchrig, aber einzelne stufige Verzerrungen waren vorhanden, was zu einem Relief-losen und im allgemeinen flachen Kanalboden führte. Wenn der Calcit von der Fe-Lösung durch eine semipermeable Membran getrennt wurde, trat eine Ausfällung vor allem auf der Calcitseite bzw. auf der Eisenseite der Membran in dem Fe^{2+} - bzw. Fe^{3+} -System ein.

Fe-Oxyhydroxide fielen aus $\text{Fe}(\text{ClO}_4)_3$ - und $\text{Fe}(\text{ClO}_4)_2$ -Lösungen durch verschiedenen Mechanismen aus. Im $\text{Fe}(\text{ClO}_4)_3$ -System wurde der Hauptteil des schlecht kristallisierten Ferrihydrites durch Hydrolyse von Fe-Polymeren in Suspension gebildet, obwohl der Beginn der Reaktion wahrscheinlich auf der Calcitoberfläche stattgefunden hat. Die Neutralisierung fand eher bei der Reaktion mit basischen Produkten einer Oberflächen-kontrollierten Auflösung des Calcites und weniger durch eine direkte Reaktion des sauren Polymers mit der Calcitoberfläche statt. Im $\text{Fe}(\text{ClO}_4)_2$ -System bildeten sich Lepidokrokit oder Goethit durch die teilweise Hydrolyse von Fe^{2+} oder Fe^{3+} bei der Reaktion mit Calcit oder mit den basischen Produkten der Calcitauflösung und durch die darauffolgende Ausfällung von einfachen Fe-Verbindungen auf existierenden FeOOH -Keimen. [U.W.]

Résumé—De la perchlorate ferreuse ou ferrique, 0,01 M, a été réagie avec de la calcite dans des suspensions aqueuses melangées qui ont été vigoureusement boillonnées avec un gaz à purge oxidant. Deux et trois équivalents de CaCO_3 ont été dissous par môle de Fe^{2+} et Fe^{3+} neutralisés, respectivement. Avec $\text{Fe}(\text{ClO}_4)_2$, les produits d'oxide Fe cristallin recouvraient partiellement la surface calcite. Les produits dominants étaient la lépidocrocite et la goethite lorsque le gaz purgeant était l'air ou 20% CO_2 (le reste étant de l'air), respectivement. Après la réaction avec Fe^{2+} , les bords et les coins des cristaux de calcite étaient généralement marqués non-uniformément; après la réaction avec Fe^{3+} , cependant, un cliché mosaïque avec des arêtes et des canaux distincts était évident sur la calcite. Ces arêtes étaient quelque peu trouées, mais des dislocations à marches distinctes étaient présentes menant à un lit de canal terne et généralement plat. Lorsque la calcite était séparée de la solution Fe par une membrane semi-perméable, la précipitation s'est produite de façon prédominante du côté de la calcite et du côté Fe de la membrane dans les systèmes Fe^{2+} et Fe^{3+} , respectivement.

Des oxyhydroxides Fe se sont précipitées à partir des solutions $\text{Fe}(\text{ClO}_4)_3$ et $\text{Fe}(\text{ClO}_4)_2$ par des mécanismes différents. Dans les systèmes $\text{Fe}(\text{ClO}_4)_3$, quoique la réaction initiale ait pu être à la surface de la calcite, la plupart de la ferrihydrite pauvrement cristallisée a été formée par hydrolyse des polymères Fe en suspension. La neutralisation s'est produite par réaction avec les produits de base d'une dissolution de calcite contrôlée à la surface, plutôt que par réaction directe de polymères acides avec la surface calcite. Dans le système $\text{Fe}(\text{ClO}_4)_2$, la lépidocrocite ou la goethite a été formée par hydrolyse partielle de Fe^{2+} ou Fe^{3+} par réaction avec la calcite ou les produits de base de la dissolution calcite et la précipitation subséquente d'espèces Fe simples sur des noyaux FeOOH existants. [D.J.]