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NICKEL AND LEAD RELEASE TO DRINKING WATER – DANISH AND EUROPEAN RESULTS

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Abstract

For the last decade numerous investigations have been carried out in Europe in order to assess metal release to drinking water. Generally metal concentrations are low when the water leaves the waterworks, but during transportation and storage in the distribution net the metal concentration may increase considerably. In the mains the storage time and the area to volume ratio is low, so normally metal concentrations will only increase very little. In domestic installations stagnation times may be very long, temperature is higher and the surface to volume ratio is higher, so metal concentrations may increase considerably. This paper will focus on nickel and lead release to drinking water as measured in domestic installations and in a test rig according to DS/EN 15664-1, modified for product testing. Surveys in Denmark, Germany and the Netherlands have shown that lead and nickel concentrations in domestic drinking water installations may be very high, especially in new installations. Lead may be released from lead piping, but also leaded brass parts may contribute to high lead concentrations in new installations. In 2008 a Danish survey of metals in drinking water from domestic installations was carried out. The survey showed that lead and nickel was primarily released from the mixer taps, and the concentrations were highest from mixer taps less than 2 years old.

Nickel is mainly released to drinking water from nickel-chromium plated brass products such as mixer taps, valves and fittings, from where it may continue to be released for several years. A co-normative research work was carried out in Germany and Denmark to assess nickel release from nickel-chromium plated mixer taps by rig testing. Two different types of kitchen mixer taps were tested for 26 weeks showing different nickel release patterns. Nickel release patterns were very similar in the two different water types used for the test, as nickel will not passivate in drinking water. This is in good accordance with previous investigations, indicating very little dependency of nickel release on water type. For one product nickel release decreased after 3-4 months and stabilised at a low level. Nickel release from the other product increased for the first 2 months and continued at a relatively high level for the full test period of 26 weeks. Based on the results from the co-normative research work, a European standard for testing of nickel release from construction products for drinking water will be written.

Keywords

Metal release, nickel, lead, drinking water, rig-test

Introduction

For the last decade numerous investigations have been carried out in Europe in order to assess metal release to drinking water [1-9]. The investigations have focused on measurement of the metals limited by the parametric values in the European drinking water directive (DWD) [10]. The directive specifies maximum metal concentrations at the consumer's tap, whereas the parametric values of the previous directive were only specified for the water leaving the waterworks. Generally metal concentrations are very low when the water leaves the waterworks, but during transportation and storage in the distribution net the metal concentration may increase considerably. In the mains the storage time and the area to volume ratio is low, so normally metal concentrations will only increase very little. In domestic installations stagnation times may be very long, temperature is higher and the surface to volume ratio is higher, so metal concentrations may increase noticeably. Therefore construction products for domestic installations have been given special attention.

The following parameters govern the metal release from metallic products:

- Stagnation time
- Water quality (including variations in composition)
- Material (composition, corrosion resistance, surface finish)
- Design (dimension, placing, other metals)
- Water consumption (consumer's own and the neighbours' consumption pattern)
- Water consumption at start-up of installation
- Temperature
- Age of installation

This paper will present data on release of lead and nickel to drinking water, as these two metals have been in focus for the last years. The paper only briefly describes materials and metal release principles. For a more detailed description of metal release from the commonly used materials, we refer to [11] and the references herein.

Sources of lead

In Denmark lead is primarily released to drinking water from the copper alloys' brass and gunmetal, as they contain lead as an alloying element. Furthermore lead may be released from leaded solders in older installations (more than 30 years old) and from the zinc layer of older hot-dip galvanised steel pipes. Today both the lead and cadmium contents of hot-dip galvanised steel pipes' zinc layer are very low and the release of the metals from this material is negligible. Lead release from dezincification resistant brass (DZR brass) is often high for the first 2-3 months due to release of smeared lead from the surfaces as a result of machining [9]. After this initial period lead release ususally declines to an acceptable level. However in some cases lead release begins to increase again, for example due to special corrosion forms, e.g. intergranular corrosion. Gunmetal is nobler than the brasses and it normally has a higher lead content. Though lead release from gunmetal may be high during the first months, the surface is then passivated, and lead release declines to a very low level, well below the parametric value of 10 µg/L as weekly average.

Sources of nickel

Nickel is used in many parts of domestic water installations. Brasses contain nickel as a trace metal and in gunmetal nickel is an alloying element. Generally nickel release is low from modern brasses and gunmetal, as the nickel content is low in the copper alloys. Stainless steel types used in drinking water installations usually have nickel contents of 10-14%, but nickel is not released to the drinking water as stainless steel is passive, and no measurable metal dissolution will take place as long as a sufficiently corrosion resistant alloy has been selected.

Brass components such as mixer taps and valves are normally nickel-chromium plated on the outside for improved corrosion and wear resistance and for better appearance. However the inside of the components will also get nickel plated near the apertures, and this nickel may be released to the water during the components' service life, see figures 1 and 2. Previous investigations have shown that nickel release may be very high for new faucets, and that this release may continue to be relatively high for several years [4].

Furthermore water from some waterworks has high nickel concentrations, and in some cases it must be precipitated at the waterworks in order to meet the parametric value of 20µg/L as weekly average.

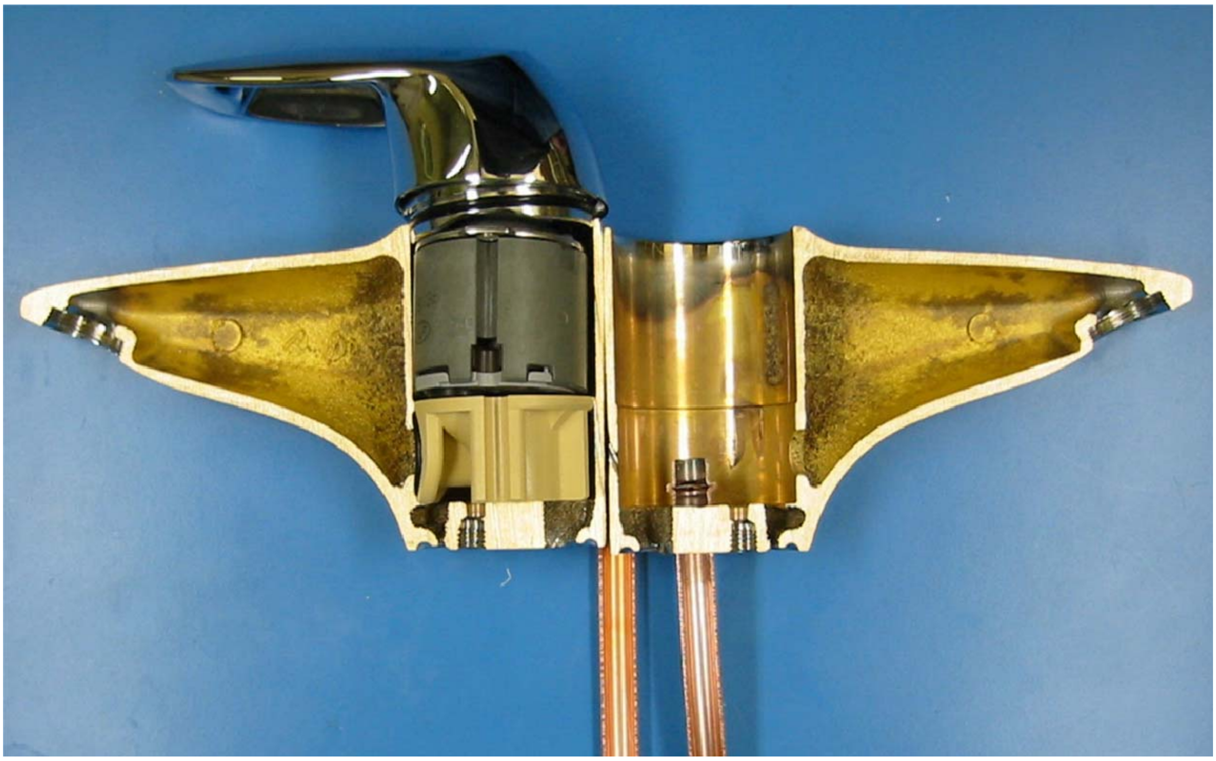

Figure 1: Example of nickel-chromium plated mixer tap. Nickel is observed at the inside of apertures.

Figure 2: Close-up of aperture on mixer tap spout showing nickel at the inside.

Part 1: Survey of metal release in domestic installations

In 2008 a screening survey of metal release at consumers' kitchen taps was carried out in 51 domestic installations on Zealand, Denmark [12]. The scope of work was to analyse the metal concentration in fractioned water samples in order to identify the possible sources of metal released to drinking water in domestic installations.

Due to the relatively low number of installations involved, it must be emphasised that the investigation was a screening only, and that it cannot be considered representative of metal release in all Danish domestic water installations.

All samples were taken from installations on Zealand, Denmark, and primarily in the vicinity of Copenhagen. The drinking water in these areas is characterised by high conductivity (80-120 mS/m) and high contents of hydrogen carbonate and dissolved salts. In these water qualities copper and zinc releases are higher than seen in water qualities with less hydrogen carbonate and dissolved salts. The release of other metals is less dependent on water quality.

To be able to separate the contribution of metals to drinking water from different sources, fractioned sampling was used. Three water samples were taken representing water from respectively mains, stagnation water from mixer tap and stop valve, and stagnation water from remaining installation. For practical reasons fixed sample volumes were used despite the different types and sizes of installations. The fully flushed sample represents water from waterworks/mains, and was used also for blind values that were subtracted from stagnation samples to calculate net contribution from different sections of the installation. However it is worth noting that stagnating water may react chemically with the pipe materials or by chemical reactions in the water phase itself, which may change the water characteristics in different ways. Metal contents may increase or decrease during stagnation. The most well-known example of decreasing metal content in stagnating water is probably the reduction in copper concentration due to deposition of metallic copper in hot-dip galvanised steel pipes.

Sampling procedure

The water samples were taken by the test persons as fractioned samples from the kitchen mixer tap as follows:

Sample A: Fully flushed (FF) 500 mL sample taken after 5 minutes of flushing with the tap fully open. This sample represents the water delivered from the mains to the consumer's premises.

Sample B: Fixed stagnation 200 mL sample taken after 4 hours' stagnation during which no water was drawn from any place in the domestic installation. This sample represents stagnation water from the mixer tap, the small connecting pipes and the last stop valve.

Sample C: Fixed stagnation 800 mL sample taken after 4 hours' stagnation (immediately after the B-sample), representing stagnation water from the remaining installation.

Samples were analysed for arsenic, antimony, tin, chromium, cadmium, zinc, copper, lead and nickel.

Results and discussion

All results presented in this section were taken from [12]. Figure 3 shows the relative distribution of the amount of metals released in the domestic installations having mixer taps less than two years old. The majority of the zinc and copper arises from the pipe materials in the installation (last 800 mL), whereas the first 200 mL accounts for the majority of the lead and nickel released to the first litre of stagnating water. This shows that in new installations the mixer taps and stop valves are the primary source of nickel and lead release although these components only constitute a minor part of the installation.

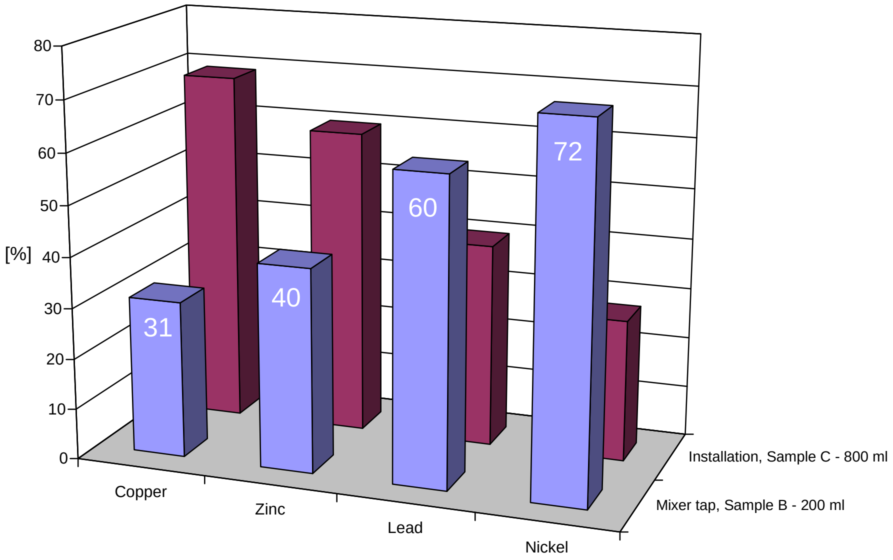

Figure 3: Relative distribution of metal release in the installations, calculated for a 1 litre sample taken after 4 hours' stagnation. Distribution was calculated from average net values from installations having mixer taps that are less than two years old. Thus 72% of the total nickel released to the first litre taken after 4 hours' stagnation was released from materials in contact with the first 200 mL water in the installation (e.g. mixer tap, connecting pipe and stop valve).

Lead release

Table 1 shows an overview of the results on lead release. In Denmark and in the DWD the parametric value for lead is 10 µg/L as weekly average.

The A-samples had low lead contents, the maximum value being 2.6 µg/L. The C-samples also had low lead contents in most cases, and only 1 sample was above 10 µg/L. The lead contents of the B-samples were higher with 7 samples being above 10 µg/L. The maximum lead content was 110 µg/L in a B-sample, table 1.

The highest lead concentrations were found in the stagnation water from the mixer taps, though the difference in average lead concentration was not very large (table 1). The high lead content in the B-samples must be caused by lead release from the brass mixer taps and valves. The high lead release in some of the C-samples is more difficult to explain. Large valves of brass or gunmetal may be the source of lead, but the highest concentrations are higher than would be expected. Other sources could be old leaded solders.

The average lead release was considerably higher in B-samples taken from installations where mixer taps were less than one year old, see figure 4. Figure 3 shows that for installations with mixer taps less than 2 years old, 60 % of the total lead was released to the B-samples. The high lead release from new brass products is known to be caused by smeared lead on the brass surfaces. Previous investigations have shown that the surface lead is usually dissolved during the first months of operation.

Table 1: Overview of results on lead release

	As analysed				**Net values**	
	A Fully flushed [µg/L]	**C** 4 h stagnation [µg/L]	**B** 4 h stagnation [µg/L]	**(C+B)**[1] 4 h stagnation [µg]	**C** 4 h stagnation [µg/L]	**B** 4 h stagnation [µg/L]
Average	0.6	2.8	7.3	3.7	2.2	6.8
Max.	2.6	37	110	32	36	109
Min.	0.2	0.0	0.5	0.1	0[2]	0[2]

Note 1: Weighted average based on sample volumes. The total sample volume is approximately 1 litre.
Note 2: Calculated net values showing negative values, e.g. due to precipitation, are reported as 0.

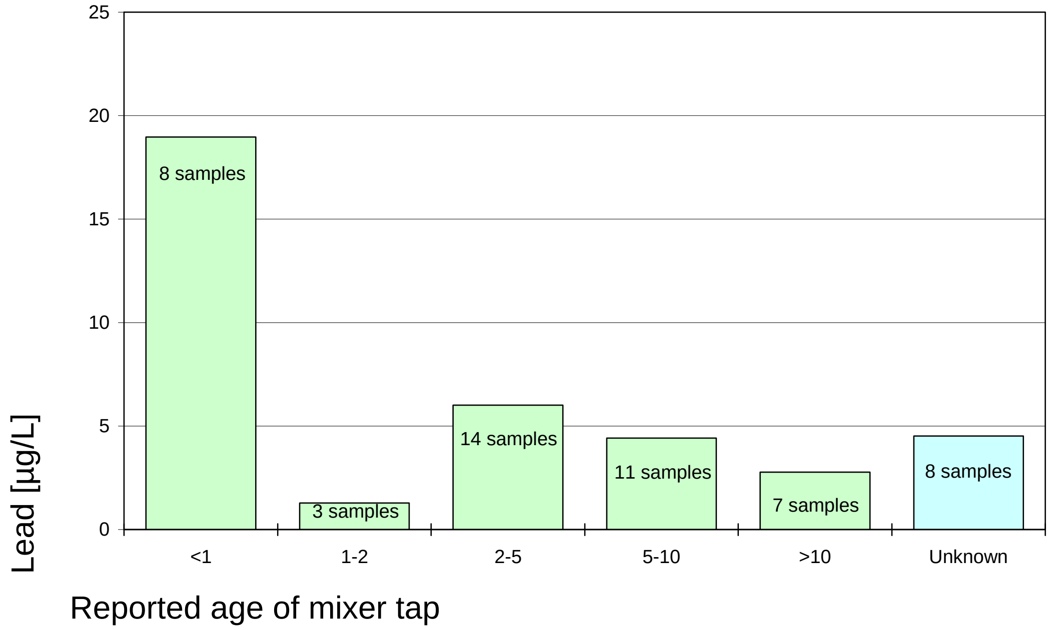

Figure 4: Lead as a function of the reported age of the mixer tap. Average lead released in the first 200 mL. 4 hours' stagnation samples.

Nickel release

Table 2 shows an overview of the results on nickel release.
In Denmark and in the DWD the parametric value for nickel is 20 µg/L as weekly average.

Table 2: Overview of results for nickel release.

	As analysed				**Net values**	
	A Fully flushed [µg/L]	**C** 4 h stagnation [µg/L]	**B** 4 h stagnation [µg/L]	**(C+B)**[1] 4 h stagnation [µg]	**C** 4 h stagnation [µg/L]	**B** 4 h stagnation [µg/L]
Average	3.5	4.9	12.1	6.4	1.5	8.6
Max	27	27	68	26	17.4	61
Min	0.6	0.8	1.0	0.8	0[2]	0[2]

Note 1: Weighted average based on sample volumes. The total sample volume is approximately 1 litre.
Note 2: Calculated net values showing negative values, e.g. due to precipitation, are reported as 0.

The nickel concentration was generally low in the A-samples, but in 7 cases it was above 5 µg/L and in 2 cases even above 20 µg/L, meaning that the water from the waterworks did not fulfil the DWD. Generally the nickel concentration did not increase much in the C-samples, but in 4 cases the concentrations were above 20 µg/L; the maximum value being 27 µg/L. The average concentration of A-samples was 3.5 µg/L, and of the C-samples 4.9 µg/L, table 2.

The B-samples had the highest nickel concentration. 11 of the B-samples were above 20 µg/L, the average was 12.1 and the maximum value was 68 µg/L. Though the B-sample only has a volume of 200 mL it contributes with a large fraction of the total nickel released in the installations. In most cases the first 200 mL contains more than half of the nickel released in the installation. For all installations the average fraction of the total nickel released to the B-samples was 61 %, and for installations where mixer taps were less than 2 years old, the B-samples contained 72 % of the total nickel released in the installations, Figure 3. This confirms that the majority of the nickel released to the water often originates from nickel-chromium plated mixer taps and brass valves.

Figure 5 shows nickel release as a function of the reported age of the mixer tap. As a lot of other parameters change from one installation to another, the picture was not very clear, but still some general remarks may be made. It may be observed that nickel release was higher from the mixer taps for the first 1-2 years; hereafter it declined to a lower level. Even for mixer taps older than 10 years some nickel release was observed, the average level being around 5 µg/L. When compared to previous investigations, the nickel concentrations measured were rather low in the first 200 mL. In previous investigations overnight stagnation has been the most commonly used, meaning that stagnation times were in the range of 8-16 hours. As the nickel release rate is normally constant up to at least 16 hours, this means that the net concentrations should be multiplied by a factor of 2-4 for comparison with previous data. Previous investigations have shown values of about 200 µg/L from mixer taps after 1 year, and about 50 µg/L for mixer taps of the same make after 5-7 years [ref. 1 and references herein].

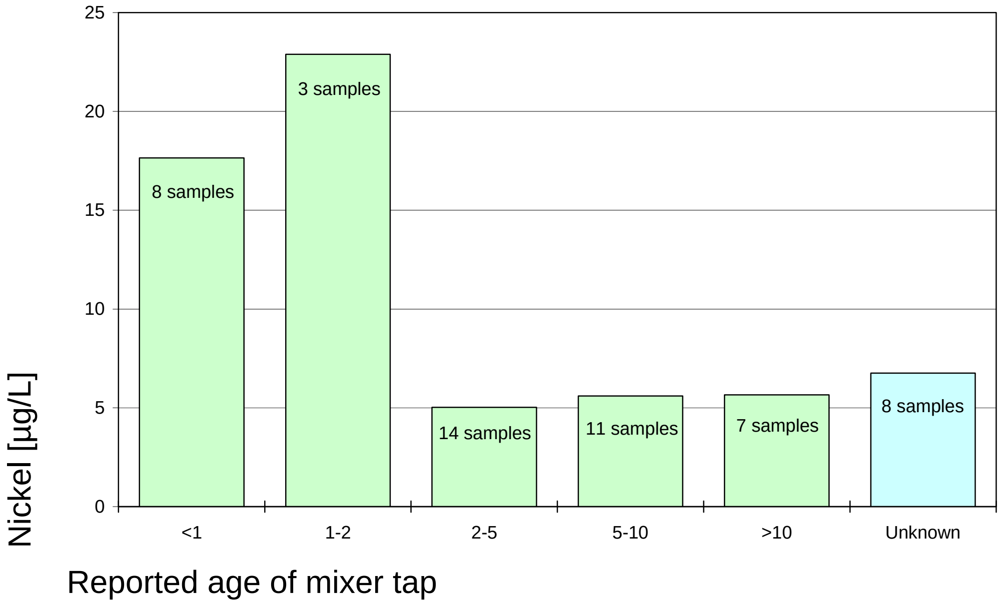

Figure 5: Nickel as a function of the reported age of the mixer tap. Average nickel released in the first 200 mL. 4 hours' stagnation samples.

Conclusions

Metal release was measured in 51 domestic drinking water installations on Zealand, Denmark. Water samples were taken by fractioned sampling, taking a fully flushed sample (A-sample) and two 4-hour stagnation samples of 200 mL (B-sample) and 800 mL (C-sample), respectively.

Lead release

The lead concentration was low in the A-samples, and generally increasing in the B- and C-samples. The maximum concentration found was 110 µg/L in a B-sample. The average lead concentrations were 2.8 µg/L in the C-samples and 7.3 µg/L in the B-samples. Sources of lead in domestic water installations are copper alloys' brass and gunmetal, and in older installations leaded solders may also contribute.

The average lead release was considerably higher in B-samples taken from installations where mixer taps were less than one year old. As average for all installations 44 % of the total lead was released to the B-samples (mixer tap and stop valve). For installations with mixer taps less than 2 years old, 60 % of the total lead was released to the B-samples. The high lead release from new brass products is known to be caused by smeared lead on the brass surfaces. Previous investigations have shown that the surface lead is usually dissolved during the first months of operation.

Nickel release

The nickel concentration was low in most of the A-samples, but in 7 cases it was above 5 µg/L and in 2 cases even above 20 µg/L, which is the parametric value for weekly average. In general, the nickel concentration did not increase much in the C-samples, but in 4 cases the concentrations were above 20 µg/L. The average concentration for A-samples was 3.5 µg/L and for the C-samples it was 4.9 µg/L.

The B-samples had the highest nickel concentration with 11 of the B-samples being above 20 µg/L. The average concentration was 12.1 µg/L and the maximum value was 68 µg/L. In most cases the first 200 mL (B-samples) contained more than half of the nickel released in the installation. For all installations the average fraction of the total nickel released to the B-samples was 61 %. For installations where mixer taps were less than 2 years old, the B-samples contained 72 % of the total nickel released in the installations. This confirms that the majority of the total nickel released to the water originated from nickel-chromium plated mixer taps and valves of nickel plated brass.

The average nickel release was higher from mixer taps less than 2 years old; hereafter it declined to a lower level.

Part 2: Long-term rig testing of nickel release from mixer taps

For the determination of the long-term behaviour of metals and alloys in contact with drinking water, a European Standard of two parts, EN 15664-1:2008 and pr EN 15664-2, was developed. Pr EN 15664-2 is now in the inquiry phase. In a co-normative research work experiments with two different types of nickel-chromium plated kitchen taps from two different producers were carried out with test rigs according to the European test rig standard EN 15664-1 [13]. Test rigs simulate operation conditions for a mixer tap installed in the kitchen at a consumer's drinking water installation. Operation conditions are characterised by rather short flowing and comparably long stagnation periods. The test rigs were operated by two laboratories:

- FORCE Technology / Denmark in Regnemark Waterworks and
- TZW / Germany in Karlsruhe

Operation and sampling of test rigs

Experiments were carried out according to the operation protocol described in the European test rig standard EN 15664-1. Physical and chemical data of the test waters are reported in table 3.

Table 3: Water analyses of water used in rig testing. Selected parameters.

		Regnemark August 2007	**Karlsruhe August 2007**
Parameter	Unit		
pH-value	pH units	7.4 (12 °C)	7.1 (13 °C)
Specific electrical conductivity	mS/m	81 (12 °C)	83 (25 °C)
Oxygen	mg/L	8.8	10
Total alkalinity	mmol/L	6.2	6
Total organic carbon (TOC)	mg/L C	3.0	1.3
Free carbon dioxide	mmol/L	0,8	1,16
Calcium	mg/L	127	138
Magnesium	mg/L	24	13
Potassium	mg/L	6	4
Sodium	mg/L	73	23
Chloride	mg/L	110	43
Nitrate	mg/L	3	26
Sulphate	mg/L	78	59
Phosphorous	mg/L	< 0.01	< 0.01
Silicon dioxide	mg/L	26	5,0

The test rig experiments were carried out for 26 weeks. Every week the taps were sampled after a stagnation period of 4 hours. In weeks 2, 12/16 and 26 a complete sampling procedure of 8 single stagnation periods was carried out.

The measured nickel concentrations in the contact water of the taps were normalised referring to a volume of 500 mL.

Results and discussion

All results presented here were taken from the co-normative research work [13].
The inlet concentration of nickel was below the detection limit of 2 µg/L.
The nickel concentrations in the contact water of all taps increased linearly with stagnation time, see figure 6. In the first weeks of operation maximum nickel concentrations of more than 900 µg/L may be observed. Because of the dilution of contact water in direct contact with the taps (< 200 mL) during sampling (sampling volume 500 mL) nickel concentrations in the water stagnating in the taps may have been up to 5 mg/L. Up to these concentrations no saturation effects concerning the solubility of nickel can be observed.

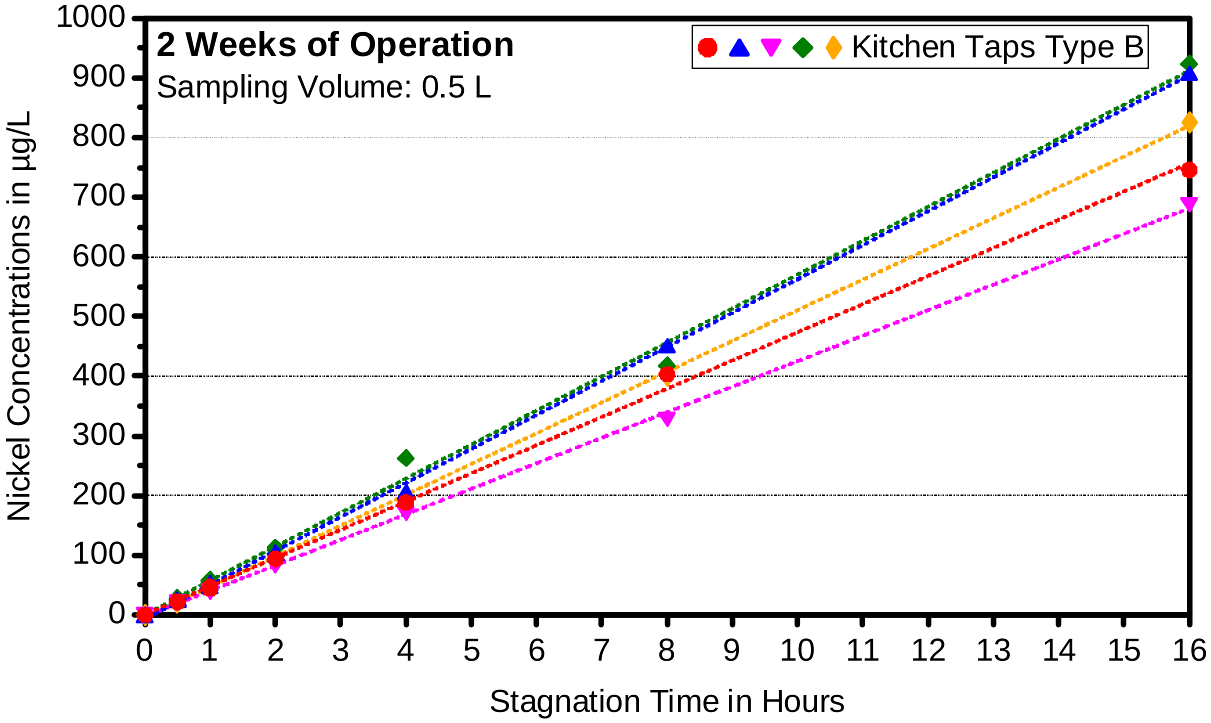

Figure 6: Stagnation curve for kitchen taps type B in Karlsruhe test water after 2 weeks of operation.

The nickel concentrations measured in the contact water of the kitchen taps showed considerable scatter, as may be observed in figures 6-8.

In figures 7 and 8 only a minor difference between the results for the different test waters can be observed. However the nickel release patterns of the different taps of producers A and B showed significant differences.

The nickel concentrations measured for the taps of producer A were not changing significantly during the 26 weeks of operation (figure 7). A maximum of the nickel release may be recognised between the 8th and 14th week of operation. The measured nickel concentrations were in the range of 30 to 160 µg/L after 4 h stagnation and for a sample volume of 0.5 L. After 26 weeks of operation the nickel concentrations were still 30 to 60 µg/L.

The nickel release pattern of the taps of producer B was different (figure 8). During the first weeks of operation a very high nickel release may be observed. In Regnemark the highest concentrations were measured in the 2nd and 3rd week of operation whereas for the TZW water in Karlsruhe, the highest concentrations were determined in the 8th week of operation. After this the measured nickel concentrations decreased, and after 26 weeks of operation the nickel concentrations were in the range of 8 to 20 µg/L after 4 h stagnation and with a sample volume of 0.5 l.

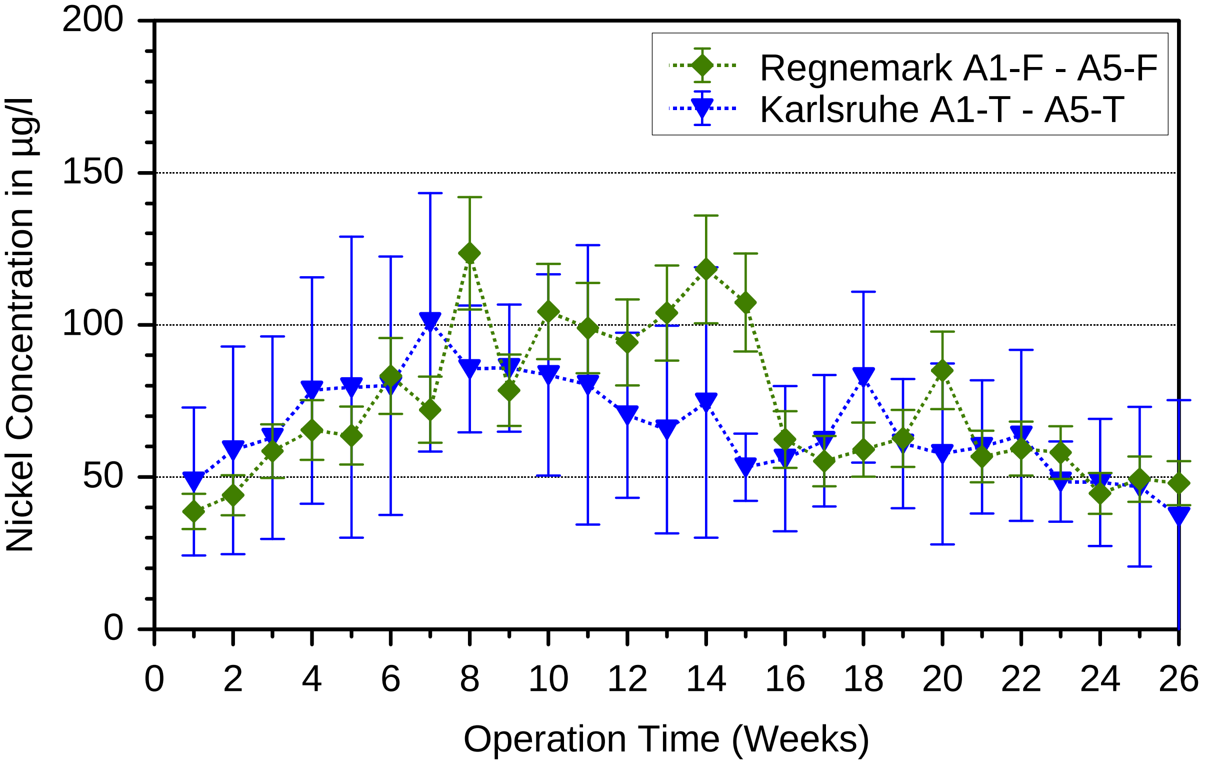

Figure 7: Nickel release from mixer taps type A as a function of operation time in two different water types.

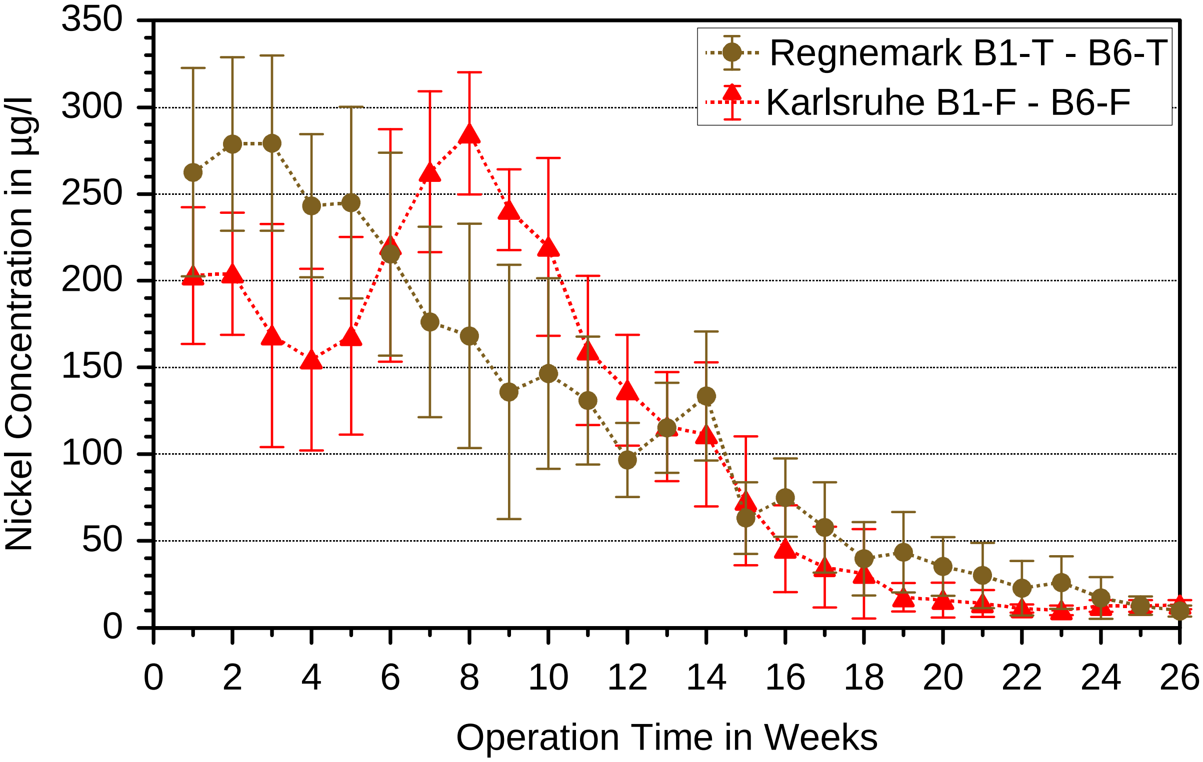

Figure 8: Nickel release from mixer taps type B as a function of operation time in two different water types.

Conclusions

Nickel release from two different kitchen taps for drinking water was determined by a long-term test rig simulating the long-term behaviour of the products in contact with drinking water in domestic installations.

The nickel release patterns of the two products were very different. Nickel release from products A did not change considerably during the 26 weeks of operation, whereas nickel release from product B was very high at the beginning and declined to a very low level by the end of the test.

Nickel release from the kitchen taps was investigated in two different waters. The results show that the water composition has only a very small or no influence, which is in good accordance with previous investigations of nickel release.

Based on the results of the co-normative research work on nickel release a new European standard is now being written for long-term rig testing of nickel release from nickel-chromium plated products for drinking water installations. The standard is based on EN 15664-1 with weekly sampling of 4 hour stagnation samples, so the number of water samples for analysis is reduced considerably compared to EN 15664-1. The test duration will be 26 weeks.

Acknowledgement

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