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Model for estimation of copper release to drinking water from copper pipes

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ABSTRACT

Modelling and prediction of the copper concentration released from copper plumbing tubes due to corrosion, dissolution, precipitation and other processes has not previously been successful. The model presented here is based on a set of dissolution and precipitation reactions, equilibrium between species in solution and solids, mass balance, kinetic expressions, adsorption isotherms, and surface area coverage by precipitates.

The model developed has created two major outputs: first; it is the most conclusive collection of mechanistic considerations to date; and second; reasonable correlations between the model and actual data have been obtained for a broad range of waters.

1. Introduction

Water chemistry and copper corrosion results in the release of copper to drinking water. The release of copper to water generally decreases with age and use of the plumbing system. Water composition, disinfection chemicals (like chlorine), and operating conditions influence the resulting copper concentration. Some combinations involving low pH, soft and organic matter containing waters have been observed to give copper concentrations that exceed existing regulations [1].

Specific conditions may facilitate the elevation of the copper concentration in water. For instance, during the winter, in cold climates, copper plumbing tubes age very little since water may be under 10 °C, and precipitation (specifically nucleation), is very slow. Another example is that of tubes of large diameter, for instance in large buildings or housing complexes, where the copper concentration may not reach supersaturation levels in the given stagnation times and therefore precipitation of solids is negligible (there is no test protocol for these tubes). This has been observed even for very long stagnation times. A third example is that of unstabilised water obtained from reverse osmosis plants which have very low content of salts. Under these conditions copper compounds cannot form or precipitate, leading to a surface without film protection, fast release of copper and pitting [2].

The need to understand the effect of water composition, temperature, disinfection chemicals, and water use patterns, on copper release, motivated research to advance understanding of experimental and field data with a mathematical formulation based on mechanistic descriptions of the processes involved.

Earlier modelling approaches were carried out by several researchers. Several published thermodynamic models predict copper concentration for the specific water data studied [3–5], focusing on the effects of temperature, pipe diameter, stagnation time, and anion concentration. Several kinetic models were proposed improving the understanding on copper release since most processes are not in equilibrium [6–8]. These studies were dependent on the tube exposure methods applied, specifically “sit and soak” methods, including NSF/ANSI 61 [9], “rig test methods” like DIN 50931-1 [10], now denominated EN 15664-1. The latter methods yield more reproducible results since they avoid tube manipulation during testing [11–17].

Schock et al. and Edwards et al. [3,4] successfully developed a copper release model denominated the “cupric hydroxide model”, for relatively new copper tubes containing drinking water, based on copper release control by cupric hydroxide solubility where higher bicarbonate concentrations exacerbate copper corrosion rates and copper release. The model was tested with laboratory data and with monitoring experiences of large utilities in the United States. This model could not fit European studies that generated copper levels reaching maximum concentration and decreasing with time afterwards [11].

Alex and Johannsen [11] developed a thermodynamic and kinetic copper release model for copper tubes containing drinking water, and successfully applied it to two water compositions using the DIN 50931-1 test. The model is based on copper oxidation, copper dissolution, and formation of malachite. This model does not include intermediate formation of cuprous scales.

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Merkel [8] successfully developed a kinetic copper release model for copper tubes containing drinking water based on copper oxidation, copper dissolution, and scale formation of malachite, and applied the model to literature and pipe rig experimental data obtained after different periods of water stagnation.

An accurate simulation model describing the corrosion of copper would reduce the amount of fundamental tests and their evaluation [3]. The development of this copper tube release model (CTRM), over several years, led us to include an increasing number of mechanistic steps in order to analyse case studies originated in many locations throughout the world.

The CTRM includes as variables those that have the most influence on copper release from copper pipes, such as water composition and temperature, stagnation time, diameter, aging time and water use patterns [3,18–24]. The model includes physicochemical processes such as kinetics of dissolution and precipitation reactions, as well as the effects of diffusion, species equilibrium, complexation, adsorption and inhibition, nucleation and crystal growth, and surface coverage over time.

The experimental data for which the CTRM was tested was obtained from DIN 50931-1 test rigs [10], from the Wieland Bench Scale Corrosion Test, WBSCT [25], that simulates the DIN test, from NSF/ANSI 61 experiments published (sit and soak test) [9], from an assortment of data obtained with a variation of these tests, and from field data. Unfortunately, data is almost always incomplete and most times it was necessary to make broad assumptions regarding the value of certain variables, such as dissolved oxygen and temperature, over time. Reliable oxygen consumption data, for instance, is only available for a small set of experiments. The CTRM developed cannot predict the copper concentration adequately when the laboratory and field data are incomplete or of poor quality. Moreover, the validity of the CTRM includes only certain water composition ranges where high quality data is available.

2. Methodology – model development

The CTRM includes modules with the aqueous chemistry and corrosion, dissolution and diffusion processes, the oxygen consumption, solid precipitation and scale formation, various adsorption processes including natural organic matter (NOM), sulphate, chloride, phosphate, and nitrate interference with scale development. These processes interact with one another, and these modules may be refined by changing a particular equation. Thus the model can be improved stepwise without having to start from scratch.

2.1. Physico-chemical definition

The CTRM developed is complex because the observations are complex. The inputs to the CTRM are variables which are measured frequently, namely alkalinity, the concentrations of calcium, chloride, sulphate, phosphate, nitrate, copper, NOM, pH, and dissolved oxygen in water. The model also requires the tube age, its diameter, water temperature and the water use pattern, including stagnation periods during the day and night. For the latter we used that specified by the DIN 50931, test protocol [10].

Once the input parameters have been assigned a value, the model calculates copper complexation by NOM and calculates equilibrium for aqueous species, checks for charge balance and performs mass balance calculations. It then performs kinetic calculations, including adsorption isotherms, coupled in time, with diffusion calculations for the oxidation and dissolution precipitation reactions of copper and copper compounds, establishing new concentrations for species. The model simultaneously estimates the surface coverage by copper and other solids which have precipitated during the time interval. At this stage the CTRM provides a new copper and other species concentration at the interface between the tube and water. It is assumed that all liquid–liquid reactions are in local thermodynamic equilibrium and that the solid–liquid reactions depend on time.

The aqueous corrosion of copper is generally an electrochemical process [19]. Yet, the proposed model does not contain half-cell reactions and may be described as a purely chemical model. There are several reasons for selecting a chemical rather than electrochemical formulation of the reactions. Firstly, electrochemical reaction rates generally depend on the electrochemical potential and an electrochemical formulation would use the electrochemical potential as some kind of master variable. The corrosion potential is not measured in conventional tests for copper release, thus introducing the potential as a variable does not seem satisfactory. Secondly, the model is mainly concerned with oxidised copper surfaces and the processes can be given an adequate description in chemical terms. Thirdly, for these oxidised surfaces, some steps may actually be chemical rather than electrochemical.

2.1.1. Solid–liquid reactions

Copper metal in contact with drinking water undergoes a fast oxidation by dissolved oxygen [20], and forms an adherent scale of cuprite (Eq. (1)). The inner scale of cuprite is thin and compact, and the outer is porous, allowing diffusion of molecules and ions through it [20–23]. According to Callot et al. [24], cuprite is the unique scale that remains in contact with copper metal surface and plays a major role in copper corrosion [6], since the oxidation of cuprous to cupric ion is the step controlling copper oxidation [26]. Dissolved oxygen continues oxidizing cuprite (Eq. (2)) [20] and if the stagnation time is long enough, dissolved oxygen may be eventually consumed. After this the synproportionation reaction (Eq. (3)) may occur, where dissolved cupric ions precipitate as cuprous oxide after reacting with metallic copper [6,27], or precipitation of oxides and basic salts start [28–29]. Precipitation of cupric oxide and basic salts (Eqs. (4)-(13)) should decrease the copper concentration in water [3,5,7,27,30–35]. Dissolution of cuprite in order to form dissolved cuprous ions is not considered in the model due to the very low solubility of cuprite. Calcium can influence the rate of copper release due to the formation of calcium carbonate by occlusion of dissolution and precipitation sites on the tube inner surface (Eq. (14)) [22,36]. In copper pipes exposed to water containing phosphate, some calcium phosphate solids have been found, and thermodynamic calculations support the assumption that a solid calcium phosphate phase (hydroxyapatite) precipitated on the copper surface (Eq. (15)) [12–14].

The following are reactions which express what we described above, although some of them can be inactive in the CTRM (Table 1 shows the solid–liquid reactions).

There are at present two mechanism for the reduction of oxygen and the associated release of Cu(II) into the water. In the first mechanism $Cu_2O(s)$ dissolves chemically and reacts with O_2 in the water to form Cu(II). This process is well known from natural waters and should be relatively fast [38–39]. By this mechanism the aqueous Cu(II) is formed without dissolution of any cupric solid (Eq. (2)). In the second mechanism, O_2 is incorporated into an outer hydrated layer of the Cu_2O. The result is the formation of a compound similar to $Cu(OH)_2{}^*{}_{(s)}$. The asterisk in the $Cu(OH)_2{}^*{}_{(s)}$ indicates that it is considered to be an unstable reaction intermediate and that it does not necessarily have the same properties as crystalline $Cu(OH)_{2(s)}$. $Cu(OH)_2{}^*{}_{(s)}$ is not usually converted to a more stable phase, but undergoes dissolution to Cu(II) up to the equilibrium activity of Cu^{2+}. The second mechanism was introduced in order to explain the observations by Werner [16].