



# Article Reduction of Chlorinated Ethenes by Ag- and Cu-Amended **Green Rust**

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Abstract: Chlorinated ethenes have been used extensively as solvents, degreasers, and dry-cleaning agents in a range of commercial and industrial applications. This has created a legacy of contaminated soils and groundwater, particularly with respect to perchloroethylene (PCE; a.k.a. tetrachloroethene-C<sub>2</sub>Cl<sub>4</sub>), and trichloroethylene (TCE; a.k.a. trichloroethene-C<sub>2</sub>HCl<sub>3</sub>), prompting the development of a wide array of treatment technologies for remediation of chlorinated ethene-contaminated environments. Green rusts are highly redox-active layered Fe(II)-Fe(III) hydroxides that have been shown to be facile reductants for a wide range of organic and inorganic pollutants. The reduction of chlorinated ethenes [vinyl chloride (VC); 1,1-dichloroethene(11DCE), cis-1,2-dichloroethene (c12DCE), trans-1,2-dichloroethene (t12DCE), TCE, and PCE] was examined in aqueous suspensions of green rust, alone as well as with the addition of Ag(I) (AgGR) or Cu(II) (CuGR). Green rust alone was ineffective as a reductant for the reductive dechlorination for all of the chlorinated ethenes. Nearcomplete removal of PCE was observed in the presence of AgGR, but all other chlorinated ethenes were essentially non-reactive. Partial removal of chlorinated ethenes was observed in the presence of CuGR, particularly 11DCE (34%), t12DCE (51%), and VC (66%). Significant differences were observed in the product distributions of chlorinated ethene reduction by AgGR and CuGR. The effectiveness of Ag(I)- and Cu(II)-amended green rusts for removal of chlorinated ethenes may be improved under different conditions (e.g., pH and interlayer anion) and warrants further investigation.

Keywords: reductive dechlorination; catalysis; perchloroethene; tetrachloroethene; trichloroethene; dichloroethane; vinyl chloride

### 1. Introduction

Green rusts are layered Fe(II)-Fe(III) hydroxides with a pyroaurite-type structure with alternating positively charged Fe(II)-Fe(III) hydroxide layers and hydrated anion layers with the general composition:  $[Fe(II)_{1-x} Fe(III)_x (OH)_{12}]^{x+} [(A)_{x/n} yH_2O]^{x-}$ , where A is an *n*-valent anion (e.g.,  $Cl^-$ ,  $F^-$ ,  $SO_4^{2-}$ , or  $CO_3^{2-}$ ), *x* is the molar fraction of Fe(III) typically ranging from 0.25 to 0.33, and y denotes varying amounts of interlayer water (y = 2 to 4) [1]. Green rusts are key components of the biogeochemical cycling of Fe in aquatic and terrestrial systems and are formed during microbial reduction of Fe(III) oxides [2-12], during direct microbial or coupled biotic/abiotic oxidation of Fe(II) under anoxic conditions by denitrifying bacteria [13–16], and during abiotic and microbially induced corrosion of iron and steel [17–20]. As such, they are found in Fe(II)–Fe(III) transition zones in a variety of natural and engineered environments including surface waters [21], groundwater [22,23], soils [24-29], sediments [30-32], and permeable reactive barriers [33-38], often as the minerals fougérite, trébeurdenite, and mössbauerite [39-41]. Furthermore, green rusts are highly redox-active and have been shown to be facile reductants for a wide range of organic and inorganic pollutants including nitrate, toxic metals, metalloids, radionuclides, azo dyes, nitroaromatics, and halogenated hydrocarbons [42-65].



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Chlorinated methanes, ethanes, and ethenes have been used extensively as solvents, fumigants, degreasers, and dry-cleaning agents, with annual production in the millions of tons. Their use in a range of commercial and industrial applications, as well as from improper disposal, has created a legacy of contaminated soils and groundwater, particularly with respect to carbon tetrachloride (CT; a.k.a. tretrachloromethane-CCl<sub>4</sub>), chloroform (CF; a.k.a. trichloromethane-CHCl<sub>3</sub>), methylene chloride (DCM; a.k.a. dichloromethane-CH<sub>2</sub>Cl<sub>2</sub>), 1,1,1-trichloroethane (111TCA;  $C_2H_3Cl_3$ ), 1,2-dichloroethane (12DCA;  $C_2H_4Cl_2$ ), perchloroethylene (PCE; a.k.a. tetrachloroethene— $C_2Cl_4$ ), and trichloroethylene (TCE; a.k.a. trichloroethene— $C_2HCl_3$ ) [66–68]. Many of these chlorinated compounds are acute toxins, carcinogens, mutagens, and endocrine disruptors [69], prompting the development of a wide array of treatment technologies for remediation of contaminated environments, which often entail reductive dechlorination to non-chlorinated products [70,71].

The reductive dehalogenation of halogenated hydrocarbons by green rust has been the focus of several studies, beginning with the work by Erbs et al. [46] showing reduction of CT to CF and PCE by sulfate green rust ( $GR_{SO4}$ , i.e., green rust with sulfate as the interlayer anion). CF was also the main product of the reduction of CT by chloride green rust (GR<sub>Cl</sub>), along with methane (CH<sub>4</sub>) and a trace of ethane ( $C_2H_6$ ) [72]. O'Loughlin et al. examined the reduction of the entire series of chlorinated methanes by GR<sub>SO4</sub> and found that CT was readily reduced to CF and carbon monoxide (CO), as well as trace amounts of methane and PCE; CF was minimally reactive and only trace amounts of methane, DCM, ethane, and ethene ( $C_2H_4$ ) were observed and DCM and chloromethane (CM; CH<sub>3</sub>Cl) were non-reactive [73]. Hexachloroethane (HCA; C<sub>2</sub>Cl<sub>6</sub>) is readily reduced to PCE by  $GR_{SO4}$  and minor products consisting of pentachloroethane (PCA:  $C_2HCl_5$ ), TCE, ethene, and ethane [45,57]. As with the chlorinated methanes, the extent of reduction of lesserchlorinated ethane analogs by GR<sub>SO4</sub> generally decreased with decreasing number of chlorines [57]. In contrast to the facile reduction of CT and HCA by green rust, most studies of the reduction of PCE (the fully chlorinated endmember of the chlorinated ethene series) by green rust indicate no or very limited reduction [74–78]; however, modest reduction of PCE (<35%) has been reported [53,72]. Likewise, green rusts have typically been found to support limited to no reduction of lesser chlorinated ethenes [53,72,76-78].

Several approaches have been developed to enhance the rates and extent of reduction of chlorinated methanes, ethanes, and ethenes by facilitating electron transfer from green rust to the chlorinated hydrocarbon. O'Loughlin et al. found that the addition of Ag(I), Au(III), or Cu(II) to green rust suspensions increased the reduction rates of chlorinated methanes and ethanes by up to three orders of magnitude [57,73]. Furthermore, the overall extent of transformation was enhanced, both in terms of the amount of parent compound reduced, as well as the fraction of reactions products consisting of non-chlorinated products. Likewise, the addition of Cu(II) or Pt(IV) to green rust suspensions increased the rates, extents, and fraction of non-chlorinated reaction products of PCE and TCE [72,75,79]. Ayala-Luis et al. reported that the reduction of CT by green rust intercalated with the surfactant dodecanoate ( $GR_{C12}$ ) was 27-fold faster than with unaltered  $GR_{SO4}$  and that the final products were primarily CO (>54%) and formic acid (>6%), with only minor amounts of CF (<6.3%) [80]. The addition of Cu(II) to GR<sub>C12</sub> lead to CT reduction that was 37-fold faster than with  $GR_{C12}$  alone and the formation of DCM and CM [81]. The presence of graphene oxide increased the reduction of CT relative to green rust alone; however, CF is the end product of the reaction [82]. Recently, Ai et al. reported that the addition of bone char to green rust suspensions resulted in the near-complete reduction of PCE, TCE, *cis*-1,2-dichloroethene (c12DCE: C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub>), and *trans*-1,2-dichloroethene (t12DCE: C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub>) to acetylene (>85%) [78]; no reduction was observed in the presence of either bone char or green rust alone. These results show that modified or amended green rust may be effective agents for the reductive dechlorination of chlorinated hydrocarbons including chlorinated ethenes.

No previous studies of chlorinated ethene reduction by green rusts (native or modified) have examined the entire chlorinated ethene series. Therefore, the objective of this study is to examine the potential of native and metal-amended [Ag(I) and Cu(II)] green rust for reductive dechlorination of PCE, TCE, 1,1-dichloroethene (11DCE:  $C_2H_2Cl_2$ ), c12DCE, t12DCE, and chloroethene (a.k.a. vinyl chloride (VC)— $C_2H_3Cl$ ).

### 2. Materials and Methods

## 2.1. Chemicals

PCE (99.9+%), TCE (99.9+%), (99%), c12DCE (97%), t12DCE) (98%), iron(II) sulphate heptahydrate (99+%), Cu(II) chloride (99.999%), Ag(I) acetate (99.999%), propene (C<sub>3</sub>H<sub>6</sub>; 99+%), *n*-heptane (C<sub>7</sub>H<sub>16</sub>; 99+%), 1-butene (C<sub>4</sub>H<sub>8</sub>; 99+%), and a mixture of *cis*and trans-2-butene ( $C_4H_8$ ; 38.1% cis and 61.6% trans) were obtained from Aldrich. A multi-component gas mixture containing methane, ethane, ethane, and acetylene (each at 1.0 mole% in N<sub>2</sub>), propane ( $C_3H_8$ ; 1.002% in N<sub>2</sub>), *n*-butane ( $C_4H_{10}$ ; 1.0% in N<sub>2</sub>), and VC, (0.1% in N2) were purchased from Scott Specialty Gases. Sulfate green rust was synthesized by air oxidation of a 1.0 M Fe(II)SO<sub>4</sub> solution as described by O'Loughlin et al. [83]. X-ray diffraction (XRD) analysis of the  $GR_{SO4}$  suspension showed it to be free of other crystalline Fe-bearing solid phases (e.g., goethite, lepidocrocite, magnetite) [83]. The  $GR_{SO4}$ consisted of nominally hexagonal, platy, 100-500 µm wide crystallites (Figure S1) with a surface area of 14.1 m<sup>2</sup> g<sup>-1</sup>, as determined by five-point Brunauer–Emmett–Teller (BET) N2 adsorption [73]. Ag-amended and Cu-amended GR<sub>SO4</sub> (AgGR, and CuGR, respectively) were prepared by spiking the  $GR_{SO4}$  suspension with either 10 mM Ag(I), or 10 mM Cu(II) [73], resulting in the formation of Ag(0) or Cu(0) nanoparticles and partial oxidation of the  $GR_{SO4}$  to magnetite (Fe<sub>3</sub>O<sub>4</sub>) [58].

### 2.2. Experimental Setup

The experiments were conducted in 160 mL serum bottles as described by O'Loughlin and Burris [57]. Initial solution concentrations were 30 mM Fe(II) as  $GR_{SO4}$  and 100  $\mu$ M Ag(I) or Cu(II) (except for controls containing green rust only). Reactions were initiated by the addition of 2  $\mu$ L of a 1.0 M methanolic solution of the chlorinated ethene of interest, resulting in 2  $\mu$ mol of halogenated ethane in each bottle. The pH of the experimental systems was 7.6  $\pm$  0.1. Chlorinated ethenes and the main non-chlorinated products of their reductive dechlorination (Figure 1) are sufficiently volatile that their concentrations in the experimental system can be monitored by measuring their headspace concentrations [84]. Therefore, at selected times, 200  $\mu$ L headspace samples were removed from the serum vials for analysis using a Hewlett-Packard 5890 Series II gas chromatograph (Avondale, PA, USA) as described by O'Loughlin and Burris [57].



**Figure 1.** Potential pathways for the reduction of chlorinated ethenes (modified from [85]). The blue arrows designate  $\beta$ -elimination reactions (RCl = RCl +  $2e^- \rightarrow R \equiv R + 2Cl^-$ ), red indicates  $\alpha$ -elimination (R = RCl<sub>2</sub> +  $2e^- \rightarrow R \equiv R + 2Cl^-$ ), green designates hydrogenation (R = R +  $2e^- + 2H^+ \rightarrow HR = RH$  or R = R +  $2e^- + 2H^+ \rightarrow HR = RH$ ), and black designates hydrogenolysis (R = RCl +  $2e^- + H^+ \rightarrow R = RH + Cl^-$ ). PCE = perchloroethene; TCE = trichloroethene; 11DCE = 1,1-dichloroethene; c12DCE = *cis*-1,2-dichloroethene; and trans-1,2-DCE = *trans*-1,2-dichloroethene.

### 3. Results and Discussion

# 3.1. Reduction of Chlorinated Ethenes by GR<sub>SO4</sub>

Plots of concentration versus time for the chlorinated ethenes in aqueous suspensions with  $GR_{SO4}$  are shown in Figure 2 and mass recoveries of the reactants and volatile products (chlorinated ethenes, acetylene, ethene, and ethane) are given in Table 1. No reaction products were detected, although water-soluble reactions products such as acetate and acetaldehyde (for which our headspace analysis would have had low sensitivity) have been observed or postulated as minor products of chlorinated ethene reduction [86,87], and may have been present. The absence of volatile reaction products and >95% recovery of the chlorinated ethenes (except for 86% PCE recovery) at the end of the experiment indicate that  $GR_{SO4}$  was not an effective reductant for any of the chlorinated ethenes under our experimental conditions. The incomplete mass recovery for PCE is not likely due to chemical transformation of PCE, rather, minor amounts of PCE may have been lost to sorption to the septum or to green rust [53].



**Figure 2.** Reduction of chlorinated ethenes in aqueous suspensions containing 2 µmol of the indicated compound and 0.5 g of  $GR_{SO4}$  either without (GR) or with the addition of 10 µmol of Ag(I) (AgGR) or Cu(II) (CuGR). Lines are for visualization purposes only. PCE = perchloroethene; TCE = trichloroethene; 11DCE = 1,1-dichloroethene; c12DCE = *cis*-1,2-dichloroethene; t12DCE = *trans*-1,2-dichloroethene; and VC = vinyl chloride. The data for Figure 2 is provided in Table S1.

**Table 1.** The extents of chlorinated ethene removal, final product distributions, and carbon recoveries in aqueous suspensions of unamended green rust (GR), and green rust amended with  $10^{-4}$  M of either Ag(I) or Cu(II) (AgGR and CuGR, respectively).

Compound <sup>a</sup>	System	Final Sampling (h)	Compound Remaining	Products <sup>a</sup>	Carbon Recovery <sup>b</sup>
РСЕ	GR	502	85.7%	ND	85.7%
	AgGR	189	1.5%	TCE(87.4%), t12DCE(7.3%), AC(7.4%), and EE(0.5%)	104.2%
	CuGR	627	67.9%	TCE(6.3%), EE(3.3%), and EA(0.3%)	77.7%
TCE	GR	501	97.4%	ND	97.4%
	AgGR	501	87.6%	AC(1.8%) and EE(1.1%)	89.9%
	CuGR	625	79.9%	EE(11.1%) and EA(1.1%)	92.1%
11DCE	GR	499	95.7%	ND	95.7%
	AgGR	501	93.8%	EE(0.3%)	94.1%
	CuGR	624	66.1%	EE(30.2%) and EA(2.8%)	99.1%
c12DCE	GR	500	100.0%	ND	100.0%
	AgGR	501	97.4%	EE(0.1%)	97.5%
	CuGR	625	83.1%	VC(1.0%), EE(14.9%), and EA(1.5%)	100.5%
t12DCE	GR	504	95.2%	ND	95.2%
	AgGR	499	94.2%	AC(0.8%), EE(0.3%), and EA(0.1%)	95.3%
	CuGR	623	48.9%	EE(42.6%) and EA(4.5%)	96.9%
VC	GR	497	100.0%	ND	100.0%
	AgGR	501	99.5%	ND	99.5%
	CuGR	622	34.2%	EE(58.2%) and EA(7.4%)	99.8%

<sup>*a*</sup> PCE = perchloroethene; TCE = trichloroethene; 11DCE = 1,1-dichloroethene; c12DCE = *cis*-1,2-dichloroethene; t12DCE = *trans*-1,2-dichloroethene; VC = vinyl chloride; AC = acetylene; EE = ethene; EA = ethane; and ND = no products detected. <sup>*b*</sup> Carbon molar balance of identified products and any remaining parent compound relative to the initial moles of parent compound.

Our results are consistent with previous studies showing no reduction of polychlorinated ethenes by green rusts (GR<sub>SO4</sub>, GR<sub>CO3</sub>, GR<sub>C1</sub>, and GR<sub>F</sub>) [75,77,78]; however, others have reported significant, if not complete, reduction of polychlorinated ethenes and vinyl chloride by green rusts [53,72,74,76,88]. The variability in the reactivity of green rust with chlorinated ethenes has been attributed to multiple factors including the type of interlayer anion, surface area, pH, Fe(II)/Fe(III) ratio, and amount of Fe(II) sorbed on the green rust, and artifacts from GR preparation and handling [53,72,76,77,88]. Interlayer anion composition has been shown to affect the rate of reduction of nitrate, chromate [Cr(VI)], and U(VI) by green rust [43,48,52], and Liang et al. [76] observed faster rates of PCE and TCE reduction with GR<sub>Cl</sub> relative to GR<sub>SO4</sub>, which they attributed to the greater surface area of the GR<sub>Cl</sub> used in their study. Han et al. [88] observed a decrease in the reduction rates of c12DCE and VC with increasing pH, which they ascribed to increasing amounts of Fe(II) on the green rust surface with increasing pH. Conversely, both Lee and Batchelor [53] and Maithreepala and Doong [72] reported a decrease in the rates of TCE and PCE reduction with increasing pH. Lee and Batchelor suggested their results could be explained by an increase in the overall thermodynamic driving force of the reaction at high pH due to the lower concentration hydrogen ions, a product of the dechlorination reaction, or to the increase in formation of hydroxide functional groups on green rust, which are presumed to be more reactive reductants. The lack of a consistent pattern in the reactivity of chlorinated ethenes with green rusts suggests that the observed differences in reactivity are perhaps due to multiple, often interrelated, factors.

### 3.2. Reduction of Chlorinated Ethenes by Ag-Amended GR<sub>SO4</sub>

As with the un-amended GR, there was essentially no dechlorination of VC and the DCEs by AgGR (Figure 2), as reaction products accounted for only 0.1-1.1% of the carbon mass balance (Table 1). TCE concentration decreased by ~12% over 501 h in the presence of AgGR, but only 3% was recovered as reaction products (acetylene and ethene). However, within 189 h, PCE was nearly completely transformed to TCE (87.4%), t12DCE (7.3%), and acetylene (7.4%). The distribution of the reaction products suggests that PCE is primarily transformed to TCE via hydrogenolysis (Figure 1), with TCE being essentially a terminal product as reduction of TCE by AgGR was minimal (Figure 2). However, some transformation of PCE to dichloroacetylene via  $\beta$ -elimination (Figure 1) is suggested by the formation of t12DCE and acetylene. Dichloroacetylene was not observed as an intermediate; however, this is not surprising given that it is rapidly dechlorinated to chloroacetylene via hydrogenolysis and to t12DCE via hydrogenation [89]. Given that t12DCE is essentially unreactive with AgGR, it is unlikely that  $\beta$ -elimination of t12DCE contributed significantly to the observed production of acetylene during PCE reduction (Figure 1). Rather, acetylene was likely the result of hydrogenolysis of chloroacetylene. As with dichloroacetylene, chloroacetylene was not observed as an intermediate; however, like dichloroacetylene, it is easily dechlorinated via hydrogenolysis, resulting in acetylene [89,90]. The formation of acetylene from the dechlorination of TCE by AgGR and the non-reactivity of lesser chlorinated ethenes suggests transformation of TCE to chloroacetylene via  $\beta$ -elimination, with subsequent reduction to acetylene (Figure 1). Reductive dechlorination of PCE and TCE by transition metal species often results in the formation of non-chlorinated  $C_3$ - $C_6$ alkanes and alkenes [85,86,90–93] attributed to radical coupling reactions; however, no such products were detected resulting from PCE reductive dechlorination by AgGR.

### 3.3. Reduction of Chlorinated Ethenes by Cu-Amended GR<sub>SO4</sub>

With the exception of PCE, chlorinated ethene reduction by CuGR was enhanced relative to AgGR or unamended GR (Figure 2). Over 622 h, 65.6% of VC was reduced to ethene (58.2%) and ethane (7.4%), consistent with dechlorination of VC via hydrogenolysis followed by hydrogenation of ethene to ethane (Figure 1). Approximately 50% of t12DCE was transformed to ethene (42.6%) and ethane (4.5%). These products could result from t12DCE dechlorination via  $\beta$ -elimination resulting in acetylene, and hydrogenation of acetylene to ethene or via sequential hydrogenolysis reactions forming VC then ethene; however, in either case, the initial transformation product (acetylene or VC) never accumu-

lated at detectable concentrations. CuGR was less effective at dechlorination of c12DCE, with >80% remaining after 625 h. The product distribution (VC (1.0%), ethene (14.9%), and ethane (1.55) is consistent with c12DCE dechlorination via sequential hydrogenolysis reactions, although the potential for dechlorination by the  $\beta$ -elimination pathway cannot be discounted. Within 624 h, ~44% of 11DCE was dechlorinated in the presence of CuGR, resulting in ethene (30.2%) and ethane (2.85). Ethene could be produced directly from 11DCE via an  $\alpha$ -elimination reaction or via serial hydrogenolysis (Figure 1).

Although greater than in the presence of AuGR or unamended GR, the dechlorination of TCE in the CuGR system was limited, with ~80% remaining after 625 h. No lesser chlorinated intermediates were detected, but the formation of ethene (11.1%) and ethane (1.1%) suggest the potential for multiple reaction pathways as shown in Figure 1. PCE concentrations decreased by ~32% within 627 h accompanied by the formation of TCE (3.6%), ethene (3.3%) and, ethane (0.3%). Similar to TCE, the observed products of PCE reduction may result from multiple reaction pathways. As with AgGR, there was no evidence of the formation of radical coupling products.

### 3.4. Comparison with Other Studies of Chlorinated Ethenes by Metal-Amended Green Rust

This is the first study to examine the dechlorination of the entire series of chlorinated ethenes by metal-amended green rusts; however, other studies have focused on PCE and TCE. No prior studies have examined chlorinated ethene reduction by Ag-amended green rust; however, Choi and Lee observed enhanced reductive dechlorination of PCE by green rusts amended with Pt(IV) [75]. PCE was essentially completely transformed to acetylene by chloride, fluoride, carbonate, and sulfate green rusts amended with Pt(IV), unlike our system with AgGR, in which TCE was the dominant product, with lesser amounts of t12DCE and acetylene (Table 2). Maithreepala and Doong examined the reduction of PCE and TCE in the presence of Cu-amended chloride green rust [72]. Within 35 days, >85% of PCE was removed, with TCE (16.6%) and ethene (31.95) as the major transformation products. Over the same period in TCE-amended systems, ~50% of TCE was removed, with ethene (11%) and ethane (1%) as products. Although the overall extents of reaction were greater, the products formed were similar to those observed in our study.

Compound <sup>a</sup>	Products <i>a</i> , <i>b</i>	This Study <sup>c</sup> AgGR <sub>SO4</sub>	Choi and Lee [79] <sup>d</sup> PtGR <sub>F</sub> , <sub>Cl, SO4</sub> , <sub>CO3</sub>	This Study <sup>e</sup> CuGR <sub>SO4</sub>	Maithreepala and Doong [72] <sup>f</sup> CuGR <sub>Cl</sub>
PCE		$2.30 \pm 0.09 \times 10^{-2}  h^{-1g}$	$9.93\pm0.58\times10^{-2}~h^{-1}$	$5.96 \pm 0.69  imes 10^{-4} \ h^{-1}$	$3.06\pm0.39 imes10^{-1}~h^{-1}$
	PCE	1.5%	~1–15%	67.9%	12.4%
	TCE	87.4%	-	6.3%	16.6%
	t12DCE	7.3%	-	-	-
	acetylene	7.4%	~71–90%	-	-
	ethene	0.5%	-	3.3%	31.9%
	ethane	-	-	0.3%	0.1%
	Carbon recovery	104.2%	81-95%	77.7%	61.0%
TCE		$2.44 \pm 0.53  imes 10^{-4} \ h^{-1}$	-	$3.59\pm0.23 imes10^{-4}~h^{-1}$	$\sim 9.58 \times 10^{-4} \ h^{-1}$
	TCE	87.6%	-	79.9%	51.0%
	acetylene	1.8%	-	-	-
	ethene	1.1%	-	11.1%	11.0%
	ethane	-	-	1.1%	1.0%
	Carbon recovery	89.9%	-	92.1%	63.0%

 Table 2. coducts in metal-amended green rust systems.

<sup>*a*</sup> PCE = perchloroethene; TCE = trichloroethene; and t12DCE = *trans*-1,2-dichloroethene. <sup>*b*</sup> Carbon molar balance of identified products and any remaining parent compound relative to the initial moles of parent compound. <sup>*c*</sup> Experimental conditions: pH ~7.6, 3 mmol Fe(II), 10 µmol Ag(I), 2 µmol PCE or TCE, and 8 and 21 day incubation period at 25 °C for PCE and TCE, respectively. <sup>*d*</sup> Experimental conditions: pH ~7.5, 2.0–2.2 mmol Fe(II), 24.3 µmol Pt(IV), 6 µmol PCE, and 5–26 day incubation period at 25 °C. <sup>*e*</sup> Experimental conditions: pH ~7.6, 3 mmol Fe(II), 10 µmol Cu(II), 2 µmol PCE or TCE, and 26 day incubation period at 25 °C for PCE and TCE. <sup>*f*</sup> Experimental conditions: pH ~7.2, 12.9 µmol Fe(II), 25 µmol Cu(II), 0.9 µmol PCE or TCE, and 35 day incubation period at 25 °C for PCE and TCE. <sup>*g*</sup> Pseudo-first-order rate constants for the reduction of PCE and TCE. The rate constant for PCE reduction from Choi and Lee [79] is from the PtGR<sub>SO4</sub> system.

As discussed in Section 3.1, differences in the reactivity of unamended green rusts with respect to dechlorination of chlorinated ethenes has been linked to several factors, several of which have been investigated in relation to the efficiency of chlorinated ethene reduction by metal-amended green rusts. As with unamended green rust, pH was found to affect PCE removal efficiency, and the relationship between pH and PCE removal efficiency was not consistent among experimental systems. Maithreepala and Doong [72] reported that the rates of PCE removal by Cu(II)-amended GR<sub>Cl</sub> increased from pH 5.5 to 7.2, but decreased at pH 9, while Choi et al. reported the rates of PCE removal by C(II)-amended GR<sub>F</sub> highest at pH 11, with decreasing rates at pH 9 and 7.5 [79]. It is possible that the differences in pH effect on PCE removal rates between these two studies is related to the type of interlayer anion in the green rusts used in each, as differences in PCE removal rates have been reported for Cu(II)- and Pt(IV)-amended green rusts (F<sup>-</sup> >> CO<sub>3</sub><sup>2-</sup> >> SO<sub>4</sub><sup>2-</sup> > Cl<sup>-</sup> and F<sup>-</sup> > Cl<sup>-</sup> > SO<sub>4</sub><sup>2-</sup> > CO<sub>3</sub><sup>2-</sup>, respectively) [75,79].

Maithreepala and Doong reported that both the removal efficiency and the rate of PCE removal by Cu(II)-amended GR<sub>Cl</sub> increased with increasing amounts of green rust at a fixed Cu(II) concentration of 0.5 mM [72]. Similarly, the rates of PCE and TCE removal by Cu(II)- and Pt(IV)-amended green rusts increased with increasing metal loadings [72,75,79], although in many cases the rates decreased at the highest metal loadings examined, which may have been due to corresponding decreases in Fe(II) levels under these conditions [72,79]. Choi et al. [79] observed an initial increase followed by a leveling off of PCE removal rates by Cu(II)-amended fluoride green rust consistent with saturation of PCE sorption sites at the higher PCE concentrations.

The product distributions of chlorinated ethene reduction by metal-amended green rusts varied based on the metal amendment (Tables 1 and 2), as has been reported for the reduction of chlorinated methanes and ethanes [57,73]. Enhanced reduction of chlorinated hydrocarbons has been reported for Ag(I)-, Au(III)-, Cu(II)-, and Pt(IV)-amended green rust, and in each system the metals are reduced by green rust to their zero valent (ZV) forms (i.e, Ag(0), Au(0), Cu(0), and Pt(0)) [58,72,75]. The enhanced reduction of chlorinated hydrocarbons by green rust-ZVAg/Au/Cu/Pt systems may be comparable to the enhanced chlorinated hydrocarbon reduction observed with bimetallic reductants [94-99] consisting of a ZV noble metal (e.g., Pd(0), Pt(0), or Ni(0)) with a more active metal (e.g., Fe(0) or Zn(0)). The specific mechanism(s) leading to the enhanced effectiveness of these bimetallic systems have not been fully characterized [100]. However, it is known that coupling a noble metal with a more reactive metal accelerates the oxidation of the more reactive metal, forming a galvanic cell wherein the active metal serves as the anode and the noble metal acts as the cathode (where electrons are transferred to the oxidant (e.g., chlorinated hydrocarbons). Such a process has been proposed for the catalytic activity of bimetallic reductants [101], and a similar process may be occurring in the green rust-ZVAg/Au/Cu/Pt systems. Furthermore, Liu et al. have reported that the kinetics and product distribution of the electrolytic reduction of carbon tetrachloride varies with the metal used for the cathode [102], which is consistent with the differences in the rates/extents and product distributions observed with different green rust-ZV metal systems.

### 3.5. Potential Utility of Metal-Amended Green Rusts for Remediation of Chlorinated Ethenes

Ag(I)- and Cu(II)-amended green rusts have been shown to be effective reductants for the dechlorination of many chlorinated methanes and ethanes [57,72,73]. Under our experimental conditions, these materials (with a couple of notable exceptions) did not demonstrate a level of reactivity that would make them suitable for use in remediation of chlorinated ethene contamination. However, under different conditions (e.g., pH and interlayer anion), metal-amended green rusts have demonstrated much higher levels of PCE and TCE removal [72,75,79] than observed in this study, suggesting that the effectiveness of Ag(I)- and Cu(II)-amended green rusts for removal of chlorinated ethenes could be improved and warrants further investigation. Given the potential ecotoxicology issues involved with the use of Ag and Cu, as well as the costs associated with precious metals like Ag, Au, and Pt, the use of metal-amended green rusts for remediation of chlorinated hydrocarbons is probably best suited to ex situ applications, as this would limit the release of metals to the environment and allow for easier recovery of the Ag, Au, or Pt.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/article/10 .3390/min12020138/s1, Figure S1: Scanning electron micrograph of sulfate green rust (GR<sub>SO4</sub>) and Table S1: Data for Figure 2.

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