

White Papers

The Reductive De-chlorination of Chlorinated Compounds Using Iron Powder

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H. Ito, T. Kimura - DOWA Mining Company, Ltd.

J.J. Liskowitz - ARS Technologies, Inc.

INTRODUCTION

In recent years, chlorinated volatile organic compounds (CVOC's) such as trichloroethylene (TCE), tetrachloroethylene (PCE), or 1,1,1-trichloroethane (MC) have caused serious contamination to soils and groundwater. Several treatment methods against this problem have been considered and one innovative approach is reductive degradation using zero-valence iron. Previous works showed the reduction of 14 kinds of chlorinated solvents with iron powder (IP)¹ and the kinetics of the reduction for carbon tetrachloride (CT) with IP². In our laboratory a process for treatment of industrial waste water for heavy metals or COD by IP (DOWA IRON POWDER Method) has been developed and commercialized as a laboratory treatment equipment³. In this study it was concluded that chlorinated solvents, such as TCE, PCE, or MC, could be degraded by IP in aqueous solution. Furthermore, the degradation of TCE and PCE with IP could be enhanced with reductants which show weak acidity, like sodium hydrogen sulfite (NaSO₃).

Experimental Section

Chemicals. The chemicals used were TCE, PCE, MC, 1,1,2-trichloroethane (1,1,2-TCA), sodium hydrogen sulfite, sodium sulfite (Wako Pure Chemical Industries, Ltd., Japan), 1,1-dichloroethene (1,1-DCE), cis-1,2-dichloroethene (c-DCE), vinyl chloride (VC), and 1,1,2,2-tetrachloroethane (TeCA) (GL-Sciences Inc., Japan). IPs used here were E-200, DE, DNC-240 (DOWA Iron Powder Co., Ltd., Japan) for the reduced iron, and cast iron powder (Wako Pure Chemical Industries, Ltd., Japan). DE was pre-reduced one for DNC-240 through the manufacturing process. Surface area for each IP, determined by BET analysis, was 2.2 m²/gram for E-200, 0.5 m²/gram for DE, and 0.1 m²/gram for DNC-240.

Model Reaction Systems. All CVOC's reaction experiments were carried out in 120-ml glass hypovials as batches at 25°C. Appropriate amounts of IP (no treatment) and 100 ml of de-ionized water were added to hypovials. The hypovials were then crimp-sealed immediately with aluminum caps with Teflon-lined septa. CVOCs were taken with glass syringe and injected into the hypovials through the septa to be 100 mg/l. Then 20 ml of head space was left. The reactions were then started with mixing by a shaker at 120 min⁻¹. To measure the concentrations for CVOCs and their intermediates, 100 micro-l of the head space gas was taken by gas-tight syringe and injected into a gas chromatograph with flame ionization detector (FID). At the same time, 2-micro-l of benzene was added to each hypovial as an internal standard.

RESULTS AND DISCUSSION

The Degradation of TCE and PCE Using IP.

Figure 1 shows the time course for 100 mg/l of TCE (7.6×10^{-4} M) mixed with various amounts of E-200 (0, 1200, 6000, 12000 mg/l). The concentration of TCE was decreased exponentially in accordance with the amount of IP. So the reaction was expected to follow pseudo first-order process described below;

$$\ln C / C_0 = -k_1 t$$

$$k_1 = k_2 [\text{Fe}]$$

More than 80 mol% of TCE was degraded by 12000 mg/l of IP after two weeks. And the chlorine, which were to be displaced from TCE, existed in the aqueous solution as Cl^- ion (97% of the yield). However, Table 1 shows that k_2 values do not correspond to the amount of IP and they decreased constantly with it. This might be caused from that mixing of IP in those systems was not complete enough to show a homogenous reaction.

PCE was also degraded by IP, whose k_1 value was about one eighth times as large as that of TCE.

It was clear that TCE or PCE could be degraded by IP in aqueous solution, however approximately 20 intermediates were also detected in the systems simultaneously through the degradation. So more details for the TCE or PCE degradation pathways have to be considered.

The Effects of Reductants Such as Hydrogen Sulfite Ion. It is generally known that about 8 mg/l of oxygen exists in water as dissolved oxygen (DO) at room temperature. DO was thought to oxidize IP to ferric oxide and inhibit degradation of CVOCs. In order to remove DO from the systems, reductants (deoxygenating agents) were mixed into the system. And also, in our previous work it was obvious that controls of pH in the system could effect the reduction by IP on its surface significantly. The effects of the reductants which showed weak acidity (NaHSO_3) or weak basicity (Na_2SO_3). It appeared that the k_1 values showed remarkable increases along with NaHSO_3 concentration. On the other hand, Na_2SO_3 showed less increase compared to NaHSO_3 .

Enhanced degradation of TCE and PCE might have arisen from the IP surface that was more reductive by NaHSO_3 . Other reductants which showed weak acidity like sodium pyrosulfite ($\text{Na}_2\text{S}_2\text{O}_5$) or sodium hydrosulfite ($\text{Na}_2\text{S}_2\text{O}_4$) in aqueous solution were confirmed to increase CVOCs' degradation rates as well as NaHSO_3 .

TABLE 2: The comparison of k_1 and k_1 -r among four kinds of IP.

Table 2 shows the k_1 (without NaHSO_3 in the system) and k_1 -r (with 2000 mg/l NaHSO_3) values degrading PCE using four kinds of IP. Thought these values varied with the IPs, NaHSO_3 was expected to increase k_1 values in any cases except for DNC-240 (see the last column of k_1 -r / k_1). Furthermore, significant differences of k_1 values were shown clearly with each IP.

Application to other CVOCs. As described above, chlorinated ethenes like TCE and PCE were degraded by IP in aqueous solution. In our laboratory applications to other types of CVOC degradation, such as chlorinated methanes, ethanes or aromatics using IP were also conducted. As a result, chlorinated ethanes like MC, 1,1,2-TCA, TeCA could be degraded

via de-hydrochlorination with IP. Chlorinated methanes or aromatics, however, could not be degraded by IP in the same condition.

CONCLUSIONS

Based on the investigations, the following conclusions were made:

1. Chlorinated ethenes like TCE and PCE were degraded by IP in the aqueous solution. The degradation might follow a pseudo first-order process with respect to the amount of IP through second-order rate constants, k_2 , could not correspond to each amount of IP.
2. TCE or PCE degradation rates using IP were highly increased adding weak acid reductants such as NaHSO_3 to the systems, where weak base reductants could not increase the rates in the same conditions.
3. Degradation rates, k_1 , varied with the different sorts of IP. From the results, E-200 was found to be the most reactive of the four IPs used in this test.
4. Applications of IP to other CVOCs like chlorinated ethanes, methanes, or aromatics were investigated and chlorinated ethanes such as 1,1,2-TCA or TeCA could be degraded via de-hydrochlorination with IP.

Further analysis of the intermediates for the degradation of CVOCs is under investigation and then the degradation mechanisms can be considered in more detail.

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