By Jacques Jumeau 2010-02-15

1/ Introduction:

There is an actual trend in water heaters manufacturer to move from 304L or 316L stainless steel to 444 because of raw material cost. This trend started 3 years ago during the stainless steel raw material price peak driven by the nickel price. These heaters have welded parts, fittings and heating elements.
These circulation heaters are used to heat the water in swimming pools, spas, and whirlpools, and as booster heaters or main heaters in home central heating.
-Swimming pool and spas heaters water temperature will vary from about 18° C. to about 43° C, the latter being temperatures which have been described as being used in hot tubs. The pH of recreational water will optimally range between about 7.2 and 7.6 for bather comfort and efficiency of disinfection by chlorine (Cl^{+}) sanitizers.
Water is usually sanitized with chemicals to eradicate disease-carrying bacteria and algae. Chlorine and certain compounds containing chlorine are the foremost sanitizers used for disinfecting water. Chlorine gas, sodium hypochlorite solutions, calcium hypochlorite and chloro-isocyanurates are the most commonly used water sanitizers that provide free available chlorine in water to be disinfected. Bromine and certain compounds containing bromine are used similarly but to a much lesser extent. Free chlorine can also be directly injected in water by hydrolysis chlorinators using salt (Nacl).
The recommended free chlorine concentration in swimming pools is between about 1 and about 3 ppm. In hot tubs, and spas, the recommended free available free chlorine concentration is between about 1 and about 5 ppm
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Most of time, this water has unknown levels of chlorine, chloride, bromine, ozone, and other unknown additives.
-Domestic central heating main heaters or booster heaters are filled with tap water, anticorrosion additive, and antifreeze additives like glycol. They are used at temperature between 50 and 65°C. Tap water content in free chlorine vary, depending of local regulation (See annex)
Free chlorine is the most corrosive ingredient that can be found in water used in these applications, and initiates pitting and crevice corrosion..

To evaluate the chlorine corrosion resistance of stainless steel sheets, Ultimheat has set up a comparative corrosion testing process. This test is made with constant chlorine level, using piping with no or low chemical reaction with free chlorine.
It is not possible to test in exact final application, as the residual free chloride level in the circuit depends of the volume, piping material, and water composition, and decrease with time.
Accelerated testing is made at higher temperature and concentration to reduce testing time. *For more about chloride consumption by piping material, refer to: Combined chlorine dissipation, pipe material, water quality and hydraulic effects, by Ginasyio Mutoti and others, published in American water Work association journal, October 2007*

2/ Existing documentation and studies

-There is just a few comparative studies made on 444, 201, 304 and 316 raw material for chloride pitting or crevice corrosion resistance.
Some of them, supplied by raw material manufacturers are commercially oriented, and conclusion depends of the type of tests made. More, a major concern about the 444 alloy is that the pitting and crevice corrosion resistance in ferritic stainless steels are related to the addition of some minor component at levels lover than 1%. *(Effect of Alloying Elements and Residuals on Corrosion Resistance of Type 444 Stainless Steel, by N.J.E. Dowling, Y.-H. Kim, S.-K. Ahn, and Y.-D. Lee, published in "Corrosion", Volume 55, Number 02, February, 1999)* . This means that some 444 stainless steel will provide much better corrosion resistance than others.
-The most interesting report was issued by Ancome Polytechnical University (Italy) , published in 2008 in *"material and corrosion, 59, number 9 (see annex 1),* and was related to 444,304 and 316 comparative corrosion results in contact with tap water. Conclusions of this report show that 444 can replace 316 if a specific passivation is made (fluonitric passivation followed by a second nitric passivation) but cannot replace it if just a standard fluonitric passivation is made and of course if there is no passivation. This passivation process was optimized by authors to provide the best corrosion resistance results.
But a major concern about available tests is that all these tests are made **only** on specimens fully immersed and without welding.
Only a few documents are providing advice about how the welding can modify the corrosion resistance on ferritic grades . For more see: *Solar waters heaters, the ferritic solution (http://www.worldstainless.org)*

By experience, we found that corrosion in stainless steel was not due solely to the raw material used, but was **mainly** initiated by the following aggravating factors:
1/ Welding: no or not appropriate welding shield gas
2/ Interface between liquid and air: this happens often because of degassing, air is trapped inside pipe fittings or heater
3/ Edges effect
4/ Iron contamination during process not removed by passivation

5/ Wrong passivation
6/ Wrong surface pickling (sand blasting)
7/ Iron oxide and sludge contamination after installation coming from other components of the equipment, and deposited in low flow area and in the welding and fittings interstices

3/ The Ultimheat corrosion testing process conditions on flat sheets

- The accelerated corrosion testing is made to check the corrosion resistance to chloride and chlorine, including interface with air and liquid, on plain raw material, edges, welding, with and without passivation, with and without mechanical pickling by sand blasting. Passivation is made using our standard citric acid passivation process.
The same test made on Titanium sheets did not show any corrosion in any of the test conditions.
The Ultimheat method (based on ASTM G48 Practice B specification), is as follow:

Test description

- Test specimens (200 x 160mm) were made of 1.2 mm thickness. BA surface finish.
- Test specimens have a longitudinal TIG welding made on automatic welding equipment, at same welding speed.
- Test specimens are welded with 2 different protection gas: welding side with Argon, other side with Argon+ 3% Hydrogen,
- Test specimens have been carefully high temperature degreased and rinsed and handled with gloves until they were immersed.
- Test specimens surface has been prepared as follow: 50% of one side has been sand blasted, other side of the same face without sand blasting. The other side has not been sans blasted. These specimens have been passivated on half their height.
- Sand blasting has been made with aluminum oxide, (aluminum oxide grit powder, mesh 120, without iron or iron oxide content). This sieve size is usually what is recommended to avoid corrosion.
- Test specimens have been immersed in the testing solution (5% active chloride= 50.000 ppm) made by dilution of a 10% solution with distilled water), during 96 hours at 70°C.
- PH was checked and adjusted to 7.3 +/-0.2
- About 20 mm on the top side were not immersed to check the liquid/ air interface corrosion resistance.
- Specimen weigh loss has been recorded after 48h and 96h (the weight loss is the full specimen weigh loss)
- Weight measurement has been made with a 0.001 gr resolution, and is average of weight loss of two identical samples tested together
-Pictures have been made with the same high resolution camera, at same distance, with same light. The same amplification ratio has been used on all pictures used in this document.
-The testing equipment is made in PVC to avoid equipment corrosion by high concentration chloride and contamination, and the chemical decay of chlorine corresponding to its reaction with ferrous ions released by iron dissolution.
- Chemical composition of initial Chlorine solution is given in annex

JPCI high chlorine corrosion specimens testing equipment	Testing specimen
	Sand blasting on the left side Passivation on lower half 

Analysis of the corrosion results on samples will give relative influence of:

- Sand blasting pickling
- Passivation
- Welding
- Air interface
- Side effect
- Protection gas efficiency

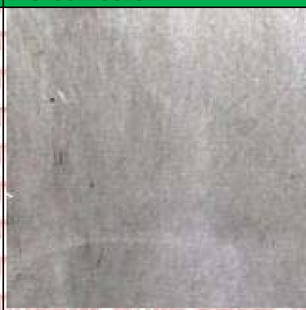
4/ Test results, sheets, 50.000 ppm chlorine content, 96 hours immersion at 70°C

4-1: average weight loss

material	201	304L	444	316L
Sample set 1: Total weight loss (%)	10.21	3.83	3.61	2.38
Weight loss, gr/cm²	0.041	0.018	0.016	0.011
Sample set 2: Total weight loss (%)	9.92	3.86	3.85	2.47
Weight loss, gr/cm²	0.040	0.018	0.017	0.011
Average weight loss, gr/cm²	0,0405	0,018	0,0165	0,011
Percentages compared to 316L	368%	164%	150%	N/A

Weight loss results: They give a weight loss about 20 times higher that values for similar tests on fully immersed and not welded specimens provided by raw material suppliers.
The worst is 201, the best is 316L, and 444 and 304L have similar results
Special comment: because of testing conditions, this weight loss is an **average of every surface condition**: passivated, not passivated, welded, not welded, sans blasted, not sand blasted.
It reflects the "in field average conditions"

4-2: corrosion results on fully immersed and un-welded parts

PASSIVATION and SAND BLASTING INCIDENCE				
		Not passivated		
Material condition	**201**	**304L**	**316L**	**444**
not sand blasted				
comments	Slight corrosion	Slight corrosion	No corrosion	No corrosion
sand blasted				
comments	Slight corrosion	Slight corrosion	Slight corrosion	Slight corrosion
		Passivated		
not sand blasted				
comments	No visible corrosion	No visible corrosion	No corrosion	No corrosion
sand blasted				
comments	Slight color change, with small red oxide dots	Slight color change	No corrosion	No corrosion

Tests conclusion:

1/ The 201 and 304L are corroded when they are not passivated , with or without sand blasting

2/ The passivation on un-welded areas of specimen gives similar corrosion resistance for every type of stainless steel

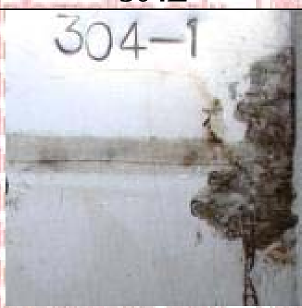
2/ The sand blasting is a corrosion aggravating factor on non passivated stainless steel

4-3: corrosion results on fully immersed welded parts

PASSIVATION and SHIELD GAS incidence on welding				
Argon protection gas				
	201	**304L**	**316L**	**444**
Not passivated				
comments	Huge corrosion	Medium corrosion	Medium corrosion	Medium corrosion
Passivated				
comments	Huge corrosion	Medium corrosion	No corrosion	Slight corrosion
Argon+ 3% Hydrogen protection gas				
not passivated				
comments	Huge corrosion	Medium corrosion	Slight corrosion	medium corrosion
passivated				
comments	Huge corrosion	Slight corrosion	No corrosion	Medium corrosion

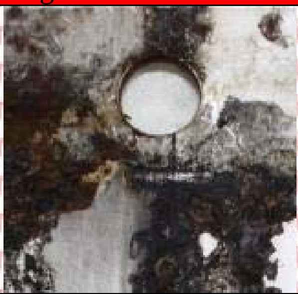
Conclusion: Without passivation, corrosion is initiated on all types of stainless steel.
201 does not resist to corrosion after welding with any type of protection gas
304L shows better corrosion resistance with 3% hydrogen shielding gas , but is slightly corroded
444 shows better corrosion resistance with argon shielding gas, but is slightly corroded. Hydrogen is not recommended
316L: No corrosion with both types of shielding gas

4-4: Corrosion results on air/liquid interface on un-welded parts

Not passivated				
	201	**304L**	**316L**	**444**
not sand blasted				
comments	Huge corrosion	Medium corrosion	Medium corrosion	Medium corrosion
sand blasted				
comments	Huge corrosion	Huge corrosion	Huge corrosion	Huge corrosion
Passivated				
	201	**304L**	**316L**	**444**
not sand blasted				
comments	Huge corrosion	Medium corrosion	Slight corrosion	Sligth corrosion
sand blasted				
comments	Huge corrosion	Huge corrosion	Huge corrosion	Huge corrosion

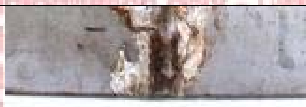
Conclusion:
Interface corrosion extends about 15 mm on both side of air/water interface, and is more important on edges
Sand blasting is an aggravating factor on all types.
201 does not resist to interface corrosion in any configuration
304, 316 and 444 are corroded when not passivated. When passivated, Best resistance is 316L and 444

4-5: Corrosion results air/liquid interface on welded parts

	Non passivated			
	201	**304L**	**316L**	**444**
Welding protected with Argon + H2				
comments	Huge corrosion	medium corrosion	Medium corrosion	Medium corrosion
Welding protected with Argon				
comments	Huge corrosion	Huge corrosion	Huge corrosion	Huge corrosion
	Passivated			
	201	**304L**	**316L**	**444**
Welding protected with Argon + H2				
comments				
Welding protected with Argon				
comments				

Conclusion:
-Interface corrosion extends about 15 mm on both side of air/water interface, and welding is an increased corrosion factor.
-201 does not resist to interface corrosion after welding in any configuration
-Hydrogen gas shielding provide a better corrosion protection on 304L and 316L

4-6: Edge corrosion results on immersed welding

Passivated*				
	201	**304L**	**316L**	**444**
Sand blasted left side, not sand blasted right side				
comments	Huge corrosion	Slight corrosion	No corrosion	Medium corrosion

Conclusion:
201: does not resist to edge effect corrosion.
316L is not corroded
444 and 304 are corroded
*Due to specimen configuration, testing on non passivated parts was not possible

5: Corrosion tests conclusions

- 201 is not recommended to use in waters with chlorine contents.
- Sand blasting must be avoided on all parts in contact with liquid
- The most oxidizing and corroding place is the air/water interface.
- Welding is the preferred corrosion starting place when wrong protection gas and wrong passivation is made.
- When tested on plain, un-welded and passivated condition, 304L, 316L and 444 have similar corrosion resistance.
- After welding, 316L has a better corrosion resistance than 444
- 3% Hydrogen shield gas reduces the 444 corrosion resistance, but improves 316L and 304L corrosion resistance

6: Welding

-For welding 444, it is essential that welding procedures minimize the pickup of oxygen, carbon, and nitrogen, in order to maintain the corrosion resistance and ductility of the alloy.
Argon shielding gas is preferred for 444 and the shielding gas should not contain hydrogen or nitrogen.
Using pure argon for welding produce slightly colored welding. Removing the welding coloration has to be made by mechanical or chemical pickling. And this is an extra cost that should be considered when using this stainless steel. Of course as shown by these test, the mechanical pickling by sand blasting must be avoided.
-There is no welding gas problem for 201, 304L and 316L

7: Forming

-The 444 elongation in annealed condition is 20 to 30%. The forming process used to make circulation heaters without cracks needs 55 to 65 % elongation.
This elongation is reached with 304L and 316L.
Because of this elongation characteristic difference, 444 cannot replace 304L or 316L without major changes in production process and product design .This is an extra cost that should be considered when using 444.

8: Availability

-444 is very difficult to find in annealed conditions needed for crack free forming conditions.
There is no availability of 444 in rod or tubes for fittings. So fittings and other components made from tube must be 304L or 316L. Welding dissimilar metals is a corrosion initiating process.
-201, 304L and 316L are easily available

9: Raw material price comparison and evolution

Estimated relative cost of 1.2mm thickness stainless steel sheets, BA surface finish and annealed condition.
Prices are based on raw material prices on 20/11/2009 and 20/11/2007.

	Versus 304L				**Versus 316L**			
	201	**304L**	**316L**	**444**	**201**	**304L**	**316L**	**444**
30/10//2009	0,63	1	1,53	1,05	0,41	0,65	1	0,68
30/10/2007	0,43	1	1,82	0,54	0,24	0,55	1	0,30

10: General conclusion

- Corrosion: We have found that chloride corrosion resistance of 444 does not match the 316L resistance level in welded parts, but is roughly equivalent to 304L. Sand blasting must be avoided. Right passivation and protection gas must be used.
- 444 could be a replacement for 304L in domestic heating, but not in spa and swimming pools, as its corrosion resistance will not match these conditions.
- Production process: Changing to 444 will induce important changes in the production process and a higher corrosion risk
- Final price difference: with actual stainless steel market price, changing to 444 small size heaters will only reduce the total of about 10%. This price reduction is limited because the fittings and heating elements, (they represent up to 50% of tank weight in a dia125 x 300 mm tank) cannot be made in 444.
This price gap has reached a much bigger percentage 2 or 3 years ago. But until the raw price difference between 304L and 444 stays under 2, there is no advantage to change.
A more important price discount can be achieved in larger size tanks, like 150L or 200L accumulation heaters, where the stainless steel weight used for the tank can rise 25 kg to 35 kg, for the same fittings size.

13: Annex

13-1: Regulations about the maximum free chlorine content in tap water:
EU: The European drinking water guideline 98/83/EC does not contain guidelines for chlorine.
*WHO (World Health Organisation):*The WHO drinking water standards state that 2-3 mg/L chlorine should be added to water in order to gain a satisfactory disinfection and residual concentration. The maximum amount of chlorine one can use is 5 mg/L. For a more effective disinfection the residual amount of free chlorine should exceed 0,5 mg/L after at least 30 minutes of contact time at a pH value of 8 or less. *(WHO, Guidelines for drinking water quality. 3rd edition)*
USA: The national drinking water standards state that the maximum residual amount of chlorine is 4 mg/L.
Australia: Maximum free chlorine water level is 5 mg/L *(*Australian Drinking Water Guideline ADWG 2006)
Other countries: Most of them use the European directive or the WHO standard. In some Asian countries, the level can rise to 100 mg/L and up to1000mg/L in some Indian cities.

13-2: The different types of chlorine:
-*Free chlorine:* the amount of chlorine present in water as dissolved gas (Cl_2), hypochlorous acid (HOCl), and/or hypochlorite ion (OCl^-) that is not combined with ammonia or other compounds in water. This is the most oxidant ingredient.
-*Chlorine residual:* the concentration of chlorine species present in water after the oxidant demand has been satisfied.
-*Combined chlorine:* the sum of the species resulting from the reaction of free chlorine with ammonia (NH_3), including monochloramine (NH_2Cl), dichloramine ($NHCl_2$), and trichloramine (nitrogen trichloride, NCl_3).

13-3: Chlorine checking process: EN ISO 7393-3:2000 (Water quality. Determination of free chlorine and total chlorine).

13-4: Chlorine solution composition (before dilution)

Free chlorine (Cl2+HOCl+ OCl-)	Alcali (NaOh)	Iron (Fe)
10.3%	0.6%	0.006%