Calcite Supersaturation and Precipitation Kinetics in the Lower Colorado River, All-American Canal and East Highline Canal

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INTRODUCTION

Predictions of calcium and alkalinity levels in rivers flowing through arid lands are particularly important for municipal and agricultural uses alike. The objectives of this investigation were to determine the state of calcite saturation in the lower Colorado River system and whether CaCO₃ precipitation occurs, and, if so, whether it affects downstream water chemistry.

The irrigation of agricultural lands under conditions of minimized leaching [van Schilfgaarde et al., 1974] reduces the total salt load of the drainage water, producing, in particular, less Ca and alkalinity after ion exchange equilibrium is established in the root zone. The effect that this will have on downstream water quality depends in part on the extent to which calcium carbonate precipitates in arid land river systems. Assuming chemical equilibrium in the river receiving the drainage water, Suarez and Rhoades [1977] evaluated the effects of reduced leaching for specific water types.

Earlier studies have shown evidence of rapid precipitation for supersaturated spring waters upon CO₂ degassing [Barnes, 1965; Jacobson and Udistowski, 1975]. However, calcium carbonate precipitation from supersaturated waters may not be a rapid process. Back and Hanshaw [1970] observed calcite supersaturation in Florida groundwaters. Suarez [1977] found that the drainage waters beneath irrigated lands were supersaturated with respect to calcite, with a mean ion activity product (IAP) value of 10⁻⁸.₄₇ [Jacobson and Langmuir, 1974]. Also, precipitation of CaCO₃ in the Wellton-Mohawk Drainage Canal does not occur despite more than tenfold calcite supersaturation in the 20-km section examined [Suarez, 1976]. It thus appears that waters with a short residence time (hours-weeks) may not precipitate calcium carbonate as theoretically predicted. The present study was undertaken to determine the downstream compositional changes that result from mixing drainage waters from the Palo Verde Project back into the Colorado River.

Drainage waters in the Palo Verde Project and the Colorado River from Parker Dam to Yuma and the All-American Canal and East Highline Canal were analyzed to ascertain if measurable precipitation of CaCO₃ occurs in agricultural drainage waters during conveyance to, or after mixing with, the Colorado River. Figure 1 shows the geographical location of the study area.

Above the Palo Verde Valley, water flow in the lower Colorado River ranges from 9.8 x 10⁶ to 220 x 10⁶ m³ yr⁻¹ [Irelan, 1971]. The climate is dry and warm, with mild winters (occasional frosts) and hot summers (commonly ≥38°C or higher at midday). Rainfall of about 7.5-13 cm yr⁻¹ derives from either local summer thunderstorms or gentle winter rain. The river cuts into mostly reworked alluvial sediments with outcrops of resistant igneous and metamorphic rock in isolated stretches. No saline deposits have been detected in this region [Metzger et al., 1971]. Groundwater recharge below Parker Dam is quite low and consists mostly of irrigation drainage. There are numerous washes along this stretch of the river, but they supply insignificant quantities of water and only during large storm events. Siltation in the river has been extensive. The river is generally less than 1 m deep (with numerous sandbars), and at low flow, water meanders within the channel.

PROCEDURE

River Sampling Study

River locations and mileages were taken from the Bureau of Reclamation Colorado River maps. The starting point for this study, kilometer 0.0, corresponds to mile 240 on the Bureau maps and is just south of Needles, California. The Colorado River was sampled initially on February 7-8, 1977, to evaluate diurnal fluctuations in CO₂ and pH during the winter. River water samples were collected above the Palo Verde Drain at kilometer 215 just north of Horace Miller Park. Over a 24-hour period, a total of 18 samples were taken at a depth of 10 cm and 1 m out in the river from the bank. A few samples were taken at the surface and at a depth of 50 cm. In situ pH (±0.01) was continuously measured, 1 m out from the riverbank, with a Beckman Expandomatic connected to an Omniscibe chart recorder. One portion of each water sample was immediately
filtered through a 0.1-μm Millipore filter using 0.5% CO₂ gas in the pressure filtration unit and then immediately acidified with HCl. Another portion was directly acidified, and the third was left untreated. All samples were placed in polystyrene bottles previously acid cleaned and rinsed with distilled water. The untreated samples were placed in bottles filled to the top, immediately capped, and placed in a cooler (±20°C). Water temperatures were also recorded at the times of collection. Most alkalinity titrations were made immediately on filtered and unfiltered samples. Some alkalinity titrations were made on the refrigerated samples within 6 hours. There were no differences, indicating that the temperature reductions and capping procedures prevented precipitation after collection. Dissolved oxygen in the river water was measured occasionally using a Yellow Springs model 51A oxygen meter. Measurements of specific conductance of the water were also made.

The Colorado River, Palo Verde Drain, All American Canal, and East Highline Canal were sampled extensively during the week of March 7, 1977. The sampling procedure was similar to that described above. The Orion model 451 pH meter was calibrated (±0.001) at field water temperatures using temperature-corrected pH buffers (6.00, 6.86, 7.00). The river was sampled from a boat in the center of the river at various locations between km 179 and km 207 (Imperial Dam). Other samples of the river and all canals and drain samples were taken near the edge. Samples were taken by boat near both banks of the river, beginning just downstream from the Pago Verde Drain and continuing downstream until the river was relatively well mixed, as determined from specific conductance measurements.

A summer sampling of the river was carried out September 19–21, 1977, at the same sites as before. The summer data cycle was evaluated by sampling the river for 24 hours on September 19–20. The samples were collected by the procedure described previously.

Analyses of Ca and Mg were performed by atomic absorption with addition of Na to the samples to prevent interferences [Brown et al., 1970]. Na and K were determined directly by atomic absorption [Brown et al., 1970]. Alkalinity was determined by titration, Cl by potentiometric titration with an American Instruments chloride titrator, SO₄ by the BaSO₄ turbidimetric procedure [American Public Health Association, 1955], and NO₃ by direct measurement with an Orion solid-state NO₃-specific electrode.

Thermodynamic calculations of ion activities are based on the use of an extended Debye-Hückel equation [Truesdell and Jones, 1974] and correction for ion pairs considering temperature-dependent dissociation constants [Stauffer, 1977]. As a check on the degree to which Ca is complexed in the river, Ca²⁺ activities (calculated as aₐₐ) were determined directly with an Orion Ca²⁺ specific electrode on the samples collected in March 1977 (in addition to calculation of aₐₐ). From total Ca by correction for activity coefficients and complexing, direct measurements were made to ensure that the calculated Ca²⁺ activity values were not in error due to possible complexing by organic species. The measured values are somewhat different and on the average slightly lower (4%) than the calculated ones (data not shown). The difference for any given sample is within the precision of the Ca electrode (±15%) error. The calculated Ca²⁺ activity values are considered accurate and were used for
calculation of degree of calcite supersaturation. Use of electrode-measured Ca\(^{2+}\) activities would not significantly change the results.

Precipitation Rate Study

Plummer et al. [1979] pointed out that calcite dissolution experiments at low P\(_{\text{CO}_2}\) will result in CO\(_2\) dis-equilibrium if the rate of dissolution exceeds transport of CO\(_2\) across the air-liquid interface and CO\(_2\) hydration. They observed that in dissolution experiments at 3 x 10\(^{-3}\) atm P\(_{\text{CO}_2}\) where PH\(_{\text{H}_2\text{CO}_3}\) changes were recorded (free drift method). Additionally, they observed slow removal of H\(_2\text{CO}_3\) from solution for PH\(_{\text{H}_2\text{CO}_3}\) > 70 (production of CO\(_2\) during dissolution) in experiments in which PH\(_{\text{H}_2\text{CO}_3}\) was controlled by addition of acid (PH-stat method).

Despite potential experimental complexities, precipitation kinetic studies on river water require low P\(_{\text{CO}_2}\) experiments, because rivers are at low P\(_{\text{CO}_2}\). At high P\(_{\text{CO}_2}\), Colorado River water is undersaturated instead of supersaturated. In order to properly simulate river conditions, experimental PH\(_{\text{H}_2\text{CO}_3}\) and P\(_{\text{CO}_2}\) values should match field values.

Under most natural conditions, PH\(_{\text{H}_2\text{CO}_3}\) ranges between 6.8 and 8.5, and HCO\(_3^-\) is the predominant carbonate ion. For these conditions the calcite precipitation reaction can be written as follows:

\[
\text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2\]

Previous precipitation experiments used free drift methods; thus P\(_{\text{CO}_2}\) increased during the reaction, as was pointed out by Plummer et al. [1979]. Fortunately, precipitation experiments can be conducted at low P\(_{\text{CO}_2}\) under fixed conditions using the PH-stat method. In this study I used Na\(_2\text{CO}_3\) as the titrant in this reaction.

\[
2\text{Na}_2\text{CO}_3 + \text{CO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Na}_2\text{CO}_3 + 2\text{H}_2\text{O} + \text{CO}_2\]

The Na\(_2\text{CO}_3\) was prepared in CO\(_2\)-free water with a specific conductivity of <0.05 μmhos/cm -1. The titrating container was completely filled with solution, minimizing the gas phase. Also, the back-pressure to the titrant container was connected to an aseptic trap to remove incoming CO\(_2\). This procedure enables PH control by replacement of the precipitated CO\(_2\); thus H\(_2\text{CO}_3\) and P\(_{\text{CO}_2}\) remain constant.

Filtered (0.1 μm) and unfiltered Colorado River water samples were collected from the Ati- American Canal and stored at 2°C. Solutions were analyzed for major species as described earlier. Orthophosphate was analyzed in 0.10-μm filtered and unfiltered samples. A synthetic phosphate-free water was prepared which had the same major ion composition and PH, and thus the same P\(_{\text{PO}_4}\), Na\(_2\text{CO}_3\), and CaCO\(_3\) IAP as Colorado River water. Additionally, Ca-HCO\(_3\)-Cl water was prepared which had the same Na\(_2\text{CO}_3\), P\(_{\text{CO}_2}\), and CaCO\(_3\) IAP.

The Brinkman E52-ES65 PH stat was calibrated within ±0.01 pH units of the reference buffers. All experiments were run in a temperature-controlled room in a temperature-controlled stirrer apparatus (±0.2°C). A Teflon stir bar was rotated at 100 rpm. Precipitation rates were independent of stirring rate. This is consistent with the observations of Plummer et al. [1978] that only at PH ≤ 5 do stirring rates affect reaction rates. The initial solution pH values were adjusted between 8.20 and 8.50 by varying the P\(_{\text{CO}_2}\). Solutions (usually 20 ml) were maintained with the PH stat at the initial pH values. Negligible amounts of Na\(_2\text{CO}_3\) were required to stabilize the pH at the desired level. Calcite seed material, washed with distilled water and then dried, was subsequently added to the solution. Different concentrations of Na\(_2\text{CO}_3\) (5 and 10 mmol 1\(^{-1}\) ) and quantities of calcite (0.05 to 0.2 g) were used to ensure that the PH-stat could maintain constant PH during runs. Experiments at different PH values were conducted with Colorado River water, synthetic Colorado River water, Ca-HCO\(_3\)-Cl water, filtered Colorado River water, synthetic Colorado River water spiked with phosphate, and Ca-HCO\(_3\) waters. Additional runs were made in which calcite was not added; negligible amounts of Na\(_2\text{CO}_3\) were titrated.

Calcite surface area was determined on Mallinckrodt reagent grade CaCO\(_3\) previously washed in distilled water to remove fine material. Preliminary wet sieving removed all >100-μm particles; subsequent washing and decanting removed all material less than 20 μm in size. The calcite was subsequently resuspended in distilled water, and hydrometer measurements were continuously taken during settling. These readings allowed calculation of particle size in 2-μm intervals. For each interval, a surface area was calculated by assuming rhombohedral particles and multiplying by the particle frequency in that interval. Total surface area was calculated by summing the surface areas in each size fraction. Sixty percent of the particles were within the range 25-35 μm in size. The average surface area of the material was calculated at 0.070 mm\(^2\) g\(^{-1}\). There was excellent agreement between dissolution rates using this material and dissolution rates observed with coarser wet-eroded calcite from lookout spur (data not shown).

Discussion

River Diurnal Fluctuation

Schmolz and Swanson [1969] noted that carbonate supersaturation of ocean surface waters could be explained by the chemical CO\(_2\) cycle. They suggested that the ratio of CO\(_2\) could exist between the most soluble calcium carbonate phase present and the water at the highest CO\(_2\) level. During the daytime at low CO\(_2\) levels, the ocean surface waters were supersaturated, but at the same Ca and alkalinity levels as during the nighttime. We needed to determine if the Colorado River is at CaCO\(_3\) equilibrium at night and if precipitation is occurring during the day. If CaCO\(_3\) does not precipitate during daylight hours when the water is most supersaturated with respect to calcium, it can be safely assumed that precipitation occurs during the entire 24-hour period.

Analyses of the Colorado River samples collected at km 215 in February 1977 indicate that the chemical composition was uniform with time. Diurnal fluctuations in P\(_{\text{CO}_2}\) were relatively small, with values close to the atmospheric level, 3 x 10\(^{-4}\) atm. The minimum P\(_{\text{CO}_2}\) of 0.34 x 10\(^{-4}\) atm occurred at 1905; the maximum P\(_{\text{CO}_2}\) of 7.19 x 10\(^{-4}\) atm occurred at 0330 (see Figure 2). Maximum P\(_{\text{CO}_2}\) occurs just before daylight. Apparent, low water temperatures during winter limit bacterial respiration, and large amounts of suspended sediment limit algal photosynthesis; hence CO\(_2\) levels are low, and diurnal fluctuations are small. Even though P\(_{\text{CO}_2}\) and PH fluctuated slightly over the 24-hour period, Ca and HCO\(_3^-\) levels remained quite constant as shown in Figure 2. The river was supersaturated with respect to calcium throughout the 24-hour period.

Determined values for PH (log IAP) and, thus degree of river supersaturation with CaCO\(_3\), varied diurnally with P\(_{\text{CO}_2}\); however, there was no evidence of CaCO\(_3\) precipitation, such as loss of Ca. Samples with the highest pH and lowest PHstat values, 7.41-7.73, showed no evidence of CaCO\(_3\) precipitation (no decreases in Ca or alkalinity) despite the increased degree of
super saturation. The river was at or near saturation with CO₂ during the entire cycle, indicating good aeration (data not given).

Partial analyses of samples collected in September 1977 at the same location are given in Figure 1. There was some variation in the composition of the river with time. The chloride concentration (shown in Figure 3) was lowest between 2200 and 0300. Based on depth measurements made in the river, maximum flow in the river occurred at least 8 hours before the time of the maximum chloride concentration. Releases from Parker Dam are made in a daily cyclical manner, primarily to generate hydroelectric power at times of peak demand. Downstream from Parker Dam, the Poston Drain (drainage return flow from the Colorado River Indian Irrigation Project) enters the Colorado River at km 1380.8. The lowest chloride value would be expected to occur at maximum flow (when there is the largest amount of upstream dilution) immediately below the drain. Within the 64 km distance between the Poston Drain and our sampling site, however, the pulse of water moves ahead of the river (and salinity front). Consistent with this salinity pulse being caused by a mixture of drainage water with the river, the fluctuations in alkalinity (shown in Figure 3) mirror the changes in chloride. Figure 3 shows a sharp decrease in CO₂ after 0600 due to the onset of photosynthesis at sunrise. The decrease in CO₂ between 0600 and 1400 would cause a similar decrease in HCO₃⁻ if precipitation were occurring. As shown in Figure 1, alkalinity did not drop during these hours. CO₂ levels fluctuated between 1.12 and 249 x 10⁻³ atm. These values are about 4 times the atmospheric value but still relatively low and quite constant. It appears that the large amounts of suspended sediments in the river reduce photosynthesis by algae. The higher level of CO₂ in the summer is interpreted as the result of higher temperatures which allow for higher rates of bacterial respiration.

The pH values obtained for the summer cycle, shown in Figure 1, ranged from 7.70 to 7.93, indicating supersaturation throughout the 24-hour cycle. The level of supersaturation in the summer months was thus lower than in winter, because of higher CO₂ levels in the summer. The highest extent of supersaturation occurred during the afternoon (around 1500 to 1800) for both winter and summer. No corresponding decrease of alkalinity or Ca were observed during that interval. Apparently, the diurnal change in the CO₂ level in the river is insufficient to cause CaCO₃ precipitation or a daily precipitation-dissolution cycle between Parker Dam and the Palo Verde Drain.

Downstream River Composition

Partial results of the March 1977 samplings of the Colorado River waters are given in Figures 4 and 5. Sample 1 (km 7.1), sample 2 (km 4.38), and sample 3 (km 6.9) were taken along the edge of Lake Havasu, and sample 4 was taken at Parker Dam, km 76.8. The estimated residence time of water in Lake Havasu is approximately 2 months (Slawson, 1972). On the basis of these limited data, CaCO₃ precipitation in Lake Havasu under winter conditions was not detected. The minimum daytime-CO₂ level is expected to be considerably lower in the summer, and CO₂ might be sufficiently depleted in the surface waters to cause precipitation. The sample taken at Parker Dam was likely more representative of the entire lake than the first three samples from shore.

The data in Figure 4 show the effect of additions of Palo Verde drainage water to the Colorado River (at km 242.6). Downstream from the drain, samples were taken from the east and west banks of the river at each of several sampling locations along the river (drainage water is indicated by open triangles in Figures 4 and 5) until no differences in specific conductance between the east and west banks were observed.

Figure 4 shows the CO₂ concentrations in the Colorado River, All-American Canal, and East Highline Canal on March 8-9,
1977. The values given in the figure correspond to the concentrations at those locations. High Cl values at km 243.5 to km 251 correspond to samples of the Palo Verde Drain. Cyclic fluctuations of the pH are due to downstream from the Palo Verde Drain reflect the changes in the relative proportions of Palo Verde Drain water to upstream Colorado River water, whose flow is controlled by the daily cyclic water release from Parker Dam. Fluctuations below Parker Dam (km 768) and above the Palo Verde Drain reflect inputs of small volumes of water from the Poston Drain at km 1308. Concentrations of Na, Mg, K, SO₄, and NO₃ were 4.50-5.92, 1.23-1.14, 9.123-0.131, 3.05-3.69, and 0.083-0.125 mmol/L respectively.

Fluctuations in pH, FCO₂, and pALP for the first three samples are due to inability to properly sample the river from the banks as indicated earlier. The pH levels were lower in the drain waters than in the river; FCO₂ levels and all other dissolved species were higher in the drain waters, as expected. The small fluctuations in Cl, alkalinity, and Ca downstream from the Palo Verde Drain (Figure 4) coincided, as did pH (Figure 5). The pH values were determined during the day so the fluctuations downstream reflect changes in the relative proportion of drain water to river water and not the diurnal CO₂ cycle. Similar fluctuations in the ion activity product $a_{CO_3}^2 - a_{HCO_3}^-$ were found (see Figure 5). The reactive degree of saturation of CaCO₃ increased in the river immediately below the Palo Verde Drain and then depended on the proportion of drainage to river water.

Despite the lack of further inputs to the river below the Palo Verde Drain, the level of calcite saturation showed no evidence of decreasing downstream from the drain, a distance of 220 km (Figure 5). The calcium and alkalinity concentrations also indicate no measurable precipitation. There was also no measurable suspended CaCO₃ in the river, on the basis of analyses of filtered and unfiltered samples. X-ray analyses of the filters revealed the presence of calcite in suspension when large quantities of water were passed through the filters from samples that had a high turbidity and high suspended solids. Montmorillonite and quartz were abundant on these filters. Filters from waters with low suspended load did not have X-ray detectable calcite (or any other carbonate phase) despite filtering of large quantities of water (about 2 L in some instances). It is concluded that suspended calcite, when present, was not a fresh chemical precipitate but part of the sediment load of the river. The presence of suspended calcite is expected, since the soils in the region contain abundant calcite.

The relative proportion of upstream Colorado River water and Palo Verde drainage making up each downstream water sample can be calculated from the chloride concentrations of upstream water, downstream water, and Palo Verde drainage waters using the relationship

$$X = \frac{[Cl]_{downstream} - [Cl]_{Pardo}}{[Cl]_{drainage} - [Cl]_{Pardo}}$$

where X is the fraction of drain water in the downstream samples. Approximately 4 to 10% of the downstream Colorado River water volume consisted of Palo Verde drainage. On the basis of these percentages, expected solute concentrations were calculated for each downstream sample. Predicted minus observed concentrations for each solute were correlated to downstream distance for all samples below Palo Verde Drain. Some variation still existed; however, it was not cyclical, and there was no statistically significant correlation with distance even at the 20% confidence level. The variation was within the range ±0.06 mmol/L for all but three samples. These values correspond to less than ±2.7% of the Ca concentrations. These values, calculated from differences in concentration, are within analytical error. This is a further indication that during the winter months there is no evidence for CaCO₃ precipitation occurring in the lower Colorado River following drainage inflow.

Results of the September 1977 sampling along the lower Colorado River are shown in Figures 6 and 7. Chloride levels along the river are shown in Figure 6. Above the Palo Verde Drain at km 243 the mixing of Colorado River water and Poston Drain water can be detected by Cl fluctuations. Below
the outfall the chloride concentrations were more pronounced and dependent on the ratio of Colorado River water to Palo Verde drainage water. Sampled were collected for a short distance downstream from the Palo Verde Drain banks from opposite banks. The CaCO₃ values were higher for the drainage water (Figure 7) and fluctuated only slightly downstream. Calcium and alkalinity concentrations (Figure 6) were higher in the drainage waters than in the river; hence they increased in the river below the dam. Figure 6 shows no evidence for supersaturated CaCO₃ precipitations. As found in the westerer, the variations in Ca and HCO₃ were similar to those of Ca (Figure 6) and reflect the varying ratio of river water to drainage water. The pH value was lower for the drainage waters (more supersaturated) than the river water. The river became more supersaturated upon receiving the drainage water and remained essentially constant thereafter (see Figure 7). Thus appears that despite considerable supersaturation, CaCO₃ does not precipitate in measurable quantities in the Colorado River upon receiving irrigation drainage below Parker Dam.

**Precipitation Rate Study**

Laboratory precipitation studies provide the opportunity to examine the reasons for lack of precipitation in the river. Laboratory experiments were conducted within the pH range observed for the river. The Colorado River water used in the study was within the concentration range determined earlier. The pH was 8.27, and the following values were calculated:

\[ \text{pH} = 8.27 \]

The orthophosphate concentration in filtered Colorado River water was 10 \( \mu \text{g} \text{P} \text{L}^{-1} \). The 3h looking data for Colorado River water, synthetic Colorado River water, and the Ca-Cl-HCO₃ water are given in Figure 8. Each value represents the means of 8 to 16 replicate runs. As expected, the rate of precipitation was faster at higher pH values, lower \( \text{CaCO}_3 \) for Colorado River water the rate at pH 8.20 was \( 5.0 \times 10^{-17} \text{ mmol} \text{ L}^{-1} \text{ cm}^{-2} \). At pH 8.50 the rate, \( 2.8 \times 10^{-18} \text{ mmol} \text{ L}^{-1} \text{ cm}^{-2} \), was 38 times greater than the rate at pH 8.20. Synthetic Colorado River water increased from 0.65 \( \times 10^{-17} \text{ mmol} \text{ L}^{-1} \text{ cm}^{-2} \) at pH 8.20 to 4.20 \( \times 10^{-17} \text{ mmol} \text{ L}^{-1} \text{ cm}^{-2} \) at pH 8.50, an increase of about 6.5 times. Colorado River water precipitated at a rate of 78 and 66% of the rate for synthetic Colorado water. This reduction in rate can be explained completely by PO₄ inhibition. When 1.0 \( \mu \text{g} \text{P} \text{L}^{-1} \) of NaPO₄ was added to synthetic Colorado River water precipitation rate was slightly below those found for PO₄-free synthetic Colorado River water and Colorado River water (data not shown). It thus seems possible that some of the determined phosphate in the river water is complexed with soluble organic.

The precipitation rates for Ca-HCO₃-CI water, also given in Figure 8, were between 3 and 4 times greater than those for Colorado River water. These results are consistent with the substantial reductions in precipitation in the presence of Mg and Sr, at constant \( \text{Ca}^{+2} \) and \( \text{HCO}_3^- \), and pH (D. L. Saurer, unpublished data, 1974). Assuming Mg has as much affinity as Ca for calcium sites (Kerker, 1966) reduces expected precipitation growth rates by 40% (from calculated \( \text{Ca}^{+2} \) and \( \text{HCO}_3^- \), (values). These results show in Figure 8 indicate that most of the inhibition to crystal growth for Colorado River water is inorganic rather than organic. This is concluded from the fact that the Colorado River water and the PO₄ and organic-free synthetic Colorado River water had precipitation rates within 30% of each other and the Ca-HCO₃-CI water precipitated up to 4 times faster than Colorado River water.

The very low or nonexistent precipitation rate in the Colorado River must reflect the unavailability of clean calcite rather than inhibition by dissolved species. Calcite is abundant in the sediment but is apparently coated by precipitation-inhibiting material. As pH values higher than 8.5, is the laboratory when LAF precipitation, precipitation (heterogeneous nucleation) occasionally occurred. Fast precipitation rates in earlier field studies (Burnes, 1965; Jacobson and Usdowski, 1957) were likely due to heterogeneous nucleation.
probably algal-induced precipitation in regions of depleted CO$_2$. The calcite kinetic rate equation of Plummer et al. [1978] was used to predict precipitation rates for Colorado River water, synthetic Colorado River water, and Ca-HCO$_3$-Cl water. The following expression from Plummer et al. [1978] was used:

$$R = k_i \cdot a_{CO_2} \cdot \left( k_i - k_k \cdot a_{Ca} - k_k \cdot a_{CO_3} - k_k \cdot a_{Cl} \right)$$

where

$$k_i = k_k \cdot \frac{1}{a_{Ca}}$$

and

$$k_k = 2.0 \times 10^{-13} \text{ mole}^{-1} \text{ liter}^{-1} \text{ sec}^{-1} \text{ atm}^{-1}$$

at 25°C, $k_i = 0.051$, $k_k = 3.45 \times 10^{-12}$, $k_k = 1.18 \times 10^{-13}$, $K_k$ is the second dissociation constant of carboxylic acid, equals $10^{-1.63}$, and $K_k$ is the carbonate constant for calcite $= 10^{-4.67}$ (Plummer et al. [1978]) suggest that a value of $k_i$ of 10 to 20 times $k_k$ be used. The value $k_i = 0.51$ was used, although in the $P_{CaCO_3}$ and pH range of the present experiment its effect on $k_k$ was minor. The term $a_{CO_3}$ is the H$^+$ activity at the surface. It is assumed to be the $a_{CO_2}$ at calcite saturation where $P_{CaCO_3}$ of the surface equals $P_{CaCO_3}$ in the bulk solution. These values were calculated using a modified version of the program described by Source [1977]. $P_{CaCO_3}$ between 10 and 20 is constant and for solving the saturation values $a_{CO_2}$, $a_{Ca}$, $a_{CO_3}$, and $a_{Cl}$.

The solid curve in Figure 8 represents the calculated precipitation rates. The fit of the model to the Ca-HCO$_3$-Cl water at pH 8.20, 8.27, and 8.33 is remarkable. Experimental runs at pH 8.4 and 8.5 showed higher precipitation rates than predicted (although only by a factor of less than 2). The sharp increase in precipitation beginning at pH 8.40 is not predicted by the model.

The present data do not support the suggestion by Plummer et al. [1979] that for precipitation experiments at low $P_{CaCO_3}$, the surface $P_{CaCO_3}$ values differ from those in the bulk fluid. This was given as an explanation for the 10 to 20 times lower than predicted precipitation rates found by Reddy [1975, un-published data, 1978] (as given by Plummer et al. [1979]). In the earlier precipitation experiment (free drip), $P_{CaCO_3}$ increased during the reaction; in contrast it remained constant in the present experiment (pH-stat using Na$_2$CO$_3$). The present data are very close to predicted values at the lower pH values. If $P_{CaCO_3}$ at the calcite surface exceeded solution $P_{CaCO_3}$ it would result in observed rates dropping below predicted rates at the higher pH values (when the rates are fast). As seen in Figure 8, experimental rates were greater than predicted rates for the higher pH measurements. An additional $a_{CO_2}$, $a_{CO_3}$, back reaction term could account for the break in slope. Leakage of CO$_2$ into the Na$_2$CO$_3$ titrant was not a factor, since values of titrant pH did not change. Also, reactions with any of the Colorado River water were below those at pH 8.33 for Ca-HCO$_3$-Cl water; thus the deviations from the Plummer et al. [1978] model were not related to the quantities of Na$_2$CO$_3$ added.
Lack of measurable precipitation downstream from the lake (despite higher levels of Ca and HCO₃-) is due to short residence times and the high sediment load which limits algal photosynthesis and thus prevents sharp drops in CO₂ levels. The pH of this precipitation was not measured. However, monitoring data from the Colorado River (located close to Lake Havasu) indicates that, while the lake levels fluctuate, the pH remains relatively constant, suggesting that the alkalinization of the lake is driven by other factors such as the buffering capacity of the lake basin.

In conclusion, the algal blooms in Lake Havasu and Lake Mohave are likely influenced by a combination of factors including increased nutrient inputs from agricultural runoff, reduced flow rates, and changes in water quality due to increased temperatures and lower flow velocities. Addressing these issues would require a comprehensive management strategy focusing on both upstream prevention and downstream mitigation techniques.


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