

Effect of Global Warming on the Dissolution of Limestone

○A.K.M. Adham Akira Kobayashi

1. Introduction

Chemical dissolution of bed rock/minerals (limestone) plays a central role in determining the geochemistry of natural waters. The major source of dissolved species to natural water is the rocks coming in contact with water (Yadav and Chakrapani, 2006). The dissolution rates of limestone in CO₂ containing aqueous solutions are determined by three rate-containing processes: (1) the kinetics of dissolution at the mineral surface; (2) mass transport by diffusion; and (3) conversion of CO₂ into H⁺ and HCO₃⁻ (Kaufmann and Dreybrodt, 2007). Again the pH, temperature and intensity of rain are changing due to global warming. As acid rain causes the dissolution of carbonaceous stones so determining those effects is very important for the stability of the underground dam construction in the limestone, which is the main geology of the islands having the underground dam in Japan. So the objective of this research is to identify at what extent the effect of global warming (pH, intensity of rain and temperature) on the dissolution of limestone. Firstly the dissolution behavior of limestone is simulated in this research. For that CHMTRNS Code (Norishad *et al.*, 1987) has been used. Then, examine the effect of pH, intensity of rain and temperature on the dissolution of limestone.

2. Numerical Conditions

As a reference case, it is assumed that recharge water, with pH of 5, at equilibrium with soil-zone CO₂ ($P_{CO_2} = 3.1623 \times 10^{-2}$ atm) flows through a limestone-lined tube. The initial composition of this water is firstly calculated. The fluid, with the calculated concentrations: $C_{H_2CO_3} = 1.473 \times 10^{-3}$ M and $C_{HCO_3} = 5.637 \times 10^{-5}$ M enters the calcite-lined tube with a velocity of 1.0 m/year. Temperature is set at 293 K. The tube length is 10 meters, variably discretized in 20 segments. The simulation time is 1 year. For examining the effect of global warming on the dissolution of limestone the pH is set 4 at boundary condition for checking the acid rain. To examine the effect of rain intensity, velocity of inlet water is set at 2 m/year. Then, to investigate the effect of temperature change, temperature is set at 303 K. Temperature in the entire region is changed to examine the effect.

3. Results and Discussion

Table 1 shows the percent change of chemical concentrations for changing the pH. Results show that the dissolution increases on decreasing the pH as H⁺ activity increases. This indicates that as the acidification of the rain water progresses, the dissolution of limestone increases. Simulation results show that concentrations of H⁺, Ca²⁺ and H₂CO₃ increase while those of CO₃²⁻, HCO₃⁻ and CaCO₃ decrease. Results also show that dissolution is more at the shallow area and it is decreasing towards deeper area. Due to limestone dissolution, underground soil porosity will increase so that more water will be stored in the shallow aquifer but the mechanical strength of the underground dam will be decreased. The percent change of each chemical concentration due to change in velocity is shown in Table 2. The results show that concentrations of CO₃²⁻, Ca²⁺, HCO₃⁻ and CaCO₃ decrease, while concentrations of H⁺ and H₂CO₃ increase. The results also show that the increase of intensity of rain, which coincides with the increase of velocity of inlet water, caused the decrease in the dissolution of limestone, as shown in Table 2. Table 3 provides the percent change of chemicals due to change in temperature. The results indicate that the dissolution increases with increasing temperature. It is also clear that concentration of CO₃²⁻, Ca²⁺ and HCO₃⁻ increase and concentration of H⁺, H₂CO₃ decrease.

Table 1: Percent change of chemical concentrations due to change in pH

Distance, m	H ⁺	CO ₃ ²⁻	Ca ²⁺	HCO ₃ ⁻	H ₂ CO ₃
0	613.8	-97.9	266.2	-85.2	5.5
0.005	598.2	-97.8	264.8	-84.9	5.6
0.012	576.2	-97.7	264.1	-84.4	5.7
0.023	546.3	-97.5	262.4	-83.6	5.8
0.037	506.4	-97.1	258.5	-82.5	6.0
0.058	454.9	-96.5	251.0	-80.8	6.2
0.088	391.9	-95.6	238.3	-78.3	6.4
0.131	320.3	-93.9	218.9	-74.6	6.7
0.192	247.6	-91.1	192.0	-69.2	6.9
0.278	183.7	-86.6	157.2	-62.2	7.1
0.401	135.0	-80.5	114.6	-54.2	7.4
0.577	100.0	-72.8	64.3	-45.9	7.9
0.827	56.1	-55.1	20.6	-30.0	9.2
1.184	27.6	-30.4	4.0	-11.2	13.4
1.692	14.6	-10.9	0.6	2.1	17.0
2.416	0.7	-0.5	0.1	0.2	1.0
3.448	0	0	0	0	0.1
4.918	0	0	0	0	0
7.014	0	0	0	0	0
10	0	0	0	0	0

Table 2: Percent change of chemical concentrations due to change in velocity

Distance, m	H ⁺	CO ₃ ²⁻	Ca ²⁺	HCO ₃ ⁻	H ₂ CO ₃
0	7.2	-12.3	-49.3	-6.0	0.8
0.009	7.8	-13.3	-49.3	-6.5	0.8
0.021	8.6	-14.5	-49.3	-7.1	0.9
0.037	9.7	-16.1	-49.4	-7.9	1.1
0.060	11.2	-18.2	-49.4	-9.0	1.3
0.091	13.3	-21.0	-49.6	-10.4	1.6
0.134	16.3	-24.5	-49.8	-12.2	2.2
0.193	20.5	-29.1	-50.4	-14.4	3.2
0.274	27.1	-35.1	-51.4	-17.3	5.2
0.386	38.6	-43.2	-53.5	-21.2	9.4
0.540	63.6	-55.4	-57.5	-26.7	20.1
0.752	144.0	-73.9	-64.4	-35.9	57.0
1.044	496.2	-91.0	-69.7	-45.5	226.4
1.447	4995	-98.8	-56.0	-39.8	2986.1
2.001	55266	-100	-27.0	82.2	1011123
2.764	6377	-95.8	-7.2	174.6	17711.0
3.815	20.1	-2.6	-1.0	21.8	52.4
5.263	2.0	-0.5	-0.4	1.6	3.7
7.256	-0.8	1.9	1.2	1.0	0.3
10	0	-7.7	-1.8	0	0

Table 3: Percent change of chemical concentrations due to change in temperature

Distance, m	H ⁺	CO ₃ ²⁻	Ca ²⁺	HCO ₃ ⁻	H ₂ CO ₃
0	-2.2	4.6	17.0	2.3	-0.06
0.005	-2.3	4.8	17.0	2.4	-0.06
0.012	-2.5	5.1	17.0	2.5	-0.06
0.023	-2.7	5.5	17.0	2.7	-0.07
0.037	-2.9	6.1	17.0	3.0	-0.08
0.058	-3.3	6.9	16.9	3.3	-0.10
0.088	-3.8	7.9	16.8	3.8	-0.12
0.131	-4.3	9.1	16.5	4.4	-0.13
0.192	-5.0	10.6	15.9	5.1	-0.17
0.278	-5.7	12.3	15.0	5.8	-0.22
0.401	-6.3	13.6	13.4	6.4	-0.29
0.577	-6.3	13.7	10.6	6.4	-0.40
0.827	-5.2	10.7	6.2	4.9	-0.62
1.184	-4.6	8.1	3.4	3.1	-1.69
1.692	-4.8	6.0	2.5	0.8	-4.07
2.416	-1.8	3.5	2.3	1.6	-0.02
3.448	-1.6	3.5	2.31	1.8	0.10
4.918	-1.6	3.4	2.3	1.7	0.12
7.014	-1.7	3.8	2.5	1.9	0.13
10	0	-1.6	-0.5	0	0

4. Conclusion

The effect of global warming on the dissolution of limestone was observed using numerical simulation. The dissolution of limestone increased with acidification of the rain water and increased temperature. Porosity of limestone increased with increase in dissolution of limestone. These findings indicated that more water were stored into the aquifers but mechanical strength of the underground dam decreased. So the damage probability of underground dam was high. Increase of intensity of rain, which coincides with the increase of velocity of inlet water, caused decrease in the dissolution of limestone.

Reference

- Kaufmann, G., and Dreybrodt, W. (2007): *Geochim. Cosmochim. Acta*, 71(6), pp.1398-1410.
- Noorishad, J., Carnahan, C.L., and Benson, L.V. (1987): LBL-22361.
- Yadav, S.K., and Chakrapani, G.J. (2006): *Current Science*, 90(7), pp.932-937.