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Improving monochloramine performance with innovative sensor-controlled dosing

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ABSTRACT: Monochloramine (MCA) has become one of the major oxidant chemistries for biological control in the paper industry. Feedback control, such as oxidative-reductive potential (ORP), is often used to provide better control of a dosing scheme.

The trademarked Ackumen MCA-i is a chemical-digital solution that uses artificial intelligence with actionable insights to stabilize the wet-end process, providing improved performance and reduction in overall chemical costs. Accurate sensor-controlled dosing can be tied to multiple inputs, such as production rates, grade changes, pH, ORP, chlorine residual, freshwater usage, and more. In this study, a case history will be presented to demonstrate how this technology provided a more consistent MCA molecule throughout the process, resulting in a higher level of efficacy and reduction in chemical costs.

Application: Through advanced multiparameter dosing controls, monochloramine feed rates can be adjusted as the paper machine process changes. This leads to the right amount of chemistry being applied at the right time, maximizing efficiency of the biocide program.

The use of monochloramine for microbial control in the paper industry is not a novel idea. In 1929, Clark T. Henderson applied for a U.S. patent for the generation of monochloramine [1]. The method involved dissolving chlorine in water, passing it through calcium carbonate, and then mixing it with ammonia. He recommended monochloramine for the control of slime and other consequences of uncontrolled bacterial growth in the paper and pulp industry. Although the patent was not granted until 1933, the use of MCA for slime control did begin in 1930 [2]. Monochloramine was found to be more effective and more persistent than chlorine. Its popularity continued to grow during the 1930s and early 1940s [3-6], and the use of either chlorine or chloramine for slime control was considered a standard practice [7].

In the mid-1940s, the use of monochloramine started to decline for several reasons, including corrosion, reduced efficacy, break-point chlorination, and the introduction of alternative organic disinfectants. Issues with severe corrosion were reported by Grant [8] and Rampel [9]. However, the mills were using a dual program of chlorine and monochloramine on the machines. King [10] noted a reduction in efficacy downstream from the application of the monochloramine, but also stated the loss of control was partially due to the use of reductive bleaching. Data collected over several years indicated that certain bacterial species were not killed or suppressed when either chlorine or monochloramine was used for slime control [11]. A third reason for the decrease in the use of chloramine was break-point chlorination, a phenomenon discovered in 1939 [12] that quickly replaced monochloramine for potable water disinfection. When applied properly, break-point chlorination provided better microbial control than the chloramine program [13,14]. The decline in the use of MCA was also due to the introduction of organic biocides. Beginning in 1942, multiple laboratory and mill studies were conducted to determine the best combination of commercially available organic disinfectants to reduce or eliminate microbial slime [8,10,15-19]. Combinations of mercury compounds, e.g., phenylmercuric acetate, and chlorophenates provided both bacterial and fungal efficacy [20,21].

Monochloramine overview

Monochloramines (MCA) are formed in situ by mixing an ammonia source (i.e., monochloramine precursor or MCAP) with industrial grade sodium hypochlorite in water. Depending on the molar ratio of the chlorine-to -ammonia source and the pH, three species of inorganic chloramines can be formed.

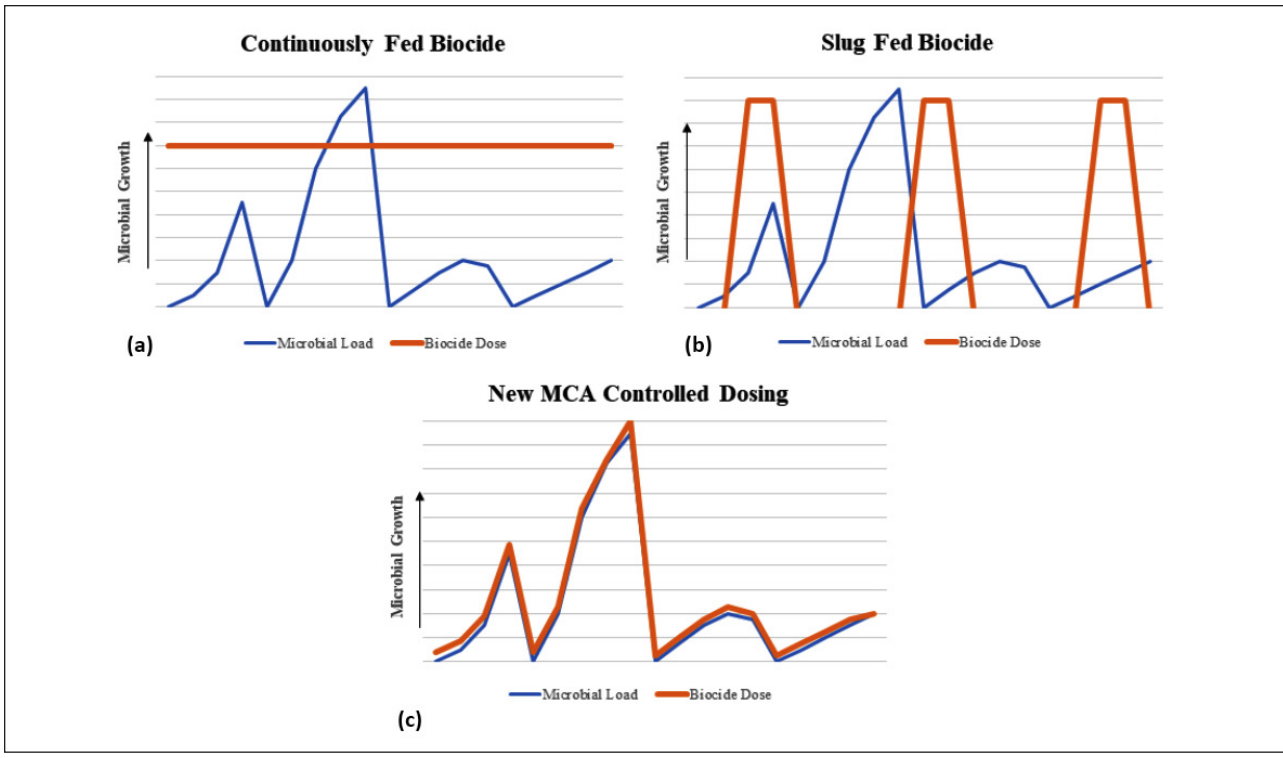
According to White [22], monochloramines are formed at a pH ≥ 7 and at a 1:1 molar ratio of the MCAP to chlorine. This equates to a weight ratio of ≤ 5:1 molecular chlorine: ammonia.

NH_3 (ammonia) + NaOCl (sodium hypochlorite) →
NH_2Cl (monochloramine) + NaOH (sodium hydroxide)

Dichloramine formation occurs at a pH range of 5–6 but can also occur at a pH 7–8 if the molar ratio of chlorine to ammonia is 2:1 (or 10:1 by weight).

$NaOCl + NH_2Cl \rightarrow NHCl_2$ (dichloramine) + NaOH

Nitrogen trichloride is formed at pH 7–8 if the chlorine-to-ammonia molar ratio increases to ≥ 3:1; i.e., 20:1 weight



1. Biocide dosing schemes: (a) Continuous dosing scheme offers a consistent microbial control; however, the biocide may be overfed frequently or underfed when a high concentration of microbial load is introduced. (b) Slug or "timed" dosing scheme is very cost-effective but allows significant periods of time when there is not biocide being added to the process. (c) The new monochloramine (MCA) controlled dosing scheme optimizes the biocide dosing rate by utilizing multiple sensor and process data.

ratio. It is also formed when the pH of the process drops below 5.

$$HOCl + NHCl_2 \rightarrow NCl_3 \text{ (nitrogen trichloride)} + H_2O$$

Monochloramines are considered weak oxidizers when compared to other oxidizers used in the paper manufacturing process, such as chlorine dioxide, hypochlorous acid, hypobromous acid, and peracetic acid. Because they are considered to be "combined" forms of chlorine, monochloramines react to a lesser degree or not at all with other wet-end additives such as dyes, optical brighteners, starch, retention aids, and sizing agents. The primary mode of action of monochloramine is the reaction with sulfhydryl groups (i.e., thiols) in amino acids. They can also react with the amino acid tryptophan and nucleic acids, but not sugars [23]. Other studies have shown that there is no interaction between monochloramines and extracellular polysaccharides [24]. Because of these attributes, MCA chemistry has become one of the major oxidant biocides used in the paper industry.

Monochloramine in today's paper industry

The use of monochloramine for biological control was reintroduced to the paper industry in 2000 [25]. Since then, MCA has become one of the major oxidant chemistries for microbial control in neutral and alkaline processes. Commonly used MCAPs include ammonium bromide, ammonium sulfate, and ammonium carbamate. Dedicated generators mix the MCAP, industrial bleach, and water in a controlled manner to generate the chloramine solution and deliver it to various areas of the process. Depending on the chemical supplier, dosing may be "slug" (i.e., timed) or continuous. The flow of an application point may be controlled via a single feedback control signal, such as oxidative-reductive potential (ORP), to provide better control of a dosing scheme. Many chemical suppliers offer real-time online monitoring, as well as cloud-based predictive analytics, for the papermaker's process.

MCA DOSING VIA ADVANCED SENSOR CONTROL

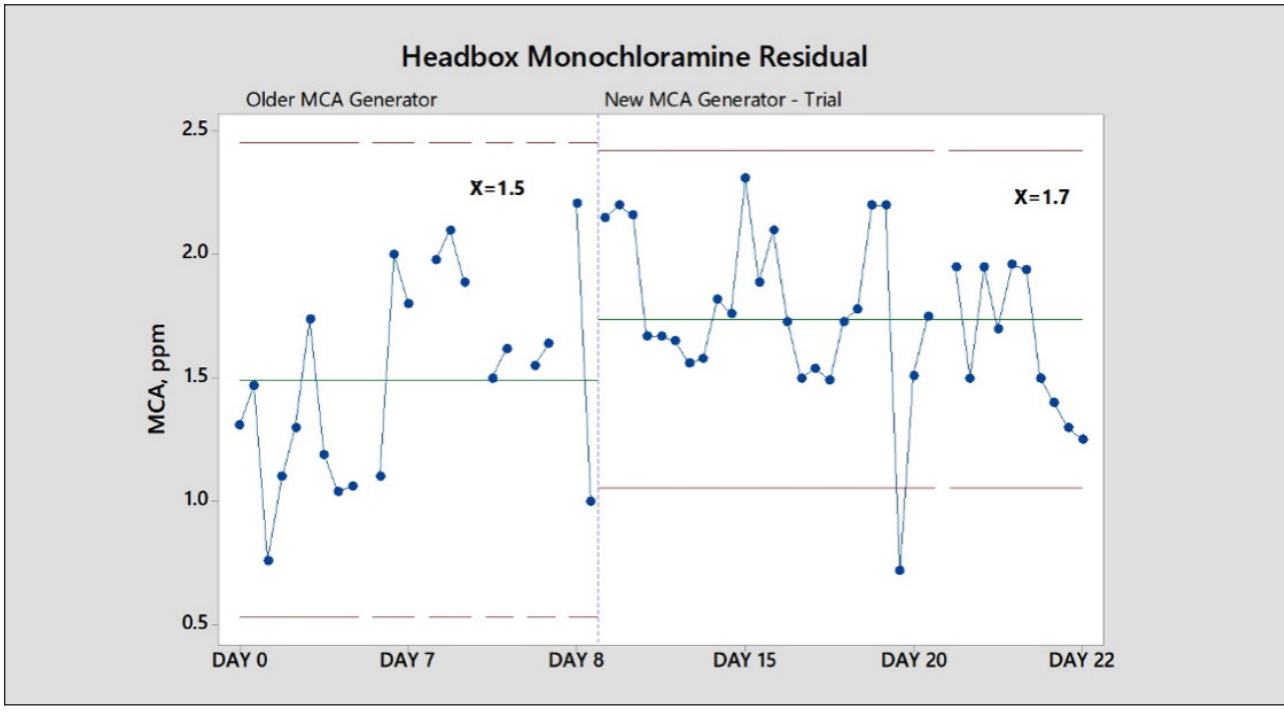
Paper mills are being challenged to reduce freshwater usage, increase on-machine efficiency, and maintain or improve product quality while minimizing process variability, unscheduled shutdowns, and additional costs. These can lead to the use of more chemistries to supplement final product specifications and influent/effluent efficiency. In response to these challenges, a chemical-digital solution that uses artificial intelligence with actionable insights to stabilize wet-end processes was developed. This program combines monochloramine chemistry with an advanced sensing technology, cloud-based data analytics, 24/7 monitoring and analysis, and accurate predictive modeling.

The new MCA generator is capable of utilizing multiple sensor data, as well as mill process data, to automatically adjust the biocide program. This minimizes the overfeeding or underfeeding of the biocide as the process changes. Most biocides, whether organic or oxidant, are applied on a timed (slug) or continuous basis. Both dosing schemes have advantages and disadvantages, depending on where the biocide is applied. Continuous feeding of MCA offers a fairly consistent control over microbial contamination (**Fig. 1a**). However, if the microbial load is low, the biocide is being overfed. If there is a "shock" of microbial contamination, there is not sufficient biocide to provide an effective kill. A "slug" dose is a more cost-effective way of applying a biocide but offers a less effective control over the microbial contamination (Fig. 1b.). Utilizing multiple sensor and process data, the new MCA program optimizes the biocide dosage by feeding the right amount of chemistry as the process changes (Fig. 1c). Mill personnel can view key operational parameters of the generator and key performance indicators (KPIs) from their computer or mobile devices.

CASE HISTORY

A three-phase trial of this new MCA technology was conducted at a paper mill in North America. Phase 1 was initiated to compare the new generator's performance against an older MCA generator. With both, MCA is generated via a controlled and precise reaction of the MCAP and industrial bleach with water. The next generation has incremental improvements, including additional safety features and state of the art components. One major difference between the generators is the order of chemical addition.

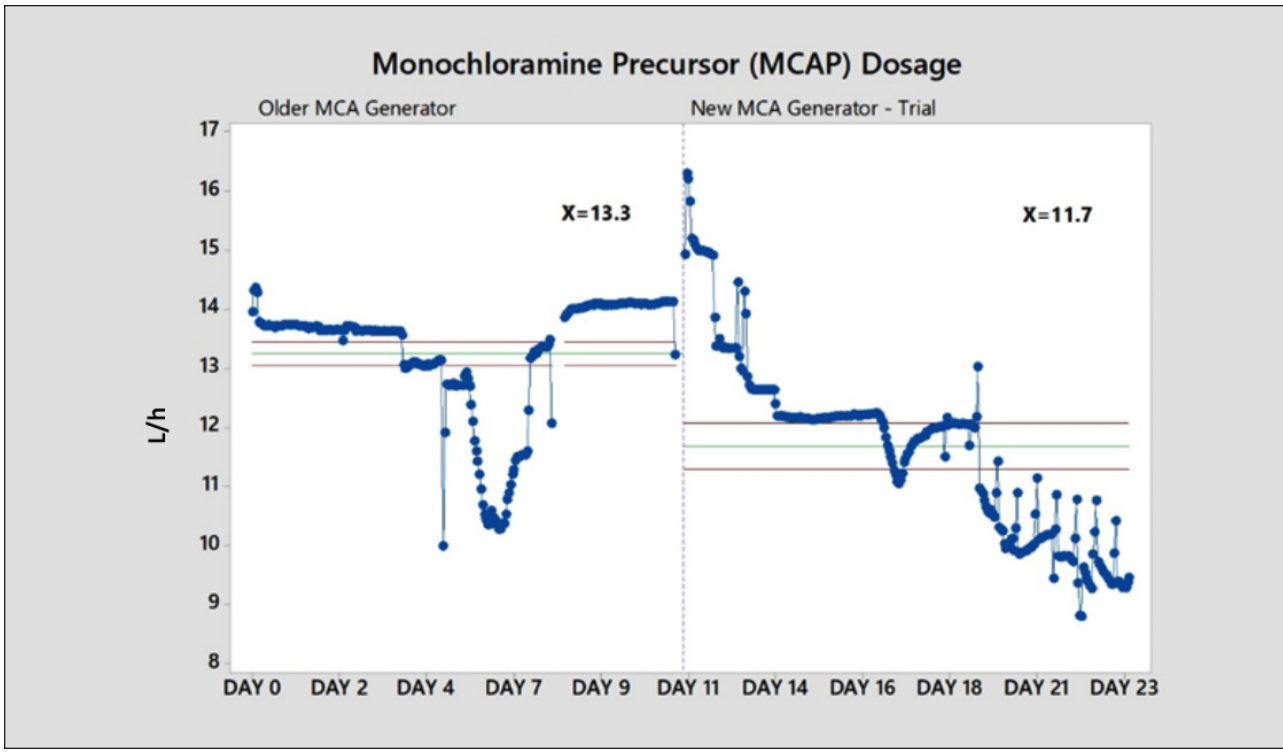
A primary goal of Phase 1 was to maintain a similar MCA residual at the headbox while maintaining key performance indicators (KPIs) such as machine runnability. In order to accomplish this, application points and dosing strategies were not changed during this phase. Results of Phase 1 are shown below in **Figs. 2–4** and summarized in **Table I**. With the new unit, headbox MCA residuals were maintained (Fig. 2), while a reduction in the MCAP usage (12.0%) was achieved (Fig. 3). With regards to controlling microbial activity, headbox adenosine triphosphate



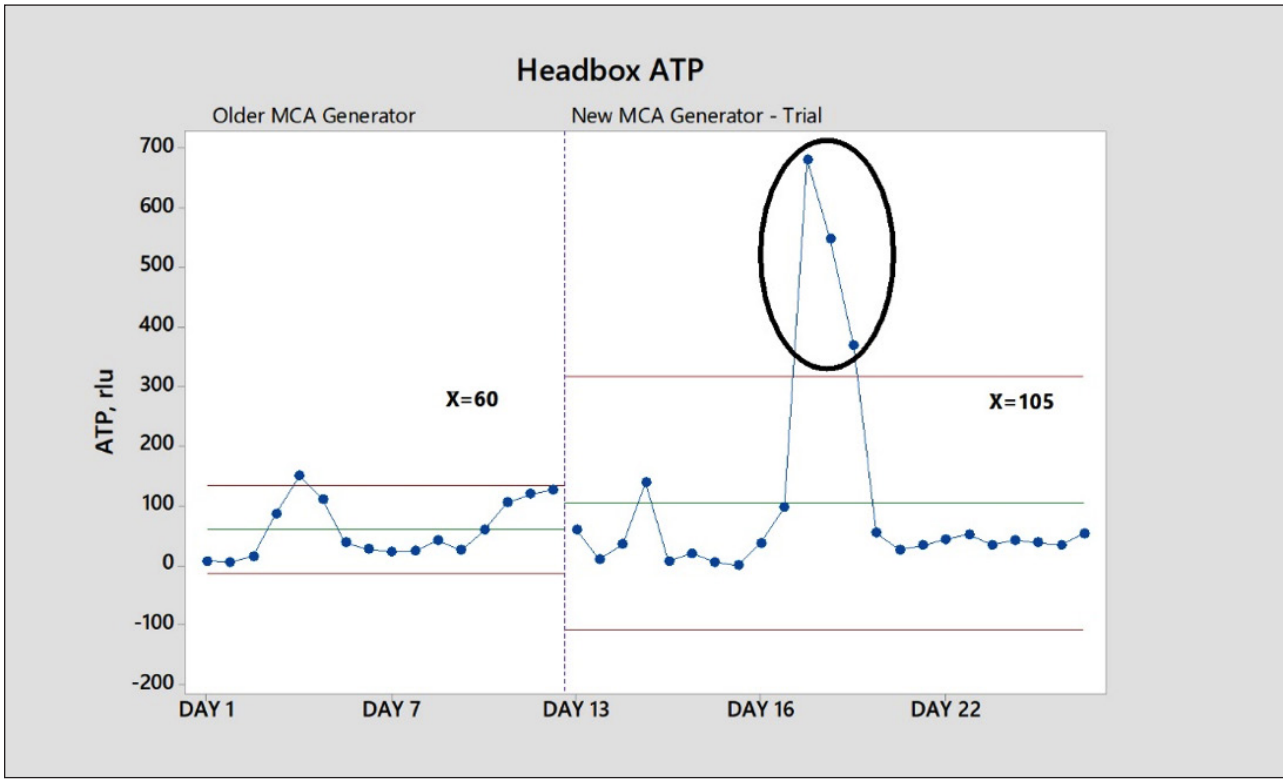
2. Phase 1 trial evaluation of headbox MCA residual. When comparing the performance of the new generator with the older generator, similar MCA residuals were achieved during both periods.

	Older MCA Generator	New MCA Generator	Difference	% Change
Headbox MCA residual, ppm	1.5	1.7	+0.20	13.3
MCAP flow rate, L/h	13.3	11.7	-1.6	-12.0
MCA: monochloramine; MCAP: monochloramine precursor				

I. Summary of key findings from Phase 1 trial evaluation.



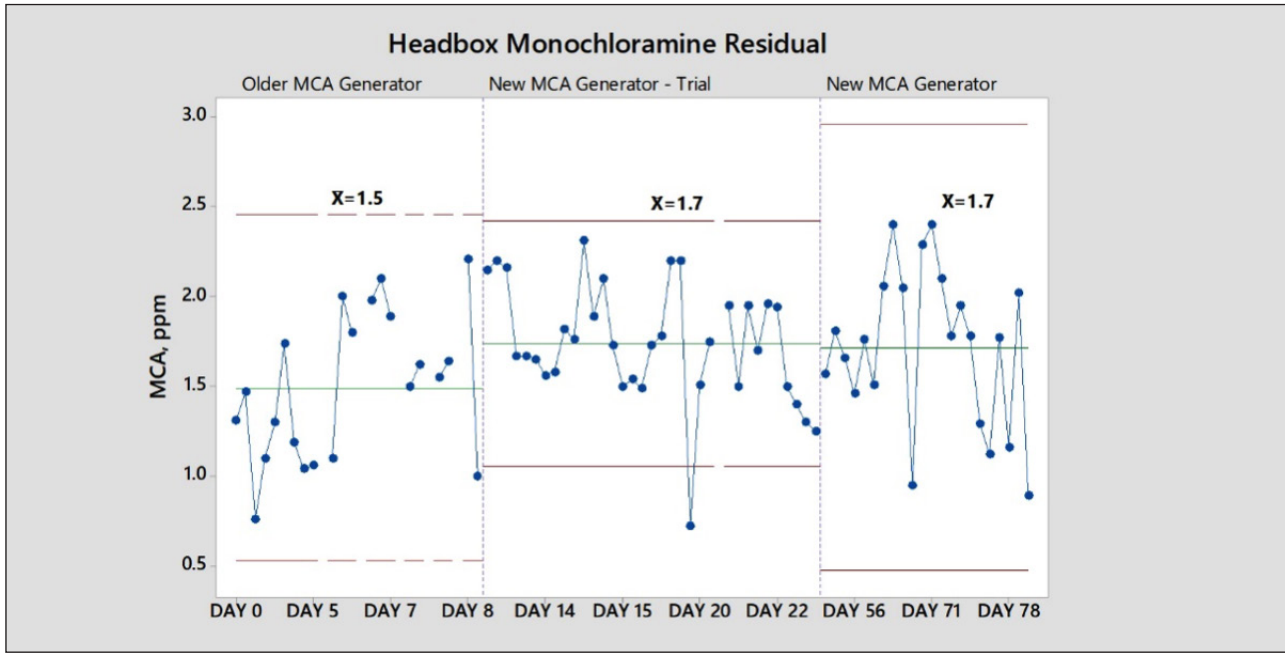
3. Phase 1 trial evaluation of monochloramine precursor (MCAP) dosage rate. For the new generator, the MCAP chemical flow rate was reduced while maintaining a similar headbox MCA residual (Fig. 2) as compared with the older generator.



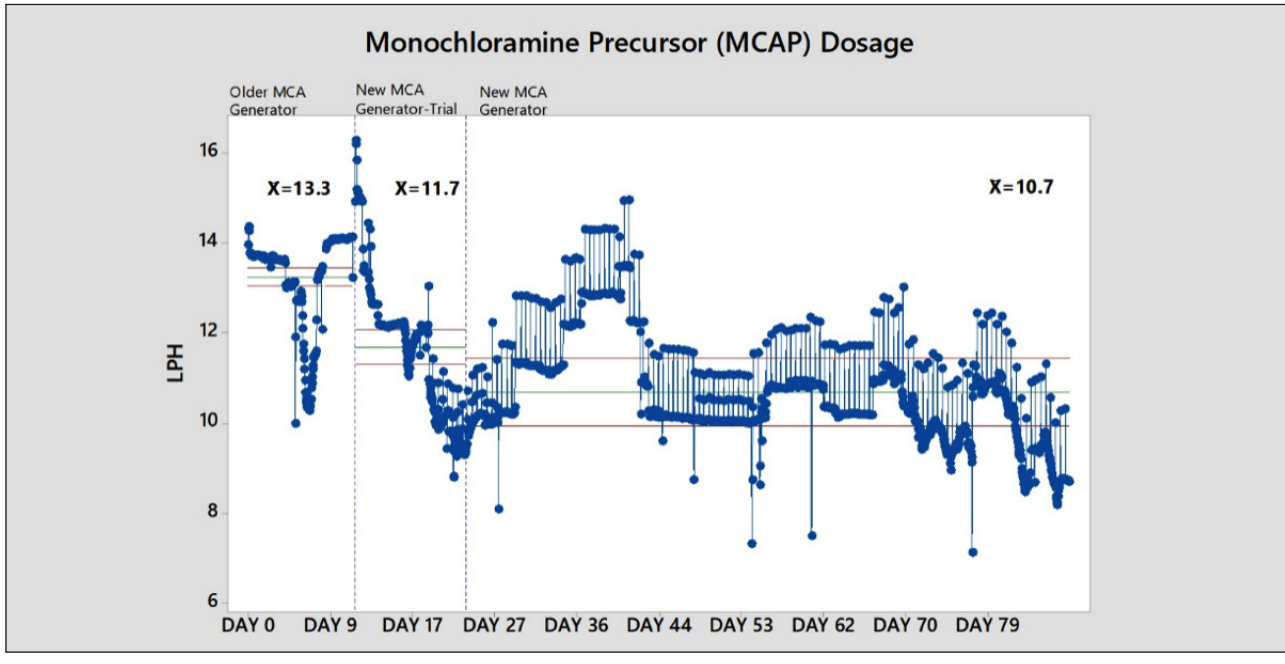
4. Phase 1 trial evaluation of microbial control via adenosine triphosphate (ATP) analysis. With the older generator, ATP numbers measured at the headbox were well below the mill's established upper limit of 500 relative light units (rlu). The new generator produced similar results. The three outliers (circled) occurred after an unplanned downtime and correlate to slightly lower MCA headbox residuals during the same time period (Fig. 1).

	Older MCA Generator	New MCA Generator	Difference	% Change
Headbox MCA residual, ppm	1.5	1.7	+0.20	13.3
MCAP flow rate, L/h	13.3	10.7	-2.6	-19.5
MCA: monochloramine; MCAP: monochloramine precursor				

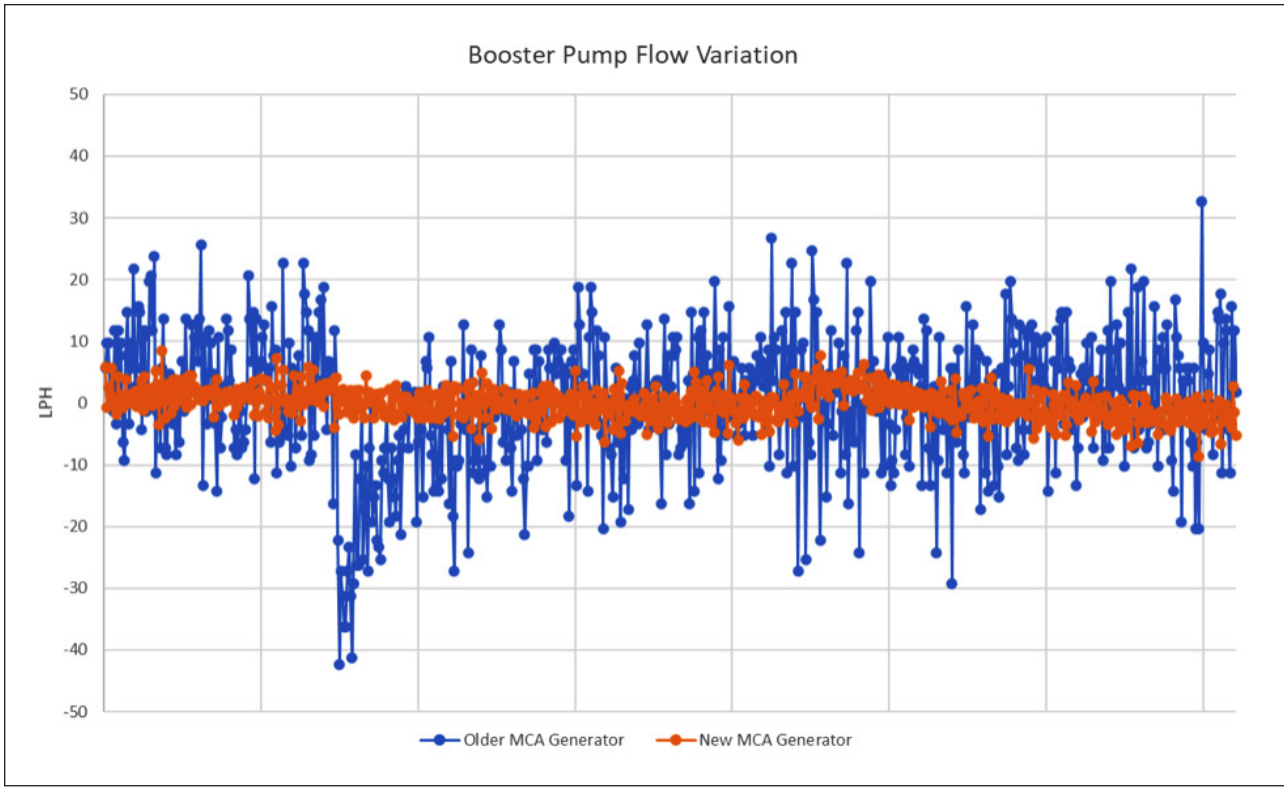
II. Summary of key findings from Phase 2 trial evaluation.



5. Phase 2 evaluation of headbox MCA residual. The headbox residuals were maintained during this phase while the MCAP flow rate was further reduced (Fig. 6).



6. Phase 2 evaluation of MCAP dosage rate. The MCAP chemical dosage rate was reduced further while the MCA headbox residuals were maintained (Fig. 5).



7. Phase 2 evaluation of the proportional–integral–derivative (PID) flow control valves. The water booster pump variation over a 12-h period was compared between the older and new generators. The flow variation was reduced by 75% due to the use of the PID flow control valves in the new unit.

(ATP) remained well below the mill's established upper limit of 500 relative light units (rlu) (Fig. 4). The outliers (above 100 rlu) occurred after an unscheduled down and correlate to lower headbox MCA residuals (Fig. 2) during the same time period. These results can be attributed to the improved reaction efficiency due to the change in order of chemical addition.

For Phase 2, the biocide program was further optimized utilizing several of the new unit's key features: a proprietary automated ratio control of the chemicals and proportional–integral–derivative (PID) flow control valves. Results are summarized in **Table II**. During this phase, the MCA headbox residuals were maintained at 1.7 ppm (**Fig. 5**), while the flow rate of the MCAP was further reduced (**Fig. 6**). The speed of response with the new generator provided a more consistent biocide dosing, less variation in MCA residual, and reduced variability throughout the process, resulting in a higher level of efficacy and a reduction in chemical usage. Through the use of the automated ratio control, the new unit adjusted the MCAP:sodium hypochlorite ratio in real time. This maintained the proper 1:1 molar ratio of both chemicals to produce a very stable MCA molecule. The addition of PID flow control valves eliminated drifts that can occur with the use of manual flow valves. **Figure 7** shows a comparison of the water booster pump variation over a 12-h period between the older and new generators. The PID flow control valves reduced flow variation by 75%. This translates to having the right amount of MCA chemistry in the process at the right time.

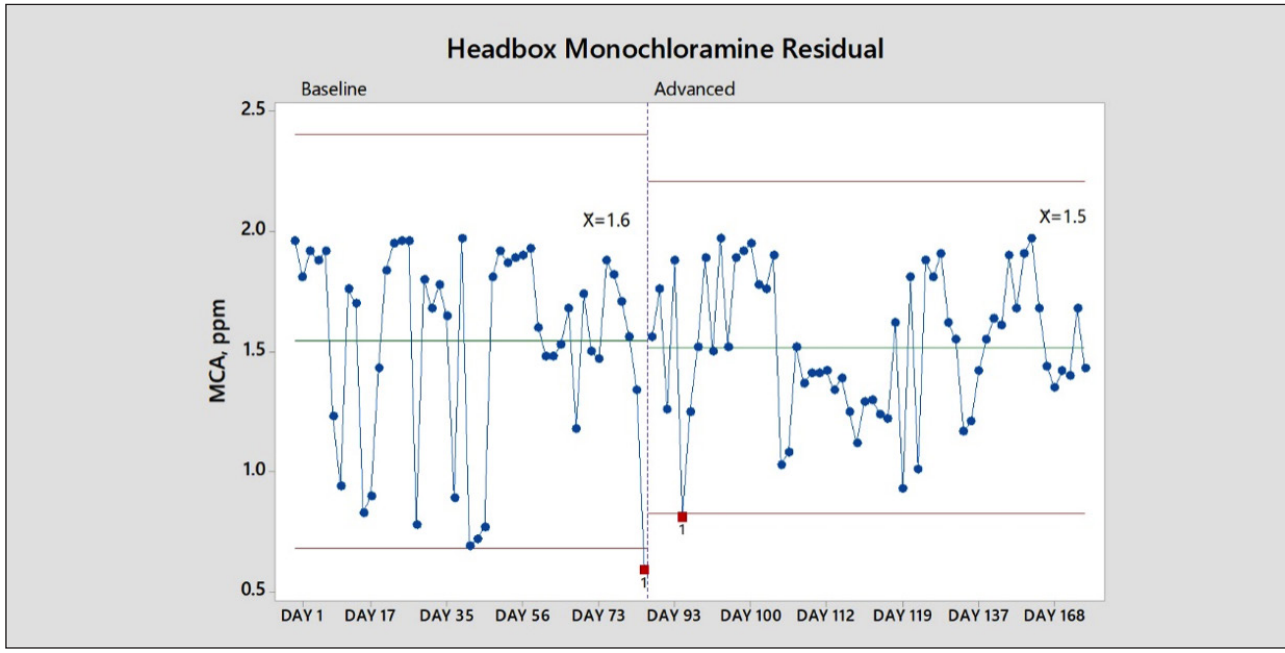
The objective of Phase 3 of the evaluation was to apply the MCA more effectively in the mill process. Using advanced controls available on the new generator, the goal was to reduce variability in the established KPIs for the biocide program. Instead of relying on constant flow dosing, the MCA dosage was continuously adjusted by the generator by changing the flow rate controlled by two of the mill's process variables. Thus, the MCA dosage would adapt continuously to the changing mill process conditions.

The two process signals sent to the unit via 4-20mA analog signals were paper machine production rate and machine grade. Biocide program performance for the new control modes was defined as variability of headbox MCA residual and headbox ATP. To accurately compare the impact of the dosing modes on the KPIs, the MCAP chemical usage was kept the same for both the baseline and advanced controls; however, with the advanced controls, the MCA dosage was continuously adjusted as the demand of the process changed. Results of the advanced control dosing mode compared with baseline dosing mode (used in Phases 1 and 2) are shown below in **Table III** and **Figs. 8–9**.

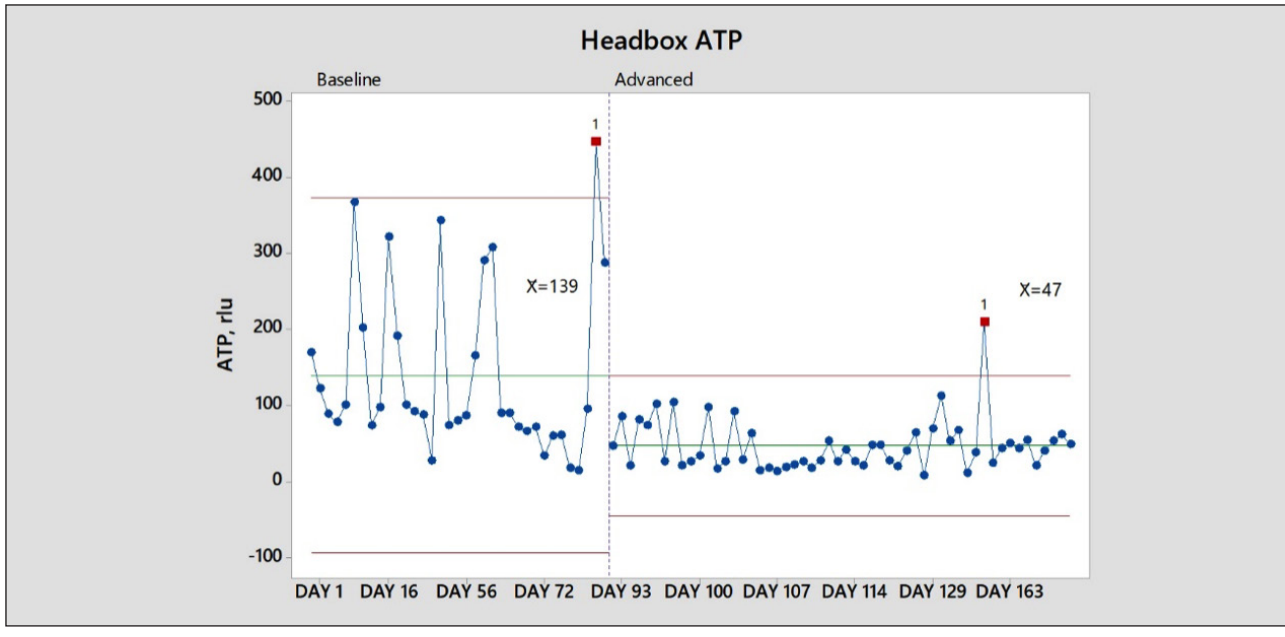
Although the average headbox MCA residual was approximately the same during both evaluation periods (Fig.

KPI	Control Method	Mean	Standard Deviation
Headbox MCA, ppm	Baseline	1.6	0.4
	Advanced	1.5	0.3
Headbox ATP, rlu	Baseline	139	111
	Advanced	47	35
MCA: monochloramine; ATP: adenosine triphosphate; rlu = relative light units.			

III. Summary of key findings from Phase 3 trial evaluation.



8. Phase 3 evaluation of headbox MCA residual. Although the headbox residuals were similar for both the baseline and advanced control dosing modes, the standard deviation for the baseline was 0.4 ppm compared to 0.3 ppm for the advanced control period.



9. Phase 3 evaluation of headbox ATP. Both dosing modes resulted in headbox ATPs below the mill's requirement. Lower variability was achieved with the advanced control dosing mode.

8), the standard deviation for the advance control (0.3 ppm) was significantly lower than the baseline period (0.4 ppm). This represents a 31% reduction in variability.

Both control modes provided microbial control as measured by the headbox ATPs; the ATPs were well below the mill's requirement of < 500 rlu (Fig. 9). However, the advanced control mode greatly reduced both the variability and level of headbox ATP. The ATP during the advanced control mode was 66% lower compared to the baseline period.

With a biocide program using no feedback control to control application flow rates, manual adjustments are required to maintain target MCA residuals and other KPIs. It may take hours or days for the program adjustments to respond to the changing demands of the process. Large variations in headbox MCA residuals can occur, allowing opportunities for slime growth on the paper machine and thus quality and runnability issues. Biocide usage is then increased to bring the residuals back to target levels. This type of control is reactive rather than proactive. By adapting to changing process conditions, the advanced dosing controls on the new MCA generator reduced the variation in both the headbox MCA residual (Fig. 8) and ATP values (Fig. 9). Eliminating periods of high ATP and low MCA residuals allows fewer opportunities for microbial-related deposition on the paper machine.

ABOUT THIS PAPER

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SUMMARY

Two of the key features on the new MCA generator, PID flow control valves and automated chemical ratio control, were evaluated in Phases 1 and 2 of the case history. When compared with the older generator, the new generator produced a more stable MCA molecule as indicated by the reduction in MCAP chemical usage (~10%). Both MCA headbox residuals and headbox ATPs were easily maintained. For Phase 3, an advanced control mode utilizing multiple inputs to control the flow of one application point was implemented to reduce the variability of the mill's biocide program KPIs. The headbox MCA residuals were similar to those determined in Phase 2, but the standard deviation was smaller. The variability of the headbox ATP numbers was lowered during this phase.

The new MCA generator offers more than feedback control via one sensor for dosing control. It allows the use of multiple inputs to any application point, and these can be customized to fit the mill's process without additional programing from the mill. For this case history, the advanced control mode utilized the mill's process information — production rate and grade changes. The dosing rate at that one application point was automatically adjusted as the mill's process changed. The ultimate goal is to feed the right amount of chemistry at the right time to provide the mill with a higher level of efficacy and efficiency while reducing chemical costs. **TJ**

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ABOUT THE AUTHORS

We chose to present this case history to highlight the progress of applying monochloramine (MCA) chemistry in the paper industry. This paper presents an innovative means of controlling an MCA chemistry through multiparameter dosing control.

In this case history, the new MCA generator's flow control valves and automated chemical ratio control provided a significant reduction in chemical usage. This information will be beneficial for mills looking to optimize their MCA program.

In the future, we will apply the advanced control mode to other key application points to determine if a further reduction in KPI variabilities can be achieved.

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