Formation of hydroxysulphate and hydroxycarbonate green rusts in the presence of zinc using time-resolved *in situ* small and wide angle X-ray scattering

I. A. M. Ahmed*, S. Shaw and L. G. Benning

School of Earth and Environment, University of Leeds, Leeds, LS2 9JT, UK

ABSTRACT

The formation and transformation of hydroxysulphate ($GRSO_4$) and hydroxycarbonate ($GRCO_3$) Green Rusts were studied *in situ* using synchrotron-based time-resolved small and wide angle X-ray scattering. The time-resolved data revealed, for the first time, the pH dependent transition from poorly-ordered schwertmannite (pH <6.5) into $GRSO_4$ (pH ~6.8) followed by $GRCO_3$ (at pH ~9.6). These data also showed that the addition of Zn to the starting sulphate Fe^{2+}/Fe^{3+} solution resulted in a change in size of the GR unit-cell due to substitution of Zn into the GR structure.

Introduction

IRON oxides and oxyhydroxides are common components within soils and aquifers where they can form *via* the weathering of Fe-bearing silicate (e.g. olivine) and sulphide (e.g. pyrite) minerals. Green Rusts (GR; e.g. $Fe_4^{2+}Fe_2^{3+}(OH)_{12}SO_4.xH_2O$) are a class of mixed-valent Fe oxyhydroxides that tend to form during aqueous corrosion of metallic-iron, or in reductomorphic soils (Trolard *et al.*, 1997) as a result of both abiotic and biotic processes (Genin, 2004). Their structure consists of layers of positively charge octahedrally coordinated Fe, intercalated with anionic species (e.g. SO_4^{2-}, CO_3^{2-} or Cl^-). The structural Fe^{2+} (Fe^{2+}/Fe^{3+} may vary between 0.5 and 3, but typically = 2) within GR serves as a powerful electron donor for the reductive transformation of many redox sensitive elements (e.g. $Cr^{6+} \rightarrow Cr^{3+}$). Also some divalent transition metals (e.g. Ni and Zn) can substitute directly for the Fe^{2+} within the octahedral layers. The reduction and/or absorption of these elements leads to reduced mobility and bioavailability and therefore GR is potentially important for the immobilization of toxic (e.g.

Se) and radioactive (e.g. U) species within contaminated land environments (O'Loughlin *et al.*, 2003; Pepper *et al.*, 2003; Refait *et al.*, 2000; Williams and Scherer, 2001).

However, the formation and stability of GR phases in the environment are still poorly understood. This is primarily due to fact that GR particles are highly reactive and oxidize rapidly in air making them difficult to study using conventional *ex situ* techniques. In this study we have characterised the formation of GR *in situ* using synchrotron-based time-resolved small and wide angle X-ray scattering (SAXS/WAXS). The aim was to explore the kinetics and mechanism of the abiotic $GRSO_4$ and $GRCO_3$ formation (nucleation and growth) and their transformation under controlled conditions, and also evaluate the effect of Zn on these processes.

Materials and methods

A programmable reaction system was used to precipitate GR at a fixed temperature (21ºC) and within an anoxic environment using a continuous flow of pure N_2 gas. This system allowed accurate addition of base and continuous logging/control of pH and redox potential (Eh). Pure $GRSO_4$ and $GRCO_3$, as well as Zn-containing $GRSO_4$ and
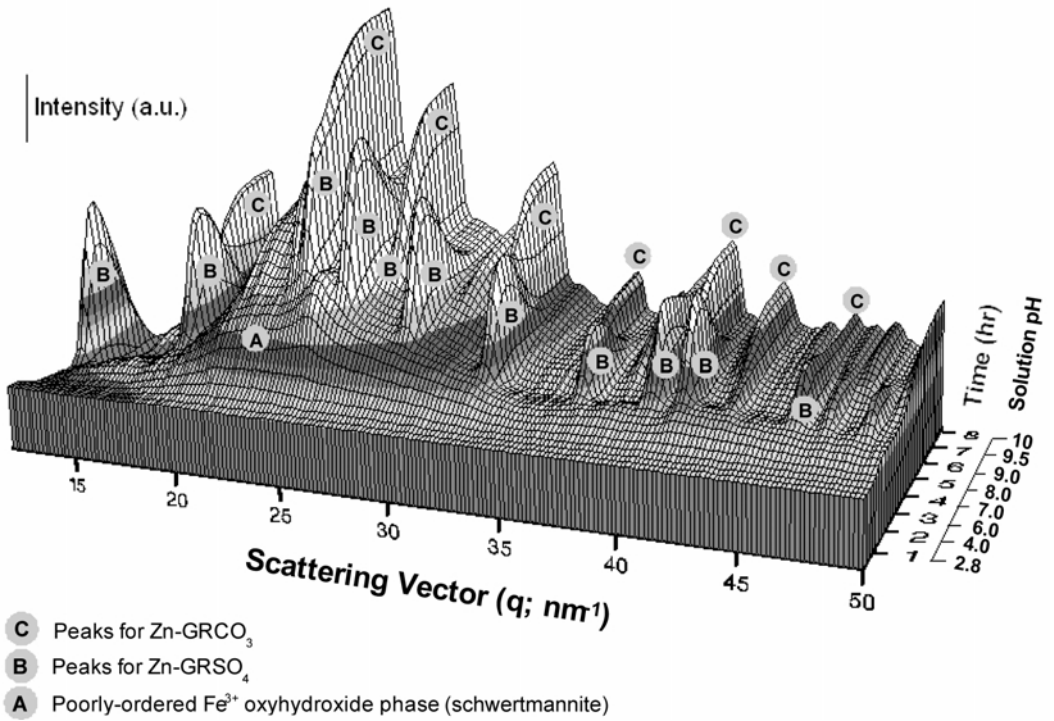
* E-mail: i.ahmed@see.leeds.ac.uk

FIG. 1. Three-dimensional plot of WAXS data for the formation of Zn-GRSO$_4$ and Zn-GRCO$_3$.
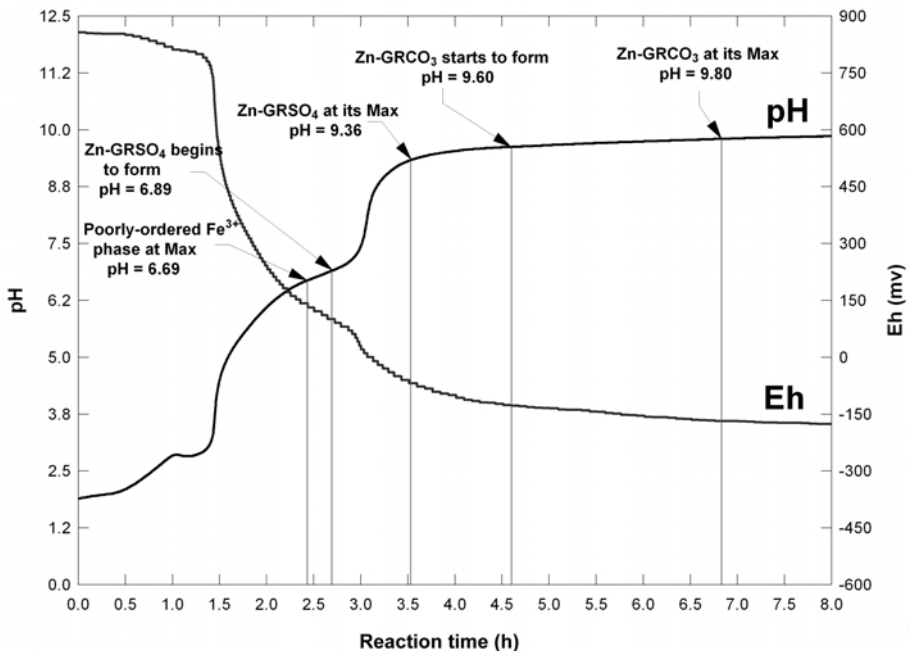

FIG. 2. Eh-pH vs. time profile for the isothermal synthesis of Zn-GRSO$_4$ and Zn-GRCO$_3$.

GRCO$_3$ (designated Zn-GRSO$_4$ and Zn-GRCO$_3$, respectively) were synthesized by the controlled addition of Na$_2$CO$_3$ to a mixture of 0.15−0.2 M FeSO$_4$, 0.1 M Fe$_2$(SO$_4$)$_3$ and 0−0.05 M ZnSO$_4$ (initial solution composition (Fe^{3+}/(Fe^{2+}+Zn^{2+}) = 1). The Zn concentration is representative of high acid-mine-drainage contamination levels (Druschel *et al.*, 2004). The initial solution pH (~1.8) was increased to pH 10 over 10 h by the addition of Na$_2$CO$_3$. All experiments were carried out on beamline MWP6.2 at the Synchrotron Radiation Source (SRS) Daresbury Laboratory, where time-resolved SAXS and WAXS patterns of the reacting suspension were collected every 2 min.

Results and discussion

The time-resolved WAXS patterns for the formation of Zn-GRSO$_4$ and Zn-GRCO$_3$, are shown in Fig. 1. Data from the pure GRSO$_4$ and GRCO$_3$ formation experiment showed almost identical trends. During the first stage of the reaction (pH 5.5−6.7), poorly-ordered schwertmannite (ferric (oxy)hydroxy-sulphate) formed, while Zn-GRSO$_4$ formed in the second stage at pH >~6.9, with the XRD peaks reaching their maximum intensity at pH ~9.4. The third stage of the reaction was marked by the formation of Zn-GRCO$_3$ which reached its maximum at pH ~9.8. This three stage process was consistent with the results from the pH and Eh data shown in Fig. 2. Data also show that the Eh decreases with

increasing pH due to the decreasing Fe^{3+}/Fe^{2+} ratio within the solution during the precipitation of schwertmannite and GR.

The WAXS data showed that the Zn-GRCO$_3$ was stable up to pH ~11 without any indications of further transformation into other Fe-phases (e.g. magnetite). To evaluate the effect of Zn on the crystal structure of the GR phases, data from the Zn-containing experiment were compared to the experiment performed in the absence of Zn. Dimensions of the GR hexagonal unit-cell refined from XRD data were a = 3.202 Å, c = 10.881 Å for pure GRSO$_4$ compared with a = 3.152 Å , c = 10.721 Å for Zn-GRSO$_4$ and a = 3.192 Å , c = 22.634 Å for pure GRCO$_3$ compared with a = 3.145 Å, c = 22.30 Å for Zn-GRCO$_3$. These data indicate that in both the GRSO$_4$ and GRCO$_3$ there is an average 1.48±0.05% decrease in the unit-cell parameters in the presence of Zn. This suggests that the smaller Zn (ionic radius = 0.74 Å) is directly substituting for the larger Fe^{2+} (ionic radius = 0.78 Å) ion within the octahedral layers of the GR structure.

Kinetic data on the formation and transformation reactions described above were derived from changes in the normalized diffraction peak areas (α) using the Johnson-Mehl-Avrami-Kolmogorov (JMAK) kinetic model:

$$\alpha = 1 - \exp(-(k(t - t_0))^n)$$

where k is the reaction-rate constant, t is time, t_0 is induction time and n is a parameter related to the
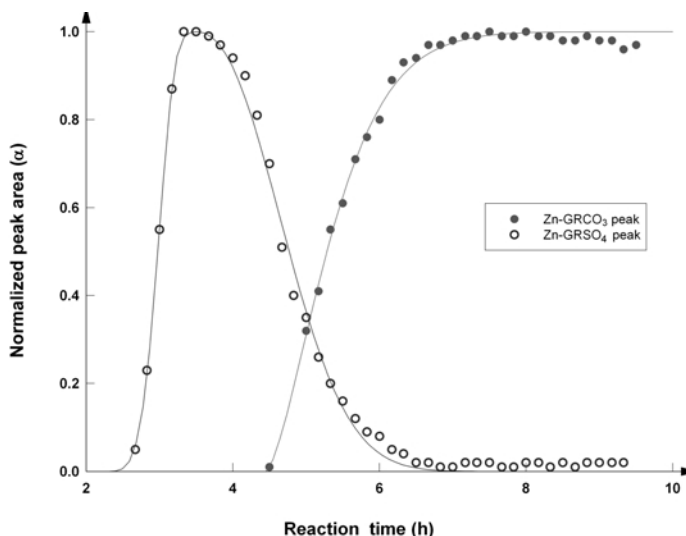

FIG. 3. JMAK model (solid lines) fitted to the decline and/or growth of the (012) Zn-GRSO$_4$ and (004) Zn-GRCO$_3$ diffraction peaks.

reaction mechanism. Model fits (Fig. 3) revealed an induction time of 2.2 h prior to the formation of Zn-GRSO$_4$ and an *n* value for Zn-GRSO$_4$ formation of ~1.5, indicating a two-dimensional phase-boundary controlled reaction. This is consistent with the plate-like morphology of GR particles.

Conclusion

We have demonstrated the use of a novel experimental system for the *in situ* characterization of GR formation under anaerobic conditions. The data showed that the GRSO$_4$ transformed to GRCO$_3$ at high pH and carbonate concentrations. Results indicated that Zn became incorporated into the Fe octahedral layers of GR during the formation of GRSO$_4$ and remained within the structure during the transform to GRCO$_3$. Thus, GR could provide a promising solution for metal remediation in sub-oxic Fe-rich systems, e.g. Fe^0 permeable reactive barriers.

Acknowledgements

References

Duschel, G.K., Baker, B.J., Gihring, T.M. and Banfield, J.F. (2004) Acid mine drainage biogeochemistry at Iron Mountain, California. *Geochemical Transactions*, **5**, 13–32.

Genin, J.M.R. (2004) Fe(II–III) hydroxysalt green rusts; from corrosion to mineralogy and abiotic to biotic reactions by Mössbauer spectroscopy. *Hyperfine Interactions*, **156–157**, 471–485.

O'Loughlin, E.J., Kelly, S.D., Cook, R.E., Csencsits, R. and Kemner, K.M. (2003) Reduction of Uranium(VI) by mixed iron(II/iron(III) hydroxide (green rust): formation of UO$_2$ nanoparticles. *Environmental Science and Technology*, **37**, 721–727.

Pepper, S.E., Bunker, D.J., Bryan, N.D., Livens, F.R., Charnock, J.M., Pattrick, R.A.D. and Collison, D. (2003) Treatment of radioactive wastes: an X-ray absorption spectroscopy study of the reaction of technetium with green rust. *Journal of Colloid and Interface Science*, **268**, 408–412.

Refait, Ph., Simon, L. and Génin, J.M.R. (2000) Reduction of SeO$_4^{2-}$ anions and anoxic formation of iron(II)-iron(III) hydroxy-selenate green rust. *Environmental Science and Technology*, **34**, 819–825.

Trolard, F., Génin, J.M.R., Abdelmoula, M., Bourrie, G., Humbert, B. and Herbillon, A. (1997) Identification of a green rust mineral in a reductomorphic soil by Mössbauer and Raman spectroscopies. *Geochimica et Cosmochimica Acta*, **61**, 1107–1111.

Williams, A.G.B. and Scherer, M.M. (2001) Kinetics of Cr(VI) reduction by carbonate green rust. *Environmental Science and Technology*, **35**, 3488–3494.