

Dashboard / ... / FC Chlorine Precipitation

Fall 2008 Semester Summary and Conclusions

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As time progressed this fall, we began to understand more fully the problem that was presented to us. It became apparent that adding another chemical to the current AguaClara water treatment system was not a reasonable solution to the precipitation problem. While adding hydrochloric acid (HCl) to the solution of calcium carbonate (CaCO_3) would be an effective way to reduce pH and prevent the CaCO_3 from forming, it would not be very cost effective. Using HCl would not only add to the cost of water treatment in terms of money spent, but also in terms of complicating plant operation. As a result, a different solution was pursued.

Next, the thought of settling out the CaCO_3 before it enters the hypochlorinator was investigated. If the precipitated CaCO_3 could be removed or reduced from solution before it comes into contact with the flow control device (FCD), this would ideally solve the problem. The fact that this chlorination treatment process will be expanding to many more communities, made investigating these problems more crucial, especially in communities that do not operate with full AguaClara water treatment plants. We began by examining the flow restrictions that may arise in the Honduran communities that expressed interest in adding an AguaClara FCD to their chlorine treatment systems. The first solution proposed was to design a settlement basin that could be implemented into the system which would allow the CaCO_3 to precipitate out before it entered the FCD like the one that can be observed in (Figure 1).

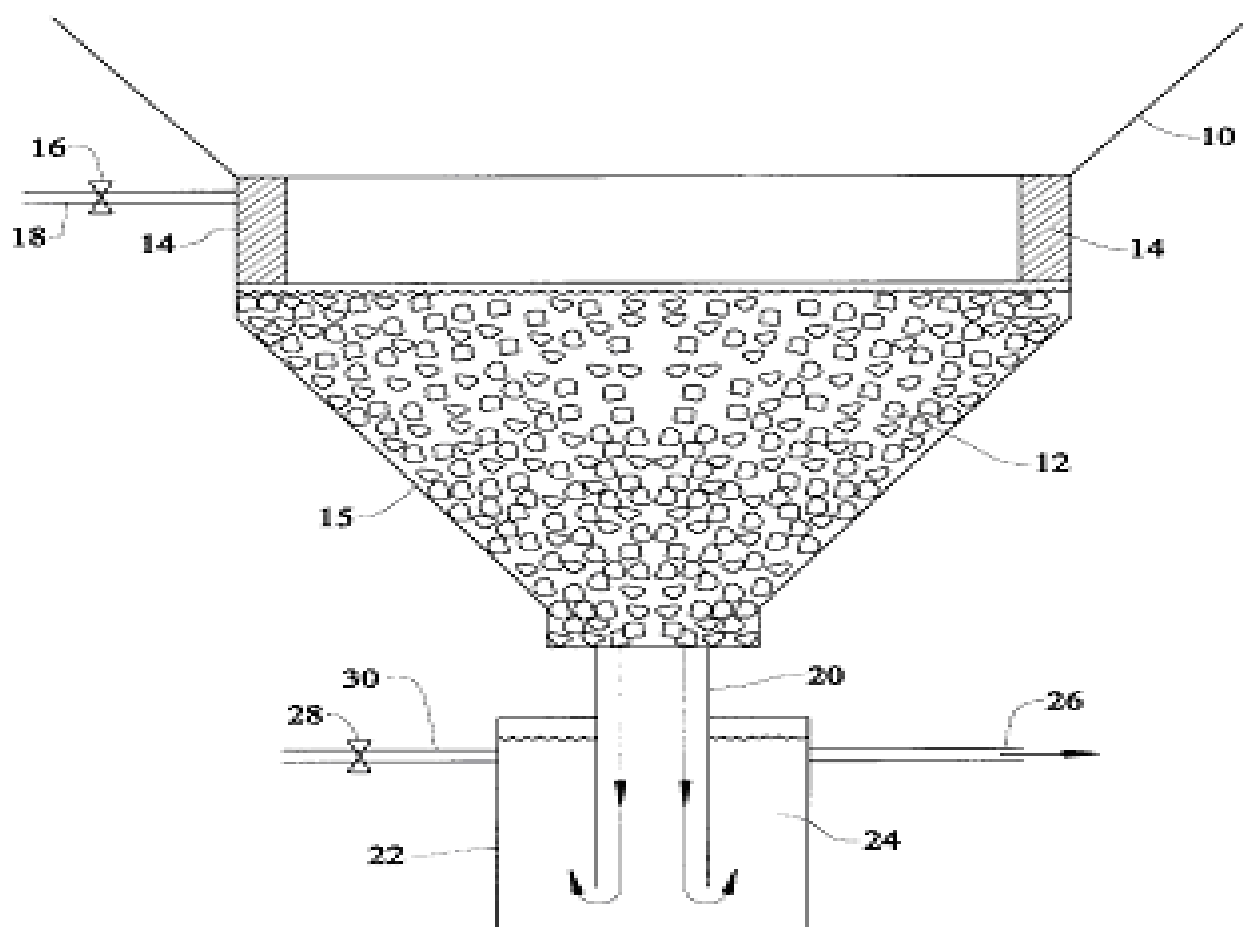


Figure 1. Calcium Hypochlorite Feeder designed by Ralph Morrison and company (US Patent Number 6,045,706).

We decided that a device like this would be costly to design and build for each community, but the idea of removing the CaCO_3 before the FC was not completely discredited.

Initially we separated the restriction of flow problem into two categories. Communities that are experiencing the problem that currently have AguaClara plants, and communities that could experience the problem that are going to use the AguaClara FC in there existing chlorine feed system. The reason we separated the problem into two categories was that we assumed that the logistics of adding a settling basin of some type to an already existing AguaClara plant would be different than adding it to a chlorine system from a chlorine stock tank in a community that is strictly chlorinating there water.

We then moved on to the restriction of flow in the FC problems faced by communities with full AguaClara water treatment plants. As is discussed in the flow control precipitation experiment Calcium Carbonate Settling Observations laboratory, the higher the concentration of calcium hypochlorite($\text{Ca}(\text{ClO})_2$), the larger the concentration of precipitate that initially settles out. If the solution of $\text{Ca}(\text{ClO})_2$ is created and left to settle, it was observed that the amount of precipitate stops forming after three days, as long as the solution is not flowing or being mixed with the atmosphere. As was observed in the Final Restriction of Flow of Hypochlorinators experiment, when the $\text{Ca}(\text{ClO})_2$ solution comes into contact with the atmosphere after initial settling, mixing or being forced through a small orifice (such as the one located in the float valve) will result in the precipitation of CaCO_3 again. It is believed that this is the result of the solution coming into contact with CO_2 in the atmosphere which results in the formation of CaCO_3 (Equation 1). This happens at pH's above around 8. The presence of $\text{Ca}(\text{OH})_2$ that also forms when $\text{Ca}(\text{ClO})_2$ is added to water (Equation 2) results in a pH increase to around 11 for a solution of $\text{Ca}(\text{ClO})_2$ of 30 grams/liter. This is high enough for the precipitation of CaCO_3 .

Equation 1. $2\text{Ca}(\text{ClO})_2 + 2\text{CO}_2 \rightarrow 2\text{CaCO}_3 + 2\text{Cl}_2 + \text{O}_2$

Equation 2. $\text{Ca}(\text{ClO})_2 + 2\text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2 + 2\text{HOCl}$

As was observed in the Carbonate Settling Observations laboratory, more precipitate can form after a concentrated solution of $\text{Ca}(\text{ClO})_2$ is diluted with non-distilled water as the result of the calcium's interaction with CO_2 (Equation 1). Precipitate could also form as a result of its interaction with other chemical species located in the dilution water.

We have now come to the conclusion that if the majority of the precipitant is removed from settling, the only other way that the flow will be impeded will be as a result of $\text{Ca}(\text{ClO})_2$ solution coming into contact with the atmosphere. Locations where this could happen are at the surface of the stock tank that holds the $\text{Ca}(\text{ClO})_2$ solution, the surface of the constant head bottle where the float valve is located, and the orifice located in the float valve where the solution is forced into the constant head bottle.

As was examined in the "Restriction of Flow of Hypochlorinators" experiment, if there is a solid material present like plastic or metal when the $\text{Ca}(\text{ClO})_2$ solution comes into contact with the atmosphere, the precipitate will form on the surface of the plastic or metal (Figure 2).



Figure 2. The precipitant that formed on a plastic surface after the solution of $\text{Ca}(\text{ClO})_2$ was leaking out of the bottle.

If precipitation forms in the stock tank or at the surface of the constant head bottle over time after the initial settlement, it would flow out of the tanks with the rest of solution or settle out at the bottom of the containers, as was observed in the Final Restriction of Flow of Hypochlorinators experiment. If it continued through the system with the flow of solution we are confident that this small amount of precipitate would not build up, or impede flow at any point in the system. This leaves us with the float valve orifice. Every instance where we were able to restrict flow from the orifice in the float valve there was a buildup of precipitate all over the surface of the float and the arm holding the float to the rest of the valve. It appears that precipitate is slowly forming in the orifice where the solution first comes into contact with the atmosphere after leaving the tube that flows from the stock tank, eventually restricting flow (Figure 3).

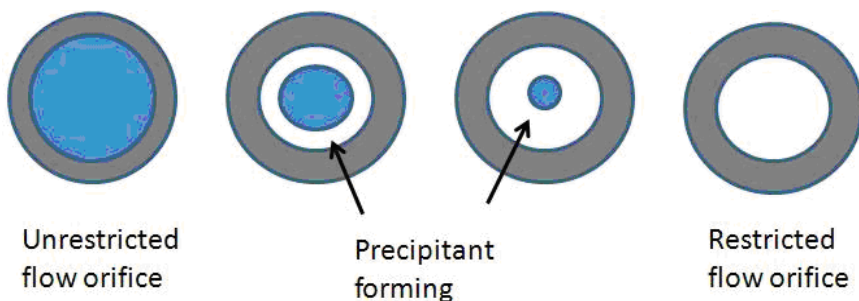


Figure 3. Restriction of flow through an orifice over time by the formation of a precipitant of CaCO_3 .

It was decided that to deal with this occurrence, we would raise the level of the solution in the constant head bottle to a level above the orifice. This would result in the solution not coming into contact with the atmosphere at the orifice. The orifice would be submerged and calcium would not come into contact with CO_2 until getting close to the surface of the solution in the constant head bottle.

In our laboratory experiments this has kept the system functioning with relatively high concentrations of $\text{Ca}(\text{ClO})_2$ for periods of time lasting more than a week as can be observed in "Restriction of Flow of Hypochlorinators" experiment. Presumably the experiment would have continued to function without obstruction, but it was terminated so a new test could be organized.

Another issue involved with the use of $\text{Ca}(\text{ClO})_2$, is safety. Calcium hypochlorite is considered a strong oxidizer. It is corrosive and causes burns to any area of the body it comes into contact with. It is harmful if swallowed or inhaled and it will react with

water. The MSDS recommends goggles, a ventilated hood, and proper gloves when in contact with this chemical. Specifically when inhaled it is extremely destructive to tissues of the mucous membranes and upper respiratory tract. Symptoms may include a burning sensation, coughing, wheezing, laryngitis, shortness of breath, headache, nausea and vomiting. Inhalation may be fatal as a result of spasm inflammation and edema of the larynx and bronchi, chemical pneumonitis and pulmonary edema (J.T. Baker, MSDS 2008). There were instances this semester where individuals that were working with this chemical in the laboratory here at Cornell felt sick and or nauseous after accidental inhalation. These occurrences were the result of improper fume hood operation by the students. They were operating the fume hood with the window (or front door) open to high.

Another issue that was considered is if the $\text{Ca}(\text{ClO})_2$ solution is going to be pre-settled before being applied to the chlorine solution stock tanks, a sufficient volume of water must be added to the chemical in the container that the solution is being settled out of to completely dissolve the $\text{Ca}(\text{ClO})_2$ in solution. The solubility of $\text{Ca}(\text{ClO})_2$ is 210 g/L. In certain communities the concentration of $\text{Ca}(\text{ClO})_2$ required for chlorination of the water supply necessitates a large enough weight of $\text{Ca}(\text{ClO})_2$ that the amount will not dissolve in a 20 liter bucket of water, which is the procedure that some operators have been implementing.

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