Calcium Carbonate Settling Observations

Abstract

We ran several experiments to determine the amount of precipitate settling out of Calcium Hypochlorite solution at 10 g/L, 20 g/L, and 30 g/L concentrations. The precipitate forming in solution was found to mostly settle to the bottom of solution, but some did stay suspended on the top of solution. From these experiments, we were able to come up with a safety height of 6 cm, which should be the minimum height the exit valve is placed at in the stock tank to minimize clogging at the stock tank exit. Also from these experiments, it was found that by allowing the solution to settle out for 3 days before running it through the hypochlorinator, a lot of the precipitate will just sit in the bottom of the stock tank. The precipitate that settles in the stock tank won’t interfere with the rest of the hypochlorinator and cause clogging in other areas, such as the float valve.

Introduction and Objectives

The Calcium Carbonate Settling experiments were done in order to determine the amount of precipitate forming at various concentrations of calcium hypochlorite solution after allowing the solution to settle for varying amounts of time. From this data, the residual masses of calcium left in solution with potential to clog the hypochlorinator were calculated. Additionally, the effects of starting with a higher concentration of calcium hypochlorite and then reducing that concentration by the addition of water, were examined to determine whether that method changes the amount of precipitate settling out.

Procedures

In this experiment, we filled three 1 liter graduated cylinders with varying concentrations of Calcium Hypochlorite. The graduated cylinders consisted of a 10g/L, 20g/L, and 30g/L solution of Calcium Hypochlorite solution. The solutions were mixed well and allowed to sit for up to 3 days in order to observe the height and weight of precipitate forming in the bottom of each cylinder after each day.

The weight of precipitate in each solution was found using vacuum filtration. The contents of each cylinder were poured through a filter and the liquid was vacuumed out. The precipitate left on the filter paper was then weighed. Due to the fact that the samples of precipitate filtered out were not heated in the oven, there is probably a small margin of error in this part of the experiment.

In another part of this experiment, a 100g/L solution of Calcium Hypochlorite was made and allowed to settle for one day. The heights of precipitate after one day were determined and then the concentration was brought down to 30g/L with the addition of tap water to the supernatant of this solution. The new height readings were taken and compared to those resulting from starting with 30g/L initially.

One more variation to this experiment was set up in which rocks were placed inside the graduated cylinders with Calcium Hypochlorite solution and the solution was allowed to settle out for a day, as before. This was done in hopes that with more surface area, which the rocks provided, nucleation sites would allow for more precipitate to settle out of solution. Results from these experiments however, were inconclusive.

Results and Discussion

After allowing the cylinders to stand for a three days, most of the precipitate settled to the bottom, but some did float as a film on the very top of the solution. This film is likely the result of carbon dioxide diffusing through the surface and immediately precipitating with the calcium. Some flocs of precipitate could be seen floating throughout the solution. After three days the amount of precipitate settling to the bottom of the cylinders did not increase.

Small bubbles were observed floating to the top of the cylinder, which sometimes would attach to flocs of the precipitant. These flocs would either float to the top or stay suspended somewhere between the bottom and the top of the graduated cylinder depending on the floc size.

For the first three days, the height of precipitate in the bottom of each cylinder increased (Figure 1). These measurements were all taken from 6.35 cm diameter graduated cylinders, to minimize error. At day four, the amount of precipitate did not increase from day three. The height of precipitate was found to increase non-linearly from with increasing concentration. The height of precipitate doubled from 10 g/L solution to 20 g/L, but just approximately 7 times greater from 10 g/L to 30 g/L. This could perhaps be due to the fact that 10 g/L is below the saturation point of calcium hypochlorite in the 1 liter graduated cylinder used, whereas at 30 g/L the solution is closer to saturation, and thus some of the solid found at the bottom could also be calcium hypochlorite.

Figure 1: Height of Precipitate over Time with Varying Concentration of Solution
In the future, the 55 gallon drums that hold the Calcium Hypochlorite solution should have exit flow valves installed at a height high enough from the bottom, so that any precipitant formed and settled does not flow out of the tank at this valve.

Measuring the height from the bottom of a container, to the top of the settled precipitant that forms, helped us determine the height to place the exit valve (Figure 2). This height was calculated to be approximately 10 cm, which is the result of maximum precipitate height found to settle out of a 30 g/L solution multiplied by a safety factor of 2. This height was determined by the fact that the ratio of solution height to precipitant height in solution should be equal at equal concentrations. The height of solution in a 1 liter graduated cylinder was found to be 29 cm and the height of precipitate in this graduated cylinder with a 30 g/L solution, was found to be 1.55 cm after 3 days. Using this ratio and the fact that height of solution in a 55 gallon drum is approximately 87 cm tall, the precipitate height was found to be 4.66 cm. Multiplying by a safety factor of 2 yields a exit valve height of approximately 10 cm.

Figure 2: Picture of Stock Tank with Exit Valve
The fact that after 3 days no more precipitate settles out, gave us a good estimate of time to wait before sending the calcium hypochlorite solution into the plant. However, waiting only 1 day is not enough time, because it results in 50% less precipitate settling out as opposed to after 3 days at some concentrations.

The masses of Calcium Carbonate precipitate resulting from vacuum filtering varying concentrations of Calcium Hypochlorite solution are graphed below. The masses were found to be 0.3, 0.72, and 1.93 grams at 10 g/L, 20 g/L, and 30 g/L, respectively. The mass of precipitate was found to increase with increasing concentration of solution. From these resulting masses and the known molecular weights of Calcium Hypochlorite going in, the amount of Calcium Carbonate that could precipitate out was calculated. And based on the amount of Calcium Carbonate we found that actually did precipitate out of solution, we were able to find the residual mass of Calcium left in solution that could potentially settle out at a later time and clog the hypochlorinators.

For every mole of calcium hypochlorite (Ca(ClO)2) one mole of calcium carbonate (CaCO3) precipitates out in solution. Using this and the fact that the molecular weight of calcium hypochlorite is 142.98 g/mol and the known masses of calcium hypochlorite added were 10, 20, and 30 g, the moles of calcium added were found to be 0.7, 0.14, and 0.21, respectively. Therefore the mass of calcium (molecular weight: 40.08 g/mol) going into solution was found to be 2.8, 5.6, and 8.4 g, respectively. Then using the molecular weight of calcium carbonate (100.09 g/mol) and the known masses of calcium carbonate coming out of solution (0.3, 0.72, and 1.93 at 10 g/L, 20 g/L, and 30 g/L, respectively as mentioned above), the moles of calcium carbonate and thus calcium coming out were found to be 0.003, 0.007, and 0.019, respectively. From this the mass of calcium coming out of solution was found to be 0.12, 0.29, and 0.77 g respectively. By subtracting the amount of calcium going into solution from the amount of calcium going into solution, the residual mass at each concentration was found.

These masses were found to be 2.68, 5.32, and 7.64 g at concentrations of 10g/L, 20g/L, and 30g/L, respectively (Figure 3). This also revealed an increase in potential for clogging with an increase in concentration of solution.

Figure 3: Mass of Residual Calcium and Precipitation forming with Varying Concentrations of Solution
When starting with an initially high concentration of Calcium Hypochlorite and reducing the concentration after initial settling by adding tap water, the resulting amount of precipitate in solution was found to decrease from 0.12 in height to 0.01 in a 30g/L solution. These are dimensionless heights measured as the height of precipitate forming divided by the height of solution. This data reveals a 80% reduction in precipitate found to accumulate. The full results are shown below (Figure 4).

Figure 4: Height of precipitate forming at 100g/L solution and diluted 30g/L solution.
From this data, it can be inferred that in the first day that the 100 g/L solution was allowed to sit, a lot of the precipitate did settle out. However, reducing the supernatent of the 100 g/L concentration to 30 g/L after the first day and allowing it to settle again did result in the additional formation of precipitate. This additional precipitate was a result of an additional day of settling, due to the fact that this test was done in less than the 3 suggested days. This was done because of a time constraint. It is also possible that some of what was measured in the initial 100 g/L concentration as precipitate was actually calcium hypochlorite that didn't dissolve due to the saturation of solution. Thus adding additional water to the supernatant of that solution would result in more calcium hypochlorite dissolving and more precipitate forming.

Conclusions

With increasing concentration of Calcium Hypochlorite Solution, the threat of clogging becomes greater due to increased amount of precipitate forming. There are several ways however to reduce this threat.

Waiting 3 days to use the solution and pouring out only the liquid at the top of the precipitant and below the film formed at the top of the container should decrease the amount of precipitate in the system and help to eliminate clogging. Further we would recommend some type of filtration of the solution to remove the floes of precipitant that are suspended in the middle of the holding container.

The 55 gallon drums that hold the Calcium Hypochlorite solution should have exit flow valves installed at a height greater that approximately 10 cm in order to be above the line of precipitate forming on the bottom of the container. This should reduce clogging at the bulkhead fitting at the exit of the 55 gallon drum.