Development of leaching tests for (recycled) metal surfaces: theory, test results and practice

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Abstract

Based on developments at European level (TC 351) and discussions with both regulators and the industry, ECN is involved in investigating the possibilities for the development of short-term (laboratory) leaching tests that are suitable to estimate the leaching of metals from (bare) metal products. Both laboratory and field data indicate that the dominant leaching mechanisms for metal surfaces are quite different from those found in "monolithic" and "granular" products (either predominantly diffusion- controlled or percolation-controlled, respectively). Leaching from metal surfaces seems to be controlled by solubility control, either in equilibrium or non-equilibrium, influenced by factors such as pH. Existing test methods for monolithic- or sheet-like products (e.g., a tank diffusion test) would need modification to be applicable to metal products.

Keywords: metal products; construction products; leaching; release; test methods

1 Introduction

Recycled or new metal construction products used outdoors may release metals due to contact with (rain)water, a process that we further address with the term “leaching” (in the specific literature, the term “runoff” is also common). Examples of such products are zinc gutters, lead slabs used in construction, copper roofs, galvanized crash barriers. Although regulations exist with respect to drinking water quality (e.g., copper pipes), there is in the EU member states no regulation specifically based on leaching of elements from metal construction products to be used outdoor, but this might change in the future. For instance, in several countries, use of metal products is restricted based on ad-hoc decision basis that often lacks consistency. Also, CEN/TC 351 (European standardization committee on the Assessment of release of Dangerous Substances from Construction Products) is standardizing test methods to be used under the Construction Products Directive (CPD, Council Directive 89/106/EEC) to determine the release of "dangerous substances" (DS) from all construction products to soil, surface water and groundwater, but guidance on test methods for metal products so far has not been filled in.

Existing estimates of metal leaching from metal products are based on costly field tests usually conducted by the industry. The leaching in terms of mg metal leached / m^2.year of metal surface is fairly well known for most “common” metal surfaces such as zinc gutters or copper roofs for which extensive field measurements have been done. Literature data show rather low variation when the mg/m^2 number is normalized for annual precipitation (e.g., Odnevall Wallinder et al., 2004; Odnevall Wallinder et al., 2007; RIZA, 2003; Robert-Sainte et al., 2009). However, such information is available only for a limited number of products, and always has a site- and conditions- specific character. A standardized laboratory test method, even though it will not improve existing estimates for common metal surfaces, would enable a consistent comparison between metal surfaces under standardized conditions and fill the knowledge “gap” for less often applied metals, alloys or new metal products brought to the market with different properties. A well-designed test would also shed more light on leaching behaviour under different types of conditions (e.g., leaching as a function of residence time, pH etc.) that are hard to derive from field data.

2 Leaching mechanisms

Before choices on (modifications to existing) test methods can be made, it is necessary to first investigate whether the leaching of metals from metal surfaces can be understood based on similar physical and chemical mechanisms as seen for the many other construction materials, for which more experience is available.

Field data indicate that metal construction products leach substances mainly through dissolution of the outer "weathered" layer of metal, the so-called patina (Odnevall Wallinder et al., 2004). However, the release rate by “leaching” should not be mixed up with the corrosion rate. The corrosion rate is initially much higher than the release rate by leaching, and gradually slows down with time. Contrary, the release rate through leaching is a constant process over long time periods (Odnevall Wallinder et al., 2004).

Many studies have indicated that the leaching from new, naturally patinated and artificially patinated metal surfaces is quite similar (RIZA, 2003; Faller & Reiss, 2005; Bertling et al., 2006; Sandberg et al., 2006; Robert-Sainte et al., 2009; Odnevall Wallinder et al., 1998). This can be explained, as when a fresh (uncorroded) metal surface is exposed to water and air, almost immediately corrosion products (metal precipitates such as oxides, hydroxides, carbonates) are formed. Release by leaching is caused by the (partial) dissolution of these corrosion products, although also particles can be released from the corroded surface. The leaching process is governed by a large number of factors and conditions, including the rain water quality (most importantly pH) and amount of rainfall. As with other products, the actual leaching of metals is not dependent on the total amount of metal in or on the product, but is governed by chemical processes at the surface of the products. As such, the leaching of metals from alloys (e.g., Cr- steel, brass, bronze) cannot be predicted based solely on the composition of the bulk of the product (Herting et al., 2005; Herting et al., 2008).

In summary, existing data indicates that the dominant leaching mechanisms for metal surfaces are quite different from those found in "monolithic" and "granular" products (either predominantly diffusion- controlled or percolation-controlled, respectively). As solubility control, either in equilibrium or non-equilibrium, is the dominant process, existing test methods for monolithic- or sheet-like products that are based on diffusion as the dominant leaching process (e.g., a tank diffusion test) would need modification to be applicable to metal products.

3 Materials and methods

Preliminary test results were collected using a modified protocol for the diffusion test (e.g., NEN7375, TS2 in TC351). Modifications to the existing protocol included the device itself (i.e. making it suitable to test a flat metal surface), the liquid-to-area (L/A) ratio (L/m^2), renewal of the eluates (no renewal versus renewal), equilibration times, pH, and contact with air (closed vessel versus open vessel with thorough aeration). Tests were conducted with several variations in the above listed parameters and conditions. Tests are conducted with demineralised water, and pH was not adjusted in most of the experiments. To enable comparison with existing field data, the tests were performed for metal surfaces for which a large amount of field data is available (zinc, aluminium, copper and lead).

4 Results

An important observation is that leaching from metal surfaces cannot be expressed in units that are used for either a percolation test (mg/kg) or a diffusion test (mg/m^2). Expression in mg/kg is obviously not possible as the leaching is not dependent on the thickness or weight of the sample (comparable to the situation for monoliths). Expression in mg/m2 as is done for monoliths in a tank diffusion test is not possible either, because as a result of solubility control, the amount leached will be dependent on the L/A ratio in the tank (in principle contrary to the situation for diffusion control). The concentration unit mg/L seems to be a suitable choice. In this respect it should be noted that although field leaching tests are expressed in mg/m^2.year, these values are based on individual runoff-rainwater samples in which concentrations are measured in mg/L, cumulated and normalized over exposed area.

When a test vessel is used, both equilibration time and the liquid-to-area (L/A) are extremely important parameters for the end result. After the metal surface is exposed to water, dissolved

concentrations increase and level off towards a plateau (Figure 1, left). The lower the L/A ratio, the quicker an equilibrium or better "steady state" will be reached between the concentration in solution and the metal surface. The "plateau" concentration itself should be insensitive to L/A ratio, but whether the plateau is reached depends on the equilibration time.

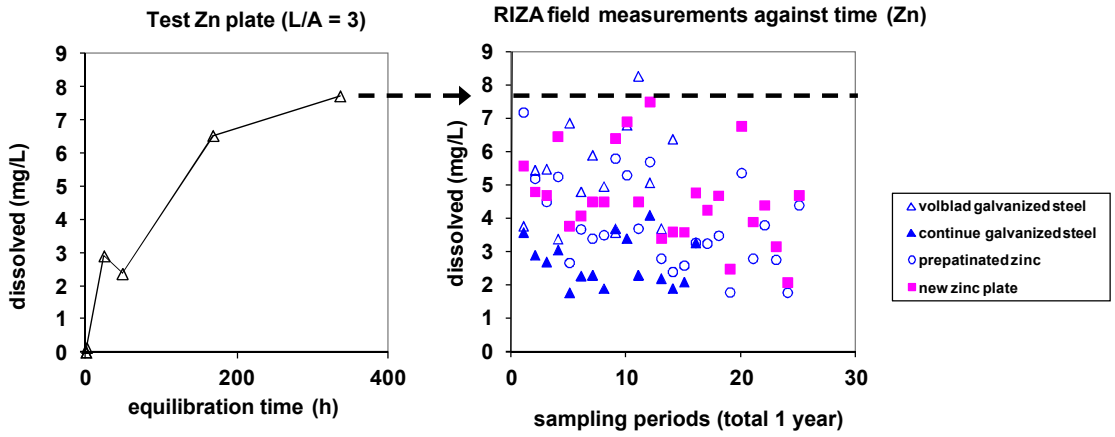

Figure: Results of a batch test using demineralized water and a new zinc surface (left), L/A ratio 3 L/m^2. The leachant on top of the metal surface was continuously and thoroughly aerated. No leachant renewal was performed, instead small aliquots were taken over time in which concentrations were measured. The pH in the eluate during the test was not adjusted, and was around pH 6-7, which was similar as the pH of the field data shown in the right diagram. Field data are shown in the right diagram (RIZA, 2003) and was collected at a location in the Netherlands, with metal plates mounted under an angle of 45 degrees during one year exposed to weather. Runoff rainwater was collected in vessels and analyzed on their concentrations of metals.The arrow between the left and ight diagram indicates that the end concentration in the test (a near-plateau value) is quite similar to the upper concentrations as found in the field study.

A first comparison of test results and concentrations measured in the field (Figure 1) shows that concentrations in the test are surprisingly similar to concentrations found in field experiments (see e.g., Figure 1 for zinc). This observation would imply that any estimate for field leaching expressed in mg/m^2.year based on the concentration as found in the test would be rather close (when based on the plateau concentration a bit on the upper side). Such estimates can be made based on the amount of water on the surface derived from the annual precipitation (examples will be shown at the conference). Note also that there is only a small difference between galvanized steel, prepatinated (artificially aged) galvanized steel and a new zinc plate. Similar observations and similarity between lab and field were also made for lead, copper and aluminum.

An interesting question is why results from the laboratory and field experiments are so close to each other. One appealing conclusion would be that concentrations found in field tests are close to equilibrium/steady state with similar metal precipitates as are formed on the surface in the test method (upon aeration of the eluates during the test). Of course, contact times in field experiments are usually much shorter than in the laboratory. One can imagine that during a rain event, contact times with a zinc plate would be in the order of hours to minutes, and maybe even shorter (depending on angle of exposure, size etc.). At the same time, however, also the L/A ratio in practice is extremely small. During a rain event, the thickness of the water layer on the surface is probably in the order of millimeters (L/A ~0.01 L/m^2 versus L/A = 3 L/m^2 in the test). Equilibrium between solution and surface is reached more quickly when the amount of water on the surface decreases, i.e. with decreasing L/A ratio. Based on these considerations it is not unlikely that contact times in practice are still long enough to establish near-equilibrium values as found in the test. On the other hand, it can be expected that many concentrations will be lower than a plateau value due to non-equilibrium (e.g., see Figure 1), but concentrations higher than the plateau value are expected to be rare. A plateau value in the test may therefore be an overestimate of concentrations occurring in practice.

At the conference, extended test results will be presented. Test conditions, results and possible modifications to existing test methods will be critically discussed. Recommendations will be made for further work in order to support choices with respect to parameters and conditions.

Acknowledgements

This work was partially funded by the basic funding from the Dutch Ministry of Infrastructure and Environment for the Environmental Research Program of ECN.

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