

Remarkable effect of Co substitution in magnetite on the reduction removal of Cr(VI) coupled with aqueous Fe(II)

YING LI^{1*}, XIAOLIANG LIANG², HONGPING HE³, YUJI ARAI⁴

¹ Department of Natural Resources and Environmental Sciences, University of Illinois at Urbana-Champaign, Illinois, 61801, USA (*correspondence: yingl@illinois.edu)

² Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangdong, 510640, PR China (liangxl@gig.ac.cn)

³ Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangdong, 510640, PR China (hehp@gig.ac.cn)

⁴ Department of Natural Resources and Environmental Sciences, University of Illinois at Urbana-Champaign, Illinois, 61801, USA (yaraia@illinois.edu)

The interaction between magnetite and aqueous Fe(II) profoundly impacts the mineral recrystallization, trace-metal sequestration, and contaminant reduction. The iron ions in natural magnetite are extensively substituted by other cations. It is still unclear whether the substitution with thermodynamically favorable redox repairs (e.g., $\text{Co}^{2+}/\text{Co}^{3+}$) plays a vital role in the reducing capability of the coupled system. Herein, a series of Co-substituted magnetite samples ($\text{Fe}_{3-x}\text{Co}_x\text{O}_4$, $0.00 \leq x \leq 1.00$) were synthesized and tested for the reductive removal of Cr(VI) in the presence of Fe(II). $\text{Fe}_{3-x}\text{Co}_x\text{O}_4$ had a spinel structure with the preferential occupancy of Co^{2+} on octahedral sites. The surface site density increased gradually with Co substitution. Cr(VI) was found first adsorbed on the $\text{Fe}_{3-x}\text{Co}_x\text{O}_4$ surface and then reduced to Cr(III) by the structural Fe^{2+} and the adsorbed Fe(II), accompanied by the oxidation of bulk Fe^{2+} and surface Fe(II) in $\text{Fe}_{3-x}\text{Co}_x\text{O}_4$ without phase transformation. The Cr(III) was precipitated on the $\text{Fe}_{3-x}\text{Co}_x\text{O}_4$ surface with Fe(III), or substituted octahedral Fe in $\text{Fe}_{3-x}\text{Co}_x\text{O}_4$. Both the reaction kinetics and the electron transfer efficiency revealed that Co substitution significantly improved the reactivity of $\text{Fe}_{3-x}\text{Co}_x\text{O}_4/\text{Fe(II)}$ towards Cr(VI) reduction. This was ascribed to the presence of the redox pairs $\text{Co}^{2+}/\text{Co}^{3+}$ and $\text{Fe}^{2+}/\text{Fe}^{3+}$ accelerating electron transfer from the $\text{Fe}_{3-x}\text{Co}_x\text{O}_4$ interface to Cr(VI). The results obtained will not only be beneficial for the application of Co-substituted magnetite in the remediation of anoxic environments, but also of great importance in reaching a deeper understanding of the fate of Cr species in anaerobic matrices.