



A World Leader in Water Purification

**Rouging of Stainless Steel High Purity Water
Systems in the BioPharm Industry**

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Introduction

Water and steam systems in the BioPharm industry are normally fabricated of austenitic stainless steel, typically 316/316L grade. Operating temperatures vary from ambient for many USP Purified water systems, to 80° C - 85° C for most WFI systems, to as high as 155° C for pure steam generators and distribution piping. Many, if not the majority, of these systems develop surface deposits or staining known in the industry as Rouge. While the FDA has no formal position on rouge, some drug manufacturers are concerned about particulate matter contamination of their products, and routinely clean and re-passivate their systems, at a considerable cost and downtime.

In the quest to identify the source and remedy for rouge, many embark on a “smoking gun” and “silver bullet” approach respectively, often with disappointing results. There are many possible sources and causes for rouge, and the effect is additive. A better understanding of the various possible contributors and the influencing factors will go a long way in addressing the problem, and hopefully in saving time and cost.

What is Rouge

Rouge is rust, which is the byproduct of corrosion that occurs on stainless steels surfaces that are exposed to a corrosive environment, in this case high purity water or pure steam. The main constituents of rouge are iron oxides (ferric oxide Fe_2O_3 , or ferrous oxide Fe_3O_4), but may include iron, chromium, nickel and other elements.

Where Rouge is Commonly Found

Although rouge may be found in ambient water systems, it is more prevalent in hot high purity water systems, in pure steam generators, and pure steam distribution piping. Typical locations in water systems where rouge first appears include:

- Heat exchangers, particularly hot ends
- Pump casings and impellers
- Spray nozzle orifices and spray areas of WFI storage tanks
- Deadlegs and condensate collection areas
- Heat affected zone (HAZ) of welds
- Areas that have been ground or mechanically polished but not properly cleaned and passivated
- Valve diaphragms
- Stress Corrosion Cracking (SCC) affected areas

Rouge Characteristics

Although the name means red, rouge is found in many colors. As the temperature increases, the color becomes darker. In pure steam systems, it may appear gray or black. In the early stages, rouge is powdery loose and can be easily wiped off. Some rouge sloughs off and disperses throughout the system downstream. In a water system, installing 0.2 or 0.45 micron filter on a sample point and letting it run for a few hours will easily detect loose rouge. Eventually, rouge becomes adherent to the surface, and may appear as baked-on glossy coating that is not removed by wiping. At that point, the stainless steel surface is coated, rouging is stabilized, and no more rouge is formed or dispersed in the system. This can be verified by the filter test. In a pure steam system, the filter is fitted to a sample cooler.

Why “Stainless” Steel “Stains”

Rouge is the observed evidence of corrosion. The various types of corrosion that may occur in a high purity water or pure steam system include:

- General Corrosion due to chemical attack, normally uniform in nature. An example is corrosion from low pH, and aggressive cleaning and passivation chemicals that etch the stainless.
- Pitting Corrosion, typically due to chlorides.
- Crevice Corrosion, such as under gaskets and “O” rings.
- Galvanic Corrosion, associated with dissimilar metals. Can also occur at weld boundaries when excessive heat alters the properties of the metal so that it is no longer stainless.
- Stress Corrosion Cracking (SCC), common when a chlorine or high chloride environment exists, especially at elevated temperature.
- Intergranular Corrosion, such as in sensitized weld areas.
- Contact Corrosion, due to surface contamination by deposited foreign particles from the surroundings, such as contact with carbon steel, grinding particles, or just plain grease and dirt.
- Erosion-Corrosion, typical in cavitating pumps, and in high velocity areas such as valves and orifices of spray balls and nozzles.
- Corrosion due to localized biological effect. Occurs under deposits and biofilm.

A useful approach to understanding rouge is to consider the various phases the stainless material goes through, and what factors influence rouge formation in each phase. These phases are:

- The Mill and Material Composition
- Fabrication
- Process Environment
- Maintenance

The Mill and Material Composition

Austenitic stainless steel has a small amount of sulfur. Manganese sulfide inclusions may form during cooling of the melt at the mill. Pitting corrosion of stainless steel is related to these inclusions. Due to a difference in the cooling rate between the inclusions and the base metal, depletion of chromium occurs around the inclusion, rendering the alloy in that region to be no longer stainless.

Some mills may add aluminum to the melt in order to minimize porosity. Traces of aluminum on the stainless surface become corrosion sites.

Mills clean and pickle stainless steel to remove surface inclusions and contaminants, and to form a chromium-rich passive film on the surface. Damage to the passive film during fabrication or in service exposes additional inclusions, which become corrosion sites.

Also, mills formulate stainless steel content to meet established standards such as ASTM, ASME, or equivalent standards. These standards were established long ago, and allow a range for each of the constituents. The range reflects the ability to control content with the technology available at the time the standards were established. Current technology permits the control of the most expensive elements at very near the minimum requirement. It happens that these elements are most responsible for the corrosion resistance of stainless steel. In general, the higher the chromium to iron ratio on the surface, the higher is the corrosion resistance.

Fabrication

Fabrication steps such as machining, shearing, welding, mechanical polishing and grinding all damage the passive film formed at the mill, and may result in surface contamination. Abrasive tools used in mechanical polishing, such as Silicon Carbide and Aluminum Oxide (corundum) are an example.

Small particles from fabrication tools or from the surrounding environment may become impeded in the stainless steel and become Contact Corrosion sites, unless removed during cleaning.

Welding produces oxides in the “heat affected” zone. The zone can have different metallurgy than the base metal, which results in Galvanic Corrosion. Sensitized weld areas are also susceptible to Intergranular Corrosion.

Process Environment

Rouge in this category is associated with the affect of the prevailing process environment on stainless steel process equipment and components. In addition to the high purity water and steam, the following process factors influence the susceptibility of stainless steel to rouging:

- **Feedwater pH and level of CO₂**

Feedwater from single-pass Reverse Osmosis or some ion exchange systems, such as weak acid beds, may have low pH, which is likely to cause rouging on the feed side of stills and pure steam generators.

- **Chlorine in the Feedwater**

Of all possible causes of corrosion, chlorine is probably the most destructive, since it results in Stress Corrosion Cracking (SCC). Although rouge will appear in areas affected by SCC, the rouge problem becomes a mute issue, since SCC causes catastrophic failure that would call for replacing the affected area, or part of, if not the whole piece of equipment. For these reasons, chlorine demands particular and careful attention, and deserves more explanation.

The higher the operating temperature the more severe and accelerated is the attack. Stainless steel in the affected area becomes very brittle, and welding cannot repair the cracks. Applying heat will cause the cracks to propagate further, and the welder will be “chasing the crack”. The crack always wins. If SCC were localized, a successful repair, if practical, would require cutting out the whole affected area until virgin metal is reached, then welding a new section. Where ASME vessels are involved, repair must be done at a facility with an “R” stamp certification.

One important fact to remember is that there is no such a thing as a low safe level of chlorine. Some mistakenly think levels of 1.0 mg/lit or less in their feedwater should not be of concern. The fact is chlorine at any detectable level migrates to minute crevices and concentrates to form highly acidic cells, which result in minute pitting. When the affected area remains mostly submerged under water, with prolonged exposure to chlorine, pits become deeper and larger, eventually visible to the naked eye. When the area is wet and dry, such as in the wall of a vessel above the water level, and in ducts and distribution piping, cracks initiate at the minute pits. The crack then propagates and enlarges to exhibit the familiar branching and “lighting bolt” appearance of SCC.

It is important to differentiate between chlorine and chloride. The USP dictates that all pharmaceutical water must be obtained from water which meets EPA “Drinking Water” standards or comparable standards of the European Union or Japan. Chlorine is normally present in drinking water as a disinfectant, typically at levels of 0.5 – 3.0 mg/l. The chlorine should be removed in the pretreatment system, while the water is still at ambient temperature. Most common removal methods are carbon filtration or sodium bisulfite injection.

On the other hand, chlorides such as in sodium chloride (common salt) may be present in the feedwater at much higher levels compared to chlorine. Chloride levels of 100 – 200 mg/l are common in drinking water. Many pharmaceutical installations use softened water feed to stills, and have been operating for many years, some for over 25 years with the same system. Inside the evaporator, the water is concentrated 5 – 6 times, which means the chloride level can be as much as 1000 mg/l or more.

Another example of using stainless steel with high chloride service is seawater evaporators. There are numerous seawater desalination plants of stainless construction. Standard seawater has approximately 19,000 mg/l chloride. Due to concentration inside the evaporator, chloride levels are in the 30,000 – 35,000 mg/l range, at temperatures of 70° C - 95°C. The common provision utilized for avoiding chloride pitting corrosion is to avoid stagnation by maintaining flow velocities of one meter (3 ft) per second or higher, and to drain the system and possibly fresh water flush it, during shutdown. These same plants would experience significant, and likely catastrophic, damage if the feedwater had a continuous level of chlorine at a fraction of mg/l.

One cause of confusing chloride with chlorine is when a stainless steel part that failed due to SCC is sent to the laboratory for analysis, invariably the report states failure is due to chloride. This is understandable since chlorine does not remain around as “chlorine”, and the telltale evidence detected by the laboratory is the chloride ion that is the byproduct of the reaction involving chlorine.

- **Erosion-Corrosion**

Some areas of the water system are subject to this type of corrosion, which can yield significant amounts of rouge. Typical examples of rouge contributors are:

- **Pump Cavitation.** Simply described, cavitation is the formation of small gas bubbles in the water due to a lowering of the pressure in the pump suction. The bubbles eventually make their way to the surface where they literally explode, with sufficient force to tear away small particles of metal. These particles corrode turning into rouge. The major cause is insufficient pump NPSH, something that should be addressed at the design stage, for it is too costly later to raise that 10,000-gallon tank couple more feet, or find a way to lower the pump.

- **High Velocity flow.** The inherently high velocity in some valves and orifices such as in spray balls and nozzles prevents formation of the passive film. Additionally, velocities beyond the critical velocity for the material erode the surface and remove minute particles of metal, which corrode and turn into rouge.

Cavitation is not the only cause for erosion in pumps. The pressure developed by a pump is directly proportional to the square of its impeller tip speed (\approx impeller outside diameter X pump RPM). High tip speeds that exceed the material's critical speed are likely to cause erosion at the OD of the impeller and tips of vanes. While cavitation damage appears as round pitting, high-tip-speed-caused erosion appears on the outer edge of the impeller disk as linear file marks extending outward in the same direction as water flow, and vane tips may have saw-teeth appearance.

Note that metal particles removed by erosion are carried downstream and disperse throughout the system. This type of corrosion is more responsible for suspended rouge particles than, for example, rouge forming on a sensitized weld, which is more likely to remain adherent to the surface. To use the medical analogy, erosion-caused rouge is a very communicable disease, while other forms of rouge are not, or much less so.

Maintenance

High Purity Water and Steam systems, during their lifetime, are subject to repairs, alterations, cleaning, and passivation. Common sense and general practices call for cleaning and passivating newly installed piping runs or equipment before connecting to the existing system. This does not always happen. There are many instances of grinding particles and metal shavings, from newly installed piping or components, that have found their way into the system, because the added section was not isolated during the cleaning.

Some de-rouging and cleaning chemicals are very aggressive and will etch stainless steel if the exposure time, temperature, and concentration are not controlled very carefully, which is not always easy to do. Because of system configuration, quick thorough flushing of all areas in a limited amount of time may be very difficult. Even with the best controls, some etching will take place. An example of these chemicals is oxalic acid, and ammonium bi-fluoride (ABF). Stainless steel surfaces that were electro-polished at significant cost are not likely to retain their electro-polish after cleanings with these chemicals.

Some de-rouging chemicals leave behind a blackish, greasy, carbonaceous deposit sometimes referred to as "Smut", which requires removal using alkaline and detergent type cleaners. Certain de-rouging procedures list a "De-Smut" step. If not effectively removed, smut-covered surfaces do not form a passive film, and can contaminate the system downstream.

Another rouge producing corrosion related to maintenance is that due to localized biological effect, referred to as Microbiologically Influenced Corrosion (MIC). Pitting may occur under deposits and biofilm. However, BioPharm facilities normally have Standard Operating Procedures for cleaning and sanitization to control microbial growth and avoid biofilm formation in USP Purified systems and ambient loops, while WFI is often produced and maintained at 80° C - 85° C.

Finding The Source of Rouge

When rouge is detected, one of the first questions asked or pondered is: what is the source? Did the rouge form where found, or did it migrate from upstream? This is the search for the “smoking gun” mentioned earlier. One observer who found a rouged pump and observed rouge in a vessel upstream of the pump insisted the rouge migrated upstream, but could not explain how that was accomplished, considering the flow is one way, without circulation.

Certainly not all rouge forms where we see it. Rouge found on Teflon diaphragms of valves, or on glass observation windows explains why.

Consider a typical WFI system consisting of Pretreatment, Final Treatment, and Storage and Distribution.

- The Pretreatment can be softening and carbon bed filtration, but may include Reverse Osmosis and ion exchange polishing, depending on the type of still being used.
- The Final Treatment is Distillation using Vapor Compression or Multi-Effect still.
- The Storage and Distribution consists of a tank, dual pumps, and a loop with use points and the associated valves, controls, and instrumentation, and possibly heat exchangers.

Since the search for the source of rouge normally begins after rouge is detected in the loop or at the point of use, we will start there and work our way upstream.

Storage and Distribution

The recommended first is step to check the WFI at the inlet to the storage tank. It is important to keep in mind that rouge can be introduced into the tank as well as generated within the tank and loop. If there is rouge entering the tank, determine if the level explains those levels found downstream, by filtering equal amounts of water at the tank inlet and each of the points downstream.

On-line or grab sampling can be performed at various points in the loop in order to determine if there is a sudden and significant increase in rouge level, which will point to a suspect area for closer scrutiny, including visual or boroscope aided inspection. Other than weld joints, traditional contributors to rouge are:

- Loop pumps, particularly with cast parts. High ferrite levels in castings are believed to be a cause for rouging, although there are few suppliers of castings who disagree.
- Cast valves or valve components
- Heat exchangers
- Tank spray balls

One factor in the amount of suspended rouge build up in the tank and loop is the circulation/withdrawal ratio. Rouge occurs when the aggressive high purity water attacks a susceptible stainless steel site. Accordingly, the more water that passes over the site, the more rouge produced. In a one-way system, the water passes over the site only once. In a circulation loop, the water may pass over the same site many times before leaving the system. With every pass, more rouge is picked up. If the amount of WFI withdrawn from the loop is small compared to that circulated, the concept of rouge build up in the system becomes obvious.

Consider a 2" circulation loop with 1000 gallons (3,785 liters) of total water volume, and an average velocity of 5 feet per second. That means a flow rate of approximately 40 gpm, and the full volume of water is turned over every 25 minutes (1000/40).

For illustration purposes, let's assume that during one cycle (25 minutes) the WFI picks up 0.1 mg of rouge. This amount raises the level by $0.1 \text{ mg} / 3,785 \text{ lts} = 0.0264$ part per billion (ppb). This would be the rouge level if the system were once through, instead of circulating. To most, the 0.0264 ppb is not noticeable.

Now consider the circulation system:

Daily circulation = $40 \text{ gpm} \times 24 \text{ hrs} \times 60 \text{ min/hr} = 57,600 \text{ gallons/day}$

Rouge entering the WFI in 24 hour day = $(0.1 * 24 * 60 / 25) = 5.76 \text{ mg / day}$

If for example average water usage is 20% of the circulation volume (11,520 gpd), rouge will accumulate at the rate of 4.6 mg/day, every day. This corresponds to an increase of 1.2 ppb per day.

It is worth noting that there are systems that feed patch processes with relatively high instantaneous demand, but overall weekly usage of less than 1% of the circulation rate.

Other systems may experience abnormally high circulation/withdrawal ratio during initial qualification and validation, since no water is used for production but the loop is operational. One such system showed marked improvement when the withdrawal rate was increased.

In reality, not all the generated loose rouge remains in suspension in the water. A portion deposits on the system surfaces. Also, rouge generation does not remain at a constant rate. When hard and adherent rouge forms, it acts as a coating and protects the surface from further rouging.

The WFI Still

The still is the process step upstream of Storage and Distribution, and is often the object of investigation to determine if it is a source of rouge.

Although the loop is normally in continuous circulation, the still is most likely alternating between ON and OFF, responding to a level signal from the storage tank. Almost all systems are configured to dump the WFI to waste for several minutes at each startup, in order to flush the line before diverting the WFI to the tank. Representative samples are best taken after the still has been operating for 15–20 minutes or longer, although sampling the water being dumped to waste may provide useful information on rouge accumulation during standby periods.

If rouge is detected at the outlet of the still, visual and boroscope inspections as well as sampling at various points can be performed. Selection of sampling points is similar to that for the loop, normally before and after the distillate pump and the heat exchangers, and at the edge of the skid. Samples at the distillate pump inlet are representative of evaporator/condenser outlet. In a Multi-Effect still, the individual effects can be sampled if necessary.

Whenever rouge is observed on the feedwater side of the still, it becomes a suspect source for rouge downstream. The hypothesis is that colloidal iron in the feedwater is carried with the steam, which later condenses into WFI. There is more than one argument against this hypothesis. If the evaporation and separation processes allow carry over of colloidal iron, one would expect endotoxin and light mineral elements like sodium to also carry over with a resultant rise of WFI endotoxin and conductivity levels respectively. However, there is no such evidence. The phase change and separation mechanisms involved in distillation are very effective in removing dissolved and suspended solids and yielding high purity steam, which condenses into WFI.

Theories aside, there is a simple and undisputable method to determine if rouge is carried with the steam from the feedwater side to the distillate side. The steam exiting the separator/mist eliminator can be captured before it has the opportunity to contact the stainless steel contact surfaces. The captured steam is condensed and sampled. If rouge is detected, then it can only have come from the feed side, assuming the sample cooler was rouge free. Either way, this sampling settles the issue. The author was involved in a case where iron was in the feedwater, and the user's consultant thought the rouge was being carried with the steam. Sampling over 3 days period showed no sign of any iron or rouge carryover. Typical sampling setup is shown in Figure 1.

Pretreatment

Pretreatment systems upstream of the still are designed to achieve the following functions:

- 1) Enable the still to produce WFI quality water by removing volatile impurities that are not removed by distillation. An example is the removal of ammonia from chloramines treated drinking water.
- 2) Prevent corrosion. An example is the removal of chlorine, and to some extent carbon dioxide.
- 3) Prevent scale formation in the still. An example is the removal of hardness and silica.

Only the second function, corrosion prevention, is directly relevant to the rouge issue. The importance of chlorine removal was addressed above.

Carbon dioxide was also mentioned under Process Environment as a contributor to corrosion and rouge formation. Most drinking waters have neutral or above neutral pH. The lowering of the pH and increased concentration of CO₂ occurs when the water is treated with reverse osmosis (RO), or certain ion exchange processes such as weak acid or strong acid beds. RO membranes do not reject the CO₂, which ends up concentrated in the permeate feeding the still. There is ample observed evidence of the effect of CO₂ on rouge formation in stills. Unlike suspended and dissolved solids, the CO₂ does carry over with the steam and eventually is vented with other non-condensable gasses, but only after it has passed over the distillate contact surfaces, which provides the opportunity for rouging. Some RO systems provide for CO₂ removal through caustic injection ahead of the RO, where the reaction converts the CO₂ into alkalinity, which is removable in the RO.

Some Vapor Compression (VC) stills are fitted with deaerators/decarbonators, which significantly reduces the free CO₂ in the feed before entering the evaporator. Some CO₂ is generated inside the evaporator due to the breakdown of alkalinity, and is also removed through the vent. In addition to contributing to rouge, CO₂ if not removed effectively in the still will contribute to increased conductivity.

Surface Finish and Affect on Rouge

Reasonably good surface finish is common practice in the BioPharm industry. The question is whether a surface finish of 10 or 15 Ra is necessary, or if such finish measurably reduces the tendency to rouging.

There is no consistent evidence to show that very smooth finish or electropolish make a significant difference, or based on some observations a difference at all. Surfaces with 15 Ra finish and Electropolished can rouge just as much as non-polished surfaces with 25 Ra finish. Many older stills, which mostly have mill finish, were observed by the author to have more resistance to rouging than mechanically polished or electropolished newer generation stills. The passive film achieved by pickling at the mill appears superior to passive films that occur after mechanical polishing or electro polishing. See Reference (1), which supports this position and concludes that *mill finish and non-polished surfaces that are pickled only or pickled and passivated show a greater resistance to surface discoloration when exposed to pure steam*

Some mechanical polishing is unavoidable in order to smooth welds, repair scratches, and eliminate crevices. However, there is no good evidence to justify excessive mechanical polishing and electro-polishing, which for the most part migrated to the BioPharm industry from the Dairy industry.

It is helpful to remember that water does not adhere to stainless steel surfaces in the manner milk and cheese whey do.

Rouge Removal

Various chemicals and recipes are used to remove rouge.

- Effectiveness depends on:
 - Type of chemical or formulation
 - Concentration
 - Temperature
 - Exposure time
 - Method applied: Flooding / immersion, spraying, circulation, swiping, etc.

Rouge Removal Chemicals

- Phosphoric acid
 - Fairly effective
 - Does not etch the metal
 - Best overall
 - Often used as cleaning and passivating agent

Combining the effectiveness of phosphoric and that it does not etch the stainless, it is probably the best overall choice.

- Citric acid
 - Slow acting
 - Safe to handle
 - Not effective on hard baked-on rouge
- Oxalic acid
 - Very effective
 - Quick acting
 - Used for the worst cases of rouge
 - Can, and often does etch stainless steel
 - Length of exposure must be carefully controlled
 - Passivation is required after an oxalic acid cleaning and rinse
- Ammonium citrates
 - Similar to citric acid
 - More often used as passivation agent
- Proprietary formulations used by professional cleaning companies
 - Formulations depend on the severity of the problem
 - Phosphoric and oxalic acids and chelating agents are often part of the formulation
 - Chelating agents are mostly EDTA

Rouge Removal Methods

- One of the following methods or a combination may be used depending on the type, size, and configuration of equipment or parts to be cleaned.
 - Circulation
 - One way intermittent flow
 - Spraying
 - Flooding
 - Tank immersion
 - Swabbing / wiping
- Rinse surfaces very well after cleaning. Use DI, distilled or other good quality water.

References and Recommended Readings

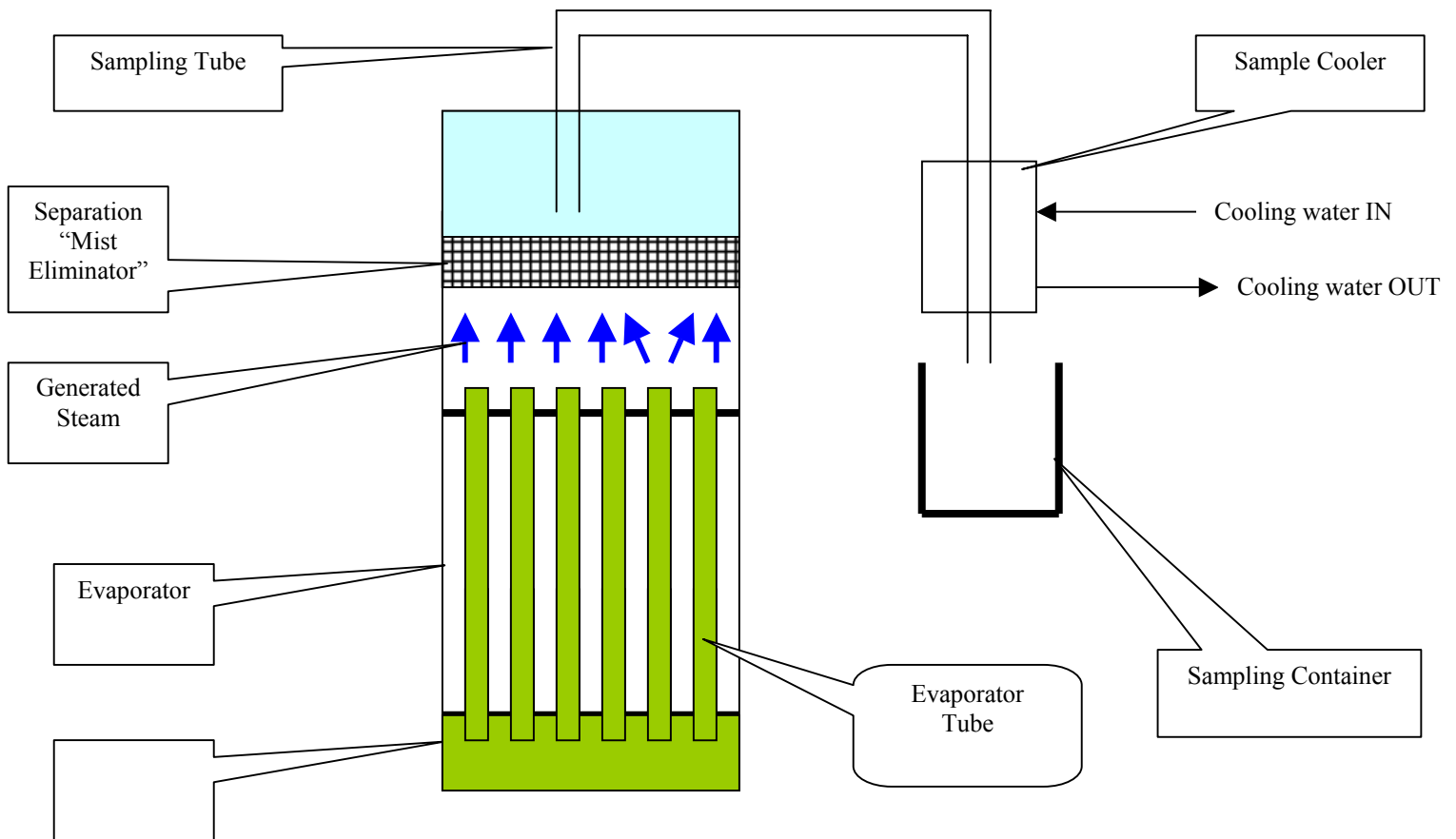
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Figure 1



Sampling of Steam from Stills or Pure Steam Generators



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