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Post-fabrication cleaning of stainless steel in the pulp and paper industry

Scope

All owners and operators of pulp and paper mills want to keep their facility continuously and reliably on stream for as long as possible with the minimum of maintenance. Post-fabrication cleaning maximizes technical and corrosion performance.

Stainless steel relies on its invisible, exceedingly thin, passive film of chromium oxide to protect its surface against the onset of corrosion. Post fabrication cleaning is the single most important factor in maximizing and maintaining the corrosion performance of fabricated stainless steel in any particular application, not just in the pulp and paper industry.

Safety precautions

Refer to the “Health and Safety Concerns” section and Appendix F.

Definitions and expressions

Post fabrication cleaning is the process of cleaning after fabrication to remove all contamination associated with the fabrication process. Contamination might include foreign metals, excessively thick oxide films, grease and oil. Cleaning generally involves various different chemical and mechanical processes either individually or in combination.

Pickling is the removal of the heavy oxide film or metallic contamination and some stainless steel using aggressive acid solutions.

Passivation is defined in ASTM A 380 (1), and more recently in ASTM A 967 (2), as a treatment that is effective for removal of foreign material (not originating from the stainless steel) from the surface of the stainless steel. Free iron, usually resulting from contact with steel tooling during fabrication or shipment is the most common concern. The protective chromium oxide film forms immediately and spontaneously on the clean surface of the stainless steel with exposure to oxygen in the environment, a process sometimes called auto-passivation. A clean stainless steel surface will form the passive film when exposed to oxygen and does not require chemical treatment to achieve the passive film. Some “passivation” methods also chemically promote and strengthen the inherent protective oxide film on the surface of the stainless steel, simply by increasing the oxygen content close to the surface.

Fabrication may reduce the overall corrosion performance of stainless steel to below its “normal” level because of transfer of foreign material to the surface of the stainless steel. In reality, it is difficult, if not impossible, to complete the fabrication of a significant facility or piece of equipment without some surface contamination.

Further discussion is provided in Appendix A.

Economic benefits

Cost of cleaning is small compared to the initial capital expenditure on a piece of equipment and compared to the continuing operational cost of not cleaning. The economics of post fabrication cleaning can be considered in two stages, the cost of cleaning and the economic implications of cleaning to long-term performance.

Cost of cleaning

Stainless steels are the material of choice in large areas of the pulp and paper industry because of its superior characteristics in comparison with carbon steels with regard to:

- Corrosion resistance
- Cost of maintenance
- Service life
- Good life cycle cost characteristics

Areas that have not been post fabrication cleaned are essentially the weak link in the chain as they generally have relatively poor corrosion performance compared to the surrounding passivated material. Consequently, if post fabrication cleaning is not completed, the owner/operator is not maximizing the payback on the investment.

Post fabrication cleaning is not expensive. In the context of constructing a vessel, post fabrication cleaning might cost as little as 1-3% of the cost of material and fabrication depending on the extent of cleaning required (3).

Economic implications of post fabrication cleaning

Some time ago in Canada, most bleach plant equipment was put into service without pickling or cleaning after fabrication primarily because it was believed that the process environment itself would provide the cleaning of the stainless steel in service. Much more corrosion was experienced in these Canadian mills than in similar mills in the U.S. where most bleach plant equipment was cleaned. The severe corrosion problems in Canada led to the use of electro-chemical protection systems, with their associated ongoing operating costs, in an effort to reduce the corrosion rate (4). The overall experience suggests that cleaning after fabrication could have been a more economical approach to avoiding corrosion.

This example clearly illustrates how avoiding a relatively small capital expenditure resulted in considerable and continuing operating expenditure. The basic premise should be to “justify why post fabrication cleaning should not be carried out” rather than having to justify the cost of cleaning.

Classification of surface cleaning need

Systematic approach

Many owner/operators are not well acquainted with the concept of cleaning; thus discussions of and decisions about cleaning are sometimes difficult. In many cases cleaning is decided after the fact, as a remedy, based on the amount of oxide formed. The decision is often based on the color of the oxide; an indication of how much damage was done to the corrosion resistance by the fabricating process. For example a “light straw” color implies relatively little damage to corrosion resistance and opens the possibility of leaving this light fabrication oxide in place, while a “burnt sugar” color indicates sufficient loss of effective chromium in the surface that removal of this oxide scale is necessary to obtain the expected corrosion resistance from the stainless steel grade selected. Absolute reliance on these color differences of oxide scales to determine when or how to clean is not recommended.

A classification system established ahead of time enables the equipment owner to decide and specify the necessary cleaning at the time of purchase. By specifying the required cleaning, this essential economic decision is not left to the equipment seller or service supplier, and can be accomplished with minimal cost.

The working group for this TIP recommends the following approach:

- Classify the need of cleaning, equipment-by-equipment, surface-by-surface

Based on the classification for each surface:

- Select cleaning method
- Select inspection method
- Decide unambiguous acceptance criteria

Classification of cleaning need

As mentioned, stainless steels rely on the continuity and integrity of its exceedingly thin oxide passive layer or film to provide corrosion resistance. The integrity of the oxide film can be damaged by:

- Retained heat treatment oxide scale (much coarser and thicker than the passive film)
- Welding heat tint (also much coarser than the passive film but not as coarse as the heat treatment oxide scale)
- Contamination, particularly by other metals, but by any non-stainless material
- Localized chromium reduction from extended high temperature exposure sometimes called “chromium depletion”

To maximize corrosion performance of stainless steels all of these damages should be identified and should be removed by an appropriate cleaning procedure. In many cases it is clearly impractical and uneconomical to apply the same cleaning procedure in every situation; preferably a system should be applied where different pieces of plant or equipment in the pulp and paper mill will have different requirements in terms of cleaning.

Given a systematic classification system, both surfaces of each piece of equipment can be classified and a cost effective system put in place to apply the post fabrication cleaning policy.

Table 1. Basic rules of cleaning for different operating conditions

<i>Require post fabrication cleaning</i>	<i>May not require post fabrication cleaning</i>
▪ Wetted surfaces	▪ Fully dry surfaces
▪ Process contact surfaces	▪ Non-contact surfaces
▪ Surfaces in contact with halogens or halides, particularly chlorine or chlorides	
▪ Surfaces in contact with alkali and caustic solutions	
▪ Low temperature surfaces (temperatures <~280°F / 140°C)	▪ High temperature surfaces (temperatures >~1000°F / 550°C)
▪ Aesthetic surfaces	
▪ Vessels, etc., where the implications of failure or coming off stream for extended periods of maintenance are prohibitive	▪ Vessels where there are no significant health and safety or production implications

The deciding factor is the corrosion environment in which each surface is operating. The TIP has classified a total of 111 surfaces from 1 (most stringent requirements) to 6 (least stringent) in the following process environments:

- Kraft pulping
- Kraft recovery systems
- Tall oil acidulation process
- Magnesium sulfite processing
- Mechanical pulping
- Recycled fiber pulping
- Bleach plant systems
- Paper machines

An example of the classification system for different equipment in the pulp and paper industry can be found in Table 2.

Every piece of steel has two sides, so one side may be in a severely corrosive environment, in which case post fabrication cleaning will be essential, while the other side may be in a relatively benign environment in which case post fabrication cleaning is not critical. Therefore, both the “internal” and the “external” surfaces need to be described (see Figure 1).

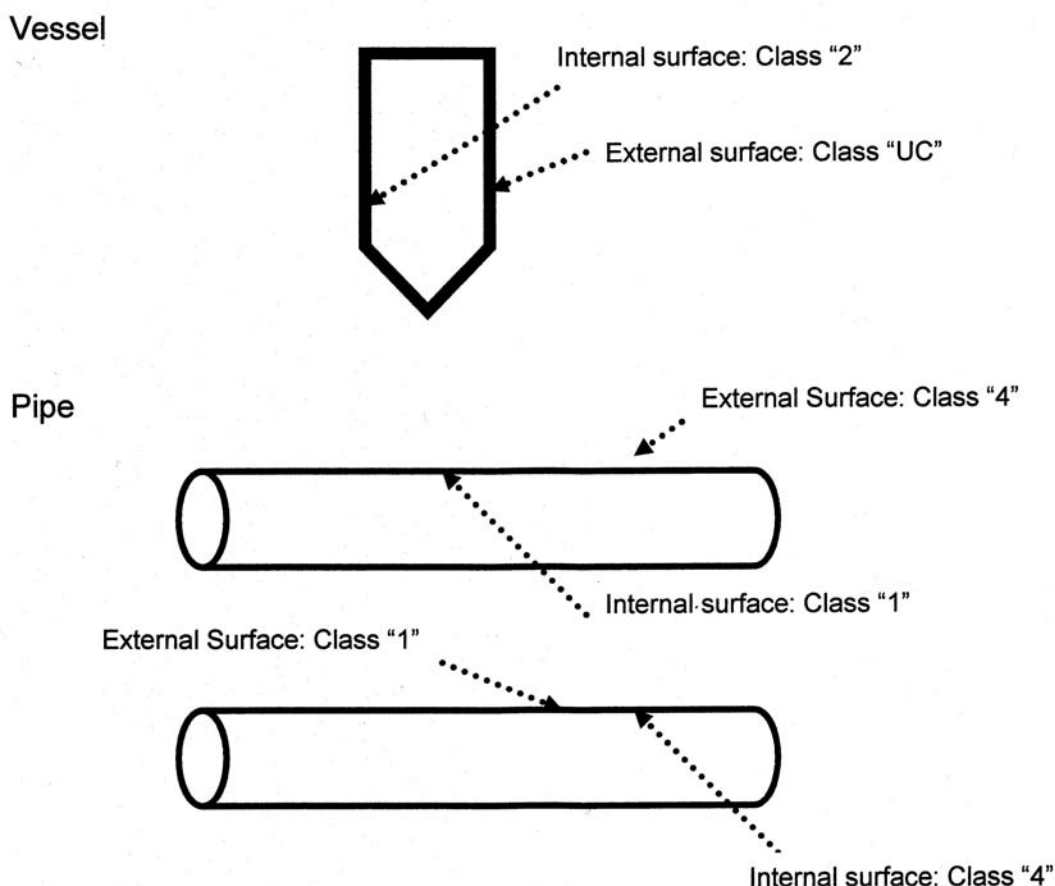


Fig. 1. External and internal equipment surfaces

From Table 2 it can be seen that the peroxide reactor, for example, has the most stringent need of cleaning. The Kraft pre-steamer is classified as “3” as later described after normal pre-cleaning operation, the surfaces will be mechanically cleaned, and the formation of the passive film chemically promoted. In contrast, the liquor heater shell would normally be electro polished. No information was available as a basis for suggesting an appropriate practice for the chlorination tower. An interval is given for the brown stock washers based on diverging views.

Detailed consideration is given to specific pieces of equipment and plant in Appendix B.

These classifications are intended to serve as a first approximation of the cleaning need. A plant operator may adopt the TIP classifications or create an internal scale based on experience. In the future we hope to update and extend the list.

Table 2. Examples of classification: 1= most stringent, 6 = least stringent.

Section	Equip	Equipment	Classification	Special Requirements	Process Stream
1	1	Pre-Steamer	3		Kraft Paper
1	3	Liquor Heater Shell etc	3		Kraft Paper
1	6	Brown Stock Washers	2-5		Kraft Paper
1	8	Chlorination Tower	No Data		Kraft Paper
1	9	Peroxide Reactor	1	Ferroxyl test	Kraft Paper
2	7	Soap Storage	Unclassified		Kraft Paper
4	1	Reactor Shell	4		Tall Oil: Acidulation Process
4	1	Reactor Paddle	4		Tall Oil: Acidulation Process
4	2	Spent acid/brine Neutralizing Tank	4		Tall Oil: Acidulation Process
6	5	Red Liquor Tank (From Washers)	2		Mg Sulfite Processing
6	6	Sulfur Burner Gas Cooler	2		Mg Sulfite Processing
6	7	Fortification Tower	2		Mg Sulfite Processing
7	2	Digester	No Data		Neutral Sulfite Pulping
8	2	Steaming Tube	4		High Yield Mechanical Pulping
8	3	Refiners	4		High Yield Mechanical Pulping
8	4	Separators	Unclassified		High Yield Mechanical Pulping
9	1	Pulper	2-4		Waste Paper Recycling
9	2	Heavy Duty Cleaner	4		Waste Paper Recycling
9	3	Coarse Screens	4		Waste Paper Recycling

Corrosion performance of different cleaning methods

The more stringent the classification, the cleaner the surface needs to be. The influence of the surface cleanliness on the corrosion performance is well documented (3-7).

The corrosion performance of 316L stainless steel is dramatically reduced in some environments by the presence of an oxide film that is normally regarded as a good quality “light straw” colored welding heat tint (3). The localized corrosion performance of the weld is improved with the removal of the heat tint. The performance continues to improve as the final surface is left with a smoother and smoother surface (Fig. 2).

When pickling is used after mechanical cleaning, the corrosion performance is essentially independent of the surface roughness. The pitting corrosion performance of the weld is brought back to parent material levels. The chemical cleaning operations are much less intensive, time consuming and skill sensitive than mechanical cleaning techniques (Fig. 3).

The chromium content at the surface of the stainless steel is reduced (“chromium depletion”) as a result of oxidation during hot processing. This loss of corrosion resistance is associated more with solution annealing heat treatment than with hot rolling. In cases where significant chromium depletion has occurred during processing, the corrosion rate was increased by a factor of as much as 50 times as a result of this chromium depletion. (6)

Any of the post fabrication cleaning techniques used improved the corrosion performance but the degree of improvement was different from one treatment to another (6). Pickling gave the greatest improvement and always considerably improved the corrosion performance. Passivation or chemically enhancing a new passive layer, using

less aggressive chemicals, had a small beneficial effect but, on its own, passivation is not effective at removing coarse oxide contamination or chromium-depleted areas. Belt grinding resulted in better corrosion performance than silica sand grit blasting, and the corrosion performance as a result of sand blasting was better than that from chilled-iron grit blasting. Grit blasting should never be used unless followed by pickling or passivation because the grit itself may transfer to the cleaned surface and act as a site for corrosion.

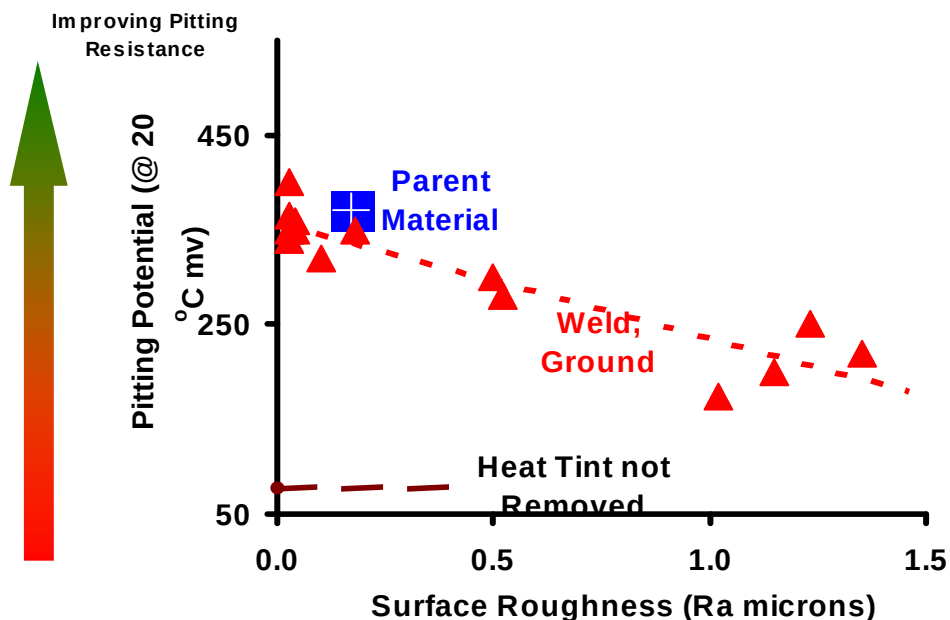


Fig. 2. Effect of mechanical cleaning and surface roughness on the pitting corrosion performance of 316L (5)

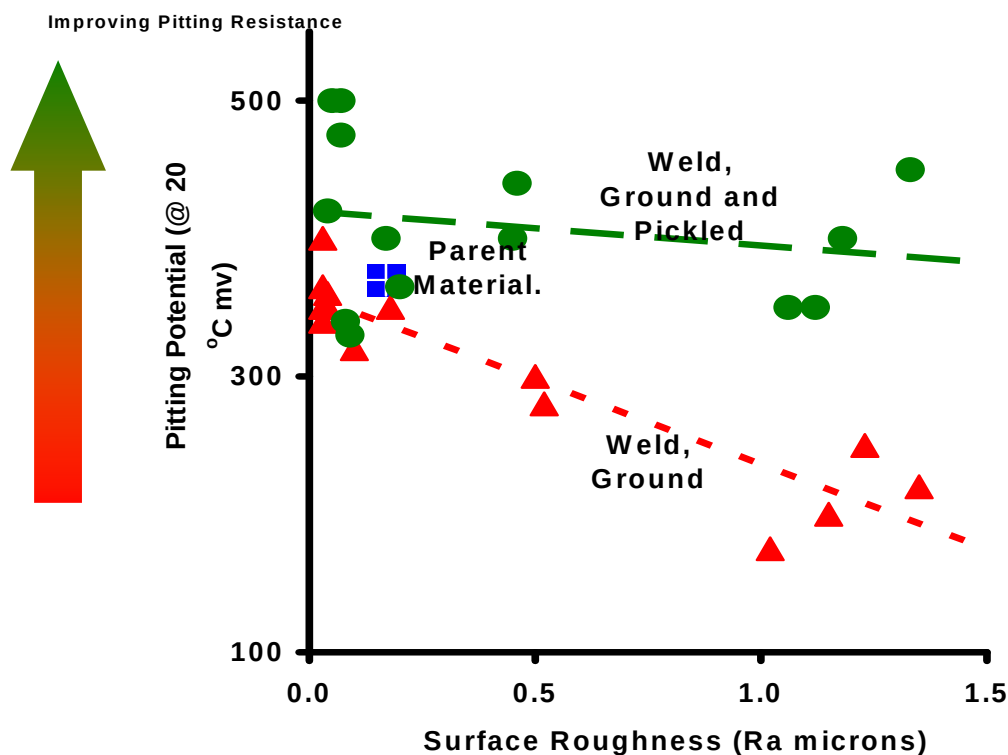


Fig. 3. The effect of pickling of mechanically cleaned surfaces on their pitting corrosion performance (3, 5)

Various grades of welded stainless steel with different post fabrication cleaning finishes were exposed to the corrosive environment of a paper mill. Pickled surfaces always gave superior corrosion performance compared to stainless steel wire brushed surfaces; glass bead blasted surfaces probably performed better than the wire brushed surfaces although this improvement was not as consistent or conclusive (4).

The effects of various cleaning techniques on the corrosion performance of 2205 duplex stainless steel were considered (7). There was very little difference in the corrosion performance of ground (60-120 grit) and blasted (blasting angle 45-60° off horizontal) surfaces. In contrast, pickled surfaces gave very good corrosion performance, (Fig. 4).

It is clear that:

- Post fabrication cleaning should be completed and completed effectively.
- The corrosion performance of both the parent material and the welded joints can be improved by mechanical cleaning techniques but there is considerable variability from one technique to another.
- The mechanical techniques are skill sensitive and labor intensive and are often difficult to apply evenly over larger surfaces.
- The best method available to achieve the full value of stainless steels is to pickle after fabrication.
- The most practical method to maximize the corrosion performance of welded stainless steel typically involves mechanical cleaning (usually grinding) followed by pickling.

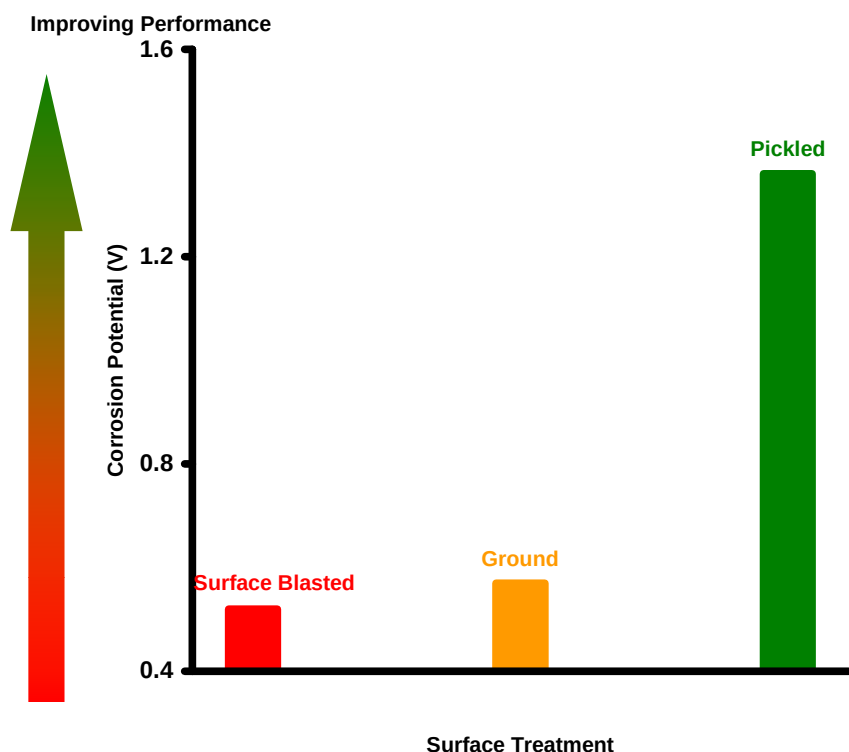


Fig. 4. The effect of different post fabrication cleaning methods on the corrosion performance of duplex stainless steel 2205 [data after Gumpel (7)]

Surface smoothness influences the in-service characteristics and service costs.

The rougher the surface, the greater is the tendency for crevice corrosion associated with deposits to occur. This effect may be due to the roughness acting as micro crevices, thus initiating crevice corrosion on their own, or by acting as sites that can hold product or other deposits, thus encouraging crevice corrosion.

A smoother surface drains better than a rough surface. There are obvious benefits in relation to reduced adhesion of product to the surface, (5, 8, 9). For example, a relatively smooth surface, ASTM No 4 finish (a 2K finish in EN 10088) required ~80% less time and water to clean it than a rougher surface (ASTM 2B) (10).

Selection of cleaning method or combination of methods

The basis of all cleaning is that all material that is not stainless steel must be removed from the stainless steel surface. Stainless steels cannot extend their protection to non-stainless material on the surface or maintain the corrosion resistance of any area blocked by a deposit, so any deposits help to initiate corrosion.

For the more stringent classifications the outermost chromium-depleted layer must be removed to restore the surface to its original corrosion resistance. The efficiency with which any operation is carried out and the effectiveness of that operation is crucial for the result (Table 3). For optimum results a combination of methods is used (Table 4).

Table 3. Effectiveness of common cleaning methods

<i>Method</i>	<i>Effectiveness</i>	<i>Skill sensitivity</i>	<i>Labor Intensity</i>
Grinding, Polishing	Metallic contaminations may remain	Very high	Very intense
Blasting	Soft contaminations may remain	Medium	Low
Brushing	Deposits not completely removed	Low	Low
Mechanical polishing, flat surfaces	Heavy oxide cannot be removed	Low	Low
Manual polishing of weld areas	Heavy oxide cannot be removed	High	High
Electro-polishing	Smoothens surface	Low	Low
Passivation	Removes light metallic contamination	Low	Low
Pickling by dipping, spraying, pumping methods	Removes heavy metallic contamination and chromium depleted layer	Low	Low
Pickling by painting method	Removes heavy metallic contamination and chromium depleted layer	Low	Medium

One of the main obstacles to properly applied cleaning is adequately addressing the health and safety issues. These might include noise, vibration, thermal and chemical burns, disposal of dusts and waste products and electrical hazards. The section “Health and Safety Concerns” and Appendix F discusses this in detail.

Grinding is a common method often regarded as a simple operation. From the clean surface point of view though, grinding requires good judgment and high manual skill as there are no visible signs when both oxide and chromium depleted layer are removed. Further, the grinding depth has to be the same at all locations, sometimes over large areas, which requires manual skill. Chemical methods are usually regarded as difficult because health and environmental training is required to handle the acids and the hazardous waste. From the clean surface point of view though, once training is performed, chemical methods follow recipes, can be repeated, requires low manual skill and the removal of material is the same over the exposed surface.

The basis of all mechanical cleaning operations is that all non-stainless steel material must be removed.

It is important to match the cleaning method to the surface classification

Table 4. Selection of cleaning methods for optimum results

Classification (Most stringent to least stringent classification)	Cleaning method					
	Pre- Cleaning	Mech. Cleaning	Pickling ^a	Chemical promotion of new passive film	Additional Cleaning Method ^b	None, As-is
1	Yes	(Yes)	Yes	Yes		
2	Yes	(Yes)	Yes			
3	Yes	Yes		Yes		
4	Yes	Yes				
5	Yes			Yes		
6	Yes					
Unclassified						Yes

^a Any additional cleaning method, e.g., electro-polishing, to be specified at contract stage

^b Any additional tests are to be specified as required

Key

Yes

Should be used

(Yes)

Optional, use as appropriate

Pre-cleaning

Pre-cleaning should be regarded as an essential first step for all cleaning methods.

Oil, waxes, hydrocarbon contamination, etc., retained on the surface to be cleaned can be either smeared further onto and into the surface by mechanical cleaning or act as a barrier layer to the chemical cleaning methods.

Cleaned surfaces should be Inspected, see the “Selection of inspection methods and coverage” section.

Mechanical cleaning

Grinding and polishing

Grinding and polishing, as manual or mechanized techniques, are very common methods of cleaning a surface. The finish achieved depends on the grit size used and on the skill of the operator (Fig. 5). The final finish should be obtained using fine grit sizes, assuming complete removal of prior surface roughness in each step, and be as smooth as possible (as shown in the previous section “Corrosion performance of different cleaning methods”) in order to maximize corrosion performance

In addition to the roughness of the final surface, the final grinding direction can also be important in relation to efficiency and speed of surface cleaning and draining.

Grinding and polishing do not necessarily remove all metallic contamination. Irrespective of recontamination, existing contamination can be smeared across a surface rather than removed.

These operations are very skill sensitive and labor intensive. The moisture test, as described in the ASTM specifications, is a simple, straightforward and effective method for identifying the presence of free iron contamination on the surface of the stainless steel.

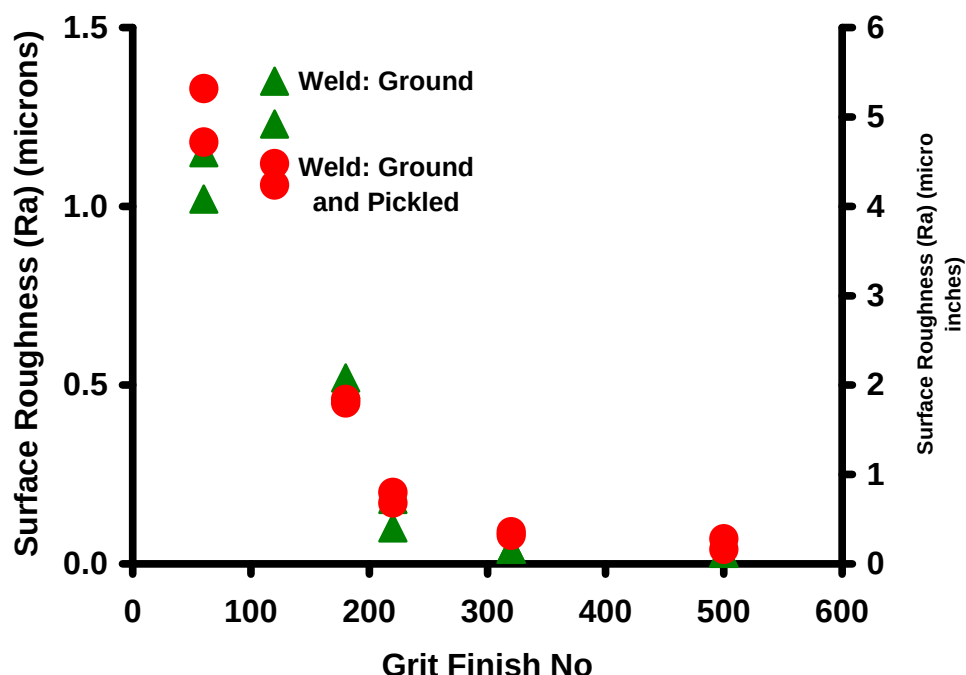


Fig. 5. Typical surface roughness produced with different sized grits (11).

Blasting

If blasting is not to be followed by chemical treatment, the grit or shot should be corrosion resistant, either a stainless steel resistant to the operating condition, or a non-ferrous product, such as alumina, carbide or glass bead. It should be dedicated to stainless steel to avoid cross contamination.

When blasting, care should be taken to assure the efficiency of the demisters in removing (particularly) hydrocarbons from the blasting air. Blasting will not necessarily remove “soft” contamination like grease etc.

The blasting angle should be vertical or just off vertical. Blasting at an angle is highly unlikely to fully remove contamination and is likely to smear contamination into the surface.

Care should be taken to ensure that coverage is even and consistent and that all contamination is removed. A typical blast finish is “Near White Metal” finish as a minimum acceptance criterion (12).

Brushing (manual and power brush)

Brushing, be it power brushing or manual brushing, is normally **not** adequate for post fabrication cleaning because it does not completely remove deposits and it certainly does not remove metal. Likewise, brushing does not remove heat treatment oxides or welding heat tint. Instead, brushing superficially polishes the oxide smooth and making it invisible, but it does not remove any areas of chromium depletion resulting from oxidation. In this condition a subsequent exposure to a reactive environment may cause corrosion.

A combination of brushing and polishing can remove dust, much gross debris, and possibly some weld spatter. Brushing by itself is appropriate only for general cleaning.

Mechanical polishing

The objective when mechanically polishing or buffing is to produce a smooth surface and, as such, it is used in combination with other methods that remove the gross oxides which polishing cannot. This technique is probably most commonly applied as a mechanized process to flat plate, before fabrication rather than to a complex shape. Weld zones, etc., are then (generally) manually polished to the required finish, which can be a fairly labor intensive and skill sensitive operation. There may be issues of consistency of aesthetic appearance over large areas.

Electro-polishing

Electro-polishing is a specialized technique that is useful for chemically cleaning the surface, for smoothing the surface, and for improving the aesthetic appearance of a surface. It does not necessarily “flatten” the surface. Electro-polishing can smooth a surface as it eliminates short wavelength roughness, e.g. removing the peaks, but it does not substantially alter long wavelength roughness.

Chemical techniques

Pickling is a method for cleaning and removing heavy oxide layers, such as heat treatment scale and heat tint from welding, and heavy metallic contamination. In contrast, some forms of passivation remove relatively low levels of metallic contamination.

Passivation

Passivation is a phrase sometimes applied to two different operations. One is the removal of exogenous contamination. The clearer definition is the re-growth of the passive, protective film. As soon as the surface is clean the passive film will form by auto-passivation in the presence of oxygen in the environment, either in air or water, but does not require a separate treatment of the surface. The suggestion that a separate treatment is necessary to establish stainless steel corrosion resistance is the cause of a lot of confusion.

Passivation is defined in ASTM A 380 as “the removal of exogenous iron or iron compounds from the surface of stainless steel by means of a chemical dissolution, most typically by a treatment with an acid solution that will remove the surface contamination, but will not significantly affect the stainless steel itself” (1). Free iron, resulting from contact with steel tooling during fabrication or shipment is the most common concern. For this purpose nitric acid (HNO_3), stabilized hydrogen peroxide solution (H_2O_2), citric acid, and phosphoric acid have all been used.

The protective oxide film forms spontaneously on the clean surface of the stainless steel during the first minutes or hours after passivation (13).

Passivation also chemically promotes and strengthens the inherent protective oxide layer on the surface of the stainless steel, simply by increasing the oxygen content close to the surface. For this purpose, passivation is undertaken either with an oxidizing mineral acid, frequently nitric acid (HNO_3), or with stabilized hydrogen peroxide solution (H_2O_2). Citric acid and phosphoric acid may be effective for cleaning the surface from free iron but are inefficient for speeding the formation of the passive film. Concentration and temperatures are discussed in the “Selection of Cleaning Materials” section.

A passivation solution, by definition, is incapable of pickling, i.e., the dissolution of stainless steel or oxides resulting from high temperature exposure, as in welding heat tint or heat treatment oxides. Passivation, by definition, does not produce solutions that are hazardous in the sense of containing chromium or other heavy metals.

Although significantly less aggressive than pickling solutions, passivation acid solutions should be handled, used, washed off and disposed of in the same way as pickling solutions.

Hydrogen peroxide solution can be run directly to drain under normal circumstances (subject to any local restrictions).

Pickling

Pickling is an aggressive chemical cleaning capable of removing oxides from the surface of stainless steels, both the inherent protective oxide formed by auto-passivation in the presence of oxygen, and the oxides that has been formed and thickened by welding, heat treatment, or other exposure to high temperatures. Pickling also removes metallic contamination from the surface of stainless steels, as well as removing some of the stainless steel surface.

Pickling is best applied to a pre-cleaned surface to assure that the exposure of the metal to this aggressive solution is as uniform as possible. The most common pickling solution for stainless steels uses a solution of nitric (HNO₃) and hydrofluoric (HF) acids, followed by rinsing in water. The presence of the hydrofluoric acid is what enables the dissolution of heat tint and heavy oxides and removal of the surface layer where chromium has been reduced by formation of the oxide, often called the chromium depleted layer. In special cases, other acid solutions are sometimes used. Because some stainless steel is dissolved, carrying chromium and other heavy metals into the pickle liquor, the resulting product is typically considered to be a hazardous waste requiring special precautions in disposal. Because the pickling solution is so aggressive, special safety precautions are required for personnel safety.

Once training in acid handling and waste disposal are completed, pickling is not a skill sensitive process nor is it a particularly labor intensive process.

Pickling can be used as a cleaning process on its own although it is frequently used in conjunction with a pre-cleaning and mechanical cleaning technique to improve the efficiency and throughput of the cleaning processes.

There are various pickling methods available as described below. The distinguishing characteristics of these methods generally relate to the method of application of the pickling solution and the subsequent rinsing procedures

Dipping / pickling bath method

Dipping the components to be cleaned into a pickling bath is arguably the most efficient and least labor-intensive method of removing oxides and contamination from stainless steel when the components are small enough or suitably shaped.

The component to be cleaned is dipped into the acid solution, held at the appropriate temperature until it is clean. The time taken to clean the stainless steel will depend on the grade of stainless steel, the extent of oxide to be removed, and the strength and temperature of the acid.

There must be full and efficient drainage of all pickling solutions and wash down waters. Great care must be taken with air pockets to ensure full treatment, possibly using a separate second stage treatment.

Spraying method

The spray method of pickling is used when a) it is not possible or practical to dip the component; b) there are large surface areas to be cleaned or c) special production or installation situations make spraying the most effective or the most economical approach.

Pickling acid is sprayed onto the surface to be cleaned. A thickener may be added to the solution to help it adhere to the surface to be cleaned. After the required contact time, the acid is washed off with high-pressure water hoses.

It is preferable to perform spray pickling in a dedicated facility and with equipment designed especially for spraying, where practical. Spray ball systems, for example, can be utilized for internal surfaces of vessels.

Painting method

Pickling pastes and gels can be painted onto components to be cleaned. This method is particularly appropriate for cleaning small or local areas, such as weld seams.