Adsorption and (induced) desorption of Cd(II) from the corrosion scales of water distribution pipes, following a deliberate contamination event

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ABSTRACT

Intrusion of toxic heavy-metal cations into water-distribution systems (WDS) may cause severe adverse health-effects on large populations, along with an undesirable psychological impact. The corrosion (scale) layer, that invariably develops on the pipes’ inner walls, is capable of adsorbing a significant mass of metal-cations and releasing them thereafter via diffusion to the water once operation is resumed, thereby causing a secondary contamination event. To overcome this, the contaminant should be completely removed, in a controlled fashion, from both the aqueous and scale phases, with minimum damage to the pipe’s physical stature. This study determined the range of the Cd(II) adsorption capacity of corrosion-scales and quantified alternative treatments for desorbing it, using an assortment of metal water-pipes, extracted from the WDS. Batch, water-recirculation and flow-through experiments were conducted to determine the extent of Cd(II) adsorption and the best way to desorb it. Corrosion-scales showed substantial Cd(II)-absorption capacity (up to 0.75 mg Cd(II)/g scale) with an approximately linear relation between the aqueous Cd(II) concentration and the adsorbed mass. Desorption experiments included dosages of various acids. Sequential rinsing (eight pipe-volumes) by pH3 solution was found to be the best approach, releasing close to ∼100% of the adsorbed Cd(II), with only a minor effect on the pipes’ integrity.

Key words | Cd(II) adsorption, Cd(II) desorption, corrosion scales, water distribution systems, water terrorism

HIGHLIGHTS

- Cd(II) adsors on the pipe’s scales upon the dissolution of cadmium salts in water.
- An adsorption capacity of up to 0.75 mg Cd(II)/g scale was found.
- The adsorbed Cd(II) mass has to be removed to prevent a secondary contamination event.
- Sequential rinsing by pH3 solutions released ∼100% of Cd(II) without damage to the pipe.

GRAPHICAL ABSTRACT

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INTRODUCTION

Water distribution systems (WDS) may be contaminated intentionally as an act of terror, or unintentionally, by human error or system failure. To name a few incidents, in 2002, an attempt to poison drinking water by cyanide was averted in Italy (Carroll 2002); in 2012, 140 Afghan students and their teachers were admitted to a local hospital after drinking contaminated water from their school’s water tank (Popalzai 2012); in 2018, an attempted ricin/anthrax water-poisoning terror attack was reported in Italy (Xuequan 2018); and recently in Israel, a cyber-attack was recorded in an attempt to manipulate drinking-water chlorine-dosing pumps (Kerstein 2020).

Once a contamination event is identified, the contaminated section of the WDS should be immediately isolated and then cleaned, before it is returned to service (Qiu et al. 2020). Potential water contaminants, as related to terrorism activity, may be divided into four groups, based on their source and chemical properties, as follows: (1) organic micro-pollutants; (2) fuel products; (3) microbial agents; and (4) toxic metal ions (Israel Ministry of Health 2013). Depending on the nature of the contamination, the cleaning process may include flushing, absorption of the contaminants by surfactants, complexing agents or activated carbon, and application of oxidation/reduction and/or disinfection measures.

This paper focuses on contamination by heavy metal ions, and specifically on Cd(II) salts. The cadmium ion was chosen as a representative metal contaminant because of its high toxicity to humans – the World Health Organization (WHO) recommends a maximal concentration of 5 μg/l in drinking water (WHO 2011). Additionally, Cd(II) has a relatively high solubility in water, as demonstrated by its $K_{sp}$ values: $10^{-15.7}$, $10^{-12.1}$ and $10^{-2.6}$ for Cd(OH)$_2$ (s), CdCO$_3$ (s) and CdCl$_2$ (s), respectively, which makes it an easy chemical to apply to a WDS without the contamination being discovered immediately (Charlton & Parkhurst 2011; Powell et al. 2011; Tchounwou et al. 2012). Assuming a fairly ‘common’ drinking water composition (total inorganic carbon concentration ($C_T$) of $10^{-3}$ M, pH = 7.5, [Cl$^-$/] = 2·10$^{-3}$ M; and temperature of 25 °C), these $K_{sp}$ values translate into a maximal dissolved value of 0.1 mg-Cd(II)/l, i.e. 33 times higher than the allowed drinking-water threshold.

In addition to being relatively soluble, the cadmium ion is stable only at an oxidation state of +2 (i.e. Cd(II)). Thus, theoretically, its intrusion to the WDS cannot be treated by dosing an oxidizing or reducing agent, but rather, by flushing the WDS, as previously suggested by Ohar et al. (2015). In other contamination events, the toxicity can be minimized by reduction (e.g. Cr(VI)) or oxidation (e.g. As(III)), however in most cases toxic metal ions are unaffected by the redox value (e.g. Cd(II), Be(II), Ni(II)) (Bruce & Odin 2001; Fawell 2005; Tchounwou et al. 2012). Generally speaking, since applying a vigorous treatment procedure can also cause severe damage to the pipes, in-situ treatment is not necessarily the best solution, and it might make sense to first remove the contamination from the pipe and then (if required) to treat, or otherwise discard the solution, in a safe fashion. However, if a fraction of Cd(II) (or any other heavy metal), gets adsorbed on the pipe’s corrosion scale, treating only the aqueous phase will not completely remove the contaminant and a secondary contamination event may unfold by a subsequent gradual release of the adsorbed Cd(II) once the system is put back into operation. Such a phenomenon was observed before by Munk & Faure (2004), who reported the desorption of metal ions (zinc, copper, nickel, molybdenum, and cadmium) previously adsorbed on sediments composed primarily of iron and aluminum (oxy)hydroxides. In Munk and Faure’s work, the release of the ions was caused by pH fluctuations of merely 0.2 units. To understand this phenomenon as it relates to the pipe’s corrosion scales, the current work focused on the adsorption/desorption of Cd(II) from the pipes’ scales, in varying operational conditions.

Any contaminant that is dosed into the distribution system or any treatment that is applied on a contaminated distribution system (which still consists primarily of iron-made pipes) may affect the deposited scale that invariably develops on the pipe walls after a relatively short period of time (several years). Corrosion scales typically consist of a mixture of various Fe(hydr)oxides, metal carbonates, trace
inorganic elements (Peng et al. 2010; Peng & Korshin 2011; Yang et al. 2012) and organic matter (Peng et al. 2010). The deposition of corrosion products, along with other minerals (e.g. CaCO$_3$(s)), on the pipe’s wall forms a layer on the inner side of the pipe, which is commonly denoted corrosion scale. The composition, structure and depth of the scale vary significantly from system to system and are mainly a function of the age of the pipes and the water quality that flowed in them during their lifespan, along with the hydraulic conditions (Sarin et al. 2004). The quantity, the reactivity and the fractionation between different iron corrosion products (e.g. magnetite, lepidocrocite, siderite, hematite, goethite, etc.) may vary significantly between different pipes, depending on the corrosion scale structure and age, and the source water quality (Yang et al. 2012).

Previous studies have shown that while inorganic contaminants, including Cd(II), are typically present only at trace levels in treated water, they can accumulate on the pipe scales (Peng & Korshin 2011; Peng et al. 2012; Gao et al. 2019). A part of the Cd(II) found in the scale due to adsorption from the water was shown to be relatively easily released (by immersing the scale in a 1 M Mg(NO$_3$)$_2$ solution at pH 7) and another part was described to be bound to carbonate species on the scale (Peng & Korshin 2011; Peng et al. 2012; Gao et al. 2019). Other works looked into the adsorption of Cd(II) on synthetic goethite (Mustafa et al. 2004, 2006) and ferricydrate (Yao et al. 2014), yet the adsorption of relatively high Cd(II) concentrations (i.e. concentration higher than the drinking-water threshold) on pipeline scales has not been investigated thus far. That said, the main factors which were found to affect Cd(II) adsorption/desorption on/from synthetic iron compounds were solution pH, Cd(II) concentration, ionic strength, competing ions in solution, temperature, and the adsorption period (Mustafa et al. 2004, 2006). It was also shown that Cd(II) adsorption was more pronounced in waters with a high carbonate concentration, likely as a result of precipitation and subsequent adsorption of CdCO$_3$(s). Previous studies (Peng et al. 2012; Gao et al. 2019) also reported on the potential adsorption capacity of pipeline scale when it was exposed to extremely low Cd(II) concentrations, emphasizing the importance of a controlled Cd(II) desorption in order to prevent secondary contamination. It thus seems important to develop a desorption procedure that does not damage the pipe’s integrity nor dissolve its corrosion layer considerably, taking into consideration that the same factors that promote Cd(II) desorption can also act to decompose the corrosion scales and may cause a lingering red water event (Lahav & Birnhack 2007).

In the current paper, we aimed at investigating Cd(II) adsorption and desorption from pipeline corrosion scales in order to identify a method that would maximize the release of the adsorbed Cd(II) while not jeopardizing the pipe’s integrity. Due to the high heterogeneity of pipeline scales and the difficulty in working with undisturbed corroded pipes, the work started by performing batch experiments on representative corrosion layers that were peeled from a variety of old iron pipes before executing experiments on ‘real’ old and corroded pipes. Because of the large heterogeneity between the corrosion scales found on live pipes, the experiments in this work may serve for establishing a reasonable working range for the possible adsorption capacity value of the scales for Cd(II) and particularly for determining the best method to be used for removing the adsorbed Cd(II) from the scale following the contamination event.

**MATERIALS AND METHODS**

**Collection and stabilization of solids extracted from pipeline corrosion scales**

Peeled scales from old corrugated iron (CI) pipes (previously used for cold water transport in northern Israel) were collected, sieved (104 μm) and rinsed with desalinated water for 27 h. The aqueous phase was replaced five times during the rinsing period and the discharged solutions were analyzed for Fe, turbidity, TDS and pH. After the stabilization period, the wet scales (~75% solids) were kept refrigerated. The surface area of the stabilized scale was measured (BET) at 45.5 ± 6.4 m$^2$/g.

**Batch adsorption experiments**

A 500 ml beaker comprising the examined water quality combined with the desired Cd(II) concentration and 1 g of
stabilized scales was placed in a rotating shaker (temperature range 24–26 °C). In each set of experiments, the water content of the scale and the total suspended solids (TSS) concentration were analyzed (Method 2540D in Standard Methods 2010). The results indicated that no significant mass loss occurred during the adsorption experiments.

**Batch desorption experiments**

Desorption experiments were carried out in closed beakers placed inside a Julabo SW22 water bath shaker (temp = 25 ± 0.2 °C). Each desorption experiment was preceded by an adsorption stage with an initial Cd(II) concentration of 0.64 mg/l. After 24 hours of adsorption, 450–470 ml of the Cd(II)-contaminated solution was separated from the scale using a magnet (neodymium 80 × 80 × 20 mm) and 200 ml of fresh solution (free of Cd(II)) was added to the beaker (that contained the scale and the remaining solution from the adsorption step). Based on the resulting water volume, the required dosage of the desorption agent was calculated and added.

**Water-recirculation batch experiments on live CI pipes (pipes #1–#3)**

A corroded CI pipe (one metre in length, 0.0254 m diameter), extracted from the water distribution system just prior to the experiment, was connected to a flow rotameter, a Masterflex peristaltic pump (pump head model 77601–00), a ten-litre feeding tank and a sampling point. Between the extraction from the distribution system and the experiment, the pipes were kept filled with local water and sealed. First, a stabilization stage was performed, in which local groundwater (the same water that the pipe was exposed to during its lifespan) was circulated through the pipe at a flow velocity of 0.2 m/s for four hours (inline pressure of 2.7–3.0 bar) followed by 48 h in which the groundwater was retained stagnant in the pipe. Next, two adsorption experiments were performed with the same water, spiked with initial Cd(II) concentrations of 0.16 mg Cd(II)/l and 5.0 mg Cd(II)/l (chemical added: Cd(NO₃)₂). The flow regime in each experiment was 8 h of 0.2 m/s circulated flow, followed by an overnight stagnant period, followed by 1 h of circulated flow at 0.2 m/s.

After the adsorption experiments, the following sequential desorption treatments were applied using a similar flow regime: (1) desorption by raw source water (groundwater); (2) desorption by a pH5 solution (groundwater to which HCl was added); (3) desorption by pH3 acidified tap water; (4) one or two additional rinses by pH3 water.

**Single-pass flow-through experiments on live pipes (pipes #4–#7)**

Three ~ten-metre (diameter = 0.019 m) live CI pipes were extracted from the WDS and connected to a peristaltic pump that pumped water from a 500 l feed container at a pressure of 2.7–3.0 bar. The water flowing out of the pipe was collected in a second 500 l container (after being sampled). A stabilization stage was performed before the experiments, similar to the one applied in the recirculating-flow experiments: tap water was introduced in the pipe at a flow velocity of 0.2 m/s for 4 h followed by a stagnation period of 48 h. Table 1 summarizes the experimental steps and flow regimes that were applied in each step. The steps were performed sequentially following the stabilization phase.

<table>
<thead>
<tr>
<th>Experimental step</th>
<th>Flow regime</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(II) adsorption with tap water to which 0.64 mg Cd(II)/l was added</td>
<td>Three 20-min flowrate phases at 0.2 m/s, followed by 2 h stagnation. Then an additional overnight stagnation phase (the solution in the pipe was replaced between the two stagnation periods).</td>
</tr>
<tr>
<td>Flush with raw tap water</td>
<td>Similar to the Cd(II) adsorption flow regime.</td>
</tr>
<tr>
<td>Intentional desorption of Cd(II) by a pH3 solution (tap water acidified by HCl)</td>
<td>The contaminated pipe was rinsed three times in a row, each lasting 2 h at batch conditions, followed by an overnight stagnant phase. The procedure was conducted twice, a total of eight rinses (six 2 h rinses and two 18 h rinses).</td>
</tr>
</tbody>
</table>
Distinguishing between adsorption of dissolved Cd(II) and of CdCO₃(s) (pipes #8 and #9)

The first stage of this phase comprised circulating tap water at ∼2.7 bar and 55 °C through eight new black iron pipes (length ∼24 m, diameter 1") for enhancing scale formation for two months under a daily flow regime of a solution circulating for eight hours followed by retaining the water in the pipe until the next morning. During this time, air was added to the solution via a diffuser and the Ca²⁺ and alkalinity concentration were maintained such that the CaCO₃(s) precipitation potential was always slightly positive. For the experiment report here two pipes were separated from the system for Cd(II) adsorption with tap water to which 10 mg Cd(II)/l was added. The experimental flow regime was similar to the one described in Table 1 for the adsorption phase.

Approximating the average scale mass in the pipes

The average mass of scale in the pipes used in the recirculated and live-pipe flowthrough experiments was estimated by carefully peeling 20 cm length of pipe scales and weighing the obtained dry (three hours at 60 °C) sample.

Solution and scale characterization

Four types of water solutions were used in the adsorption and desorption experiments: (1) desalinated water from the BWRO plant in Ma’agan Michael, Israel; (2) groundwater from Yagur, Israel; (3) tap water from Haifa, Israel; and (4) deionized water with EC < 1 μS/cm. The characterization of the first three water sources is shown in Table 2.

Analyses

The cation and sulfate concentrations were analyzed by Thermo Fisher Scientific ICP-AES. The chloride and nitrate ion concentrations were analyzed by a Metrohm 950 compact IC Flex ion chromatography unit operated with a Metrosep A supp7 250/4 column. The BET surface area measurements were conducted using a NOVA touch surface area and pore size analyzer of Quantachrome Instruments. Water chemistry calculations (e.g. ion speciation, acid dosages, CdCO₃ precipitation potential PP) were performed using the PHREEQC software (phreeqc.dat database) (Charlton & Parkhurst 2014). The cation composition of the scale was characterized following a procedure suggested by Schwertmann & Cornell (2000). An amount of 200 mg of the stabilized scale was dried for 1 h at 105 °C. The dried scale was then dissolved in 20 ml 32% HCl acid (analytical grade) at an elevated temperature (60–80 °C) for 1.5 h and analyzed by ICP to obtain the cationic composition. The total organic carbon concentration was measured by a Sievers M5310C (Suez Water Technologies, Boulder, CO, USA) TOC Analyzer.

RESULTS AND DISCUSSION

Characterization of the mixed scales used in the experiments

Elemental analysis of the solution obtained from the dissolution of the mixed scales confirmed that they were made predominantly from iron. Much lower fractions of zinc, calcium, sodium, and potassium were also observed. The results are summarized in Table 5. No significant difference

<table>
<thead>
<tr>
<th>Solution Units</th>
<th>Alkalinity mg/l as CaCO₃</th>
<th>pH</th>
<th>0.64 mg Cd/l dose</th>
<th>5.0 mg Cd/l dose</th>
<th>Ca²⁺ mg/l</th>
<th>Mg²⁺ mg/l</th>
<th>Na⁺ mg/l</th>
<th>Cl⁻ mg/l</th>
<th>SO₄²⁻ mg/l</th>
<th>NO₃⁻ mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>Desalinated water</td>
<td>81–85</td>
<td>7.9–8.1</td>
<td>0.576–0.582</td>
<td>4.95–4.96</td>
<td>26.6</td>
<td>0.8</td>
<td>62.0</td>
<td>89.5</td>
<td>2.4</td>
<td>1.8</td>
</tr>
<tr>
<td>Groundwater</td>
<td>311–328</td>
<td>7.3–7.6</td>
<td>0.576</td>
<td>4.98</td>
<td>102.1</td>
<td>49.4</td>
<td>106.7</td>
<td>286.4</td>
<td>52.5</td>
<td>23.8</td>
</tr>
<tr>
<td>Tap water</td>
<td>147–156</td>
<td>7.5–7.8</td>
<td>0.576</td>
<td>4.96</td>
<td>51.1</td>
<td>25.5</td>
<td>107.0</td>
<td>130.1</td>
<td>50.5</td>
<td>0.16</td>
</tr>
</tbody>
</table>
was found in the composition of scales before and after the applied stabilization procedure.

Speciation of Cd(II) in the examined conditions

An equilibrium-based analysis was carried out using PHREEQC (Parkhurst & Appelo 1999) to determine the fractionation of Cd(II) species in the applied experimental conditions. Figure 1 presents the Cd(II) main complexes that form at the relevant pH range (desalinated water was used as the background solution and the pH was altered in PHREEQC by simulating dosages of HCl).

Figure 1 shows that introduction of soluble CdCl₂ or Cd(NO₃)₂ into the water would invariably result in conditions of super-saturation with respect to CdCO₃(s) (otavite), even at relatively low alkalinity values. When CdCO₃(s) forms at a considerable concentration upon the addition of a large mass of Cd(II), the turbidity of the water will increase, the contamination will become apparent and the water will not be consumed. To avoid such an occurrence, which is unwanted from the perpetrator standpoint, the adsorption experiments in the current work were carried out with Cd(II) dosages resulting in low CdCO₃(s) supersaturation, in which condition no turbidity was expected to form due to both limitations related to slow homogeneous phase nucleation kinetics and the high adsorption rates on the scale surface, as reported by Bucca et al. (2009) and Riechers et al. (2017). Evidently, no turbidity was observed in the batch experiments after 24 h and an (initial) cadmium concentration of up to 5 mg Cd(II)/l.

Adsorption of Cd(II) on mixed corrosion scales, peeled from old water pipes

Figure 2 shows the normalized results (mg Cd(II)/g scale) obtained in 24 h batch, isotherm-like experiments (room temperature), that were performed with the mixed scales, with two water quality backgrounds. The results follow a rough linear trend up to a concentration of ∼0.5 mg Cd(II)/l in the aqueous phase. The highest adsorption capacity that was observed at this concentration was ∼0.4 mg Cd(II)/g of mixed scales. No change was apparent in the results that were obtained with either desalinated water or groundwater as the background water, while the experiments that were carried out with distilled water yielded lower adsorption points, corroborating the notion that CdCO₃(s) precipitation, which invariably occurred under realistic water conditions (see Figure 1), increased the overall Cd(II) adsorption. It is emphasized that the scales used in this experiment were peeled from many different pipes and thus represent various conditions with respect to the corrosion

Table 3 | Elemental composition of the mixed scales used in Cd(II) adsorption and desorption tests

| Cation mass fraction out of overall cation mass (%) |
|-----|-----|-----|-----|-----|-----|
| Ca  | Fe  | K   | Na  | Zn  |
| 5.1 ± 0.4 | 82.9 ± 4.1 | 1.9 ± 0.2 | 2.9 ± 3.0 | 7.2 ± 1.7 |
| 8.5 ± 1.7 | 82.4 ± 0.4 | 0.0 ± 0.0 | 2.0 ± 1.2 | 7.0 ± 2.6 |

Figure 1 | Distribution of Cd(II) species as a function of pH at equilibrium with CdCO₃(s) (background solution: desalinated water, see Table 1); phreeqc.dat database. Temp = 25°C.

Figure 2 | Normalized results of batch Cd(II) adsorption on mixed scales, peeled from old CI water pipes, with three background water qualities, at room temperature (pH = 8.0, ORP = −450 mV).
layers that developed on the original pipes. Clearly, the layered structure of the original scales was different, as was also probably their age and composition, due to both redox reactions (e.g. oxidation of ferrous-containing iron oxides to ferric oxides) and the fact that the scales were intensely rinsed during their ‘stabilization’ phase, which invariably led to a change in the solids composition and layer structure. It is also noted that ‘old’ corrosion scales are expected to be less reactive than ‘fresher’ precipitates (Sarathy et al. 2008). Nevertheless, the results indicate that the applied procedure is capable of supplying information (albeit semi-qualitative) on the ability of pipe corrosion scales to adsorb Cd(II). Figure 2 shows that corrosion scales have a considerable capacity for adsorbing Cd(II). This observation was further corroborated by batch (water recirculation) adsorption experiments that were conducted with live pipes (pipes #1–#3), that showed higher (normalized) adsorption capacity at similar water quality conditions.

Pipes #1–#3, that were used in these experiments, were extracted from the WDS just prior to the experiments and thus their corrosion scales could be considered almost undisturbed. The results, summarized in Table 4, show that the adsorption capacity of the live-pipe scales was higher than the results obtained with the mixed, peeled scales (Figure 2). This was particularly apparent in the experiments that were conducted with a high initial Cd(II) concentration of 5.0 mg/l. In the experiments in which an initial concentration of 0.16 mg Cd(II)/l was applied, practically all the Cd(II) was adsorbed by the scales after 24 h. It is noted that at the water quality applied, from a thermodynamic perspective, practically all of the Cd(II) (at both concentrations) was expected to precipitate as CdCO3(s) (Figure 1), and therefore the majority of the adsorption on the scales could be assumed to be of this species.

The results listed in Table 4 seem to indicate that ‘fresh’ scales have a higher capacity for Cd(II) adsorption than the older (and mostly oxidized) mixed scales. They also indicate that when the Cd(II) concentration is relatively low, and sufficient time is allowed for adsorption, practically all of the metal ion can be expected to be adsorbed by the scales, a fact that would render it almost non-detectable in the aqueous phase. However, once Cd(II)-devoid freshwater flows in the pipe the adsorbed Cd(II) mass can be expected to diffuse gradually to the aqueous phase over time and contaminate the water. Such an occurrence may even be more challenging from a water-safety aspect than the case

<table>
<thead>
<tr>
<th>Pipe #</th>
<th>Final solution concentration [mg Cd(II)/l]</th>
<th>Adsorption capacity [mg Cd(II)/g-scale]</th>
<th>Final solution concentration [mg Cd(II)/l]</th>
<th>Adsorption capacity [mg Cd(II)/g-scale]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>Non-detectable</td>
<td>0.017</td>
<td>0.15</td>
<td>0.500</td>
</tr>
<tr>
<td>#2</td>
<td>Non-detectable</td>
<td>0.023</td>
<td>0.116</td>
<td>0.693</td>
</tr>
<tr>
<td>#3</td>
<td>Non-detectable</td>
<td>0.024</td>
<td>0.046</td>
<td>0.748</td>
</tr>
</tbody>
</table>
in which the contamination is quickly recognized, and steps are immediately taken to abate it.

Next, in order to test more realistic contamination conditions, flow-through experiments were conducted with three live pipes (denoted pipes #4, #5 and #6). Figure 3 depicts the adsorption results obtained over time with these pipes, which were disconnected from the WDS just before the start of the experiment. The pipes were left at their original position, and were thus almost entirely undisturbed. Horizontal cross-sections from the three pipes, showing their developed corrosion scales, appear underneath the graph. Water contaminated with 0.64 mg/l was pumped through the pipes using the flow pattern described in Table 1. The integrative results of these experiments show that the pipe with the most developed corrosion scale (pipe #5, with 0.180 g scale per cm pipe length or 10.25 g scale/cm² of inner surface of the pipe's wall) showed the highest adsorption capacity under the experimental conditions, i.e. ~21 mg Cd(II)/m² inner surface area of the pipe. Pipe #4 (0.145 g scale per cm pipe length or 9.16 g scale/cm²) and pipe #6 (0.172 g scale per cm pipe length or 10.25 g scale/cm²) also showed a considerable adsorption capacity. For reference, the same experimental conditions were applied also to a brand new pipe (pipe #7) with similar dimensions, and the recorded Cd(II) adsorption capacity was five to six times lower (3.77 mg Cd(II)/m²). The normalized amount of Cd(II) that was adsorbed on the scale in these experiments (overall contact time = 2 h) was approximately one order of magnitude lower than that recorded in the batch experiments (contact time 24 h), emphasizing the effect of the contact time on the adsorption results.

As mentioned, at typical tap water quality conditions most of the Cd(II) is expected to precipitate as CdCO₃(s).

Figure 3 | Results of flow-through Cd(II) adsorption experiments on 'live' CI water pipes and an image of the corresponding surface area of the pipes (horizontal cross-sections).
To test the difference between adsorption of dissolved Cd(II) and adsorption of CdCO₃(s), a side-experiment was conducted on two pipes that were exposed to similar conditions and that were assumed to have an almost identical corrosion layer. Tap water was dosed with CdCl₂ to result in 10 mg-Cd(II)/l. In the experiment performed on pipe #8, the solution pH was reduced to pH6, to attain negative precipitation potential with respect to CdCO₃(s). On the other, in the experiment performed on pipe #9, the water was allowed to stand for 1 h after the CdCl₂ addition to allow for full precipitation of CdCO₃(s), before the water was pumped through the pipe. Turbidity-based side-experiments showed that 1 h was sufficient for the CdCO₃ precipitation to attain its full extent. The results, shown in Figure 4, indicate that Cd(II) adsorption from the CdCO₃(s)-dominated solution was twice as high relative to the Cd(II) adsorption from the solution that contained only dissolved Cd(II) species. Combined with previous reports on the role of carbonate alkalinity on the extent of Cd(II) adsorption on iron oxides (Gao et al. 2019) and the fact that when distilled water was used within this study (Figure 2) Cd(II) adsorption was much lower, these results corroborate the conclusion that both Cd(II) forms get adsorbed on the corrosion scales but also that dissolved Cd(II) species adsorb to a much lesser degree than CdCO₃(s). The high normalized adsorption capacities recorded in these experiments were attributed to the very high reactivity associated with the fresh corrosion scales present on the pipes used in these runs.

**Cd(II) desorption alternatives**

**Desorption of the Cd(II) from the mixed scales**

Multiple Cd(II) desorption experiments were carried out both on the mixed scales and the live pipes (pipes #1–#7), using a variety of desorption methods. All the experiments were conducted on scales that had previously been in contact with a Cd(II) solution and thus adsorbed a certain mass of Cd(II). Due to the large inherent variability in the origin, age and structure of the scales, the experimental conditions during the desorption experiments and the previous adsorption conditions, there was no logic in reporting on the exact mass of Cd(II) that desorbed in each experiment. Rather, the percentage of Cd(II) that was desorbed from the mass that was previously adsorbed is reported, with the aim of identifying the conditions that would allow for extracting and rinsing out close to 100% of the previously adsorbed mass. Since all the methods that were assessed to release the Cd(II) from the scales could also have a potential adverse impact on the integrity of the pipes, the mass of iron and zinc that dissolved into the water in the course of desorbing the Cd(II) is also reported.

The first set of experiments was conducted on mixed scales loaded with Cd(II) and its purpose was to identify the best desorption treatment. Desorption experiments were attempted by acidifying the background water with a strong acid (HCl), leading to an initial pH5, pH4 and pH3. The acidified solution was brought into contact with the scale and the solution was allowed to stabilize for 24 hours. The pH value increased to around pH6 after about two hours in all of these tests and remained there throughout the experiment, indicating that the dissolution effect wears off after ∼2 h. Weak acids (acetate and citrate) were also tested in the same fashion at pH4 and pH5. These organic acids have a relatively high buffering capacity around the target pH values tested and citrate also forms stable soluble complexes with divalent metal cations. Finally, the effect of dissolving a sulfide salt (Na₂S) was also tested, with the underlying hypothesis that the formation of CdS(s), which has a very low $K_{sp}$, would desorb the Cd(II) from the scales and maintain it as a CdS colloid in the water, which could be readily washed out.

The results of these experiments, which were conducted at a water volume to scale-mass ratio of ∼0.357 L/g, are
summarized in Table S1 in the Supplementary Information file. Generally speaking, Table S1 shows that the most efficient Cd(II) recovery (>80%) was attained when the mixed scales were flushed with a pH3 solution. Right after the acidification, the pH of the solution went up, specifically due to dissolution of carbonate solids, and generally stabilized at ~pH6 after two hours. The redox value, measured in one experiment, stabilized around 225 mV, predominantly due to the low pH value. The dissolved oxygen concentration was close to saturation throughout the run. Table S1 shows that the use of organic acids for desorbing Cd(II) was less effective, as was the use of Na2S. Moreover, the release of iron from the scales, which was limited when HCl was used to bring the water to pH3, was much more pronounced when the organic acids were added. Note that in these experiments no intentional attempt was made to release 100% of the Cd(II) mass from the scales, but rather the purpose was to find the most efficient method, out of the ones tested. The combined conclusions from these experiments led us to abandon all the methods, apart from HCl addition to pH5 and pH3. Eventually, the desorption experiments conducted on live pipes focused on finding the number of pH3 rinsing cycles that would result in close to 100% recovery of the adsorbed Cd(II) mass. No attempt was made to rinse with more acidic solutions, to avoid harming the pipes.

Desorption of Cd(II) from live CI pipes

Two types of experiments were conducted with live pipes. First, the live pipes that were used for adsorbing Cd(II) in the water-recirculation experiments (pipes #1, #2, and #3) were subjected to five rinses: a rinse with untreated groundwater, then a rinse with the same water acidified to pH5, and then three sequential pH3 rinses (apart from pipe #1, on which only two pH3 rinses were done) under water recirculation conditions, for 24 hours. The volume of the recirculated water was ten litres, yielding ratios ranging from 0.11- to 0.15-litre solution to 1 g of scale. The results, summarized in Table S1, show that passing untreated water caused a release of only a small Cd(II) mass, and rinsing with a pH5 solution had the effect of releasing ~30% of the Cd(II) mass. However, after three pH3 rinses practically all of the Cd(II) that was previously adsorbed on the scales was released to the aqueous phase and the effect on the integrity of the scales, as manifested by the iron mass that was carried over to the water, was not dramatic, implying that the application of such conditions would not endanger the operational functioning of the pipe. The importance of these experiments is that they show that the adsorbed Cd(II) can be fully released from the scales by rinsing with pH3 solutions, without causing damage to old and highly corroded pipes. It is also apparent that without applying a treatment at all, the Cd(II) would be desorbed at a slow rate from the scales, contaminating the water for a relatively long time.

To test more realistic conditions, a second set of experiments was performed on the single-pass flow-through live pipes (pipes #4–#7). The water volume to scale-mass ratio (single rinse) applied in these experiments was 0.015-0.02 l/g, which is around one order of magnitude lower than the ratio applied in the desorption experiments on pipes #1–#3. The duration of each rinse was also lower (2 h in the first six rinses and then 18 hours for rinses 7–10). The results of these experiments are summarized in Table 5.

Table 5 | Results of 24 h water-recirculation desorption experiments conducted on CI pipes #1–#3 (recycled water volume – 10 litres)

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Pipe #1 Cumulative Cd released [%]</th>
<th>Pipe #1 Cumulative dissolved Fe [g]</th>
<th>Pipe #2 Cumulative Cd released [%]</th>
<th>Pipe #2 Cumulative dissolved Fe [g]</th>
<th>Pipe #3 Cumulative Cd released [%]</th>
<th>Pipe #3 Cumulative dissolved Fe [g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rinses with raw groundwater</td>
<td>2.11%</td>
<td>Non-detectable</td>
<td>2.66%</td>
<td>Non-detectable</td>
<td>1.33%</td>
<td>Non-detectable</td>
</tr>
<tr>
<td>pH5 rinse</td>
<td>36.52%</td>
<td>0.019</td>
<td>36.44%</td>
<td>0.022</td>
<td>36.92%</td>
<td>0.013</td>
</tr>
<tr>
<td>1st pH3 rinse</td>
<td>74.41%</td>
<td>0.442</td>
<td>86.25%</td>
<td>0.43</td>
<td>74.68%</td>
<td>0.445</td>
</tr>
<tr>
<td>2nd pH3 rinse</td>
<td>87.02%</td>
<td>0.43</td>
<td>94.39%</td>
<td>0.61</td>
<td>91.02%</td>
<td>0.377</td>
</tr>
<tr>
<td>3rd pH3 rinse</td>
<td>–</td>
<td>–</td>
<td>100.00%</td>
<td>0.853</td>
<td>100.00%</td>
<td>0.221</td>
</tr>
</tbody>
</table>
and 8) in comparison with the 24 h applied in the water-recirculation experiments. The first rinse (rinse #0) was done with untreated water and resulted in the release of ∼15% to 20% of the adsorbed Cd(II) mass. The pH value of the acidified rinsing solutions after two hours approached pH6 in all the runs, indicating again that the dissolution potential of the solution was almost exhausted after two hours. The results, shown in Figure 5, indicate that regardless of the type of the pipe inner surface area (new vs highly corroded; different previously adsorbed Cd(II) mass), the attainment of close to 100% Cd(II) recovery required at least eight full pipe-volume rinses, and a cumulative desorption period of at least 48 h. It therefore appears that both the volume of the water that is required in this procedure (that needs to be eventually discarded to a hazardous waste site) and the period of time that is required for the desorption can be considered realistic.

The zinc and iron concentrations recorded in the rinsing water are listed in Table S2 in the SI file. The low iron mass that was released is an indication that the dissolution/breakdown of the iron oxides in the corrosion layer was minimal. Zn(II), on the other hand, was released from the scales at a higher mass, indicating that it had adsorbed on them over time, after being released from the ZnO coating of the inner (galvanized) pipe surface. Either phenomenon is not alarming from the pipe-integrity point of view and, although these experiments should clearly be repeated with larger-diameter pipes, the conclusion thus far is that the suggested procedure is not overly damaging to the pipe's physical condition. The calcium, iron, and zinc percentages out of the dry scale mass in pipes #4–#6 and the mass per surface area of the total inorganic and organic carbon in the scale of the same pipe are shown in Table S3 and Table S4 (SI file), respectively, before and after the adsorption/desorption treatment sequence. The relatively small changes in the scale composition before the adsorption period and after the eight pH3 rinses corroborates the observation that no irreversible damage occurred to the pipes as a result of the suggested treatment procedure.

**CONCLUSIONS**

An act of terrorism that involves the dissolution of heavy metals into the water distribution system may carry unwanted consequences. One of the related phenomena is the possible adsorption of the heavy metal ions on the pipe's corrosion scales and its subsequent release over time. Consequently, a positive outcome of a Cd(II)-related contamination event would have to result in complete removal of the contaminant from the aqueous and solid phases alike. This work shows that the mass of Cd(II) that adsorbs onto pipe corrosion scales is roughly proportional to both the concentration of the Cd(II) in solution and the mass of scales on the pipe walls. Both dissolved Cd(II) species and CdCO₃(s) are adsorbed, with the latter, that would invariably form in typical drinking waters upon Cd(II) contamination, adsorbing more preferably. The normalized adsorption capacity of realistic corrosion scales for Cd(II) was found in this study to be (roughly) up to 1 mg of Cd(II) per g of corrosion scales. Since according to our study old pipes may develop a corrosion scale layer of up to ∼10 g/cm² inner pipe surface area, the Cd(II) mass that can be adsorbed on the pipes' walls is substantial, as indeed shown in the adsorption experiments conducted in this work.

Desorption experiments showed that the most efficient method for desorbing the Cd(II) without overly harming the pipes is to consecutively rinse it with tap water acidified to pH3 by strong acid dosage. Eight sequential rinsing periods (six 2 h periods followed by two 18 h periods)
were found to extract close to 100% of the cadmium without dissolving a large mass of iron from the scales. Zinc, on the other hand, was released in larger quantities, but the overall integrity of the pipes was not (at least visually) compromised. The experiments described in this work should be repeated with other toxic heavy metals (Ag⁺, Co²⁺, Hg²⁺, Cu²⁺, etc.) and also larger and more diverse types of metal pipes installed in water distribution systems, before a formal procedure could be recommended for application in heavy-metal-based contamination events. A further challenge would be to upscale the problem from a local contamination-event treatment to dealing with rehabilitation of a contaminated portion of a real water distribution system. This will require constructing an optimal decision support model on locations where treatment chemicals should be injected into the network, as well as their concentrations, injection times, flow rates and drainage outlet locations, which is based on the topology and topography of the system.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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