FLORAN® clearitas safer. cleaner. better.™

INTRODUCTION

Blue Earth Labs is the leader in innovative approaches to water quality standards. Our suite of products reduces chlorine demand and disinfectant byproducts (DBPs) in water systems by eliminating organic and inorganic scale, enabling utilities to comply with EPA Stage 2 DBP rules.

Clearitas (formerly RE-Ox) is a proprietary formulation of oxidized chlorine that is added to drinking water distribution systems. Used in conjunction with existing disinfectants, Clearitas has been shown to effectively lower chlorine demand and improve DBP levels in many municipal settings.

Below are the differences between Clearitas and other chlorine based disinfectants, as well as the "mode-of-action" of the products and laboratory results. Field studies of Clearitas are available in our case studies.

CLEARITAS SYNTHESIS AND ANALYSIS

Clearitas is synthesized in a similar manner to bleach with a number of key differentiators. First, the manufacturing techniques employed during Clearitas's synthesis allow for the production of chlorine oxidants that reach higher oxidation states than sodium hypochlorite (NaClO). In addition to being able to oxidize different molecules present in water distribution systems, these higher oxidation states can be more hydrophobic in nature than ClO^-, which allow them to interact more strongly with organics that are present in water distribution systems and scale.

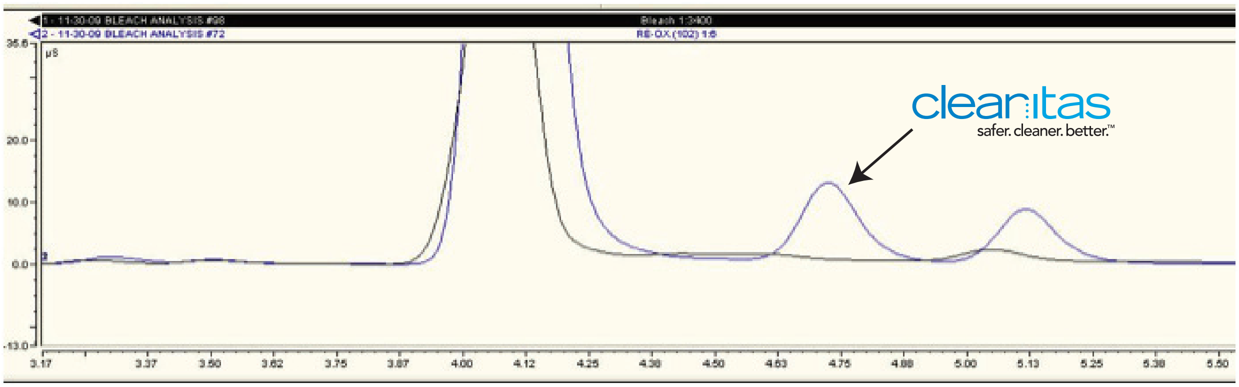

Figure 1 - Ion chromatography of bleach and Clearitas

Clearitas has been analyzed and compared to existing standards (such as bleach, NaClO, ClO_2, ClO_3, etc.) with a number of different analytical methods including chromatography, mass spectrometry, etc. Figure 1 presents two ion-chromatograms performed on Clearitas and bleach using identical methodologies and normalizing both solutions to total free chlorine. In this experiment, the x-axis is time and the y-axis is conductance. The methodology was set up so that ions progress down an ion-exchange column at very high pH. Thus, the hydration status of the ions can be determined relative to one another, even if ions have an identical charge. The methodology is set up so that ions that are retained on the column for longer dwell times are either at higher oxidation (+2 charge instead of +1), more hydrophobic in nature, or both. This particular comparison demonstrates that Clearitas contains ions that are clearly different than those present in bleach. Note: The very large peak at four (4) minutes is actually chloride; ClO^- comes off the column before the Cl^- and has very poor conductance.

MUNICIPAL SCALE ANALYSIS

In order to understand the mode of action of Clearitas, actual scale from municipal water supplies (from replaced pipe sections) was obtained from a number of different locations for analysis.

The scale was evaluated by soaking the scale (with periodic agitation) for 72 hours in hypochlorous acid (ClO), ClO2, ClO3, conventional bleach, and Clearitas. Bleach was analyzed both at pH 12 (which was the pH when it was simply diluted) and pH 7 (through the addition of hypochloric acid (HCl)). Clearitas was pH 7 in these experiments. In each case, the samples were normalized to 100 ppm of total chlorine and all analysis was completed in duplicate. At 24-hour intervals, a small sample of the eluent was removed from each sample and analyzed for total Ca+ using ion chromatography. A number of different scale samples were analyzed. Additionally, experiments were completed where the scale was left in whole chunks and where it was ground to a powder with a mortar and pestle.

Sample ID	Integration Area (uS*min)	Calcium Concentration in Solution (ppm)	
A. 100 ppm ClO	0.3312	25	pH 6
B. 100 ppm ClO	0.4015	29	pH 6
A. 100 ppm ClO2	0.342	26	pH 6
B. 100 ppm ClO2	0.3388	26	pH 6
A. 100 ppm ClO3	0.4211	30	pH 6
B. 100 ppm ClO3	0.5148	36	pH 6
A. 10X Diluted Bleach	0.0296	8	
B. 10X Diluted Bleach	0.0365	8	
ClO (5000 ppm)	0.4427	32	
ClO2 (5000 ppm)	1.7584	107	
ClO3 (5000 ppm)	2.2157	134	
A. Clearitas	**4.3705**	**258**	
B. Clearitas	**5.1239**	**301**	

Table 1 - Calcium release results of 72 hour scale soaking experiment

Table 1 shows the results from one such experiment (using ground scale) after 72 hours. In this experiment, very high levels of the standards were also run. As can be seen from the data, Clearitas had a huge effect on the production of free Ca^{+} from this particular scale. In fact, even 50 times more concentrated standards did not have the same descaling effect as Clearitas.

In the experiments on whole scale, similar trends have been noted but with much slower descaling in all cases. This trend is not surprising since the whole scale has much smaller surface area relative to the ground scale.

Clearitas has also been shown to be effective on inorganic scale that is composed of other metals. For example, iron rich scale, formed in a distribution system, was studied and showed similar trends with Clearitas. For example, in one type of scale, Clearitas removed 3.7 ppm of soluble iron (Fe) after soaking, compared to only 1.5 ppm of Fe using bleach.

It has been noted that the seeming catalytic effect of Clearitas is more pronounced with certain scale. In all of the municipal scale analyzed thus far, Clearitas has always produced higher free Ca+ compared to the standards. However, certain industrial scale analyzed seemed to produce much smaller differences.

In order to investigate the mechanism of action, eluents from these experiments were analyzed using mass spectrometry at The California Institute of Technology. Two of the resulting scans from one experiment are shown in Figure 2. Both the bleach and Clearitas were also examined using the identical methods (data not shown). Neither bleach nor Clearitas contains molecules at high molecular weight (< 300 amu). Generally, in scale, inorganic components will have relatively small molecular weights when measured with mass spectrometry. High molecular weight molecules will generally be mixed organics. Based on the above, for the scans shown in Figure 2, the high molecular weight molecules present in the eluent are organics being released from the scale. As can be seen, the eluent from the Clearitas contains much higher concentrations of large molecular weight molecules.

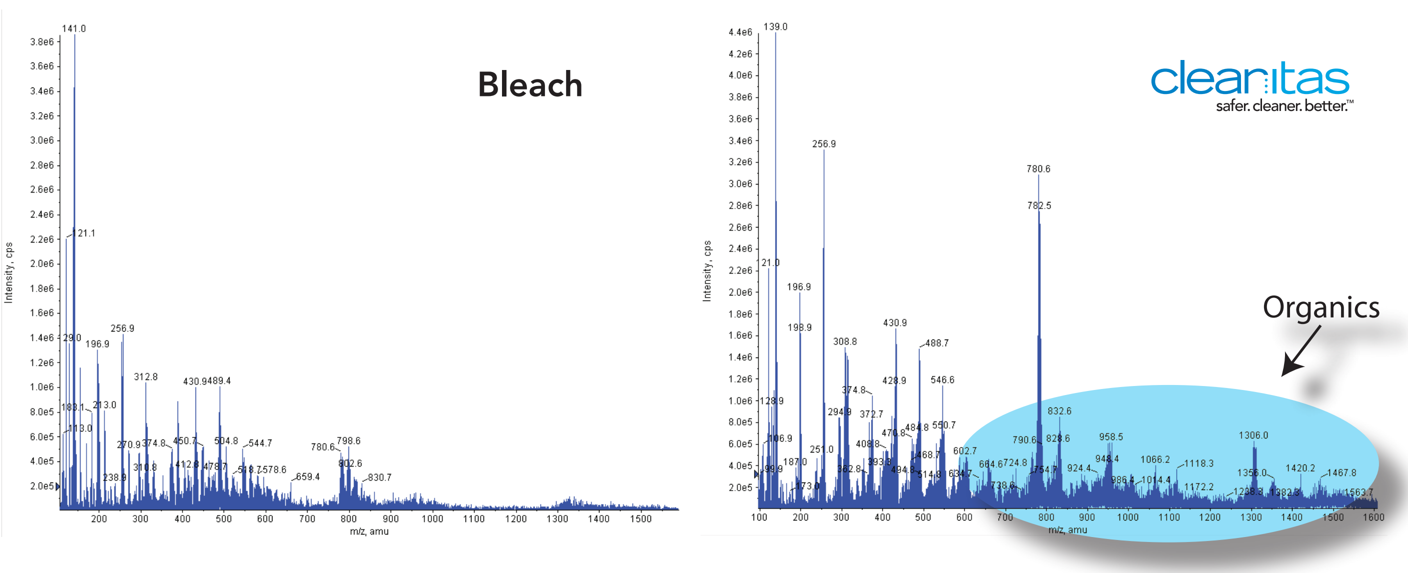

Figure 2 - Mass spectragraphs of eluent from scale soaking experiments

IN SITU SCALE ANALYSIS

In order to further understand the mechanism of action, Blue Earth Labs contracted with Puckorius and Associates to analyzed laboratory synthesized scale. Briefly, a dynamic scale tester (DST) was constructed in which calcium carbonate scale forms in a heated Pyrex glass coil from flowing simulated scale-forming cooling water. The DST is normally used to study the effectiveness of various commercial scale inhibitors and determine the dosages required. A schematic of the equipment is shown in Figure 1.

Two types of scales were made in duplicate. One type of scale was made using deionized (DI) water (which is organic free); the other was synthesized using water from an actual cooling tower in Colorado (which contains organic molecules). In both cases, the water used contained1500 ±1% parts per million (ppm) of calcium as CaCO3 and 275 ±1% ppm of bicarbonate alkalinity also as CaCO3, plus normal concentrations of magnesium, chloride, sulfate, sodium and silica, mimicking concentrated cooling tower water. Scale was formed in the DST at 120°F.

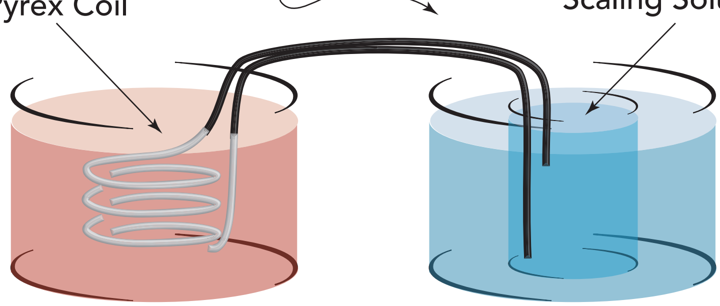

Figure 3 - Simplified schematic of dynamic scale tester (DST)

After the scale was fully formed and rinsed, a solution of Clearitas at +800 mV oxidation-reduction potential (ORP) was flushed through each of the coils at 100°F. The coils were discharged into different beakers. When the ORP went below +600 mV, additional Clearitas was added. The coils were flushed for two hours.

Very quickly, particles were noted in the beaker that was discharging from the scale made with cooling tower water. It was also noted that during the two-hour flush cycle, the ORP of the solution cleaning the scale made with deionized (DI) water never fell below +650 mV. Additionally, very little scale appeared to remain on the coils containing scale made with cooling tower water. At the end of the flush, the Ca^{+} concentration was measured in both flushing beakers. Additionally, the coils were cleaned with acid to remove the remaining scale and the Ca^{+} content of the cleaning fluid was measured.

The results of this test appear in Table 2. As can be noted from the data, some scale was removed using water distilled with Clearitas. However, the cleaning effect was much more dramatic when the scale was synthesized using cooling tower water.

	Ca in Eluent	Ca remaining on Coils	Total
Scale (distilled water)	84	528	612
Scale (cooling tower water)	623	0	623

Table 2 - Results from DST laboratory descaling experiment

DISCUSSION

It is well understood that oxidizing agents can convert solidified calcium (and other scale forming compounds) into solubilized form. The above experiments also demonstrate that fact, since some Ca^+ is released by the standards used. This oxidation occurs in a stoichiometric manner (one oxidizing molecule removes one calcium molecule). However, in an environment where the water chemistry is "scaling" rather than "corrosive," the amount of deposition that occurs greatly outweighs the ability to remove calcium in a stoichiometric manner. Thus, scale builds up over time.

Based on the experiments described above, it appears that Clearitas is able to oxidize and destroy organic compound that act as nucleation sites during scale formation. By removing the "glue" that holds the scale together, large amount of Ca^+ can be released into the water in soluble form, thus reversing the total scale formation over time. In this manner, a very low dosing of Clearitas into a water distribution system can have a very impactful effect.

The effectiveness of Clearitas on these scales will depend on a number of factors, including the water chemistry within the system. Additionally, the effectiveness of Clearitas will be more pronounced in systems where the organic content is higher during the scale forming process.