Surface chemical reactivity in selected zero-valent iron samples used in groundwater remediation

Nancy Ruiz [a,1], Sudipta Seal [b,*], Debra Reinhart [c]

[a] *GeoSyntec Consultants, 2100 Main St., Suite 150, Huntington Beach, CA 92648, USA*
[b] *Advanced Materials Processing and Analysis Center (AMPAC), and Mechanical Materials and Aerospace Engineering (MMAE), The University of Central Florida, Orlando, FL 32816, USA*
[c] *Department of Civil and Environmental Engineering, The University of Central Florida, Orlando, FL 32816, USA*

Abstract

Permeable iron barriers have become a popular choice as a passive, cost-effective in situ remediation technology for chlorinated solvents. However, loss of reactivity over time, due to a build up of corrosion products or other precipitates on the iron surface, is a great concern. Because first-order rate constants for trichloroethylene (TCE) degradation have differed by iron pre-treatment and sonication history, X-ray photoelectron spectroscopy (XPS) was used to explore the changes in near surface chemistry of several iron samples. Both sonicated and unsonicated filings were analyzed in unwashed and groundwater-soaked conditions. Unsonicated acid-washed iron, with the highest first-order rate constant for TCE degradation, was characterized by greater surface oxygen content and was more ionic relative to the unwashed samples. The unsonicated, unwashed sample, with the lowest rate constant, exhibited a mixture of nonstoichiometric iron oxide and oxyhydroxide species. Sonication of groundwater-soaked iron removed weakly bonded iron hydroxide species and decreased the ionic character of the surface as was observed in the unwashed samples. Thus, this type of study might provide a better understanding of the chemical reactivity of selected iron samples and design better material in remediation technology. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: XPS; Zero-valent iron; Trichloroethylene (TCE); Sonication; Remediation technology

1. Introduction

According to the US Environmental Protection Agency (EPA), there are approximately 5000 Department of Defense, Department of Energy and Superfund sites contaminated

---

* Corresponding author. Tel.: +1-407-823-5277; fax: +1-407-823-0208.
E-mail addresses: nruiz@geosyntec.com (N. Ruiz), sseal@pegasus.cc.ucf.edu (S. Seal).
[1] Tel.: +1-714-969-0800; fax: +1-714-969-0820.

with chlorinated solvents-hydrocarbons widely used in a range of industries including dry cleaning, metal parts fabrication, electronic equipment manufacturing, and insecticide and herbicide production. The persistence and mobility of these hydrocarbons from the surface to the subsurface was largely unanticipated, and traditional disposal practices of chlorinated organic compounds such as trichloroethene (TCE) and tetrachloroethene (PCE) — the groundwater pollutants most often present — contributed to groundwater contamination throughout the world [1–3].

Economic considerations and the concern about effective long-term disposal are contributing to a shift away from historic pump and treat remediation systems and towards in situ methods — specifically enhanced biodegradation [4] or abiotic transformation. In biotic environments, microorganisms attach to metal surfaces and change the surface chemistry via biofilm formation [5]. Such metals present a unique opportunity to provide passive or near passive in situ treatment to degrade chlorinated organics. The permeable iron wall, for example, has emerged as a cost effective, passive remediation tool to treat groundwater contamination [6].

Iron, a readily available transition metal, provides an opportunity to degrade chlorinated organics under reducing conditions, rather than simply transfer them from the subsurface to another medium [7,8]. However, loss of reactivity over time, due to a build up of corrosion products or other precipitates on the iron surface, is a great concern. Reduction in dechlorination rates and flow problems have been linked to the deposition of material, mainly carbonates in highly alkaline water, on the iron surface [9–11]. Reactivity also decreases as reaction occurs on the surface of the iron [12]. If such reaction products can be removed, the lifetime of a barrier can be significantly extended. The application of ultrasonic energy may be a direct approach, which cleans the iron surface and restores its reactivity. To evaluate this approach, it is necessary to understand the iron surface chemistry, where the chemical reactions are primarily taking place and altering the performance of the zero-valent iron wall barrier.

Ultrasonic energy was employed to restore the reactivity of an iron surface. Batch studies were used to investigate the capacity of coarse iron filings to degrade TCE before and after sonication [13]. Because first-order rate constants for TCE degradation differed by iron pre-treatment and sonication history, X-ray photoelectron spectroscopy (XPS), a surface-sensitive tool, was used in this study to explore the changes in near surface chemistry of several iron samples. Both sonicated and unsonicated filings were analyzed in unwashed and groundwater-soaked conditions. Unsonicated acid-washed filings were also examined. This type of study is aimed to provide insight into the chemical reactivity of selected iron samples and might improve groundwater remediation technology efficiency.

2. Experimental

2.1. Materials

Reagents were obtained from Fisher Scientific, all were at least 99% pure and were used as received. Coarse uncrushed iron filings (surface area: $0.77 \, \text{m}^2/\text{g}$ as received) were obtained from Peerless Corporation (Cincinnati, OH). Natural groundwater was obtained

Table 1
Major physical and chemical parameters of native groundwater from proposed field site on east coast of central Florida

Parameter	Value	Method
pH	7.32	Field
Temperature	27.3 (°C)	Field
Dissolved oxygen	0.1 (mg/l)	Field
Conductivity	1923 (S)	Field
Turbidity	0.72 (NTU)	Field
Ca — ICP method	81.4 (mg/l)	EPA 6010
Fe — ICP method	0.059 (mg/l)	EPA 6010
Mg — ICP method	57.7 (mg/l)	EPA 6010
K — ICP method	18.6 (mg/l)	EPA 6010
Na	228 (mg/l)	EPA 6010
Cl	480 (mg/l)	EPA 325.2
NO_3^-	<0.01 (mg/l)	EPA 325.2
SO_4^{2-}	71 (mg/l)	EPA 300
Total alkalinity	289 (mg/l as $CaCO_3$)	EPA 310.1
Total dissolved solids	1100 (mg/l)	EPA 160.1
Total inorganic carbon	29.9 (mg/l)	SM 505
Total organic carbon	3.64 (mg/l)	EPA 415.1

from the East Coast of Central Florida and the detailed analysis of this water is shown in Table 1.

2.2. Iron pre-treatment

A bag containing a known mass of iron, measured prior to the pre-treatment was placed in a 1.0 l Tedlar bag with 500 ml of water and purged with nitrogen gas for 30 min to emulate low oxygen levels typical of groundwater. The bag was then either sonicated for a specific period of time or immediately dosed with a stock solution to bring the TCE concentration to approximately 14 mg/l. After dosing, the bag was placed on a shaker table set at a rate of 160 shakes/min to ensure adequate mixing. TCE degradation experiments were conducted with deionized water and natural groundwater using 100-mesh iron powder and course Peerless iron filings were analyzed in three different conditions: untreated, washed with a 5 wt.% sulfuric acid and rinsed with deionized water, or untreated and soaked in deoxygenated groundwater for several months. Additionally, some untreated and groundwater-soaked filings were sonicated for 2 h in a 25 ml screw-cap borosilicate vial filled with deoxygenated deionized water using a 600 W, 20 kHz Branson Ultrasonic water bath with an ultrasonic intensity of 0.32 W/cm². After sonication, the samples were drained of water and dried under nitrogen. All samples were stored under nitrogen to preclude atmospheric oxidation.

2.3. XPS methodology

XPS was performed using a PHI 5400 XPS system. Aluminum K α radiation of 350 W was used for this analysis. The sample filings were pressed as a flat wafer and mounted on

a sample holder. All samples which had been acid-washed or sonicated were stored under nitrogen to avoid atmospheric contamination and oxidation and will be referred as 'proper care' of the sample in the later section. Pass energies for the survey and high-resolution scans were 44.75 and 35 eV, respectively. To correct for sample charging all binding energies were referenced against the adventitious C(1s) peak at 284.6 eV [13]. An electron take-off angle of 50° between the sample surface and analyzer entrance was used for the surface analysis of all samples. Quantification was performed by determining the peak position, height, width, and shape as described in the literature [14]. The satellites were included automatically in the synthesis [15]. A Shirley background subtraction was also conducted for each peak in the spectral region under quantification analysis [16].

3. Results and discussion

Samples were removed from the bags periodically and analyzed for TCE and daughter products. TCE disappearance rate constants were calculated after 24 h of exposure to TCE to allow equilibration with the iron surface. All correlation coefficients for the calculation of rate constants exceeded 0.99. More details describing TCE removal during batch testing can be found elsewhere [17]. First-order rate constants are provided in Table 2. Table 2 also summarizes several general parameters developed during the XPS analysis of the iron samples: the ratio of adventitious carbon to carbon double-bonded to oxygen [(C–H)/(C in C=O)], full width half maximum (FWHM) energy information for C(1s), O(1s), and Fe(2p), and the iron to oxygen ratio (Fe/O). The ratios and FWHM values were obtained from the survey spectrum for each iron sample.

3.1. Impacts of pre-treatment on iron surface chemistry

With the exception of the Fe(2p) peak, which broadened after sonication [18] and narrowed after acid-washing, exposure to ultrasonic energy and washing with sulfuric acid

Table 2
Detailed XPS analysis of iron filings in various conditions

Parameter	Unwashed, no US	Unwashed, US	Acid-washed, no US
First-order constant for disappearance, k_{obs}, ($h^{-1} \times 10^{-3}$)	Rate 2.70 TCE	3.36	4.74
XPS core level[a]			
Fe(2p)	4.5	4.7	4.0
C(1s)	1.9	2.3	2.0
O(1s)	4.0	4.5	4.2
Quantification			
Fe/O	0.351	0.244	0.252
C–H/C in C=O	4.62	3.93	3.99

[a] Full width half maximum (FWHM) (± 0.2 eV).

produced similar changes in the surface chemistry of iron samples. In both cases, the C(1s) and the O(1s) peaks broadened and the Fe/O and C–H/C in C=O ratios decreased.

The broadening of the carbon C(1s) peak due to the presence of multiple elemental species, determined from the calculated (FWHM) value for carbon, and from the decrease in the [C in C–H]/[C in carbonyl (C=O)] ratio may be evidence of the removal of carbonyl oxygen (C=O), identified at O(1s) with binding energy of approximately 531.6 eV (8), exposing a surface which becomes more reactive for TCE degradation. This results in high first-order rate constants (see Table 2).

One of the more notable features of the iron sample surfaces is that the Fe/O ratio is not stoichiometric, indicating a mixture of Fe^{2+} and Fe^{3+} (as detected by change in Fe FWHM) combined with oxygen. If only FeO is on the surface, the ideal Fe/O ratio would be 1. If only Fe_2O_3 is on the surface, the Fe/O ratio would be 0.660. However, Fe/O ratios in the present study, ranging from 0.244 for sonicated unwashed filings to 0.351 for unsonicated unwashed filings, represent a hybridization of iron oxidation states. The Fe/O ratios calculated from sonicated unwashed filings and unsonicated acid-washed filings, 0.244 and 0.252, respectively, represent vacancies in the oxide lattice structure created during sonication and acid-washing. The removal of iron atoms, whether due to acid-washing or sonication, disturbs the stoichiometric surface, and apparently increases iron surface activity for TCE degradation, as demonstrated by increased first-order degradation constants.

The decrease in the [C in C–H]]/[C in C=O] ratios indicates that sonication or acid-washing of iron filings removes surface oxides but concurrently increases the spontaneous formation of highly reactive hybrid (nonstoichiometric) oxides due to the exposure of fresh reactive surface. The hybrid oxide layer indicates activation of the iron surface, perhaps essential for the reductive dechlorination of chlorinated solvents in a low-oxygen subsurface environment. Activation of the metal surface, actually the initiation of corrosion, is a basic step in organometallic chemistry [16].

3.2. Valence band studies

Spectra were developed for three iron samples in the valence band region from 0 to 20 eV: unsonicated acid-washed filings and unwashed filings, which had soaked several months in natural groundwater before and after sonication. The binding energy associated with the FWHM for $Fe(2p)_{3/2}$ in the acid-washed iron is the lowest of all the samples, and also indicates a very reactive surface. The valence band scans for acid-washed iron (Fig. 1) shows a broad band from 2 to 8 eV, characteristic of highly reactive nonstoichiometric iron oxides. The broad band is characteristic of a hybridization in the electron density of states between the O(2p) and the localized Fe(3d) bands and the difference in relative intensity of these peaks is an indication of vacancy formation in the oxide lattice structure in the subsurface, leading to defects in the oxide lattice and creating a flowpath for ionic species to interact with the iron. The creation of lattice defects by sonication has also been noted in lithium [19], zinc [20], and copper catalysts [21].

The valence band scans for the unwashed iron samples show sharper peaks for iron, indicating a small presence of 'O' valence orbital vacancy states. Based on information from the unwashed iron samples, the groundwater-soaked iron filings, which were also unwashed, would probably demonstrate similar reactivity for TCE degradation. As illustrated by Fig. 2,
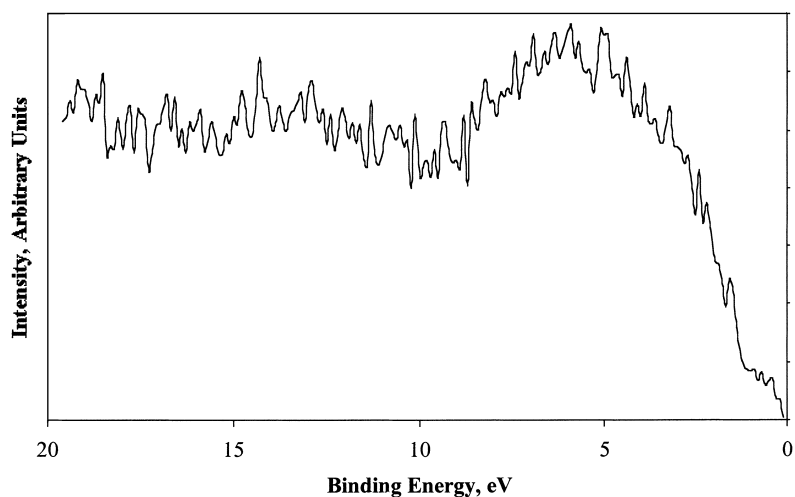
Fig. 1. XPS/ESCA 0–20 eV valence band spectra for unsonicated acid-washed Peerless filings.

a broad iron peak in the valence band region indicates that unsonicated groundwater-soaked iron should show little reactivity. The typically broad valence band iron oxides emerge, indicating the hybridization of Fe(3d) and O(2p) density of states. However, sonicated filings should exhibit much greater reactivity for dechlorination, as evidenced by a narrow

Fig. 2. XPS/ESCA 0–20 eV valence band spectra for unsonicated unwashed Peerless filings after several months in natural groundwater.
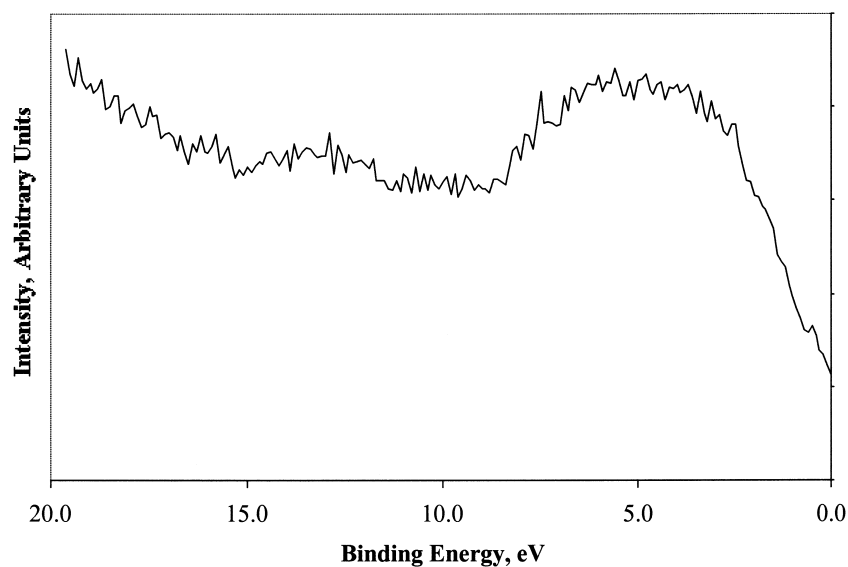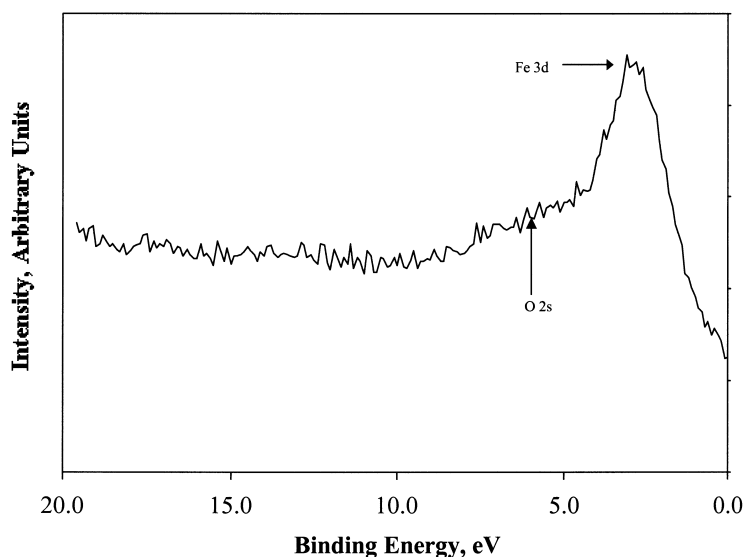
Fig. 3. XPS/ESCA 0–20 eV valence band spectra for sonicated unwashed Peerless filings sonicated after several months in natural groundwater.

iron peak in the valence band scan in Fig. 3. Localized to the Fe(3d) density of states, sonicated material removal of oxide layers thus making the surface more reactive for high first-order rate constant for effective TCE disappearance. Thus, these valence band studies were quite useful to bring out the subtle details in the iron surface chemistry not indicated in the core level XPS to understand the changes in the first-order rate constants.

Table 3 presents a detailed XPS analysis (binding energy, bonding state, and surface concentration) for major elements of interest on the filings: C, Fe, O, and Si. Band gap energy information [22] calculated from the valence band region, 0–20 eV, is also presented. The C(1s) peak at 284.6 eV, common to all samples, represents a nonreactive (adventitious) carbon present on the surface of materials exposed to the atmosphere, and is used essentially as an internal standard [14]. There may be a slight variation in the binding energy information developed from this analysis, probably due to the irregular shape of the filings, which affects the photoemission process, due to both elastic and inelastic scattering processes [15].

Acid-washed iron, with the highest first-order rate constant for TCE degradation, was characterized by a greater surface oxygen content and was more ionic relative to the unwashed samples, as noted by a relatively high binding energy for Si(2p), 102.6 eV, coupled with a relatively low binding energy for O(1s), 531.3 eV. The unsonicated, unwashed sample, with the lowest rate constant, exhibited a mixture of nonstoichiometric iron oxide and oxyhydroxide species. The O(1s) binding energies for oxygen in iron hydroxide and oxyhydroxide were found to be 533.1 and 529.8 eV, respectively. Although there was only a slight change in overall surface composition, the relative presence of specific oxygen species was quite different after sonication. Sonication of groundwater-soaked iron removed weakly bonded iron hydroxide species and decreased the ionic character of the surface (O(1s) bind-

Table 3
Qualitative and quantitative XPS results of iron filings in various conditions[a]

Sample	Band gap (eV) (±0.1)	C(1s)			Fe(2p)			O(1s)			Si(2p)		
		Binding energy (eV) (±0.2)	State	Surface (%) (±1)	Binding energy (eV) (±0.2)	State	Surface (%) (±1)	Binding energy (eV) (±0.2)	State	Surface (%) (±1)	Binding energy (eV) (±0.2)	State	Surface (%) (±1)
Acid-washed, no US	1.9	288.5	C=O	7.5	710.7	Fe–O	5	531.3	C=O	13.2	102.6	SiO_2	4.5
		284.6	C–H	56.5				529.7	Fe–O	12.8			
Unwashed, no US	2.0	288.0	C=O	6	711.2	Fe–OH	3	533.1	Fe–OH	4.0	101.6	SiO_2	4
		284.6	C–H	63.9				531.8	C=O	7.5			
								529.8	Fe–O/OH	10.1			
Unwashed, US	1.3	288.3	C=O	7	710.5	Fe_2O_3	2	531.6	C=O	12.3	101.6	SiO_2	5
		284.6	C–H	64				529.6	Fe–O	8.7			
GW-soaked, no US	1.9	288.1	C=O	5.2	710.5	Fe–O	3	531.0	C=O	15.7	102.2	SiO_2	6
		284.6	C–H	55.1				529.9	Fe–O	14.6			
GW-soaked, US	1.5	288.3	C=O	6.3	710.3	Fe–O	2.5	531.0	C=O	10.9	N/A	SiO_2	2.7
		284.6	C–H	66.1				529.6	Fe–O	11.4			

[a] US: ultrasound; GW: groundwater; N/A: not available.

ing energy of 529.6 eV), as was observed in the unwashed samples. Thus, it is clear that the pre-treatment and sonication history of the iron used impact both the relative surface presence and the bonding nature of an element. These alterations in surface chemistry, in turn, are reflected in changes observed for first-order rate constants for TCE degradation.

3.3. Acid-washed iron

In acid-washed iron, the atomic concentration of C=O type carbon is greater than the other samples, and indicates an increase in natural surface oxidation. Acid-washed iron is characterized by a greater surface total oxygen concentration relative to the unwashed samples, and indicates the process creates reaction sites for oxidation. Acid-washing leaves the surface more ionic, as shown by the high binding energy for the Fe(2p) peak, 710.7 eV. The high band gap from the Fermi energy line, 1.9 eV, may be due to immediate oxide formation and again suggests a chemically active surface. The high first-order rate constant for this iron further confirms the surface's activity.

3.4. Unwashed iron

In the unwashed samples, the unsonicated sample is characterized by a mixture of non-stoichiometric Fe–O and FeOOH species (Table 3), which is confirmed by an increase in Fe(2p) binding energy, 711.2 eV, due to the ionic nature of the hydroxide species as compared to the sonicated sample, 710.5 eV (Table 3). Although there are small differences in overall surface composition between the unwashed samples, the relative presence of specific oxygen species (i.e. Fe/O in Table 2) is quite different after exposure to ultrasound. Substantial amounts of hydroxide/oxide are present in the unsonicated-unwashed sample, but are not found in the sonicated-unwashed sample. There are also more Fe–O oxygen type bond units in the unsonicated material relative to its sonicated counterpart. The band gap decreases after sonication, indicating a movement of Fe(3d) density of state towards the Fermi edge, resulting in a more conductive surface due to oxide removal (see Table 3) and hence more reactivity. This increased conductive nature may be reflected in this sample's increased first-order rate constant for TCE degradation relative to its unsonicated counterpart (see Table 2).

3.5. Groundwater-soaked iron

In groundwater-soaked samples, sonication reduces the amount of Fe(2p) (see Table 3), indicating removal of weakly bonded iron hydroxide species. Sonication yields a slight loss in the ionic [23] character (i.e. reduction in the overall O(1s) binding energy in the groundwater soaked sample: see Table 3), as was observed in the unwashed samples. After exposure to ultrasound, there is slightly more Fe–O-type bonding and somewhat less C=O bonding (carbonyl type species), indicated by the change in atomic oxygen species surface concentrations. Also, SiO_2 concentration in the unsonicated sample is three times that found in its sonicated counterpart (Table 3), indicating that ultrasound removes weakly adsorbed (physisorbed) silica species. As was also seen in the unwashed iron, a sonicated

Ionic		Covalent	
Acid-Washed	Groundwater-Soaked	Unwashed	
102.6	102.2	101.6	Si(2p), eV
529.7	529.9	533.1	O(1s), eV

Fig. 4. Schematic representation of the relative nature of the bonding environment for Si(2p) and O(1s) binding energy (0.1 eV) on unsonicated iron surfaces.

surface is more prone to adventitious carbon uptake. It must be noted, however, due to the heterogeneous nature of the iron filings, that the amount of sample analyzed can impact the change in concentration observed, but 'proper care' (see Section 2) during XPS analysis care has been taken in the sample preparation to circumvent this problem.

3.6. Role of silica

Surface silica formation emerges as a sentinel of the general bonding character [23] of the sample surfaces. A schematic of the bonding nature for the unsonicated iron samples is presented in Fig. 4. The lowest Si(2p) binding energy is noted in the unwashed iron, the sample with the lowest rate constant, and demonstrates the most covalent bonding nature. The Si(2p) binding energy is highest in acid-washed iron, the sample with the highest first-order rate constant for TCE degradation, and indicates the most ionic nature of the three samples. This increasingly ionic nature is echoed in the decreasing binding energy for (Fe–O) oxygen from the unwashed iron to the acid-washed samples. Oxygen is covalent at higher binding energies, such as seen in water, at 533.1 eV [15].

4. Conclusions

Use of XPS was successfully illustrated in understanding the chemical reactivity of zero-valent iron in remediation technology. XPS is particularly suitable to this kind of work, because it alone permits simultaneously monitoring of surfaces of the iron filings at different stages of pre-treatment. From XPS qualitative and quantitative information presented in this paper, it is concluded that sonication removes the surface oxide layer making the surface more reactive. This active surface is essential for the reductive dechlorination of chlorinated solvent in a low oxygen subsurface environment. While unwashed iron shows a mixture of non-stoichiometric iron oxide species; acid-washed iron presents more reactive (ionic) surface, with a high first-order rate constant, i.e. more efficient in TCE disappearance. The ultrasound was found to effectively remove the weakly absorbed silica species, thus increasing the performance of a zero-valent iron barrier wall. XPS chemical shifts in the Si(2p) and O(1s) photolines represent a systematic variation of covalent to ionic character in selective iron surfaces resulting in increasing first-order rate constants. In summary XPS analysis of iron samples provides important surface chemistry information in relation to

first-order rate constants for TCE in zero-valent iron performance. It is clear that iron pre-treatment and sonication history change both the relative presence and the bonding nature of an element on the iron surface. These changes are reflected, in turn, in changes observed for the first-order rate constants for TCE degradation.

Acknowledgements

References

[1] J.J. Westrick, J.W. Mello, R.F. Thomas, J. Am. Water Works Assoc. 76 (1984) 52.

[2] T.O. Hirara, M. Nakasugi, M. Yoshida, K. Sumi, Water Sci. Technol. 25 (1992) 9.

[3] D.W. Blowes, C.J. Ptacek, J.A. Cherry, R.W. Gillham, W.D. Robertson, Geo-Environment 2000, Vol. 2, Geotechnical Special Publication no. 46, ASCE, New York, 1995, p. 1588.

[4] P.L. Palmer, in: E.K. Nyer et al. (Eds.), Reactive Walls in situ Treatment Technology, Vol. 271, CRC/Lewis, Boca Raton, FL, 1996, p. 288.

[5] A.K. Tiller, in: S.C. Dexter (Ed.), Biologically Induced Corrosion, NACE, Houston, 1986, p. 8.

[6] R.W. Gillham, D.R. Burris, in: Proceedings of the Subsurface Restoration Conference, The 3rd International Conference on Ground Water Quality, Dallas, TX, 1992.

[7] R.W. Gillham, S.F. O'Hannesin, Presentation at modern trends in hydrogeology, in: Proceedings of the Conference of the Canadian National Chapter, International Association of Hydrogeologists Hamilton, Ont., Canada, 1992.

[8] L.J. Matheson, P.G. Tratnyek, Environ. Sci. Technol. 28 (1994) 2045.

[9] P.D Mackenzie, S.S. Baghel, G.R. Eykholt, D.P. Horney, J.J. Salvo, T.M. Sivavec, Pilot-scale demonstration of chlorinated ethene reduction by iron metal: factors affecting iron lifetime, Presented before the Division of Environmental Chemistry, American Chemical Society, Anaheim, CA, 1995 (preprinted extended abstract).

[10] S. O'Hannesin, R. Gillham, Ground Water 36 (1998) 164.

[11] R.D. Powell, D. Blowes, R. Gilham, D. Schultz, T. Sivavek, R. Puls, J. Vogan, P. Powell, R. Landis, in: Permeable Reactive Barrier Technologies for Contaminant Remediation, EPA/600/R-98/125, 1998.

[12] T.L Johnson, P.G. Tratnyek, Dechlorination of carbon tetrachloride by iron metal: the role of competing corrosion reactions, Presented before the Division of Environmental Chemistry, American Chemical Society, Anaheim, CA, 1995 (preprinted extended abstract).

[13] N.E. Ruiz, D. Reinhart, C.A. Clausen, C.L. Geiger, N. Lau, in: Proceedings of the 1st International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA, 18–21 May 1998.

[14] T.L. Barr, S. Seal, J. Vac. Sci. Technol. A 13 (3) (1995) 1239.

[15] D. Briggs, M.P. Seah, Practical Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy, Wiley, New York, 1983, p. 533.

[16] D.A. Shirley, Phys. Rev. B 5 (1972) 4709.

[17] N. Ruiz, Ph.D. Thesis, UCF, 1998.

[18] B. Pugin, A.T. Turner, in: T.J. Mason (Ed.), Advances in Sonochemistry, Vol. 1, 1990, pp. 81–118.

[19] P. Lindley, in: T.J. Mason (Ed.), Chemistry with Ultrasound, Critical Reports on Applied Chemistry, Vol. 28, Elsevier, New York, 1990.

[20] K.S. Suslick, S.J. Doktycz, in: T.J. Mason (Ed.), Advances in Sonochemistry, Vol. 1, 1990, pp. 197–230.

[21] J. Lindley, T.J. Mason, J.P. Lorimer, Ultrasonics 25 (1987) 45.

[22] C.A. Wert, R.M. Thomson, Physics of Solids, 2nd Edition, McGraw-Hill, New York, 1970.

[23] T.L. Barr, Modern ESCA, CRC Press, Boca Raton, FL, 1994.