Norwegian aspects regarding corrosion and constituent leaching from metallic materials in contact with drinking water

Christian J. Engelsen

Senior Scientist, PhD, SINTEF Buidling and Infrastructure, P.O. Box 123 Blindern, N-0314 Norway.

Sverre Gulbrandsen-Dahl

Chief Scientist, PhD, SINTEF Raufoss Manufacturing AS, P.O. Box 163, N-2831 Norway.

Abstract

The Norwegian practice for brass products regarding the leaching properties (health requirements) is to use the NKB Product rules. Since a fixed composition for the test water is normal for this type of test method, challenges are faced due the variation in the chemical composition of actual drinking waters. Most of the raw water in Norway is soft with relatively low alkalinity due to water supply mainly from surface water. According to the latest investigations, the drinking water in Oslo was found to have an average hardness and alkalinity of 19.3 mg Ca/L and 0.69 mmol/L, respectively, which in general is compatible with the test water used in the NKB test regarding. However, the fundamental leaching principle applied in these types of batch tests and what is believed to be disclosed by short-term tests in general, are important to consider. Regarding the typical corrosion types in Norway the failures analysis indicates that the main corrosion mechanism has changed from dezincification to stress corrosion cracking over the last 20 years. The main causes of failure are residual stresses from manufacturing, component design, installation error, and component mismatch. The development of brasses has progressed significantly, both regarding the thermo-mechanical properties in the processing phase and regarding the mechanical and leaching properties in the user phase.

1 INTRODUCTION

More than 90% of the Norwegian water supply is based on surface water due to its easy access and general good quality. Thus, most of the Norwegian raw water is soft, except for some groundwater sources within lime rich bedrock located in certain regions in Norway. The given water quality is obviously important to consider during the treatment and distribution for drinking water. This means that the materials and components in contact with drinking water (DWMC) need to be compatible with the given water qualities. Brass is commonly used in a range of DWMC (e.g. valves, fittings, faucets etc.) and an inadequate material choice may cause both corrosion and metal release to drinking water. Around 67% of the waterworks in Norway are public according to a survey from 2006/2007 [1]. These waterworks supply water to 96% of the Norwegian population. The survey also disclosed that most of the waterworks with insufficient water quality were found among the remaining 4% which are private co-operative waterworks. Thus, it can be expected that the public drinking water is of good quality. This paper emphasise some important aspects with brass used in DWMC regarding corrosion, metal release and approval testing in Norway.

2 Corrosion challenges in Norway

Corrosion is the second most frequent failure mode in water installation systems in Norway next to "Age and Wear" [2]. Corrosion of materials in contact with drinking water is typically either one of the types listed in the Table 1, or a combination of these corrosion types.

Table 1 The most common types of corrosion of metallic materials in contact with drinking water

Corrosion type	Cause	Countermeasure
Uniform Corrosion	Uniform corrosion of the exposed surface due to a corrosive environment.	Reduction of water corrosivity.
Erosion	Corrosion due to high flow rates.	Design of that reduces turbulence, and reduction of particles in the water.
Galvanic Corrosion	To materials with different galvanic potential has an electrical connection.	Choice of materials with overlapping galvanic potential, ensure no electrical contact, design with a favourable anode/cathode surface area ration.
Stress corrosion	The material is exposed to tensile stress and a corrosive atmosphere.	Reduced stress level is the most efficient relief measure, either by design or installation practice.
Dealloying	Selective corrosion of one of the alloying elements, i.e. dezincification of brasses.	Use of dezincification resistant alloys with proper state.

Dealloying, and dezincification of brasses in particular, was the most frequent corrosion form in Norwegian water supply until the 1980's. With introduction of requirements for use of dezincification resistant (DZR) alloys in these systems, dezincification failures have decreased dramatically. However, dezincification still appears from time to time and is typically due to use of alloys with not the correct chemistry or thermal mechanical treatment to achieve dezincification resistance. It is vital to maintain dezincification resistant properties in materials in contact with drinking water in Norway to avoid these failures also in the future.

Based on the experience from failure analyses at SINTEF Raufoss Manufacturing over the last 15 years the most frequent corrosion forms in Norway today seems to be stress corrosion and galvanic corrosion. The latter corrosion failures are typically due to connection of non-compatible materials with respect to galvanic potential. Figure 1 shows galvanic corrosion of aluminium due to contact with brass. This corrosion failure was accelerated due to unfavourable combination of a large brass (noble) surface areas electrical connected to an aluminium component with a smaller surface area.

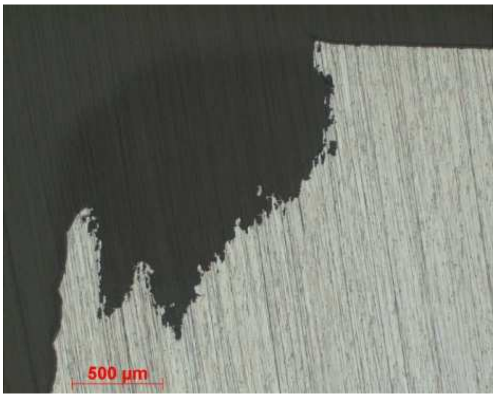

Figure 1 Galvanic corrosion of aluminium which was directly connected to a large brass component.

In the later years stress corrosion of brass has been a one of the most frequent failure modes of corrosion in drinking water systems in Norway. Stress corrosion failure is caused by constant stress exposure of the component above a critical level, and combined with a corrosive atmosphere, which can be ammonia, amines, water and moist. The stresses can be either residual or external, and the most efficient relief measure is reduced stress level [3] Stress concentrations at the crack tip causes a micro galvanic cell which cause an accelerated crack propagation and results in brittle fractures in a sound material. An example of stress corrosion cracking in a component without material failures is shown in Figure 2, secondary cracks is seen below the main failure and is typical for this failure mode.

The causes for stress corrosion can be residual stresses from manufacturing such as deformations from to hard machining, wrong design of the component which results in to high internal stresses during normal service conditions (i.e. too thin wall thickness), wrong assembly due to high moment, or component mismatch during assembly. Machined threaded parts seem to have an overrepresentation within stress corrosion failures.

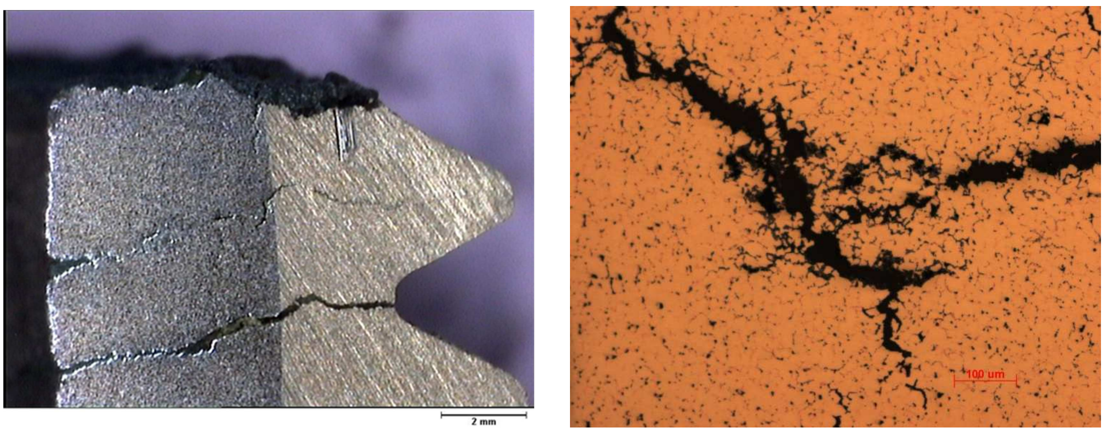

Figure 2 Stress corrosion cracking in brass caused by to high moment during assembly

3 Leaching mechanisms and challenges with tests used in Norway

Leaching may be defined as the transfer of a chemical substance from a solid phase to the aqueous phase. Solubility controlled, diffusion controlled and surface wash-off leaching are the main leaching processes occurring in most of the solid-aqueous systems encountered (bedrock in groundwater and surface water, concrete in contact with water, metals in contact with drinking water etc.). Solubility controlled leaching depends mainly on the chemical stability of the parent chemical complex and the main leaching mechanisms are usually precipitation and dissolution, ion exchange, sorption to reactive surface and complex formation to humic substances [4, 5]. This can mechanistically be described by thermodynamic reaction constants when approaching chemical equilibrium conditions. Diffusion controlled leaching is driven by the concentration gradient (i.e. the chemical potential) of the substance in the solid and aqueous phases. In addition, concentration gradients occur within the solid phase due to depletion. The mechanism can be described by Fick's second law of mass diffusion. Surface wash off is a physico-chemical process where the substance is rapidly transferred to the aqueous phase without following the diffusion law's or the solubility. It may be closely related to erosion.

If the leaching processes and mechanisms mentioned above are applied for describing the release of metals from brass surface to drinking water, several of the mentioned mechanisms may come in force. Depletion of a target element in the outermost brass layer will cause diffusion controlled leaching which actually slows down with the square root of time. Species in water (dependent on water quality) may form complexes with corrosion products that cause solubility controlled leaching for normal stagnation times like 8-12 hours. Lead release from brass alloys forms secondary corrosion products like hydroxide and carbonate species e.g. $PbCO_3$, $Pb_2(OH)_2(CO_3)_2$ and $Pb(OH)_2$ [6]. These species may form protective layers on the surface. Thus, in a stagnation period the aqueous concentration of Pb is dependent on the solubility of the parent species. This is controlled by the stability constant and pH is therefore one of the main solubility controlling factors. In analogy, the leaching of Cu from cupper pipes is controlled by the solubility and thus pH of the corrosion products e.g. Cu_2O, CuO, $Cu_4SO_4(OH)_2$ or $Cu_2(OH)_2CO_3$. In addition, the concentration of oxygen, sulphate and bicarbonate in the water will also determine which minerals that are formed. $Cu(OH)_2$ is medium soluble and is normally transformed to malachite at appropriate pH and bicarbonate concentration. At pH lower than 6.5, most of the layers are dissolved (or not forming) and Cu^{2+} is directly released. In addition, natural organic matter (NOM) like humic substances has strong complexing properties that may increase the solubility of Cu^{2+} and most likely other metal cations like Zn^{2+} and Pb^{2+}.

Hence, the release of metals from brass to drinking water depends on many factors and mechanisms. It can be summarised that the main mechanisms may be a combination of electrochemical (corrosion), chemical (leaching) and the wear process which are all interconnected to various extent [7]. The interconnection means that for instance a corroded brass (e.g. by dezincification) may have higher potential for release of Pb than the same brass type with no corrosion but it also depends on the type of lead complex formed which in turn depends on the water composition. From a more practical point of view, it can be deduced that the metal species are released to the drinking water to an extent that is dependent on the water composition, the operating conditions in domestic drinking water installations and the material characteristics.

In Norway, most of the raw water is soft because the water supply is mainly based on surface water. Only in certain parts of Norway the water is hard and alkaline due to groundwater supply from sources with lime rich bedrock. Quality parameters for drinking water in Oslo are shown in Table 2. It can be seen that the average hardness and alkalinity are 19.3 mg Ca/L and 0.69 mmol/L, respectively.

Table 2 Average concentrations in drinking water for Oslo [8]

Parameter	Unit	Avarage concentration	Measurement frequency
Alkalinity	mmol/L	0.69	Weekly
Acidity	pH	7.69	Weekly
Conductivity	mS/cm	10.9	Weekly
Hardness	mg Ca/L	19,3	Every third month

In general, soft water is aggressive in terms of corrosion and metal leaching to drinking water. For brass products (e.g. fittings and taps) the reduced carbonate concentration in soft water decreases the tendency to form stable lead carbonate species in the protective layer which obviously influence the release of Pb.

Thus, water composition is not only essential in in the service life of DWMC, but also in the approval stage before entering into use. This is due to the Norwegian regulation that requires the following. In order to be able to place building products, including DWMC, on the market and to use the products in works, relevant technical documentation should follow. Note that it is the building owner that eventually decides if the product is fit for use or not. A part of the required technical documentation is to demonstrate that DWMC are suitable for their intended use. The practice in Norway is to document the release of Pb and Cd according to NKB product rules [9]. The short-term batch leaching test under these rules is an in-product exposure by demineralised water containing 50 mg/L NaCl, Na_2SO_4 and $CaCO_3$ and a final pH of 7.0. The exposure last for 10 days with renewal of the test water every day. Other short-term tests in other countries have different test waters and exposure regimes like for instance ANSI/NSF 61 (USA) and AS/NZS 4020 (Australia). In the former, the test water depends on the product types and is in the pH range from 5-10. The pH of the test water for taps is 8 with high alkalinity whereas pH 5 and 10 are normally used for fittings. The latter test method applies demineralised water with a hardness of 50 mg/L (as $CaCO_3$) with a pH around 7.0-7.5 by using reagents of $NaHCO_3$ and $CaCl_2$. Hence, the water composition in the leaching tests determines to a large extent which products that finally are placed on the market.

The leaching of lead from brass fittings as function of exposure time (ANSI/NSF 61) is shown in Figure 2. The results strongly indicated that saturation was approached after relatively short exposure time (6h). The decrease in lead concentration may be explained be re-precipitation as temperature was held at 82 ^{o}C for the first 30 minutes before normal cooling to room temperature. Thus, to choose one single approval method, with a fixed test water, which aims to represent the water quality, is therefore challenging due to the fact that different corrosion and leaching mechanisms predominate at different water conditions (pH, alkalinity, hardness, NOM, etc).

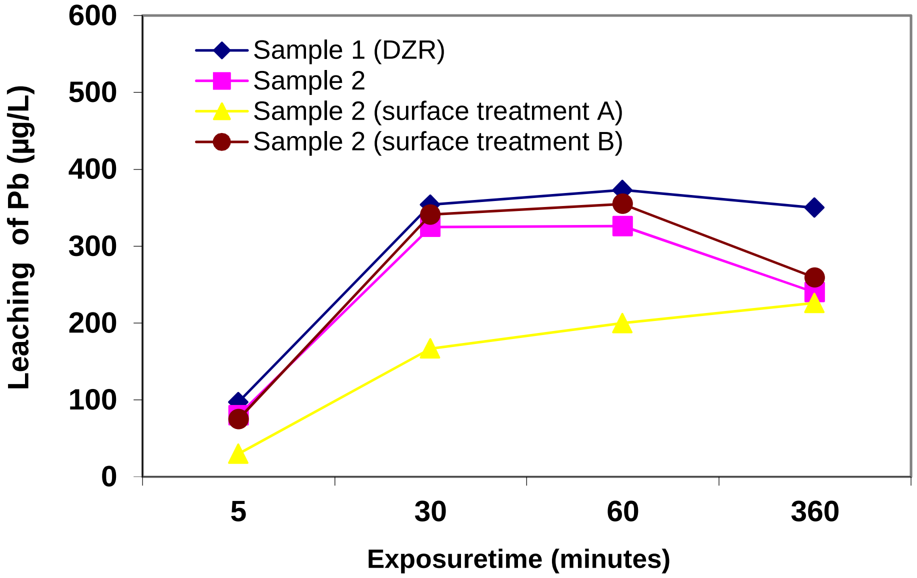

Figure 3 Leaching of Pb from brass fittings according to ANSI/NSF 61 section 4 (pH 10). Lead concentrations were determined as function of time for 6 h in parallel assemblies of fittings. Concentrations are not normalised.

4 Brass with improved properties

The new alloy RA455 from ISIFLO/Raufoss Water and Gas is an optimization of CW625N and RA450 with respect to corrosion properties and leaching. The alloy is within the composition window of CW625N. Hence, the material is within the 4MS common approach regarding material composition and leaching from metallic materials in contact with drinking water (Acceptance of metallic materials used for products in contact with drinking water – Part B: 4MS Common composition list). The key-enabler in this development process has been to develop an efficient thermo-mechanical processing scheme that can handle the tight compositional tolerances and provide a final product with dezincification resistant properties.

Furthermore, some interesting results have already been achieved for low lead brass alloys regarding leachability. Obviously, the positive lead leaching properties gained by decreasing the lead content in the alloy have a negative counter reaction by increasing the processing costs (e.g. increased wear). The leaching from brass alloys with different Pb contents is shown in Figure 4. The experiments were conducted according to NKB product rules. The leaching of lead from brass alloy with 0.35% Pb was small compared to alloys with higher lead contents. In addition, promising results has been achieved with acid extraction of surface Pb conducted according to EN 16057 for a brass with lead content of < 0.2% [10].

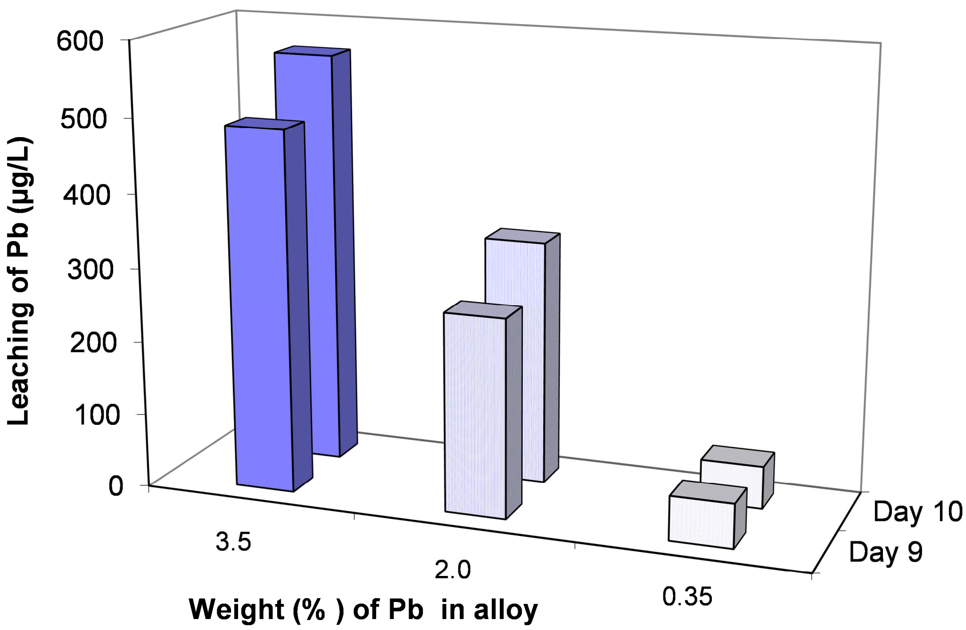

Figure 4 Leaching of Pb from brass fittings with different content of Pb according to NKB product rules. The concentrations are not normalised.

4 Conclusions

Placing DWMC on the market requires technical documentation in most countries and it is mandatory in Norway. The Norwegian practice for brass products regarding the leaching properties (health requirements) is to use the NKB Product rules. Since a fixed composition for the test water is normal for this type of test method (batch test), challenges are faced due the variation in the chemical composition of the drinking waters. Most of the raw water in Norway is soft with relatively low alkalinity due to water supply mainly from surface water. According to the latest investigations, the drinking water in Oslo was found to have an average hardness and alkalinity of 19.3 mg Ca/L and 0.69 mmol/L, respectively, which in general is compatible with the test water used in the NKB test regarding the mentioned parameters. However, the fundamental leaching principle applied in these types of batch tests and what information is believed to be disclosed by short-term tests is important to consider.

Regarding the typical corrosion types in Norway the failures analysis indicates that the main corrosion mechanism has changed from dezincification to stress corrosion cracking over the last 20 years. The main causes of failure are residual stresses from manufacturing, component design, installation error, and component mismatch. The development of brasses has progressed significantly, both regarding the thermo-mechanical properties in the processing phase and the mechanical and leaching properties in the user phase.

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