

The Dechlorination of Hydrocarbons

PALLADISED IRON UTILISED FOR GROUND WATER PURIFICATION

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The pollution of groundwater and soils by industrial chemicals is a cause of significant environmental concern. Treatment with palladium is suggested as a means of decontaminating certain occurrences of polluted soil and groundwater. Palladium can be chemically deposited onto zero-valence iron (Fe^0) and the resulting bimetal is very effective in dechlorinating many of the toxic chemicals, produced as industrial effluents, that are found in soils and groundwater. With a palladium content of 0.05 per cent (w/w), the rate at which trichloroethene is dechlorinated is one to two orders of magnitude faster than with iron alone. Similarly, a bimetal made of palladium/iron readily dechlorinates dichloromethane and polychlorinated biphenyls which are not easily reduced by Fe^0 .

This report describes the treatment of contaminated water with a palladium/iron bimetal. Such contaminated water is typically the legacy of past practices in which chlorinated degreasing solvents were discharged to soils following use. These solvents have been used in dry-cleaning, all aspects of metals manufacturing, metal plating, engine maintenance, and in many other cleaning and fabrication applications. Consequently, thousands of sites have been affected. Other common chlorinated hydrocarbon pollutants include pesticides and herbicides, chlorophenols used in the wood-treatment industry, and polychlorinated biphenyls (PCBs) which were used in electrical capacitors and as heat transfer fluids.

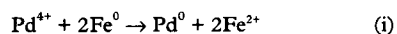
Our recent studies have demonstrated that palladium/iron rapidly dechlorinates toxic hydrocarbons, such as chlorinated ethenes, phenols and biphenyls (1–3). This research began after the publication of a report suggesting the use of zero-valence iron as a means of dechlorinating contaminated groundwater in situ (4). Iron

alone, however, suffers from relatively slow reaction rates and does not dechlorinate important compounds, such as dichloromethane and PCBs.

By chemically plating iron filings with palladium to approximately 0.05 per cent (w/w), the dechlorination rate for trichloroethene is increased by one to two orders of magnitude (5), and the dechlorination reaction is extended to include recalcitrant compounds, such as PCBs.

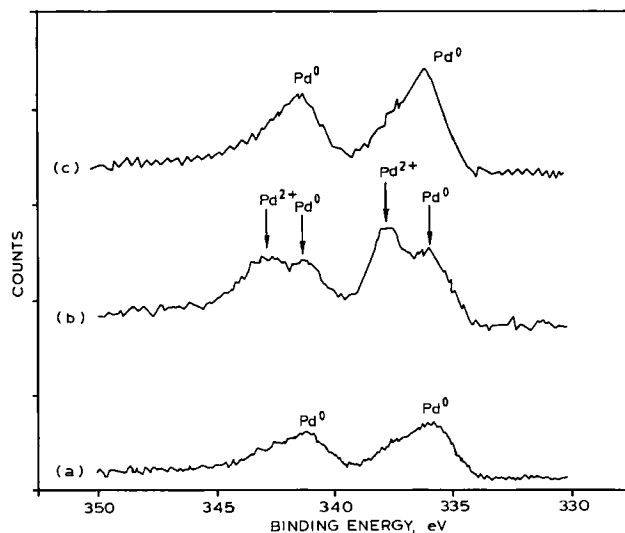
Experimental Work

The majority of the experiments conducted to date have employed 0.05 per cent (w/w) palladium. Zero-valence iron, nominally 40-mesh size, is palladised by reacting it with a solution of 99 per cent hexachloropalladate (K_2PdCl_6), according to the following reaction:



The solution at first exhibits the red-orange colour of the hexachloropalladate(IV) ion, which changes to pale yellow or clear as the reaction proceeds. X-ray photoelectron spectroscopy,

Fig. 1(a) Binding energies of the Pd 3d_{3/2} and the Pd 3d_{5/2} peaks in the X-ray photoelectron spectrum of elemental palladium deposited on the iron surface.
(b) Pd 3d peaks of elemental palladium and Pd²⁺ species after deposition of a very low surface concentration of palladium. The presence of Pd-O-Fe bonds is evident from the binding energies of the Pd²⁺ species.
(c) Pd 3d peaks after the iron surface with the Pd-O-Fe bonds was allowed to stand overnight in an ultra high vacuum

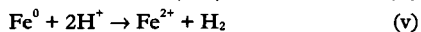
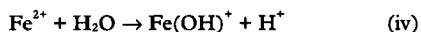


see Figure 1, has shown that the Pd(IV) ion sorbs onto the iron surface, followed by rapid reduction to Pd(0) (6). The reduction potentials of iron and palladium:



are such that the reaction is rapid and results in a stable surface which is relatively impervious to most chemical agents.

When produced in bulk, it is important to manage the production of hydrogen caused by the water-induced corrosion of iron:



Similarly, following palladisation, the material should be dried under an inert atmosphere to minimise corrosion by atmospheric oxygen. Dechlorination kinetics for volatile compounds were measured with batch studies using zero-headspace extractors (ZHEs) which prevent losses due to the leakage of volatile compounds (7). The essential components of a ZHE are a stainless steel cylinder and piston. The upward movement of the piston is controlled by applying a positive pressure at the bottom. At a given time during the reaction, a sample can be with-

drawn or displaced by slowly raising the piston, such that there is no headspace, thus assuring the gaseous by-products are collected; they are then analysed by gas chromatography.

Dechlorination Results

The dechlorinations of 1,1,2-trichloroethylene by iron and palladium/iron are compared in Figure 2. The rate constant for the reaction was approximately 0.0931/hour with iron, but improved to 1.17/hour with 0.05 per cent (w/w) palladium/iron (5). Figure 2 also shows that there is a difference in the by-products observed from the two reaction conditions. Intermediates 1,1-dichloroethene and 1,2-dichloroethene are observed when iron is the reductant. However, neither of these two compounds is observed when 1,1,2-trichloroethylene is reduced by palladium/iron. Similarly, although vinyl chloride is observed in both instances, the persistent concentration is reduced by approximately an order of magnitude when palladium/iron is used instead of iron. These results demonstrate that palladium/iron has a potential applicability to a wide variety of domestic and waste waters.

Unfortunately, not all chlorinated compounds are dechlorinated as readily as 1,1,2-trichloroethylene. For example, PCBs are notoriously

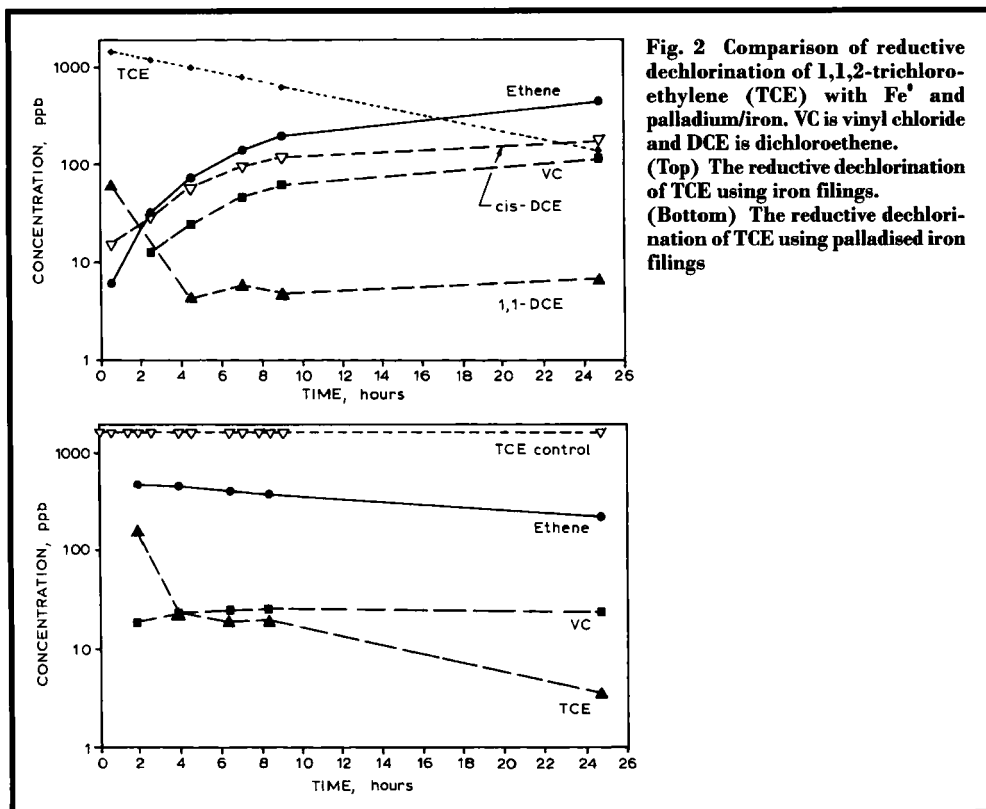


Fig. 2 Comparison of reductive dechlorination of 1,1,2-trichloroethylene (TCE) with Fe and palladium/iron. VC is vinyl chloride and DCE is dichloroethene. (Top) The reductive dechlorination of TCE using iron filings. (Bottom) The reductive dechlorination of TCE using palladised iron filings

difficult to degrade (8). A recent study required equipment comprising sealed ampoules and a temperature of 400°C for dechlorination to occur (9). With palladium/iron, however, all of the PCB congeners in Aroclor 1260 and 1254 – PCBs were typically sold and used commercially in mixtures called Aroclors – were dechlorinated within 10 minutes by reacting a methanol: water:acetone solution (mixed in a 1:3:1 volume ratio) with the 0.05 per cent w/w palladium/iron bimetal (3). Biphenyl, the principal reaction product, was identified in a hexane extract of the reaction mixture using gas chromatography/mass spectrometry, GC/MS. PCBs were not detected by GC/MS from hexane or methanol extractions of the palladium/iron following use. Parallel experiments were performed with unpalladised iron particles of size 10 µm. PCBs were detected in the hexane and methanol extracts of the unpalladised iron, but not biphenyl.

Preliminary work has also been performed with

chlorophenols. As shown in the Table, a number of chlorophenols are easily degraded with palladium/iron. Present work is concentrating on pentachlorophenol (PCP), which is a widespread water and soil contaminant in the United States of America. The dechlorination of PCP from a solvent solution is shown in Figure 3. A solvent or surfactant is required because of the low aqueous solubility of PCP. Detoxifying contaminated soils by extraction with a solvent or surfactant is considered very expensive because of the cost of reclaiming the surfactant. This experiment, therefore, suggests that palladium/iron may solve the problem by providing a convenient means of degrading the contaminants within the original extraction solution.

Mechanism

Work with zero valence iron has suggested that the reductive dechlorination reaction is a simple electron transfer, following the sorption of

Fig. 3 (a) Water-diluted 100 per cent ethanol extract of soil contaminated with pentachlorophenol; note the large pentachlorophenol peak at 6.8.

(b) Water-diluted, 100 per cent ethanol extract of soil contaminated with pentachlorophenol after contact with palladium/iron for 2 hours. The pentachlorophenol peak is absent.

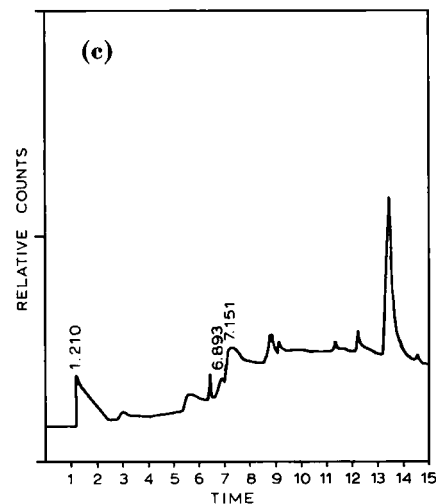
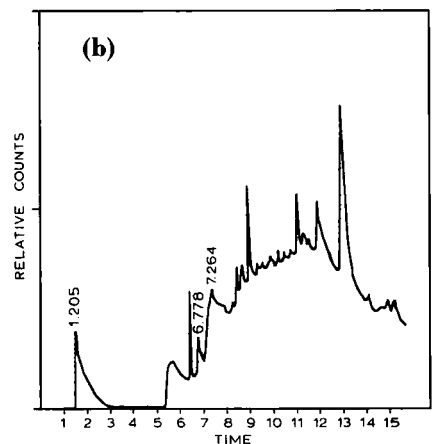
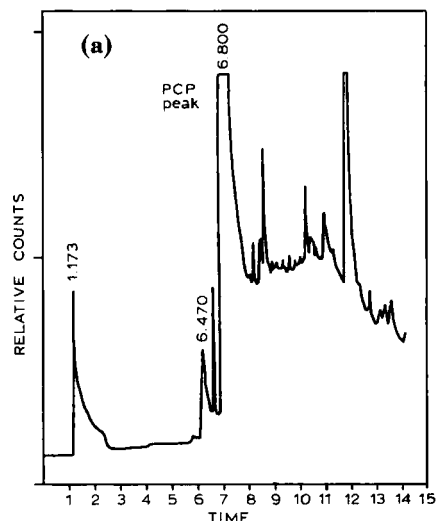
(c) Hexane extract of the palladium/iron following reaction with the pentachlorophenol extraction solution. The peak for pentachlorophenol is absent

the contaminant on the iron surface (10). A rapid two-electron transfer is suspected, based on thermodynamic calculations (11) and failure to observe free radical formation by electron spin resonance – as was attempted by the authors of this communication.

The precise role of the palladium has not been determined, however, two approaches are being considered. First, palladium may serve as an electron shuttle and may act in a manner similar to certain hydroquinones, such as jugalone. Research has shown that an azo-dye which is easily reduced by Fe^0 is not reduced when the compound is prevented from sorbing directly to the iron.

The addition of jugalone to the system, however, facilitates electron transfer and the reduction then proceeds rapidly (12). Palladium may act in a similar fashion while bound to the iron. However, such an electron shuttle effect would essentially be an enhancement for the electron transfer process. The reaction rate for compounds which are reduced by zero valence iron would be increased. The effectiveness of palladium/iron for circumstances where zero valent iron is ineffective, such as for surfactant/solvent solutions or for dichloromethane and PCBs, can not, however, be explained by an electron shuttle effect.

Thus, it is believed that the propensity of palladium to sorb hydrogen (at 80°C it can sorb 900 times its own volume at a pressure of 1 atmosphere (13)) explains the increased reactivity of the palladium/iron. Hydrogen, formed as shown in Equation (v), is sorbed by the



Chlorophenols Degraded with Palladium/Iron		
Compound	Reaction time, min	Product
2-Chlorophenol	2	Phenol
4-Chlorophenol	3	Phenol
2,3-Dichlorophenol	2	Phenol
2,4-Dichlorophenol	3	Phenol
2,6-Dichlorophenol	2	Phenol
2,3,4-Trichlorophenol	3	Phenol
2,3,5-Trichlorophenol	4	Phenol
2,4,6-Trichlorophenol	4	Phenol

palladium forming a powerful reducing species that dechlorinates the chlorinated organic compound once it adsorbs onto the bimetal surface.

Future Research

Additional research is being conducted to determine whether the use of palladium/iron has commercial value. First, little work has yet been performed regarding the selection of the iron base metal and the optimum palladium coverage. It is known that the reductive dechlorination occurs on the palladium/iron surface. However, the inter-relationships among iron surface area, palladium coverage and reactivity have not been adequately evaluated. Moreover, work with zero valence iron (5) has demonstrated that carbon impurities enhance the dechlorination of 1,1,2-trichloroethylene. Thus, impregnating carbon with palladium/iron or simply using a less pure, carbon-contaminated iron source may offer advantages both in terms of reactivity and cost.

The second major area where research is needed is with respect to the regeneration of the surface following use. Laboratory studies do not adequately simulate long-term field use. For example, clogging occurs with long-term use of zero-valence iron (14). Thus, because palladium/iron is more costly, it is expected that for viable commercial use, the surface will require periodic regeneration. Research in this area is centring on mineral acids and complexing

agents, such as citric acid. It is hoped that these agents will remove iron oxides and other iron precipitates (such as carbonates and sulfates) which may accumulate when groundwater is passed through the palladium/iron.

It should be noted that sulfide is known to poison palladium catalysts. Fortunately, groundwaters used for domestic purposes rarely contain sulfide. Some potable waters do, however, contain sulfate which might be reduced by the sulfur-reducing bacteria that thrive in the reducing conditions created by the palladium/iron. This possibility is currently being investigated.

Finally, research is needed to determine the best method for deploying the palladium/iron material during a field-scale trial. Present work is evaluating packed bed reactors (15) but the use of foam iron or slurry reactors may have significant advantages for cost and ease of regeneration.

Acknowledgement

The work described in this communication was supported by funds received from the Environmental Restoration Programs at the Portsmouth and Paducah Gaseous Diffusion Plants, and from the Office of Technology Development within the Department of Energy Office of Environmental Management, under the In Situ Remediation Integrated Program. The support of Jay Clausen from Paducah and Frank Anderson and Tom Houk at Portsmouth is gratefully acknowledged.

This is publication No. 4617, Environmental Sciences Division, Oak Ridge National Laboratory (ORNL). ORNL is managed by Lockheed Martin Energy Research Corp. for the U.S. Department of Energy under contract No. DE-AC05-96OR22464.

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Colloidal Palladium/Nickel Bimetallic Clusters

Nanoscope metal particles, such as clusters, have different properties to bulk metals. The dispersion of noble metal clusters can be achieved by reducing noble metal ions in water, in the presence of water-soluble polymers, such as poly(*N*-vinyl-2-pyrrolidone) (PVP). It is more difficult to produce clusters and colloids of non-noble metals. Palladium/copper clusters have been prepared, but nickel clusters have proved difficult.

Now, however, researchers at the University of Tokyo and the Science University of Tokyo, have managed to prepare colloidal dispersions of palladium/nickel bimetallic clusters by a modified polyol reduction method (N. Toshima and P. Lu, *Chem. Lett. Jpn.*, 1996, (9), 729–730).

At palladium molar contents of 20–80 per cent, the dispersions contained fine particles of narrow size distribution and average diameter 1.89 nm, with little aggregation, which suggested alloy structure formation. Both palladium-palladium and palladium-nickel bonds may exist simultaneously within each particle of the palladium/nickel bimetallic clusters.

The catalytic activity of the PVP-protected palladium/nickel colloids was studied during nitrobenzene hydrogenation to aniline. Clusters with palladium ratios ranging from 40–80 per cent had much higher catalytic activities than both nickel and palladium monometallic clusters. The palladium:nickel (3:2) colloid showed

the highest activity, around 4.2 times that for monometallic palladium clusters. Interactions between palladium and nickel in the cluster may affect the catalytic activity.

Palladium Aids Insulator Metallisation

Minute copper and nickel patterns can be produced on glass, silica and other insulating materials by using laser-assisted surface activation.

Now investigators at the C.N.R.S., Marseille, France, have reported a simple process in which visible continuous-wave and pulsed lasers can activate spun-on seeding layers of palladium acetylacetonate dissolved in chloroform (G. A. Shafeev, J.-M. Themlin, L. Bellard, W. Marine and A. Cros, *J. Vac. Sci. Technol., A*, 1996, **14**, (2), 319–326). The focused laser beam changes the chemical state of the palladium precursor by pyrolysis. The patterned catalytic film can then promote electroless metal growth.

The quality of the adhesion of the metal deposit to the underlying insulator is very important, and this is determined by the palladium clusters formed when the laser beam activates the catalytic seeding layer. After thermal decomposition the remaining palladium atoms are bonded to one of the two acetylacetonate "wings" of the parent molecule. Removing these ligands by treatment with hot acetic acid allows wear-resistant metal deposits to be formed on insulators.