Effect of water and sulfide on magnesium carbonate crystallization

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8a. Mineral growth and dissolution: modern approaches to molecular-level reaction mechanism determination with implications for toxic metal sequestration, biomineralization, and engineering

Magnesium is the second most widely occurred metal component in carbonates next only to Ca, but low temperature precipitation of anhydrous Mg-CO_3 phases has proven virtually impossible. The difficulty encountered herein is often attributed to the highly hydrated character of Mg^{2+}. The seemingly clear understanding in the role of water leads to an interesting question: will magnesite precipitate if the formation of aqueous hydration shell is breached or prevented? Meanwhile, a plethora of literature data documented the occurrence of dolomite in the presence of sulfur reducing bacteria SRB, leaving no lucid explanation for the kinetic effect of water. The ultimate goal of our research is to address these issues through experimentally testing the follwoing hypotheses: (1) weakend solvation shell around Mg^{2+} will lead to $MgCO_3$ crystallization if dehydration is the kinetic hindrance and (2) sulfide is the ultimate mediating agent for SRB facilitated dolomite formation.

Crystallization experiments were carried out in dry organic and organo-aqueous binary solvents and in the presence of sulfide ions. Experimental results indicate (1) Anhydrous $MgCO_3$ precipitates under dry conditions but appears in amophous form instead of crystalline magnesite. (2) Crysalline anhydrate only forms when both Mg and Ca are present in organic solvent. XRD identifies the occurrence of dolomite with ~37% $MgCO_3$ in solutions containing 1:1 ratio of Mg and Ca. (3) The presence of minute amount of water in organic solvents leads to the precipitation of hydrated magnesium carbonate. (4) Tri-hydrate Mg-CO_3 nesqhehonite is the dominant phase in binary solvent, similar to the result in pure aqueous environments. However, the presence of organic solvent greatly accelerate the crystallization kinteics. (5) Input of solutions with Mg/Ca = 5 instantly halts the growth on seeded calcite crystals in saturated solutions. However, in situ AFM observations on the (104) faces reveals the inhibation tackles primarily nulceation but not step flow despite the change of hillock morphology. (6) The retardation effect of Mg is greatly alleviated, if not eliminated at all, when the input solutions contains 0.5 mM sulfide. Initial effect of Mg changes the hillock from the rhombic to a tear-drop mophology, but continued growth leads to step bunching in the $< \bar{4}41 >$ directions and ultimately a return to the cleavage form.

These observations indicate that the crystallization of Mg-containing carbonate may be inhibited both kinetically and energetically. The kinetic effect is shown by the formation of metastable hydrous phases in the presence even minimal amount of water. However, the inhibition on step nucleation but not step flow, as well as the lack of crystalline $MgCO_3$ phase in dry solvents, suggest the difficulty for Mg^{2+} and CO_3^{2-} to establish ordered long-range structures.

The Leaching of Heavy Metals from Steel Slag in Panzhihua Region

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Introduction

From 1970s to nowadays, approximately 3000000 t/a steel slag were dumping in Panzhihua region. [1] Heavy metals such as V, Cr, and Ni will influence environmental quality when they leach from slag pile. [2] In order to investigate the leaching of heavy metals from steel slag, some experiments were carried out.

Material and Method

The steel slag was selected in Baguanhe slag pile in Panzhihua region, and the chemical composition was Al_2O_3 1.69%, CaO 51.2%, Cr_2O_3 0.11%, FeO 10.66%, MgO 4.55%, MnO 1.54%, P_2O_5 0.37%, SiO_2 10.05%, TiO_2 5.33%, V_2O_5 6.35%. The steel slag was grounded and seived through d<0.075 mm, then 7 steel slag samples (each sample weight was 140 g) were put into 7 beakers which were added 100 ml pH=1, 3, 5, 7, 8, 10, 12 acid or alkali solutions, respectively. After 14 days soaking and shaking, heavy metals in the solution were detected by ICP-MS.

Results and Discussion

The leaching of heavy metals from slag was shown in Figure 1. When the pH value of solution was 1, the leaching of heavy metals was highest. And when the pH value of solution was 3, 5, 7, 8, 10, and 12, the concentration of heavy metals varied not obviously. Cr and Ni in leaching solution exceeded to Identification standards for hazardous wastes - Identification for extraction toxicity (GB5085.3-2007), which threatend regional environmental safety.

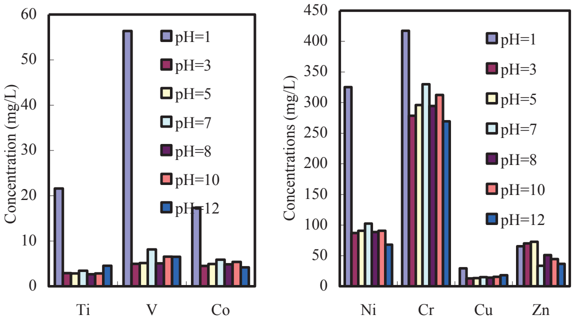

Figure 1: Heavy metas in solution after 14 days slag leaching

Conclusion

The steel slag which contained some heavy metals was hazardous waste. Heavy metals could release from the leaching of steel slag, especially, Cr and Ni would pollute water and soil.

Acknowledgement

This study is granted by NSFC project (No.41073068).

[1] Teng, et al (2006) *Chinese Journal of Geochemistry* **25(4)**, 378-384. [2] Proctor, et al (2002) *Human and Ecological Risk Assessment* **8(4)**, 681-711.