Influence of calcium ion and pH on oxidation rates and secondary mineral formation on pyrite surface

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Abstract

Pyrite is one of the most widely distributed sulfide minerals in the volcanogenic massive sulfide ore deposits, and it contributes greatly to the formation process of groundwater here. Many studies have been extensively investigated its oxidation mechanisms and kinetics in acidic conditions ($pH<4$) in term of acid mine drainage generations. However, the influence mechanisms of pyrite oxidation with calcium ion (Ca^{2+}) which is abundant in groundwater and hydroxyl ion are not clearly understood yet. In this work, we investigated the initial pyrite oxidation process with or without calcium ion at pH 6, 9 and 12 to clear those interactions. The result showed a significant increase of dissolved total sulfur concentration at pH 12 in both Ca addition and non-Ca addition systems. On the other hand, at pH 12 the dissolved total Fe showed low concentration in Ca^{2+}-existed system and simultaneously accompanying with the rapid decrease of Ca^{2+}. Shrinking core model was introduced into the description of the pyrite oxidation process, the fitting rate constant also reflected Ca^{2+} had a remarkable effect on pyrite oxidation process at pH 12 but a weak influence on it at pH 6 and 9, separately. The formation of goethite, magnetite, and hematite on the pyrite surface after the reaction in all conditions were confirmed by X-ray photoelectron spectroscopy (XPS). The proportion of goethite increased rapidly when the pH value of the reaction system rose. Moreover, Ca^{2+} facilitated the transformation of pyrite to other iron oxides at each pH value, especially the proportions of goethite and magnetite were increased remarkably. Therefore, the existence of Ca^{2+} facilitated the dissolution and oxidation of pyrite with increasing hydroxyl ions, which in turn accelerated the phase transfer reaction from ferrihydrite to goethite. Then the goethite converted into hematite and magnetite which are more thermodynamically stable and more crystalline phases. These secondary mineral formations on pyrite surface could control the dissolution rate of pyrite surface and depress the diffusion of other toxic metal ions in groundwater with their higher adsorption abilities.