

# Valmet Technical Paper Series

## Paper Mill Boiler Chemical Cleaning – Why, When and How

### Executive Summary

A pulp and paper mill's operation requires that its boilers operate reliably and efficiently. Excess deposits within boiler tubes can cause failures of the tubes, which not only result in lost production, but can also place mill personnel and equipment at risk of injury and damage, particularly in the case of a chemical recovery boiler.

This paper addresses how deposits and their thicknesses, densities and compositions affect boiler reliability and efficiency. Methods to measure deposit thickness, density, and composition using ultrasonic and tube sampling techniques are discussed.

Methods to remove deposits are described, which will prevent tube failure and increase heat transfer efficiency. For large boilers, the removal of deposits by chemical means during an outage has been proven to be the most effective and efficient method. The steps required to plan and execute a boiler chemical cleaning program are discussed in detail. How to choose the chemicals to use based on the nature of the deposit are also reviewed. Effective chemical cleaning methodologies designed to provide the shortest outage duration are described for various boiler configurations. The means to minimize and/or eliminate hazard exposure to personnel and the environment are presented.

## Introduction

Valmet is the largest supplier of recovery and power boilers for the pulp and paper industry and has been offering inspections and chemical cleaning advisory services for boilers in North America for more than 35 years.

Boilers and their reliable performance are essential for every operating unit of a pulp and paper mill. However, excess deposits inside a boiler's tubes may cause failure of the tubes which not only results in lost production but also, in the case of recovery boilers, places mill personnel and equipment at risk of injury and damage.

Upon obtaining a threshold deposit weight density, deposits should be removed to prevent tube failure and increase efficiency. The removal of deposits by chemical means during an outage has been proven to be the most effective and efficient method.

This paper presents information to help the reader determine why a boiler requires chemical cleaning and when chemical cleaning is needed. Also presented and discussed are factors that contribute to a boiler chemical cleaning program.

## Definitions

**Beaker tests** – Laboratory tests to determine the solubility of the deposit in various cleaning solutions. These tests are done under the same conditions (temperature, concentration, etc.) as may be used on the cleaning project.

**Chemical cleaning** - The removal of deposits by dissolving or disintegrating the deposits in chemical solutions.

**Corrosion inhibitors** – Substances added to acids and other corrosive liquids to mitigate corrosion of the boiler materials of construction that occurs during cleaning.

**Deposit** – Unwanted solid matter, which separates out of fluids in a process stream, coating equipment surfaces and interfering with process efficiency.

**Deposit weight density (DWD)** – The weight of deposit material per boiler tube internal surface area unit. It is generally expressed as grams per square foot (g/ft<sup>2</sup>).

**Neutralization** - The elevation of the pH of the cleaned metal surfaces to above 7.0 in order to prevent acid corrosion during post-cleaning activities including operation.

**Passivation** - The formation of a thin, nonporous layer of magnetic iron oxide on the surface of the cleaned metal in order to prevent rusting before startup.

**Solvent** – Any liquid, aqueous or non-aqueous, used to chemically clean boilers.

## Why chemically clean?

Boilers are primarily chemically cleaned to prevent tube failures caused by under deposit corrosion or overheating due to the insulating effect of a deposit. Another reason for chemically cleaning a boiler is to reduce fuel costs also caused by the insulating effect of a deposit. Refer to **Table 1 (next page)**.

### Energy loss due to scale deposits\*

Scale thickness (inches)	Fuel loss (% of total use)		
	Scale type		
	"Normal"	High iron	Iron plus silica
1/64	1.0	1.6	3.5
1/32	2.0	3.1	7.0
3/64	3.0	4.7	-
1/16	3.9	6.2	-

Note: "Normal" scale is usually encountered in low-pressure applications. The high iron and iron plus silica scale composition results from high-pressure service conditions.

\* Extracted from *National Institute of Standards and Technology, Handbook 115, Supplement 1*. On well-designed natural gas-fired systems, an excess air level of 10% is attainable. An often-stated rule of thumb is that boiler efficiency can be increased by 1% for each 15% reduction in excess air or 40 °F reduction in the stack gas temperature.

**Table 1. Energy loss due to scale deposits**

## When to chemically clean?

The timing for chemically cleaning a boiler may be based on the following:

1. **After a feed water condition upset** – black liquor incursion, pH excursion, raw water incursion  
These events will result in inconsistent boiler water chemistry and possible corrosion both short and long term. Chemically cleaning should be performed boiler as soon as possible after these events.
2. **When the DWD becomes a threshold value.** Deposit weight density is determined by dividing the weight of a deposit by the tube area the deposit covers. The result is reported as grams per square foot (g/ft<sup>2</sup>)

The DWD threshold value depends on operating pressure.

Accepted thresholds are:

Below 1000 psi – 40 to 20 g/ft<sup>2</sup>

1000 to 2000 psi – 20 to 12 g/ft<sup>2</sup>

Chemical cleaning should be scheduled when any DWD measurement of the cold or hot side of a tube becomes a threshold value.

3. **When thick, localized deposits are present.** Thick, localized deposits can result in tube failure due to tube wall thinning and crack propagation caused by under-deposit corrosion. An example of a thick localized deposit is shown in **Figure 1**.



**Figure 1. Example of thick localized deposit**

## Deposit weight density determination

Deposit weight density is determined by weighing the deposit in a section of tube and dividing the weight by the area of the surface to which the deposit was adhering. The precursor to this requires a section of tube being removed from a water wall having the highest heat influx. The exterior deposits are removed from the section. A 1 to 1 ½" length is cut from the section and weighed. The interior deposit is removed either by brushing or, preferred, bead blasting. The length is reweighed. The weight loss of the length is the weight of the deposit. The DWD is then calculated by dividing the weight loss in grams by the area in square feet of the surface to which the scale was adhering.

Determining where to collect the tube section is usually an educated guess. However, the uncertainty as to where to collect the section can be eliminated by employing recently introduced ultrasonic technology. This technology detects deposit thickness and is applied very similarly to that method employed to determine tube metal thickness.

This system (**Figure 2**) is a combination of advanced UT hardware and software that was developed to measure and record thicknesses of the internal deposit layer and remaining tube wall in the water wall tube. The tube thickness and deposit layer are accurately measured by the difference in the wave form through the materials. Boiler tubes are prepared through the use wire wheel and a 1" X 1" area is cleaned near the crown of the tube shown in **Figure 3**. The detection process involves running a specially designed probe over the cleaned surfaces of tubes deemed to contain the greatest deposit weight density. The software interprets the ultrasonic wave reflections to a deposit thickness. A large number of tubes may be scanned over a 12-hour shift thus yielding a profile of deposit thickness across the scanned zones. The tube with the highest deposit thickness can then be targeted for section removal. If the approximate deposit composition is known, the software can be adjusted and the result can be used to calculate the DWD accurately.

There is reluctance to section a tube. However, a tube sample also provides the following benefits:

- A tube section allows determination of whether the deposit can be removed from the metal surface even though it may not all be dissolved. This will show that multiple solvent stages may not be necessary as previously thought.
- A cross section of the deposit on the metal may reveal layers which cannot be removed by a single solvent stage.
- In solubility tests, loose deposits in the beaker may react differently with the solvent than the deposit on a metal surface, such as a boiler tube.
- The surface of the cleaned tube section can be examined.



**Figure 2. Boiler tube deposit inspection system in use**



**Figure 3. Tube preparation completed**

If a current tube cut cannot be obtained, a sample from the most recent opening of the boiler may be submitted for analysis. Historical information from past cleanings is also helpful, but both of these approaches may fail to account for later episodes of contamination of the boiler water that can cause layers of deposit which may be more difficult to remove. Water samples, and deposit samples taken from drums, provide only limited information about the deposits in boiler tubes.

## How to clean?

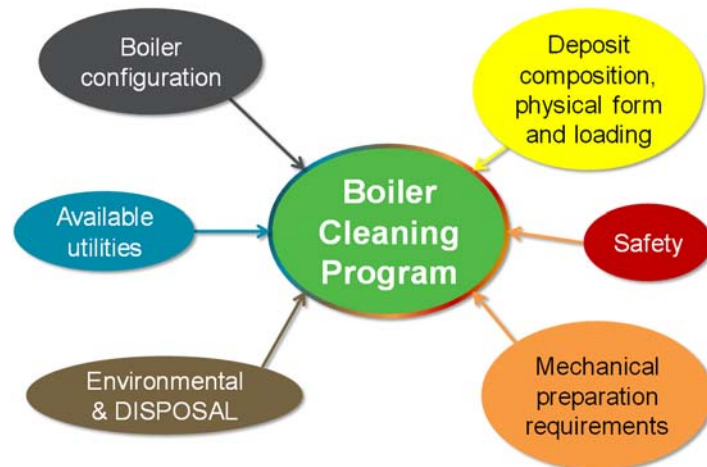
Several contributing factors must be considered when creating a boiler chemical cleaning program. These factors are illustrated in **Figure 4**.

### Safety

Personnel protection must be integrated into project engineering. The following steps should be taken:

- Barricade the boiler, manifold area, injection hoses, and temporary equipment in order to prevent nonparticipants from entering areas where they may be exposed to the chemicals.
- No welding or torch cutting is allowed on the boiler during the cleaning process, nor in the immediate area, because chemical cleaning usually generates flammable hydrogen gas.
- Personal protective equipment including chemical proof clothing, goggles, and respirators should be worn when entering the barricaded areas when chemical exposure is a risk.
- Hydrogen sulfide monitors should be in place.
- Escape routes should be planned and communicated.
- Personnel in adjacent operating areas should be informed of the operation and associated hazards.
- First aid and eye wash facilities should be immediately accessible.
- A safety meeting, with both plant and cleaning contractor personnel attending, should be held before the project starts.
- Check valves should be on all water and steam supply lines.
- All temporary piping and hoses should be hydrotested prior to introduction of solvents to the boiler.

### Contributors to boiler cleaning program



**Figure 4. Contributing factors**

### Solvent choice vs. deposit type

All acids and chelants must be used with corrosion inhibitor additives. All solvents indicated are used as dilute solutions in water. Concentrations of solvents, solution temperatures and other parameters will vary, depending on the specific solvent used, DWD, deposit composition and other factors.

The typical solvent used in the chemical cleaning of paper mill boilers is hydrochloric acid based. The prevalent use of this solvent is due to its relatively low cost and the ease of disposal of the waste solvent. The waste solvent is usually placed into a mill's process sewer after neutralization. For the purpose of this writing, the information which follows will be aligned with a hydrochloric acid based cleaning program.

## Corrosion of base tube metal by chemical cleaning

Corrosion of base tube metal during chemical cleaning is a valid concern. However, selection of the proper corrosion inhibitor and quantity keeps solvent corrosion to a minimum. There are many corrosion inhibitors on the market. They are generally complex proprietary mixtures. The chemical cleaning consultant will often recommend an inhibitor suitable for the project at hand. The owner may want to request supporting corrosion test data from the party making the inhibitor recommendation. A widely accepted criterion is that static lab tests, run within the proposed cleaning procedure parameters, yield metal loss rate data not greater than 500 mg/dm<sup>2</sup>/day (0.01 lb/ft<sup>2</sup>/day), with no visible pitting of the metal test specimens. Proper inhibition will allow no more than an average 0.00008 inch (0.002 mm) of metal loss during a typical hydrochloric acid solvent stage.

Deposits	Commonly used solvents
Magnetite, Fe <sub>3</sub> O <sub>4</sub>	Hydrochloric acid, HCl; Chelants: EDTA salts, citric acid salts
Copper oxide, CuO	Ammonium hydroxide, HCl + thiourea
Copper metal + oxide	Buffered ammonium hydroxide + oxidizer; ammoniated citric or EDTA salts + oxidizer
Water scale, mainly calcium carbonate, CaCO <sub>3</sub>	Hydrochloric acid, HCl; Chelants: EDTA salts; organic acids: formic, acetic
Black liquor scale	A separate stage of sodium hydroxide + potassium permanganate solution.
Silica, SiO <sub>2</sub> , or high silica water scale	HCl + ammonium bifluoride
Calcium sulfate anhydrite, CaSO <sub>4</sub>	HCl

**Table 2: Choices of solvents vs. boiler waterside deposits and metals**

Prior to introducing the solvent into the boiler, the solvent is to be tested for corrosion inhibitor effectiveness. This is done by collecting a sample of the solvent from its storage tank and diluting the sample to proper strength. The diluted sample is then subjected to tests to determine the effectiveness of the corrosion inhibitor. If the tests indicate that corrosion inhibition is inadequate, then the storage tank is agitated to ensure the contents are thoroughly mixed and the solvent is retested. If the test again indicates that corrosion inhibition is not adequate, then additional inhibitor is to be added to the solvent, the solvent further agitated, and the solvent retested.

Another form of corrosion which is concerning is ferric ion corrosion. When iron oxide dissolves, ferric ion (Fe<sup>+3</sup>) is released and corrodes the exposed tube metal. As the weight density of iron oxide increases, the amount of ferric ion corrosion increases. However, even for a high iron oxide weight density, the total average metal loss is less than 0.050 inch or 1.3 mm. Nevertheless, this form of corrosion can be eliminated by the addition of a reducing agent such as sodium erythorbate to the iron oxide solvent. This material will reduce the ferric ion before the ion reacts with the base tube metal.

Corrosion rates during a chemical cleaning project are sometimes measured by inserting metal test specimens in the boiler or testing a sample of the solvent collected from the boiler.

## Tube leaks occurring during chemical cleaning

In older boilers that have not been chemically cleaned, leaks in tubes and permanent drain piping sometimes occur. The leaks are usually the result of exposure of existing holes or cracks by the removal of the deposit.

## Neutralization and passivation

Neutralization involves filling the boiler with a high pH solution of soda ash, caustic or ammonia. This step is performed to ensure any residual low pH solvent is neutralized.

Passivation is the formation of a nonporous, tightly adhering thin film of magnetite on the cleaned boiler surfaces. This film is important to prevent rusting and is helpful for inspection. The formation is achieved by filling the boiler with a high pH solution at an elevated temperature and containing a passivator such as sodium nitrite. Alternatively, the film may be formed by firing the boiler to a minimum of 10.6 kg/cm<sup>2</sup> (150 lb/in<sup>2</sup>) while filled with a soda ash or caustic solution, and maintaining this pressure for a specified minimum amount of time.

## Boiler configuration and flow circuitry

The configuration of a boiler will greatly affect the means that the boiler will be filled, drained, and circulated.

Some boilers require a specific circulation method. For example, screen pendent sections in chemical recovery boilers require a circuit that will allow circulation of this boiler section separately from other boiler sections.

## Filling and draining

Systems should be properly sized in order to allow filling and draining to be rapidly performed. Filling should usually be done in less than 90 minutes and draining should take not more than two hours. Rapid boiler filling and draining reduces overall base metal loss by reducing unnecessary amounts of time a corrosive solvent contacts the boiler metal. Rapid filling and draining also results in a shorter outage schedule thus minimizing lost production.

A typical filling and draining system, incorporating a chemical-blending manifold, is used for the simultaneous injection and heating of a solvent as well as for the proper dilution of solvent concentrates. This system also provides important control of filling temperature, pressure and flow.

For safety, welded carbon steel or stainless steel piping and components should be used. The initial cost of piping may be greater than hose, but piping will prove to be less costly over the life of the boiler if the boiler is cleaned routinely on a 5- to 7-year basis. Also, welded piping greatly reduces the possibility of leaks.

The manifold is connected to pressurized hot condensate or feed water supply for heating of the liquid to temperatures up to 93 °C (200 °F) as the boiler is filled with the solvent. In order to prevent overheating of the solvent and also to supply proper dilution of the solvent concentrate, pressurized cool condensate, treated water or demineralized water is also piped to the manifold.

Flow meters are used in order to monitor total flow and to quickly obtain the proper dilution of the solvent concentrate. A sample point is installed for sampling the solvent for active component concentration analysis. Distribution of the solvent during filling from the manifold is by separate lines to the lower water wall headers, lower pendent screen header, downcomers and economizer inlet header.

The manifold also allows for used solvent draining via piping leading to a sewer or to used solvent storage tanks. If waste solvent neutralization is required, 50% liquid caustic may be injected (metered) into the chemical concentrate injection nozzle while the used solvent is draining from the boiler.

## Solvent circulation or agitation

After the boiler is filled with the solvent at proper concentration and temperature, agitation of the solvent is required in order to maintain uniform heat distribution and to increase the dissolution rate of the deposit.

The means of solvent agitation include:

- Circulation by external pump
- Circulation by gas lift with nitrogen or air
- Thermal circulation by firing and cooling the boiler
- Draining a portion of the solvent from the boiler to an external tank and pumping the drained solvent back into the boiler

### *Circulation by external pump*

Circulation by external pump normally consists of pulling suction from the lower water wall headers and discharging into the lower screen pendent header and lower header of the first economizer. This method's disadvantage is higher piping costs. For hydrochloric acid based solvent, circulation is intermittent to minimize corrosion. For ammonia based copper solvents and passivation solutions, continuous circulation is acceptable and often desired.

### *Gas lift*

Gas lift yields excellent temperature, solvent concentration uniformity and the least amount of sludge. The gas flow to yield the required circulation rate can be calculated. The gas is injected into the downcomers creating lift of the solvent. The solvent rises and flows into the steam drum. From the steam drum the solvent flows into the upper water wall headers and down the water walls. This fills the partial vacuum in the lower portion of the downcomers created by the solvent lift. The exact flow rate of the solvent can be observed using a Doppler ultrasonic flow meter. If proper venting is not available for exhausting the gas from the boiler, only low flow of the solvent can be obtained.

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## WARNING:



**Air is never to be used to circulate iron oxide solvents because the corrosion properties of the solvent will be greatly increased.**

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### *Draining and pumping back into the boiler*

Draining and pumping back into the boiler is a relatively inexpensive method of solvent agitation and may be used when unusual circumstances prevail. This method has the inherent disadvantages of:

- Intermittent contact of the upper headers and connecting wall tubes of some boilers by the solvent
- Cooling of the solvent during the draining and pumping if an external heat exchanger is not utilized
- Non-uniform mixing of the solvent in the boiler resulting in concentration differences in the solvent

## Mechanical preparation requirements

Proper mechanical preparation is imperative for a successful project. The items described in the following text are minimum mechanical requirements.



## Solvent level indication in the steam drum

Monitoring of the solvent level in the steam drum is very important to ensure that the liquid level is high enough that the upper wall headers and riser relief tubes are filled. Level monitoring is also important to ensure the solvent does not completely fill the steam drum and exit the vents or enter the superheater. Solvent steam drum level monitoring is done by use of a temporary sight gauge. Use of the permanent level indicator could result in damage to this instrument.

## Lower header hand hole cap removal

Sludge will also settle in lower pendent screen and water wall headers. To remove this sludge, access to the interiors of the headers is necessary. This access requires removal of hand hole caps or inspection nipple caps.

## Nozzles for filling and draining

As previously stated, rapid filling and draining is necessary. This requires chemical cleaning nozzles of proper size and locations. Each boiler to be chemically cleaned should be examined to ensure proper nozzles exist. If not, then proper nozzles must be installed.

## Steam drum internals

Sludge laying in the near horizontal tubes of the boiler bank of two drum boilers is normal following the chemical cleaning of these types of boilers. To prevent solidification in place of this sludge after startup, the sludge has to be removed by hand flushing. These tubes need to be flushed with a hose from the steam drum in order to successfully remove this sludge. To access the tubes in the steam drum requires the steam drum internals to be removed.

## Pendent screen circulation

Pendent screen circulation requires a separate circulation line being installed from a pump discharge if the existing lower pendent header drains are of small diameter. Also, the supply tubes in the lower drum must be plugged or severely restricted to prevent the flow from short circuiting.

## Available utilities

Utilities are necessary for the execution of a boiler chemical cleaning project. Project planning must include that utilities will be available for the cleaning.

Boilers have to be preheated before being filled with solvent. The solvent itself must be heated to a temperature that will effectively remove a deposit - yet minimize its corrosive properties. These require either steam or feed water.

Pumps for circulating solvents may need electricity for their power. Compressed industrial grade and oil free air are required for transfer pump operation and solvent circulation. Proper lighting is required. Demineralized or cool treated water is required for solvent tempering, boiler rinsing and post-cleaning hand flushing.

## Environmental requirements and solvent disposal

Integral to any boiler chemical cleaning project are the following questions:

1. How are waste solvents to be disposed?
2. What condition do waste solvent have to be in to be disposed?
3. What chemicals may be allowed on site?
4. Are spill containment and removal measures in place?
5. How will boiler leaks be managed?

## Other prerequisites

In addition to those discussed previously in this paper, other prerequisite items are important:

### A procedure covering each aspect of the project

The entire chemical cleaning procedure should be in place and understood by personnel involved in the project. The procedure should be flexible in order to accommodate unusual occurrences. It should include practical contingency plans for upset conditions.

### Schedule allowing sufficient time for the project

The schedule should be developed well before the project begins. However, means of keeping the project schedule as brief as possible should be examined and, if technically and mechanically sound, implemented.

### Solvent sampling

Samples of the solvent should be collected on a periodic basis in order to determine the progress of the cleaning. Hourly sampling is adequate for most projects, while 30-minute sampling intervals should be used for low pH cleaning solutions. When a deposit dissolves in the solvent, metal ions of the deposit are released into the solvent. The concentrations of these ions will continuously increase until all of the deposit is dissolved or the solvent is spent. If the solvent spends, additional acid may be added or the boiler may be drained and filled with fresh solvent. The time for solvent contact termination is indicated when the concentration of the ions stabilizes and there is adequate free solvent. Therefore, analysis of the solvent should be performed for dissolved ions and solvent concentration while the solvent is in the boiler. Properly placed sampling points should be provided in order that samples of the solvent may be collected.

If the solvent is being circulated, sampling the solvent from the steam drum will be adequate due to the uniformity of the solvent within the boiler. This sample should be collected from the drain on the bottom of the steam drum temporary sight gauge. (When using high temperature solvent [greater than 93 °C / 200 °F], sample coolers should be installed at the sample points.) Solvent samples may also be collected from the temporary piping if external circulation is employed.

For the case where the solvent is drained to a tank and pumped back into the boiler, samples should be collected from the steam drum and from the solvent drained to the tank. This is because the concentrations of components within the solvent at the top and bottom of the boiler may be non-uniform resulting in a termination indication at one sampling point that is not indicated at the other sample point.

When the concentrations of the analyzed components do not change (i.e. they stabilize) over at least three sample periods, then the adhering deposit is deemed removed from the interior boiler surfaces.

In chemically cleaning boiler with a high deposit weight density, high dissolved iron concentrations (> 1.0 wt-%) may occur. If the iron concentration exceeds 1.2 wt-% without indication of stabilization, then an accelerated corrosion condition exists and the solvent should be immediately removed from the boiler.

### Superheater protection

Superheater protection is of utmost importance since allowing solvent to spill into the superheater can result in permanent damage. At a minimum, the superheater should be filled with high quality water containing an oxygen scavenger. Although this will not prevent solvent from entering the superheater, it will provide some protection by diluting any solvent that may enter the superheater from the steam drum. If solvent enters the superheater, immediately backfilling the superheater with high quality water from the superheater outlet to the steam drum will likely flush the solvent from the superheater. To fill the

superheater with water, first fill the boiler with water to an indicated level in the steam drum. Then backfill the superheater with high quality water into the superheater outlet line just upstream of the non-return valve. The water will flow through the superheater to the steam drum. Indication that water is flowing into the steam drum from the superheater is by noting a rise in the level of the water in the steam drum as indicated by the temporary sight gauge.

A well-designed and constructed temporary steam drum level gauge that is constantly monitored by a person in good communication with the cleaning crew will greatly reduce the possibility of superheater contamination.

Added protection of the superheater can be achieved by installing plugs at the steam drum in the superheater inlet header supply lines, or in individual inlet tubes.

## Personnel

Engaging an independent consultant is recommended. This individual will plan a safe, environmentally responsible program that will result in a clean boiler at the least overall cost. Personnel involved must be briefed and certain of their duties. The chemical cleaning contractor and mill must provide around-the-clock coverage by experienced supervisors and operators. The boiler operator should assign two operators per shift to operate permanent equipment and coordinate with other mill departments.

## Temporary equipment

All equipment should be proven and mechanically capable of performing its designed function. Also, all temporary equipment must be inspected and cleaned of all foreign material before it is made part of the cleaning project.

## Personnel briefing

All personnel, including those not involved in the project but in the area or in adjacent areas, should be fully briefed on the associated hazards. A loss prevention plan should be implemented and understood by all personnel.

## Inspection

Hand flushing should be followed by a thorough inspection to look for any excessive pitting and other anomalies.

## Conclusion

Boiler reliability and efficiency are necessary for a pulp and paper mill's profitability. The growth and analysis of boiler deposits should be part of any boiler reliability and inspection program. When boiler deposits reach a DWD threshold value or feed water upsets occur, then the chemical cleaning of the boiler should be planned and executed as soon as possible by knowledgeable and experienced personnel.

*This white paper combines technical information obtained from Valmet personnel (Dewey Johnson, David Kittel) and published Valmet articles and papers.*

*Valmet provides competitive technologies and services to the pulp, energy and paper industries. Valmet's pulp, paper and power professionals specialize in processes, machinery, equipment, services, paper machine clothing and filter fabrics. Our offering and experience cover the entire process life cycle including new production lines, rebuilds and services.*

*We are committed to moving our customers' performance forward.*