

Impact of stagnation time on metal dissolution from plumbing materials in drinking water

D. A. Lytle and M. R. Schock

ABSTRACT

Studies were conducted to evaluate the impact of stagnation period on the metal dissolution from plumbing materials including lead, copper and brass. Experimental data showed that metal levels increased exponentially with time, with the sharpest increase occurring over the first 20–24 h. Metal levels may continue to increase following well beyond 24 h of stagnation. Copper levels increased until dissolved oxygen fell below 1 mg l^{-1} after which copper levels fell. Results showed that stagnation behaviour is complex in nature, difficult to predict and dependent on water chemistry. Experimental data fit well to a radial diffusion model when a diffusion barrier term is considered.

Key words | brass, copper, corrosion, diffusion, lead, stagnation time

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INTRODUCTION

Lead and copper tap water monitoring requirements under the US Environmental Protection Agency's (USEPA's) Lead and Copper Rule (LCR) (Federal Register 1991a, b, 1992), require that first draw water samples must be taken at defined sites following at least 6 h of stagnant contact with the plumbing materials. The time frame was intended to represent a 'worst case' lead or copper exposure such as in the morning after an overnight stand period.

The effect of stagnation period on the amount of metal in the water is important in several respects. A systematic model for describing metal concentration versus stagnation time (stagnation profile) would be useful in more accurately predicting human exposure. Similar information would be useful in explaining discrepancies between theoretical metal levels predicted by solubility models and field monitoring data, and within-house and between-house drinking water metal concentration variability. Also, such models would be important to assure proper conclusions when comparing alternative corrosion control treatments.

The objectives of the research presented in this paper are to: (1) investigate the impact of the stagnation period on metal release from copper, lead and brass, in several

test waters; (2) compare experimental stagnation profiles with radial diffusion model predictions; and (3) discuss the practical implications of the results.

BACKGROUND

Several investigators have reported on the impact of stagnation time on copper concentration. Tronstad and Veimo (1940) examined changes in copper and dissolved oxygen concentrations in water in contact with copper pipe after different stand periods. They found that copper levels increased to a maximum value after a certain amount of time depending on experimental conditions, then decreased asymptotically towards a limiting value which was believed to be dependent on the corrosion products formed and the consumption of dissolved oxygen. Maximum copper concentrations were reached in as little as 2–3 h to about 15 h. At the same time the oxygen concentration decreased asymptotically to a minimum of $0.1\text{--}0.3 \text{ mg l}^{-1}$ (initial values ranged from 5 to 6 mg l^{-1}) after approximately 48 h. The loss in oxygen was slower in aged pipes in comparison with 'fresh' pipes.

Yamauchi *et al.* (1982) briefly examined the impact of stand time and temperature on copper leached from copper tubing. They found that copper levels increased to a maximum value after a certain period (6–9 h), then decreased at all three temperatures studied (10°C, 30°C and 50°C). The time to reach the peak decreased with increasing temperature. The authors suggested that copper dissolution rates decreased with corresponding decrease in oxygen concentration. The lowering of copper levels was believed to result from copper (II) (cupric) ions in the water reacting with metallic copper to form copper (I) (cuprous) ions.

Like Yamauchi *et al.* (1982), Harju and Holm (1992), at two different field test sites with different water qualities, found that copper levels leached from copper pipes reached a maximum value after about 4 h then gradually dropped off. The decrease in copper levels was thought to be a result of a presumed decrease in dissolved oxygen.

A 1988 KIWI report (van den Hoven and van Eekeren 1988) showed that copper concentration generally increased gradually to a maximum level after a period (about 22 h stand time for 19.8 mm diameter pipes) of standing after which copper levels became independent of stand time. In exceptional cases, however, no saturation level was reached. Instead, copper levels decreased after a certain maximum value was reached over a long stand period. The authors attempted to quantitatively predict the dissolution of copper over time with a diffusion-based model which incorporated the contact time, copper diffusion coefficient, maximum copper level (based on water quality) and pipe diameter. They strictly considered aged pipes, i.e. pipes which had a stabilized layer on the inside.

Werner and colleagues (1994) presented the most interesting and revealing work on stagnation impact on copper and dissolved oxygen levels. They examined the impact of three water flow scenarios: (1) continuous flow; (2) 12 h flow; 12 h stand; and (3) 1 hour flow, 23 h stand; on stagnation profiles and dissolved oxygen levels. Results showed that after 3 h, copper levels increased to a maximum value while the dissolved oxygen levels decreased. When dissolved oxygen levels decreased from an initial value of 8 mg l⁻¹ to 1 mg l⁻¹, copper levels began to decrease. Under flow condition (1), copper levels reached

a maximum then dropped to undetectable after 23 h, while dissolved oxygen was gone by 8 h. During flow regime (2), copper dropped to undetectable levels after only 4–5 h and dissolved oxygen was gone within 10 h. In flow (3), copper was still observed after 24 h and dissolved oxygen depletion was low. The highest copper maximum was observed in flow regime (1) while the lowest was observed in flow regime (3). These studies showed that the character of the scale differed with different flow/stand schemes, which also implies difficulty for reliably comparing data on metal levels from different sites, pipe loops or systems. Further, it raises a clear question about what equilibrium really means in dynamic systems of oxidizing agents and reducing materials (metal pipes).

Numerous international researchers have also investigated various aspects of stagnation curves for lead pipe, and many of these studies have been reviewed by Schock *et al.* (1996). One of the most common observations of this research was that lead levels in treated drinking water rapidly increased but ultimately approached a fairly constant 'equilibrium' value after approximately 'overnight' periods of stagnation. The rapidity of increase was somewhat variable over the first few hours of stagnation, and most researchers believed that this difference in slope of the initial limb of the stagnation curve was mostly caused by the formation of corrosion scales or diffusion barriers on the pipe surfaces, rather than by changes in the rates or extent of oxidation of the lead metal to Pb²⁺ ion. Early studies by Schock (1980, 1981) and Schock and Gardels (1985) showed that the rate of depletion of chlorine residual was related to the effectiveness of corrosion inhibition by pH and alkalinity adjustment on tests with new pipe. Some researchers felt that the shapes of the stagnation profiles could best be described purely statistically, and cases where particulate release was significant made all stagnation curve models difficult to apply quantitatively to predict lead levels at the tap. Because the Lead and Copper Rule in the United States (Federal Register 1991a, b) sought to target and reduce the lead concentrations in the types of households that would tend to produce the highest lead levels, the regulation incorporated assumptions about metal stagnation profiles that were based on the dominant observations in the lead corrosion control research, recognizing that precise predictions of

lead levels at different standing times were impossible. Therefore, favouring conditions closest to the maximum quasi-equilibrium values under normal usage conditions would be the best strategy for the regulatory purpose. Thus, a minimum stagnation time of 6 h was required by the regulation, and guidance that accompanied the regulation (US Environmental Protection Agency 1992) suggested that samples should be taken after the pipes were fully flushed followed by between 6 and 16 h of standing time.

MATERIALS AND METHODS

The data presented in this paper were gathered from corrosion studies conducted by researchers at the USEPA's National Risk Management Research Laboratory (NRMRL) in Cincinnati, Ohio, between 1991 and 1996.

Study A

The objective of Study A was to examine the impact of domestic ion exchange water softeners on the corrosion of plumbing materials (Sorg *et al.* 1999). A pipe loop test system was installed at the Indian Hill water treatment plant in Indian Hill, Ohio (USA). Indian Hill's raw water is a relatively hard groundwater (water quality shown in Table 1).

Two pipe loop boards were used; one was supplied with raw water and the other received ion exchange softened water (Table 1). The pipe loop systems were designed similarly to the system described in the American Water Works Association's *Lead Control Strategies* manual (AWWARF 1990). Each pipe loop board contained two loops of lead pipe, copper tubing, copper pipe with 50 : 50 tin : lead solder, galvanized pipe, and two brass kitchen taps. A pipe diameter of 12.7 mm and lengths of 15.2 m (1,950–2,300 ml capacity) were used. Each individual pipe section or tap was separated from the main feed manifold by a check valve, followed by a needle valve, flowmeter, and a sample port. A second sample

port was located after the pipe section. Water passing each pipe section was directed to a common drain which was controlled by a solenoid valve/timer mechanism.

The system was pressurized to 1,525–1,660 kPa and the flowrate through each loop during the flow periods was approximately 3.8 l min^{-1} . Three 30 min and one 15 min flow periods were set daily and were separated by 1.5–2 h stand periods. One litre first-draw samples were taken bi-weekly after the remaining stand period of approximately 17.5 h after sending 500 ml to waste. Pre- and post-softened water was monitored on each day that samples were collected (twice per week). Wet chemistry and metal samples were analysed at the EPA's facility in Cincinnati, Ohio, while pH, dissolved oxygen and temperature were measured at the Indian Hill facility at the time of sampling. Normal system operation was interrupted twice during the study period (at 161 and 455 days into the study) to collect special stagnation profile samples. Over 1-week periods, normal flow operation was altered such that 7–8 different samples with stand times of up to 90 h were taken. The samples were analysed for metal content and dissolved oxygen.

Study B

The study objectives were to examine the impacts of water quality and stagnation time on copper concentrations. The experimental system consisted of three heavy-duty polyethylene plastic 200-l water reservoir tanks with floating lids to reduce water contact with the atmosphere. Test water held in each reservoir was manually chemically adjusted to the desired quality. Water was continuously mixed by a magnetic drive pump recirculation system in order to assure complete chemical dispersion. Each tank was connected to a parallel set of three 24 m (370 ml capacity) lengths of 12.7 mm ID type M hard drawn copper pipe by a series of Schedule 80 PVC pipe and fittings. Pressure demand pumps were used to maintain pressure (at 207 kPa) and flowrate (11.4 l min^{-1}) through the pipes. Each set of pipes fed to a common drain. Flow was controlled by a timer activated solenoid valve positioned between the pipes and the drain line. Timer activation opened the solenoid valve resulting in a system pressure

Table 1 | Mean test water quality parameters

Analyte	Study A		Study B		
	Softened	Non-softened	System 1	System 2	System 3
Lead ($\mu\text{g l}^{-1}$)	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0
Calcium (mg l^{-1})	0.32	83.6	36.8	36.6	36.7
Copper (mg l^{-1})	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Iron (mg l^{-1})	0.002	0.002	< 0.05	< 0.05	< 0.05
Potassium (mg l^{-1})	3.14	2.98	2.79	2.80	2.81
Magnesium (mg l^{-1})	0.12	24.2	9.66	9.67	9.68
Manganese (mg l^{-1})	0.001	0.001	< 2.0	< 2.0	< 2.0
Sodium (mg l^{-1})	177	40.7	21.0	22.9	25.1
Zinc (mg l^{-1})	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Alkalinity ($\text{mg CaCO}_3 \text{ l}^{-1}$)	261	262	46.4	47.8	48.1
Sulphate ($\text{mg SO}_4 \text{ l}^{-1}$)	46.3	46.2	70.3	70.4	70.4
Chloride (mg l^{-1})	73.8	73.5	26.4	29.3	32.9
Silica ($\text{mg SiO}_2 \text{ l}^{-1}$)	7.28	7.39	5.78	17.9	28.3
Nitrate (mg N l^{-1})	2.07	2.13	1.09	1.09	1.10
Phosphate (mg P l^{-1})	0.08	0.09	< 0.03	< 0.03	< 0.03
Dissolved oxygen (mg l^{-1})	3.47	3.47	—	—	—
Total inorganic carbon (mg C l^{-1})	69.7	69.6	11.0	10.9	10.9
Free chlorine ($\text{mg Cl}_2 \text{ l}^{-1}$)	—	—	0.50	0.52	0.52
pH, pH units	7.45	7.33	7.49	7.51	7.50
Hardness ($\text{mg CaCO}_3 \text{ l}^{-1}$)	1.3	300			

drop, pump activation and water flow. Each valve opening or flow period lasted approximately 1 min and passed approximately 11.4 l of water through each pipe.

Flow periods were set for five times a day on weekdays and twice a day over the weekend. Flow period times were based on collecting 1, 2, 4, 8 and 11 h stagnation

time samples from each pipe and reservoir filling needs. Stagnation samples were taken on Monday (11 h samples) and Tuesday (1, 2, 4 and 8 hour samples). Results from a series of sequential samples suggested that the sampling should consist of wasting the first 30 ml (water in contact with the PVC sample port) and, immediately afterwards,

collecting approximately 100–125 ml for copper analysis to assure a sample in contact with the copper. In addition, a 25 ml sample was taken from each pipe for chlorine analysis. Reservoir water samples were taken each Tuesday and consisted of a 250 ml sample for background metals, 250 ml sample for anions, and a 30 ml TIC (total inorganic carbon) sample. Free chlorine and pH were monitored and adjusted (if necessary) daily.

Flow requirements required the reservoir tanks to be filled three times a week (Monday, Wednesday and Friday). Test water was chemically adjusted, carbon cartridge filtered Cincinnati tap water. The original goal of this study was to evaluate the impact of silica on copper corrosion at two pH values: phase 1 at pH 7.5 and phase 2 at pH 8.5. Chemical adjustment to meet pH, free-chlorine, and silica target levels were made with 8 M NaOH, 6 M HCl, sodium hypochlorite, and Type 'N' sodium silicate addition. Water quality analysis for the two study phases are shown in Table 1.

Study C

The objective of this study was to evaluate the impact of pH and orthophosphate on the amount of metal leached from pipe and tap materials, and has been reported in detail elsewhere (Lytle and Schock 1996) The test apparatus consisted of a large water reservoir connected to 12 parallel test loops.

Each test loop was constructed of PVC Schedule 80 and high-density polyethylene (HDPE) valves, fittings and pipe. The systems each contained a three-way valve, a sample holding cell and tubing made of Teflon®. The holding cell was sized to hold tightly one 25 × 51 × 3.2 mm metal coupon (Metal Samples, Inc., Munford, Alabama) in order to maximize the ratio of coupon surface area to volume of water in contact with the coupon. The coupon surface area was $3.06 \times 10^{-3} \text{ m}^2$ and the volume of water was 26 ml, resulting in a surface area to volume ratio of $1.18 \times 10^{-4} \text{ m}^2 \text{ ml}^{-1}$. Six differently composed brass coupons, plus, a pure copper, pure zinc, pure lead and 60 : 40 Sn : Pb solder coupon were simultaneously tested. The different brass coupons were chosen because they represent common materials used to manufacture brass

taps and other fixtures used in drinking water systems. Test water was chemically adjusted as needed to maintain test water quality goals. Test water quality is shown in Table 1 for two test phases. Test water was fed to the loops by a magnetic drive pump.

Approximately 38 l of test water was flushed through the loops simultaneously at a flowrate of approximately 0.15 l min^{-1} for a brief rinse period. The valves in the loops were then closed, holding the water in the cells in contact with the metal coupons for approximately 22–24 h. Next, the cells were sampled by opening the labcock above the cell to the air and then opening the three-way Teflon® stopcock below the cell. The total sample volume was only about 26 ml, most of which was contained in the Teflon® sample cell. The valves were then closed and newly prepared source water was again flushed through the cells, as mentioned above, repeating the procedure. Water was flushed through the cells daily (Monday to Friday), even when sampling was not done. Air was in contact with the metal coupons for a short period of time; however, the coupon surface was not exposed for long enough to become completely dry.

Test runs were generally terminated after approximately 150 days, based on apparent stabilization of metal leaching levels. At the end of each test run, the coupons were removed from the cells, the system was cleaned as previously described, new coupons were installed, and the study was repeated with a different extraction water. Water quality data for two phases of the study are shown in Table 1.

Analytical

Water samples taken for metal analyses were preserved with ultrapure nitric acid (0.15% v/v) (US Environmental Protection Agency 1979). Pipe loop samples and background metal samples were analysed for inorganic elements according to recommended techniques (US Environmental Protection Agency 1986). Background wet chemistry samples were refrigerated and analysed accordingly (US Environmental Protection Agency 1983; US Geological Survey 1985; SMEWW 1992).

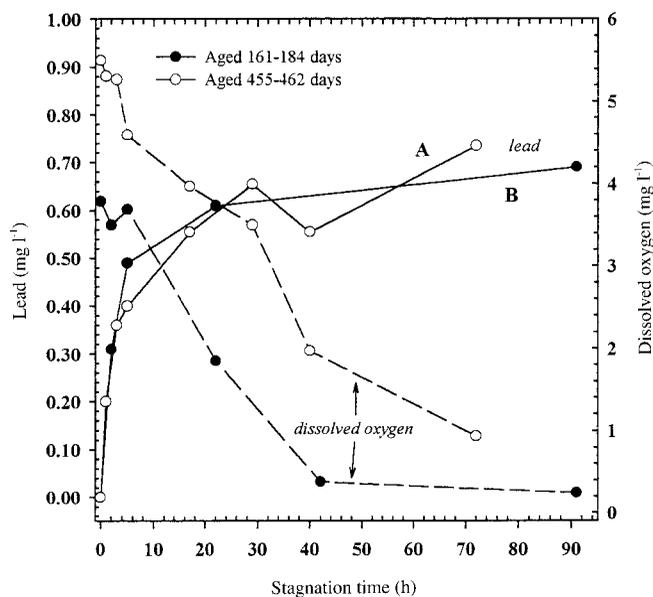


Figure 1 | Impact of stagnation time on lead and dissolved oxygen concentrations in lead pipe (13 mm diameter) exposed to softened water in Study A.

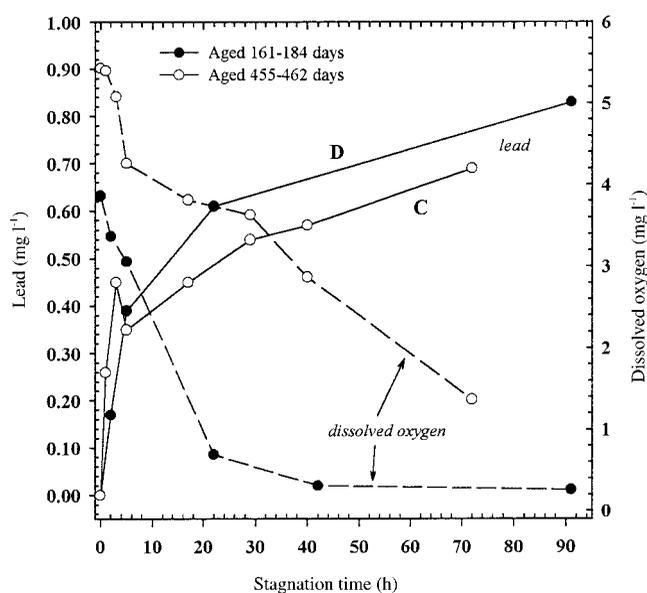


Figure 2 | Impact of stagnation time on lead and dissolved oxygen concentrations in lead pipe (13 mm diameter) exposed to non-softened water in Study A.

RESULTS

Study A

Results from Study A showed that the shape of the lead pipe stagnation curves and the maximum lead concentrations were independent of pipe age and tested water quality. Stagnation profiles (Figures 1 and 2) increased in an exponential manner with increasing time. Lead levels increased most rapidly over the first 10 h, reaching approximately 50–70% of maximum observed values. Lead levels appeared to slightly increase even up to 90 h of standing. This pattern was most prominent in the non-softened system (Figure 2). The results have noteworthy regulatory and human exposure implications. As an illustration, a sample taken after a 6-h stand period in the experimental case of the older lead pipe exposed to softened water (Figure 1) would give a lead concentration of approximately 0.40 mg l^{-1} while a sample taken after 16 h would give approximately 0.54 mg l^{-1} . The difference is a 35% lead increase over the recommended LCR sampling period of 6–16 h (US Environmental Protection Agency 1991).

Corresponding dissolved oxygen concentration profiles (also shown in Figures 1 and 2) were parallel and decreased in an almost exponential fashion. A difference in the magnitude of dissolved oxygen concentration profile with pipe age was noted. The curve shift was attributed to the 1 mg l^{-1} difference in the initial dissolved oxygen levels.

Copper pipe results showed differences in the stagnation patterns between pipes exposed to softened (Figure 3) and non-softened (Figure 4) water. The shape of both stagnation profile pairs was independent of age. Peak copper concentrations appeared to differ, although peak values may have been missed due to gaps between sampling times. Copper levels increased sharply to maximal levels after approximately 20–25 h of contact with standing water for loops exposed to softened water. Copper levels then dropped sharply to less than 0.5 mg l^{-1} by 72–92 h. Peak copper levels corresponded to the time when dissolved oxygen fell below 1 mg l^{-1} (Figure 3). Dissolved oxygen dropped sharply to undetectable levels after 30–40 h.

The stagnation profile and the dissolved oxygen results for the pipes exposed to non-softened water

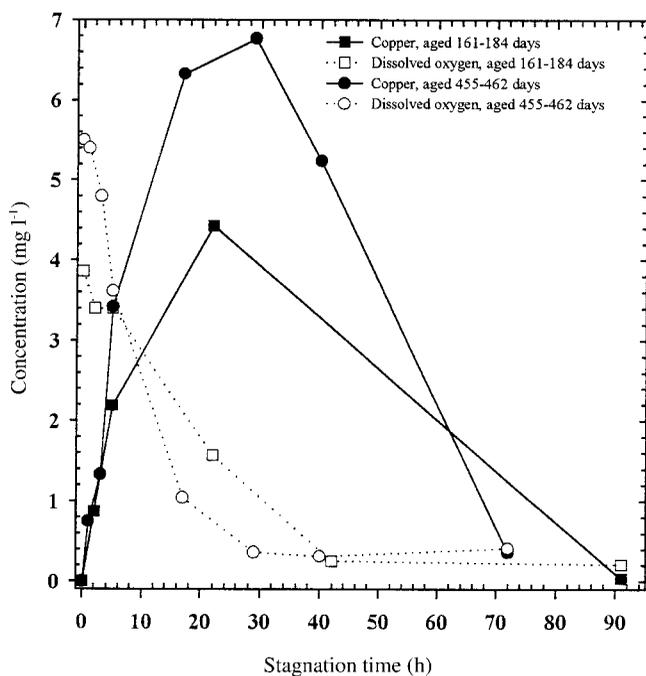


Figure 3 | Impact of stagnation time on copper and dissolved oxygen concentrations in copper tubing (13 mm diameter) exposed to softened water in Study A.

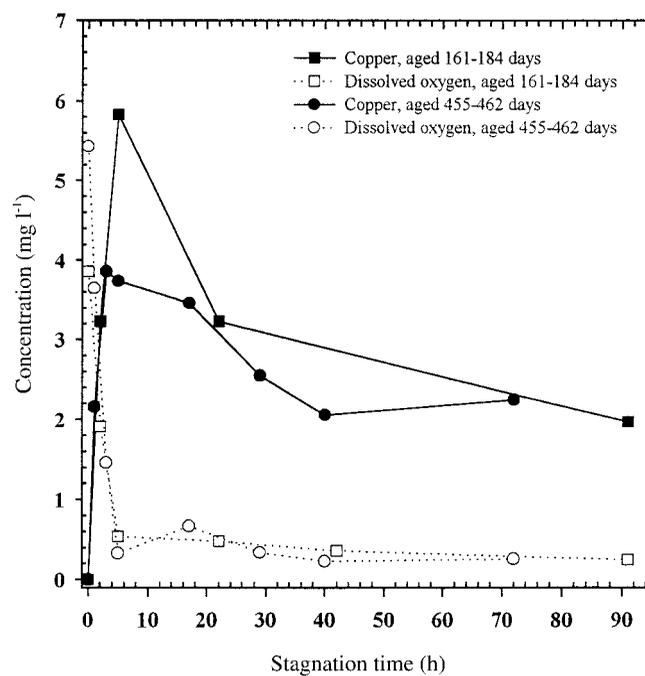


Figure 4 | Impact of stagnation time on copper and dissolved oxygen concentrations in copper tubing (13 mm diameter) exposed to non-softened water in Study A.

(Figure 4) were considerably different from those exposed to softened water. Copper levels increased more sharply, reaching maximal levels in less than 8 h. After peaking, copper levels dropped more gradually than in the softened water, reaching approximately 2 mg l⁻¹ after 72–92 h. Once again, the shift in direction in copper concentration corresponded to the point where dissolved oxygen dropped to approximately 1 mg l⁻¹. Dissolved oxygen dropped more rapidly than in the softened water system, falling to undetectable levels after only 6–8 h.

The relationship between copper and dissolved oxygen stagnation behaviour has also been observed by Werner and colleagues (Werner *et al.* 1994). Copper observations reflect electrochemical interactions between dissolved oxygen, metallic copper, surface oxidation products [e.g. Cu(OH), Cu₂O, Cu(OH)₂], cuprous (Cu¹⁺) ions and cupric (Cu²⁺) ions (Werner *et al.* 1994; Schock *et al.* 1995a, b). Metallic copper is oxidized to cuprous ion then to cupric ions under conditions of sufficient dissolved oxygen (>1 mg l⁻¹) also producing a thin

Cu(OH)₂ surface deposit. Under low dissolved oxygen conditions, cupric ions are reduced to cuprous ions and the surface film may be reduced to Cu(OH) or CuO by contact with the pipe. Copper solubility based on cupric solids can be 10–1,000-fold higher than copper solubility based on cuprous oxide or hydroxide, explaining the stagnation pattern (Werner *et al.* 1994; Schock *et al.* 1995a, b).

Analysis of the deposits on the copper pipes revealed a general absence of Cu(II)-containing solids, especially on the pipe exposed to softened water. This would be expected for the case where insufficient oxidant was available to produce a thick and uniform passivating film of the oxidized form. The absence of significant cupric hydroxide or tenorite (CuO), but the observed presence of Cu₂O (cuprite) is supportive of the reversion of Cu(II) to Cu(I) forms, or the physical retardation of oxidation by surficial materials, possibly amorphous. The pipe exposed to the hard water had only traces of Cu₂CO₃(OH)₂ (malachite) in widely dispersed random minute patches. Faster oxidation that could leave a residual Cu(II) material behind

after depletion in the water is consistent with the behaviour in Figure 4.

The metal stagnation behaviour clearly showed a strong dependence of metal concentration on stand time prior to sampling. Metal levels increased exponentially with stand time with time being most critical during the first 20–24 h. This observation has direct implications for LCR monitoring. For example, in the case of the older copper pipe, a sample taken after the minimum of 6 h would give a value of approximately 1.4 mg l^{-1} while a sample taken after 16 h would give approximately 5.2 mg l^{-1} (Figure 3). The resulting copper increase of 270% was much more dramatic than the case for lead. This illustration shows how dramatic differences in copper exposure can be over relatively short times and how inconsistencies in sampling times can explain within-house and between house sampling variability frequently observed during field sampling.

The importance of understanding the nature of stagnation behaviour in a system is clearly demonstrated by closely examining and comparing copper profiles shown in Figures 3 and 4. The plots show that the relative perceived nature of softened versus non-softened water towards copper as measured by copper concentration is a function of stand time. For example, non-softened water can be viewed as more corrosive after 5 h, softened water can be viewed as more corrosive after 12 h, while no difference can be made after 20 h.

Study B

Study B differs from Study A in that chlorine as well as dissolved oxygen was present in the test water. Plots from Phase I of the study, of copper concentration, reduction of free chlorine and reduction of dissolved oxygen, are shown against stand time in Figure 5 after the system had been operated for more than 150 days. The plots of copper concentration show that silicate enhanced copper concentrations and the stagnation profiles nearly paralleled each other. Copper concentrations increased with time even beyond 24 h with the steepest increase occurring over the first 20 h.

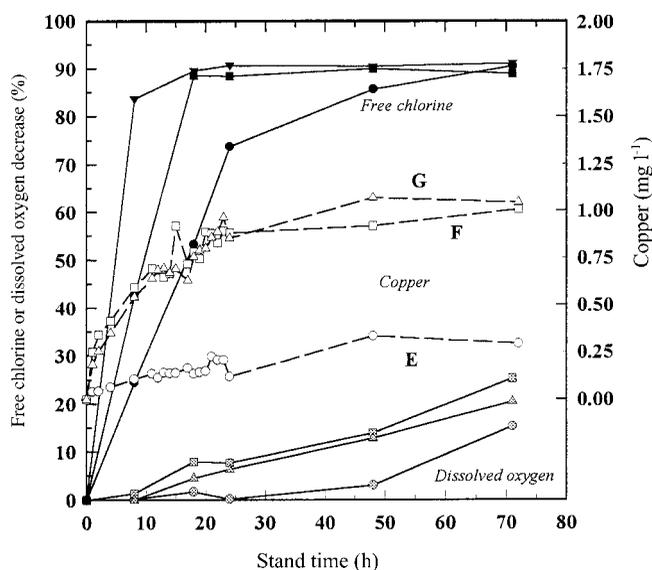


Figure 5 | Copper stagnation profile and free chlorine and dissolved oxygen depletion profiles during Phase I of Study B. The system was aged 150 days (circles, $5 \text{ mg l}^{-1} \text{ SiO}_2$; squares, $15 \text{ mg l}^{-1} \text{ SiO}_2$; triangles $25 \text{ mg l}^{-1} \text{ SiO}_2$).

The free chlorine (mean initial level = 1.4 mg l^{-1}) decreased rapidly and was essentially depleted after 10–20 h. Dissolved oxygen (mean initial level = 8.9 mg l^{-1}), however, did not decrease during the same time period. Significant decreases in dissolved oxygen were not observed until the free chlorine was gone. As a result, reduction of copper (II) and subsequent reduction in copper concentration was not observed such as in Study A because an oxidant was always present at the end of the stagnation period.

Figure 6 shows the evolution of stagnation profiles with time between 22 and 212 days. The steepness of the curves decreased with time. Equilibrium copper levels, however, also decreased with time as diffusion or passivating layers developed.

Study C

The effect of stand time (24 versus 72 h) on metal levels leached from a red brass, C84500 (79% Cu, 11% Zn, 6% Pb), a yellow brass, C85400 (65% Cu, 30% Zn, 2% Pb), and lead, copper and zinc was investigated at pH 7.0 (Table 1,

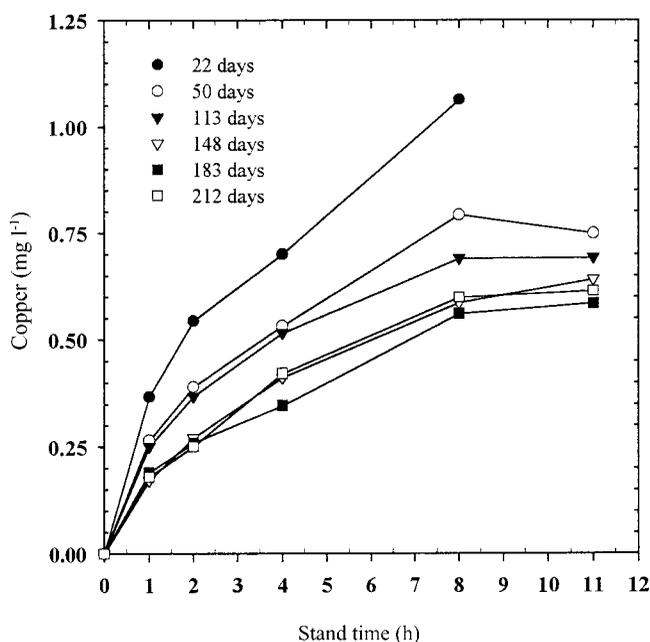


Figure 6 | Change in stagnation profile with pipe age during Phase I of Study B. Results are from a system that was exposed to $25 \text{ mg SiO}_2 \text{ l}^{-1}$.

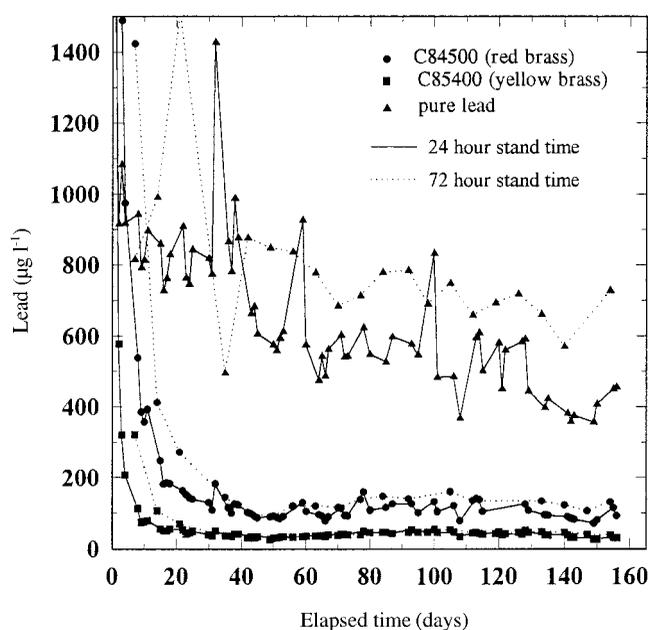


Figure 7 | Influence of stagnation time on brass and lead coupons in Phase I of Study C (pH=7.0).

Phase I) and 8.5 (Table 1, Phase II). The amount of lead leached from red brass was slightly higher ($10\text{--}25 \mu\text{g l}^{-1}$) after 72 h while yellow brass was not affected by stand time (see Figure 7 for Phase I). The amount of lead leached from the pure lead coupons in pH 7.0 water were clearly impacted by stand time, releasing as much as $100 \mu\text{g l}^{-1}$ more lead after 72 h standing than 24 h. No difference was observed between 24 and 72 h standing samples at pH 8.5.

The amount of copper leached from red brass at pH 7.0 generally increased by 0.5 to 1 mg l^{-1} between 24 and 72 h (Figure 8). This trend was also observed with the pure copper coupon. The yellow brass copper leaching trend exhibited an interesting pattern. Initially copper levels were lower at 72-h than 24-h standing time, however after 125 days the trend reversed. Stand time had a minimal effect on the amount of copper leached from both brasses at pH 8.5. Seventy-two-hour samples tended to be $0.01\text{--}0.05 \text{ mg Cu l}^{-1}$ higher at 72 h for both brasses (not shown).

At pH 7.0, zinc leached from red brass was significantly higher (by approximately 1.0 mg l^{-1}) after 72 h,

more than doubling the zinc concentration (shown in Figure 9). Yellow brass was also affected by stand time in the same fashion but at a higher scale. By the end of the study zinc levels leached from the yellow brass in 72 h were more than double the levels at 24 h (approximately 2.0 mg l^{-1} to $4.0\text{--}4.5 \text{ mg l}^{-1}$).

An exploratory study (Phase III) was conducted to further address the impact of stand time on the metals leached from brass alloys. The study was conducted in test water previously described for testing the leaching of metals from taps by the National Sanitation Foundation International (National Sanitation Foundation (NSF) 1994) (pH=8.19, DIC= $113.6 \text{ mg C l}^{-1}$, alkalinity= $501.7 \text{ mg CaCO}_3 \text{ l}^{-1}$, free chlorine= 1.9 mg l^{-1} , and sodium= 220.0 mg l^{-1}). Two brasses, yellow brass, C85200 (69% Cu, 26% Zn, 2% Pb), and red brass, C84400 (77% Cu, 11% Zn, 7% Pb), were each evaluated in duplicate. Stagnation profiles were developed from samples taken following 30 min, 1, 2, 4, 6, 8 and 15 h. Results for lead showed that stagnation profiles varied with alloy composition. Figure 10 shows that lead levels tended to still be increasing up to 15 h (following 2 months of

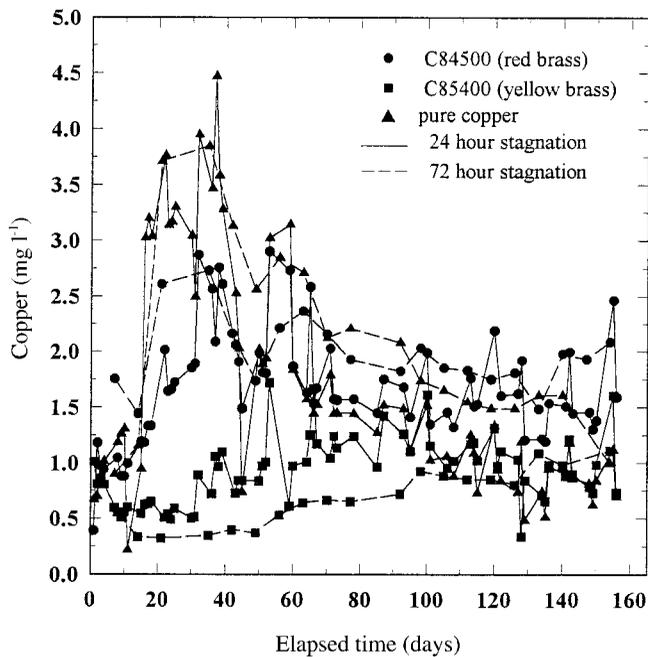


Figure 8 | Influence of stagnation time on copper leached from brass and copper coupons during Phase I of Study C (pH=7.0).

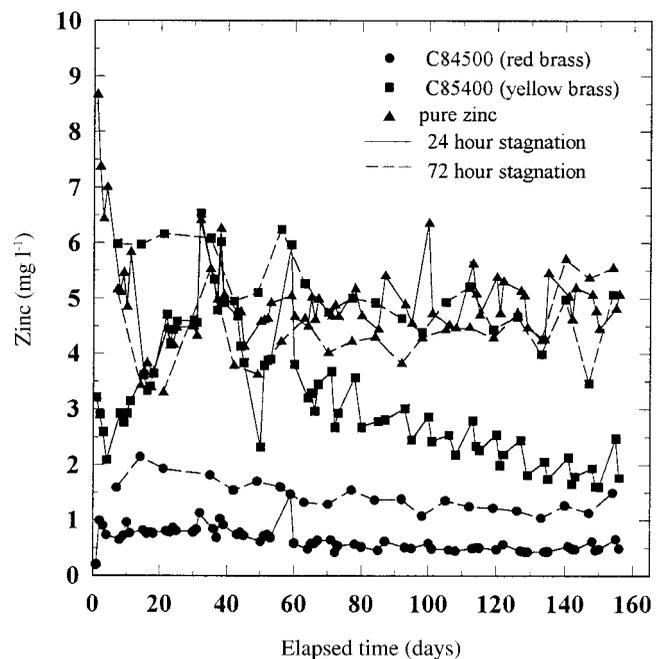


Figure 9 | Influence of stagnation time on zinc leached from brass and zinc coupons during Phase I of Study C (pH=7.0).

operation or ‘conditioning’) for the red brass. This observation may have been associated with the relatively high amount of lead leached from the alloy. Lead leached from yellow brass, however, was not largely impacted by stagnation time. Lead reached maximum levels as early as 30 min. These results suggest that the dissolution rate of lead is slowed down by factors such as alloy composition, surface area or diffusion barrier films. These observations agree with observations made between 24- and 72-h standing samples.

Stagnation profiles for copper leached from both brasses show that the most rapid increase in copper levels occurred over the first 6 h. The copper levels appeared to still be slightly increasing after 15 h. Similar observations were made with zinc stagnation profiles, but continuing increase of zinc levels after 15 h was not as apparent.

Molecular diffusion model

A radial molecular diffusion model was developed to calculate the concentration of metal (illustrated with copper) leached from a pipe with time. The model assumes

that copper concentration is constant along the pipe axis, sufficient oxidant is present to drive the copper oxidation and molecular diffusion is the rate-limiting step. Model calculations were based on non-steady state conditions for the case of stagnant water flow (i.e. only molecular diffusion will be considered). The model was derived by performing a mass balance around a control volume (entire pipe volume) as follows:

Mass balance of copper in the control volume:

$$(\text{Mass accumulation}) = (\text{Mass into}) - (\text{Mass out}) \quad (1)$$

Mass in the control volume:

$$\Delta M_{\text{Cu}} = C_{\text{Cu}} (4\pi r^2) \Delta r \quad (2)$$

Mass flow in – mass flow out:

$$\phi - (\phi + \Delta\phi) = -\Delta\phi \quad (3)$$

Mass flow:

$$\phi = -(4\pi r^2) D_{\text{Cu}} \frac{\Delta C_{\text{Cu}}}{\Delta r} \quad (4)$$

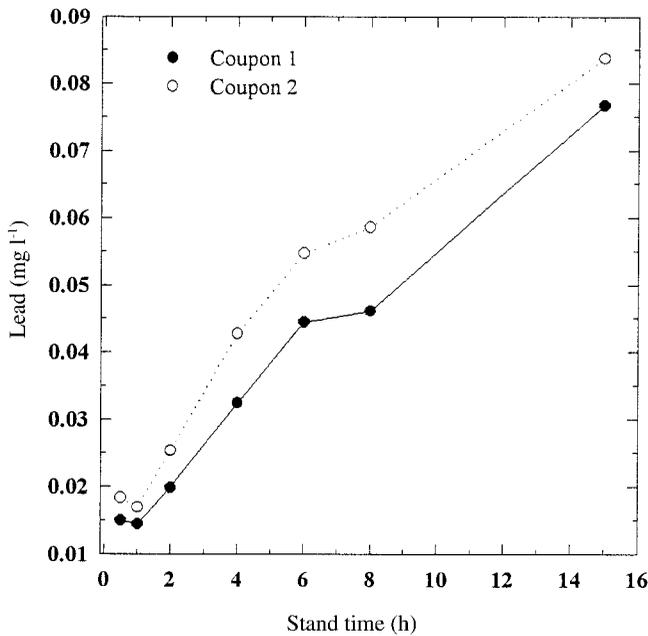


Figure 10 | Lead stagnation profile for red brass C84400 during Phase III of Study C.

Plug back into mass balance, Equation (1):

$$(4\pi r^2)\Delta r\Delta C_{Cu} = 4\pi D_{Cu}\Delta \left(r^2 \frac{\Delta C_{Cu}}{\Delta r} \right) \Delta t \quad (5)$$

Dividing by $4\pi r^2\Delta r\Delta t$ and express in terms of partial derivatives:

$$\frac{\partial C_{Cu}}{\partial t} = \frac{D_{Cu}}{r^2} \frac{\partial \left(r^2 \frac{\partial C_{Cu}}{\partial r} \right)}{\partial r} \quad (6)$$

Equation (6) can be further separated to:

$$\frac{\partial C_{Cu}}{\partial t} = D_{Cu} \left(\frac{2\partial C_{Cu}}{r \partial r} + \frac{\partial^2 C_{Cu}}{\partial r^2} \right) \quad (7)$$

For the case when the concentration of copper at the pipe surface is constant, the following initial and boundary conditions apply: (1) at $t=0$ and $r < a$, $C_{Cu} = C_{Cu,0}$; (2) at $r=a$, $C_{Cu} = C_{Cu,\infty}$; and (3) $r=0$, $\delta C_{Cu}/\delta r = 0$. The mathematical solution of Equation (7) developed by Crank (1975) describes the dependence of radial distance on concentration. The dependence of the volume average metal concentration as a function of time is more relevant,

however, to stagnation data (Kuch and Wagner 1983). A relatively simple and practical solution describing the build-up of copper concentration with stagnation time has been developed and recommended (Schlunder 1975; Kuch and Wagner 1983):

$$\frac{[C_{Cu,t}] - [C_{Cu,0}]}{[C_{Cu,\infty}] - [C_{Cu,0}]} = 1 - \exp \frac{-4 Fo'}{\frac{1}{Bi'} + \frac{1}{\sqrt{(5.78)^2 + \frac{4}{\pi} \frac{1}{Fo'}}}} \quad (8)$$

where Bi' is the Biot-number:

$$Bi' = \frac{\beta_a 2a}{D} \quad (9)$$

and Fo' is the Fourier-number:

$$Fo' = \frac{Dt}{4a^2} \quad (10)$$

The terms are defined as follows: a is the pipe radius (m), t is the stagnation time (s), D_{Cu} is the diffusion coefficient for copper in water ($m^2 s^{-1}$), $[C_{Cu,0}]$ is the initial copper concentration, $[C_{Cu,t}]$ is the volume average copper concentration after time t , and $[C_{Cu,\infty}]$ is the copper concentration at the pipe surface which is assumed to be the maximum copper concentration (i.e. the equilibrium copper concentration). The Biot-number serves as a correction factor for additional diffusion resistance such as that which might be produced by the formation of deposits on the pipe surface. The authors unfortunately do not present more detail of the β_a term nor do they give example values for different conditions, or references. Kuch and Wagner (1983) showed that model predictions were in good agreement with experimentally obtained stagnation curves in two separate cases.

Equation (8) represents the fraction of copper concentration diffused into the water after time t relative to the total copper in the water after the concentration across the radial distance of the pipe has reached equilibrium or diffusion ceases (normalized concentrations).

Experimental copper stagnation profiles from Study B (silicate treated loops only) were plotted against theoretical curves using a reported diffusion coefficient for the

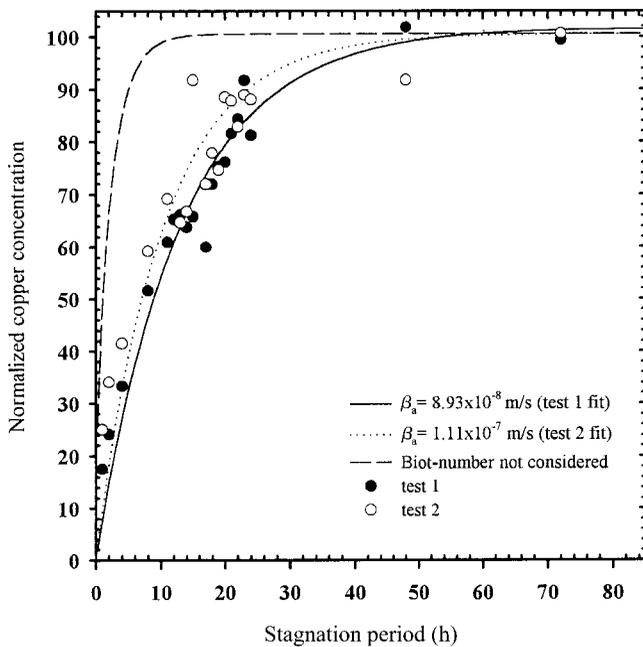


Figure 11 | Experimental copper stagnation profile data (Study B) plotted with theoretical curves.

Cu^{2+} ion in deionized water of $7.2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ (Newman 1972) in Figure 11. Curves were fit by statistically determining the best β_a term using a Solver routine incorporated in a Microsoft Excel (Redmond, Washington) spreadsheet to minimize the sum of squared residuals between actual and model predicted metal levels. Regression analysis gave R^2 values of 0.954 and 0.924 for test 1 and 2, respectively. A plot for the case where the Biot-number is not considered (i.e. no diffusion barrier or limitation) is also shown. The plots showed that experimental stagnation data can be described by radial diffusion modelling as long as a fitted diffusion resistance term was considered.

Modelling analysis was also done on labelled data shown in Figures 1, 2, 5 and 6 (Table 2) using a diffusion coefficient for lead of $1.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ (Kuch and Wagner 1983) for lead cases. Experimental data were described nicely by the diffusion model based on R^2 values with the exception of Curve C. The fit for Curve C was improved after a data point at time = 3 h was not considered (Figure 2). Best fit plots for curves A–G were

Table 2 | Diffusion model fitting summary. Curve labels represent plots shown in Figures 1, 2 and 5

Stagnation curve	Metal	Best fit $\beta_a, \text{ m s}^{-1}$	R^2
Curve A (Study A)	Lead	2.95×10^{-7}	0.898
Curve B (Study A)	Lead	5.32×10^{-7}	0.943
Curve C (Study A)	Lead	4.58×10^{-7}	0.669
Curve C (Study A) w/o data point at $t = 3 \text{ h}$	Lead	1.25×10^{-7}	0.905
Curve D (Study A)	Lead	1.32×10^{-7}	0.943
Curve E (Study B)	Copper	4.40×10^{-8}	0.827
Curve F (Study B)	Copper	1.11×10^{-7}	0.924
Curve G (Study B)	Copper	8.93×10^{-7}	0.954
22 days (Study B)	Copper	9.15×10^{-7}	0.953
50 days (Study B)	Copper	1.20×10^{-6}	0.965
113 days (Study B)	Copper	1.32×10^{-6}	0.992
148 days (Study B)	Copper	5.78×10^{-6}	0.995
183 days (Study B)	Copper	6.00×10^{-7}	0.961
212 days (Study B)	Copper	6.51×10^{-7}	0.988

normalized for comparison purposes in Figure 12. Data in Figure 6 were also described well by the diffusion model. The data did not show a pattern between pipe age and β_a term. Table 2 and the Figures show a large variability in stagnation behaviour, and a range of β_a terms can apply. This implies that diffusion modelling is not a good predictive tool for estimating stagnation behaviour. Diffusion modelling does, however, describe stagnation behaviour data taken from 'real' systems.

Particulate release is an obvious complication in the data when a quantitative diffusion model is fitted. A re-analysis of the USEPA lead pipe loop (Schock 1980, 1981; Schock and Gardels 1983) obtained from 1978–1982 using waters of different alkalinities in the pH range of 8–9.5 showed that while it could be explained by the

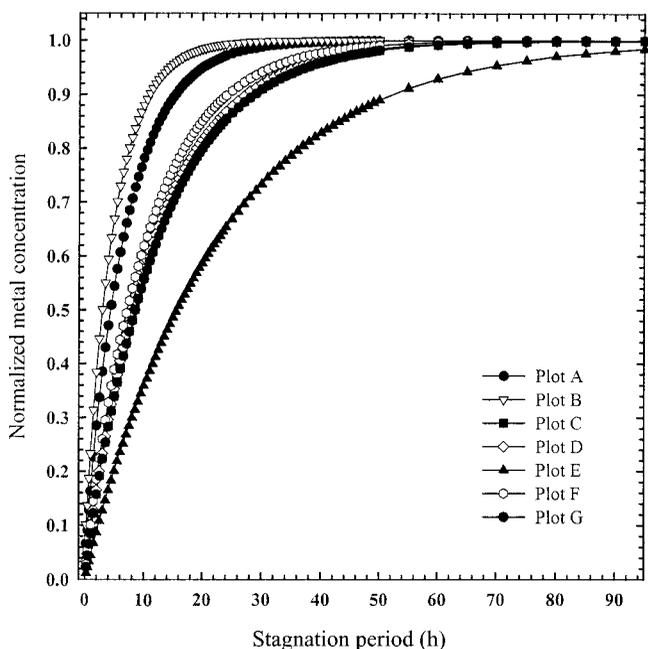


Figure 12 | Best fit normalized stagnation plots of experimental data.

diffusion model described here, the actual data had considerable scatter from particulate release. Similarly, there was loop to loop variability in studies performed for an AWWARF guidance manual (AWWARF 1990). In these copper studies, particulate release played a lesser role, making the curve fitting more precise. The small volumes of water used in the coupon studies and the infrequency of sampling make it impossible to enumerate any particulate effect that might be present. In pipe loop research studies for comparisons of corrosion treatment performance, the investigators must be aware of the effects and be able to assess their relative significance.

DISCUSSION

The studies described herein have important implications for many aspects of corrosion control, including: describing and understanding the corrosion and metal release processes in pipe loop and coupon studies; devising appropriate sampling schemes to assess either

acute or chronic human exposure; assessing the quality and success level of applied corrosion control programmes; diagnosing problems of metal release in houses, buildings, or isolated parts thereof; and in interpreting regulatory monitoring results within or among water distribution systems.

The study results showed that water chemistry and the ageing of the scales on the metal surfaces clearly play a significant role in the shapes of the stagnation curves, and the metal concentrations reached. These findings help to explain commonly encountered discrepancies between solubility model predictions and experimental or field metal levels. It also helps explain within-house and between-house drinking water metal variability. Special attention must be given in these situations to ensuring consistent and appropriate sampling protocols designed accordingly for the questions being asked.

Lead and Copper Rule sampling criteria may have to be revisited, especially for copper, because the presumptions about conditions producing ‘worst case’ exposure scenarios do not follow those of lead very well. Similarly, presumptions of sampling protocols for determining health exposure issues probably need considerably more investigation, as misleading results could readily be obtained. The biases caused by the sampling protocols could be either high or low and vary with the materials and metals of interest, as well as the specific water qualities. Exposure estimates, without accounting for these factors of materials, water chemistry and time, could be off by a factor of 2–10, or even more.

CONCLUSIONS

The study results illustrate the complex nature of lead and copper dissolution rates from pipe and coupons. Water quality, oxidizing agent, material age and alloy composition were all demonstrated to have significant impact on the shape of stagnation profiles and time to reach an equilibrium state. Corrosion control study results illustrated the importance of understanding stagnation profiles and how improper research conclusions can be drawn when this information is not considered. The findings help to explain commonly encountered discrepancies

between solubility model predictions and experimental or field metal levels, and within-house and between house drinking water metal variability. The results also bring into question presumptions made about health exposure issues.

The results demonstrated that mass transfer modelling can be used to describe a stagnation profile. The results, however, demonstrated that the theoretical curves are extremely variable. Water quality and pipe age, which are probably associated with the type and development of corrosion products on the pipe surface, were associated with the variability.

While the mass-transfer modelling approach could lead to numerically descriptive results for the experimental systems studied, it is not necessarily accurate, mechanistically. The mass-transfer modelling essentially makes the implicit assumption that physical surface conditions are the controlling factor in metal release into solution. Studies by several researchers implicate solution chemistry as important in affecting the rate of oxidation of Cu(I) to Cu(II). In turn, in natural waters this would be important in enabling dissolution and passivation. Further research is needed into the factors affecting the kinetics of oxidation of Cu(I), and Cu(I) to Cu(II), to accurately understand its behaviour in drinking water systems. Similar research needs exist for other metals of interest (e.g. iron, lead, zinc), for which even less kinetic information is available. Such studies need to include both oxygen and chlorine species as oxidants, as well as different background aqueous chemistries.

ACKNOWLEDGEMENTS

The authors wish to express thanks to the following members of the USEPA staff: Tom Sorg, Leslie Ostrozny, Kelly Mayhew, Chris Keil, Leo Fichter, Herb Braxton and Kenneth Kropp for construction, daily operating, and sampling of the test systems, and Keith Kelty, James Doerger, James Caldwell, Louis Trombly and Patrick Clark for analytical support. Additional thanks go to Greg George, Steve Harmon, John Damman and Roger Rickabaugh of Dyncorp/Technology Applications Inc.

and Kim Brackett and Cory Demaris of IT Corp. for additional analytical support and technical discussions, and to Tom Sorg (USEPA) for helpful comments and input.

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency. Mention of trade names or commercial products is for explanatory purposes only, and does not constitute endorsement or recommendation for use.

NOTATION

a	pipe radius (mm)
β_a	correction factor to account for additional diffusion resistance (m s^{-1})
C_{Cu}	copper concentration at location r , and at time, t (moles l^{-1})
$C_{\text{Cu},\infty}$	copper concentration at pipe wall (which may be assumed to be maximum equilibrium copper concentration after stagnation) (moles l^{-1})
$C_{\text{Cu},0}$	copper concentration at $t=0$, $r < a$ (moles l^{-1})
C_{Cu}	t volume average copper concentration after time t (moles l^{-1})
D_{Cu}	diffusion coefficient of copper in water ($\text{m}^2 \text{s}^{-1}$)
M_{Cu}	mass of copper in unit volume of pipe at time t (mg)
n	counter term
r	distance in radial direction from centre of pipe (mm)
t	time (s)
V	pipe volume per unit width (m^3)

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