Control of Deposition Risks in High-Silica Boiler Waters:
A Novel Approach Using Purified Tannin Chemistry

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ABSTRACT

The use of make-up water sources having a high-silica concentration has proven to be a major challenge for the operation of industrial steam boilers. Despite advances in conventional deposit control technologies, high-silica boiler water (>150 mg/L as SiO_2) continues to have a major impact on the operation and efficiency of boilers. The primary concern is avoiding silica/silicate-based deposits which are thermally insulating and significantly reduce heat transfer. Conventional treatment requires limitations on boiler silica levels which can result in operation at low cycles of concentrations, excessively high make-up water and blowdown rates, and high fuel usage rates.

Here, case studies show that Purified Tannin treatment (a green chemistry process) not only allows boiler operations at significantly higher silica levels while inhibiting formation of scale, but also shows visual evidence suggesting removal of previously deposited scale. Moreover, laboratory results using photometric dispersion analysis (PDA) and dynamic light scattering (DLS) show that silica/tannin are still stable at silica levels well above any established industry guidelines.

This work provides a new model for steam boilers that utilize high-silica water for their make-up. It demonstrates that operation at higher cycles of concentration and boiler silica levels is attainable while controlling deposition risks in the boiler. Finally, operational guidelines are proposed for boilers operating with Purified Tannin.

KEYWORDS

Green chemistry, tannin molecules, silica, colloids, steam boilers, scale, corrosion inhibition

INTRODUCTION

Control of corrosion and scale is critical for the protection of capital assets throughout industry and society. It is especially important for the treatment of industrial steam boilers where metal surface temperatures exceed the boiling point of water at the boiler operational pressure. It is well known that temperature increases the potential for corrosion of metals and scale deposition. Generally speaking, methods to control scale and corrosion have been on-going processes in many industries.

Because of economic concerns and climate change, water and energy usage and exhaust gas emissions have become major factors that must be considered in the overall benefits of water treatment. For industrial

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steam boilers, not only the cost of the boiler treatment is considered, but we can now calculate the savings from reducing the use of fuel and water, and the amount of greenhouse gas (GHG) emissions (depending on the state, province, or country). Interestingly, in the near future it is expected that the industry will be able to estimate the disability-adjusted life years (DALYs), resulting from water treatment, through life cycle impact assessment methodologies. Nonetheless, we must calculate as precisely as possible the following savings: energy, GHG, and water!

One of the difficult aspects of scale and corrosion inhibition in steam boilers is to minimize scale formation on the tube surface, i.e. below the critical point where heat transfer efficiency is reduced. The industry has been able to correlate, and in some cases, quantify the additional amount of fuel required for steam generation per thickness of boiler tube scale. Obviously, this correlation is a function of the type of metal and the chemical composition of the scale, i.e. organic and/or inorganic (e.g. carbonates, hardness salts, silica-based, and phosphates). Scaling is not specific to boilers or equipment, it also occurs in plants and living organisms, e.g. inside daphnia. Scale formation at high pH and temperature is easier to trigger and normally a challenge to prevent and difficult to remove. Several ways to remove scale can be used, but may cause challenges and safety issues. Some of the approaches can be performed during normal operation or only when the boiler and associated equipment are shut down, which can be very expensive. Obviously, a hybrid approach is possible, for example, an acid cleaning followed by an on-line addition of synthetic or natural chelating/dispersing agents or polymers.

There is a consensus among industry experts that high-silica concentration is a major challenge for the operation of steam boilers. Despite advances in conventional deposit control technologies, high-silica boiler water (>150 mg/L) continues to have a major impact on the operation and efficiency of boilers. The solubility of crystalline silica (quartz) is quite low with 5-6 mg/L at 25°C and pH < 9, with the solubility of amorphous silica ranging from 120-150 mg/L at 25°C and pH 8-8.5 [1]. Colloidal silica that enters equipment with the feedwater can settle on the boiler tubes in form of silicates [2]. Silica-based deposits are highly insulating and greatly reduce heat transfer. For instance, deposits composed of silicates were found to be responsible for the failures of boiler tubes in thermal power plants and it is also a great problem in geothermal energy utilization [3]. It is widely accepted that the polymerization of silica monomers is the formation mechanism of amorphous silica deposits [4,5]. Conventional treatment requires limitations on boiler silica levels which can result in operation at low cycles of concentrations, excessively high make-up water and blowdown rates, and high fuel usage rates. Hence, the control of deposition risks in high-silica boiler water is a challenging task that has not yet been fully addressed.

This work describes case studies to support the possibility to control deposition risks in high-silica boiler water using Purified Tannin chemistry. The second part of this work conveys scientific evidence that silica/tannin are still stable at silica levels well above any established industry guidelines. Finally, we will propose operational guidelines for protecting steam boilers when using green chemistry through tannin treatment and compare them with ASME guidelines.

MATERIALS AND METHOD

Chemical and Solutions

The Purified Tannin solution was prepared by diluting concentrated TG-3106, provided by TGWT Clean Technologies Inc., using Reversed Osmosis (RO) water. Pure colloidal silica nanoparticles (30 nm, 50%

(wt/wt) Ludox TM-50) were purchased from Sigma Aldrich, Ontario, Canada. Nissan Chemical America kindly gifted a sample of aqueous colloidal suspension of 200 nm pure silica nanoparticles (40% (wt/wt) MP-2040). The size of silica nanoparticles was measured with DLS, and their diameters were found to be 35±2 and 207±2 nm, with a polydispersity (PD) index of 0.19 and 0.03, respectively. Ferrous sulfate, ferric sulfate, sodium sulfate, sodium chloride, magnesium chloride, and calcium chloride were supplied by Sigma Aldrich, Ontario, Canada. For pH adjustment, concentrated sodium hydroxide and sulfuric acid from AquaPhoenix, Pennsylvania, USA, were used.

Photometric Dispersion Analyzer (PDA)

Changes in the stability of silica and/or Purified Tannin, hereinafter referred to as tannin, were monitored with a Photometric Dispersion Analyzer (PDA 2000 Rank Brothers, Cambridge, UK) [6,7]. The silica/tannin suspension was pumped through a transparent 3 mm diameter tubing into the photocell of the PDA, which monitors the fluctuations in intensity of transmitted light (figure 1). In the present study, the suspension was pumped using a peristaltic pump at a constant flow rate corresponding to an average shear rate (G) of ~200 s^{-1}. This experimental setup allows measurements of the aggregation and break-up kinetics.
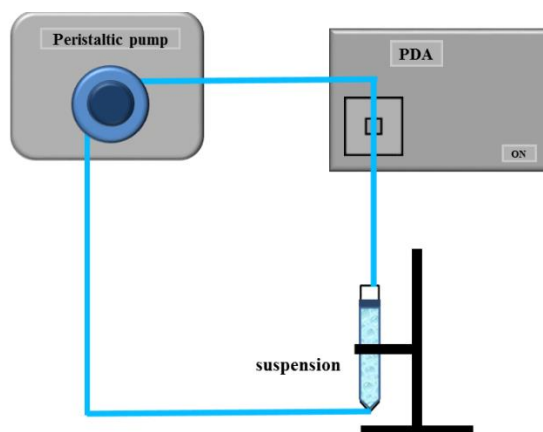

Figure 1: Experimental set-up for the Photometric Dispersion Analyzer (PDA).

The transmitted light intensity has two major components: $\bar{V}$ which represents the average transmitted light intensity (DC; direct current) and a much smaller component (V_{rms}) defined as the standard deviation around the mean signal. The V_{rms} increases considerably as particles aggregate, whereas the aggregation only slightly changes $\bar{v}$. Therefore, a significant increase in the ratio (R), also referred to as aggregation index (AI), is a clear indication of particle aggregation, with R defined as:

$$R = \frac{V_{rms}}{\bar{V}}$$ **Eq. 1**

For dilute systems, R varies linearly with the square root of the concentration, and for polydisperse systems R is approximately linear with the particle radius, a [6,7]:

$$R \cong CN^{1/2}a \qquad\qquad \textbf{Eq. 2}$$

where N is the number of particles per unit volume, and C is a constant. Changes in R (ΔR) correlate with changes in size (Δa) measured by static light scattering/diffraction [8]. PDA is a powerful technique to monitor particles stability at various shear rates in real time [9-13]. Interestingly, the PDA detection limit of about 0.5 micron is about 100 times smaller than what a human eye can actually see.

Dynamic Light Scattering (DLS)

Particle size analyses were performed using a Brookhaven 90Plus particle size analyzer. DLS results are average of three measurements without stirring at 25 ± 0.1 °C. Measurements were carried out at an angle of 90° from the incident beam.

RESULTS AND DISCUSSION

This work is divided into three parts. The first part is to present case studies showing the use of tannin for the control of deposition risks in high-silica boiler waters. The second part is to present some scientific evidence for the stability of silica/tannin at conditions well above industry guidelines for boiler water operation. Finally, operational guidelines are proposed for protecting steam boilers when using tannin, and those guidelines are compared to ASME guidelines.

Case Studies

Three steam boiler case studies are presented where the source for make-up was high-silica water. In all cases, conventional treatment technology was replaced with tannin technology, and the boiler cycles of concentration were significantly increased, hence boiler silica content were much higher than traditional limits [14]. A few critical boiler water parameters were plotted to show the trends before and after tannin treatment was implemented. The average and standard deviation were calculated for the pH, silica concentration, un-neutralized (UN) and neutralized (N) conductivities, M-Alkalinity, and residual tannin. The data of the transition period between treatments were excluded to prevent any skewed average. Pictures of boiler tubes, taken during openings/inspections, are provided to show visual depiction of the boiler conditions before and after tannin treatment.

Poultry Industry Feedmill (USA)

A poultry industry feedmill was using a 200 HP fire-tube boiler for process and heating applications. The boiler was operating at approximately 100 psig and burning propane (LPG) for fuel. The mill called for about 30,000,000 lbs per year of steam and returned about 20% of that to the boiler as condensate. The well water used as the source of make-up for the boiler contained high levels of silica that ranged seasonally between 25 and 40 ppm as SiO_2. Along with the low percentage condensate return, the high-silica in the make-up limited the boiler operation to about 15 cycles of concentration. A conventional sulfite, polymer, caustic, and amine program was used to treat the boiler system. At those 15 cycles, as depicted in figure 2, some deposition was noticed at annual boiler inspections and the boiler silica levels climbed above 150 ppm (table 1).

Figure 2: 2014 inspection of top (left and middle) and bottom (right) tubes while using conventional treatment.

After the inspection in late November of 2014, the boiler treatment was switched to a tannin program on December 2nd. The conductivity control range was increased significantly while using the same make-up water source. Table 1 summarizes the boiler operational data while using conventional treatment up to 12-01-2014 and while using the tannin treatment from December 2nd 2014 to the date of the writing of this paper (June 2016). It can be seen that the conductivity, M-alkalinity, and silica levels in the boiler were maintained well above established industry guidelines while using tannin.

Table 1: Boiler water parameters before and after using tannin.

Boiler water parameter	Conventional treatment	Tannin treatment
Cycles of concentration*	15 (*10*)	50 (*35*)
% Blowdown	6.4 (*10*)	1.9 (*2.9*)
pH	10.5 ± 0.3	11.7 ± 0.3
Silica as SiO_2 (ppm)	179 ± 80	$1,288 \pm 235$
Un-Neutralized conductivity (μmhos cm^{-1})	$2,348 \pm 403$	$10,720 \pm 1026$
M-alkalinity as $CaCO_3$ (ppm)	355 ± 129	$1,497 \pm 605$
Residual tannin (ppm at 420 nm)	Not Applicable	171 ± 60

*Based on Un-Neutralized conductivity and (Neutralized conductivity).

Several benefits of switching to tannin treatment and operation at significantly higher cycles are reduction in boiler blowdown and sewer water discharge, make-up water requirements, propane usage for fuel, and level of greenhouse gas (GHG) emissions. These results were tabulated and documented as boiler house budgetary savings for the feedmill. Figure 3 depicts the condition of the boiler in November of 2015, after one year of operation using tannin treatment. The UN conductivity control set-point was typically 12,000 μmhos cm^{-1} and the typical boiler silica level was 1,200 ppm as SiO_2. It can be seen in figure 3 that pre-existing scale on the tubes seen in figure 2 has been partially removed.

In conclusion, the poultry industry feedmill boiler was allowed to safely operate at much higher conductivity and cycles of concentration, and at extremely high-silica levels. The boiler inspection revealed that the tannin treatment not only inhibited scale formation, but also showed visual evidence of scale removal.

Figure 3: 2015 inspection of top (left and middle) and bottom tubes while using tannin treatment.

Figures 4 to 12 are presented to show the key data trends for the feedwater and boiler water for the periods before and after the tannin treatment. Charts depict raw data trends and calculated boiler cycles going back several years of operation to current date. To minimize space in this paper, certain feed water and boiler water data sets were plotted together. To emphasize important points during the operation using tannin treatment, data sets starting in December of 2014, were isolated and plotted.
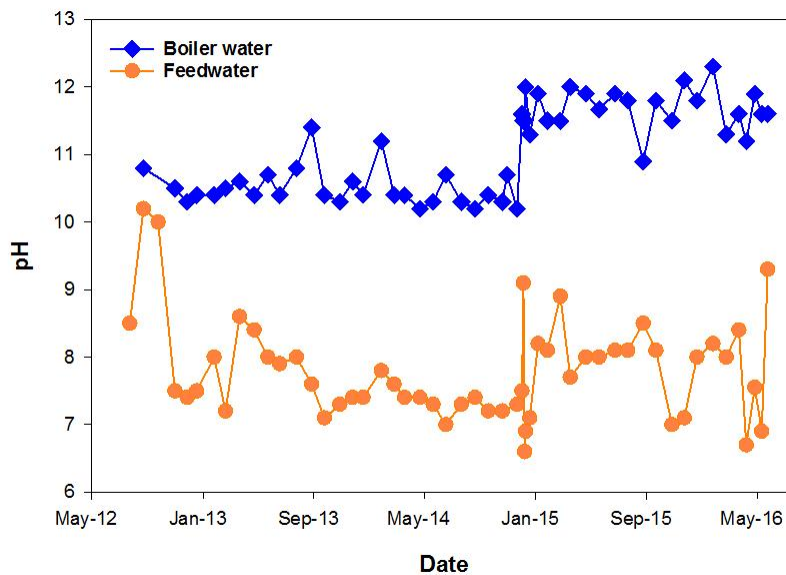
Figure 4: Boiler feedwater and boiler water pH versus time (tannin treatment started 12/02/2014).
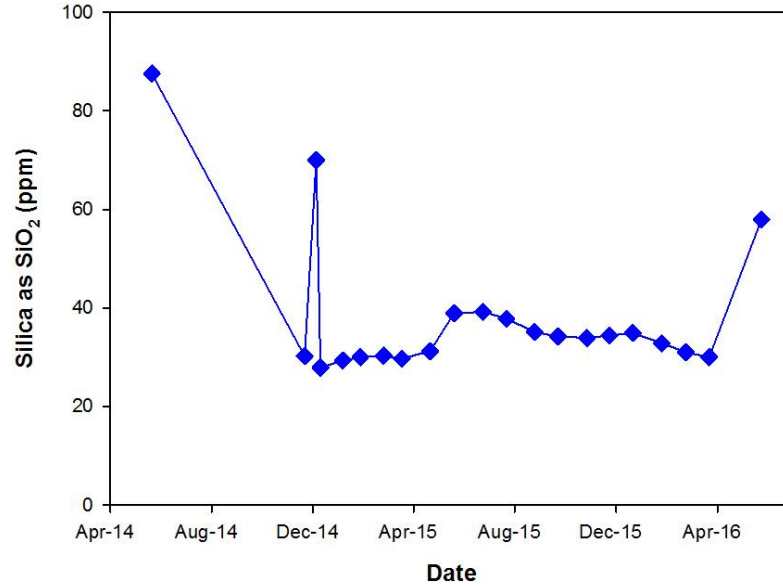
Figure 5: Boiler feedwater silica levels versus time (tannin started 12/02/2014).
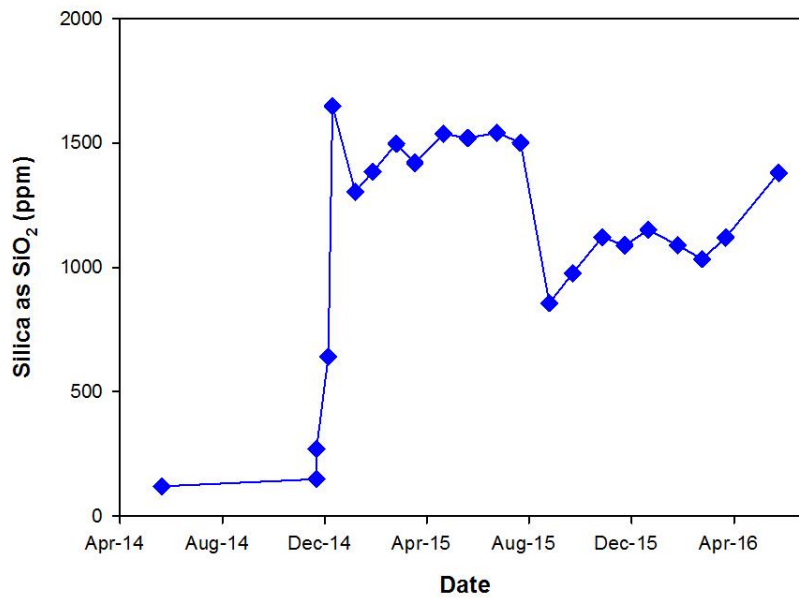
Figure 6: Boiler water silica levels versus time (tannin started 12/02/2014).
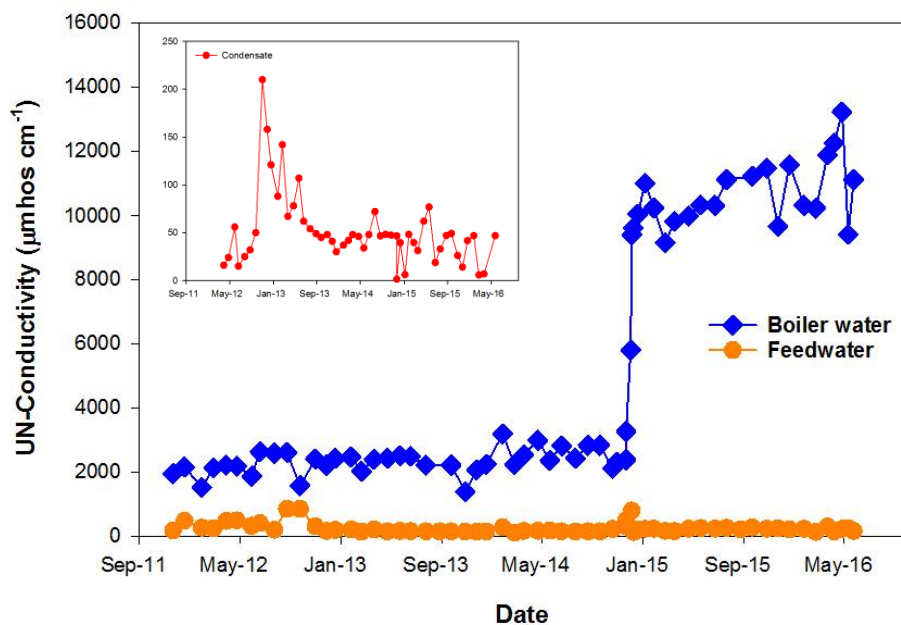
Figure 7: Boiler feedwater and boiler water (Un-Neutralized) conductivity versus time (condensate conductivity inset).
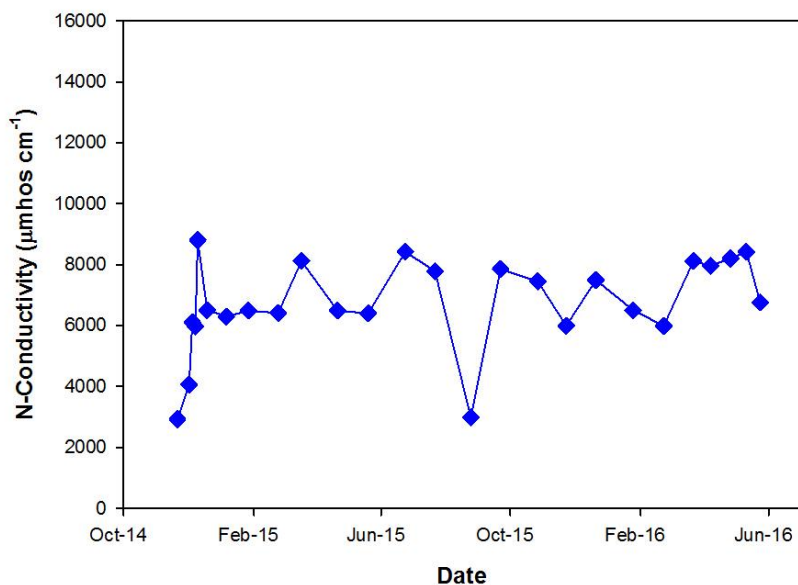
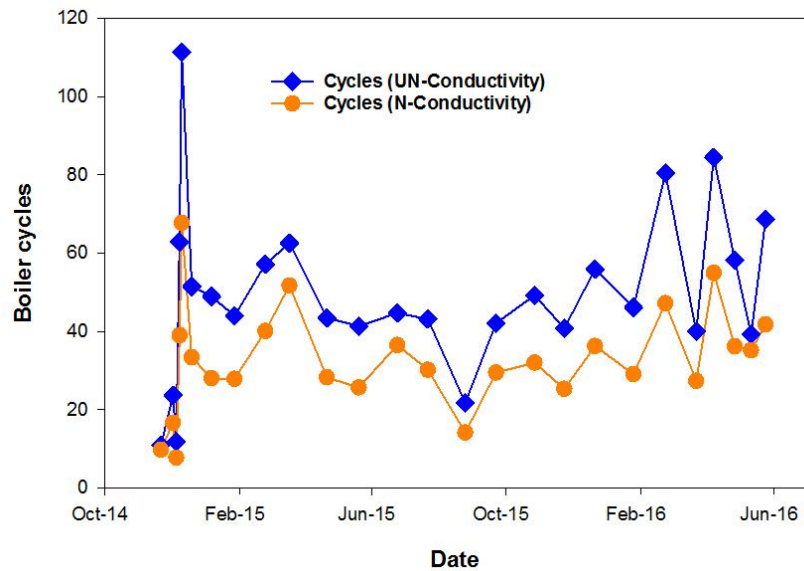**Figure 8: Boiler water Neutralized conductivity versus time.**

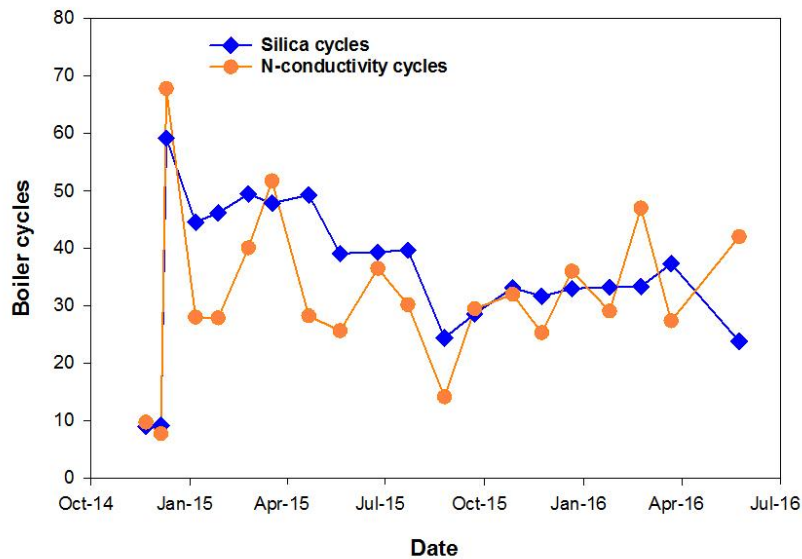**Figure 9: Boiler cycles versus time (based on Un-Neutralized and Neutralized conductivities).**

Figure 10: Boiler cycles versus time (based on silica and Neutralized conductivity).

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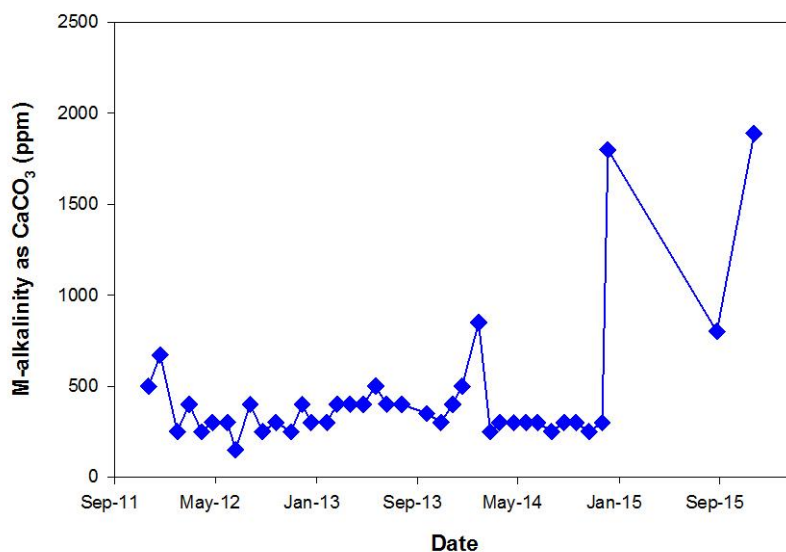
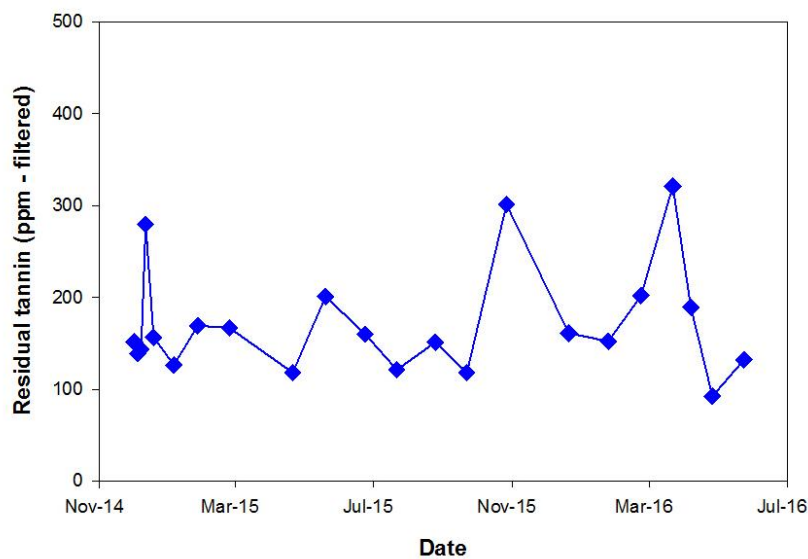**Figure 11: Boiler water M-alkalinity versus time.**

Figure 12: Boiler water residual tannin versus time (using Hach DR 890 Unit at 420 nm wavelength).

Textile Industry (Mexico)

Mexico is known for having volcanic formations which result in many regions of the country having ground water containing significant levels of silica. This has caused silica control to be a major issue for steam boiler operation throughout the country. Silica levels can range from 40 to 105 ppm in ground water. A textile manufacturer in Mexico has been dealing with this issue for many years, and utilized make-up water containing $60 - 80$ ppm of silica as SiO_2.

The facility has a 3 fire-tube boilers burning natural gas for fuel: a 200 HP and a 400 HP operating since 1998, and a 500 HP operating since October of 2014. The operating pressures for the boilers range from 87 to 116 psig, and the condensate return for all 3 boilers was approximately 33%. The low condensate return rate and high-silica levels of the make-up water significantly limited the number of boiler cycles of concentration. Even at low cycles, boiler scale was encountered requiring periodic acid cleanings.

The boilers were treated with a conventional phosphate, caustic, and silica dispersant program until June 2015. The low cycles of operation resulted in a high blowdown rate, and a huge requirement for make-up water and natural gas for fuel. On June 8th 2015, the boiler treatment program was switched to tannin to address the deposit issues and to allow operation at higher cycles of concentration.

Under the tannin program, pH, silica, conductivity, residual tannins, chlorides, and the boiler cycles of concentration were initially monitored on a weekly basis, followed by monitoring on a monthly basis. Typical values for all data monitored are listed in table 2. Caustic feed for boiler alkalinity control was not required with the tannin program. Although the tannin program does not require measurement of either P, M or OH alkalinity, the M-alkalinity was measured to provide comparison with conventional treatment.

Table 2: Boiler water parameters before and after tannin treatment.

	Boiler 200 HP		Boiler 500 HP	
Boiler water parameters	**Conventional treatment**	**Tannin**	**Conventional treatment**	**Tannin**
Cycles of concentration*	5	13	5	16
% Blowdown	20	7.7	20	6.1
pH	11.0 ± 0.4	11.4 ± 0.3	11.3 ± 0.5	11.6 ± 0.4
Silica as SiO_2 (ppm)	297 ± 64	748 ± 165	289 ± 47	946 ± 304
Un-Neutralized conductivity (μmhos cm^{-1})	$4,227 \pm 768$	$8,184 \pm 1,775$	$4,710 \pm 1,525$	$10,331 \pm 3,079$
M-Alkalinity as $CaCO_3$ (ppm)	$1,063 \pm 367$	$2,338 \pm 652$	$1,275 \pm 438$	$2,957 \pm 953$
Residual tannins (ppm)	Not Applicable	139 ± 80	Not Applicable	203 ± 101

*Number of cycles based on chlorides.

As a result of switching to the tannin program, the number of boiler cycles was increased from 5 to 13 (200 HP) and from 5 to 16 (500 HP). The % blowdown was reduced from 20% to 7.7% (200 HP) and 20% to 6.1% (500 HP). These higher boiler cycles resulted in significant reductions in water and natural gas requirements. The Un-Neutralized conductivity control set-point ranged from 8,000 to 10,000

μmhos cm^{-1} for the 2 boilers. The typical boiler silica levels averaged 750 ppm and 950 ppm as SiO_2, which are well above industry guidelines for fire-tube boilers operating at <300 psig.

Figure 13 shows the condition of the 200 HP boiler using conventional treatment at low cycles in comparison to that after one full year of operation using the tannin treatment at much higher cycles. On-line clean-up of old deposits was noted during inspection. Figure 14 shows the condition of the newer 500 HP boiler six months after using the tannin treatment at higher cycles. The boiler tubes are noticeably clean.

In conclusion, the textile manufacturer's boilers were allowed to safely operate at much higher conductivity and cycles of concentration, and at extremely high-silica levels. The boiler inspections revealed that the tannin treatment not only inhibited scale formation, but also showed visual evidence of scale removal for the 200 HP boiler.

Figure 13: 200 HP boiler, December 2014, conventional treatment (left); June 2016, after one year of tannin treatment (right).

Figure 14: Inspection of 500 HP boiler, December 2015, after 6 months of tannin treatment.

Figures 15 to19 are presented to show the key data trends for the boiler water for the periods before and after the tannin treatment. Charts depict raw data trends going back several years of operation to current date.
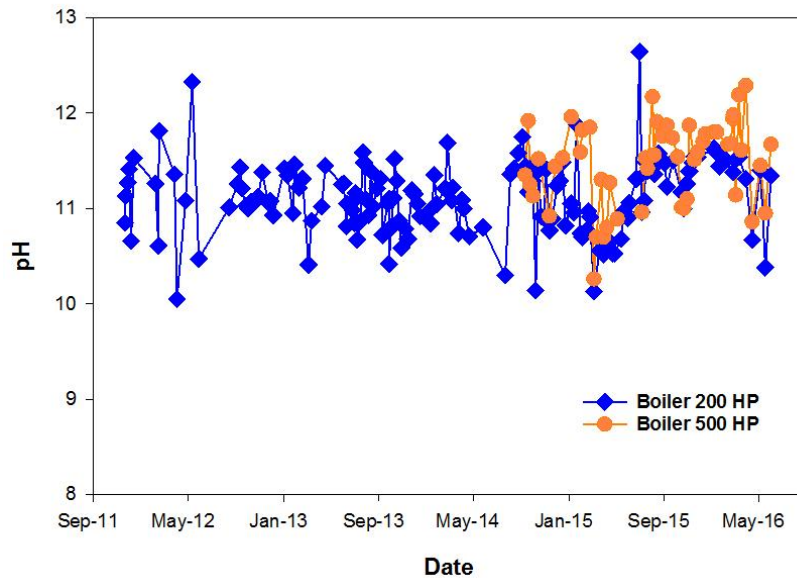

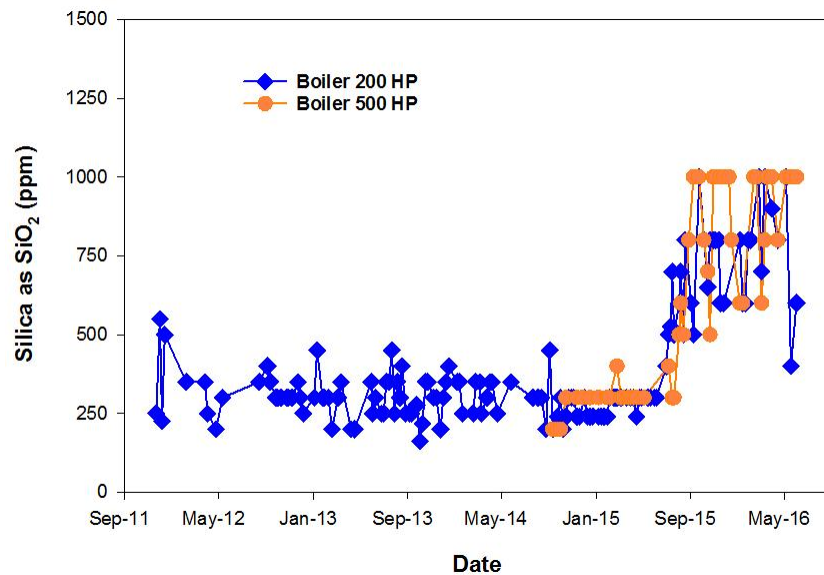**Figure 15: Boiler water pH versus time (tannin started June 8, 2015).**

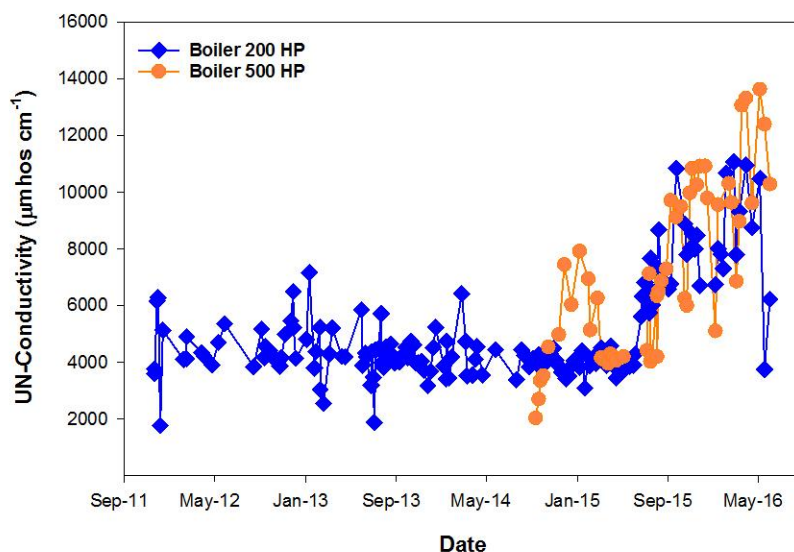**Figure 16: Boiler water silica levels versus time (tannin started June 8, 2015).**

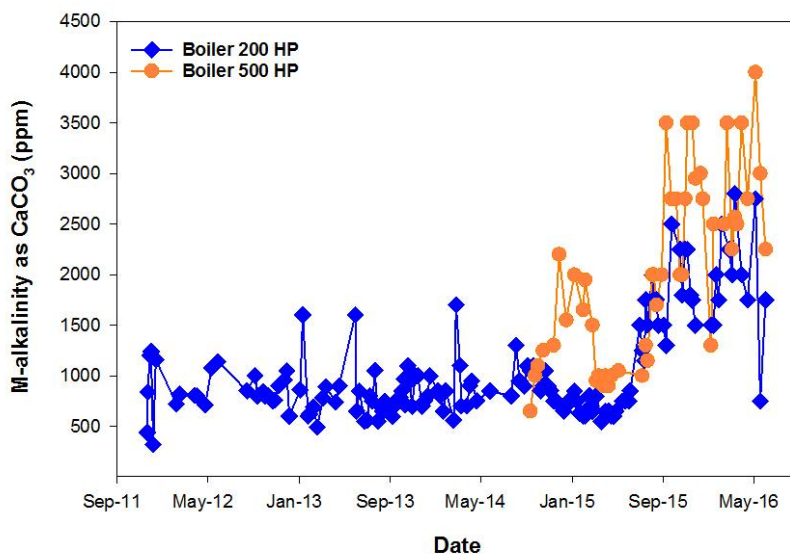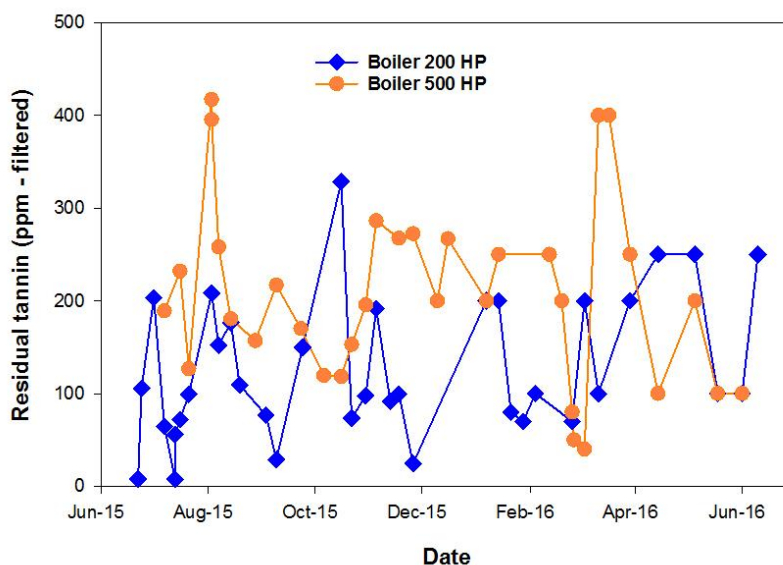**Figure 17: Boiler water Un-Neutralized conductivity versus time.**

Figure 18: Boiler water M-alkalinity versus time.

Figure 19: Boiler water residual tannin versus time.

Textile Industry (USA)

A global textile company was using four fire-tube boilers ranging 300 HP to 750 HP to generate approximately 100,000,000 lbs per year of steam for various process and heating applications. The boilers operated at 125 psig while burning natural gas for fuel, and the system returned about 30% of the steam as condensate. In the mid 2000's, the plant had been using well water for make-up that contained silica levels ranging from 15 to 25 ppm as SiO_2. Although limiting boiler cycles of concentration to a low level, the conventional treatment program in use failed to maintain clean boiler tubes. The boilers were scaled with heavy Ca, Mg, and Silicate deposits. In 2006, a decision was made to attempt to clean up the boilers on-line. The make-up source was switched to city water which was more expensive but contained significantly less silica, and the boiler treatment was switched to a chelant based program. The boiler cycles of concentration remained low, with an Un-Neutralized conductivity control point of 1,600 µmhos cm^{-1}, and a 7% blowdown rate. After 2 full years of running, the boiler make-up water costs were hurting the budget, and the on-line cleaning was deemed to be too slow and unsuccessful. Figure 20 depicts the condition of the boiler tubes after two years of trying to clean up the scale with an on-line, chelant treatment.
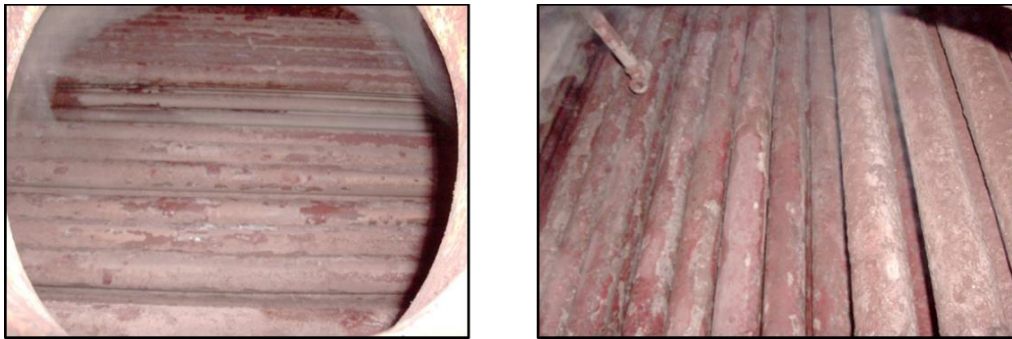
Figure 20: 2008 boiler tubes inspection after 2 years of on-line chelant clean up.

In late 2008, the boiler treatment was switched to a Purified Tannin program to speed up the on-line cleaning. From day 1, the make-up source was switched back to the well water containing high silica levels. The boiler conductivity control point was initially raised to 6,000 µmhos, yielding higher cycles of concentration and a much lower blowdown rate of 2.5%. In early 2009, two of the boilers were opened for inspection after 4 months of Purified Tannin treatment to evaluate conditions. The engineering and maintenance teams were impressed with the cleaning progress, especially at the higher boiler cycles and silica levels. Figure 21 depicts the condition of the boiler tubes after just 4 months of operation where some bare tube surface was already exposed.

Figure 21: 2009 boiler tubes inspection after 4 months of Purified Tannin treatment.

With the positive results from the inspection and the blessing of the plant personnel, the conductivity control point for the boilers was raised to 10,000 µmhos for the duration of the on-line cleaning process. The Purified Tannin treatment cleaned up the boilers to satisfactory levels and continues to maintain the boilers clean while being on-line for approximately 8 years. The conductivity control point since late 2008 has ranged from 8,000 to 12,000 µmhos, while the boiler silica levels and M-alkalinity have ranged from 450 to 850 ppm as SiO_2 and from 690 to 2700 ppm as $CaCO_3$, respectively (table 3).

The use of well water versus city water for boiler make-up represented significant savings for the plant. The increased boiler cycles further reduced the cost of make-up water as the blowdown rate was reduced from 7.1% to 2.3% (table 3). The plant also realized savings on their sewer bill, as less water was being discharged to the city sewer. With clean boiler tubes and boiler operation at much higher cycles of concentration, the requirement for natural gas to fuel the boilers was also reduced, resulting in measured savings on gas purchases.

Table 3: Textile Industry: Comparison between Conventional and Purified Tannin treatment.

Water treatment program		Conventional treatment	Purified Tannin treatment
Boiler operation	Cycles of concentration*	14	44
	% Blowdown	7.1	2.3
Boiler water quality	pH	11.8	12.3
	UN-Conductivity (µmhos cm-1)	1,600	10,480
	Silica as SiO_2 (ppm)	66	706
Type of Feedwater		City Water	Well Water

*Based on UN-conductivity.

Stability of Tannin and Silica (PDA characterization, with shear)

The goal of this laboratory investigation is to shed light on the stability of purified tannin in high-silica boiler water. Tannins are macromolecules having their size in the colloidal range that do not settle. Because they experience about 10^{21} collisions per second with water molecules [15], they are constantly moving randomly. Moreover, these macromolecules have functional groups that become highly negatively charged at high pH, which keeps them stable in solution [16,17]. Silica also becomes more negatively charged as pH increases [18-20], hence they both behave similarly, e.g. they are stable at higher pH.

Silica solubility drastically increases at pH above ~10 [21,22]. Then, polymerized silica and silicate salts of metal ions or other cations, can be formed, which can trigger the nucleation of crystals in the bulk solution.

There are two possible mechanisms to induce scaling: 1) scale can be either directly induced on metal surfaces (e.g. boiler tubes); and 2) indirectly in the bulk of process water and subsequently depositing on the tubes. We performed PDA experiments to gather useful information on bulk nucleation. In other words, the destabilization/aggregation of silica/silicate/tannin in solution gives information about the propensity of precipitation in solution, which can subsequently deposit on the boiler metal surfaces. Thus, the following investigation is an attempt to get insights on how to minimize the propensity of high-silica level to scale boilers.

Tannin

Tannin solutions, without silica, are stable in all investigated conditions, i.e. pH ranges from 7 to 12, NaCl concentration up to 0.15 M (14,200 µmhos cm^{-1}), conductivity up to ~50,000 µmhos cm^{-1} (0.5 M Na_2SO_4), 50 ppm $Fe^{2+/3+}$ as Fe, 100 ppm Ca^{2+} as Ca, and 50 ppm Mg^{2+} as Mg (not shown here).

Silica 30 and 200 nm

Table 4 shows the stability of colloidal 30 nm silica nanoparticles (up to 5000 ppm), without tannins, in the pH range of 7 to 12 and NaCl concentrations up to 0.15 M (14,200 µmhos cm^{-1}) [19]. Then, additional experiments were performed with larger 200 nm SiO_2 nanoparticles. The 200 nm silica nanoparticles behave differently than the 30 nm SiO_2 nanoparticles, the former having a faster aggregation rate and lower dissolution rate. In other words, at pH 12, the 30 nm nanoparticles dissolve faster, while the 200 nm nanoparticles aggregate before they are completely dissolved. In any case, aggregates that are formed are temporary and easily disappear when subjected to shear/agitation (table 4).

Tannin and silica

Similar results were observed for a mixture of tannin and silica nanoparticles under the same conditions. Under most conditions, the tannin and silica nanoparticles are stable (table 4). These findings are in agreement with the chemical properties of both tannin and silica nanoparticles, i.e. having a highly negative charge density at higher pH, which enhances their stability through electrostatic repulsion. However, at extremely high conductivity, e.g. ~50,000 µmhos cm^{-1} (0.5 M Na_2SO_4), 5000 ppm colloidal silica (30 nm) starts to aggregate at pH ~10 and as pH increases aggregation tends to occur at lower silica concentration, e.g. 300 ppm at pH~12. Those aggregates are permanent since they do not break up under experimental shear of ~200 s^{-1} (Tables 4 and 5).

Table 4: Silica and tannin/silica (30 and 200 nm) stability (PDA characterization, with shear).

Parameters	30 nm Silica		200 nm Silica	
	Silica up to 5000 ppm	Tannin (275 ppm), silica as SiO_2 (up to 5000 ppm)	Silica as SiO_2 (up to 5000 ppm)	Tannin (275 ppm), silica as SiO_2 (up to 5000 ppm)
pH 7-12	stable	Stable	stable	stable
Cond. up to 14,200 µmhos cm^{-1} (0.15 M NaCl)*	stable	Stable	stable	stable
Fe^{2+} as Fe; up to ppm	stable	Stable	stable	stable
Fe^{3+} as Fe; up to ppm	stable	Stable	stable	stable
Ca^{2+} as Ca; up to 100 ppm	temporary aggregates[1]	permanent aggregates[2]	stable up to 150 ppm of SiO_2	stable up to 500 ppm of SiO_2
Mg^{2+} as Mg; Up to 50 ppm[3]	temporary aggregates[1]	temporary aggregates[1]	stable up to 150 ppm of SiO_2	stable up to 150 ppm of SiO_2
Cond. 50,000 µmhos cm^{-1}, pH 12 (0.5 M Na_2SO_4)	permanent aggregates[3]	permanent aggregates[3]	N.D.	N.D.

[1] Temporary aggregates are reversible and disappear after few hours or days.
[2] Up to 70 ppm of Ca^{2+} (as Ca^{2+}) and pH 7-12 stable aggregates below PDA detection limit, 80 ppm and pH>11 permanent aggregates.
[3] Up to 300 ppm of SiO_2 no aggregates. Higher silica concentration aggregates start to appear.
N.D.: Not determined.

Tannin, silica and calcium ions

The effect of calcium on the stability of silica was investigated and the results show the presence of temporary settled aggregates. These temporary aggregates could be due to the bridging of partially dissolved outer layers of silica nanoparticles by calcium ions. They easily break up because the bridges might be weakened as more silica gets solubilized, resulting in a distribution of Ca^{2+} ions over more partially solubilized chains [18]. On the other hand, figure 22 shows that permanent settled aggregates of silica 30 nm/tannin are induced at calcium concentrations equal or greater than 80 ppm (as Ca^{2+} or 200 ppm $CaCO_3$). Moreover, figure 23 shows that 70 ppm of calcium (pH 7 to 12) does not induce aggregates, i.e. the baseline of the aggregation index (AI) does not change (larger AI corresponds to the presence of bigger aggregates). Interestingly, 80 ppm calcium ions (as Ca^{2+}) initiate fast aggregation of silica nanoparticles, reversible up to pH 11 (about 8100 seconds), but irreversible at pH>11.
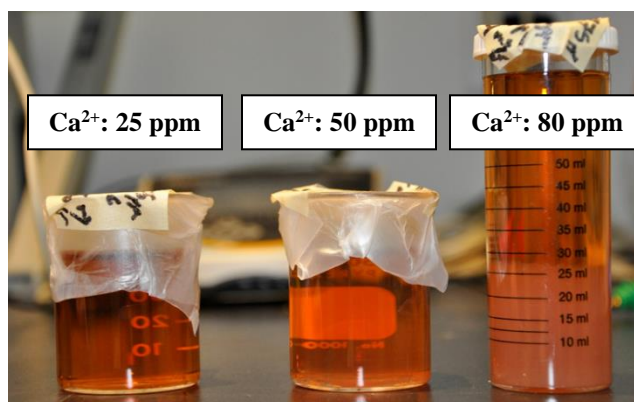
Figure 22: Effect of calcium on tannin/silica stability: 25, 50 and 80 ppm Ca^{2+} as Ca, 5000 ppm SiO_2 (30 nm), pH~12.

However, the results from 200 nm SiO_2 differ, wherein no aggregation occurs at silica levels of 150 ppm or less, while at a higher silica concentration aggregates start to appear. In the presence of tannin and at 100 ppm Ca^{2+}, tannin improves the stability limit from 150 to 500 ppm of silica (table 4).
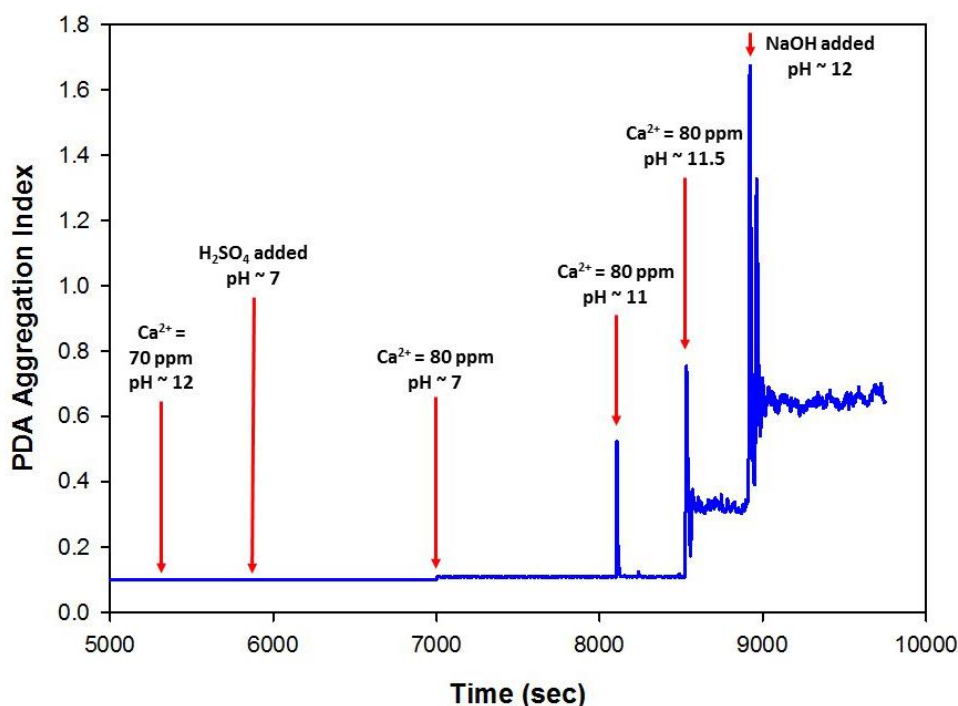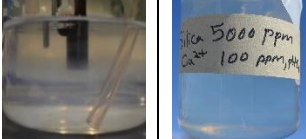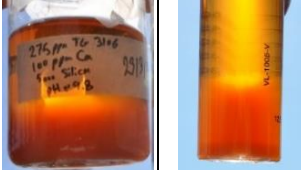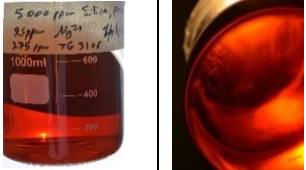
Figure 23: PDA Aggregation Index of silica/tannin suspension: 275 ppm Purified Tannin and 5000 ppm SiO₂ (30 nm) in the presence of Ca²⁺ ions, shear rate (G) of ~200 s⁻¹. Note the results were truncated to after 5000 seconds to accommodate eventful results.

Tannin, silica, iron, and magnesium ions

Both tannin and silica nanoparticles maintained their stability in the pH range 7 to 12, up to 50 ppm of Fe^{2+} and Fe^{3+} as Fe, most likely due to the precipitation of ferrous and ferric hydroxide at pHs higher than 8 (table 4). On the other hand, magnesium (50 ppm as Mg^{2+} or 173 pm as $MgCO_3$, pH 7 to 12) triggered temporary destabilization of silica nanoparticles at higher pHs, which leads to the formation of temporary aggregates (tables 4 and 5). The observed aggregates disappear after few hours, i.e. the time needed that silica nanoparticles fully dissolve.

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Table 5: Summary of stability of tannin and silica (30 nm).

Type of system /aggregation	Concentration* (ppm)	Aggregates	Photos of solution/suspension
Tannin	275	NO	
Silica	5000	NO	
Tannin-silica	275-5000	NO	
Tannin-calcium	275-100	NO	
Silica-calcium	5000-80	Temporary (left)/ few hours later (right)	
Tannin-calcium-silica	275-80-5000	Permanent	
Tannin-Fe^{2+}/Fe^{3+}-silica	275-50/50-5000	NO	
Tannin-Mg^{2+}-silica	275-25/50-5000	NO at 25 ppm/temporary at 50 ppm	
Tannin-silica-Na_2SO_4 (0.5 M), cond. of 50,000 μmhos cm^{-1}	275-5000	Permanent	

*Silica as SiO_2

Particle size (DLS characterization, without shear)

The next series of experiments were performed to determine the particle size of SiO_2, Purified Tannin and a mixture of SiO_2 and tannin, hence to validate whether tannin shows dispersive properties. Figure 24 shows that silica particles at 5000 ppm concentration have a bimodal size distribution, in which one peak, ~25 nm, corresponds to individual nanoparticles and the other, ~80 nm, corresponds to doublets or triplets (concentration effect) of nanoparticles. As previously mentioned, the average size of silica nanoparticles is 35±2nm. Purified Tannin, on the other hand, exhibits a broad size distribution from 80 nm to 1200 nm probably due to the association of tannin macromolecules [23]. Interestingly, mixing Purified Tannin and SiO_2 results in a size distribution similar to that of SiO_2, because silica particles outnumber tannin macromolecules in the mixture and their stability is not influenced by the presence of tannin.
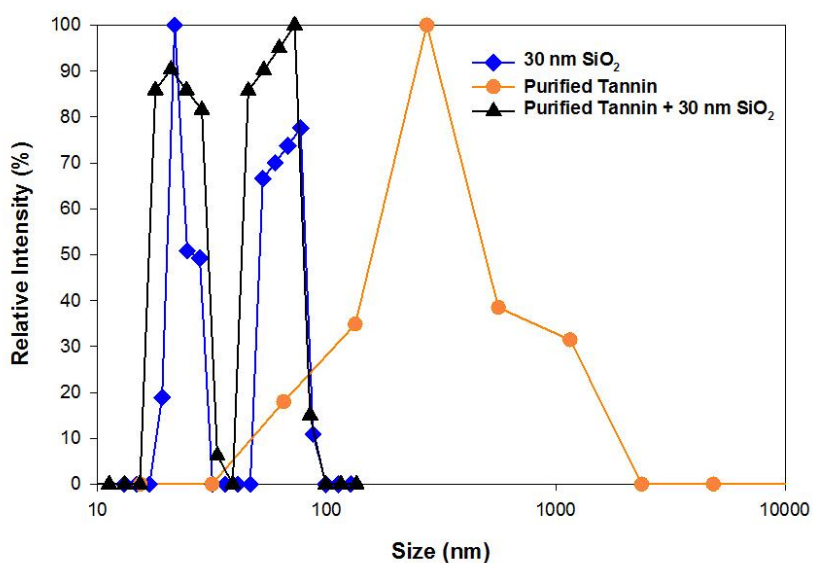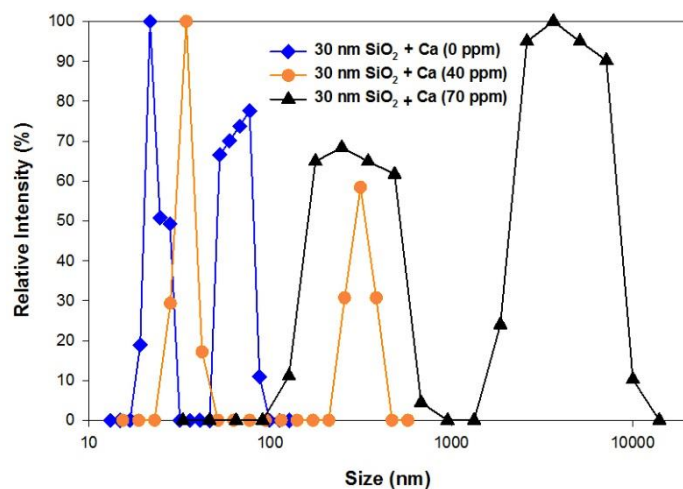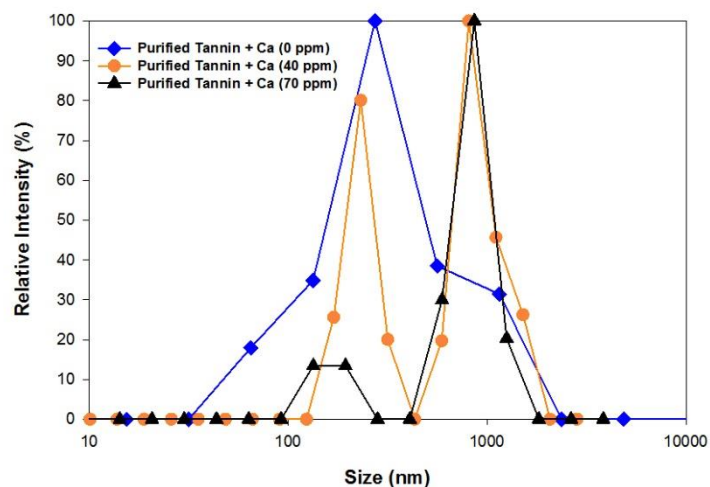

Figure 24: Size distribution of 30 nm SiO_2, Purified Tannin, and mixed suspension of 5000 ppm of 30 nm SiO_2 and 275 ppm of Purified Tannin. DLS results attest to the presence of silica doublets and triplets.

The effect of calcium ions was also studied and as seen in figure 25(a) silica nanoparticles aggregate up to 70 ppm of calcium ions after which the aggregates start to settle within few minutes. Similarly, Purified Tannin shows an increase in its size with addition of calcium; however, it maintains its stability (figure 25(b)). Interestingly, by comparing figures 25(a) and (c) one can notice dispersive effect of Purified Tannin on silica nanoparticles aggregates which leads to break-up of aggregates into smaller entities, which do not settle and remain stable in the bulk suspension as confirmed by PDA method. Results when using magnesium instead of calcium showed qualitatively similar effect.
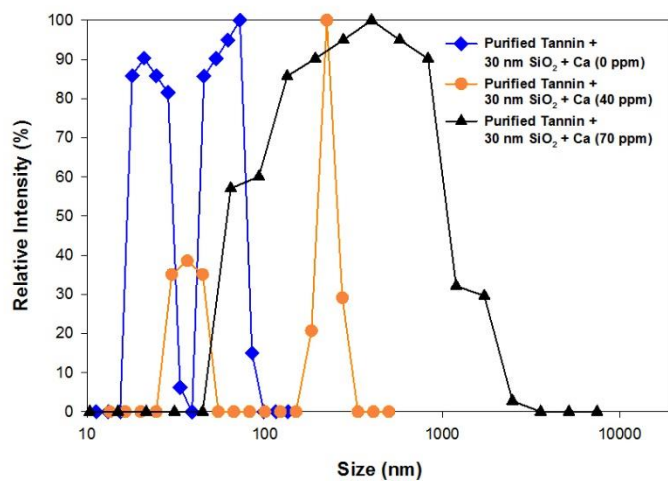
(a)

(b)

(c)

Figure 25: Effect of calcium on size distribution of (a) 30 nm SiO₂, (b) Purified Tannin (c) mixture of 5000 ppm of 30 nm SiO₂ and 275 ppm of Purified Tannin at pH~12.
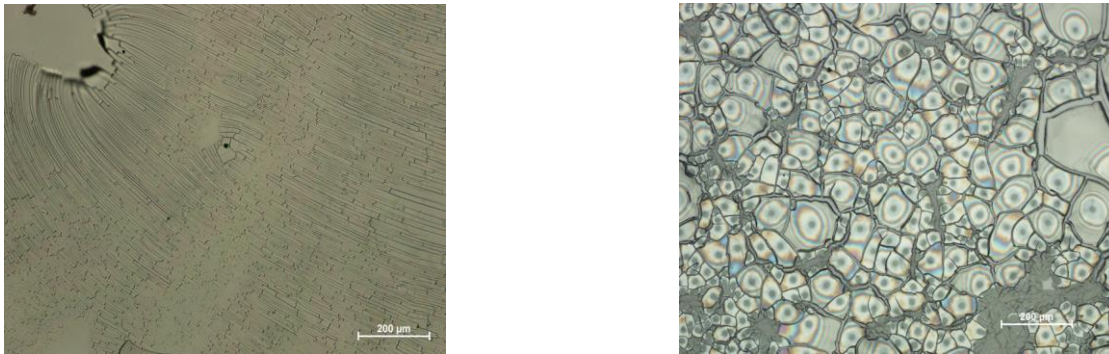
Figure 26: Optical microscopy (dry state): left) pure silica 5000 ppm as SiO₂ (30 nm); and right) 275 ppm Purified Tannin, 80 ppm calcium as Ca²⁺, and 5000 ppm of silica as SiO₂ (30 nm).

Optical microscopy

Preliminary optical microscopy images show typical striped patterns for dried colloidal silica [24] and aggregates of tannin/silica-silicates in the presence of 80 ppm of Ca^{2+} (figure 26). Further investigation is under way to obtain a better understanding of these images.

Finally, although this laboratory investigation supports that tannin/silica suspensions are stable at silica levels well above any established industry guidelines, additional research is needed to elucidate the underlying mechanisms.

Boilers operational guidelines

Based on case studies presented in this work, supported by more than 10 years of industrial field experience in North America, as well as scientific evidence from previous publications and this work, operational guidelines are proposed. Consequently, tables 6 and 7 show the ASME guidelines as well as the proposed guidelines for boilers operating with Purified Tannin. These are conservative guidelines since Purified Tannin can perform at higher silica and conductivity shown in table 7.

Table 6: Conventional treatment: ASME guidelines for modern industrial fire-tube boilers for reliable continuous operation [14].

Drum pressure (psig)	Boiler water		
	Silica (ppm as SiO_2)	Total alkalinity (ppm $CaCO_3$)	Conductivity (μmhos cm^{-1}) (Un-neutralized)
0−300	≤ 150	<700	<7,000

These apply when total hardness <1 ppm and oxygen concentration <7 ppb.

Table 7: Purified Tannin treatment: Proposed guidelines for modern industrial fire tube and water tube boilers for reliable continuous operation.

Drum pressure (psig)	Boiler water			
	pH	Silica (ppm as SiO_2)	Conductivity* (μmhos cm^{-1}) (un-neutralized)	Residual tannins (ppm at 420 nm)
0−300	11.5±1.0	≤ 750	<10,000	175±25

*Function of boiler blowdown rate. Targeted residual tannin for scaled boilers is 225±25 ppm (measured at 420 nm). These apply when total hardness <1 ppm and oxygen concentration <7 ppb.

CONCLUSIONS

Here, case studies show that a green chemistry treatment with Purified Tannin not only allows boiler operations at significantly higher silica levels while inhibiting formation of scale, but also shows visual evidence of removal of previously deposited scale. Laboratory results show that silica/tannin are still stable at silica levels well above any established industry guidelines. Laboratory studies also show that Purified Tannin has a dispersive effect on silica nanoparticles aggregates both in the absence and presence of ions such as Ca, Mg and Fe, which minimizes the propensity of precipitation in the bulk solution, and subsequently decreases the deposition risks on the boiler metal surfaces. Several benefits of switching to green chemistry through tannin treatment and operating at significantly higher cycles are: a reduction in boiler blowdown and sewer water discharge, make-up water requirements, propane usage for fuel, and level of greenhouse gas (GHG) emissions. Finally, guidelines for boilers operating with Purified Tannin are proposed.

ACKNOWLEDGEMENTS

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