Höganäs

Brazing filler metals for low metal ion leaching in drinking water applications

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Abstract

The quality of drinking water is affected by metal ions introduced through leaching from materials that come in contact with it, such as pipes, fittings and heat exchangers. Regulatory authorities have established maximum permissible quantities of metal ions in drinking water. In brazed components, the leaching of metal ions can be observed due to the interaction of both the base material and the brazing filler metal in contact with the water. With the correct selection of base material and brazing filler metal this effect can be minimized. The metal ion leaching of AISI 316L components brazed with different filler metals, Cu-foil (99.9% Cu), BNi-5, BrazeLet® Ni613, BrazeLet F300-20 and BrazeLet F86, was investigated and compared to suggest the best choice for minimizing the amount of metal ions leached into the water. Cu, Cr, Fe, Mn, Mo and Ni concentrations in water were measured by ICP every two weeks over a total test period of 12 weeks. The effect of water temperature on the metal ion leaching rate was investigated by comparative testing at room temperature and 80 °C. At 80 °C, the total metal ion leaching over a period of 12 weeks was highest for Cu-foil. BrazeLet F300-20 performed best with no measurable leaching. At room temperature, the total leaching of Cu and Ni ions was higher than at 80 °C for all the alloys tested except BNi-5. Cu-foil showed highest leaching of Cu ions, while BNi-5 showed the highest leaching of Ni ions. The passivation of the brazed joint, which leads to the decrease in the metal ion leaching with time, was accelerated with higher temperature. Metallographic examination showed that for Cu-foil corrosion can be observed in both the base material and filler metal, while for BNi-5 it was only seen in the eutectic structure of the brazing filler material. No significant corrosion could be observed for BrazeLet Ni613, BrazeLet F300-20 or BrazeLet F86.

Introduction

The United Nations recognizes the right to safe and clean drinking water as a human right [1]. Drinking water guidelines and standards exist to enable the provision of clean and safe water for human consumption [2][3][4], based on scientifically assessed acceptable levels of toxicity to humans or aquatic organisms. One class of water contaminants are metal ions. These can be present in the groundwater but can also be introduced into the water through leaching from materials that come in contact with it, such as pipes, fittings and heat exchangers. It varies between the regulations whether the limits shall be considered for worst case (single analysis value after long stagnation period), or of a representative human consumption pattern over a given period of time (e.g. 1 week).

Table 1: Regulatory limits for elements relevant to stainless steel brazed components. All values in µg/L.

Element	EU directive 2020/2184	WHO Guideline2017	U.S. EPA 2009
Fe	200	-	-
Cr	50	50	100
Cu	2000	2000	1300
Ni	20	70	- (Note 1)
Mn	50	-	-

Note 1: EPA have not specified a limit for Ni in the current regulation. In previous revisions, a limit of 100 µg/L was specified, but this has been remanded back to EPA for furtherconsideration and no limit is currently specified.

With the threshold values established as shown in Table 1, the question then becomes how to test the brazed components in a relevant way to ensure that they are suitable for the application. There are a number of test standards available. Most commonly referred to is SS-EN 15664-1/2 [5][6], but SS-EN 15664-1 is only applicable for individual materials and not for the overall product. For brazed components, SS-EN 16058 [7] is sometimes considered a more relevant option although this test standard is developed for evaluation of products covered with a Ni layer (e.g. Ni-plating). DIN 50930-6 [8], provides a list of materials that are considered acceptable for use in contact with drinking water, but this only covers the individual materials by themselves and does not reflect how the base material interacts with a brazing filler material. DIN 50930-6 does open for use of Ni-base brazing filler metals in brazed components for drinking water applications by the 5% ordinance, allowing use of these materials if the area in contact with drinking water is not exceeding 5% of the total surface area in contact with

drinking water. Although this could be evaluated relatively easily for a simple tubular heating element design, it cannot easily be confirmed that a complex brazed plate heat exchanger will meet the same requirement. The area covered by brazing filler material will depend on numerous factors such as the base material grade, the brazing filler metal composition, the component design, the brazing filler metal application process and applied amount and the brazing process conditions. For most conventional stainless steel brazed plate heat exchangers, the plate area covered by brazing filler material exceeds 5%.

Material selection must ensure suitably low leaching of metal ions while still meeting the other functional requirements. In the recent years, Höganäs have seen an increased amount of requests from producers of brazed plate heat exchangers and other brazed components for drinking water applications to reduce the metal ion leaching, particularly of Ni and Cu ions.

A commonly used base material for heat exchangers is austenitic stainless steel, which shows good thermal properties, corrosion resistance and strength, and is suitable for use with drinking water due to its low leaching of metal ions. As for the brazing filler metals, both Cu- and Ni-based brazing filler metals are well-established in the industry. Due to the better corrosion resistance and better hygienic suitability of the brazed components with Ni-based filler materials, brazed plate heat exchangers are increasingly being joined with Ni-base brazing fillers materials [9][10]. Fe-based brazing filler metals are also used in the manufacture of heat exchangers, and former investigations on the metal ion leaching behavior of Fe-base brazing filler metals have shown improved results compared to conventional Ni-base brazing filler metals [11]. Heat exchanger units brazed with copper as brazing filler metal are considered to have shorter service spans and require more frequent replacement due to poor corrosion resistance compared to heat exchangers brazed with Ni-base brazing filler metals [12][13].

An increased focus on sustainability further promotes the exchange of Cu-brazed heat exchangers to Ni-brazed and Fe-brazed heat exchangers. Measures shall be taken to reduce the leaching of metal ions such as Cu and Ni-ions to drinking water and subsequently wastewater. A closely related consideration is circularity, as Cu is unwanted in scrap steel. This focus has led producers of brazed plate heat exchangers to select Ni- or Fe- base brazing filler materials over Cu, even for applications where it technically is not strictly required.

Standard Ni-base brazing filler materials such as BNi-5, BNi-7 and B-Ni60CrPSi (BNi-15) were evaluated by Hoyer et al., with the brazing filler material covering the complete stainless steel insert surface according to SS-EN 15644-1 [5]. They found that all the three brazing filler materials remain clearly under the tolerable level of Ni-ion leaching of 20 µg/L, but these results cannot be extrapolated to an actual brazed component. Hartmann took a more practical approach, preparing brazed plate heat exchanger samples of AISI 316L austenitic stainless steel brazed with BCu-3, BNi-5b and VITROBRAZE® brazing foil compositions VZ2150 and VZ2106, and submerging these in stagnant drinking water at room temperature for a total test duration 3 months, and observed the lowest metal ion leaching with VZ2106 [10].

All of the evaluations of metal ion leaching for Ni-base brazing filler materials for drinking water applications have shown that metal ion leaching was highest in the beginning of the test, and decrease with time due to formation of a passivation layer. Passivation is dependent on the water chemistry and temperature, and the process can take a long time before metal ion leaching is reduced to low or insignificant levels. For components where initial metal ion leaching until passivation occurs is not tolerable, a post-brazing conditioning step in an oxygen-containing atmosphere has been suggested by Rabinkin for formation of a surface oxide layer to decrease the initial Ni- ion leaching [13].

Immersion tests of brazed exchanger samples in water to relatively compare the amount of metal ion leaching for different filler metals such as performed by Hartmann [10], can give us an idea of which brazing filler metals are better suited for use in drinking water applications. Although investigations on Fe-base brazing filler materials have shown reduced metal ion leaching compared to Ni-base brazing filler materials [11], the tested alloys in this paper were not commercially available products used by the industry. To offer a more valid alternative, and to further strengthen material selection considerations for drinking water applications, Höganäs' standard Fe-base brazing filler materials BrazeLet F300-20 and BrazeLet F86 are evaluated together with standard Ni-base brazing filler materials and Cu-foil as reference materials.

Experimental procedure

AISI 316L heat exchanger plates with 0.3 mm thickness and typical fishbone pattern were provided by a manufacturer of brazed plate heat exchangers, formed by simultaneous pressing with Cu-foil. Sections of 70 x 25 mm were cut out from the provided plates. The composition of the plates was analyzed by ICP-OES, and is given in Table 2.

Table 2: Chemical analysis of AISI 316L plates

Fe	Cr	Ni	Mo	Mn	Si	Cu	C	P
Bal.	16.4	10.0	2.0	0.95	0.36	0.38	0.03	0.03

The brazing filler metals evaluated are listed in Table 3. Cu-foilof 30 µm thickness was used for the Cu-brazed sample. For theremaining samples, brazing filler metal was in the form of a water based brazing paste, applied by manual spraying, and theplates were dried in a hot air furnace prior to assembly. Eight plates were stacked in alternating direction to form each sample. Weight control of each sample was performed during each preparation step. As paste was applied by manual spraying on small plate samples, there is significant variation in the applied amount of brazing filler metal. The total amount of brazing filler metal for each sample varied in the range of 2.58 g – 7.01 g. The total base material plate weight for each sample varied in the range of 41.58 g – 44.84 g, with the resulting ratio of applied brazing filler metal weight to base material weight varying in the range of 0.06 – 0.16.

Table 3: Brazing filler materials evaluated. Nominal composition in wt%, except for Cu-foil showing actual analysis by ICP.

Material	EN ISO 17672	AWS A5.8	Ni	Cr	Si	Fe	P	Cu	Nb	Brazing temperature
BrazeLet BNi5	Ni650	BNi-5	Bal.	19	10.2	-	-	-	-	1150 °C / 2102 °F
BrazeLet Ni613	-	BNi-15	Bal.	29.5	4.0	-	6.0	-	-	1090 °C / 1994 °F
BrazeLet F300-20	-	-	20	20	4.0	Bal.	7.0	6.5	-	1100 °C / 2012 °F
BrazeLet F86	-	-	20	29	6.5	Bal.	6.0	-	0.5	1150 °C / 2102 °F
Cu-foil	-	-	0.005	0.002	0.002	0.007	0.001	Bal.	-	1120 °C / 2048 °F
Note: *BrazeLet F300-20 is a developed and patented brazing filler metal composition by Höganäs AB [14].*										

The samples were brazed in a Nabertherm VHT 40/16 Mo vacuum furnace. The ramp rate was 9 °C/min from 20 °C up to 450 °C, followed by a 30-minute hold to ensure complete removal of any polymer in the brazing paste binder. Heating was continued with the same ramp rate to the recommended brazing temperature for each brazing filler metal as specified in Table 3, where the components were held for 30 minutes followed by natural cooling in vacuum. The measured vacuum level at the brazing temperature was approximately 10^{-5} mbar for all samples, except the Cu-brazed sample which was brazed at approximately 10^{-3} mbar. A sample after brazing is shown in Figure 1.

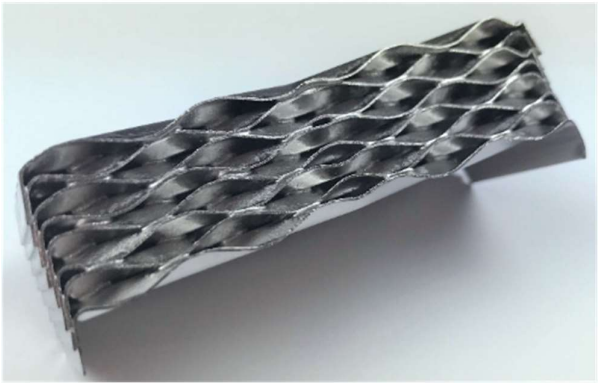


Figure 1: Brazed test sample used for immersion tests

Prior to testing each of the samples were separately rinsed for 24 h with local running tap water. Each brazed sample and the reference base material stack sample were placed into separate glass containers filled with 200 mL local tap water after two minutes flushing of the tap. Table 4 shows the average water analysis from the closest water treatment plant supplying drinking water to the Höganäs area. The containers were sealed with a plastic cover and stored either at room temperature or in a heating cabinet at 80 °C. Every second week, containers were refilled to a total volume of 200 mL with fresh tap water to compensate for any minor evaporated amount, the components were removed and water was sent for analysis. To start a new test cycle, the components were immersed in fresh tap water and the same procedure detailed above was repeated throughout 12 weeks.

At each test cycle, water was sampled and prepared for analysis on a Spectro ICP-OES ARCOS II. 0.25 mL HNO_3 and 1 mL Sc solution (200 mg/L) were added to each water sample until a total volume of 50 mL. The prepared water samples were analyzed for Cr, Cu, Fe, Mn, Mo and Ni ions with the following limits of quantification: Cr < 5 µg/L; Cu < 1 µg/L; Fe < 2 µg/L; Mn < 1 µg/L; Mo < 1 µg/L; Ni < 1 µg/L. Below these concentrations, the values are given as non-detectable (<LOQ).

Table 4: Water quality data for Höganäs drinking water (Ringsjöverket, Stehag, Sweden).

Parameter	Unit	Median value
Conductivity	mS/m	18
pH	-	8.1
Alkalinity ($HCO3^-$)	mg/L	44
Total hardness	°dH	3.4
Ca	µg/L	21.000
Al	µg/L	7.1
As	µg/L	0.105
B	µg/L	8.8
Cd	µg/L	<0.004
Cl	µg/L	26.000
Cr	µg/L	<0.050
Cu	µg/L	8.4
F	µg/L	<200
Fe	µg/L	2.6
Hg	µg/L	<0.1
K	µg/L	1100
Mg	µg/L	1500
Mn	µg/L	0.14
Na	µg/L	9300
NH4	µg/L	<10
Ni	µg/L	0.46
NO2	µg/L	<7
NO3	µg/L	<1000
Pb	µg/L	0.05
PO4-P	µg/L	<5
Sb	µg/L	<0.050
Se	µg/L	<0.5
SO4	µg/L	5800

The concentrations were given as an average value of three measurements and their standard deviation. When calculating the final results, if both sample and the pure base material were below LOQ, then values were given as <LOQ, if the sample gave a value but pure base material below LOQ, then the value of the pure base material was assumed 0 and if the value measured in pure base material is higher than or equal to the sample, the value was given as 0.

After completion of the immersion tests, the components were prepared by standard metallographic methods and investigated using a Zeiss Axio Imager.M2m Light Optical Microscope, a Leica 205M Stereo Microscope and a Hitachi SU6600 Field Emission Scanning Electron Microscope.

Results and Discussion

Cr, Cu, Fe, Mn, Mo and Ni-ion concentrations of each immersion test were obtained from ICP-analysis. The results were normalized by the amount of paste applied on each specimen. The total measured metal ion leaching is shown in Table 5, with the total leaching of each metal ion specified individually for clarity. The measured amounts of Cr, Mn and Mo were very low compared to Cu, Fe and Ni. As Fe is not of health concern, the main focus in this paper is therefore put on the Cu and Ni leaching. Focusing on the trend of Cu and Ni leaching throughout the 12 weeks test period as shown in Figure 2 and Figure 3, the specimens tested at 80 °C showed a tendency of decreasing leaching with time. This is not observed in the test at room temperature. Cu-foil showed highest Cu-ion leaching at both temperatures. Ni-ion leaching at room temperature was highest for Cu-foil, followed by BNi-5. At 80 °C, it was highest for BNi-5, followed by Cu-foil, with the other filler metals showing very low Ni-ion leaching.

Table 5: Total metal ion leaching of Cr, Cu, Fe, Mn, Mo, and Ni ions (µg/L) per 10 g of filler metal after the test period of 12 weeks at room temperature and 80 °C, with total leaching for each individual metal ion provided. →

Material	RT	80 °C
Cu-foil	7763 ± 152.4 Cr: <LOQ Cu: 6202 ± 42 Fe: 277 ± 101 Mn: 92 ± 0.6 Mo: 2 ± 0.2 Ni: 1190 ± 8.6	3451 ± 44.1 Cr: <LOQ Cu: 2523 ± 33 Fe: 61 ± 7.2 Mn: 228 ± 1.2 Mo: 10 ± 0.5 Ni: 384 ± 2.2
BrazeLet BNi5	179 ± 5.1 Cr: <LOQ Cu: 10 ± 1.4 Fe: 15 ± 2.1 Mn: <LOQ Mo: <LOQ Ni: 154 ± 1.6	1337 ± 15.1 Cr: 9 ± 0.1 Cu: 155 ± 1.5 Fe: 103 ± 4.8 Mn: 2 ± 0.1 Mo: <LOQ Ni: 1190 ± 8.6
BrazeLet Ni613	542 ± 12.0 Cr: 18 ± 0.3 Cu: 175 ± 6.9 Fe: 321 ± 2.3 Mn: <LOQ Mo: 9 ± 0.4 Ni: 28 ± 2.1	135 ± 6.4 Cr: <LOQ Cu: 30 ± 0.9 Fe: 103 ± 4.8 Mn: <LOQ Mo: <LOQ Ni: 2 ± 0.7
BrazeLet F300-20	235 ± 69.3 Cr: 67 ± 0.7 Cu: 65 ± 14 Fe: 92 ± 52 Mn: <LOQ Mo: <LOQ Ni: 11 ± 2.6	< LOQ Cr: <LOQ Cu: <LOQ Fe: <LOQ Mn: <LOQ Mo: <LOQ Ni: <LOQ
BrazeLet F86	311 ± 9.5 Cr: <LOQ Cu: 209 ± 7.6 Fe: 86 ± 0.7 Mn: <LOQ Mo: 5 ± 0.4 Ni: 11 ± 0.8	92 ± 10.4 Cr: <LOQ Cu: 14 ± 0.8 Fe: 71 ± 9.1 Mn: 4 ± 0.0 Mo: 3 ± 0.5 Ni: <LOQ

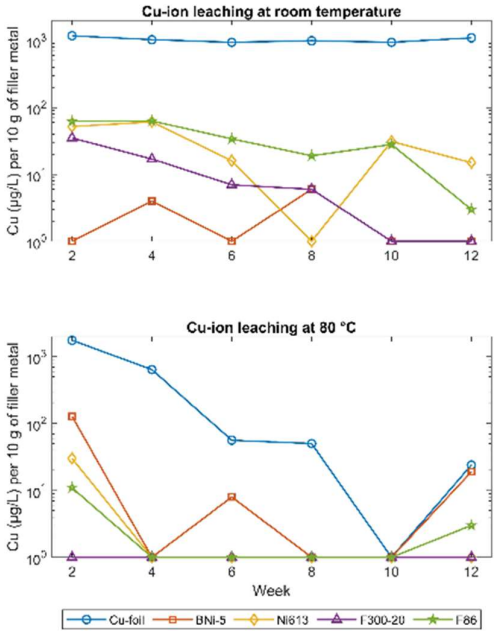


Figure 2: Measured Cu-ion leaching each sampling interval for the evaluated brazing filler metals for at room temperature and 80 °C.

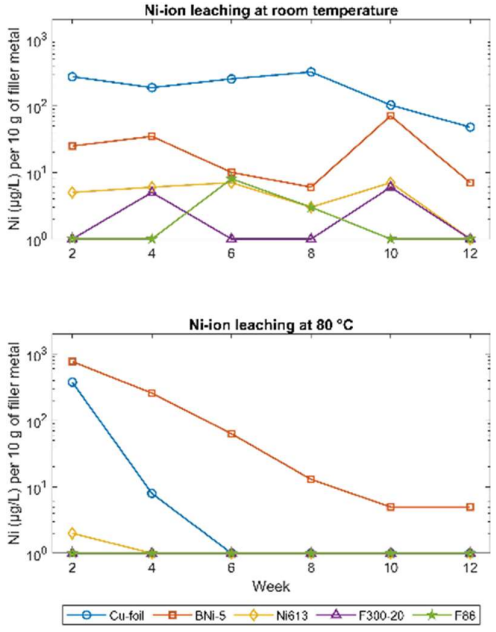


Figure 3: Measured Ni-ion leaching each sampling interval for the evaluated brazing filler metals for at room temperature and 80 °C.

Cu-foil

The specimens brazed with Cu-foil showed a high and stable Cu ion leaching at room temperature throughout the whole test period. When tested at 80 °C, the initial leaching rate is also very high, but this decreases to low values similar to the other brazing filler metals towards the end of the 12 week test period. The Cu-brazed samples also show the highest Ni-ion leaching of all the tested brazing filler materials at room temperature, with no significant decrease over time. At 80 °C a high initial Ni-ion leaching is observed, decreasing towards the end of the test period. The Cu- and Ni-ion leaching is coming from both the brazed joint fillets, but also from the other surfaces of the heat exchanger sample as most of the internal surfaces are covered with a thin layer of Cu after brazing. In the samples exposed to room temperature, the appearance of this Cu layer remains with a metallic appearance, while the sample exposed at 80 °C show visible signs of oxidation of the Cu with a green tinted layer covering the surfaces. This green colour indicates the formation of insoluble malachite ($Cu_2(OH)_2CO_3$), which acts as a protective film preventing further corrosion. The observed reduction in metal ion leaching over time for the samples exposed to 80 °C is attributed to the formation of this protective copper carbonate layer. Copper carbonate is a major factor in controlling the amount of free copper ions in solution in drinking water, and remains stable for pH 6.0 – 9.3 [15]. The absence of passivation at room temperature is consistent with the results of Hartmann, which reported high Ni-ion leaching for the Cu-brazed specimen throughout the three-month test cycle [10]. Previous investigations have established Ni- leaching from Cu-brazed joints occurs by two mechanisms [9][10]. Firstly, the full solid solubility of Ni in Cu leads to a related Ni-leaching as the Cu-brazed joint corrodes. Secondly, the exposed base material surface that has been covered with a Cu-layer is sensitive to intergranular corrosion due to Cu- penetration along grain boundaries, which can lead to detachment of base material grains. The Ni-concentration in the Cu-brazed joint is relatively low after brazing measured by EDS to max. 1.6 wt% Ni close to the interface line in the fillet area. Hence, corrosion of the Cu brazing filler metal alone does not explain the high Ni-ion leaching values observed.

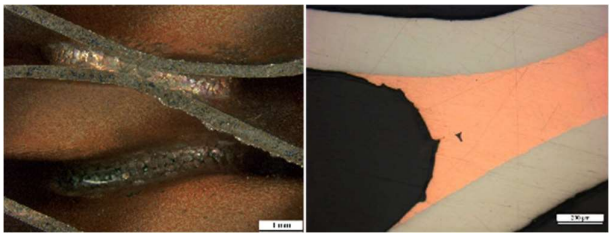


Figure 4: Cu-brazed sample - room temperature

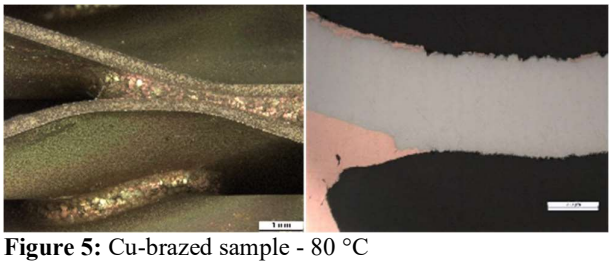


Figure 5: Cu-brazed sample - 80 °C

BNi-5

The specimen exposed at room temperature showed a moderate Ni-ion leaching, and did not show any clear passivation. The sample exposed at 80 °C showed much higher Ni-ion leaching, especially for the first two-three sampling intervals, and then decreased down to low levels from week 10 onwards. The total Ni-ion leaching over the full test duration is much higher for the 80 °C sample (1110 µg/L) compared to the room temperature sample (154 µg/L), which is also evident from the metallographic investigation. Minor corrosion attacks of the eutectic structure in the room temperature sample, while the sample exposed to 80 °C exhibits severe corrosion of the eutectic structure in the fillets. The primary Ni-Cr-Si-(Fe) (ss) growing from the base material interface remained unaffected. The Ni-(Cr)-silicides found in the eutectic structure have excellent corrosion resistance, particularly in acidic conditions, and it is likely that the difference in corrosion potential between the different phases in the eutectic structure, has promoted corrosion by micro galvanic corrosion.

BNi-5 is showing the opposite behaviour compared to all the other brazing filler metals evaluated, with higher total metal ion leaching for the sample exposed to 80 °C compared to the sample exposed to room temperature. The root cause for this cannot be concluded from these trials, and needs further investigations. Although the sample exposed to 80 °C eventually shows a passivation, the corrosion attack before coming to this point is significantly more extensive. This is consistent with the investigations performed by Fukai et al. studying the corrosion behaviour of BNi-5 at 25 °C and 80 °C [16]. At 80 °C the formation of a passivating oxide layer is suppressed and corrosion propagates by micro galvanic corrosion. At higher temperatures the potential difference between AISI 316L base material and the Cr-poor eutectic structure, led to increased corrosion rates.

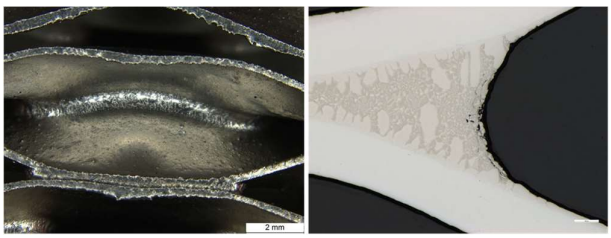


Figure 6: BNi-5 sample - room temperature

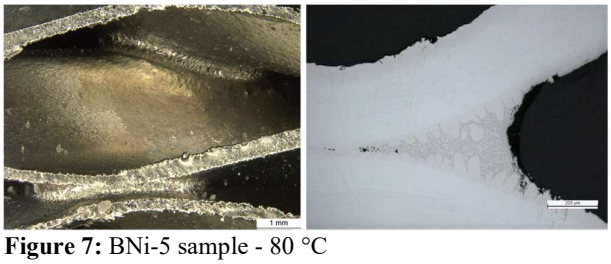


Figure 7: BNi-5 sample - 80 °C

BrazeLet Ni613

BrazeLet Ni613 is widely used as a brazing filler material with very high corrosion resistance, attributed to the high Cr content in combination with Si. The test samples exposed to room temperature showed low amounts of Ni-ion leaching, and complete passivation by week 12 at the end of the test. In the test samples exposed to 80 °C, the passivation occurs considerably faster and a low amount of Ni-ion leaching can only be measured in the first sampling, with no further measurable Ni-ion leaching for the remainder of the test period. Of other elements, some Fe-ion leaching can be measured at both temperatures, with the room temperature sample showing the highest values. As the measured Ni ion leaching results at the same sampling intervals is very low or insignificant it is considered unlikely that the Fe ion leaching originates from corrosion of the brazing filler metal, but rather is a result of minor corrosion of the base material surface. The most considerable Fe-ion leaching occurs close to or after the point of passivation of the brazing filler metal, which further supports that it is the base material corroding.

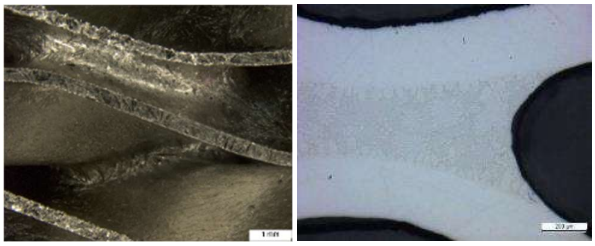


Figure 8: BrazeLet Ni613 sample - room temperature

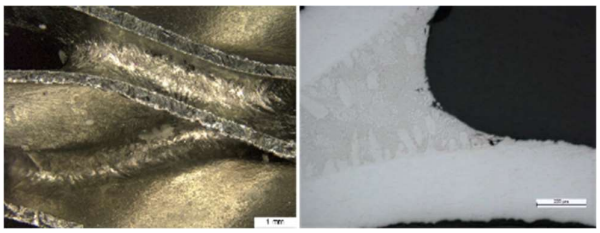


Figure 9: BrazeLet Ni613 sample - 80 °C

BrazeLet F86

The BrazeLet F86 specimens show very low amounts of metal ion leaching. For the room temperature sample, the measured total Ni-ion leaching is the lowest of all the samples tested at the same condition (together with BrazeLet F300-20). For the sample exposed to 80 °C, no measureable Ni-ion leaching is observed. Some Fe-ion leaching is measured, but to a lower extent than all other brazing filler metals except BNi-5 and BrazeLet F300-20. The metallographic investigation revealed some imperfections in the fillet surface, which might have developed further by corrosion to a minor extent although this cannot be concluded from the metallographic investigations. Such imperfections in the fillet surface can sometimes be observed in BrazeLet F86 brazed joints and can be avoided by applying less / the correct amount of brazing filler metal. In these samples, the applied amount was significantly higher than the recommended amount. Overspray is observed on the plate surfaces outside the joint area, which further indicates the potential to reduce the applied amount. The only leaching really observed for BrazeLet F86 was Cu-ion leaching at room temperature. This is likely coming from the plate surface as the AISI 316L plates were stamped together with Cu-foil, and analysis of the AISI 316L plate material showed 0.38 wt% Cu.

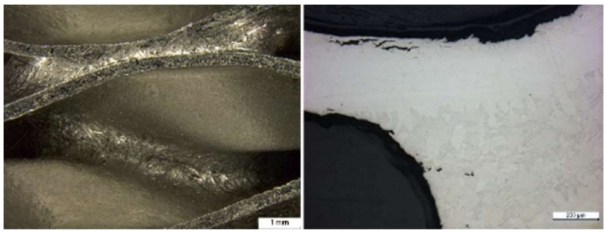


Figure 10: BrazeLet F86 sample - room temperature

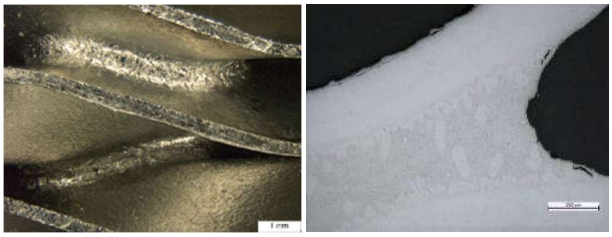


Figure 11: BrazeLet F86 sample - 80 °C

BrazeLet F300-20

The BrazeLet F300-20 specimens showed the lowest amount of metal ion leaching in the entire study. In the specimen at room temperature, only minor Cu-ion leaching was measured for the first eight weeks of the test period. The total Ni-ion leaching at room temperature was the lowest of the brazing filler metals evaluated (at the same value as BrazeLet F86). At 80 °C no metal ion leaching could be measured for any of the elements analyzed (Cr, Cu, Fe, Mn, Mo, Ni) as any metal ion concentration was lower than the limit of quantification (LOQ). From the metallographic investigation, no visible corrosion attack can be seen. Some minor defects in the fillet surface can be found and is normal for BrazeLet F300-20, particularly if the amount of brazing filler material is high as is the case here.

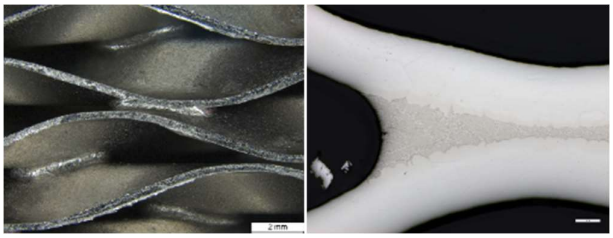


Figure 12: BrazeLet F300-20 sample - room temperature

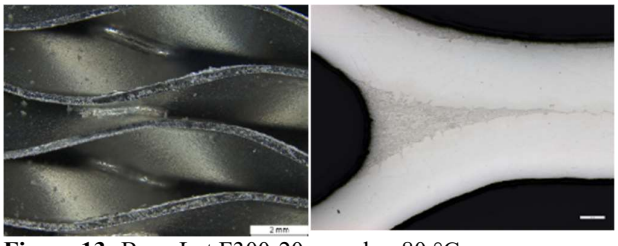


Figure 13: BrazeLet F300-20 sample - 80 °C

Effect of water temperature

A decrease in metal ion leaching with time has also been seen in other studies [9][10][11][17]. These previous studies were all performed at room temperature and attributed this decrease to the passivation of the brazed joint. The formation of a protective film inhibits further corrosion by creating a physical barrier to the contact of water with the brazing filler metal.

During this evaluation, the trend of decreasing metal ion leaching with time was clearly observed during the tests at 80 °C, but was not as evident at room temperature. Higher temperature promotes the formation of a protective oxide layer, or in the case of Cu a carbonate layer. Some of the measured leaching values were very low and any trend might have been difficult to observe due to the uncertainty of the measurement itself. In dynamic rig tests such as SS-EN 15664-1, faster passivation can be expected compared to stagnant immersion tests due to the semi-continuous supply of fresh drinking water with higher dissolved oxygen content.

Effect of brazing filler metal amount

It is important to note that in all samples a higher than recommended amount of brazing filler metal is applied and this can affect the amount of leaching observed. There are significant variations in the amount of paste and therefore brazing filler metal applied on the samples due to the application method with manual spraying and small samples. For larger scale production of brazed plate heat exchangers there are a number of more adequate methods to apply brazing paste in a controlled manner.

A larger amount of brazing filler metal applied can be found to increase the likelihood of corrosion primarily in two different ways. First, the larger amount of brazing filler metal applied will generally increase the size of the brazing fillets which increase the tendency of surface voids and defects caused by solidification shrinkage. These voids can act as initiation sites for corrosion. Second, the larger brazing fillets can also have a different microstructure, with an increased tendency for intermetallic phases. This can increase the tendency for preferential corrosion of certain phases in the microstructure. For BNi-5 this can clearly be seen with the eutectic structure corroding preferentially, while the Ni-Cr-Si-(Fe) (ss) primary phase is remaining without significant corrosion attack. Although corrosion might stop before compromising the joint integrity as the narrow joint has another microstructure, considerable metal ion leaching can result. How critical the applied amount is depends on the brazing filler metal used, and has in particular been found to affect the corrosion resistance of BrazeLet F86, BrazeLet F300-20 and BNi-5.

Summary and comparison with previous investigations

Looking to the metal ion leaching results, there are clear and significant differences between the various brazing filler metals evaluated in this work. It is found that Fe-based brazing filler metals show clearly lower amounts of total metal ion leaching, and particularly Ni-ion leaching compared to Ni-base and Cu- base brazing filler metals. This represents a technical advantage of the Fe-based brazing filler metals on top of the cost reduction compared to Ni-base brazing filler metals.

Local tap water available at the lab (Höganäs, Sweden) was used during the evaluation due to easy availability but it should be noted that the water quality used for the tests can greatly influence the results. Parameters such as dissolved oxygen, conductivity, chemical composition of the water (e.g. alkalinity, sulphate and chloride content), hardness and pH have a big impact on the corrosion phenomena that cause the metal ions leaching. Brazed plate heat exchanger manufacturers such as SWEP International AB have clear recommendations for which base material and brazing filler materials are recommended for different water chemistries [18]. For corrosion resistance in water which is closely related to metal ion leaching, we find that copper-brazed heat exchangers, are more sensitive to the water chemistry compared to Ni- or Fe-brazed heat exchangers.

Hoyer et al. and Wielage et al. evaluated test tubes where brazing filler metal was applied onto the inner surface and then brazed [9][11][17]. This does not give the same contacts and galvanic interactions as would be observed in a brazed plate heat exchanger. The relevancy of their EN 17672 Ni650 (BNi- 5) and B-Ni60CrPSi (BrazeLet Ni613) results are hard to evaluate as the microstructure of the surface layer is unknown and the brazing is performed at a higher temperature.

Conclusions

» The main metal ion species relevant for the industry is Cu and Ni-ions. Cu-ion concentration in drinking water is restricted to 2000 µg/L in EU and 1300 µg/L in US, while Ni-ion concentration is restricted to 20 µg/L in EU while US is currently reviewing the requirement and have taken the former requirement of 100 µg/L out of the National Primary Drinking Water Regulation pending a final decision.

» Existing test standards to qualify metallic materials for drinking water applications, such as SS-EN 15644-1/2 are not suitable to study metal ion leaching from brazed components due to the absence of galvanic interactions. The test standard evaluates surfaces coated only by the brazing filler metal, and therefore does not reflect the interactions with the base material.

» BrazeLet F300-20 showed the lowest metal ion leaching of all the tested brazing filler metals in this investigation.

» BrazeLet F86 also showed very low metal ion leaching values, similar to BrazeLet F300-20.

» BrazeLet Ni613 showed very low metal ion leaching values at room temperature and insignificant amounts at 80 °C with quick passivation. Most leaching at room temperature was Fe-ions, attributed to minor corrosion of base material plate surfaces and not of health concern.

» BNi-5 showed relatively high amounts of Ni-ion leaching at room temperature and very high amounts at

80 °C due to severe corrosion attack of the eutectic structure in the brazed joint fillets. Leaching of other metal ion species was very low, noting that Si was not measured.

» Cu-foil showed the highest levels of Cu and Ni leaching, mostly from the Cu-rich surface layer on the base material plates. No passivation was observed at room temperature, while at 80 °C passivation significantly reduced leaching from week 6 by formation of a green layer of malachite (Cu2(OH)2CO3). Ni-ion leaching is a result of full solid solubility of Ni in Cu, where Ni in solid solution in Cu is released to the drinking water as the joint is corroded.

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References

[1] United Nations, General Assembly, (2010), *The human right to water and sanitation, A/RES/64/292*

[2] Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption, (2020), *Official Journal of the European Union L435/1*

[3] World Health Organization, (2017), *Guidelines for drinking water quality: fourth edition incorporating the first addendum.*

[4] United States Environmental Protection Agency, (2009), *National Primary Drinking Water Regulations (EPA 816- F-09-004)*

[5] Swedish Standards Institute, (2013), SS-EN 15664-1, *Influence of metallic materials on water intended for human consumption – Dynamic rig test for assessment of metal release – Part 1: Design and operation.*

[6] Swedish Standards Institute, (2010), SS-EN 15664-2, *Influence of metallic materials on water intended for human consumption – Dynamic rig test for assessment of metal release – Part 2: Test waters.*

[7] Swedish Standards Institute, (2012), SS-EN 16058, *Influence of metallic materials on water intended for human consumption – Dynamic rig test for assessment of surface coatings with nickel layers – Long-term test method.*

[8] Deutsches Institut für Normung E.V., (2013), *Corrosion of metals – Corrosion of metallic materials under corrosion load by water inside pipes, tanks and apparatus – Part 6: Evaluation process and requirements regarding the hygienic suitability in contact with drinking water.*

[9] Hoyer, I. et al., "Nickel ions in potable water and their migration out of brazing fillers and brazed joints," *Brazing, high temperature brazing and diffusion bonding. LÖT 2013: Lectures and posters of the 10th international conference taking place in Aachen on 18th to 20th June 2013. DVS Berichte 293, pp. 176-181.*

[10] Hartmann, T., "Metal Leaching of Brazed Stainless Steel Joints into Drinking Water," IBSC 2015: *Proceedings from the 6th international brazing and soldering conference, Long Beach, CA, April, 2015.*

[11] Wielage, B. et al., "Development of iron filler metals for high-temperature brazing of materials in contact with drinking water," *Brazing, high temperature brazing and diffusion bonding. LÖT 2010: Lectures and posters of the 9th international conference taking place in Aachen on 15th to 17th June 2010. DVS Berichte 263, pp. 189-195.*

[12] Rabinkin, A., "High temperature brazing development since the time of the "Bow-Tie Generation": In memory of Robert L. Peaslee," *Brazing, high temperature brazing and diffusion bonding. LÖT 2010: Lectures and posters of the 9th international conference taking place in Aachen on 15th to 17th June 2010. DVS Berichte 263, pp. 1-8.*

[13] A. Rabinkin, U.S. Patent 6,749,104.

[14] O. Mårs and U. Persson, U.S. Patent 9,193,011.

[15] World Health Organization, (2004), *Copper in Drinking Water – Background document for development of WHO Guidelines for Drinking-water Quality, WHO/SDE/WSH /03.04/88*

[16] Fukai, Y. et al., "Corrosion Behavior of Nickel-based Brazing Filler Metal for Stainless Steel Heat Exchanger", *Journal of Smart Processing, Vol. 9, No. 3 (2019), pp. 127-132.*

[17] Hoyer, I. and Wielage, B., Advances in brazing: 18. Brazing of nickel-based filler metals for pipes and other components in contact with drinking water, Woodhead Publishing Limited (Cambridge, 2013), pp. 545-565.

[18] SWEP International AB, (2021), *Recommendations regarding water for BPHEs in district energy systems*, available from: https://www.swep.net/globalassets/support/instruction-manuals/water-recommendations_en.pdf