

This article was downloaded by: [University of Leeds]

On: 30 September 2013, At: 08:03

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Environmental Technology

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/tent20>

Immobilization of chromate in hyperalkaline waste streams by green rusts and zero-valent iron

Christine M. Rogers^a, Ian T. Burke^a, Imad A.M. Ahmed^a & Samuel Shaw^a

^a School of Earth and Environment, Earth Surface Science Institute, University of Leeds, Leeds LS2 9JT, UK

Accepted author version posted online: 20 Aug 2013. Published online: 30 Sep 2013.

To cite this article: Christine M. Rogers, Ian T. Burke, Imad A.M. Ahmed & Samuel Shaw, Environmental Technology (2013): Immobilization of chromate in hyperalkaline waste streams by green rusts and zero-valent iron, Environmental Technology, DOI: 10.1080/09593330.2013.834948

To link to this article: <http://dx.doi.org/10.1080/09593330.2013.834948>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

Immobilization of chromate in hyperalkaline waste streams by green rusts and zero-valent iron

Christine M. Rogers*, Ian T. Burke, Imad A.M. Ahmed† and Samuel Shaw‡

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

(Received 26 April 2013; accepted 8 August 2013)

Zero-valent iron (ZVI) and green rusts can be used as reductants to convert chromium from soluble, highly toxic Cr(VI) to insoluble Cr(III). This study compared the reduction rates of Cr(VI) by ZVI and two carbonate green rust phases in alkaline/hyperalkaline solutions. Batch experiments were carried out with synthetic chromate solutions at pH 7.7–12.3 and a chromite ore processing residue (COPR) leachate (pH ≈ 12.2). Green rust removes chromate from high pH solutions (pH 10–12.5) very rapidly (<400 s). Chromate reduction rates for both green rust phases were consistently higher than for ZVI throughout the pH range studied; the surface area normalized rate constants were two orders of magnitude higher in the COPR leachate solution at pH 12.2. The performances of both green rusts were unaffected by changes in pH. In contrast, ZVI exhibited a marked decline in reduction rate with increasing pH to become almost ineffective above pH 12.

Keywords: green rust; zero-valent iron; chromite ore processing residue; chromate reduction; hyperalkaline waste

1. Introduction

The removal of toxic (e.g. Cr(VI)) and radioactive (e.g. U(VI)) species from alkaline and hyperalkaline (pH > 10) waste streams/groundwaters is a problem for many industries and contaminated land remediation. Cr(VI), like other redox active contaminants (e.g. U(VI) and Tc(VII)), can be reductively immobilized using material such as zero-valent iron (ZVI) [1] and synthetic resins.[2] In this process, the highly soluble, oxidized form of the contaminant is chemically converted to a reduced form, often forming Cr(OH)₃, which has lower solubility and mobility e.g. Cr(VI) → Cr(III). The most commonly used forms of ZVI, granular and micro, have limited efficiency for reducing contaminants in hyperalkaline conditions.[1] Therefore, key to developing a remediation strategy for hyperalkaline wastes and groundwater is the development of materials which can effectively reduce contaminants at high pH.

Hyperalkaline wastes are formed during a number of metal extraction and purification processes. Examples include nuclear reprocessing wastes, currently stored at sites in the USA and Europe.[3,4] Hyperalkaline conditions will also be intrinsic to cementitious radioactive waste repositories where cement pore waters will maintain pH > 12 for thousands of years.[5] Among the most common hyperalkaline waste streams are Cr(VI) rich waters formed by leaching chromite ore processing residue (COPR). These residues are waste products generated by the high

lime process when chromite ore is roasted with alkaline carbonate (e.g. NaCO₃) to extract chromium. Historically, COPR has been discarded in poorly managed landfills, often located around urban areas.[6–8] Leachate from these wastes are typically hyperalkaline and, due to the inefficient nature of the metal extraction process, can contain toxic levels of Cr(VI), reaching 1.6 mmol L⁻¹. [9,10]

ZVI has been successfully utilized within permeable reactive barriers (PRB) to reductively immobilize Cr(VI) in groundwaters with circum neutral pH.[11,12] At higher pH, the rate of Cr(VI) reduction decreases rapidly due to the consumption of H⁺ during the Cr(VI) reduction reaction, and the formation of low solubility Cr(III)/Fe(III) oxides on the ZVI surface which limit further reduction.[13] These processes severely limit the effectiveness of ZVI for remediating high pH COPR leachates. Potential alternatives to ZVI are green rust phases. These are a family of layered double hydroxide compounds containing Fe(II) and Fe(III) with a general formula



where $x = 0.9\text{--}4.2$, $y = 2\text{--}4$ and A is an anion (e.g. CO₃²⁻ or SO₄²⁻). [14,15]

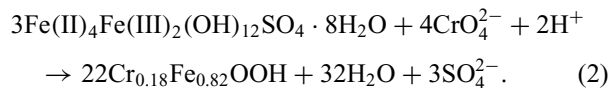
They have been shown to effectively reduce a variety of redox active contaminants including Cr(VI), [16–18] U(VI) [19] and Se(VI). [20] During the Cr(VI) reduction process,

*Corresponding author. Emails: c.m.rogers@leeds.ac.uk; christinerog@gmail.com

†Present address: Lancaster Environment Centre, University of Lancaster, Lancaster LA1 4YQ, UK.

‡Present address: School of Earth, Atmospheric and Environmental Sciences, University of Manchester, Manchester M13 9PL, UK.

the Fe(II) within green rust oxidizes to produce Cr(III) substituted α -Fe(III)OOH as the final reaction product,[21] see Equation (2)



The substitution of Cr(III) within the highly insoluble Fe(III) phase, potentially limits any further remobilization. Green rust forms plate-like particles which are typically 1–5 μm in diameter and <100 nm in thickness. The high surface area of the particles and the ability of electrons to move through the structure means that the entire particle is oxidized during the Cr(VI) reduction process, with no surface passivation.[21] Finally, recent studies have also shown that green rust can be stable up to at least pH 10,[22] suggesting it could be a candidate for contaminant reduction in hyperalkaline solutions.

The aim of this study is to test the hypothesis that green rusts will be significantly more effective than ZVI for reductive removal of Cr(VI) from strongly alkaline solutions. The primary objective was to use batch experiments to compare the rates of Cr(VI) reduction by carbonate green rust (GR-CO₃), carbonate green rust containing zinc (GR-Zn-CO₃) and granular ZVI, in synthetic alkaline fluids and COPR leachate. The results from this study show that green rust is highly effective at removing Cr(VI) from hyperalkaline solutions.

2. Experimental section

Granular ZVI (Connelly GPM, Inc., IL, USA) was prepared by sieving to produce a size fraction between 0.25 and 0.6 mm. Carbonate green rust (GR-CO₃) and carbonate green rust containing zinc (GR-Zn-CO₃) were synthesized following the methods of Ahmed et al.[22,23] GR-Zn-CO₃ was synthesized from a starting solution with a Zn/(Zn + Fe) ratio of 0.2, to form a green rust phase where 20% of the total Fe was substituted with Zn.[23] Phase purity of the green rusts was confirmed by powder X-ray diffraction (Bruker D8 $\lambda = \text{CuK}\alpha_1$). The surface areas of the green rusts and ZVI were determined using the Brunauer–Emmett–Teller (BET) method (Micromeritics Gemini V2365). The surface areas of the ZVI, GR-CO₃ and GR-Zn-CO₃ were 2.07, 21.6 and 88.5 m²g⁻¹, respectively.

Sodium chromate solutions (100 and 1000 $\mu\text{mol L}^{-1}$) were prepared using deionized water and then titrated, dropwise with sodium hydroxide solution, to achieve the desired initial pH (8, 10 or 12). Solutions were stored in septum vials and deoxygenated by bubbling with oxygen-free nitrogen immediately prior to use. Alkaline COPR leachate was collected from a waste site in the North of England (from a standpipe piezometer, screened into the COPR). The leachate had a pH of 12.2 and contained 990 $\mu\text{mol L}^{-1}$ Cr(VI).[9]

The Cr(VI) reduction experiments were performed with a solid concentration of 10 g L⁻¹ in a crimp sealed 20 mL septum vial with a nitrogen headspace. Two concentrations of chromate solution were used; 100 $\mu\text{mol L}^{-1}$ with ZVI and 1000 $\mu\text{mol L}^{-1}$ with the green rusts. The Cr(VI) concentration was increased in the green rust experiments due to the rapid Cr(VI) reduction rates observed (seconds) in these systems. In all experiments, the concentration of Fe(II) within GR was in excess relative to Cr(VI). Vials were shaken during the experiments at 21°C ($\pm 1^\circ\text{C}$). At each time step, a nitrogen filled syringe was used to extract a suspension of the reacting materials; the experiments with ZVI were sampled in triplicate, but only single measurements were possible with both green rust materials due to the fast reduction rates in these systems. The extracted suspension was filtered through a 0.2 μm nylon syringe filter and the filtrate analysed for chromate and pH. Determination of Cr(VI) concentration was achieved colourmetrically based on the reaction with diphenylcarbazide (US EPA method 7196 [24]). Measurements were made with a Cecil 3021 UV/VIS spectrophotometer at 540 nm; the detection limit was 0.2 $\mu\text{mol L}^{-1}$. The pH value reported for each experiment was taken to be the mean of the measured pH values for every time step used in the derivation of the initial rate constant (k_{obs}) for that experiment. A summary of experimental conditions is given in supporting material Table S1.

3. Results

3.1. Cr(VI) removal

The concentration of dissolved Cr(VI) as a function of reaction time and pH for reduction experiments employing green rust and ZVI are shown in Figure 1. Cr(VI) removal in the presence of GR-CO₃ and GR-Zn-CO₃ was extremely rapid in all systems. GR-CO₃ completely removed all Cr(VI) within 300 s in all solutions except the leachate. Here, there was an initial rapid reduction of chromate with 80% removal in 350 s followed by a slower removal stage lasting over 1000 s (Figure 1(a)). GR-Zn-CO₃ was the most reactive material and removed almost all (>99%) Cr(VI) within 300 s in all systems. Overall, the reactivity for both green rust materials remained relatively constant at all pH values, therefore it was not possible to determine any trend in reduction rate with pH.

In contrast to the fast reduction rates observed with green rust, the reduction of Cr(VI) by ZVI was much slower at all alkaline pH values used in the study (Figure 1(c)). In fact, at pH > 12 and with COPR leachate, Cr(VI) concentrations remained near initial values with little reduction even after several weeks (data not shown). At lower pH values, the rates of reduction were faster; at pH 7.7 there was 50% removal of Cr(VI) after 1.5 h (5.3×10^3 s) compared with 1.8 h (6.5×10^3 s) at pH 9.0. A photograph of the post experiment microcosms Figure S1 (with supporting material) demonstrates the effectiveness of green rust

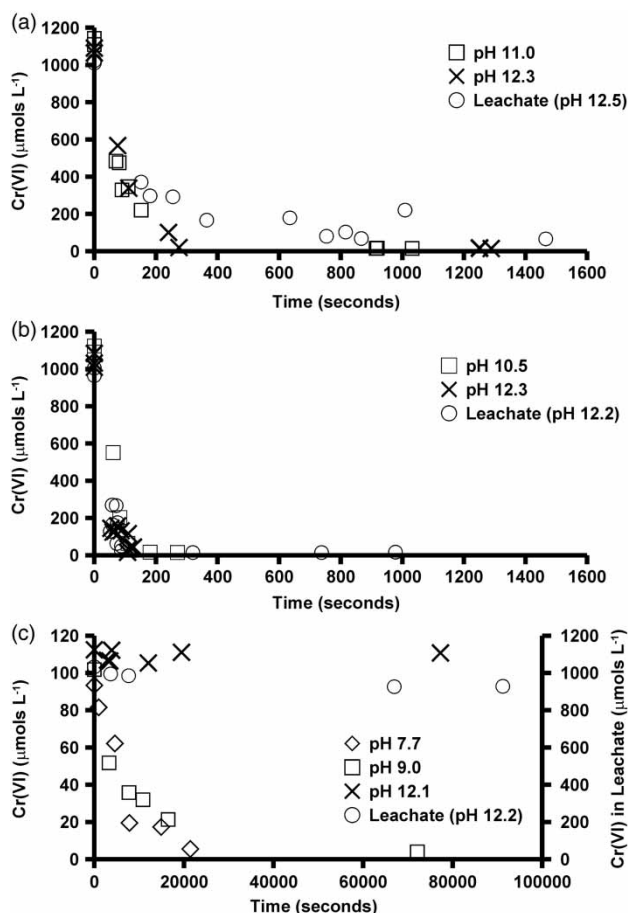


Figure 1. Cr(VI) concentration with time during reaction of (a) GR- CO_3 and (b) GR-Zn- CO_3 with synthetic chromate solutions (pH 10.5–12.3) and COPR leachate, and (c) ZVI with synthetic chromate solutions (pH 7.7–12.1) and COPR leachate.

materials compared with ZVI at removing Cr(VI) from the COPR leachate solution.

3.2. Kinetic analysis of Cr(VI) removal

Previous studies of Cr(VI) reduction by green rust [16–18] and ZVI [13] indicate that, provided the amount of reacting solid material is not rate limiting, the kinetics of Cr(VI) reduction can be described by a first order kinetic model as follows:

$$\frac{d[\text{Cr(VI)}]}{dt} = -k_{\text{obs}}[\text{Cr(VI)}], \quad (3)$$

where k_{obs} (s^{-1}) is the observed rate constant and t is the time (seconds). Equation (3) can be expanded to take into account the variation in surface area of the different solid materials used in the batch experiments.[25]

Thus,

$$\frac{d[\text{Cr(VI)}]}{dt} = -k_{\text{SA}}\rho_{\text{a}}[\text{Cr(VI)}], \quad (4)$$

where k_{SA} is the specific (surface area normalized) rate constant ($\text{L s}^{-1} \text{m}^{-2}$) and ρ_{a} is the surface area concentration

of the solid material ($\text{m}^2 \text{L}^{-1}$). The surface area concentration can be related to the surface area per gram of the solid material and the solid concentration in the system to give

$$\rho_{\text{a}} = a_{\text{s}}\rho_{\text{m}}, \quad (5)$$

where a_{s} is the specific surface area of solid ($\text{m}^2 \text{g}^{-1}$) and ρ_{m} is the mass concentration of solid (g L^{-1}).

Therefore,

$$k_{\text{obs}} = k_{\text{SA}}\rho_{\text{m}}a_{\text{s}}. \quad (6)$$

Initial rate constants for each ZVI and GR experiment were obtained by fitting the first-order rate expression (k_{obs} , Equation (1)) and normalizing for surface area and solid concentration (k_{SA} , Equation (6)). The values for k_{obs} , k_{SA} are given in Table 1.

Rate constants (k_{obs} and k_{SA}) for Cr(VI) reduction by green rust and ZVI as a function of pH are shown in Figure 2. Both the k_{obs} and k_{SA} data show that Cr(VI) reacts faster with green rusts than with granular ZVI. The k_{obs} values for GR-Zn- CO_3 are slightly higher than those for GR- CO_3 , but the k_{SA} values are almost identical. This indicates that the increased rate of Cr(VI) reduction by GR-Zn- CO_3 is simply a surface area effect, and there is no intrinsic improvement in Cr(VI) reduction caused by the addition of zinc. An almost imperceptible increase in reaction rate with pH is observed for green rusts when k_{obs} values are plotted in Figure 2(a). When corresponding k_{SA} values are plotted in Figure 2(b), the reduction rates decrease with pH. The k_{SA} and k_{obs} values for granular ZVI decrease rapidly with pH and show that at pH 10–12 green rust materials reduce Cr(VI) approximately 200 times faster than ZVI. The rate constants (k_{obs} and k_{SA}) for Cr(VI) reduction in this study correlate well with published rates for Cr(VI) reduction by green rust carbonate at pH 7.[16,17]

The results for ZVI show a steady decrease in reaction rate with increasing pH. The data are consistent with reduction rates at lower pH [13] and reveal a trend of decreasing reduction rate with increasing pH from 5 to >12. By combining the data from this and previous studies,[1,13] a linear relationship between $\log k_{\text{SA}}$ and pH can be observed. From this a model for Cr(VI) reduction rate as a function of pH (5–12) can be derived as follows:

$$\log k_{\text{SA}} = -0.50(\pm 6) \text{pH} - 0.4(\pm 5), \quad (7)$$

$$(\text{Pearson's } r = -0.94, P = < 0.001, n = 10).$$

Cao and Zhang [1] compared the rates of Cr(VI) reduction by nano-ZVI and micro ZVI at pH 11 (Figure 2). The Cr(VI) reduction rate for micro ZVI is similar to those for ZVI in this study suggesting that the granular ZVI used in this study was similar to the micro ZVI used by Cao and Zhang.[1]

4. Discussion

This study has demonstrated the highly effective nature of green rusts in reducing and removing Cr(VI) from solutions

Table 1. Experimental parameters for each Cr(VI) reduction experiment in this and previously published studies.

Material	pH	Observed rate k_{obs} (s^{-1})	BET value a_s ($\text{m}^2 \text{g}^{-1}$)	Surface area ρ_a ($\text{m}^2 \text{L}^{-1}$)	Specific rate k_{SA} ($\text{L s}^{-1} \text{m}^{-2}$)	Ref.
ZVI granular	7.65	1.31E-04	2.07	20.7	6.33E-06	
	9.02	1.06E-04	2.07	20.7	5.12E-06	
	12.11	1.65E-05	2.07	20.7	7.97E-07	
	12.17 ^a	6.97E-06	2.07	20.7	3.37E-07	
	5.50	3.06E-02	2.30	19.00	1.61E-03	[13]
	6.00	1.69E-02	2.30	19.00	8.92E-04	[13]
	6.50	7.78E-03	2.30	19.00	4.09E-04	[13]
	7.00	3.06E-03	2.30	19.00	1.61E-04	[13]
ZVI micro	7.50	1.53E-03	2.30	19.00	8.04E-05	[13]
ZVI micro	11.00	2.57E-05	1.00	10.50	2.45E-06	[1]
ZVI nano	11.00	2.35E-03	35.00	38.50	6.11E-05	[1]
GRCO ₃	10.98	1.13E-02	21.62	216.0	5.23E-05	
	12.31	9.81E-03	21.62	214.8	4.57E-05	
	12.45 ^a	6.73E-03	21.62	216.4	3.11E-05	
	7.00	2.39E-02	30.10	15.05	1.59E-03	[17]
GR-Zn-CO ₃	7.00	3.30E-03	47.00	11.80	2.81E-04	[16]
	10.49	1.73E-02	88.52	885.4	1.95E-05	
	12.29	2.86E-02	88.52	885.2	3.23E-05	
GR-Zn-CO ₃	12.19 ^a	3.16E-02	88.52	884.7	3.57E-05	

Note: Data from referenced work has been adapted to provide a direct comparison with experimental results in this study.

^aThe solution was COPR leachate.

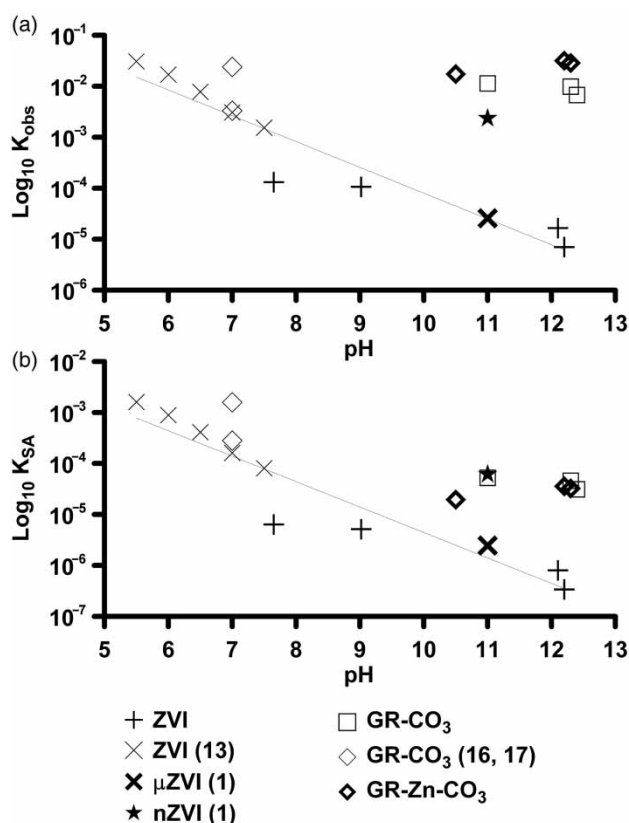


Figure 2. A comparison of (a) observed rate constants, k_{obs} and (b) specific rate constants, k_{SA} for green rusts and ZVI.

at high pH, including hyperalkaline COPR leachate. This is contrasted with the behaviour of granular ZVI, which proved to be almost completely ineffective above pH 10.

It also shows that the rate of Cr(VI) reduction by structural Fe(II) within GR-CO₃ is not significantly affected by increasing pH to hyperalkaline conditions. The effectiveness of green rust is likely to be related to the chemical, electrical and structural properties of these phases. The Fe(II) reductant is located within the octahedral layers of the green rust structure [14] with the reduction of Cr(VI) occurring at the edges of the plate-like particles.[21] We suggest that passivation of the green rust particles does not occur as electrons can easily flow along the octahedral layers [26] so permitting constant replenishment of Fe(II) at the reactive edge sites. This process allows the particles to remain reactive until all the Fe(II) has been oxidized. Also, the rapid transport of electrons along the layers would promote the fast reduction rate of Cr(VI) interacting with edges of the plate-like particles. This idea is supported by Skovbjerg et al. [21] who showed that the entire green rust particle reacts to form α -FeOOH during Cr(VI) reduction. After reduction, Cr(III) will substitute for the oxidized Fe(III) ions and become immobilized via incorporation into the FeOOH structure of the oxidation product.[21] Cr(III) within iron oxides has been observed to be very resistant to reoxidation.[8] Thus, the reduced Cr(III) will remain immobilized in the solid for the long term. These results suggest that green rusts could be an effective remediation material for high pH COPR leachates. However, it should be noted that green rusts oxidize rapidly in air, therefore emplacement mechanisms, for example, employing carbon nanotubes (CNTs), would need to be developed to minimize air exposure. The use of CNTs in this way may also contribute to the overall removal capacity of the material.[27]

The results at high pH suggest that granular ZVI can have no practical application in PRB technology for remediating hyperalkaline COPR sites. The low rates of reduction observed in this study imply that an unrealistically thick PRB would be required to achieve acceptable Cr(VI) removal, and therefore, the implementation costs would be unfeasibly large.[28] These results are consistent with other studies which have revealed the ineffectiveness of ZVI as a Cr(VI) reductant in hyperalkaline solutions [1] The reason for the dramatic decrease in reduction rate with high pH has been attributed to the decreasing concentration of H⁺, which is required for the Cr(VI) reduction reaction, and the formation of an oxidized surface layer which physically protects the ZVI surface from further reaction with Cr(VI).[13] Effective remediation of COPR sites with ZVI PRB technology could potentially only be achieved through the addition of other substances to reduce the high pH of the system into the range where ZVI is effective.[12] However, this approach has produced limited success.[11] Also, the necessary maintenance and monitoring required is contrary to the principles of long-term passive treatment.

In contrast to the results for granular ZVI, the reduction rates for nZVI were similar to those for GR. Cao and Zhang [1] suggested that the nano-size of ZVI is too small for surface oxidation effects to dominate. However, use of nZVI in the environment can lead to the development of highly reducing conditions and hydrogen generation,[29] which is not observed during green rust oxidation, and may not be desirable.

5. Conclusions

The results from this study indicate that green rusts are highly effective at reducing and removing Cr(VI) from hyperalkaline solutions (up to pH >12). Observed surface area normalized reduction rates are similar to nZVI and ~200 times faster than for granular ZVI at high pH. Green rust materials could therefore be used as potential tools for COPR leachate remediation. They may also be suitable in the reductive immobilization of other contaminants from a wide range of hyperalkaline fluids. This includes radioactive elements (e.g. U, Np and Tc) from high pH reprocessing wastes.[19] The fast rates of reaction and environmentally benign reaction products also make green rusts potential candidate materials for emergency clean-up operations following accidental spills.

Acknowledgements

Thanks are due to Dr D.I. Stewart for his helpful comments on the manuscript, Ramboll UK Limited for access to the COPR site and to Dr R. Whittleston for collecting the leachate.

Funding

This work was supported in part by NERC [grant number NE/D014026/1]; Dr C.M. Rogers is a Daphne Jackson Fellow with funding provided by the Natural Environment Research

Council and with additional support from an Alan Tetlow Memorial Bursary (The Royal Society of Chemistry, Water Science Forum).

Supplementary data

Supplemental data for this article can be accessed here <http://dx.doi.org/10.1080/09593330.2013.834948>.

References

- [1] Cao L, Zhang W. Stabilization of chromium ore processing residue (COPR) with nanoscale iron particles. *J Hazard Mater.* 2006;B132:213–219.
- [2] Ghandi MR, Viswanathan N, Meenakshi S. Synthesis and characterization of a few amino-functionalized copolymeric resins and their environmental applications. *Ind Eng Chem Res.* 2012;51:5677–5684.
- [3] Zachara JM, Ainsworth CC, Brown GE, Catalano JG, McKinley JP, Qafoku O, Smith SC, Szecsody JE, Traina SJ, Warner JA. Chromium speciation and mobility in a high level nuclear waste vadose zone plume. *Geochim Cosmochim Acta.* 2004;68:13–30.
- [4] Gregson CR, Goddard DT, Sarsfield MJ, Taylor RJ. Combined electron microscopy and vibrational spectroscopy study of corroded Magnox sludge from a legacy spent nuclear fuel storage pond. *J Nucl Mater.* 2011;412:145–156.
- [5] Savage D. A review of analogues of alkaline alteration with regard to long-term barrier performance. *Mineral Mag.* 2011;75(4):2401–2418.
- [6] Geelhoed JS, Meeussen JCL, Hillier S, Lumsdon DG, Thomas RP, Farmer JG, Paterson E. Identification and geochemical modeling of processes controlling leaching of Cr(VI) and other major elements from chromite ore processing residue. *Geochim Cosmochim Acta.* 2002;66:3927–3942.
- [7] Stewart DI, Burke IT, Mortimer RJG. Stimulation of microbially mediated chromate reduction in alkaline soil-water systems. *Geomicrobiol J.* 2007;24:655–669.
- [8] Geelhoed JS, Meeussen JCL, Roe MJ, Hillier S, Thomas RP, Farmer JG, Paterson E. Chromium remediation or release? Effect of iron(II) sulfate addition on chromium leaching from columns of chromite ore processing residue. *Environ Sci Technol.* 2003;37:3206–3213.
- [9] Whittleston RA, Stewart DI, Mortimer RJG, Tilt ZC, Brown AP, Geraki K, Burke IT. Chromate reduction in Fe(II)-containing soil affected by hyperalkaline leachate from chromite ore processing residue. *J Hazard Mater.* 2011;194:15–23.
- [10] Farmer JG, Thomas RP, Graham MC, Geelhoed JS, Lumsdon DG, Paterson E. Chromium speciation and fractionation in ground and surface waters in the vicinity of chromite ore processing residue disposal sites. *J Environ Monit.* 2002;4:235–243.
- [11] Fleury B, Frommer J, Eggenberger U, Mader U, Nachtgaal M, Kretzschmar R. Assessment of long-term performance and chromate reduction mechanisms in a field scale permeable reactive barrier. *Environ Sci Technol.* 2009;43:6786–6792.
- [12] Farrell J. Removal of hexavalent chromium from groundwater using zero-valent iron media. In: Lo IMC, Surampalli RY, Lai KCK, editors. *Zero-valent iron reactive materials for hazardous waste and inorganic removal.* Reston, VA: American Society of Civil Engineers; 2007;61–76.
- [13] Alowitz MJ, Scherer MM. Kinetics of nitrate, nitrite and Cr(VI) reduction by iron metal. *Environ Sci Technol.* 2002;36:299–306.

- [14] Christiansen BC, Balic-Zunic T, Petit PO, Frandsen C, Morup S, Geckeis H, Katerinopoulou A, Stipp SLS. Composition and structure of an iron-bearing, layered double hydroxide (LDH) – green rust sodium sulphate. *Geochim Cosmochim Acta*. 2009;73:3579–3592.
- [15] Chaves LHG. The role of green rust in the environment: a review. *Revista Brasileira de Engenharia Agricola e Ambiental*. 2005;9:284–288.
- [16] Williams AGB, Scherer MM. Kinetics of Cr(VI) reduction by carbonate green rust. *Environ Sci Technol*. 2001;35:3488–3494.
- [17] Bond DI, Fendorf S. Kinetics and structural constraints of chromate reduction by green rusts. *Environ Sci Technol*. 2003;37:2750–2757.
- [18] Legrand L, El Figuigui A, Mercier F, Chausse A. Reduction of aqueous chromate by Fe(II)/Fe(III) carbonate green rust: kinetic and mechanistic studies. *Environ Sci Technol*. 2004;38:4587–4595.
- [19] O’Loughlin EJ, Kelly SD, Cook RE, Csencsits R, Kemner KM. Reduction of uranium(VI) by mixed iron(II)/iron(III) hydroxide (green rust): formation of UO₂ nanoparticles. *Environ Sci Technol*. 2003;37:721–727.
- [20] Myneni SCB, Tokunaga TK, Brown GE. Abiotic selenium redox transformations in the presence of Fe(II,III) oxides. *Science*. 1997;278:1106–1109.
- [21] Skovbjerg LL, Stipp SLS, Utsunomiya S, Ewing RC. The mechanisms of reduction of hexavalent chromium by green rust sodium sulphate: formation of Cr-goethite. *Geochim Cosmochim Acta*. 2006;70:3582–3592.
- [22] Ahmed IAM, Benning LG, Kakonyi G, Sumoondur AD, Ter-rill NJ, Shaw S. Formation of green rust sulfate: a combined in situ time-resolved X-ray scattering and electrochemical study. *Langmuir*. 2010;26:6593–6603.
- [23] Ahmed IAM, Shaw S, Benning LG. Formation of hydroxy-sulphate and hydroxycarbonate green rusts in the presence of zinc using time-resolved in situ small and wide angle X-ray scattering. *Mineral Mag*. 2008;72:159–162.
- [24] Method 7196A Chromium. Hexavalent (Colorimetric). Washington, DC: U.S. Environmental Protection Agency; 1992.
- [25] Johnson TL, Scherer MM, Tratnyek PG. Kinetics of halogenated organic compound degradation by iron metal. *Environ Sci Technol*. 1996;30:2634–2640.
- [26] Wander MCF, Rosso KM, Schoonen MAA. Structure and charge hopping dynamics in green rust. *J Phys Chem C*. 2007;111:11414–11423.
- [27] Sharma YC, Srivastava V, Singh VK, Kaul SN, Weng CH. Nano-adsorbents for the removal of metallic pollutants from water and wastewater. *Environ Technol*. 2009;30:583–609.
- [28] Domenico PA, Schwartz FW. *Physical and chemical hydrogeology*. 2nd ed. New York: Wiley; 1998.
- [29] Furukawa Y, Kim J, Watkins J, Wilkin RT. Formation of ferrihydrite and associated iron corrosion products in permeable reactive barriers of zero-valent iron. *Environ Sci Technol*. 2002;36:5469–5475.