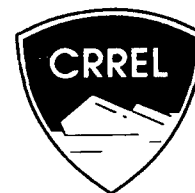


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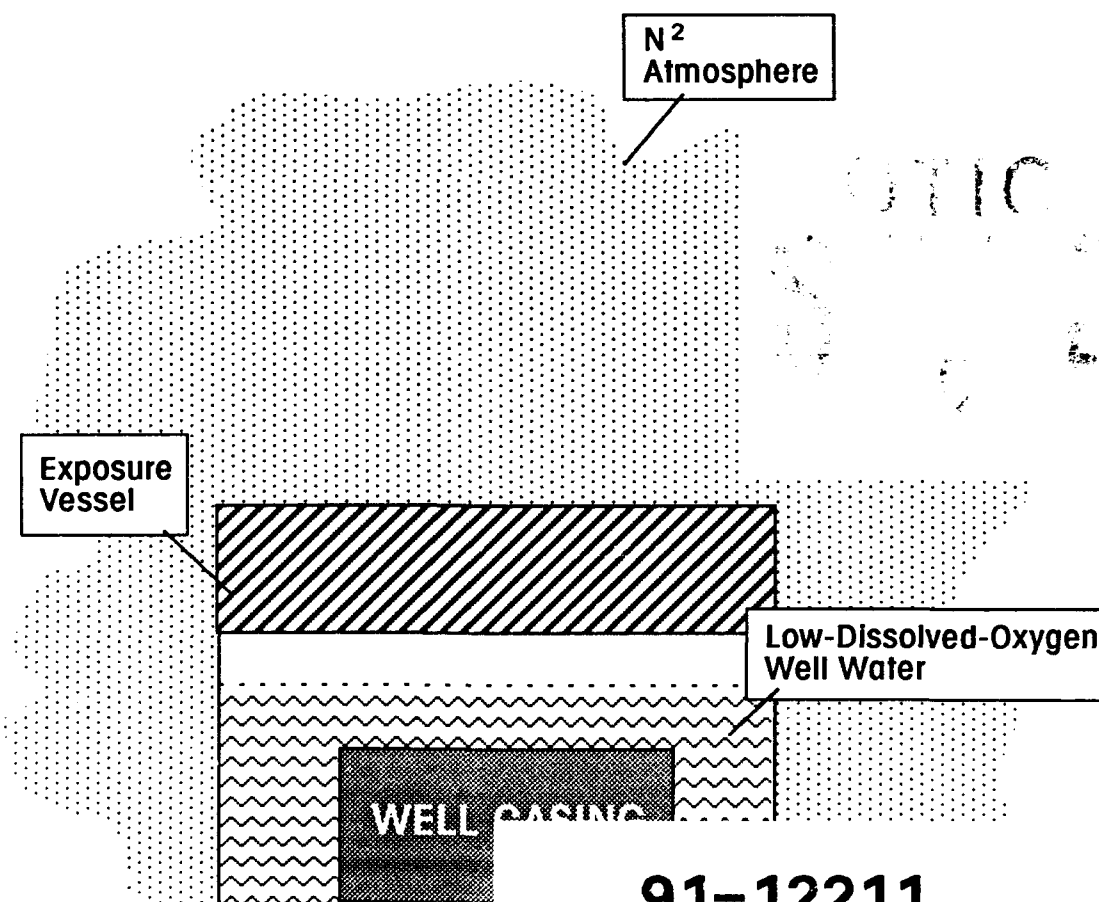


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Potential Influences of Common Well Casings on Metal Concentrations in Well Water With Low Dissolved Oxygen

Alan D. Hewitt

July 1991



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For conversion of SI metric units to U.S./British customary units of measurement consult ASTM Standard E380, Metric Practice Guide, published by the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.

Cover: Experimental setup.



**U.S. Army Corps
of Engineers**
Cold Regions Research &
Engineering Laboratory

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PREFACE

This report was prepared by Alan D. Hewitt, Research Physical Scientist, Geological Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory. Funding for this project was provided by the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA), Martin H. Stutz, project monitor.

The author thanks Louise Parker, James Cragin and Dr. Clarence Grant for their critical reviews of the text.

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Potential Influences of Common Well Casings on Metal Concentrations in Well Water With Low Dissolved Oxygen

ALAN D. HEWITT

INTRODUCTION

Recently, the representativeness of analyte concentrations collected from ground-water monitoring wells has come into question. The focus of this issue is the selection of well encasement material, stemming from the U.S. Environmental Protection Agency (EPA) recommendation for only stainless steel and poly(tetrafluoroethylene) (PTFE) in the *Resource Conservation and Recovery Act (RCRA) Ground-Water Monitoring Technical Enforcement Guidance Document (TEGD)* (EPA 1986). The basis for the omission of rigid poly(vinyl chloride) (PVC) as an encasement material has been questioned by several subsequent studies (Gillham and O'Hannesin 1990, Hewitt et al. 1989, Parker et al. 1990, Reynolds et al. 1990).

Accurate determination of the presence and concentrations of hazardous waste transported with ground water is jeopardized if the materials used in the construction of monitoring wells influence the solution chemistry. Since the pollution of ground water by organic constituents has been more common than pollution by metals and other inorganic constituents, they have received more attention. Three recent studies of rigid PVC and PTFE (Gillham and O'Hannesin 1988, Parker et al. 1990, Reynolds et al. 1990), examining the rate at which these two materials sorb organic compounds from aqueous solution, concluded that rigid PVC was superior to PTFE in this regard.

The other recommended material, stainless steel—of which formulations 316 and 304 are commonly used for ground-water monitoring—is composed of Fe, Cr and Ni. This creates problems for ground-water contamination by these metals and others that may be influenced by their presence. For this reason the application of metal versus polymeric casings has also been questioned (Houghton and Berger 1984, Barcelona and Helfrich

1986, Hewitt 1989a,b). Studies of ground water collected from wells encased with SS 304 and steel indicate that the leaching of metals from these materials is a continuous process which may or may not influence the aqueous metal chemistry after the well is purged (Houghton and Berger 1984, Barcelona and Helfrich 1986). Static laboratory experiments have shown stainless steels 304 and 316 to have the greatest potential to leach Ba, Cd, Cr, Pb and Cu or sorb As, Cr and Pb in comparison to PVC and PTFE (Hewitt 1989a,b). All of these studies attributed release or sorption of metal analytes by stainless steel and steel to be associated with corrosion. Researchers have observed surface oxidation predominantly along the pipe's weld, and secondly on freshly cut surfaces, during the laboratory studies, and they hypothesized oxidation in the field studies.

The oxidation of these ferrous metal pipes could easily account for the sorption and leaching of metals observed upon exposure to aqueous solutions. In an attempt to prevent surface oxidation facilitated by normal laboratory atmospheric conditions, PVC, PTFE, SS 304 and SS 316 well casings were tested for both the release and sorption of metals under a nitrogen atmosphere with de-oxygenated well water. The results of this study under conditions where the availability of oxygen is limited should better assess the potential for these materials to affect the chemistry of ground water sampled from deep wells.

MATERIALS AND METHODS

Materials

Well casings for ground-water monitoring, manufactured by Johnson Well Screen (SS 304, SS 316 and PVC) and MIP, Inc (PTFE), were cut in approximately 2-cm lengths from 1.2-m (4-ft) riser sections of 5-cm id (2-in.

Table 1. Physical state of stainless steel pipe rings for both experiments.

Static leaching

SS 304-1	—	SS 304-4	O/W*	SS 304-7	—	SS 304-10	—
SS 304-2	—	SS 304-5	—	SS 304-8	—	SS 304-11	—
SS 304-3	—	SS 304-6	—	SS 304-9	—	SS 304-12	—
SS 316-1	—	SS 316-4	—	SS 316-7	—	SS 316-10	—
SS 316-2	O/W	SS 316-5	—	SS 316-8	O/W	SS 316-11	—
SS 316-3	—	SS 316-6	—	SS 316-9	—	SS 316-12	—

Sorption

SS 304-1	—	SS 316-1	—
SS 304-2	—	SS 316-2	—
SS 304-3	—	SS 316-3	—

* O/W—oxidation on wall surface.

od). The exact length of the casing rings was adjusted based on the pipe's diameter and wall thickness, so as to maintain a constant 80-cm² surface area. The freshly cut ends of the casing rings represented 9% of the surface area for the stainless steels and about 17% for the PVC and PTFE materials. The weld area on the stainless steel rings accounted for approximately 2% of the surface area.

During pipe milling (cutting and edge filing), precautions were taken to prevent exposure to grease, dirt, solvents and other foreign substances. Casing rings were cleaned prior to the exposure tests by individually rinsing them several times with deionized distilled water (Millipore, Type 1) and air drying them in a Class 100 clean air station. No attempt was made to remove any surface discoloration or ink that was present on the pipes as received. All cleaning and subsequent work was conducted within a clean-room complex, and the casing rings were handled with plastic gloves or nylon tweezers. As in an earlier study (Hewitt 1989b), several sections of stainless steel casings were subjectively removed prior to setting up the experiments because of existing surface rust of greater than 1 mm². Metal casing sections with rust spots less than 1 mm² were noted (Table 1).

Polypropylene jars (69-mm od × 62-mm height, 125 mL, Model 6185-E37, Thomas Scientific) were used as exposure vessels for the individual casing rings. These vessels were cleaned by soaking in 10% v/v redistilled G. Fredrick Smith (GSF) HNO₃, rinsed several times with deionized distilled water and then air dried in a clean-air station. Other materials, i.e., 7.5-mL sample bottles (polyethylene, Nagle), pipette tips (Eppendorf), and 4-L glass bottles used for the well water collection, were also acid washed and thoroughly rinsed with deionized distilled water. Glass, tygon tubing and graduated

cylinders used for the de-aeration and transferring of well water were also cleaned by soaking and rinsing with deionized distilled water.

A glove bag (Handy-Lok, x-37-37, I²R) served as the nitrogen environmental chamber. Nitrogen from a standard zero grade 230 SCF cylinder was regulated at a constant flow of at least 0.5 L/min throughout the entire experiment. This flow was increased to roughly 3–5 L/min when the glove bag was opened for removal of samples or introduction of equipment.

Well water was collected from the overflow discharge arm of 76-m-deep domestic artesian well, located in Weathersfield, Vermont. The overflow arm, consisting of approximately 10 m of 10.2-cm od PVC pipe, was connected to the well head some 5 m below the ground surface and discharged to a low point on the property. At the time of collection, the well's discharge was flowing at about 0.5 L/min. Prior to collecting the well water for this experiment, the pH, Dissolved Oxygen (DO), and the Oxidation Reduction Potential (ORP, i.e., Eh) were measured. The in-situ pH and laboratory measured pH and conductivity of the well water collected from this location, and that collected in previous years from a faucet within the house, were similar (Table 2).

Test design and setup

Before introducing the well water to the exposure vessels, oxygen was removed from these containers by leaving them uncapped in the glove bag for 1 day. Well water that had been collected the previous day was purged with nitrogen at a flow rate of 1 L/min for about 1 hour inside the glove bag to lower the native DO concentration (9.0 mg/L) to below 1.0 mg/L. Both the sparging frit and the well water transfer tube were positioned within 2 cm of the bottom of the 4-L glass collection bottles. The low-DO well water was transferred to 100-mL graduated cylinders using positive nitrogen pressure and measured volumes were poured into individual exposure vessels. Aliquots of low-DO well water from a single 4-L bottle were used to set up each of the experiments (two 4-L bottles were collected). Because of the large number of samples, only a 60-mL volume was transferred for the static leaching experiment, while a 99-mL solution volume was used for the sorption experiment. These volumes were sufficient to submerge the well casing rings, thus creating pipe-surface-area-to-aqueous-volume ratios of 1.3 cm²/cm³ and 0.81 cm²/cm³ for the leaching and sorption tests respectively. The ratios are representative of well casings below the saturated zone; however, they are much lower than that which exists for well screens.

Tests for the static leaching of metals from PVC, PTFE, SS 304 and SS 316 well casings were performed

Table 2. Parameters measured for in-situ well water, monitoring solution and test samples.

	DO (mg/L)	pH	ORP (mV)	Conductance (μ mhos)
In-situ well water	9.0	7.4	280	*230
Static leaching experiment monitoring solutions				
Stock	0.4	8.4	190	240
2 hr	1.3	8.4	180	—
8 hr	1.2	8.4	180	—
24 hr	1.7	8.7	180	—
120 hr	0.6	8.9	170	—
Sorption experiment monitoring solutions:				
Stock	0.9	8.1	200	—
2 hr	1.8	8.1	—	—
8 hr	1.6	8.1	190	—
24 hr	0.8	8.5	170	—
72 hr	0.3	8.9	150	—
A single replicate at the conclusion of the sorption experiment				
Control-A	0.4	8.9	180	—
PTFE-A	1.3	8.9	180	—
PVC-A	0.8	8.8	190	—
SS 304-A	1.1	8.7	190	—
SS 316-A	0.8	8.8	180	—
Previously measured parameters (Hewitt 1989b)				
Stock	—	7.8	—	240

* Conductivity of well water measured in the laboratory just prior to purging.

in triplicate. Samples of the low-DO well water in contact with the well casing materials were taken after 2, 8, 24 and 120 hours. Three vessels with no well casings served as controls for each of the treatment periods. In addition to the sample and controls, four additional vessels without well casings were included, one for each treatment period, so that the following solution parameters could be monitored: pH, DO and ORP (Table 2).

The sorption study also used this setup design—triplicates of the four casing materials and control, and an individual vessel for monitoring the solution parameters (Table 2) for each treatment period. Samples for this test were taken after 2, 8, 24 and 72 hours. A 1.00-mL spike consisting of metals of interest was added to the 99-mL well water aliquots that had been transferred for this test. This spiking solution was prepared in low-DO well water with concentrations of approximately 1.0 ppm Cu, Cr and Pb, and 0.2 ppm Cd.

During the experiment, the exposure vessels were closed, shielded from natural light, kept in the nitrogen environmental chamber, and maintained at a temperature of 24°C. After the various treatment periods, samples for the static leaching experiment were obtained by

sacrificing an entire exposure vessel, whereas only a 2.5-mL aliquot was removed from each of the sorption test vessels. This sample collection protocol required 60 (3×5×4) vessels for the static leaching experiment and 15 (3×5×1) vessels for the sorption experiment.

The exposure vessels, removed after each leaching treatment period, were placed in a clean-air station and the well-casing rings were removed. The remaining 60 mL of well water was acidified with 1.2 mL of concentrated HNO₃ (GFS). The 2.5-mL aliquots removed from the sorption vessels were transferred inside of the glove bag to 7.5-mL low-density polyethylene bottles with an adjustable 5-mL pipette. Once an entire set of samples had been transferred, the sample aliquot bottles were removed from the glove bag, placed in a clean-air station and acidified with 0.05 mL of concentrated HNO₃ (GSF).

It is important to recognize that metal analyses in the static leaching experiment include both the metals in aqueous solution and those sorbed to the vessel walls, whereas the sorption study only includes the aqueous species. In earlier studies (Hewitt 1989a,b) it was shown that this acidification lowered the well water's pH below 2.0, and that this pH was sufficient to desorb metals from the polypropylene vessel walls.

Analysis

Cadmium, copper, chromium, iron, nickel and lead were determined by Graphite Furnace Atomic Absorption (GFAA) using a Perkin-Elmer (PE) model 403 Atomic Absorption Spectrophotometer (AAS) coupled with a PE model 2200 heated graphite atomizer. Instrumental procedures followed general guidelines provided in the manufacturer's instrument manual (Perkin-Elmer 1981).

Analysis procedures were designed to achieve detection limits well below 1% of the present domestic water quality levels set by the EPA (Table 3). Method Detection Limits (MDL) were established following the pro-

Table 3. EPA interim primary drinking water quality levels and the method detection limits (MDL).

Metal	EPA primary drinking water levels (μ g/L)	MDL (μ g/L)
Cd	10	0.034
Cu	1000	0.13
Cr	50	0.085
Pb	50	0.10
Fe	—	0.87
Ni	—	2.2

cedure outlined in the Federal Register (1984). These estimates require that a minimum of seven replicate determinations be made of analyte concentrations that are one to five times their estimated detection levels. The MDL is obtained by multiplying the standard deviation of the replicate measurements by the appropriate one-sided *t*-statistic corresponding to *n*-1 degrees of freedom at the 99% confidence level.

All of the metals cited above were determined for the static leaching experiment and, with the exception of Ni, for the sorption experiment. Each sample aliquot with a determined analyte concentration above the MDL was analyzed at least twice and the results averaged. Analyte concentrations were based on peak height measurements from strip chart recordings.

Aqueous calibration standards for Cd, Cr, Cu, Fe, Ni and Pb were prepared by diluting 1000-mg/L certified atomic absorption stock solutions (Fisher Scientific Corp.). Working standards were prepared in deionized water acidified to 2% v/v with HNO₃ (GFS).

Calibrations were based on three concentration standards analyzed in triplicate. Standards were randomly introduced throughout the course of sample analysis, and all of the calibration curves were linear over the concentration range examined. To see if the intercepts were significantly different from zero, we compared the residuals for the models with an intercept and for the models with zero intercept using the *F*-ratio at the 95% confidence level. Analyte concentrations in the samples and controls were determined based on the slope and intercept model only if the intercept was deemed significant. Otherwise, a zero-intercept linear model was employed.

To evaluate leaching or sorption of metals by the four well casing materials, analysis of variance (ANOVA) and least-significant-difference (LSD) analyses were carried out at the 95% confidence level. The results of these analyses for each treatment period established which well casings influenced the chemistry of a particular analyte compared to the control and the other well casings (Table 4). In addition, we identified those leached metals in the low-DO well water that exceed 1% of the EPA drinking water quality level. This low level warning criterion was chosen to highlight metals that, although not of immediate health concern, were leached from casings to the extent that the average solution concentration increase was more than an order of magnitude greater than the MDLs established or native levels, or both.

Along with the monitoring DO, pH and ORP at the setup of each experiment, and for every collection period, the conductivity of the well water was determined before and after purging with nitrogen. Dissolved oxygen was spectrophotometrically measured using high

range AccuVac reagent vials (Hach 25150) and a Dr/2 spectrometer (Hach). This colorimetric determination is designed to measure DO in the 0- to 10-mg/L range. The pH was measured with a semi-micro glass combination Ross model 81-03 electrode (Orion). We calibrated the electrode with low ionic strength buffers prior to analyzing the well water solutions. Oxidation-reduction potentials were determined with a model 97-78-00 platinum redox electrode (Orion). The response of the platinum electrode was established before each analysis by measuring 0.1-M potassium ferrocyanide and 0.05-M potassium ferricyanide solutions. A Leeds and Northrup electrolytic conductivity bridge was used to measure conductivity.

RESULTS

Static Leaching

Cadmium

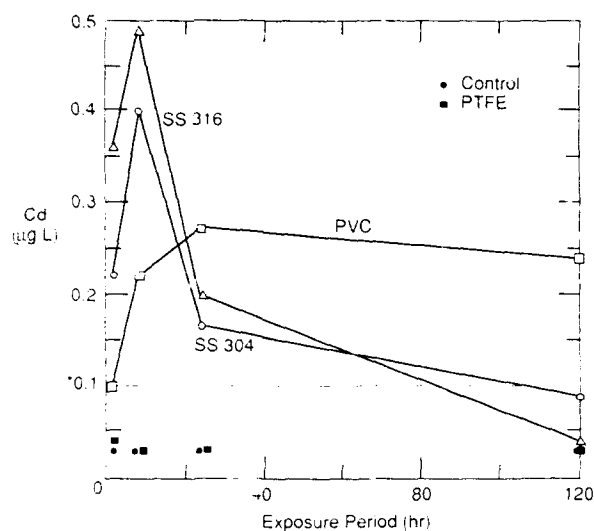
Initially, the release of Cd was significantly greater ($\alpha = 0.05$) from the two stainless steel casings than from the control and PTFE (Table 4a). By plotting (Fig. 1a) the average exposure solution concentrations for each well casing and the control, it is apparent that Cd was also released from PVC. The level contributed by PVC quickly reached a plateau and then remained fairly constant for the duration of the test. In contrast, Cd in solutions exposed to both stainless steels showed sharp maxima for the 8-hour treatment period and declined thereafter, indicating that these metal casings were capable of an initial release followed by sorption. PVC and both the stainless steels frequently showed leached Cd concentrations that exceeded 1% of the EPA drinking water quality limit, while the PTFE apparently released no Cd.

Chromium

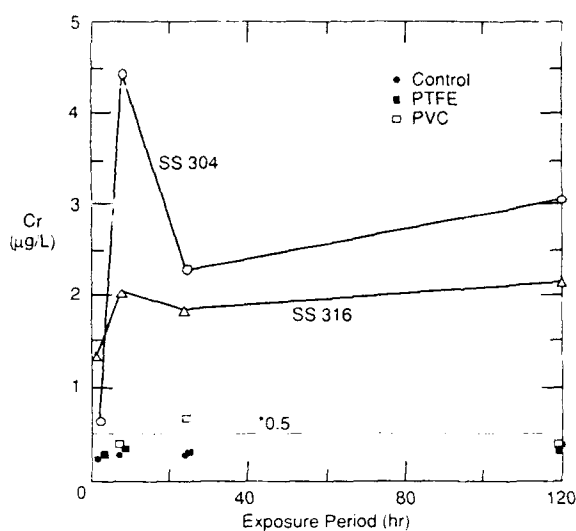
The ANOVA failed to reveal any significant difference among the materials (Table 4a). Lack of statistical significance was attributable to poor precision among the stainless steel triplicates. A plot of the average concentrations (Fig. 1b) shows no consistent trends but indicates that the two stainless steels leached more Cr than the other materials. The stainless steels and PVC casings all frequently produced mean solution concentrations that exceeded 1% of the EPA drinking water quality standard. In contrast, levels for PTFE samples were consistently similar to the control.

Copper

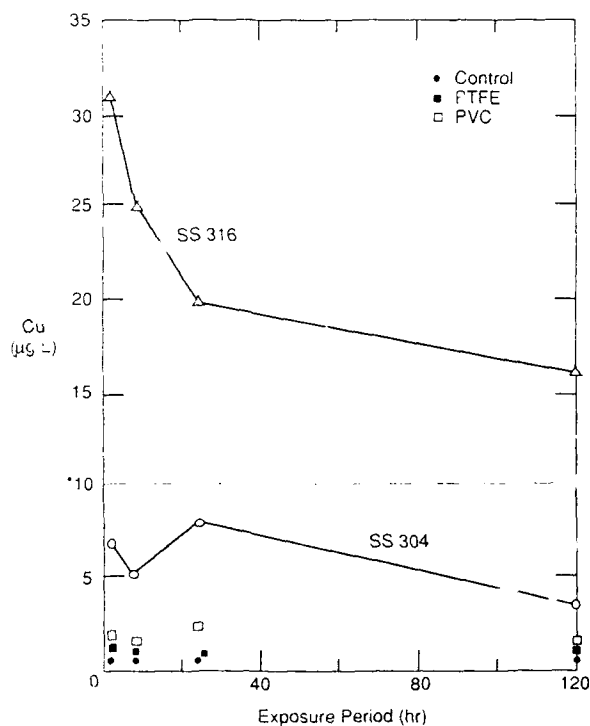
The statistical analysis consistently distinguished SS 316 as the material that contributed the greatest amount



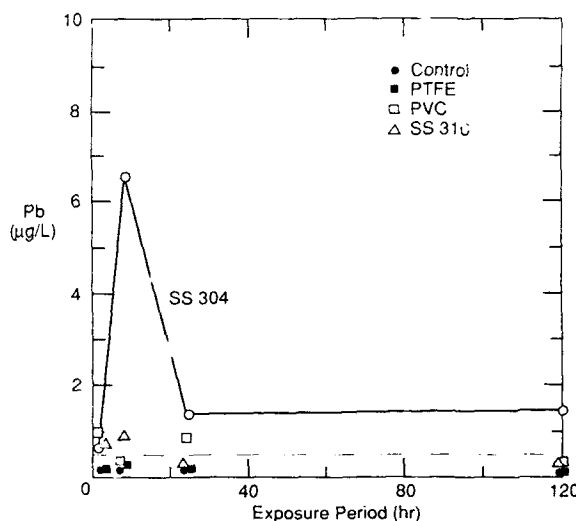
a. Cadmium.



b. Chromium.



c. Copper.

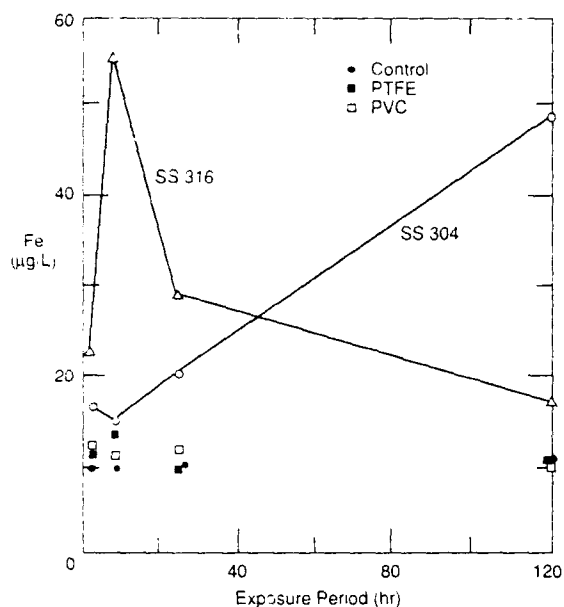


d. Lead.

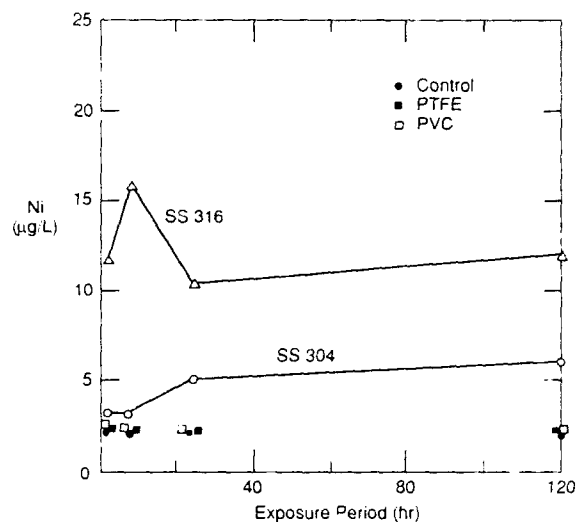
Figure 1. Well water leaching of metals from PTFE, PVC, SS 304 and SS 316 well casings. Dashed line shows the 1% concentration of the EPA drinking water quality level.

of Cu to solution (Table 4a). Although not statistically significant, SS 304 consistently showed average Cu concentrations that were greater than PVC, PTFE and the control. Figure 1c shows that the release of Cu from SS 316 was very rapid, reaching a maximum for the 2-hour treatment period, after which resorption is indi-

cated. There was no clear pattern associated with SS 304 and the release of Cu was negligible from PTFE and PVC. The levels of Cu determined in solutions exposed to SS 316 throughout this experiment were greater than 1% of the EPA drinking water quality level.



e. Iron.



f. Nickel.

Figure 1 (cont'd). Well water leaching of metals from PTFE, PVC, SS 304 and SS 316 well casings. Dashed line shows the 1% concentration of the EPA drinking water quality level.

Lead

Statistically, SS 304 for the last two treatment periods, and PVC for the 24-hour period, leached more Pb than the other materials (Table 4a). It should be noted that one of the 8-hour SS 304 exposure solutions was determined to have 17.5 µg/L of Pb. This single value is 35% of the EPA drinking water quality level. Figure 1d shows that the solution concentrations of Pb were fairly constant, if we neglect the 8-hour treatment for SS 304. Consistently, SS 304 and both SS 316 and PVC for two of the four treatments leached Pb, creating solution concentrations that exceeded 1% of this EPA drinking water quality standard. Again the release from PTFE was negligible.

Iron

Statistically, stainless steel 316 for two of the first three treatment periods contributed more Fe to solution than the other materials (Table 4a). Again poor precision among the the triplicate samples of stainless steel casings impaired the statistical analysis. Figure 1e shows that the contribution of Fe from SS 316 is initially rapid, then resorption is indicated, whereas SS 304 continues to serve as a source of Fe throughout. Neither PTFE or PVC showed meaningful differences from the control throughout the experiment.

Nickel

The statistical analysis consistently established SS 316 as the greatest source of Ni to solution (Table 4a).

Figure 1f shows that the levels of Ni from the solutions exposed to all of these materials remained fairly constant throughout, and that PVC and PTFE showed no release of Ni.

Sorption

Cadmium

The ANOVA and LSD tests statistically distinguished SS 304 as the most reactive surface for sorption of aqueous Cd for both the 8- and 24-hour treatment periods (Table 4b). Sorption was not significant for the 2-hour treatment, and poor precision among the triplicate samples of the PVC and SS 304 casings reduced the sensitivity of the statistical analysis for the 72-hour period. Figure 2a, a plot of the average concentrations for each treatment period, shows that SS 304, PVC and SS 316 sorbed Cd, and that sorption by PTFE was negligible. Sorption of Cd by the stainless steels is consistent with the observed trend for the last two exposure periods in the leaching experiment.

Chromium

Stainless steel 304 was the only material that significantly sorbed Cr (Table 4b). Sorption was statistically significant for only the first three treatments because of poor precision among the SS 304 triplicates for the final exposure period. Figure 2b clearly shows the losses of Cr for those solution exposed to SS 304.

Table 4. Summary of ANOVA and LSD determinations for average analyte concentrations ($\mu\text{g/L}$). Materials with common underlining are not different at the 95% confidence level as determined by the LSD.

Time		Well casing				
1. Static leaching experiment						
Cadmium						
2 hr	Control	PTFE	PVC	SS 304	SS 316	
	0.03	0.04	0.10	0.22	0.36	
(LSD = 0.16)						
8 hr	Control	PTFE	PVC	SS 304	SS 316	
	0.03	0.03	0.22	0.40	0.49	
(LSD = 0.36)						
24 hr	Control	PTFE	SS 304	SS 316	PVC	
	0.03	0.03	0.17	0.20	0.27	
(LSD = 0.22)						
120 hr	Control	PTFE	SS 316	SS 304	PVC	
	0.03	0.03	0.04	0.09	0.24	
(LSD = 0.28)						
Chromium						
2 hr	Control	PTFE	SS 304	PVC	SS 316	
	0.24	0.28	0.62	0.72	1.35	
(LSD = 1.12)						
8 hr	Control	PTFE	PVC	SS 316	SS 304	
	0.29	0.35	0.38	2.04	4.44	
(LSD = 5.91)						
24 hr	Control	PTFE	PVC	SS 316	SS 304	
	0.28	0.30	0.68	1.89	2.29	
(LSD = 2.59)						
120 hr	PTFE	Control	PVC	SS 316	SS 304	
	0.34	0.37	0.38	2.19	3.06	
(LSD = 3.25)						
Copper						
2 hr	Control	PTFE	PVC	SS 304	SS 316	
	0.47	1.13	1.85	6.90	31.2	
(LSD = 11.5)						
8 hr	Control	PTFE	PVC	SS 304	SS 316	
	0.49	0.73	1.44	5.02	25.3	
(LSD = 15.3)						
24 hr	Control	PTFE	PVC	SS 304	SS 316	
	0.50	0.70	2.35	8.09	20.0	
(LSD = 8.67)						

Table 4 (cont'd). Summary of ANOVA and LSD determinations for average analyte concentrations ($\mu\text{g/L}$). Materials with common underlining are not different at the 95% confidence level as determined by the LSD.

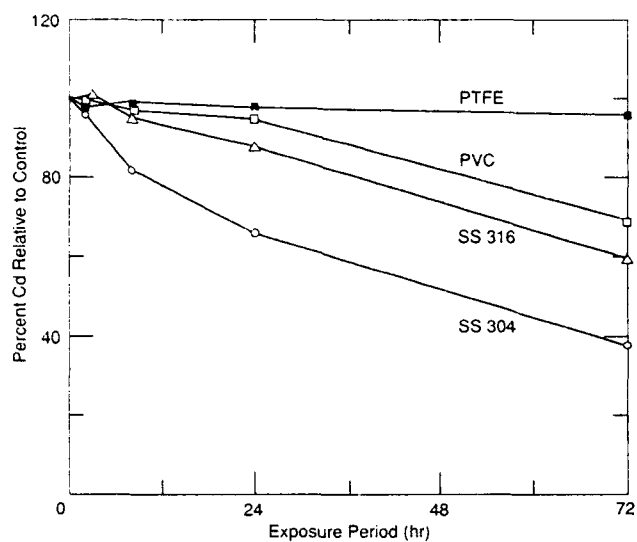
Time		Well casing				
	120 hr	Control 0.49	PTFE 0.99	PVC 1.66	SS 304 3.56	SS 316 16.2
(LSD = 7.02)						
Lead						
	2 hr	Control 0.10	PTFE 0.14	SS 304 0.55	SS 316 0.79	PVC 0.94
(LSD = 0.98)						
	8 hr	Control 0.10	PTFE 0.18	PVC 0.36	SS 316 0.95	SS 304 6.58
(LSD = 11.7)						
	24 hr	Control 0.10	PTFE 0.18	SS 316 0.27	PVC 0.93	SS 304 1.42
(LSD = 0.59)						
	120 hr	Control 0.10	PTFE 0.12	SS 316 0.34	PVC 0.36	SS 304 1.65
(LSD = 0.55)						
Iron						
	2 hr	Control 9.93	PTFE 11.4	PVC 12.0	SS 304 16.7	SS 316 22.7
(LSD = 7.65)						
	8 hr	Control 9.77	PVC 11.0	PTFE 13.4	SS 304 14.9	SS 316 55.6
(LSD = 85.8)						
	24 hr	PTFE 9.50	Control 9.80	PVC 11.5	SS 304 20.0	SS 316 28.9
(LSD = 16.1)						
	120 hr	PVC 9.10	PTFE 9.60	Control 10.0	SS 316 17.1	SS 304 48.2
(LSD = 40.8)						
Nickel						
	2 hr	Control 2.2	PVC 2.2	PTFE 2.4	SS 304 3.2	SS 316 13.5
(LSD = 6.9)						
	8 hr	Control 2.2	PTFE 2.2	PVC 2.2	SS 304 3.5	SS 316 16.0
(LSD = 5.2)						

Table 4 (cont'd).

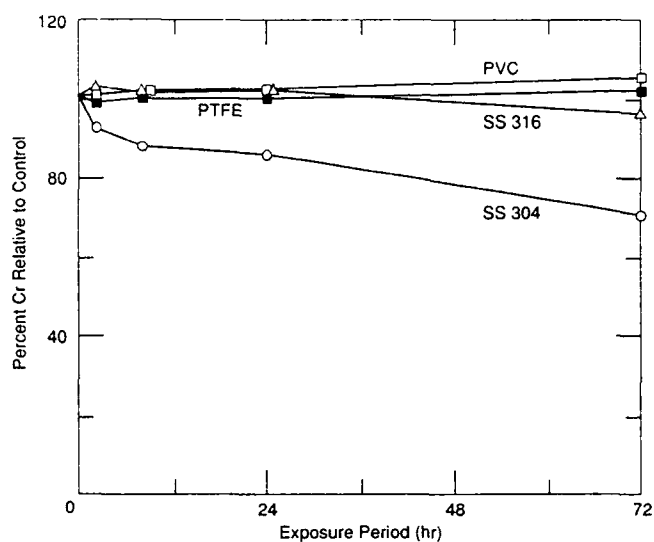
<i>Time</i>		<i>Well casing</i>				
	24 hr	Control 2.2	PTFE 2.2	PVC 2.2	SS 304 5.0	SS 316 10.4
	(LSD = 3.0)					
	120 hr	Control 2.2	PVC 2.2	PTFE 2.4	SS 304 6.1	SS 316 12.0
	(LSD = 8.7)					
b. Sorption experiment						
<i>Cadmium</i>						
	2 hr	SS 304 2.18	PTFE 2.24	Control 2.28	PVC 2.28	SS 316 2.31
	(LSD = 0.12)					
	8 hr	SS 304 1.85	SS 316 2.16	PVC 2.19	PTFE 2.22	Control 2.25
	(LSD = 0.20)					
	24 hr	SS 304 1.48	SS 316 1.96	PVC 2.11	PTFE 2.19	Control 2.23
	(LSD = 0.29)					
	72 hr	SS 304 0.82	PVC 1.27	SS 316 1.46	Control 2.04	PTFE 2.13
	(LSD = 1.42)					
<i>Chromium</i>						
	2 hr	SS 304 11.3	PTFE 12.1	Control 12.2	PVC 12.3	SS 316 12.4
	(LSD = 0.79)					
	8 hr	SS 304 10.7	PTFE 12.1	Control 12.1	SS 316 12.2	PVC 12.4
	(LSD = 1.36)					
	24 hr	SS 304 10.5	Control 12.2	PTFE 12.2	PVC 12.4	SS 316 12.5
	(LSD = 1.45)					
	72 hr	SS 304 8.36	SS 316 11.4	Control 11.9	PTFE 12.1	PVC 12.5
	(LSD = 4.36)					
<i>Copper</i>						
	2 hr	PTFE 10.4	Control 10.5	PVC 10.8	SS 304 12.2	SS 316 23.2
	(LSD = 7.42)					

Table 4 (cont'd). Summary of ANOVA and LSD determinations for average analyte concentrations ($\mu\text{g/L}$). Materials with common underlining are not different at the 95% confidence level as determined by the LSD.

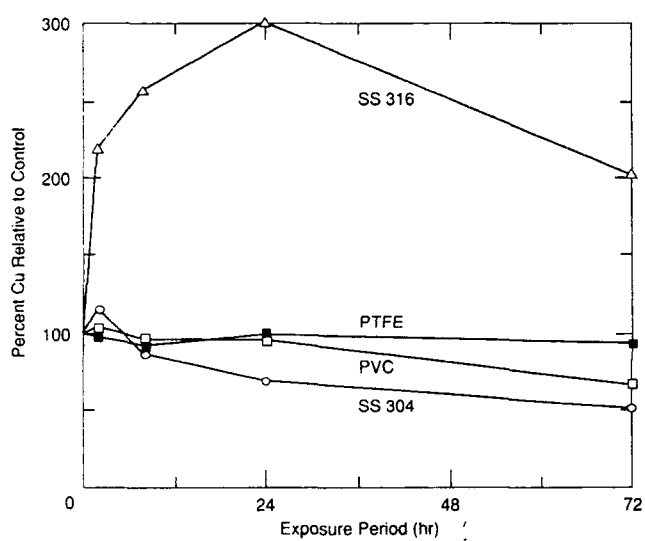
<i>Time</i>		<i>Well casing</i>				
(LSD = 7.55)	8 hr	SS 304 9.33	PTFE 9.93	PVC 10.2	Control 10.7	SS 316 27.6
	24 hr	SS 304 6.84	PVC 9.41	PTFE 9.61	Control 9.91	SS 316 30.0
	72 hr	SS 304 4.48	PVC 6.24	PTFE 8.75	Control 9.38	SS 316 18.9
(LSD = 10.9)						
<i>Lead</i>						
(LSD = 0.61)	2 hr	SS 316 8.56	SS 304 8.73	PVC 9.32	PTFE 9.83	Control 10.1
	8 hr	SS 316 5.17	SS 304 5.73	PVC 8.49	PTFE 9.54	Control 9.98
	24 hr	SS 316 2.94	SS 304 3.65	PVC 7.98	PTFE 9.11	Control 9.62
(LSD = 2.05)						
(LSD = 4.50)	72 hr	SS 316 1.64	SS 304 2.26	PVC 4.45	Control 8.42	PTFE 8.51
<i>Iron</i>						
(LSD = 16.9)	2 hr	PVC 8.76	Control 9.11	PTFE 10.9	SS 316 13.2	SS 304 19.6
	8 hr	Control 8.66	PTFE 8.71	PVC 8.97	SS 316 12.3	SS 304 19.6
	24 hr	PTFE 7.75	PVC 8.31	Control 8.08	SS 316 11.8	SS 304 18.9
(LSD = 15.6)						
(LSD = 6.61)	72 hr	PTFE 6.91	PVC 6.93	Control 7.35	SS 316 9.89	SS 304 11.3



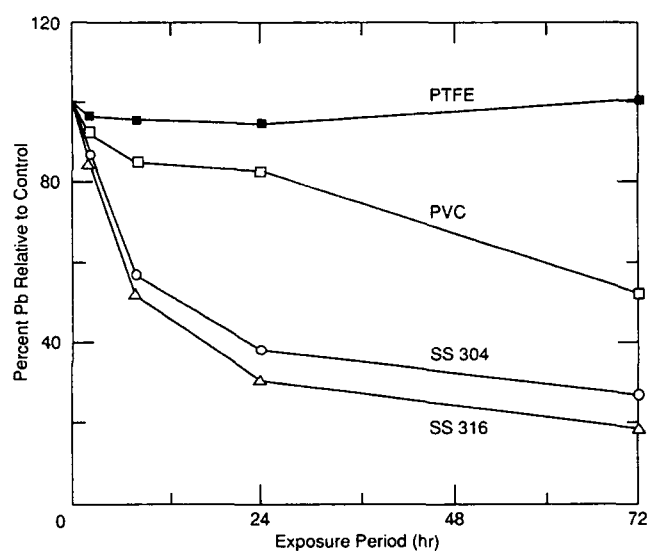
a. Cadmium.



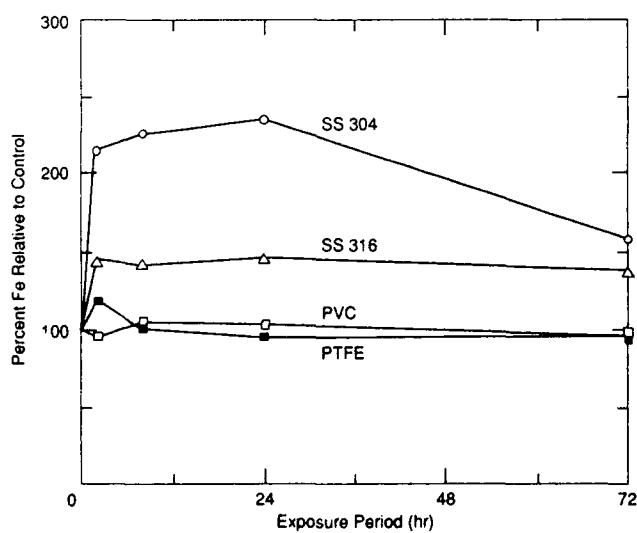
b. Chromium.



c. Copper.



d. Lead.



e. Iron.

Figure 2. Concentrations of spiked metals relative to the control for solutions exposed to PTFE, PVC, SS 304 and SS 316.

Copper

Although this test was designed to monitor sorption, the contribution of Cu to the well water exposed to SS 316 was found to be statistically significant for the first three treatment periods (Table 4b). This is consistent with the leaching experiment results. Figure 2c shows that in addition to the release of Cu from the SS 316, both SS 304 and PVC showed a sorptive tendency for aqueous Cu, and that PTFE was inert.

Lead

Statistically, both stainless steels were found to deplete the aqueous Pb levels more rapidly than PTFE and the control (Table 4b). Analysis of Table 4b indicates that the aqueous Pb concentrations decreased with time in all of the exposure vessels including the control; thus, apparently, some of casing materials as well as the polypropylene vessel walls provided sites for sorption. Figure 2d clearly shows the sorption tendency of the stainless casings and PVC, and that PTFE was inert.

Iron

The ANOVA did not establish any statistical differences among the Fe concentrations for any of the test materials or the control (Table 4b). Again poor precision among the stainless steel triplicates was the limiting factor for the statistical analysis. Table 4b indicates that all of the solutions were characterized by a slight decrease in aqueous Fe throughout the experiment; thus, as with aqueous Pb, Fe was sorbed by both the polypropylene exposure vessels and some of the casings. Figure 2e clearly shows that the average concentration of Fe in solutions exposed to the stainless steels were consistently higher than those exposed to PTFE, PVC and the control, thus indicating these materials were a source of Fe as the leaching experiment had shown.

DISCUSSION

The solution parameters in Table 2 show that during the course of the two experiments there were changes in DO (1.5 mg/L), pH (0.8) and ORP (50 mV). The greatest relative change was for DO (>400%). This parameter also showed the largest variation (%RSD) when a single replicate of each casing material and control was measured at the conclusion of the sorption experiment (Table 2).

For both experiments, the monitoring solutions for the 2-hour treatments showed a two-fold increase in DO, when compared to the levels measured just prior to dispensing. The DO remained fairly constant between 2- and 8-hours in the monitoring vessel, then decreased by at least 50% between the 8-hour and the final treatment

period. The increases in DO observed after the water was dispensed from the 4-L collection bottle were possibly caused by a combination of the actual physical process of transferring the well water and dissolution of oxygen that may have remained on the walls of the vessels (the surface area in contact with the solution was 113 cm²). The latter reason is supported by the generally higher DO levels measured in the vessels containing well casings at the end of the sorption experiment. Vessels with well casing sections contain 11% more surface area than the monitoring and control vessels. Because of the increased surface area, the well water exposed to the well casings most likely had slightly higher DO levels (≈ 0.6 mg/L) than indicated by the monitoring vessel measurements. The drop in DO seen after the 8-hour treatment period was attributed to biological activity. Nonetheless, the objective of maintaining a low oxygen environment was clearly achieved.

The variation in the pH and ORP determined for the monitoring solutions showed trends of decreasing acidity and ORP with increasing time of exposure. Comparing the monitoring solution values obtained for the final treatment period of both experiments with those obtained for the well casings and the control at the end of the sorption experiment indicates that there was no apparent well casing effect on pH or ORP.

The solution parameters maintained under the nitrogen environment had no visible influence on the surface appearance of the stainless steel casings. No new oxidation sites developed, nor did the existing sites grow visibly during the course of these two experiments. Thus, unlike the two previous studies (Hewitt 1989a,b) where frequently oxidation sites developed and increased in size, and in a couple cases, hydrous Fe precipitates formed, there were no visible changes taking place on the surface of stainless casings under this low-DO condition.

Since Fe was easily measurable in the well water, monitoring the aqueous levels throughout the experiments allows us to deduce its probable oxidation state. Table 4a shows that the randomly filled control vessels for the static leaching experiment all contained identical concentrations of Fe, indicating that it was evenly distributed in the collection vessel after purging. This was not the case previously (Hewitt 1989b), when the well water sat for several days between collection and experimental setup, and contact with laboratory air was not restricted. Under this less stringent protocol, the Fe concentrations in randomly filled controls varied by an order of magnitude, suggesting that the Fe was not dissolved, but was stratified in the collection vessel. The homogeneous Fe levels obtained for the leaching experiment controls and the lack of a precipitous decline in Fe concentrations for the sorption experiment (Table 4b)

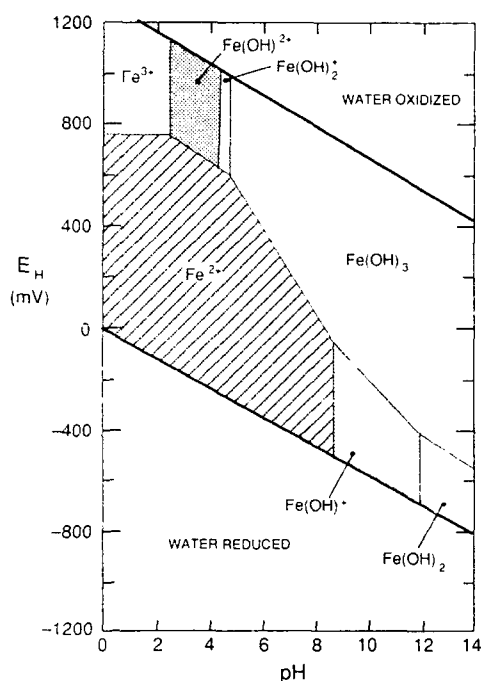


Figure 3. Diagram of iron speciation in ground water based on Eh and pH control (after Lloyd and Heathcote 1985).

indicate that Fe concentrations were not influenced, other than by the exposure to the stainless casings (Fig. 1e and 2e). Based on the range of solution parameters determined and a ground-water ORP/pH phase diagram taken from Lloyd and Heathcote (1985, Fig. 3), aqueous ferric hydroxide is the favored form. Because $\text{Fe}(\text{OH})_3$ is only sparingly soluble ($1.3 \times 10^{-14} \mu\text{g/L}$) at pH 8.8, the approximately $10 \mu\text{g}$ of Fe/L observed in the well water samples suggests that ferric iron must be uncoagulated in solution and is most likely colloidal.

The findings of this experiment, performed in low-DO well water, examining the potential of different well casing materials to influence Cd, Cr, Cu and Pb, support previous results (Hewitt 1989a,b), when presumably the

exposure solution was saturated with this oxidant. Again, PTFE was observed to be the least reactive material, and the stainless steels the most reactive in terms of releasing or providing sites for sorption of metals when exposed to well water. A summary (Table 5) of the materials that released or sorbed the greatest amount of Cd, Cr, Cu and Pb shows that one of stainless casing materials was always the most reactive. For this analysis, only SS 304, with regard to leaching Cr and sorbing Cu, was not significantly different from the control (and often PTFE and PVC) for at least one of the treatment periods. Thus, stainless steel casings show the greatest potential to alter the concentration of these metals in solution, independent of the amount of DO or presence of visible surface oxidation.

For Fe and Ni in the static leaching and Fe in the sorption experiments, the stainless well casings were again the most problematic. Statistically, both stainless steels leached more Fe than the control for at least one of the treatment periods, and SS 316 leached more Ni than any of the other materials and the control for three out of the four treatments. Although the sorption study failed to show any statistical difference among the materials, it is apparent from Fig. 2e that both stainless steels in this experiment also released Fe to solution.

For this study and previous ones (Hewitt 1989a,b), values that are often treated as outliers (i.e., Appendix A, *Static Leaching Experiment*, Pb 17.8- and Fe 138- $\mu\text{g/L}$ concentrations for 8-hour treatment samples exposed to SS 304 and SS 316, respectively) were not removed to improve the statistical comparison. These independent studies all have reported a couple of aberrant values, and in every case they were for solutions exposed to the stainless steel casings. Since all casings were handled identically, this cumulative observation suggests that the stainless steel material is more prone to indeterminate contamination. The aberrant values for this study were not associated with the stainless casing sections that had visible oxidation sites (see Table 1).

Regardless of amount of water purged or contact time, ground-water sampling wells encased with stain-

Table 5. Summary of results.

	Cd	Cr	Cu	Pb
Well casing material that released the greatest amount of metal to the well water, when averaged over the four treatment periods.	SS 316	SS 304	SS 316	SS 304
Well casing material that sorbed the greatest amount of metal from the well water, when averaged over the four treatment periods.	SS 304	SS 304	SS 304	SS 316

less steels are subject to circumstantial evidence making them a more questionable candidate for monitoring metals than either PVC or, particularly, PTFE. Considering all of our laboratory studies, this statement applies to both deep and shallow wells. PVC, although not nearly as inert as PTFE, can be characterized as performing more predictably than the stainless steels. Stainless steels 316 and 304, as determined in this study and previously (Hewitt 1989a,b), show the greatest potential to influence solution metal chemistry in ground water. PVC well casing is also now available cleaned by the manufacturers. This additional quality control step may improve its performance with aqueous metal chemistry.

CONCLUSION

The results of this study under low-DO conditions support earlier findings (Hewitt 1989a,b). Together with studies concerned with aqueous levels of organic constituents (Gillham and O'Hannesin 1990, Parker et al. 1990, Reynolds et al. 1990), one can conclude that all four commonly used well casing materials have the potential to influence ground-water chemistry. Stainless steels 304 and 316 with and without visible surface oxidation were consistently found to be the poorest choices for monitoring metals and PTFE for the poorest choice for organics. Contrarily, it appears that stainless steels may be the best choice if only organics were of concern, and PTFE for only metals. PVC, although not without some problems, is a reasonable compromise for monitoring both inorganic and organic constituents, and is available at a lower cost compared to the other materials. This cost savings could be used to support a more extensive sampling program, providing for more site information. Until a superior, universally inert material is commercially available for ground-water monitoring wells, PVC should see continued use in routine applications.

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APPENDIX A: LEVELS OF METALS DETERMINED IN WELL WATER SOLUTIONS (µg/L) FOR BOTH EXPERIMENTS.

Static leaching experiment

<i>Pipe</i>	<i>Replicate</i>	<i>Time (hr)</i>	<i>Number</i>	<i>Cd</i>	<i>Cr</i>	<i>Cu</i>	<i>Pb</i>	<i>Fe</i>	<i>Ni</i>
Control	1	2	1	<D*	0.21	0.47	<D	10.0	<D
Control	2	2	2	<D	0.18	0.47	<D	9.6	<D
Control	3	2	3	<D	0.32	0.47	<D	10.2	<D
Control	1	8	4	<D	0.30	0.52	<D	10.7	<D
Control	2	8	5	<D	0.30	0.47	<D	9.3	<D
Control	3	8	6	<D	0.27	0.47	<D	9.3	<D
Control	1	24	7	<D	0.30	0.47	<D	10.2	<D
Control	2	24	8	<D	0.30	0.52	<D	9.3	<D
Control	3	24	9	<D	0.24	0.52	<D	9.9	<D
Control	1	120	10	<D	0.39	0.47	<D	10.2	<D
Control	2	120	11	<D	0.36	0.52	<D	9.9	<D
Control	3	120	12	<D	0.36	0.47	<D	9.9	<D
PTFE	1	2	1	<D	0.27	1.04	0.21	10.5	2.8
PTFE	2	2	2	<D	0.30	1.13	<D	11.9	<D
PTFE	3	2	3	0.06	0.27	1.23	0.11	11.9	<D
PTFE	1	8	4	<D	0.33	0.78	<D	11.6	<D
PTFE	2	8	5	<D	0.33	0.57	0.27	10.7	<D
PTFE	3	8	6	<D	0.39	0.84	0.17	17.8	<D
PTFE	1	24	7	<D	0.27	0.63	0.28	9.3	<D
PTFE	2	24	8	<D	0.27	0.63	0.15	9.0	<D
PTFE	3	24	9	0.04	0.36	0.84	0.11	10.2	<D
PTFE	1	120	10	0.04	0.33	1.67	<D	8.8	2.8
PTFE	2	120	11	<D	0.33	0.57	<D	9.3	<D
PTFE	3	120	12	<D	0.36	0.73	0.15	10.7	<D
PVC	1	2	1	0.23	0.88	2.82	1.52	12.1	<D
PVC	2	2	2	0.05	0.68	1.65	0.96	11.3	<D
PVC	3	2	3	<D	0.60	1.08	0.33	12.7	<D
PVC	1	8	4	<D	0.45	0.92	0.38	10.7	<D
PVC	2	8	5	0.31	0.32	1.67	0.38	11.0	<D
PVC	3	8	6	0.33	0.38	1.72	0.31	11.3	<D
PVC	1	24	7	0.47	0.51	2.77	0.48	11.0	<D
PVC	2	24	8	0.29	0.65	2.09	0.99	11.9	<D
PVC	3	24	9	0.04	0.88	2.19	1.31	11.6	<D
PVC	1	120	10	0.22	0.40	1.88	0.27	10.2	<D
PVC	2	120	11	<D	0.36	0.66	0.30	7.8	<D
PVC	3	120	12	0.48	0.38	2.45	0.51	9.3	<D
SS 304	1	2	1	0.18	0.52	9.58	0.25	15.2	3.5
SS 304	2	2	2	0.18	0.65	8.66	0.38	13.6	4.0
SS 304	3	2	3	0.29	0.70	2.45	1.01	21.4	<D
SS 304	1	8	4	0.44	1.52	4.85	0.74	15.8	3.5
SS 304	2	8	5	0.29	9.82	4.91	17.8	16.1	4.5
SS 304	3	8	6	0.47	1.99	5.30	1.21	12.9	2.5
SS 304	1	24	7	0.15	3.60	11.7	1.27	13.0	6.9
SS 304	2	24	8	0.11	1.49	10.3	1.33	15.1	5.2
SS 304	3	24	9	0.25	1.79	2.28	1.67	31.9	3.0
SS 304	1	120	10	<D	5.95	4.07	1.34	19.3	10.9
SS 304	2	120	11	0.12	1.43	3.81	1.54	40.3	4.5
SS 304	3	120	12	0.13	1.79	2.80	2.80	85.1	3.0
SS 316	1	2	1	0.37	0.64	35.4	0.35	21.7	8.9
SS 316	2	2	2	0.37	1.03	37.1	0.94	18.6	11.9
SS 316	3	2	3	0.33	2.38	21.2	1.07	27.9	19.8
SS 316	1	8	4	0.75	3.84	13.7	2.13	138	20.3

SS 316	2	8	5	0.34	0.89	23.3	0.31	14.1	11.9
SS 316	3	8	6	0.37	1.40	39.0	0.41	14.7	15.8
SS 316	1	24	7	0.19	0.92	25.3	0.25	25.0	10.4
SS 316	2	24	8	0.11	0.76	19.5	0.18	38.6	8.9
SS 316	3	24	9	0.29	3.99	15.1	0.38	23.1	11.9
SS 316	1	120	10	0.04	2.92	20.0	0.51	21.2	18.8
SS 316	2	120	11	<D	1.04	19.0	<D	11.6	9.4
SS 316	3	120	12	0.05	2.62	9.66	0.41	18.6	7.9

* <D Less than or equal to the respective MDL.

Sorption experiment

<i>Pipe</i>	<i>Replicate</i>	<i>Time (hr)</i>	<i>Number</i>	<i>Cd</i>	<i>Cr</i>	<i>Cu</i>	<i>Pb</i>	<i>Fe</i>
Control	1	2	1	2.28	12.0	9.92	10.3	9.13
Control	2	2	1	2.30	12.3	11.5	10.2	9.09
Control	3	2	1	2.26	12.4	10.2	9.75	9.11
Control	1	8	2	2.28	12.4	10.2	10.2	8.59
Control	2	8	2	2.26	12.0	11.7	10.2	8.93
Control	3	8	2	2.22	12.0	10.3	9.53	8.47
Control	1	24	3	2.22	12.2	9.12	9.66	8.27
Control	2	24	3	2.28	12.1	10.9	9.87	7.72
Control	3	24	3	2.18	12.2	9.72	9.32	8.26
Control	1	72	4	1.76	11.6	7.52	6.99	7.02
Control	2	72	4	2.24	12.1	10.8	9.24	6.98
Control	3	72	4	2.13	12.0	9.82	9.03	8.06
PTFE	1	2	1	2.22	12.0	10.1	9.75	13.2
PTFE	2	2	1	2.26	12.2	11.2	9.87	9.54
PTFE	3	2	1	2.24	12.0	9.92	9.87	9.90
PTFE	1	8	2	2.18	12.1	9.42	9.11	9.13
PTFE	2	8	2	2.26	11.9	11.1	9.75	8.60
PTFE	3	8	2	2.22	12.3	9.28	9.75	8.40
PTFE	1	24	3	2.15	12.0	8.92	8.90	8.04
PTFE	2	24	3	2.22	12.2	11.1	9.11	7.84
PTFE	3	24	3	2.20	12.4	8.82	9.32	7.37
PTFE	1	72	4	2.07	12.5	8.12	8.26	7.55
PTFE	2	72	4	2.22	12.0	10.2	8.81	6.73
PTFE	3	72	4	2.09	11.9	7.92	8.47	6.45
PVC	1	2	1	2.20	12.3	10.3	9.32	8.77
PVC	2	2	1	2.28	12.1	10.6	9.32	8.92
PVC	3	2	1	2.36	12.6	11.5	9.32	8.58
PVC	1	8	2	2.09	12.3	10.1	8.60	8.58
PVC	2	8	2	2.20	12.1	10.1	8.47	8.66
PVC	3	8	2	2.28	12.7	10.6	8.39	9.67
PVC	1	24	3	1.95	12.3	9.02	8.05	8.57
PVC	2	24	3	2.15	12.4	9.22	7.84	8.44
PVC	3	24	3	2.22	12.5	10.1	8.05	7.92
PVC	1	72	4	0.19	12.5	2.40	1.27	6.59
PVC	2	72	4	1.49	12.4	7.11	4.87	7.20
PVC	3	72	4	2.13	12.6	9.22	7.20	7.00
SS 304	1	2	1	2.20	10.8	9.12	9.11	34.3
SS 304	2	2	1	2.22	11.8	18.0	8.60	9.88
SS 304	3	2	1	2.13	11.2	9.52	8.47	14.5
SS 304	1	8	2	1.82	9.55	6.35	6.91	34.6
SS 304	2	8	2	1.92	11.9	15.6	5.08	10.0
SS 304	3	8	2	1.80	10.3	6.01	5.21	14.2
SS 304	1	24	3	1.40	9.57	4.11	5.30	32.7
SS 304	2	24	3	1.63	11.8	12.9	2.46	9.41
SS 304	3	24	3	1.42	10.1	3.51	3.18	14.5

SS 304	1	72	4	1.07	9.01	2.81	4.24	15.2
SS 304	2	72	4	1.15	11.6	8.68	1.06	7.48
SS 304	3	72	4	0.25	4.47	1.96	1.48	11.1
SS 316	1	2	1	2.28	12.2	25.2	8.39	9.86
SS 316	2	2	1	2.34	12.4	19.3	8.47	19.0
SS 316	3	2	1	2.30	12.7	25.2	8.81	11.4
SS 316	1	8	2	2.09	12.3	29.9	4.79	8.66
SS 316	2	8	2	2.28	12.1	24.4	5.51	18.6
SS 316	3	8	2	2.11	12.3	28.5	5.21	9.74
SS 316	1	24	3	1.86	12.2	28.7	2.33	8.49
SS 316	2	24	3	2.11	12.6	33.1	3.81	16.9
SS 316	3	24	3	1.92	12.6	28.1	2.67	9.90
SS 316	1	72	4	1.34	11.5	14.6	1.19	7.50
SS 316	2	72	4	1.82	11.2	27.2	2.46	14.3
SS 316	3	72	4	1.23	11.5	14.8	1.27	7.87

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13. ABSTRACT (Maximum 200 words) Both the leaching and sorption characteristics of poly(vinyl chloride) (PVC), poly(tetrafluoroethylene) (PTFE) and two types of stainless steel (SS 304 and SS 316) well casing materials were examined by determining levels of Cd, Cr, Cu, Pb, Fe and Ni in an aqueous solution. Experiments were conducted under a nitrogen environment in well water having low dissolved oxygen, without visible surface oxidation of the stainless casings. Under conditions typical of deep wells, PTFE was inert, whereas both stainless steels significantly altered the solution chemistry for most of the metals cited above. PVC was generally more reactive than PTFE, but did not dominate solution chemistry; neither was it as variable in its influence as the metal casings.					
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