METAL LEACHING OF BRAZED STAINLESS STEEL JOINTS INTO DRINKING WATER

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Abstract

Due to hygienic considerations and improved corrosion resistance, the use of stainless steel in heat exchangers and plumbing systems for domestic drinking water installations is increasing. In Europe, and especially in Germany, stainless steel is replacing copper alloys in these applications. The hygienic suitability of stainless steel for drinking water applications is well investigated, documented and approved. However, only a few research papers can be found dealing with hygienic aspects of brazed joints made on stainless steel components, such as heat exchangers.

This paper presents an investigation made on 316L stainless steel joints where plate heat exchanger samples are brazed using a range of copper, nickel and iron based brazing alloys in form of amorphous foils. The metal leaching of these samples into drinking water was examined and the results disclose a distinct improvement in the hygienic suitability of modern VITROBRAZE® compositions over other state of the art brazing alloys.

Introduction

The primary purpose of national and international drinking water standards and guidelines [1-4] is the protection of public health. Drinking water is required for all usual domestic purposes, including drinking, food preparation and personal hygiene. A safe drinking water should not represent any significant risk to health over a lifetime of consumption. To ensure a high level of health protection, drinking water shall meet minimum requirements in the field of appearance, microbiology, radioactivity and chemistry. These values are available based on the scientific knowledge.

Drinking water contains a certain amount of heavy metals due to natural occurrence of these elements or as result of metal leaching from contact with domestic drinking water installations. The maximum concentrations for some brazing related metallic elements are listed in Table 1. Since the precautionary principle has also been taken into account, the German drinking water ordinance [3] demands the minimization principle. Only materials or components should be used for drinking water applications which release a minimum of any substances into the water and should not emit higher values of substances than would be unavoidable in compliance with the state of the art and technology. Due to these hygienic considerations, corrosion resistant stainless steel is replacing copper alloys and zinc coated steel in heat exchangers and plumbing systems for domestic drinking water installations. The hygienic suitability of stainless steel for food processing and drinking water applications is well investigated, documented and approved.

Table 1: Chemical elements of brazing alloys and their maximum concentration limit in drinking water according to the U.S. EPA regulations, the European drinking water directive and the WHO-guideline. Values are given in µg/l.

Element	U.S. EPA	EG council directive 98/83	WHO-guideline value 2011
Fe	-	200	-
Cr	100	50	50
Cu	1300	2000	2000
Ni	-	20	70
Mn	-	50	-
B	-	1000	2400

However, only a few research papers can be found dealing with the hygienic aspects of brazed joints made on stainless steel components, such as heat exchangers [10,12,13]. It is well known that brazed stainless steel structures release a certain amount of involved elements when placed in contact with drinking water [5-13]. Some statements in technical literature conclude that brazed joints on stainless steel components made with Ag-, Cu- or Ni-based brazing alloys do not meet the corrosive or hygienic requirements of drinking water installations, irrespective of the type of brazing alloy used [5,6]. Such statements caused uncertainty to the industry and end users of such components.

Germany’s Federal Institute for Material Testing examined several cases of damaged copper brazed heat exchangers after contact with drinking water [7-9]. These investigations disclosed that copper brazed stainless steel heat exchanger exhibit significant corrosion of the brazed joints as well as high copper leaching rates into the drinking water. Although both copper and stainless steel are classified as resistant towards drinking water, the brazed joint may generate corrosive problems if exposed to specific water qualities. Corrosion was always found in the drinking water circuit of such components and did not occur on the heating water circuit. Virgin heat exchangers especially, exhibit high copper leaching rates exceeding the allowable limits during the first weeks of service. Surprisingly, other investigations show that copper brazed stainless steel heat exchangers may also exhibit significant leaching of nickel into the drinking water. Furthermore, it was discovered that copper brazed heat exchangers exhibit significantly higher nickel leaching rates to the drinking water than components brazed with an nickel brazing alloy [10,11].

Due to the increasing occurrence of nickel hypersensitivity in humans as well as the permanent tightening of the general toxicity level for nickel, strict limitations can be found in some governmental drinking water regulations. In Europe especially, where the nickel limit is set as low as 20 µg/l [2] there is still some confusion as to whether brazed stainless steel components meet the European hygienic requirements. Some research work [12,13] was already done to investigate the emission of nickel ions out of various nickel- and iron based filler metal surfaces into drinking water. These investigations were carried out as a dynamic rig test according to European and German standards, using tube sections coated internally with filler metal as specimen [14,15]. The results show that the hygienic suitability of all tested brazing alloys is comparably as good as the unbrazed 316L surface. However, the specific testing method was configured to investigate individual materials, for example a tube material, where a stable material and surface condition over the whole sample was given. This test method did not reflect the different material conditions occurring on a brazed joint where we have a base material, a filler material and a reaction zone with a material mix of all involved elements. It is well known that such a reaction zone tends to be the weakest area of a brazed component in terms of corrosion resistance.

The target of this study is to provide a baseline investigation for the metal leaching of individual nickel containing brazing materials into drinking water and compare them with the metal leaching of brazed stainless steel structures with surface conditions equivalent to those of a real heat exchanger. One goal was to carry out this investigation based on heat exchanger like samples and with testing methods less complex and expensive than a dynamic rig test according to [14]. Several brazing alloys were tested with the intention of finding suitable brazing alloys where the leaching of undesired metals is minimized. The aim was to identify optimized material combinations leading to a reduced water contamination on one hand and to improved corrosion resistance and service life of the brazed component on the other.

Experimental

Today the majority of plate type, stainless steel heat exchangers are brazed in a vacuum furnace using filler metals in the form of thin metallic foils [11,16,17]. Several nickel and iron based amorphous brazing foils (ABF) as well as a crystalline Cu102 foil are considered in this investigation (see Table 2). The outstanding brazeability of the amorphous VITROBRAZE foils, the microstructural compatibility of the joints and the good mechanical durability of the brazed components are reported elsewhere [16-20]. These foils were prepared to form shims with dimensions of 25 mm x 40 mm x 0.05 mm. The compositions of the brazing foils are listed in Table 2. The austenitic stainless steel grade 316L was chosen as base material.

Heat exchanger plates with a thickness of 0.3 mm and the typical herringbone embossed pattern were provided by a heat exchanger manufacturer. Small samples of these plates, 25 mm x 40 mm were precisely machined using a wire cut EDM machine (Figure 1). To form a structure similar to a heat exchanger, the corrugated 316L samples were stacked with alternating change in direction of the embossed pattern. This results in an open structured 3-dimensional specimen in which a fluid can freely pass. Each specimen consisted of 7 steel layers with a total height of about 16 mm and a total weight of about 18.4 g. All parts are cleaned with Isopropanol in an ultrasonic bath for 15 minutes prior to assembly. One brazing foil shim was placed between each steel layer. A picture of the brazed specimen is shown in Figure 2. Each brazed specimen has 144 punctual brazed joints and a total surface of about 165 cm^2, of which 140 cm^2 is in contact with the brazing alloy. An Al_2O_3 fixture was used to compress the stack during the brazing process and to keep the plates in correct position. Brazing was carried out in a vacuum furnace with a vacuum level of about $1x10^{-4}$ mbar. Individual brazing parameters were set depending on the foil composition (see Table 2).

Table 2: Chemical composition of brazing foils and base material, brazing temperature - T_b and duration at brazing temperature - t_b

Material		**Chemical composition in weight %**								**Brazing conditions**	
ISO 17672	VITROBRAZE® designation	Ni	Fe	C	Cu	Cr	Mo	Si	B	T_b [°C]	t_b [min]
Ni610	VZ2111	75.5	4.2	≤ 0.06	-	13	-	4.5	2.8	1130	30
Ni620	VZ2120	82.3	3	≤ 0.06	-	7	-	4.5	3.1	1080	30
-	VZ2150	73.3	-	≤ 0.1	-	18.2	-	7.3	1.2	1190	30
Ni661	-	76.3	-	≤ 0.06	-	15	-	7.3	1.4	1190	30
-	VZ2106	44	35	≤ 0.1	1	11	1.5	6.4	1.5	1190	30
Cu102	-	-	-	-	99.95	-	-	-	-	1130	30
Stainless steel 316L		12	68	≤ 0.03	-	17.5	2	≤ 1	-	-	-

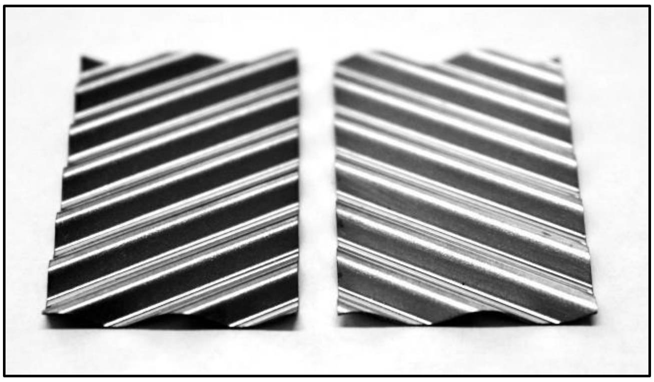

Figure 1: Embossed stainless steel 316L samples (25 mm x 40 mm) prior to assembling and brazing

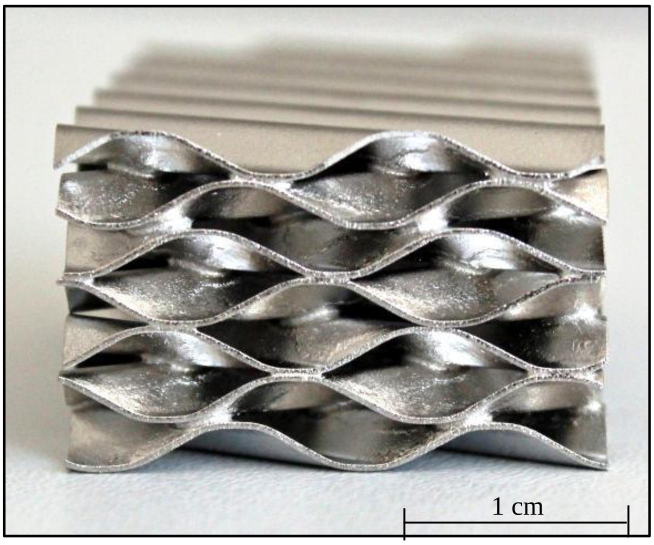

Figure 2: Vacuum brazed specimen using VZ2150 brazing foil as filler material.

To investigate the metal leaching behavior of the plain metals as well as of the brazed specimens, an immersion test using the local drinking water quality was carried out. A detailed analysis of the local water quality is given in Table 3. Due to the elevated values of hardness and electrical conductivity, this water quality may become problematic under corrosive considerations.

After cleaning and activation of the metal surface of the brazed specimens by rinsing them for 24 h with drinking water, each specimen was completely submerged for 360 h in a closed plastic beaker (Ø 68 mm, h = 80 mm) containing 60 ml of fresh local drinking water. After this test cycle, the specimen was removed from the beaker and the water samples analyzed by means of inductive coupled plasma emission spectrometry to determine the metal concentration leached into the water. For this analysis, a standard analytical instrument, an Agilent Technologies ICP-OES 720 Series Axial, was used. The accuracy of the measurement is within 1-5 % when measuring the amount of heavy metals in aqueous solutions. The lower detection limit for nickel and iron is5 µg/l, chromium 2 µg/l and for

Table 3: Quality data of the local drinking water used for this investigation (Water treatment plant II, Hanau, Germany).

Compound		**Unit**	**Averaged value**
Temperature		°C	14
pH-value			7.9
Electrical conductivity		µs/cm	637
General hardness		mmol/l	2.55
Hydrogen carbonate	HCO_3^-	mmol/l	3.06
Carbon dioxide	CO_2	mmol/l	0.2
Dissolved oxygen	O_2	mmol/l	0.3
Calcium	Ca	mg/l	75.2
Chloride	Cl	mg/l	66.5
Chlorine dioxide	ClO_2	mg/l	0.06
Iron	Fe	mg/l	0.017
Nickel	Ni	mg/l	< 0.005
Fluoride	F	mg/l	0.1
Potassium	K	mg/l	7.1
Magnesium	Mg	mg/l	15.7
Sodium	Na	mg/l	35.2
Nitrate	NO_3	mg/l	7.4
Phosphate	P_2O_5	mg/l	1.2
Sulfate	SO_4	mg/l	69.9
Total organic carbon	TOC	mg/l	1.8
Uranium	U	mg/l	0.0003

copper it is 3 µg/l. Values below these limits will be displayed as n.n. - not noticeable. To determine the time dependent metal leaching behavior of the brazed samples a long-term investigation over several test cycles was carried out, because it is well known that due to a passivation process the metal leaching rate of brazed components will reduce after some weeks in service [6,10,13].

To obtain the metal leaching of the individual plain materials the immersion test, following the same testing routine, was carried out using material samples with a total surface area of 140 cm^2. Due to the absence of grain boundaries and their better chemical homogeneity, amorphous metals offer much better corrosion resistance than their crystalline counterparts. As this will certainly influence the metal leaching rate, the amorphous VITROBRAZE® foils were converted to the crystalline state by applying a heat treatment at 500°C for 1 h, which is above the crystallization temperature – T_x of the alloys. The Cu102 foil was tested without heat treatment.

To avoid contamination, the brazed specimens as well the water sample were not in contact with any other metallic component during the entire test procedure. The water sampling was always done after rinsing the water line for 15 minutes. For each test cycle, one plastic beaker with water, but without metal specimen, was processed and analyzed for reference. The analyzed metal content of the reference water was subtracted from values of the metal samples.

Results and Discussion

Plain brazing alloys

In contact with the local drinking water, all tested brazing foils show significant metal leaching for some elements, whereas the plain stainless steel 316L did not release any measurable amount of metal ions. The obtained values for one test cycle are shown in Table 4. Dependent of the chromium and boron content, all nickel foils release different amounts of nickel into the water. The nickel values decrease from Ni620 (777.2 µg/l) → Ni610 (463.5 µg/l) → Ni661 (174 µg/l) → VZ2150 (24.4 µg/l). Metal ions of chromium or iron could not be detected. For the copper foil Cu102, a copper leaching of 754 µg/l could be measured. With the release of only 17.4 µg/l nickel, the lowest metal leaching value is obtained for the Fe/Ni-Cr foil VZ2106.

Brazed stainless steel specimens

In figure 3 a comparison of the measured metal leaching values for the first test cycle of the brazed specimens is shown. Significantly different metal leaching rates were obtained for the brazed specimens when compared to the metal leaching of the plain brazing alloys. The type, as well as the quantity of the released elements differs from alloy to alloy. The variation of the brazing alloy in the brazed specimens leads to significant differences of their metal leaching behavior. The results obtained from the first test cycle showing the highest values for all tested material combinations.

The nickel brazed specimens using the brazing alloys Ni620 and Ni610, containing a relatively high boron amount of approximately 3 wt.%, exhibit the highest metal leaching within this test, whereas the modern nickel brazing alloys containing lower boron content (≤ 1.5 %) and higher chromium concentration release substantially less metal ions into the drinking water. In addition to nickel, a fairly substantial release of iron could be measured for all nickel brazed specimens. The specimen using Cu102 as brazing alloy released a copper concentration of 1074 µg/l into the water. Furthermore, nickel concentration of 116 µg/l and iron concentration of 5 µg/l was measured. The release of nickel out of austenitic stainless steel joints brazed with copper are in accordance with the results obtained by [9,10]. The microstructural analysis (Figure 4) of the Cu102 brazed specimen exhibits a selective corrosive attack along the grain boundaries of the copper crystals even if the exposure time in drinking water was only 360 h (one test cycle). The lowest amount of 6.7 µg/l metal ions could be detected for the specimen brazed with the Fe/Ni-Cr brazing foil VZ2106.

Long term investigation of brazed stainless steel specimens

At the initial test cycle the specimens using the brazing alloys Ni661, VZ2150 and VZ2106 release substantially lower amounts of metal ions into drinking water than obtained for the Cu102 brazed specimen. To determine the time dependent metal leaching behavior of these promising specimens a long term investigation was carried out.

Table 4: Metal leaching of the individual plain alloys into drinking water. Total sample surface was 140 cm^2, immersion time 360 h. ABF's are tested in crystalline state (after heat treatment of 500°C for 1 h). Stainless steel 316L was tested in a heat treated condition at 1190°C for 0.5 h in a vacuum furnace. Values are given in µg/l.

Alloy	Cu	Ni	Fe
Cu102	754.0	n.n.	n.n.
Ni610	n.n.	463.5	n.n.
Ni620	n.n.	777.2	n.n.
Ni661	n.n.	174.0	n.n.
VZ2150	n.n.	24.4	n.n.
VZ2106	n.n.	17.4	n.n.
SS316 L	n.n.	n.n.	n.n.

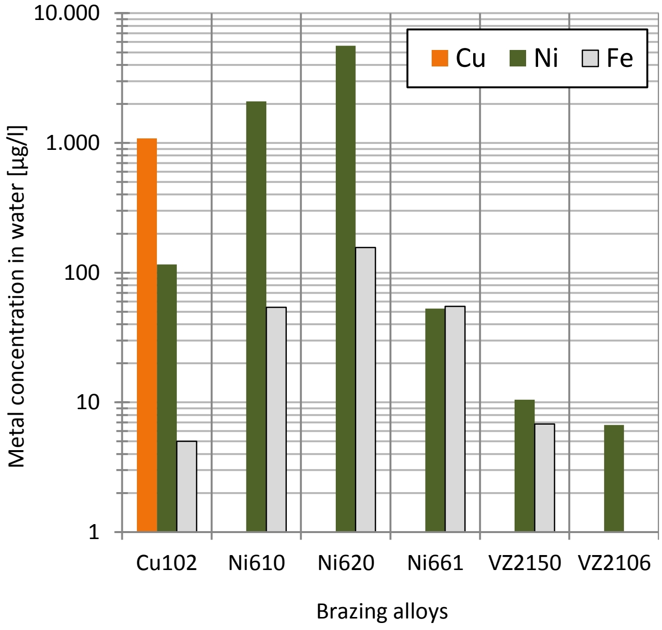

Figure 3: Metal leaching into drinking water of brazed 316L specimens joined using various brazing alloys. Values are given for the 1st immersion cycle (360 h).

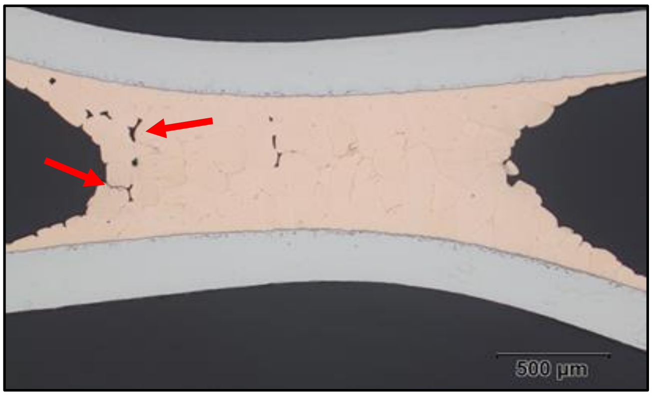

Figure 4: Microstructure of a 316L specimen brazed with Cu102 after 360 h immersion in drinking water. Selective corrosive attack could be observed at the grain boundaries of the copper crystals (red arrows).

Figure 5 compares the nickel leaching of these samples over a period of 6 test cycles. The brazed specimen using VZ2106 show a rapid passivation and did not release any detectable level of metal ions into the drinking water for all further test cycles. The metal leaching for the brazed VZ2150 specimen dropped below the detection limit at the 6th test cycle, and for the Ni661 specimen at the 5th test cycle. For the Cu102 brazed specimen, a distinct release of copper and nickel ions could be measured for all test cycles.

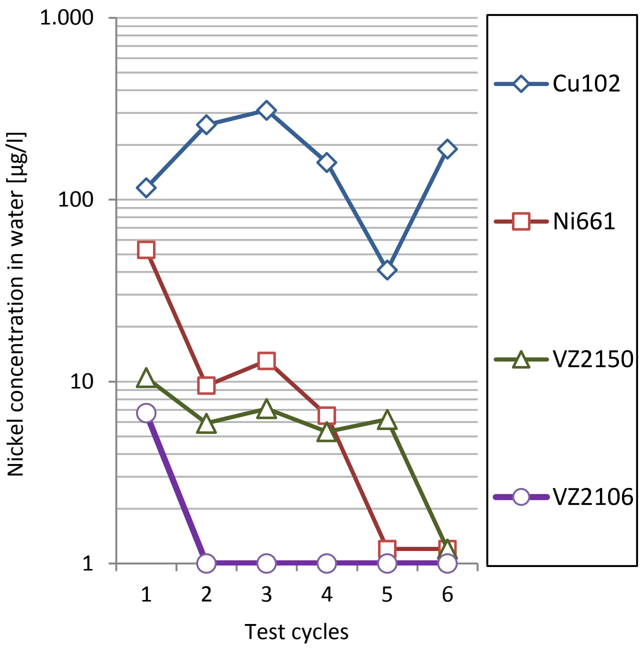

Figure 5: Nickel leaching of brazed specimens into drinking water using various brazing alloys measured over a period of 3 months (360 h per test cycle).

In table 5, the results for the 1st and 6th test cycle are compared and lead to the conclusion that the tested Ni-Cr and Fe/Ni-Cr brazing foils are promising candidates offering a lower susceptibility to corrosion and the associated metal ion leaching. With these compositions it might be possible to obtain brazed stainless steel components offering an improved hygienic suitability over the state of the art copper brazing alloys for drinking water applications.

The metal leaching of brazed stainless steel structures into an aqueous solution is a complicated process affected by many chemical, electrochemical and metallurgical variables. Unexplained today are the mechanisms leading to the significant nickel leaching of the copper brazed specimens. There is no doubt that it originates from the austenitic stainless steel, but it was unexpected that no comparable amounts of iron and chromium could be detected since a corrosion process of the stainless steel was assumed. Explanations for this phenomenon may be found on the metallurgical side of braze joint formation. nickel is soluble in copper at all concentrations, whereas iron and chromium are insoluble in copper at room temperature. During brazing operation at about 1120°C a partial dissolution of the stainless steel into the liquid copper will occur. During the following cooling and solidification of the joint, a precipitation of iron and chromium crystals will take place at the grain boundaries of the Cu(-Ni) solid solution. Thus, a local corrosion cell is formed leading to an accelerated selective corrosive attack at the grain boundaries of the affected Cu(-Ni) solid solution if they are in contact with a conductive aqueous solution. This may explain our findings of the selective corrosive attack at the copper joint visible in Figure 4. However, further studies are necessary to investigate the involved corrosion mechanisms.

The corrosion resistance of stainless steel is mainly influenced by the presence and the quality of a protective chromium oxide surface layer. Against this, the positive results of brazed VZ2106 joints are surprising. Although the chromium content of this Fe/Ni-Cr brazing foil is lower than for the Ni-Cr foil VZ2150 (11 % vs. 18 %), the metal leaching into drinking water is on an outstanding low level. The underlying corrosion mechanisms are not clear yet and will be object for further studies. Clearly, the molybdenum and copper additions of the VZ2106 alloy will have a beneficial effect to the quality of the protective oxide layer. But it is assumed that also electrochemical aspects will lead to the superior corrosion resistance of this alloy. An investigation of the current density potential of these brazed structures is necessary to complete this research work.

All obtained results can vary with the quality of the individual drinking water. For other water qualities, different results may be obtained.

Table 5: Total amount of Cu+Ni+Fe metal ions leached from brazed 316L specimens into drinking water.

Brazing alloy	Total metal leaching of Cu+Ni+Fe [µg/l]	
	Test cycle 1	*Test cycle 6*
Cu102	1195.0	820.0
Ni661	108.0	n.n.
VZ2150	17.3	n.n.
VZ2106	6.7	n.n.

Summary

The metal leaching of brazed stainless steel specimens into drinking water was examined. As part of this investigation it appears that drinking water is a corrosive environment demanding a high corrosion resistance of the brazing alloy to obtain an non-critical metallurgical bond in terms of hygienic considerations. The obtained results confirmed that it is not possible to characterize corrosive or hygienic aspects of a braze joint by studying the individual materials. It is imperative to analyze the metallurgical bond and the activities of the involved materials with respect to their thermal processing. A general statement as to whether a pure brazing alloy will release more or less metal ions into water than a brazed joint cannot be given. It was found that not all nickel brazing alloys are comparably suitable for drinking water applications. It must be assumed that the nickel brazing alloys Ni610 and Ni620, containing a high boron content of about 3 wt.%, are not applicable because they release high values of nickel into the water. The specimens brazed with the Ni-Cr alloys Ni661, VZ2150 and the Fe/Ni-Cr alloy VZ2106, containing a lower boron content of ≤ 1.5 wt.%, exhibit the lowest metal leaching rates within our tests and show them to be much more convenient for drinking water applications.

Our obtained results confirmed the assumption that copper brazed 316L joints release a significant amount of nickel in addition to copper and iron. A clear root cause for this specific characteristic could not yet be determined. For the brazed specimens using the Ni661, VZ2150 and VZ2106 brazing foils we have obtained a significantly lower nickel leaching rate than for the copper brazed specimen. The general leaching of metal ions (Cu+Ni+Fe) for the Cu102 brazed specimen is orders of magnitude higher than for the specimens brazed with the above mentioned Ni-Cr and Fe/Ni-Cr brazing foils.

The investigation of the corrosion mechanisms leading to the comparably low metal leaching of some Ni-Cr and Fe/Ni-Cr brazed stainless steel structures will be object of further research work.

With respect to the minimization principle, only materials or components releasing a minimum of substances into the water should be used for drinking water applications. It was shown that brazed stainless steel components using chromium and nickel containing brazing alloys exhibit significantly better hygienic suitability than state of the art copper brazed components.

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