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Trace Additives to Inhibit the Caking of Purple K for 3-D Firefighting

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14. ABSTRACT The use of crystal-habit modifying additives was evaluated to inhibit the caking of Purple K dry chemical fire suppression agent. Potassium bicarbonate (KHCO₃), which is the active ingredient (>99%) of Purple K, was used as the baseline compound. Micron-sized KHCO₃ powder containing additives were produced by a spray and drying technique. However, the quantity of sample produced was insufficient to conduct drop tests. A follow-up effort focused on producing salt cakes with six additives. Cakes were made by spraying 1 ml aqueous solution containing 0.0333 g of corresponding additives onto 30 g of KHCO₃ powder, followed by baking in an oven at 60oC for 16 hours. The cakes containing NH₄Cl, (NH₄)₄Ce(SO₄)₄, and K₄Fe(CN)₆ displayed improved scattering by dropping from a height of 18 inches, suggesting these additives may have weakened inter-crystalline bridges between the salt particles. These results warrant further tests, in terms of other additives, combination of additives, and additive concentration dependence, to fully assess the effect of crystal habit modifiers on the caking behavior of KHCO₃.					
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1. Executive Summary

1.1 Objective

This project investigated the use of crystal-habit modifying additives to inhibit the caking of Purple K dry chemical fire suppression agent. Specifically, this project sought to demonstrate the improvement of the anti-caking behavior of potassium bicarbonate (KHCO_3), which is the active ingredient (>99%) of Purple K, and to achieve the production of modified KHCO_3 using a technique similar to the rapid expansion supercritical solution (RESS) method.

1.2. Background

Purple K is used as a dry chemical fire suppression agent by the Air Force and throughout the firefighting industry. Although Purple K powder is effective for suppressing three-dimensional fuel fires, it is also prone to caking in humid/moist environments. This undesired behavior can lead to problems associated with the mobilization of the powder out of the storage tank. In some cases, delivery of the powder was completely prevented due to caking.

The most common method to reduce/prevent the caking of Purple K is to blend in trace amounts of silicon-based oils and water insoluble powder with the Purple K powder. These surface modifiers are effective for preventing the caking of Purple K. However, an undesired side-effect of their use is to also reduce the effectiveness of the flame suppression by breaking down the aqueous film-forming foam (AFFF) that is used in conjunction with the Purple K to suppress fires. Hence, the development of a technique for preventing cake formation that does not affect the performance of firefighting foams would be valuable to both the Air Force and the firefighting industry. This project was initiated to examine the potential for crystal habit-modifying additives to serve as anti-caking agents that have little/no effect on the performance of firefighting foams.

1.3. Approach

This project consisted of two main phases. First, the production of micron-sized unmodified and modified KHCO_3 particles was attempted from both a KOH solution and from a KHCO_3 solution, using a bench-top flow-through apparatus. The KHCO_3 solution was atomized by a CO_2 gas stream using a nozzle atomizer. The resulting spray was ejected into a heated chamber to promote evaporation of H_2O in the atomized spray and to induce $\text{KHCO}_{3(s)}$ precipitation and particle formation. After production of modified KHCO_3 was achieved, the second phase of the project examined the effect of the additives on the anti-caking behavior of the KHCO_3 particles. In this phase, drop tests were performed on cakes formed from the modified samples, according to the literature. Microscopic images were taken to verify the size of the produced KHCO_3 powder, and

digital images of the fragmentation patterns of the cakes were recorded to assess the effect of additive on the anti-caking behavior of the KHCO_3 .

1.4. Conclusions

- Micron-sized KHCO_3 particles were achieved using the KHCO_3 feed, but not with the KOH feed. The inability of the KOH feed system to form KHCO_3 particles was likely due to the inability for several mass transfer/reaction steps to proceed during the short time the atomized drops were in the air.
- Micron-sized modified KHCO_3 particles were achieved using the experimental apparatus.
- The first adapted anti-caking test proved inconclusive for determining the effect of the additives $\text{K}_4\text{Fe}(\text{CN})_6$ and $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4$ on the caking behavior of KHCO_3 due to the small weight of the cakes (400 mg), which was limited by the capability of the synthesis apparatus. Little difference in the fragmentation patterns was observed for cakes with and without an additive.
- The second adapted anti-caking test involved higher weight of the cakes (30 g), which used pure KHCO_3 to emphasize on the cake formation procedure instead of KHCO_3 power synthesis. Noticeable and repeatable fragmentations were observed in the modified KHCO_3 cakes as compared to the baseline (without an additive) KHCO_3 cake. The cakes containing NH_4Cl , $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4$, and $\text{K}_4\text{Fe}(\text{CN})_6$ displayed visually improved scattering by dropping from a height of 18 inches, suggesting these additives may have weakened inter-crystalline bridges between the salt particles as compared to the baseline cake.
- The cake formation procedure should be modified to more accurately reflect the conditions/process by which Purple-K caking occurs in the field. Results from this study warrant further tests, in terms of other additives, combination of additives, and additive concentration dependence, to fully assess the effect of crystal habit modifiers on the caking behavior of KHCO_3 .

2. Objectives and Scope

The goal of this project was to prove the concept of incorporating crystal habit modifiers to inhibit the caking of Purple K dry chemical fire suppressant using bench-top test systems. The specific objectives were as follows:

1. To demonstrate the effectiveness of crystal habit modifying additives to improve the anti-caking behavior of KHCO_3 , which is the active ingredient of Purple K.
2. To demonstrate the production of modified KHCO_3 crystals using a technique similar to the rapid expansion supercritical solution (RESS) method.

3. Background

Purple K is used by the Air Force and throughout the firefighting industry as a dry chemical agent for suppressing three-dimensional fuel fires. The main ingredient of Purple K is potassium bicarbonate, KHCO_3 , which serves as the active flame suppression agent. Purple K is produced and stored as a micron-sized powder, and delivered by compressed air from the storage tank to the nozzle. However, undesired caking of Purple K during storage has been known as a major issue in its use. Produced as a free-flowing powder, purple K can become a caked solid when exposed to moisture or humid air. Once caking has occurred, the purple K mobilization is hindered or even prevented. In fact, there have been instances of failed Purple K delivery at the scene of a fire due to caking in the storage tank.

Caking is believed to occur due to the formation of intercrystalline salt bridges between water soluble salt particles. There are three scientific methods that have been applied to minimize the formation of the intercrystalline salt bridges, and therefore preventing water soluble salts from caking. The first method involves coating the salt particles by an oily substance which serves as a barrier to block the moisture. The second method involves blending the water soluble salts with a fine, water insoluble powder, which reduces caking by creating gaps between the salt particles. While both of these methods rely on surface modifiers, the third method uses crystal habit modifiers that alter the crystal habit of the salt, so that the moisture-induced intercrystalline bridges form in a weakened condition. Hence, any salt cakes that do form are easily broken apart with little force.

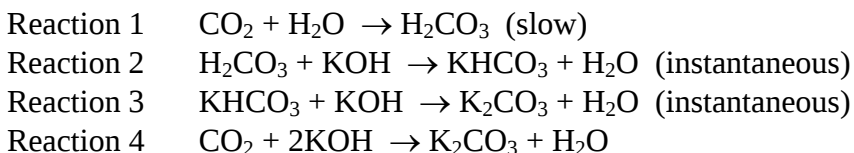
In the typical commercial Purple K formulation (such as the one manufactured by Chemguard, Inc.), the potassium bicarbonate powder (>99%) is blended with trace amounts of silicone-based oils (methyl hydrogen siloxane) and water insoluble powder (magnesium aluminum silicate). These surface modifiers are proven to be effective to prevent Purple K from caking in conventional dry chemical fire suppression applications. One of the new firefighting techniques currently being developed at Air Force Research Laboratory, Deployed Base Systems Branch (AFRL/MLQD) is that of combined agents fire fighting (CAFF), which integrates the dry chemical agent with the aqueous firefighting foam (AFFF) agent to achieve enhanced fire suppression capabilities for both three-dimensional fuel fires and pool fires. In the CAFF applications, tests have shown that silicone-based surface modifiers are also very effective for breaking down AFFF and other firefighting foams. Hence, the use of silicon oil-treated Purple K in concert with firefighting foams leads to a decrease in the performance of fire suppression. Therefore, the development of a technique that reduces the tendency for Purple K to cake, and does not affect the effectiveness of firefighting foams, is of great interest to both Air Force and commercial firefighters.

A number of crystal habit modifiers, also referred to as additives, in trace (ppm) levels have been demonstrated to be highly effective to prevent caking during storage of inorganic salts, such as sodium chloride, potassium chloride, ammonium chloride, ammonium sulfate, and potassium sulfate (Phoenix, 1966). Potassium carbonates show

similar caking tendency as that of the chloride and sulfate salts. The reported crystal habit modifiers would have a good chance to work for potassium bicarbonate as an anti-caking approach. However, no studies on crystal habit modifiers for carbonate salts have been found in the literature. Therefore, this experimental investigation focused on the method involving crystal habit modifiers to prevent potassium bicarbonate from caking. If successful, the method can be used to develop new Purple K dry chemical formulations that inhibit the tendency for caking without impeding or reducing the effectiveness of firefighting foams in the CAFF applications.

Potassium bicarbonate is commercially produced by carbonating potassium hydroxide (KOH) to potassium carbonate (K_2CO_3), which is then carbonated to $KHCO_3$. Carbonation is accomplished by injecting carbon dioxide (CO_2) gas into an aqueous KOH solution (Pierantozzi, 1993).

Two chemical pathways exist for the reaction of KOH with CO_2 in an aqueous medium. These reactions for CO_2 and KOH in water are shown below (Butler, 1982).



The first pathway, which has the potential to form the desired product $KHCO_3$, is summarized by Reactions 1-3. As indicated, the rate of the direct CO_2 hydration (Step 1) is slow and the rates of Step 2 and Step 3 are instantaneous. Therefore, the rate of the overall reaction for the first pathway can be approximated by the rate of the direct CO_2 hydration, which is the rate-limiting step. This step is controlled by the rate of CO_2 dissolution into the aqueous phase. The reaction rate for the first pathway in terms of the rate of CO_2 disappearance is given below,

$$-d[CO_2]/dt = k_{CO_2} [CO_2].$$

The second pathway, which does not form the desired product $KHCO_3$, is shown in Reaction 4. For this reaction, the rate of CO_2 disappearance is proportional to both the CO_2 concentration and OH^- concentration, resulting in the following reaction rate:

$$-d[CO_2]/dt = k_{OH} [OH^-][CO_2].$$

Therefore, the overall reaction rate for the reaction of KOH with CO_2 can be summarized as the sum of the rates for both pathways:

$$-d[CO_2]/dt = k_{CO_2} [CO_2] + k_{OH} [OH^-][CO_2]$$

The rate of reaction for the second pathway is a strong function of pH, and is insignificant below pH = 8. Hence, at pH < 8, the overall rate of reaction can be approximated as $k_{CO_2} [CO_2]$. Above pH = 10, however, the direct reaction of CO_2 with

OH^- dominates the reaction, and the overall rate can be approximated as $k_{\text{OH}} [\text{OH}^-][\text{CO}_2]$. The rate constants (k_{CO_2} and k_{OH}), half life ($t_{1/2}$), and equilibrium for the carbon dioxide-carbonate equilibrium reactions in an aqueous solution are given in Table 1. The data show that when pH is greater than 10 the formation of carbonate (CO_3^{2-}) from carbon dioxide is instantaneous even at room temperatures.

Although the second pathway does not yield the target compound KHCO_3 directly, the reaction consumes OH^- , which serves to lower the pH. The HCO_3^- ion is the dominant carbonate ion in the pH range of about 7 to 10 (see Figure 1), so that reducing the pH of a KOH solution (pH = 14) by consuming OH^- ions via Reaction 4 may be a feasible method for producing KHCO_3 from CO_2 and KOH.

Table 1. Rate Constants, Half Life and Equilibrium (CO_2) for the Carbon Dioxide-Carbonate Equilibrium an Aqueous Solution (25°C)

pH	% CO_2	k_{CO_2}	$k_{\text{OH}}(\text{OH}^-)$	$\alpha k_{\text{H}_2\text{CO}_3}$	$\alpha' k_{\text{HCO}_3^-}$	$t_{1/2}$ (s)
1	99.8	0.03	0.0000	20	0.005	0.05
2	99.8	0.03	0.0000	20	0.05	0.05
3	99.8	0.03	0.0000	16	0.38	0.06
4	99.4	0.03	0.0000	5.7	1.4	0.18
5	96.0	0.03	0.0000	0.77	1.8	1.25
6	70.6	0.03	0.0001	0.08	1.9	9.1
7	19.3	0.03	0.0008	0.008	1.9	26.0
8	2.3	0.03	0.0085	0.001	1.9	25.0
9	0.2	0.03	0.085	0.000	1.8	8.7
10	0.0	0.03	0.85	0.000	1.3	1.14
11	0.0	0.03	8.5	0.000	0.33	0.12
12	0.0	0.03	85.0	0.000	0.038	0.012
13	0.0	0.03	850	0.000	0.004	0.0012
14	0.0	0.03	8500	0.000	0.000	0.0001

The half life to attain equilibrium is given by $t_{1/2} = \ln 2 / (\Sigma k_{\text{CO}_2} + \Sigma k_{\text{carb}})$, where $\Sigma k_{\text{CO}_2} = k_{\text{CO}_2} + k_{\text{CO}_2}(\text{OH}^-)$ and $\Sigma k_{\text{carb}} = \alpha k_{\text{H}_2\text{CO}_3} + \alpha' k_{\text{HCO}_3^-}$. The α terms represent the fraction of total carbonate present as H_2CO_3 and HCO_3^- , respectively. (Adapted from Kern, 1960)

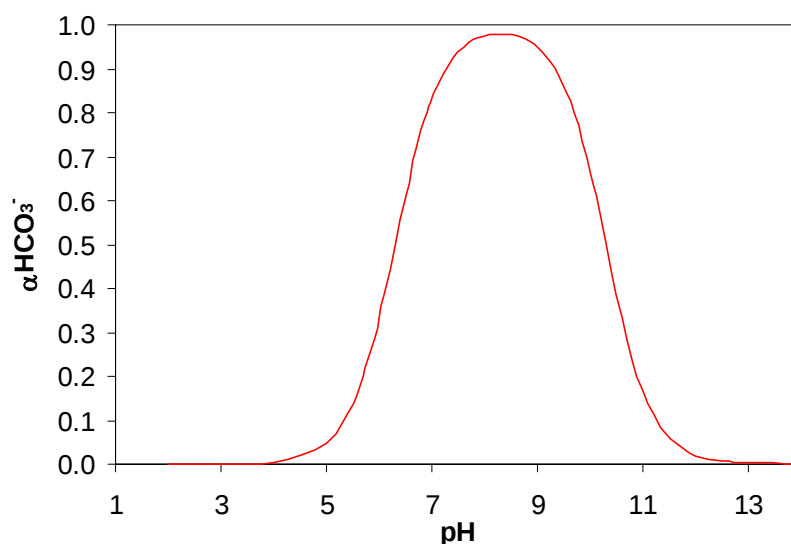
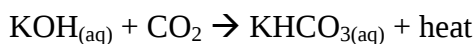


Figure 1. Effect of pH on Bicarbonate Fraction in Solution. Bicarbonate Fraction (αHCO_3^-) is equal to $(\text{HCO}_3^-)/[(\text{H}_2\text{CO}_3^*) + (\text{HCO}_3^-) + (\text{CO}_3^{2-})]$, where $(\text{H}_2\text{CO}_3^*)$ is commonly used to indicate the sum $(\text{H}_2\text{CO}_3) + (\text{CO}_2(\text{aq}))$.

4. Approach

4.1. Production of Potassium Bicarbonate

Potassium bicarbonate was used as a model compound to determine the anti-caking effectiveness of crystal habit modifiers on Purple K. Figure 2 depicts the laboratory-scale test system designed to continuously produce micron-sized particles of modified KHCO_3 . A gas-driven atomizer (nozzle) was used to contact a KOH aqueous stream containing trace amounts of the crystal habit modifier with a gaseous CO_2 stream by the following reaction pathway:



As the CO_2 gas dissolves into the atomized (KHCO_3 + additive) droplets, the exothermic reaction would occur, forming modified KHCO_3 . If there is sufficient heat, either provided by heat of the reaction or added to the system via an external heating source, the water solvent would be evaporated from the KHCO_3 solution, resulting in modified KHCO_3 particles. These particles could be collected and their size determined using a microscope. If the atomized droplets produced are small enough, then micron-sized particles can be achieved.

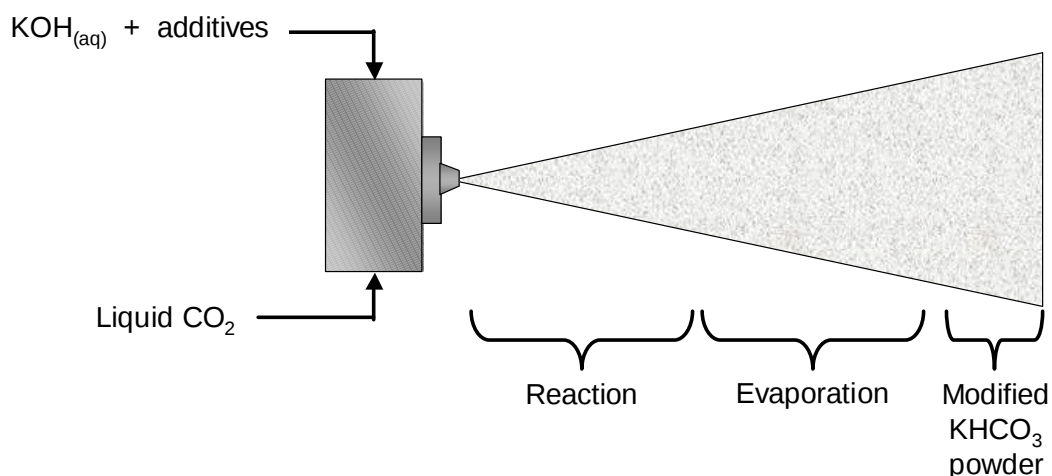


Figure 2 Proposed technique for producing modified KHCO₃.

4.2 Crystal Habit Modifiers

Phoenix (1966) examined the anti-caking effectiveness of several crystal habit modifiers on chloride and sulfate salts of sodium, potassium, and ammonium. Of the crystal habit modifiers examined in the study, potassium ferrocyanide (K₄Fe(CN)₄), cadmium chloride (CdCl₂), ammonia acetamide (N(CH₃CONH₂)₃), ferric chloride (FeCl₃), ammonium cerium (IV) nitrate (NH₄)₂Ce(NO₃)₆, and ammonium cerium (IV) sulfate ((NH₄)₄Ce(SO₄)₄) were categorized as “very good” anti-caking agents. Among these candidate additives for use in the present study, potassium ferrocyanide is commonly used in industry to inhibit the caking of sodium chloride, and only 4 ppm of the additive is required. Ammonium cerium (IV) sulfate is an effective anti-caking agent for some potassium salts (Phoenix, 1966). In the present study, potassium ferrocyanide and ammonium cerium sulfate were chosen as crystal habit modifiers.

4.3 pH of Solution

KOH is a strong base and the pH of a 50% KOH solution is 14, whereas KHCO₃ is a weak acid salt and is most prevalent in the pH range of 7 – 10. Thus, pH of the solution made from the generated particles can be used to indicate the presence of KHCO₃, and confirm its synthesis. pH strips were used to estimate pH of the solution.

4.4. Anti-Caking Test

Modified KHCO₃ particles collected from the experimental apparatus could then be subjected to a caking test to evaluate the anti-caking effectiveness of the crystal habit modifiers. The caking test, adapted from the test described by Phoenix (1966), proceeds as follows. Three hundred grams of modified KHCO₃ are mixed with 9 mL of water. The resulting wet mixture is molded into a small cake, and dried in a temperature-controlled oven for a specified amount of time. A drop test is then performed by dropping the cake onto a hard surface from 18”. The anti-caking effectiveness is then determined by observing the number of pieces into which the cake breaks up and by comparing digital images of the scattered cakes.

5. Materials and Methods

Chemicals used in the study included the following: potassium hydroxide (Oxy-Chem, 80% purity, water balance); potassium bicarbonate (Fisher, A.C.S. reagent grade); carbon dioxide (Airgas, Inc., zero grade); potassium ferrocyanide trihydrate, $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ (Aldrich, 99%), ammonium cerium sulfate dihydrate, $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ (Aldrich, 94+%), KCl (Aldrich, 99%), KBr (Aldrich, 99%), KF (Aldrich, 99%), NH_4Cl (Aldrich, 99%).

An electronic balance (xxx) was used to precisely weigh the amounts of feed salts and additives required to prepare the feed solutions. Water used to prepare the solutions was obtained from an in-house RO system (Rainsoft Model RSRO).

6. System Development

Preliminary tests were conducted using a simple experimental system to demonstrate the concept described in Figure 1. This experimental effort proceeded to develop several versions of bench-top experimental systems with improvements and upgrades to meet specific test requirements. Details of these experimental systems are provided below.

6.1. System I

The preliminary experimental apparatus assembled for modified KHCO_3 production is shown in Figure 3. A gas atomization nozzle (Spraying Systems Co., Model 1/8JSU11) was used to contact the KOH and CO_2 streams. Aqueous KOH solution was supplied from a buret, and the CO_2 gas was delivered from a CO_2 tank. The ejected spray was collected using a plastic tray, which was pitched at a downward angle so that any generated KHCO_3 particles were directed away from the ejected spray.

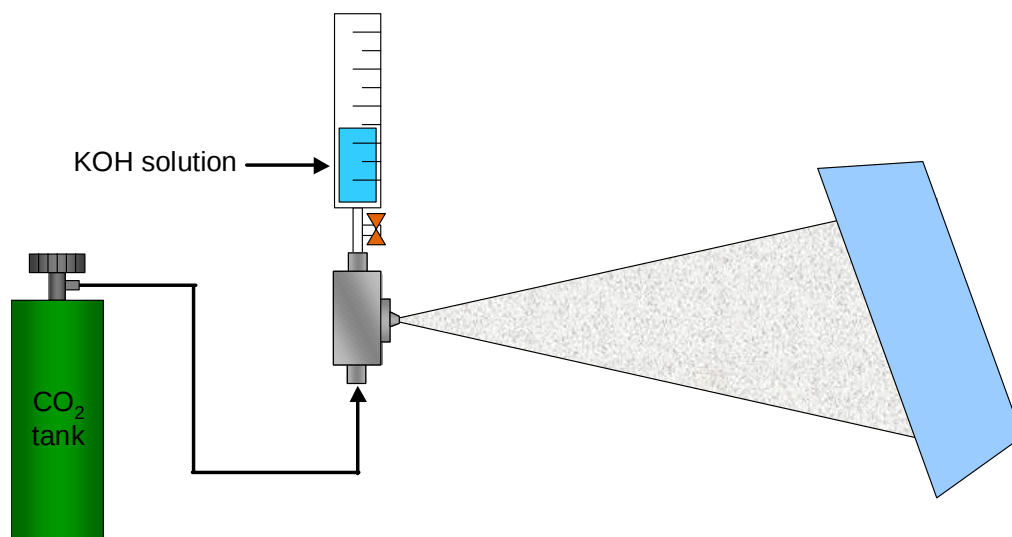


Figure 3. Schematic of Continuous KHCO_3 Production System I.

6.2. System II

The second generation system used to produce modified KHCO_3 is shown in Figure 4. In this system, a syringe pump (ISCO, Model LC-5000) was used to deliver a solution of KHCO_3 + additive to the nozzle at a constant flowrate. The CO_2 gas was heated before entering the nozzle by flowing the gas through heating coils (1/8" O.D. x 0.035" wall thickness Stainless Steel tubing) placed in a bath of boiling water. A metal tube (1" O.D. x 6" length) was attached to the nozzle to act as a drying chamber for the ejected spray. Both the nozzle body and connecting tubings were heated using a flexible (silicone rubber extruded) heating tape (Thermolyne, No. BS0051 080) rated for 120V and 209 W. To promote a drying environment after the tube, a metal plate was placed near the exit of the nozzle and was heated using a jacket heater.

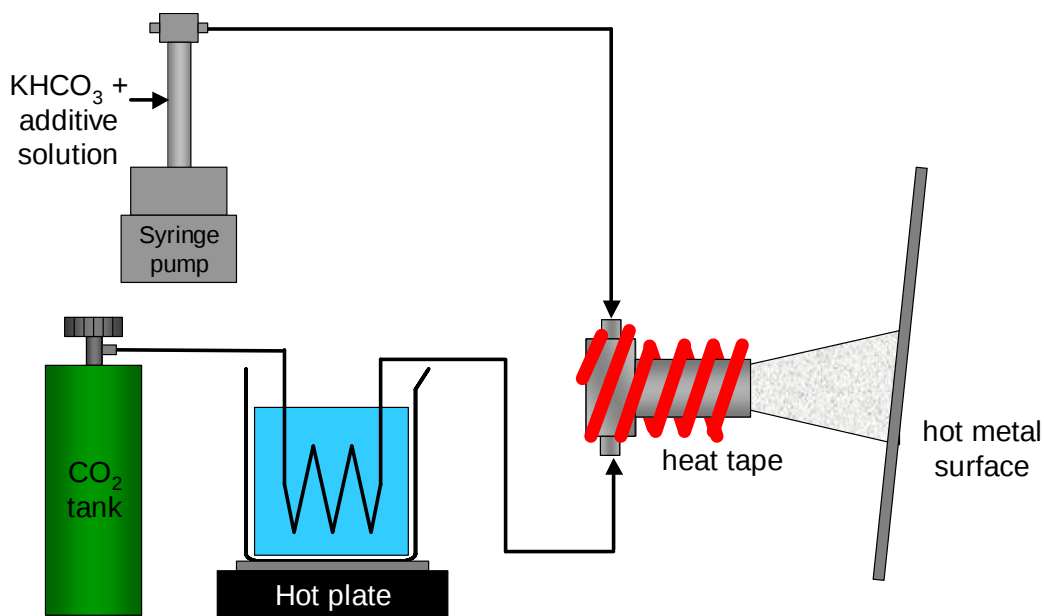


Figure 4. Schematic of Continuous KHCO_3 Production System II.

6.3. System III

The third generation bench-top test system is shown in Figure 5. To create an oven-like environment, the metal tube in system II was removed and replaced with a longer (12"), larger diameter (2.5") glass tube. The glass tube was heated by the flexible heating tape wrapped outside the glass tube. The tube was pitched at a slightly upwards angle, so that dried particles could collect on the glass surface while allowing the hot CO_2 and evaporated H_2O gases to leave the chamber.

6.4. System IV

The fourth and final generation system used in this study is shown in Figure 6. In this setup, the nozzle/glass tube arrangement used in system III was reconfigured so that the nozzle points downward. The glass tube was placed directly on top of a plastic

weighing boat. In addition to providing a simple method for particle collection, the closed end provided by the weigh boat helped to create a hot ($>100^{\circ}\text{C}$) environment inside of the glass tube.

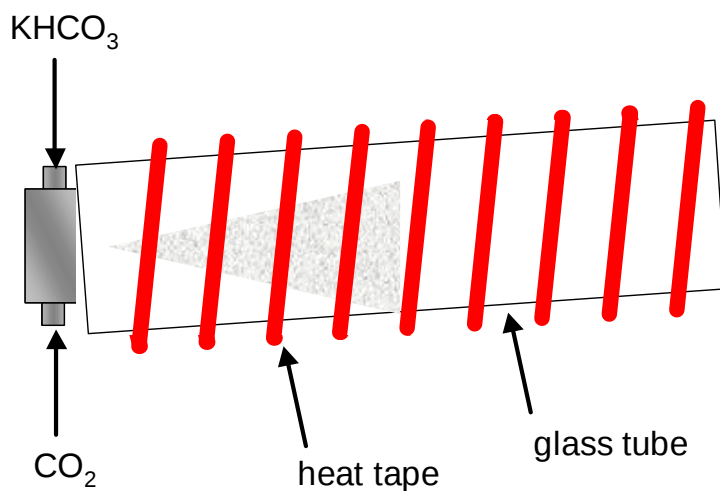


Figure 5. Schematic of Continuous KHCO_3 Production System III.



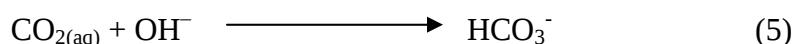
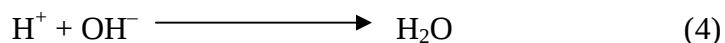
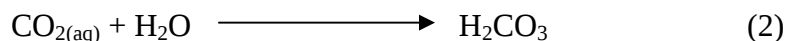
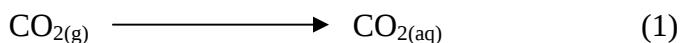
Figure 6. Schematic of Continuous KHCO_3 Production System IV.

7. Results and Discussion

7.1. KHCO₃ Synthesis via CO₂ and KOH System I

The synthesis of KHCO₃ from CO₂ and KOH was attempted using System I. A 50 wt% aqueous KOH solution was used as the feed KOH solution. This solution was atomized via the nozzle using CO₂ at delivery pressures between 5 and 20 psi. Tests using this setup consistently produced a fine atomized mist, which ended up as liquid drops collected on the plastic tray. It appeared that there was not sufficient heat nor time to evaporate the water to form salt particles. However, the pH of the collected liquid was 14, suggesting that the driving force (k_{OH}) for the reaction between CO₂ and OH⁻ was high, according to the data shown in Table 1. Therefore, efforts should be made to improve either the extent of contact between the gaseous and liquid reactants or the extent of water removal.

The kinetics described in Section 3 is a simplified treatment of the CO₂ and KOH reaction. Since the formation of KHCO₃ from CO₂ and KOH is a gas-liquid reaction, the synthesis process in an aqueous environment is likely to proceed through the mechanistic steps as summarized in equations 1-5.



Considering a solution of KOH, the first step for production of KHCO₃ is the dissolution of gaseous CO₂, as shown in equation 1. The HCO₃⁻ species may then be formed in one of two pathways. In the first pathway (steps 2 – 4), the dissolved CO₂ reacts with H₂O to give carbonic acid, H₂CO₃, as shown in equation 2. The H₂CO₃ then dissociates in step 3 to form H⁺ and HCO₃⁻. The liberated H⁺ then reacts to neutralize the KOH-provided OH⁻ ions, forming water in step 4. As the OH⁻ is neutralized, the pH decreases and HCO₃⁻ becomes the dominant carbonate species. In the second pathway (step 5), the dissolved CO₂ reacts directly with the OH⁻ to yield the HCO₃⁻ anion. At pH>10, the second pathway is much faster than the first pathway, as indicated in Table 1.

To form micron-sized KHCO₃ particles from atomized liquid drops using a 50% KOH solution (pH = 14) as in System I, the two step reaction sequence represented by equations 1 and 5 must take place inside the drop. Additionally, the H₂O in the drop must be evaporated. The short (<1 sec) time that the atomized drops are in contact with the CO₂ gas, coupled with the complexity of the steps which must occur in that short

time, suggests that KHCO_3 particle formation from CO_2 and KOH may be very difficult to achieve using system I.

7.2. Process Simplification

To address the project objectives despite the inability of system I to achieve KHCO_3 synthesis, a simplified approach was adopted. Rather than trying to form KHCO_3 in the system from a KOH + additive solution, a solution of KHCO_3 + additive was used instead as the feed solution. Making this substitution simplified the process from one that focused on both reaction and evaporation, to one that focused exclusively on evaporation. Thus, all later generation systems were designed to produce micron-sized modified- KHCO_3 particles via the drying of an atomized spray of aqueous modified- KHCO_3 drops.

7.3. KHCO_3 Particles using System II

System II was used designed to produce micron-sized modified KHCO_3 particles. Before attempting the formation of modified KHCO_3 , KHCO_3 without any additive was used as the feed to assess the ability of the system to achieve solid particles. The syringe pump was used to deliver a 23% by mass KHCO_3 solution to the nozzle. The solution was atomized with preheated CO_2 gas, as shown in figure 3, set to a delivery pressure of 10 psi. KHCO_3 solution flowrates of 15 mL/hr and higher resulted in condensation of the atomized spray on the hot metal surface. However, reducing the flowrate to 1.5 mL/hr led to the accumulation of solid KHCO_3 on the surface of the metal plate, with no condensation. The solid that accumulated on the surface was not a powder, but rather a firmly-adhered solid that could only be removed from the surface by scraping the solid with a spatula. The formation of surface-adhered solid rather than particles suggests that the atomized drops may not have been fully dry when hitting the surface. Rather, a fraction, if not all, of the water in the atomized drops had been evaporated after the drop had reached the hot metal surface. Moreover, the temperature just outside of the heat tape-wrapped metal tube was 77°C , which is likely too low to evaporate the H_2O from the droplets in the short amount of time they spend between the nozzle and the metal plate. To make conditions more favorable for evaporation, the system was redesigned to achieve higher temperatures in the path of the atomized spray.

7.4. KHCO_3 Particles using System III

Formation of KHCO_3 particles from atomized KHCO_3 solution was attempted using System III. In this system, the temperature inside of the glass tube was 90°C , and was not affected by the presence of flowing CO_2 . Additionally, the residence time of the atomized drops in the heated zone was roughly 5 times that of System II, due to the increase in length of the heated area. The syringe pump was again used to deliver the KHCO_3 (50% by mass) solution at a flowrate of 1.5 mL/hr, and the CO_2 delivery pressure was set to 8 psi. These conditions led to the formation of solid KHCO_3 on the surface of the glass tube. However, as with System II, the solid did not form as a free-flowing powder, but instead adhered to the glass tube and had to be scraped off. Despite the

increased temperature and increased residence time, particle drying was not sufficiently achieved using System III. To further promote particle drying, and to provide a surface for solid collection that was not directly heated by heat tape, the system was again modified.

7.5 KHCO₃ Particles using System IV

System IV was used to attempt the formation of solid KHCO₃ particles from the 50% KHCO₃ solution. Figure 7 shows the temperature profile observed inside of the glass tube, which was measured in the center of the tube without any fluid flowing through the nozzle. The temperatures achieved in this system were greater than 100°C for most of the ejected spray path.

To verify the drying capability of this system and determine an optimum KHCO_{3(aq)} flowrate for particle formation, a test was performed using only H₂O in the feed solution. With the CO₂ delivery pressure set to 10 psi, the H₂O flowrate was varied between 1.5 and 150 mL/hr. Insufficient drying capability was indicated by the appearance of liquid drops on the glass tube surface and by the appearance of wetness on a piece of paper towel placed underneath the glass tube. Using this test, the optimum liquid flowrate into the nozzle was determined to be 4 mL/hr.

The system was then used to attempt particle formation from a 50% by mass KCHO₃ solution. At 4 mL/hr, solid formation was observed both on the glass tube surface and on the weigh boat. After 2.5 hours at 4 mL/hr, a solid coating had formed on both the weigh boat and the glass tube (Figure 8), with a thicker coating being obtained on the glass tube and closer to the nozzle. In contrast to the previous system runs, the solid coating on the weigh boat did not have to be scraped off, but was rather easily removed using forceps. This behavior suggests that the atomized drops produced by the nozzle were dried in the heated glass tube, forming solid particles that were collected on the surface of the weigh boat.

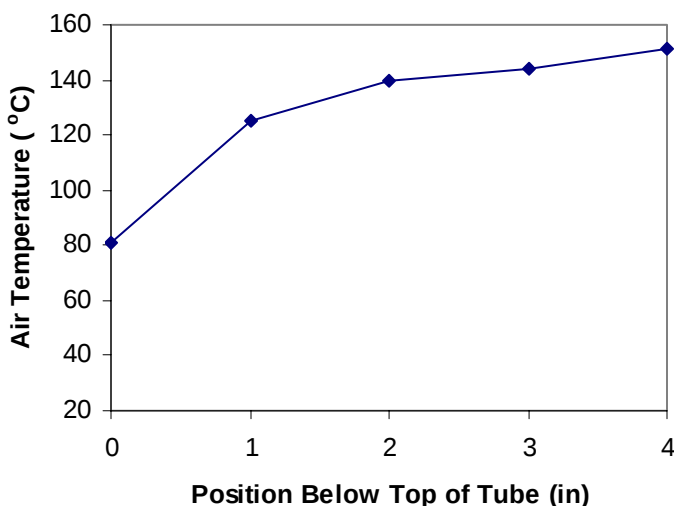


Figure 7. Temperature Profile within Heated Glass Tube.

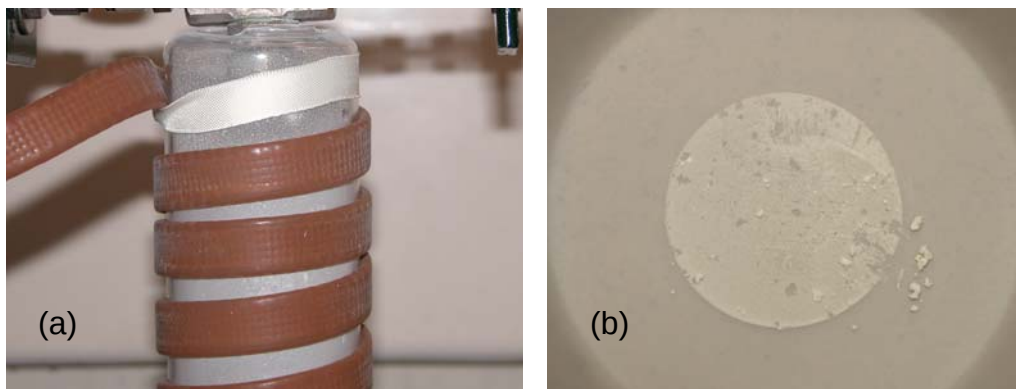


Figure 8. (a). Solid Formation on the Inner Surface of Glass Tube. ($\text{KHCO}_{3(\text{aq})}$ flowrate = 4 mL/hr for 2.5 hours). **(b). Solid Formation on Weigh Boat.**

7.6 Formation of Modified KHCO_3 Particles using System IV

Having demonstrated successful drying of $\text{KHCO}_{3(\text{aq})}$ droplets, modified KHCO_3 particles were next synthesized. Two modified KHCO_3 batches were prepared using System IV, one with 3000 ppm $\text{K}_4\text{Fe}(\text{CN})_6$ and the other with 1000 ppm $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4$. Images taken using a microscope (Nikon Labophot-2) were used to determine particle size of the modified and unmodified KHCO_3 . As shown in Figure 9 shows, the largest particle diameters from the three batches were on the order of $10\ \mu\text{m}$. Hence, modified KHCO_3 particles can be produced in the desired size using System IV.

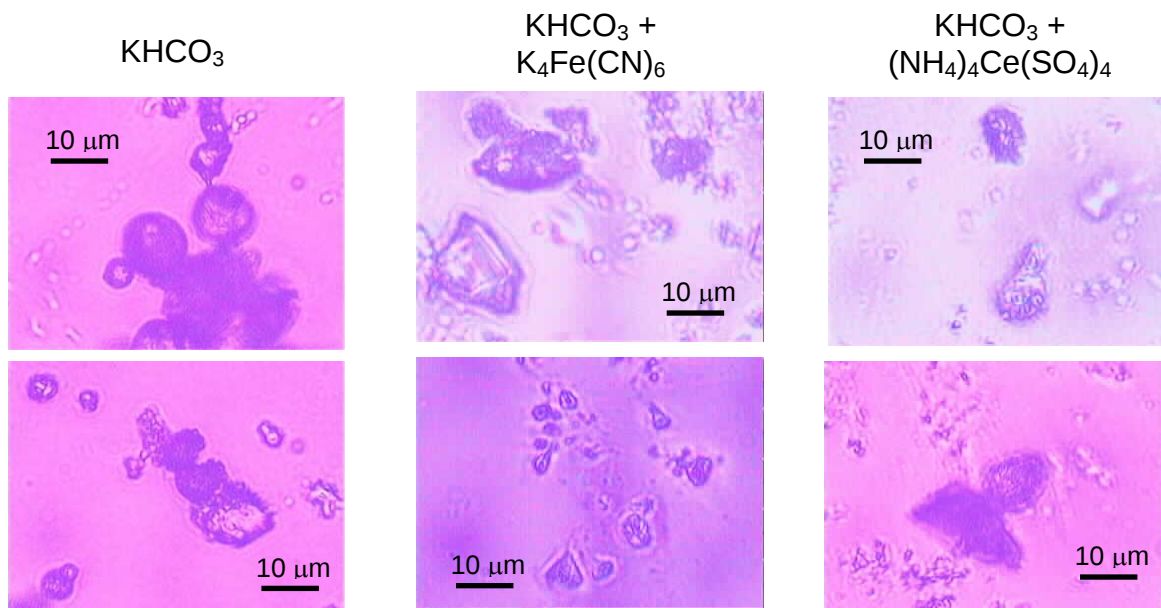


Figure 9. Microscopic Images of Collected Particles (100X Magnifications).

7.7 Adapted Anti-Caking Test I

Because only a few grams of modified KHCO_3 could be produced using System IV in a reasonable amount of time (about 24 hours), the 300 g sample test described by Phoenix (1966) was modified to be performed on a smaller scale. The first adapted anti-caking test is demonstrated in Figure 10. In this test, about 400 mg of sample are weighed measured and placed inside of an 11-mm GC vial cap with septum. H_2O is next added dropwise using a syringe, taking care to evenly distribute the H_2O over the sample. This amount of H_2O that would be added according to the H_2O :salt sample ratio used by Phoenix would be 12 μL ; however, this small amount cannot be easily or completely distributed through the salt sample. Instead, 50 μL of H_2O were used, which could be distributed more evenly through the sample. After adding the H_2O , the sample was mixed using the needle of the 100 mL syringe used to add the H_2O . Although a fair distribution of the H_2O through the solid sample could be achieved using this technique, the mixing step led to the clumping of small wet particles. The presence of these clumps demonstrates the difficulty posed in attempting to distribute the H_2O perfectly throughout the sample. The moist sample was then formed into a small cake by placing an 11-mm GC septum on top of the sample, and compressing the sample. The resulting cake was then removed from the GC vial cap by poking a syringe tip (with needle removed) into the septum on the opposite side of the cake. The molded cake was then placed in an oven at 80°C for 2 hours, and subjected to the drop test.

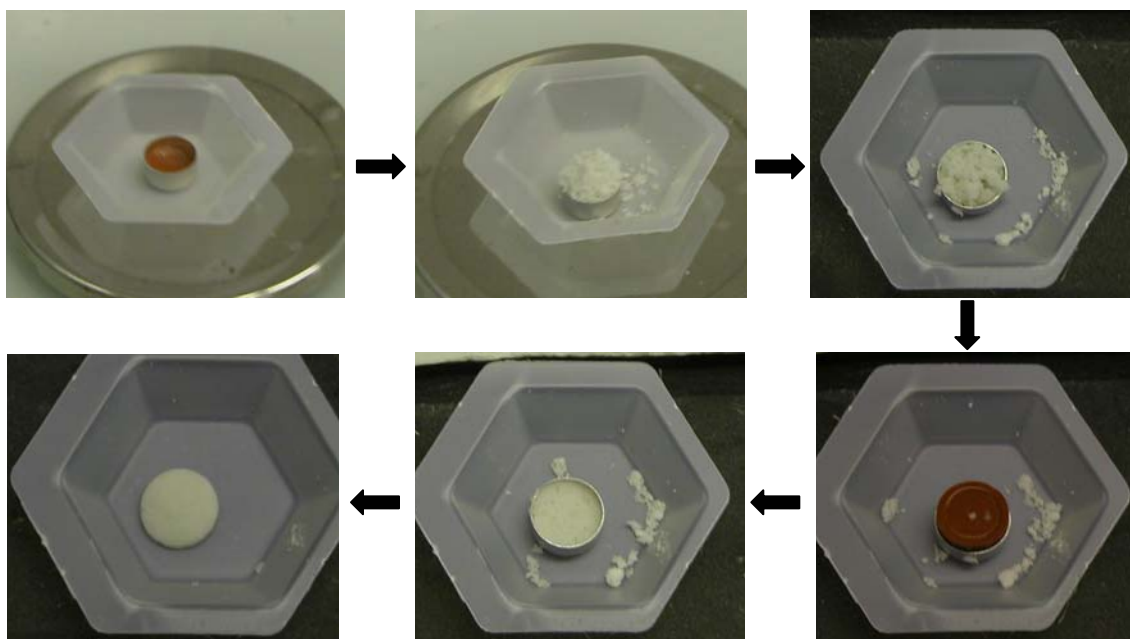


Figure 10. Cake-Forming Sequence for Adapted Anti-Caking Test I.

7.8 Anti-Caking Effectiveness of $K_4Fe(CN)_6$ and $(NH_4)_4Ce(SO_4)_4$ based on Test I

Each of the three batches was subjected to the Adapted Anti-Caking Test I. Results of the drop test, conducted from 18" and with 2 cakes from each batch, are shown in Figure 11 where each photo represents a different sample. For the $KHCO_3$ batch, each cake displayed some minor breakage. For both modified $KHCO_3$ batches, however, each of the cakes exhibited very little breakage. Based on these observations, it would seem as if the additives actually enhanced the caking tendency of the samples. However, further inspection of the sample cakes made after conducting the tests revealed that the cakes were not thoroughly dry, as shown in Figure 12. The presence of moisture in the cakes likely played a role in keeping the cakes from breaking.

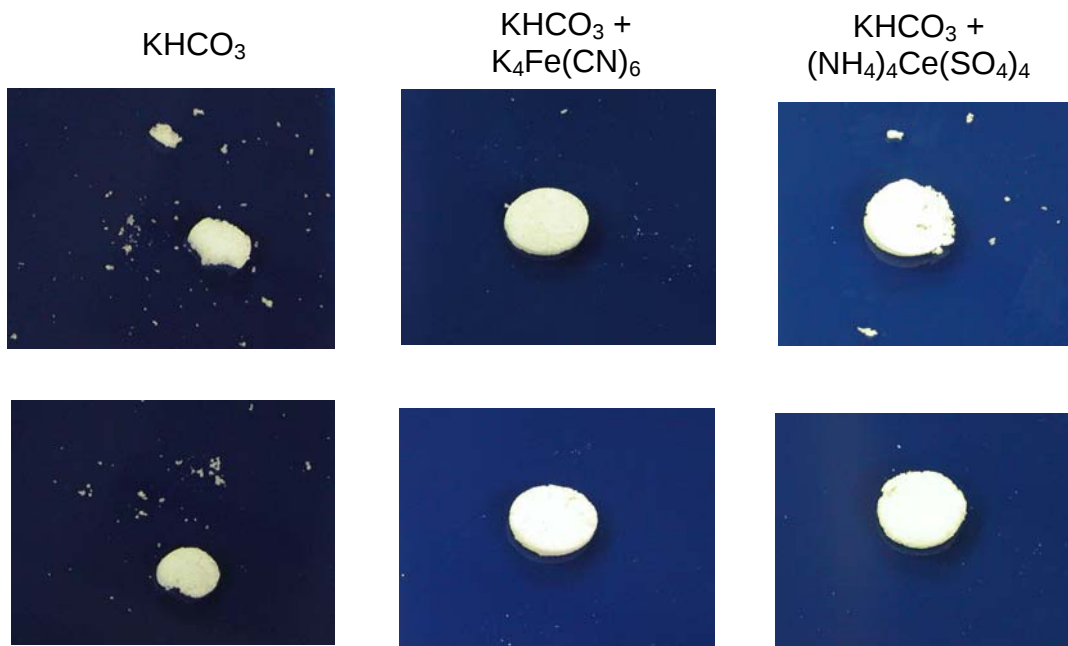


Figure 11. Adapted Anti-Cake Test I Results for the $KHCO_3$, $KHCO_3 + 3000$ ppm $K_4Fe(CN)_6$, and $KHCO_3 + 1000$ ppm $(NH_4)_4Ce(SO_4)_4$ Cakes.

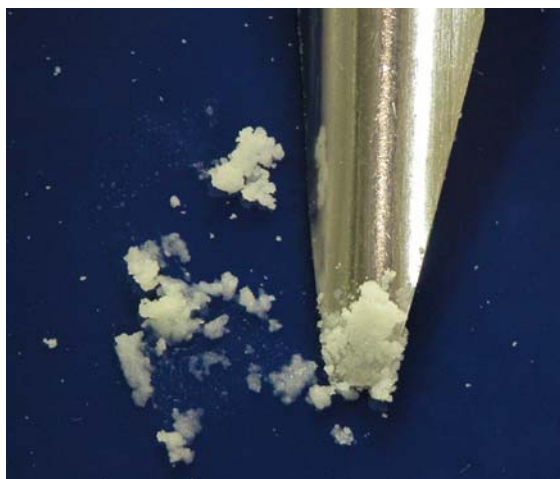


Figure 12. $KHCO_3 + 1000$ ppm $(NH_4)_4Ce(SO_4)_4$ Cake Revealing Moisture

7.9 Adapted Anti-Caking Test II

The anti-caking test was redesigned to more closely mimic what was performed by Phoenix (1966). However, the literature method called for 300 grams of salt for each cake. To choose the scale of operation more appropriate to the bench-top tests in this study, a decision was made to use 30 grams of salt, with all other key parameters scaled down accordingly, as shown in Table 2.

Table 2. Comparison of Key Parameters for Preparing Salt Cakes with Additives

Method	Salt Weight (g)	Additive Solution Concentration (g/ml)	Additive Solution Used (ml)	Drying Time	Drying Temperature (°C)
Literature	300	0.0333	9	4 days	unspecified
This Study	30	0.0333	1	16 hours	60

The following procedures were used to prepare the salt cakes containing anti-caking additives to be tested.

Spray Solution Preparation

1. Add 1.2 g of each additive and 36 ml DDI water to make a solution;
2. Store the solution in a perfume spray bottle (about 40-ml capacity); and
3. Calibration tests were conducted to correlate the amount of solution sprayed with the number of compressions (1 ml of solution was sprayed out of the bottle with six full compressions).
4. A total of six additive solutions were prepared according to the formula given in Table 2. These additives were
Potassium Chloride - KCl
Potassium Bromide - KBr
Ammonium Chloride - NH_4Cl
Potassium Fluoride - KF
Ammonium Cerium Sulfate - $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4$
Potassium Ferrate Cyanide Tri-Hydrate - $\text{K}_4\text{Fe}(\text{CN})_6$

Cake Formation Procedure

1. Weigh 30g of potassium bicarbonate (KHCO_3), which was first ground to a fine powder using a mortar and pestle;
2. cut a piece of black plastic garbage bag into a 12" x 12" sheet and lay flat on the working bench;
3. add 30 g of KHCO_3 onto the black plastic sheet and smooth out the sample evenly
4. grab the back two corners of the plastic sheet and form a cone at the rear of the sheet;
5. spray the top surface of the sample with 6 compressions;
6. pour saturated sample octagonal weigh boat (3" approximate rim diameter);

7. smooth the sample out by lightly scrapping a stainless steel spatula across the surface;
8. place the sample in the oven (preheat at 60 degrees Celsius) for 16 hours; and
9. cakes prepared according to this procedure were labeled as

Sample #1: 30 g of KHCO_3 + 1 ml of water without additive (Baseline)
 Sample #2: 30 g KHCO_3 + 0.0333 g of Potassium Chloride KCl in 1 ml of water
 Sample #3: 30 g KHCO_3 + 0.0333 g of Potassium Bromide KBr in 1 ml of water
 Sample #4: 30 g KHCO_3 + 0.0333 g of Ammonium Chloride NH_4Cl in 1 ml of water
 Sample #5: 30 g KHCO_3 + 0.0333 g of Potassium Fluoride KF in 1 ml of water
 Sample #6: 30 g KHCO_3 + 0.0333 g of Ammonium Cerium Sulfate $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4$ in 1 ml of water
 Sample #7: 30 g KHCO_3 + 0.0333 g of Potassium Ferrate Cyanide Tri-Hydrate $\text{K}_4\text{Fe}(\text{CN})_6$ in 1 ml of water

Drop Test Procedure

1. A cardboard containment frame (18" long x 12" wide x 4" tall) was placed on the working bench top to prevent over scattering of the cakes;
2. a ruler was used to indicate the height of 18";
3. each cake was hand held at the 18" mark and released from the flat position with respective to the bench surface directly above the cardboard containment frame.

7.10. Anti-Caking Effectiveness of Selected Additives Based on Test II

The results of the drop tests for the cakes formed using the second cake-forming method are shown in Figure 13. In this test, there appears to be little difference between the fragmentation observed for the pure KHCO_3 cake and that of the modified cakes. In fact, the size of the fragmented pieces appears to be slightly larger in the modified cakes when compared to the pure KHCO_3 cake. This may indicate again that the additives actually increased the tendency for caking to occur; however, Figure 13 provides no substantial evidence to suggest an effect of $\text{K}_4\text{Fe}(\text{CN})_6$ or $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4$ on the caking properties of KHCO_3 . Thus, further testing is necessary to accurately determine the effect, or lack thereof, of $\text{K}_4\text{Fe}(\text{CN})_6$ and $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4$ on the caking tendency of KHCO_3 .

This set of drop tests yielded noticeable and repeatable difference between different cakes. The differences covered both positive and negative effects on crystal growth as compared to the base line cake (Figure 13). All cakes containing the simple potassium salt additives (KCl, KBr, and KF) appeared to have enhanced the extent of caking, as shown in Figures 14, 15, and 16, respectively. The rest of the cakes containing NH_4Cl , $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4$, and $\text{K}_4\text{Fe}(\text{CN})_6$ appeared to have weakened inter-crystalline bridges between the salt particles as compared to the baseline cake, as shown in Figures 17, 18, and 19, respectively.

Table 3. Summary of Drop Test Results Based on Test II

Additive	Breakage	General Observation
Water only (Baseline)	Fair	Some pieces of the broken cake are larger than a ¼ of the full cake size
KCl	Poor	Poor breakage. Sample appears to be amplifying the baseline's crystal growth
KBr	Fair	Fair breakage. Sample appears to be identical in structure to the baseline
NH ₄ Cl	Good	Good breakage. Sample appears to break apart much easier than the baseline
KF	Fair	Fair breakage. Sample appears to be identical in structure to the baseline
(NH ₄) ₄ Ce(SO ₄) ₄	Good	Good breakage. Sample appears to break apart much easier than the baseline
K ₄ Fe(CN) ₆	Good	Good breakage. Sample appears to have some particles smaller than the baseline

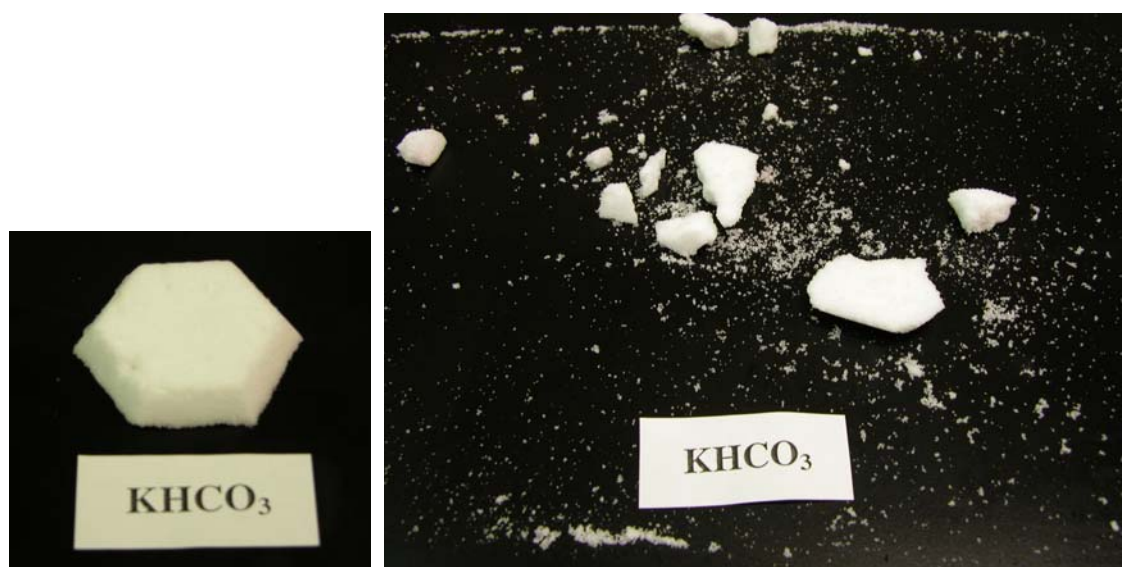


Figure 13. Adapted Anti-Cake Test II Results for the KHCO₃(Baseline)



Figure 14. Adapted Anti-Cake Test II Results for the $\text{KHCO}_3 + \text{KCl}$ as Additive



Figure 15. Adapted Anti-Cake Test II Results for the $\text{KHCO}_3 + \text{KBr}$ as Additive

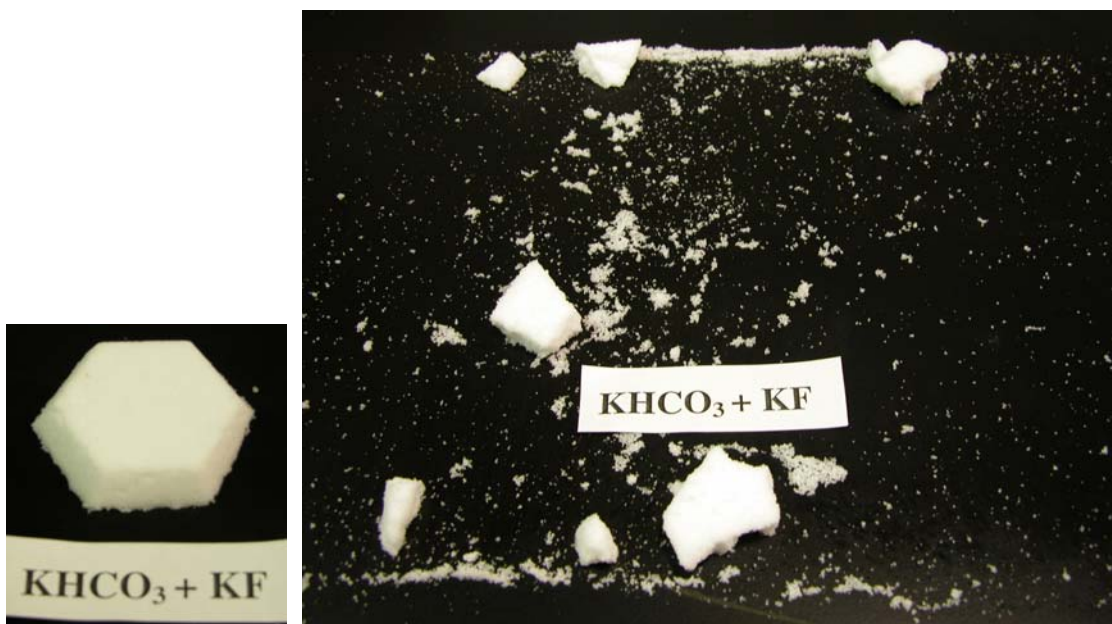


Figure 16. Adapted Anti-Cake Test II Results for the $\text{KHCO}_3 + \text{KF}$ as Additive

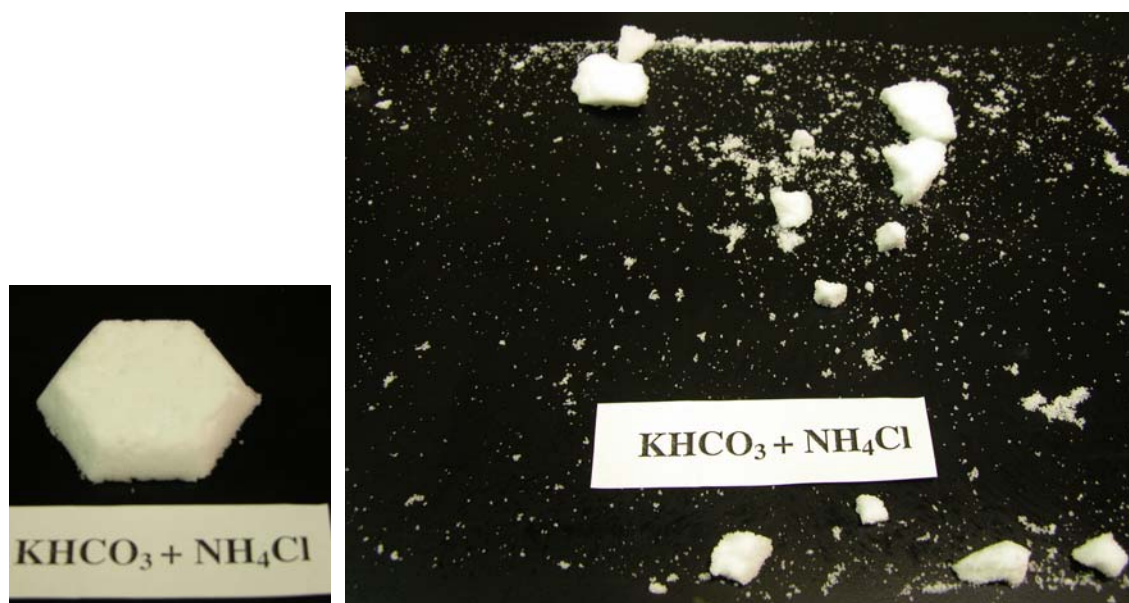


Figure 17. Adapted Anti-Cake Test II Results for the $\text{KHCO}_3 + \text{NH}_4\text{Cl}$ as Additive

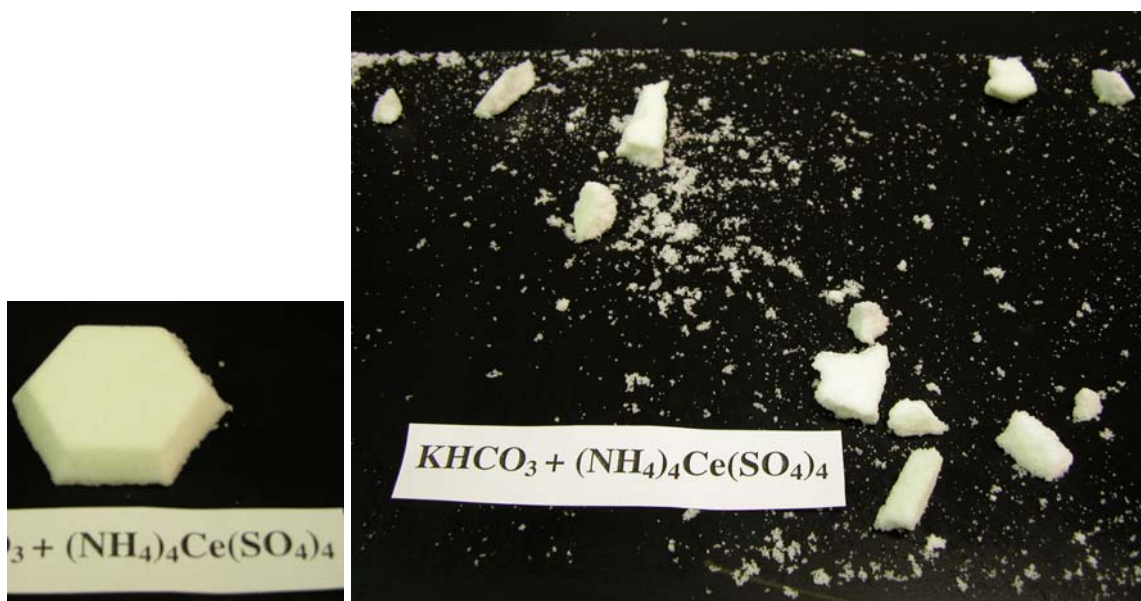


Figure 18. Adapted Anti-Cake Test II Results for the $\text{KHCO}_3 + (\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4$ as Additive

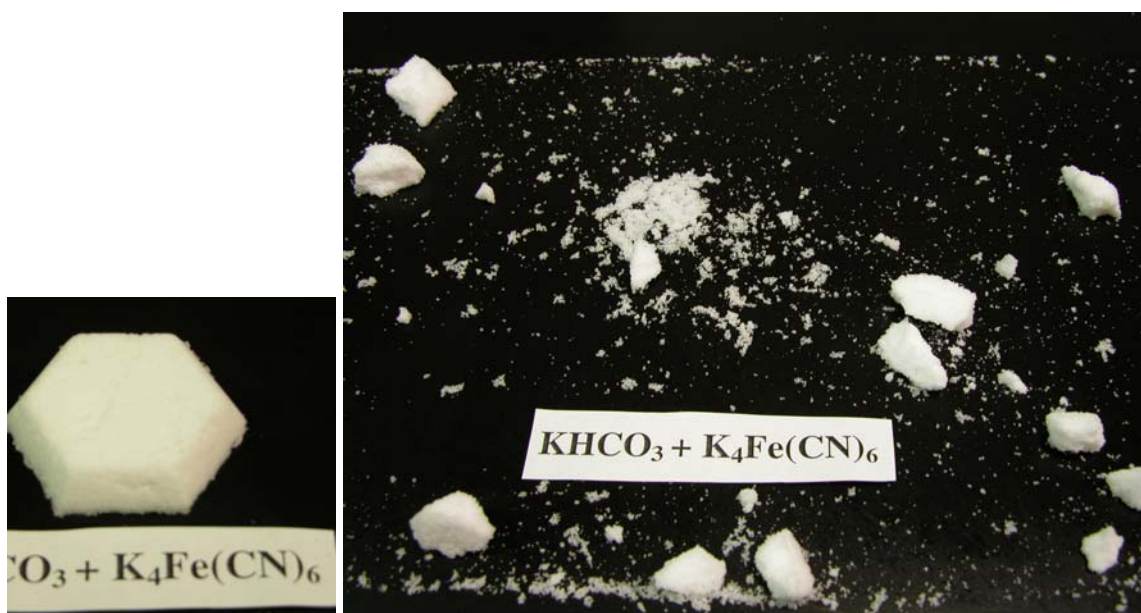


Figure 19. Adapted Anti-Cake Test II Results for the $\text{KHCO}_3 + \text{K}_4\text{Fe}(\text{CN})_6$ as Additive

8. Summary, Conclusions and Recommendations

8.1 Summary and Conclusions

An experimental investigation was conducted to study the ability of crystal habit modifiers to reduce or prevent the tendency for purple K to cake when exposed to humid air. Potassium bicarbonate, KHCO_3 was used as a model compound to represent purple K, which consists of more than 99% KHCO_3 . The first portion of the study examined the potential for modified KHCO_3 particles to be produced at the desired size of roughly 10 μm . KHCO_3 synthesis was attempted by contacting gaseous CO_2 with 50 wt% aqueous KOH solution via an atomizer as assembled in System I, which involved the simplest process configuration to validate the original conceptual design. Tests conducted using System I did not produce KHCO_3 particles. This lack of reaction was likely due to the inability for the multiple mass transfer and reactions steps to occur in the short amount of time that the atomized drops were exposed to the CO_2 before impinging on the plastic collection device.

To simplify the approach to achieving micron-size KHCO_3 particles, KHCO_3 was used in place of KOH as the feed solution. With this approach, the only step required in the atomized spray was the evaporation of H_2O from the atomized drops to form KHCO_3 particles. Systems II, III, and IV were designed to produce KHCO_3 particles using this technique. System II was unable to achieve sufficient H_2O evaporation due to inadequate heating, and no solid formed from the atomized spray. System III achieved solid formation, but the KHCO_3 that formed had accumulated on the glass tube surface, and was not a free-flowing powder. This adhesion of solid to the glass surface suggested that most of the H_2O evaporation from the atomized droplets had taken place after the droplets had reached the surface, and not while they were in the air. System IV was then designed to improve drying conditions at higher temperatures. Using System IV, micron-sized KHCO_3 particles were successfully produced from the aqueous KHCO_3 solution.

Having found a successful method for producing micron-sized KHCO_3 particles, modified KHCO_3 was next produced using System IV. Modified KHCO_3 was obtained by adding the desired crystal habit modifier to the feed KHCO_3 solution. Potassium ferrocyanide and ammonium cerium (IV) sulfate were used as crystal habit modifiers and formulated into the KHCO_3 particles at 3000 ppm and 1000 ppm, respectively.

To demonstrate the effects of the added crystal habit modifiers, an anti-caking test was performed on each sample. Based on the method described by Phoenix (1966), each sample (about 400 mg) was formed into a small moist cake and dried in an oven. The dried cakes were then each dropped from a height of 18 inches. Fracture patterns for the pure KHCO_3 cake and modified KHCO_3 cakes were similar. Further inspection revealed that the cakes were not sufficiently dry prior to the drop test, and the center of each cake was still moist. Thus, this initial test was inconclusive concerning the effect of the crystal habit modifiers on KHCO_3 caking tendency.

A second cake test was performed using larger amounts of KHCO_3 (30 g). Noticeable and repeatable fragmentations were observed in the modified KHCO_3 cakes as compared to the pure KHCO_3 cake. The cakes containing NH_4Cl , $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4$, and $\text{K}_4\text{Fe}(\text{CN})_6$ displayed visually improved scattering by dropping from a height of 18 inches, suggesting these additives may have weakened inter-crystalline bridges between the salt particles as compared to the baseline cake.

8.2 Recommendations

The results of this investigation can be used to suggest additional testing to elucidate the potential for crystal habit modifiers to reduce or prevent purple K caking, and to suggest alternative methods for preparing micron-sized modified KHCO_3 particles.

- The cake formation method should be redesigned to reflect the cake-forming process that occurs under the field conditions when purple K has been exposed to humid air. The inability of the crystal habit modifiers used in this study to prevent caking may be due to the technique used to form the cake, in which the water added was mixed throughout the KHCO_3 sample, and the resulting wet mixture compressed to form a cake. The manual force applied to compress the cake may have been too great, such that a similarly formed, well-packed cake was produced from each of the modified and non-modified samples. Another possibility is that the high oven temperatures and associated high rate of evaporation led to strong caking in each sample.
- Dependence of the additive concentration on the anti-caking effectiveness should be evaluated to optimize the formulation.
- Additives other than those reported by Phoenix (1966) and combinations of selected additives should be explored for anti-caking of KHCO_3 .
- The drying technique used in System IV can be improved to achieve micron particles more consistently and with less of the feed KCHO_3 lost to impinging on the glass tube surface. To address these issues, a larger diameter glass tube should be used in place of the 2.5" tube that was used in Systems III and IV. A sufficiently large tube (larger than the diameter of the atomized spray) would prevent the atomized droplets from contacting the glass tube, and hence no KHCO_3 would accumulate on the glass tube. Additionally, increasing the distance between the nozzle and the particle collection weigh boat would further promote particle formation by increasing the amount of time available for the atomized droplet to dry.

9. References

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