

Rapid De-Carbonation in Canned Carbonated Soft Drink Beverages

by

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ABSTRACT OF THESIS

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Carbonated beverages are engineered to contain a defined quantity range of CO₂ dissolved into the product to optimize consumer preference. Carbonation level is an integral component of carbonated soft drink beverages that significantly contributes to positive sensory attributes of sodas; the mouthfeel and taste that the consumer expects. Rapid de-carbonation is a phenomenon in which the carbonation level of a canned carbonated soft drink beverage rapidly decreases to unacceptable levels, determined by consumer best taste limits, in less than 10 minutes of opening the can. Rapid de-carbonation leads to a range of negative experiences for the consumer. This phenomenon is classified into three types of rapid de-carbonation: gushing, foaming, and active.

The objective of this thesis is to investigate factors that contribute to rapid de-carbonation through exploring the interactions between internal can coating morphology, beverage chemistry, and physical characteristics contributed by filling and processing

conditions. Each of these factors has been studied separately in the past by the beverage, can, and coating industry. The factors were studied simultaneously to evaluate the effect on the rapid de-carbonation phenomena as well as the interaction between each factor. Specific levels, or conditions, of each factor were identified as a stress factor: high initial carbonation level, high water mineral content level, and a specific coating morphology. The results show that while each separate factor increased the rate of de-carbonation; however, when the stress factors were combined the effect was not only additive but synergistic. The carbonation loss increased by more than 1.5x when compared to a system that had lowest amount of engineered stress factors.

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“The harder the conflict, the more glorious the triumph. What we obtain too cheap, we esteem too lightly; it is dearness only that gives everything its value. I love the man that can smile in trouble, that can gather strength from distress and grow brave by reflection.”

-Thomas Paine

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1. INTRODUCTION

Carbonation is an integral component of carbonated soft drink beverages that significantly contributes to an optimal consumer experience. Carbonated beverages are engineered to contain a set range of CO₂ gas dissolved into the product to elicit enhanced sensory attributes. Rapid de-carbonation is a phenomenon in which the carbonation level of a canned carbonated soft drink beverage will rapidly decrease to unacceptable levels in less than 10 minutes of depressurizing the can. Rapid de-carbonation leads to a range of negative experiences for the consumer, from unbalanced flavors and unexpected mouth feel to explosive foams.

The rapid de-carbonation phenomenon is classified into three types: gushing, foaming, and active. Gushing is characterized when foam pours out of the can within less than ten seconds of opening and a significant amount of carbonation is lost in less than 10 minutes. Foaming is characterized by foam emerging from the opening of the can within 5 minutes of opening, resulting in a significant loss of carbonation. Active rapid de-carbonation involves no foam but a significant loss of carbonation within 10 minutes of opening the can.

The root cause for rapid de-carbonation remains elusive throughout the industry. Investigations into the root cause of rapid de-carbonation looking at single contributing factors have been explored; however, the effect of the interactions has not been studied. This thesis investigates the root cause of rapid de-carbonation through exploring the interactions between internal can coating morphology, beverage chemistry, and physical characteristics contributed by filling and processing conditions. Although these theories have been studied

in other applications, this study is the first time these factors have been tested together to study rapid de-carbonation in canned soft drink beverages.

The internal can coating morphology contributes to the rapid de-carbonation phenomenon by providing nucleation sites. There are two main types of nucleation: homogeneous and heterogeneous. Homogeneous nucleation involves one phase while heterogeneous nucleation involves two or more phases. Heterogeneous nucleation is characterized by the catalysis that results in the formation of gas bubbles when a supersaturated solution comes in contact with another material. This thesis focuses on heterogeneous nucleation as it is most applicable to canned carbonated beverage system. The gas cavity must be of a specific geometry and radius for the solution to overcome critical energy barriers. When the can is opened, the pressure suddenly decreases within the system causing the liquid to become out of equilibrium. The sudden reduction in pressure catalyzes the reaction by altering the thermodynamic balance of the solution, or beverage, where bubbles generated by this sudden change create pits or defects in the internal can surface that was apparently, previously smooth (*1*). Once pressure equilibrium is again reached, bubble formation will cease.

Several theories are used to explain nucleation. Classical nucleation theory is the most widely known theory regarding nucleation. However, this theory assumes that the macroscopic features of the system are equivalent to those on the microscopic level. Microscopic features such as varying surface geometry, line tension, and surface diffusion are additional characteristics of the internal coating that contribute to this phenomenon that are not captured in classical nucleation (*2, 3*). Non-classical and pseudo-classical nucleation

theories have built on the classical theory to account for these details. The nuances between the different nucleation theories may account for the different types of rapid de-carbonation (gushing, foaming, and active).

Beverage chemistries linked to ingredients also contribute to the different types of rapid de- carbonation. Ingredients can alter the behavior of the beverage including its gas solubility, nucleating, and foaming properties (4). First, ingredients that can lower the surface tension of the liquid, such as aspartame, act as a surfactant which alters the molecular interaction of the beverage reducing the interfacial free energy between the two phases (5). Beverages containing aspartame are more likely to nucleate and form bubbles and foam (4). Second, other ingredients, such as flavors, may stabilize foams depending on what type of oils are used. Different oils have varying properties. Properties, such as whether the oils have been solubilized or emulsified and the stability of the emulsifier itself contribute to the nucleation properties of the beverage (6). Beverages contain many different flavors and oils; therefore, the impact of different beverage formulas affect the stability of foams formed in these beverages. Third, beverage density is affected by ingredients which can alter the behavior of bubbles. The presence of sugars increases the density of the beverage compared to non-sugared beverages. Changes in the beverage density effect the bubbles ability to rise (7).

The different levels of mineral content in the water used to batch, or manufacture, the beverage may also affect the beverage chemistry. Total mineral content of the water used for manufacturing the beverages can vary greatly from one manufacturing plant to another based on incoming municipal water and different water treatment processes used. Typical total

mineral content in filling plants ranges from 13 ppm to 120 ppm. Mineral content from salts can affect the solubility of gases and the stabilization of bubble coalescence. Bubble coalescence is the aggregation of smaller bubbles to form a larger bubble. Salts affect the coalescence of bubbles by altering the hydrogen bonding and thus inhibiting liquid film drainage and coalescence of the bubbles (8). Liquid film drainage occurs when the skin of two bubbles thin, enabling the bubbles to join, or coalesce. Certain salts such as NaCl, MgCl_2 and CaCl_2 inhibit coalescence, while other salts such as NaClO_3 do not. Additionally, the effect of different salts may vary based on the amount of salt in the solution. Coalescence may alter different attributes of the beverage including the size of the bubbles released, the rate at which they are released, formation of foams and ultimately the amount of gas loss from the beverage.

Each carbonated beverage formula has a specific targeted range of gas carbonation level to obtain an optimal consumer experience. On commercial filling lines, CO_2 is introduced into the beverage inline, prior to filling the beverage into the package. In carbonated soft drink beverages, other carbonated species should not coexist with the dissolved CO_2 due to the low pH (7). At low pH levels, conditions are more favorable for weak acids to remain stable due to a lack of proton donating species.

To increase the solubility of CO_2 into the beverage, the temperature is lowered as much as possible during filling. Carbonated soft drink beverages are filled at temperatures slightly above freezing ($\sim 2\text{-}4^\circ\text{C}$) to reach the targeted CO_2 level which is often at saturated conditions. As the level of CO_2 saturation increases, so does the rate of nucleation because mass transfer rates are directly proportionate to concentration. (9)

In this thesis, the interactive effects of surface morphology, beverage chemistry, and CO₂ saturation based on filling conditions on rapid de-carbonation were investigated in three DOEs (design of experiment). In the final set of experiments, the factors that were observed to have the greatest effect were tested using a randomized DOE. The factors included in all these experiments were chosen based on previous experiments and theories from adjacent scientific disciplines. This is the first time that the interactions between all these factors have been tested together to understand rapid de-carbonation in soft drink beverages.

2. LITERATURE REVIEW

The rapid de-carbonation phenomena system is comprised of three main components: the can, beverage, and gases infused into the system. Each of these components has factors that contribute to this phenomenon.

2.1. System

To understand the dynamics of rapid de-carbonation, we must first understand its system. This system is comprised of three contributing components: the can, the liquid beverage and the gas used to carbonate the beverage.

Two-piece cans are primarily used for beverages. The two-piece design allows for less metal to be used and a larger area to print graphics. Most beverage cans manufactured in the United States have an aluminum alloy body. The aluminum alloy is composed of aluminum with manganese and iron inclusions. These inclusions increase the malleability of the aluminum to allow the can to be more easily drawn during the manufacturing process.

The can body is produced by a method called drawn and wall-ironed (D&I). First cups are punched from large aluminum coils by a stamping press. Second the walls of the cup are drawn and ironed by a series of tungsten carbide rings to increase the height and thin the walls. Then the can bodies are trimmed and washed before an external priming lacquer is applied and dried in an oven. Next the cans are decorated with the respective print designs and a coat of varnish is applied to the external can end. The cans enter another oven to dry the print and varnish. Afterward an internal coating is applied to the can and cured in a third oven. The internal coatings are usually an epoxy or acrylic-based coating. Finally, the cans

are necked to reduce the diameter of the opening and prepare the can so a lid can be applied later after filling (10, 11). The cans bodies are usually manufactured in a can facility then shipped in pallets to filling plants.

At the filling plants, the syrup is batched or made by mixing ingredients in large mixing tanks. In certain formulas, ingredients must be mixed in a specific order to prevent undesirable chemical reactions. The syrup is then pumped through lines that incorporate the correct amount of water and CO₂ into the beverage before it is filled into the can at high speeds (1200 cans per minute or greater). The beverage is cooled down to slightly above freezing to increase the solubility of the gas into the liquid. Immediately after the can is filled with the beverage a lid is seamed onto the can to create a hermetic seal by folding and interlocking the can body flange and can end (12).

After the can has been sealed, the system becomes closed. Although energy may transfer in and out of the system, there is no mass transfer and, therefore, no gas enters or leaves this system (13). Within 24 hours after sealing the can, the system equilibrates. However, once the can is opened, the system is no longer closed. The system is no longer in equilibrium because gas is released and causes changes in pressure.

Two basic principles help explain how fluctuations in pressure drive changes within this system: Ideal Gas Law and Le Chatelier's Principle. The Ideal Gas Law ($PV=nRT$) helps us to understand the basic thermodynamic processes in this system. Pressure is directly affected by both temperature and the amount of gas, or CO₂, that is added to the system. As the amount of initial CO₂ is increased, the amount of pressure inside the system also increases. While the can is sealed and the system is closed, the gas is trapped inside the

can. However, once the can is opened, the gas rapidly dissipates due to the large gradient in gas concentration between the beverage and the air. This transfer speed is increased as the temperature increases, based not only on the affected increase in gas volume due to elevated temperatures but also due to the solubility of the gas. As temperature increases, the solubility of CO₂ in the liquid solution diminishes.

Le Chatelier's principle explains that when a system at equilibrium is disturbed, it will adjust itself to compensate for the change and attain equilibrium once again. When the can is opened, the total pressure of the system is changed; it dramatically drops. Gas rushes out changing the volume of gas in the system (de-carbonation) when the pressure drops to regain equilibrium. By increasing the temperature, the energy or enthalpy of the system increases hastening the shift in equilibrium. (14)

2.2. Internal Can Coating and Morphology

The internal coatings in beverage cans are primarily either epoxy or acrylic-based coatings. Cans are coated on the inside to prevent interaction between the aluminum and beverage. Without the protective internal coating, the beverage would corrode through the aluminum in weeks. The coating materials are primarily chosen based on two characteristics: 1) the coating must be compatible with the manufacturing process and 2) provide a sufficient chemical barrier between the metal and the beverage. A robust barrier should be able to withstand the corrosive nature of the beverage yet be flexible and adhere well to the can wall. Low pH, minerals, and ingredients all contribute to the corrosive nature of the beverage.

Historically, epoxy-based coatings have been most widely used in the canned beverage industry. They have high chemical resistance and are flexible. Epoxy-based coatings are made by reacting bisphenol A (BPA) with epichlorohydrin (ECH). When the ratios of BPA to ECH, all altered the molecular weight (MW) of the coating is controlled. Different molecular weights alter the viscosity thus affecting the application properties of the coating. Varying the molecular weights and using different types of cross linking also changes the chemical resistance properties of the epoxy-based coating as well as its physical properties. As cross linking increases so does density, resulting in a harder more brittle coating. However, the exact ratios of BPA to ECH and amount of cross linking are not known since most coating formulas are proprietary. (15)

In recent years, there has been a push to remove BPA from any food contact because BPA may act as an endocrine disrupter and pose as a health hazard. Despite the European Food Safety Authority (EFSA) concluding in 2015 that there is “no health concern for any age group from a dietary exposure” (16), government bans on products with BPA such as the domestic ban in France and the push for Proposition 65 (17) in California continue. Due to the public concerns and current or imminent bans, can suppliers have been developing coatings to exclude BPA from their internal can coating materials.

One type of coating that was developed to exclude BPA is a water dispersible epoxy acrylic graft copolymer coating. This type of coating can be made by reacting an acrylic copolymer with an epoxy resin in a glycol ether solvent where only a small number of the carboxyl groups react and then a phenolic resin is used as a cross linker. (15)

Several variables (i.e. molecular weight, cross linking, and components) affect the morphology of the internal can before filling with the beverage and how it reacts with the beverage after filling. Molecular weight and the coating components affect how the internal coating cures. Epoxy-based coatings cure differently from the acrylic graft copolymer coatings because the type of volatile organic compounds (VOC) released during curing are different, resulting in dissimilar surface morphology. Cross linking is made during curing process. The type and extent of cross linking as well as molecular weight changes the level of chemical resistance and thus the interaction between the beverage and the can coating. These variables also affect the final surface morphology of the coating.

Surface morphology describes the size, shape, texture, and material distribution of a material. Surface topography is a measure of the geometry of the shapes and features found in surface morphology. An atomic force microscope (AFM) is used to measure the size and shape of features found on the material surface. AFM can also measure surface roughness as well as indicate phase distribution in a material. Analyzing the size and geometry of the features is important to understanding the interaction between the beverage and the can coating. Sharp peaks and cavities can function as nucleation sites. These surfaces have high surface energy that tilts the balance of the Gibbs free energy equation to favor nucleation.

Nucleation is the initial step in the formation of a new thermodynamic phase. It is a process that can form crystals, molecules, and in this application bubbles. Nucleation occurs when a system comes out of equilibrium and is able to overcome critical energy barriers to cause a physical separation of a solid, liquid or gas (1, 18). There are two types of nucleation: homogenous and heterogeneous.

Homogeneous nucleation involves a single phase, or state of matter, and occurs spontaneously without the need of a nucleation site. The new phase is formed by fluctuations within that single phase. Homogeneous nucleation requires a large amount of energy to initiate and not dissolve back into the bulk phase compared to heterogeneous nucleation. This high energy requirement contributes to a slower initial reaction rate.

Heterogeneous nucleation is characterized by the catalysis that results in the formation of a second phase when a supersaturated material comes in contact with another material. This other material, known as a nucleating agent, serves as a catalyst and is often a particulate or the surface of a package. Nucleation sites on the nucleating agent enable the system to overcome the critical energy barriers. Heterogeneous nucleation is associated with a smaller critical size radius than those found in homogeneous nucleation. Both the geometrical effect of the catalytic surface and the smaller critical radius size contribute to a lower critical energy barrier and a faster reaction rate for heterogeneous versus homogeneous types of nucleation. (19)

Classical nucleation theory is the most common theory that predicts the rate and likelihood nucleation will occur by estimating the critical energy barrier. As described in the equation below, per classical nucleation theory, the nucleation rate is dependent on the number of nucleation sites, temperature, and amount of free energy required.

$$R = N_s Z_j \exp\left(\frac{-\Delta G^*}{k_B T}\right) \quad (\text{equation 1})$$

where ΔG^* = maximum Gibbs free energy

R = rate of nucleation

N_s = number of nucleation sites

Z = Zeldovich factor (likelihood that the bubble will nucleate)

j = rate at which molecules attach to nucleus

k_B = Boltzmann constant

T = absolute constant

This theory makes multiple assumptions that do not always translate to actual systems (20).

Classical heterogeneous nucleation theory assumes that preexisting gas cavities exist within the surface (21). Once the pressure has dropped in the system, a bubble will form in the crevice as the gas pressure within the bubble is greater than the pressure of the liquid. However, the bubble will not release from the cavity unless the following criteria have been met. The bubble must first reach a critical size radius to exceed the total free energy requirement, also known as the nucleation energy barrier. Once this radius has been reached, the bubble will continue to grow. The release of the bubble is dependent on the geometry of the defect, surface tension of the beverage, and the interaction between the phases. (21, 22) In studies that focus on the classical nucleation, a conical shaped defect is assumed for ease of modeling, ignoring the effect of geometry on nucleation. The geometrical features of a defect impact its ability to form and release bubbles. The effects of four different defect geometries on nucleation were studied by Chappell *et al* (21). They compared the effects of conical, cylindrical, elliptical and spherical defects (Figure 1) and evaluated the degree of difficulty of forming a gas pocket at the bottom of the shape to induce nucleation. This degree of difficulty is known as threshold value of liquid pressure.

The elliptical defect had the lowest threshold value of liquid pressure while the other geometrical defects had similar values. However the elliptical cavity is most conducive to the emergence of a bubble because of the smooth transition between the inside to the outside

surface of the elliptical cavity. Once the receding contact angle has been achieved within the cavity, the bubble will grow and become unstable enabling the gas pocket to emerge with ease. In cases where the gas pocket forms half way up the cavity, elliptical shaped defects have the highest threshold of pressure for nucleation making it the most ideal geometry to promote nucleation. (21)

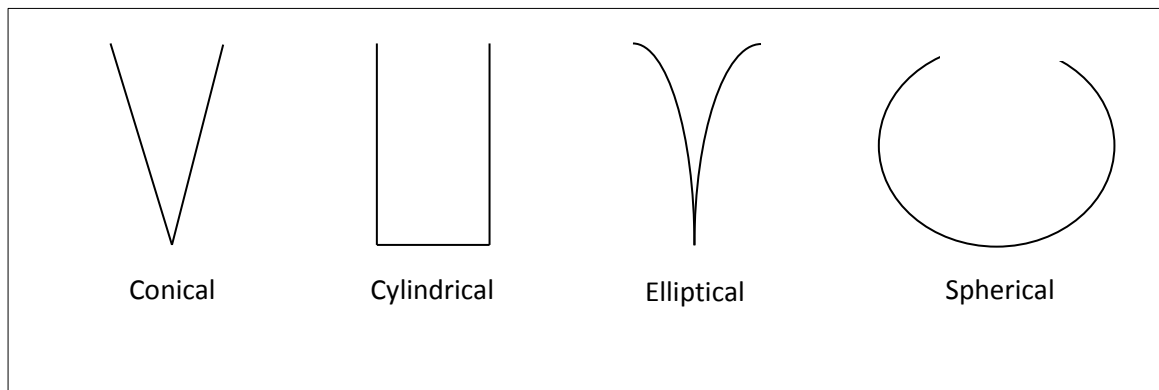


Figure 1. Chappell and Payne 2007 evaluated the effects of Nucleation energetics on cavity geometry

For the bubble to reach the critical radius, the internal pressure of the gas bubble must be greater than the surface tension of the liquid. The critical radius is the minimal size the gas bubble must reach to become thermodynamically stable and continue to grow then detach. Surface tension is the phenomena at the liquid-gas interface dictated by the attraction, or cohesive forces, of the liquid molecules to each other. These occurrences are explained by the Laplacian and Gibbs-Thomson effect.

Both of these effects are strongly linked to the geometry of the surface. Laplacian pressure is the difference in pressure between the inside and outside of the curved surface. In nucleation, this difference would be the pressure in the gas and liquid areas around the interface of the bubble that is dictated by the surface tension of the liquid between the gas

and liquid phase. We can predict how a liquid will interact with the surface using the Young-Laplace equation. The Gibbs-Thomson effect refers to chemical potential changes across the curved surface. As the curvature increases, a higher level of energy is required to form the bubble due to the existence of positive interfacial energy. Both the Laplacian pressure and Gibbs-Thomson effect are dependent on the geometry of the surface and related to the surface energy of the substrate (20).

Surface energy is the sum of all the intermolecular forces and dictates whether one material will adhere or repel to another material. This intermolecular force will determine whether or not the liquid will wet a surface. A hydrophilic surface will wet while a hydrophobic surface will not. Hydrophilic surfaces are attracted to the liquid molecules and are less likely to nucleate. Hydrophobic surfaces are the opposite and will repel the liquid enabling a faster release of a bubble. Surface energy of a material on a macro level can be measured using contact angle measurements

The classical nucleation theory fails to calculate actual nucleation rates (3, 9, 21, 23). Often the nucleation rates are under estimated because classical nucleation theories extrapolate thermodynamic parameters to molecular levels and assume systems are at equilibrium. The classical heterogeneous nucleation theory states that no gas cavities are present in the bulk or surface prior to the supersaturated state. For the bubbles to nucleate, a supersaturated system must occur for a bubble to nucleate. The non-classical and pseudo-classical nucleation theories hypothesize that there may be pre-existing gas pockets in the cavities at the surface of the package. The pre-existing gas cavities lower or eliminate the nucleation energy that the system must overcome to nucleate. The presence of pre-existing cavities would explain why actual nucleation rates exceed the predicted rates using classical

nucleation theory (1) and the inability to explain the different types of rapid de-carbonation observed in carbonated soft drink beverages packaged in cans when only classical nucleation theories are considered. Classical nucleation theory simplifies the interfacial interactions by assuming that line tension remains constant (24). However line tension at wetting is an important interaction. Line tension is the interfacial interaction between the liquid and the substrate. Gretz's (25) concluded that if macroscopic contact angles are less than 90° , the line tension effect is important. Hydrophobic surfaces give rise to negative line tensions. Negative line tensions will decrease the critical Gibbs free energy hence increasing the nucleation rates beyond those predicted by the classical nucleation theory (24).

Surface diffusion is another important factor in nucleation. According to surface diffusion, vapor molecules or gases may adsorb into a layer of the substrate. The thickness of this layer is dependent on the saturation of the system and the properties of the gas (26). These factors help explain why rapid de-carbonation has not followed predicted behaviors in previous studies that focused solely on classical nucleation theories.

2.3. Beverage Chemistry

Soft drink beverages are comprised of many different ingredients such as CO₂, caramel coloring and water. Each ingredient imparts different physical and chemical characteristics to the beverage. The beverage chemistry of these ingredients adds to the complexity of studying the behavior and root causes of rapid de-carbonation with a soft drink beverage versus plain water.

When the CO₂ is added in line to the beverage, the liquid is cooled to a very low temperature, slightly above freezing. This cooling enables the beverage to have more

carbonation than would be feasible in ambient conditions. Due to the non-polar nature of the CO₂ molecule, the water and CO₂ do not bond. Instead the water molecules form weak chains around the CO₂ molecules when they are in solution. In plain water, the CO₂ easily overcomes the weak van der Waals forces holding the water molecules together.

The chemical properties from one ingredient to the next can vary significantly. When ingredients other than CO₂ are added to the beverage, the interactions are altered due to the varying chemical properties. The surface tension (the intermolecular attractive forces between like molecules) of the liquid is what provides the necessary wall tension for the bubble to form. For example, aspartame, sugar, and flavor oils lower the surface tension of water by interfering with the interaction between the water molecules. Surface tension affects the likelihood a bubble will form, its stability, and the size it will grow to. The lower the surface tension the more easily a bubble will form.

Caramel is used in many cola beverages as a colorant. Caramel color is divided into four categories for many types of food and beverage applications. Class IV caramel colorant has been most widely used for soft drink applications (27). It is produced by heating food grade carbohydrates in the presence of ammonia and sulfite reactants in a Maillard type reaction. Maillard reaction is a desirable non-enzymatic type of browning (28). In the case of caramel coloring, the Maillard reaction refers to the reaction between sugar and naturally occurring nitrogen containing amines to form from the melanins, or brown pigments. The color intensity and polarity of the caramel is altered based on the application (29, 30). For cola beverages, the caramel used generally has a negative charge which enables it to withstand the low pH of the beverage.

Water is necessary in all beverage formulas. Water quality varies from one manufacturing plant to the next due to different types of incoming water and water treatment processes in the plant. The various types of water quality affect the total mineral content found in the water. Total mineral content, or hardness, can range from 13 ppm to 120 ppm. This affects the amount of mineral content, or hardness, that the water used for producing the beverage contains.

Water hardness affects the key chemical characteristics of the beverage including microbiological stability, nucleation, and foaming properties (31). Increased amounts of salts decreases the solubility of gases in water resulting in a “salting out effect” that causes the bubbles to be pushed out of the carbonated beverage at a faster rate (32). Increasing amounts of salts also inhibit coalescence of bubbles by reducing the attraction between bubbles and microbubbles (33). Coalescence is the process by which two or more bubbles aggregate together and join to form one bubble. Different coalescent behavior will affect the type of bubble in the beverage: small or large. It will also dictate the likelihood that a stable foam will form. Though a lesser driving force, different types of salts affect the attractive force differently depending on the ionic charge of the molecule (8).

2.4. Physical Characteristics Contributed by Filling and Processing Conditions

For many soft drink beverages, the consumer prefers a highly carbonated experience. The level of carbonation and pressure is not attainable under normal conditions. The beverage must be chilled to slightly above freezing temperatures ($\sim 2 - 4^{\circ}\text{C}$), high pressure (~ 1400 psi), and high speeds (1200 to 2000 cans per minute) to dissolve and maintain the high amount of

CO₂ into the liquid. In ambient temperatures and pressures, the CO₂ would normally escape into the atmosphere.

The amount of beverage filled into the packaging, or fill height is controlled on the filling line; however, the amount may vary up to +/-1ml. The amount of beverage filled into the can will affect the total pressure inside the package. Per the Ideal Gas Law, as the volume increases the moles of CO₂ or the carbonation will increase. Also, as the amount of carbonation increases so will the pressure. Pressure is further increased by an increase in temperature.

3. OBJECTIVES

The objective of this thesis is to investigate the factors of rapid de-carbonation in carbonated beverages filled in aluminum cans. These factors, internal can coating, beverage chemistry and physical characteristics contributed by filling and processing conditions, were identified through literature searches, industry knowledge, and a series of testing. The impact of each individual factor and their interactions on rapid de-carbonation was investigated.

4. MATERIALS AND METHODS

4.1. Materials

Calcium chloride dehydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, ACS reagent $\geq 99\%$) and magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, BioXtra, $\geq 99\%$) were purchased from Sigma-Aldrich. All ingredients used to make beverages are proprietary and were ordered from an internal source. Treated water from the PepsiCo Valhalla Technical Center was used in these experiments to make all beverages. Treated water for these experiments went through a five-stage filtration process consisting of a 50-micron pre-filter, a 0.5-micron ultrafiltration system, a carbon tower, a 1-micron post-carbon filter, and an UV light.

Aluminum cans for the design of experiment 1 (abbreviated as DOE 1) were manufactured by Rexam at the Rexam Technical Center in Elk Grove, IL. Aluminum cans for DOE 2 were obtained from stock cans in the PepsiCo Valhalla Technical Center; these cans were manufactured by Crown Cork and Seal. Aluminum cans for DOE 3 were manufactured by Crown Cork and Seal at their Olympia plant in Washington. Internal can coatings used for all three DOEs were proprietary internal can coatings obtained from Valspar.

4.2. Design of Experiment (DOE)

The experiments consist of a series of DOEs. Each set of experiments was designed to address different combinations of the factor hypothesized to have an effect on rapid decarbonation.

4.2.1. DOE 1: Fill Height, can coating, and ingredient evaluation

The effect of fill height, different internal can coating chemistries, and beverage chemistries were evaluated using a randomized design of experiment.

The cans were produced at the Rexam Technical Center. Can coatings were provided by Valspar. Each can variant was coded using a different color lacquer described in Table 1.

Coating Name	Use	Can Color Code
20Q53AP	Control	Black
40Q50AA	Negative Variant	Blue
20Q53AP	Positive Variant	Red

Table 1 Can coating variants produced in the Rexam Technical Center for DOE 1

Cans were shipped to PepsiCo Valhalla Technical Center and filled with three variants of beverage: commercial Diet Pepsi formula, Diet Pepsi with all sweeteners removed, and acidified carbonated water. All batches were made with treated water from the PepsiCo Valhalla Technical center. The carbonated water was acidified with phosphoric acid 80% and citric acid, and the solution was buffered using sodium citrate to simulate pH and TA in the commercial Diet Pepsi formula. Sodium citrate was added to the Diet Pepsi with all sweeteners removed as a buffer for the solution.

Samples were filled at three different fill levels. The fill level was determined by weighing the filled cans. The samples were divided into high (360 - 364 g), medium (355 - 359 g), and low (349 - 354 g). The samples were filled and evaluated using a 3x3 full factorial DOE

described below in Table 2. Each sample set was assigned a variant code. Samples were stored in the testing room maintained at room temperature ($\sim 21.1^{\circ}\text{C}$).

Bev Var	Can Var	Fill Var	Var Code	1 day (# of samples)	3 days (# of samples)	1 week (# of samples)	2 week (# of samples)	3 weeks (# of samples)	Total	Case Total
Acidified Carbonated Water (Beverage 1)	Can 1	Low	111	48	48	48	48	36	228	10
		Medium	112	48	48	48	48	36	228	10
		High	113	48	48	48	48	36	228	10
	Can 2	Low	121	48	48	48	48	36	228	10
		Medium	122	48	48	48	48	36	228	10
		High	123	48	48	48	48	36	228	10
	Can 3	Low	131	48	48	48	48	36	228	10
		Medium	132	48	48	48	48	36	228	10
		High	133	48	48	48	48	36	228	10
Diet Pepsi no Sweetener (Beverage 2)	Can 1	Low	211	48	48	48	48	36	228	10
		Medium	212	48	48	48	48	36	228	10
		High	213	48	48	48	48	36	228	10
	Can 2	Low	221	48	48	48	48	36	228	10
		Medium	222	48	48	48	48	36	228	10
		High	223	48	48	48	48	36	228	10
	Can 3	Low	231	48	48	48	48	36	228	10
		Medium	232	48	48	48	48	36	228	10
		High	233	48	48	48	48	36	228	10
Diet Pepsi (Beverage 3)	Can 1	Low	311	48	48	48	48	36	228	10
		Medium	312	48	48	48	48	36	228	10
		High	313	48	48	48	48	36	228	10
	Can 2	Low	321	48	48	48	48	36	228	10
		Medium	322	48	48	48	48	36	228	10
		High	323	48	48	48	48	36	228	10
	Can 3	Low	331	48	48	48	48	36	228	10
		Medium	332	48	48	48	48	36	228	10
		High	333	48	48	48	48	36	228	10
TOTAL				1296	1296	1296	1296	972	6156	270

Table 2 Variant codes for samples filled at the PepsiCo Valhalla Technical Center for DOE 1

Twenty four hours following filling, samples were tested using the gravimetric method developed by Ball Can Corporation to evaluate carbonation loss. Samples were also evaluated visually and categorized into three types of rapid de-carbonation: gushing, foaming, and active. Cans that were never filled and emptied cans after filling were measured for contact angle and evaluated using Atomic Force Microscopy (AFM). Both

contact angle and AFM methods will be described in later sections 1.2.2 and 1.2.3. Filled cans were tested using the CarboQC and following PepsiCo Method (PepsiCo TM 2000.133) to get a baseline for dissolved CO₂ in the beverage.

4.2.2. DOE 2: Investigation on effect of water quality

The effect of mineral content in the water used to manufacture the beverage was evaluated using three different targeted amounts of MgCl₂ and CaCl₂ to obtain desired total water hardness.

Cans were obtained from the stock supply at PepsiCo Valhalla Technical Center. Two batches of commercial Diet Pepsi formulation were made. Calcium chloride dihydrate (CaCl₂·2H₂O) and magnesium chloride hexahydrate (MgCl₂·6H₂O) were added to one batch of beverage to alter the hardness and alkalinity to mimic water quality at filling plants with harder water quality than the PepsiCo Technical Center. The amount of calcium chloride dihydrate needed to achieve desired hardness levels of CaCl₂ was calculated using the following equation:

$$\frac{\text{CaCl}_2 - 2\text{H}_2\text{O}(g)}{1 \text{ liter of water}} = (\text{Desired Water hardness (ppm)} - \text{Actual Water hardness (ppm)}) * \left(\frac{\left(\frac{2}{\frac{3}{2.5}} \right)}{10^6} \right) * 2.203 * \left(\frac{147.1}{40.1} \right) * 453.593$$

Similarly, the amount of magnesium chloride hexahydrate needed to achieve desired hardness levels of MgCl₂ was calculated using the following equation:

$$\frac{MgCl_2 - 6H_2O(g)}{1 \text{ liter of water}} = (Desired \text{ Water hardness (ppm)} - Actual \text{ Water hardness (ppm)}) * \left(\frac{\left(\frac{2}{\frac{3}{2.5}} \right)}{10^6} \right) * 2.203 * \left(\frac{147.1}{40.1} \right) * 453.593$$

Filled can samples were stored in a 21.1°C chamber immediately after filling and equilibrated for twenty-four hours. Cans were opened following the twenty-four-hour equilibration period. Ten samples from each variant were tested using the gravimetric carbonation loss method developed by the Ball Can Corporation.

4.2.3. DOE 3: Investigation on effect of water quality, carbonation level, and internal can coating

The effects of water hardness, initial carbonation levels of beverage and different can coating chemistries were evaluated using a randomized DOE.

Variant	Run Day	Water hardness	CO2 (gV)	Coating
1	1	High	High	BPA- NI 40Q60AA
2	1	High	High	Epoxy 9823001
3	1	High	Low	BPA- NI 40Q60AA
4	1	Low	High	Epoxy 9823001
5	1	Standard	Standard	BPA- NI 40Q60AA
6	2	Low	High	BPA- NI 40Q60AB
7	2	Low	Low	BPA- NI 40Q60AA
8	2	High	Low	BPA- NI 40Q60AB
9	2	High	High	BPA- NI 40Q60AB
10	2	Low	Low	Epoxy 9823001
11	3	Low	Low	BPA- NI 40Q60AB
12	3	Standard	Standard	BPA- NI 40Q60AB
13	3	Low	High	BPA- NI 40Q60AA
14	3	Standard	Standard	Epoxy 9823001
15	3	High	Low	Epoxy 9823001

Table 3 Variants for DOE 3

Empty cans were sent from Crown Cork and Seal. Three internal can coatings were submitted for testing: Epoxy 9823001, Acrylic-based coating 40Q60AA, and Acrylic-based coating 40Q60AB. Five cans from each coating variant were tested for internal coating thickness and dispersion using the SpecMetrix Can Stand ACS 1 purchased from Sensory Analytics, LLC prior to filling. One can from each internal coating variant was measured for internal contact angle and set aside for microscopy evaluation to get an internal coating baseline. Three separate batches of Wild Cherry Pepsi were made using the commercial formulation. All batches were tested to meet commercial beverage formulation specifications. Calcium chloride dihydride and magnesium chloride hexahydride were added to the two batches to simulate water quality found in commercial plants with higher levels of mineral content by targeting values of 70 ppm and 120 ppm of calcium carbonate (CaCO_3) water hardness. Three different carbonation levels were also targeted: low (3.4 gV), medium (3.6 gV), and high (3.8 gV). DOE is shown in Table 3. The variants were filled on three separate days to ensure that all samples could be tested using the gravimetric method within twenty- four hours of filling. Samples were transported to the PepsiCo Advanced Research Laboratory in Hawthorne, NY immediately following filling. Samples were stored and equilibrated overnight in a 21.1°C environmental chamber. Twenty-four hours following filling, thirty samples per variant were tested using the gravimetric carbonation loss method. The temperature of samples was recorded after the samples were tested using a Traceable Digital Thermometer model 61220-601 purchased from VWR. Ten samples from each variant set were tested for dissolved carbonation in closed cans using the CarboQC model 14805 purchased from Anton Paar (PepsiCo TM 2000.133).

4.3. Contact Angles

Contact angle was measured to capture the gross internal coating properties. Rectangular samples (approx. 50.8 mm by 17 mm) were cut from the side wall of a can (approx. 50.8 mm by 17 mm). Samples were mounted with internal coating facing up to glass slides using quick set epoxy, weighted, and cured overnight. Contact angles were measured on internal can coatings using the Kruss DSA30E Contact Angle Measurement Machine. The measurements were taken using a 3 μL sessile drop of water dispensed by a 0.510 mm single load syringe. The camera was set to 3 mm.

4.4. Microscopy

Rectangular samples were cut from the side wall of the can into (approx. 31.75 mm x 25.4 mm). Samples were mounted in a custom holder (see Figure 2). This holder was engineered to minimize any movement of the sample that could cause noise or false results.

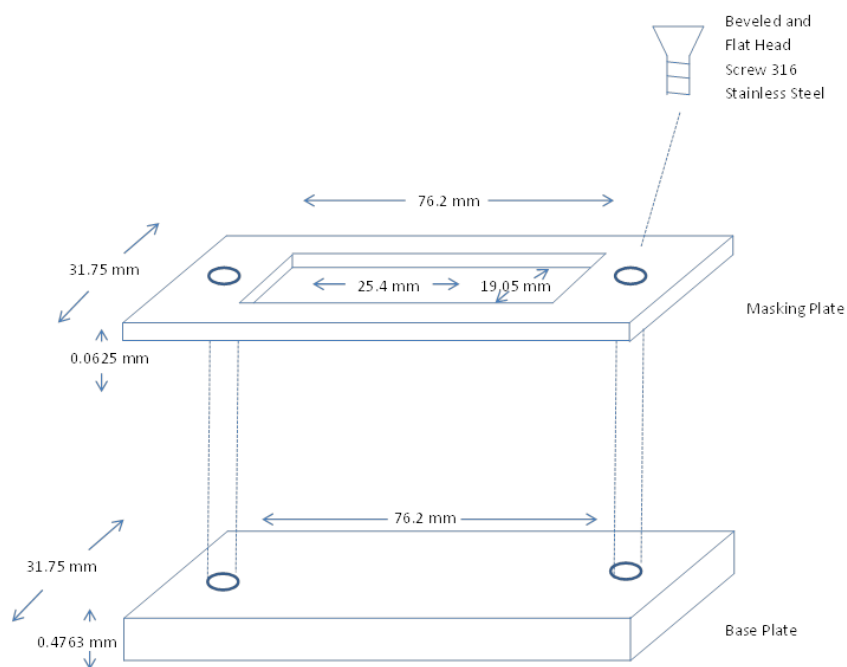


Figure 2 Custom made AFM sample holder

Atomic force microscopy (AFM) analysis was performed on internal can linings using a Bruker (formally Digital Instruments and Veeco) Dimension 3100 AFM. AFM was used to characterize the geometry of the defects in the internal coating. The analysis was performed in tapping mode with a NanoScope IIIa controller. The feedback loop maintains a constant oscillation amplitude by maintaining a constant signal from a split photodiode detector. Standard uncoated silicon tips were used with a resonant frequency of about 300 kHz, with a nominal tip radius of curvature between 5 and 10 nm. Typical acquisitions were acquired from an area of 20 μm x 20 μm , down to 1 μm x 1 μm scans.

4.5. Carbonation Testing Methods

4.5.1. Gravimetric Test Method

The gravimetric test method was used to quantify the carbonation loss of each can sample. All samples were tested at ambient room temperatures (21.1 to 23.9 °C). Cans were inverted gently two times. A top loader balance was used to measure the weight in grams to the second decimal place. An aluminum pan was placed on each balance and the balance was tared. Cans were placed on the aluminum pan to catch all spills and minimize error from spilled beverage. A full weight was recorded of an unopened can. The cans were carefully opened and the timer was started. Weights were recorded at 5 seconds, 5 minutes, and 10 minutes after the can had been opened. The operator was careful not to disturb the sample while collecting data. The CO₂ loss in grams was calculated by subtracting the 10-minute

weight from the 5 second weight. The difference was multiplied by 1.538 to convert the loss value from grams to gas volumes.

4.5.2. CarboQC Closed Can Method

The CarboQC Closed Can PepsiCo Test Method (PepsiCo TM 2000.133) is used to measure the amount of dissolved CO₂ in a beverage. It was used in these tests to verify that the samples were filled to the targeted CO₂ levels. All samples were stored in an environmental chamber maintained at 21.1°C and 50% humidity. Samples were removed from the chamber on the day of testing. Samples were inverted gently three times each, just prior to being tested to equilibrate the gases in the headspace. Samples were placed in the piercer unit, inverted (dome side up). Samples were pieced and tested following the respective method (Diet or Regular). Temperature, dissolved O₂ and CO₂ were recorded.

5. RESULTS AND DISCUSSION

The effects of three factors were evaluated on the carbonation loss in the first ten minutes of opening a can of carbonated soft drink beverage: the package, beverage chemistry, and filling processes. Each testing set evaluated hypothesized factors in different combinations. The first DOE (design of experiment) evaluated fill height, initial carbonation, and internal can coating. The second DOE evaluated the effects of mineral content in the batching water. The final DOE evaluated the following key factors identified through the other testing rounds in varying combinations: initial carbonation level, internal can coating, and mineral content in water used to batch (manufacture) the beverage. The following sections are compiled from all three sets of tests to highlight results that were consistent across multiple tests. Results that did not show significant differences will also be discussed to explain why these factors were dropped from the next set of testing.

5.1. Interfacial Interactions

Three levels of initial carbonation and mineral content were set up: low, standard and high. Samples with the lowest amount of initial carbonation and mineral content were considered to be the least stressed. Conversely samples with the highest amounts of initial carbonation and mineral content were considered to be the most stressed systems. The epoxy-based coating (Epoxy 9823001), acrylic-based coating (BPA- NI 40Q60AA), and acrylic-based coating (BPA- NI 40Q60AB) are considered to add increasing levels of stress to the system, respectively.

Results from the final DOE indicate that when stressed conditions are combined (high initial CO₂ content and high mineral content filled into a can with an acrylic-based coating) 10 minute CO₂ loss shows a statistically significant increase (95% confidence level) above the acceptable range of 1.0 gV [1 gV (gas volumes) = 355 cc of gas] loss in 10 minutes, as compared to samples filled using any other set of conditions. Samples with only one stressed condition lost significantly less CO₂ compared to samples with multiple stressed conditions (Figure 3). Results were further analyzed to show the additive effects on 10-minute CO₂ (carbonation) loss of each factor on a single type of variant coating, BPA-NI 40Q60AB. The increase in 10-minute CO₂ becomes more significantly different as the variable factors (initial carbonation level and mineral content) are stressed. This increased loss rate indicates that the phenomenon is related to a combination of multiple stressed conditions. The additive effect of these factors enhances CO₂ loss more than any single factor.

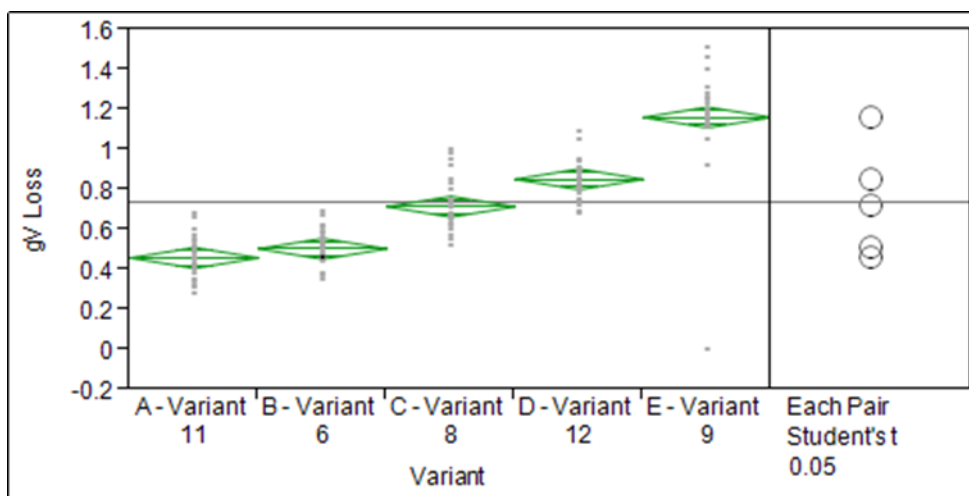


Figure 3. Plot evaluating the effect of CaCO₃ water hardness and initial CO₂ content on 10-minute gas volume loss of beverage using gravimetric loss across all samples using the BPA- NI 40Q60AB internal coating.

Samples with a combined 70 ppm CaCO₃ hardness and 3.6 gV initial carbonation level or higher have a 10-minute carbonation loss above the industry accepted value of 0.8 or less. Samples with high water hardness and high initial carbonation lost close to 3 times the amount of CO₂ in the first 10 minutes after opening (A-Variant 11 = low water hardness, low initial carbonation; B-Variant 6 = low water hardness, high initial carbonation; C-Variant 8 = high water hardness, low initial carbonation; D-Variant 12 = standard (medium) water hardness, standard (medium) initial carbonation; E-Variant 9 = high water hardness, high initial carbonation)

Initial CO₂, internal can coating, and mineral content were modified according to a randomized DOE (Table 3). The effects of initial carbonation, mineral content (water hardness) and internal can coatings were studied both individually and additively. The factors are grouped into themes: nucleating surface morphology, beverage chemistry, and processing conditions. The themes were determined by the categorical source of the factor.

5.2. Nucleating Surface Morphology

All aluminum cans used to package carbonated soft drink beverages have an internal coating, generally epoxy- or acrylic-based. This coating is used to protect the aluminum from corrosion caused by the beverage (corrosive factors include pH, colorants, and mineral content). The internal coating also helps smooth out the internal surface, because the side wall is uneven. Aluminum cans are manufactured using an alloy of aluminum, magnesium, and manganese. The manganese increases the strength and malleability of the aluminum to improve the drawing process to form the cans, but the manganese and magnesium inclusions also roughen the sidewall, creating an uneven surface morphology (Figure 4).

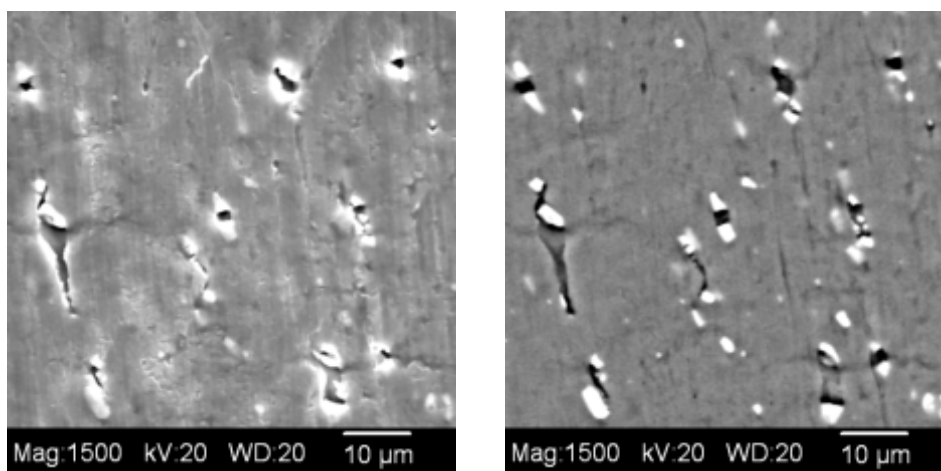
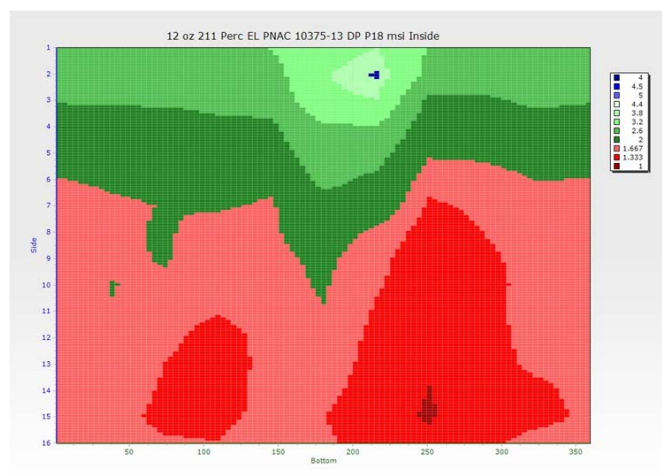


Figure 4 SEM cross section micrographs of can wall showing Mn and Fe inclusions

Wall thickness measurement were taken using the SpecMetrix Can Stand ACS 1 to ensure that the can were properly coated. The scans demonstrate varying thicknesses of coating throughout the samples; however, all internal surfaces of the can appear to have some degree of coating (Figure 5).



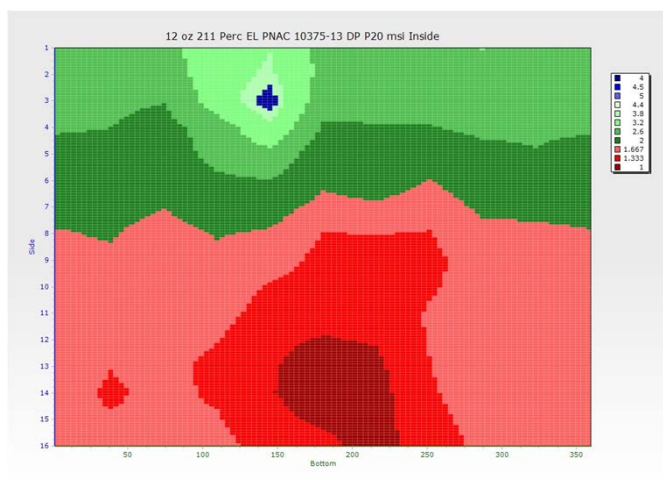


Figure 5 Internal can coating thickness measurements taken by SpecMetrix Can Stand ACS 1 demonstrates similar coating distribution across samples with no areas without coating

Figure 6 shows the topographical profiles of the internal coating of the can surfaces; these profiles were taken using an atomic force microscope (AFM).

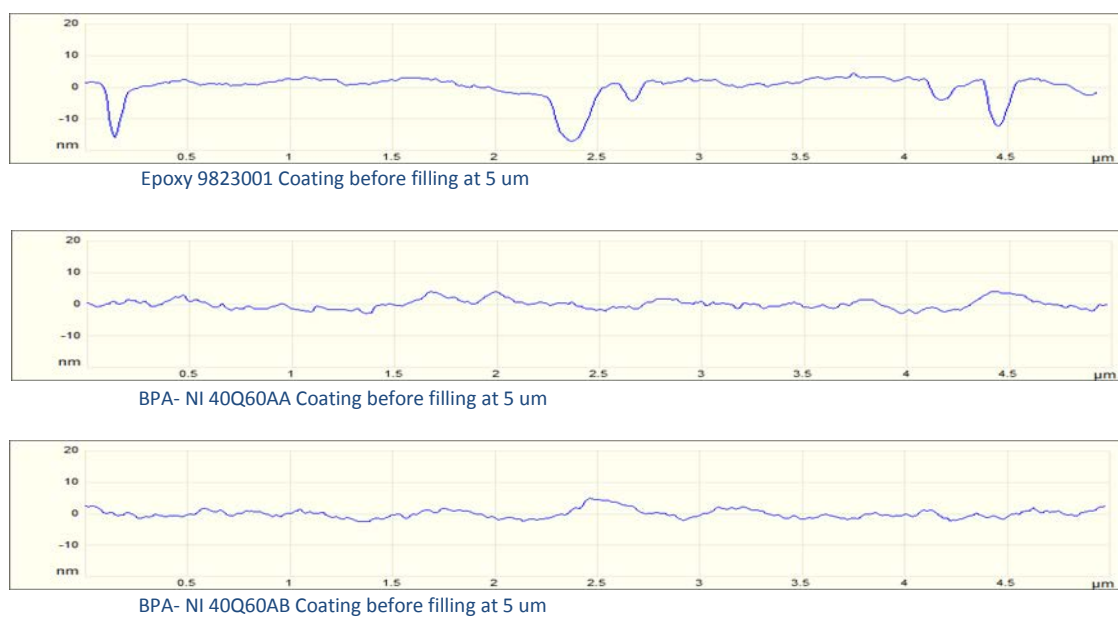


Figure 6 AFM topographies of internal can coatings prior to filling show epoxy-based coating topography is different from acrylic-based coatings.

Prior to filling the cans with beverage, the internal surfaces are relatively smooth (Figure 6). The cans coated with an acrylic-based coating are relatively smoother than the cans coated with an epoxy-based coating. The epoxy-based coatings have wide, rounded defects. These defects are not present in the acrylic-based coatings.

All internal coating samples were rougher after filling; however, the BPA-NI and epoxy-based coatings showed different surface profiles following filling. The profiles of the sample with BPA-NI internal coating can be characterized as spikey and narrow while the epoxy-based coating profile is rolling and undulating, (Figure 7). The AFM examples are from the three different internal coatings taken from samples after being filled at the same time with the same beverage that was manufactured with high mineral content and filled with high initial carbonation levels.

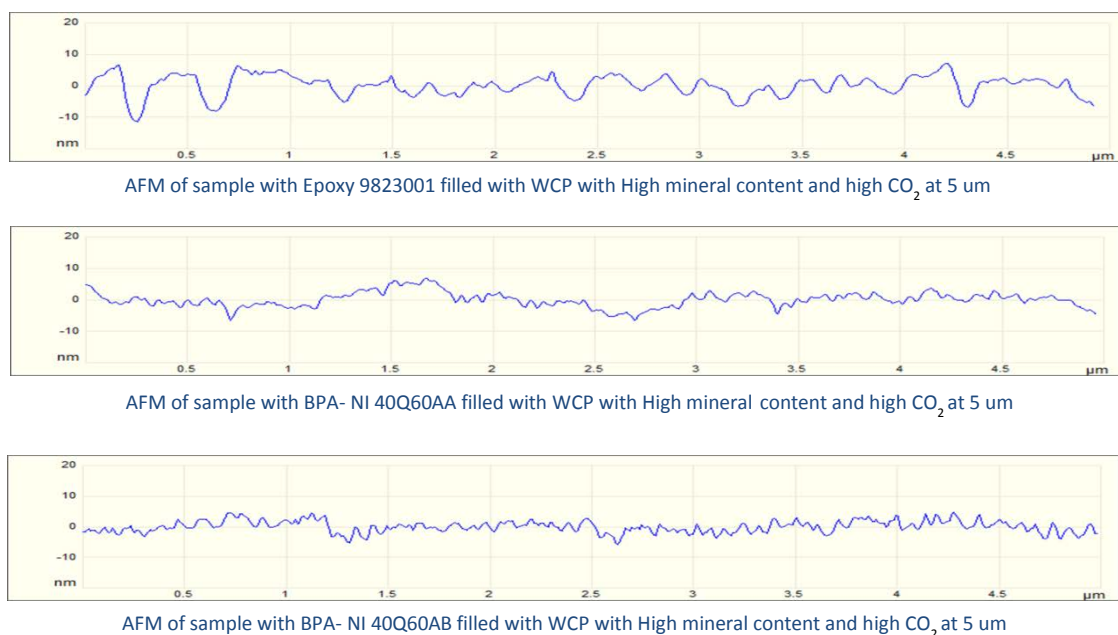


Figure 7 AFM topographies of internal can coating after filling demonstrate the varying topography changes between epoxy-based and acrylic-based coatings.

Samples from this set of cans were analyzed for carbonation loss using the gravimetric test. The analysis shows a significant statistical increase in the carbonation loss within the first ten minutes of opening samples. Both sample sets that used BPA-NI acrylic-based internal coating (Variant 9 and Variant 1) had statistically significantly higher loss rates at a 95% confidence level compared to Variant 2 samples with a standard epoxy-based internal coating (Figure 8).

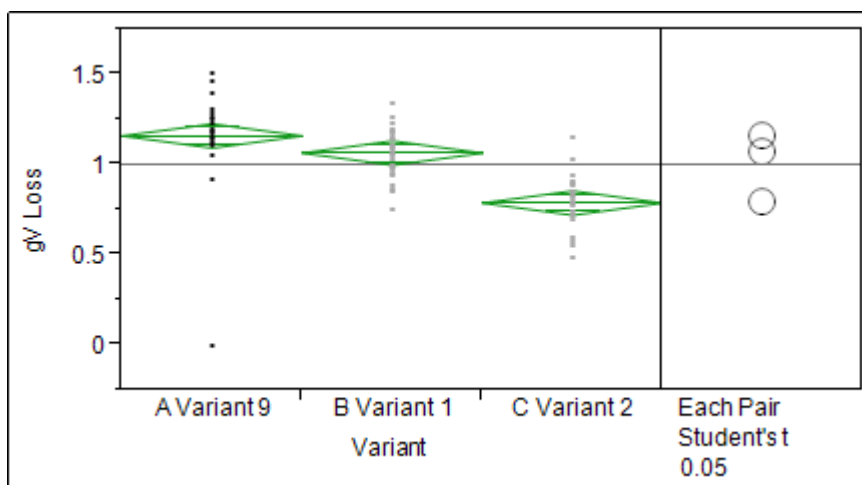
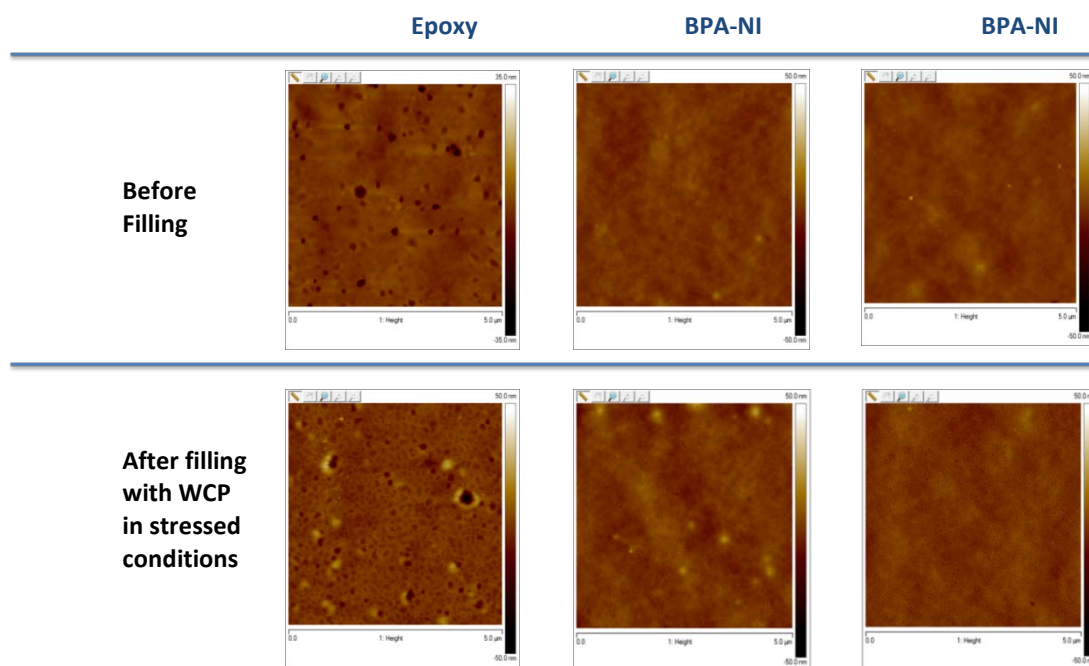


Figure 8 BPA-NI acrylic-based internal coatings (Variants 9 and 1 to left) have a statistically significantly higher carbonation loss compared to the samples that have an epoxy-based coating (Variant 2 to the right). All samples were batched with a target 120 ppm CaCO_3 Water hardness content and 3.9 gV initial carbonation.

The difference in the carbonation loss with varying coatings may be due to the differences in internal coating surface morphology. The varying geometries of defects have a direct effect on the likelihood and speed at which a bubble will form and be released (21). The three different coatings exhibited different defect geometries. The difference between the epoxy and acrylic-based is marked. Although the defects shown in the AFM micrographs cannot be ascribed to a single cavity geometry described by Chappell and Payne, it is reasonable to conclude that the differences in defect geometry between the different coatings contribute to the different carbonation loss rates.

AFM micrographs of the three internal can coatings exhibited different characteristics, post fill as shown in Figure 9. Samples with the epoxy-based internal can

coating showed large, round defects throughout the samples within 24 hours after filling. Conversely, acrylic-based coatings exhibited tiny, pinhole-like defects after twenty-four hours. According to Leung (23), to nucleate and release a bubble, a defect must be of a certain size and geometry. If a defect is too small, the physics of the system will not support the formation of a bubble. On the other hand, if the defect is too large, the bubble will not be able to release from the defect. The bubble will be trapped and eventually the gas will dissipate back into the can coating.



Theoretically the size and geometry of the defects in the acrylic-based coatings is more conducive to the formation and release of bubbles while the defects in the epoxy-based coating do not provide the necessary features to promote nucleation in this thermodynamic system. The exact dimensions of the defects using AFM, SEM, and FESEM (Field Emission Scanning Electron Microscopy) were not successfully measured. Future work to measure the specific dimensions of these defects to test this theory is recommended. Analysis using a

Figure 9 Defects and inclusions after filling differ across internal can coatings demonstrate different interactions

Transmission Electron Microscope (TEM) may provide enough detail to appropriately measure and characterize these defects, particularly a High Resolution TEM (HRTEM). Crystalline structures have been successfully analyzed using HRTEM to characterize point defects and surface structures.

AFM analysis revealed that over time, the amount and size of deposits increased. Sixteen days post filling, the deposits agglomerated at the surface (Figure 10). These deposits form a significant layer (more than 25%) over the internal coating. The deposits were further analyzed in a previous internal PepsiCo study using X-ray photoelectron spectroscopy (XPS) to investigate the components. The XPS results showed increased amounts of nitrogen and sulfur (elements used in the caramel coloring for Diet Pepsi) sixteen days after filling (Figure 11).

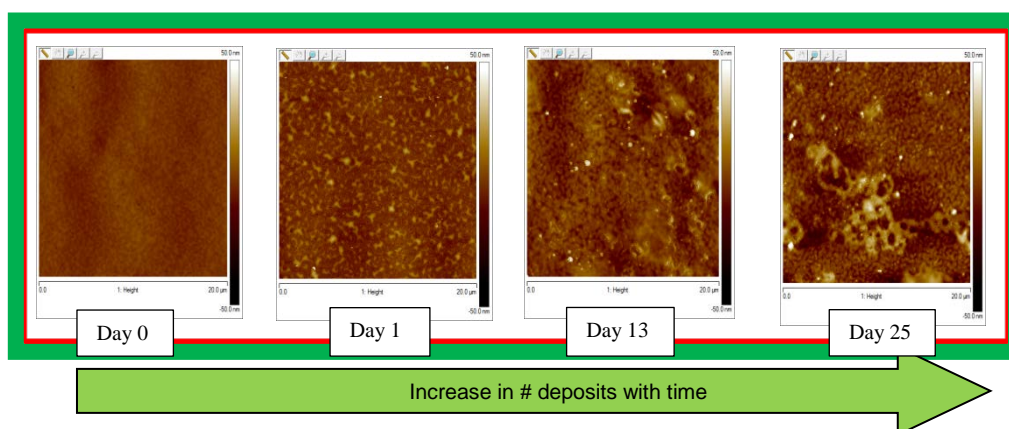


Figure 10 AFM of agglomerating deposits at 0, 1, 13 and 25 days after filling

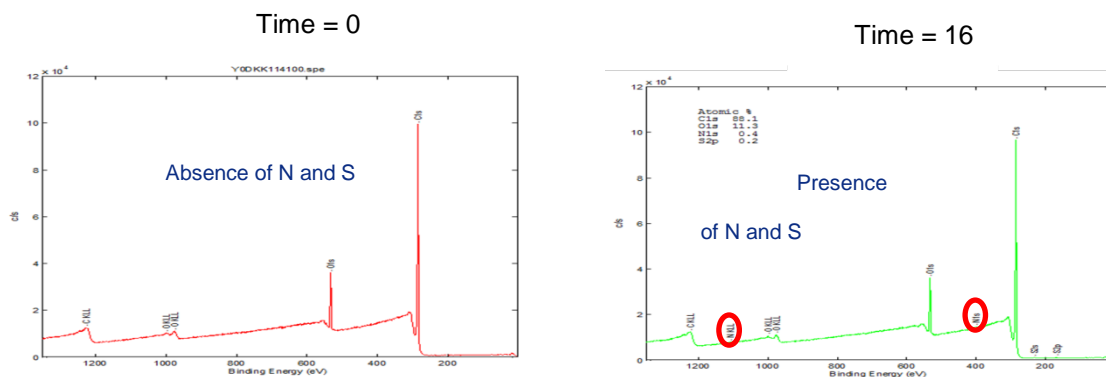


Figure 11. XPS indicating deposits contain N(nitrogen) and S (sulfur)

Samples containing the acrylic-based coatings exhibited very few deposits. The deposits that were observed were small (less than 5 μm) and scarce. The deposits also appeared far less dense than those observed in the samples with epoxy-based coating. The different chemistry of the acrylic-based liner may have less of an affinity to the substances that form these deposits.

The changes observed in the AFM surface roughness measurements after filling can be caused by two factors: (1) etching of the surface by physicochemical changes initiated by the soda and (2) deposits of coalesced particles (N and S) from the soda formulation. The time sensitive data suggests that there may be short term etching effects and longer term particle deposition processes occurring. The data shows that increased surface roughness of the liner increases the carbonation loss rate.

One theory to explaining why the epoxy-based coating has less CO_2 loss is deposits form a protective layer over the coating by covering the internal coating defects. The coated

surface has fewer possible nucleation sites. This coating would decrease the ability for the system to form and release bubbles. In cases of foaming type rapid de-carbonation, the rapid de-carbonation phenomenon dissipates around 14 days in a sealed can. The timing of this vanishing phenomenon coincides with the formation of a particulate layer across a majority of the internal coating area.

Another factor that influences the likelihood a substrate will nucleate is the wettability of the material. Wettability is the interaction between a liquid and solid based on intermolecular forces. The greater the wettability, the greater the two interfaces adhere to each other while surfaces that are described as lower in wettability have a greater repulsion to each other. Wettability can be measured using contact angles. Greater contact angles are indicative of lower wettability.

In Figure 12, a comparative graph shows the differences in contact angles measured with the different types of internal can coatings with both high and low mineral contents. The contact angles measured for the epoxy-based coating were significantly greater than the contact angles of the acrylic-based coatings, BPA-NI 40Q60AA and BPA-NI 40Q60AB. When comparing the low to high mineral content results, the trend for the epoxy-based coating and BPA-NI 40Q60AA are contradictory to the results with the BPA-NI 40Q60AB.

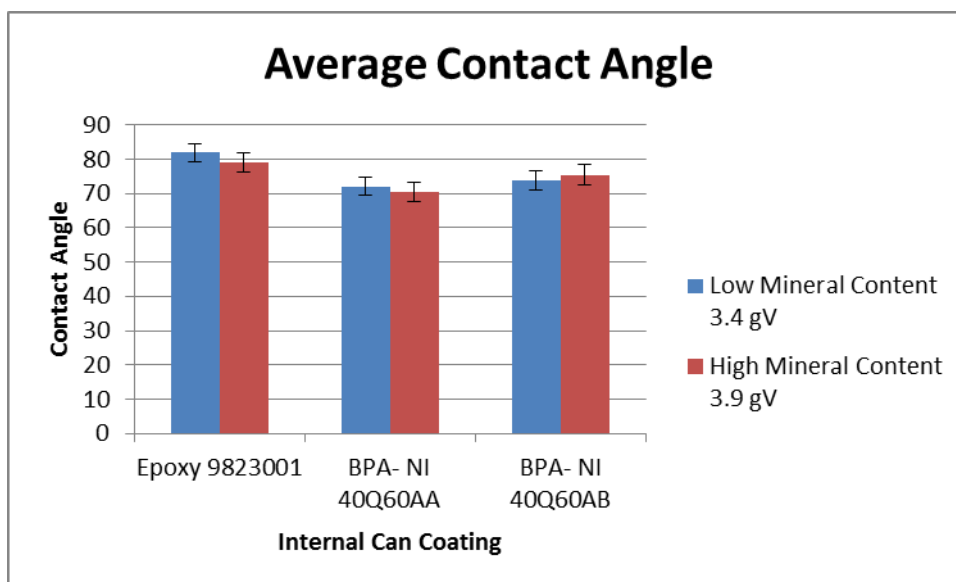


Figure 12 Comparison contact angles measured with various coatings after exposure to low and high mineral content beverages

In general as the contact angle increases the more prone a system would be to nucleate. However, the data in Figure 12 contradicts that hypothesis when comparing the results with the epoxy-based coating compared to the BPA-NI 40Q60AA and again with the low mineral content compared to the high mineral content for both the epoxy-based coating and the BPA-NI 40Q60AA. In each of these instances, the samples with the lower contact angles had the more rapid loss of CO₂, the opposite of what is expected.

There are several possible explanations for these unexpected results. One, the measurements were taken more than one day after the cans were emptied. During this waiting period, the coatings may have relaxed from their stressed state resulting in a different contact angle measurement than what was present at the time the cans were opened and the CO₂ loss was measured.

A second possible explanation is measurement error. The technician who measured the contact angles had limited experience with this equipment. Another detrimental factor is this equipment was located in an area that often had drafts and floor vibrations. Any of these factors could impact the measurement of the contact angle.

A third explanation is the geometrical surface morphology may play a significant role in the nucleating propensity of this system. The surface roughness of a substrate impacts heterogeneous nucleation. Jagged “step like” structures promote nucleation while smooth micropores inhibit nucleation. The wetting angle, and thus nucleation, is dependent not only on the contact angle but also the surface’s microstructure (34). The 3D AFM micrograph in Figure 13 illustrates this jagged structure found in the acrylic-based coating studied, while the micrograph in Figure 14 exhibits more smooth micropores found in the epoxy-based coatings.

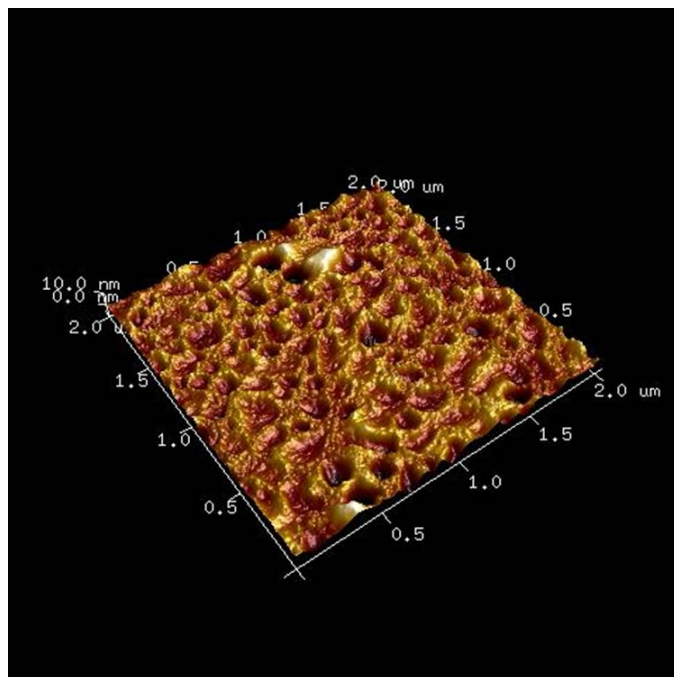


Figure 13 3D AFM micrograph of epoxy-based coating after 1 day 2 um

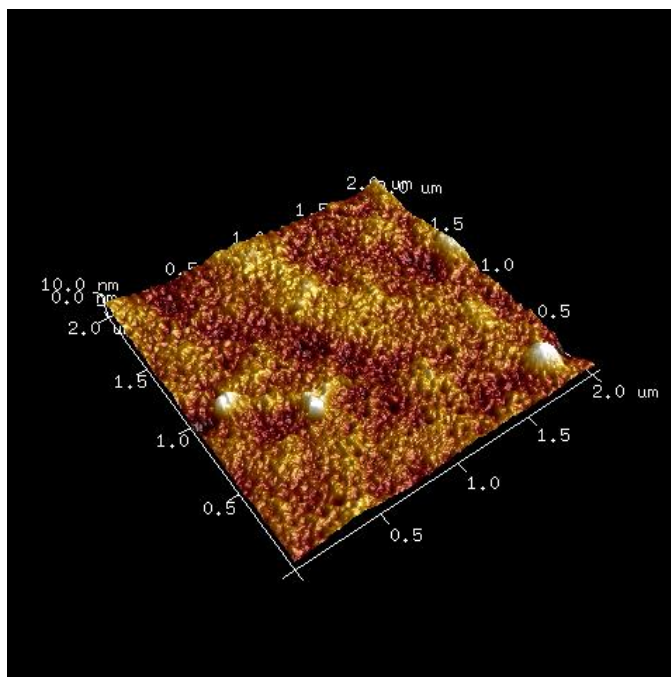


Figure 14 3D micrograph of acrylic-based coating after 1 day 2 um

5.3. Beverage Chemistry Characteristics

Results from the first set of experiments that explored the effects of fill height, beverage ingredients, and internal can coating showed a significant carbonation loss difference between acidified carbonated water and commercial formula Diet Pepsi. The acidified carbonated water, spiked with phosphoric acid to match the pH of Diet Pepsi, consistently lost twice the amount of CO₂ ten minutes after opening, compared to the samples filled with commercial formula Diet Pepsi at each time of testing (see Figure 15). There were no dissolved additives in the acidified carbonated water to bind or retard CO₂ evolution, thus resulting in higher loss rates. The optical observations validate the fact that acidified carbonated water does *not* support homogeneous nucleation in cases of foaming during times

of rapid de-carbonation. This observation provides evidence that components in the soda formulation produce nucleation sites for the generation of homogenous foam-like bubbles. Combining the homogeneous and heterogeneous nucleation experimental data suggests that the generation of foam-like bubbles in the soda results from interactions from both the bulk liquid and the liner surface.

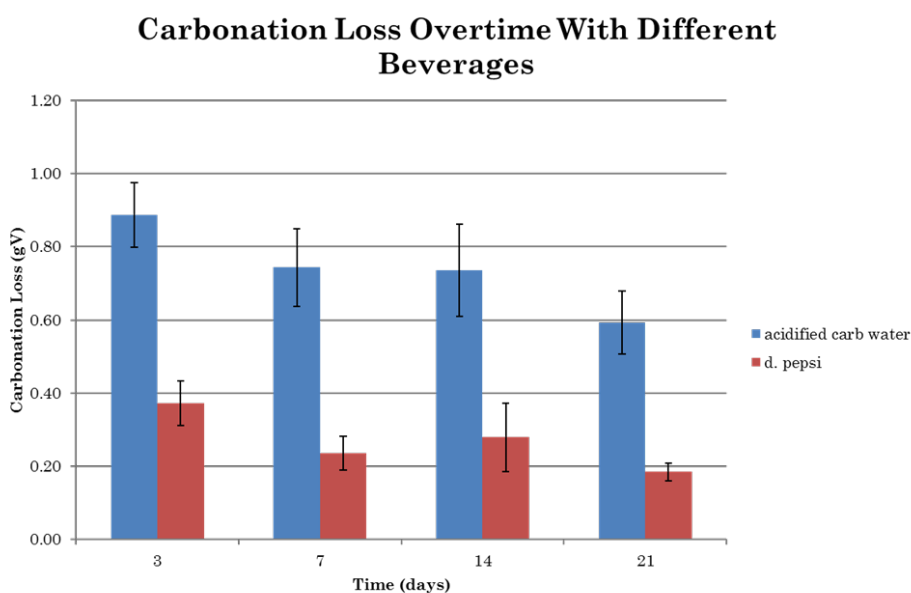


Figure 15 Comparative CO₂ loss between acidified carbonated water and commercial formula Diet Pepsi. Acidified carbonated water consistently lost double the amount of CO₂ than the commercial formula Diet Pepsi

Samples of the Diet Pepsi and acidified water were measured for surface tension following the procedure listed in the materials and methods section. Figure 16 shows that the commercial Diet Pepsi samples consistently have lower surface tensions than the acidified carbonated water due to the presence of additional surface active species in the soda formulation.

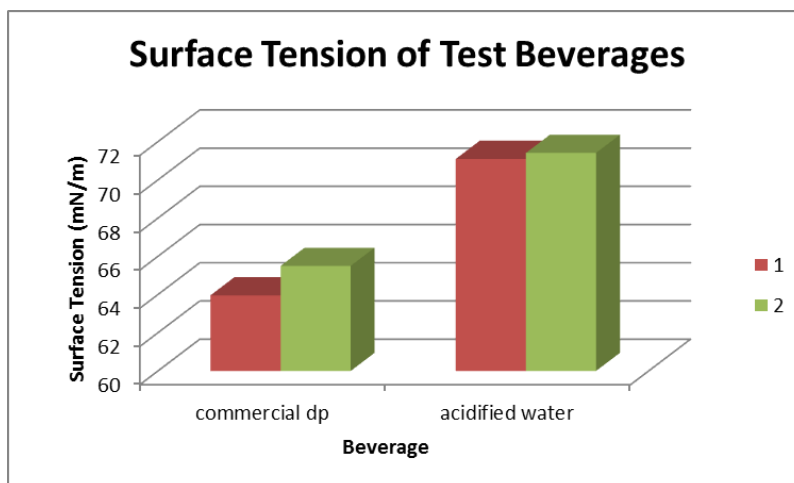


Figure 16 Comparative surface tension of commercial formula Diet Pepsi, no aspartame Diet Pepsi and acidified carbonated water

In the final set of tests investigating the effect of water quality, initial carbonation levels, and internal can coating, higher levels of mineral content correlated with higher CO₂ loss rates after ten minutes of opening the can. The carbonation loss rates were tested using the gravimetric test method. As the mineral level increases in the batch water, carbonation loss rates also increase (Figure 17).

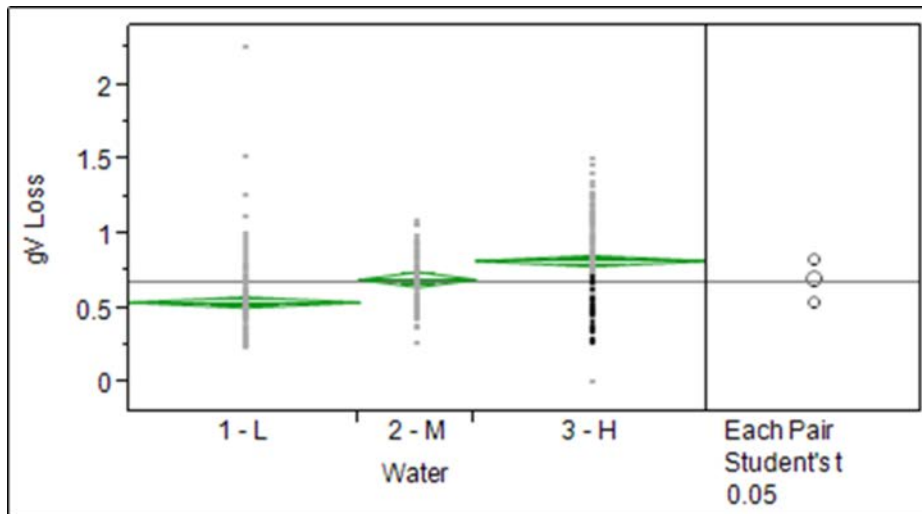


Figure 17 Carbonation loss of beverages in first ten minute after opening with increasing mineral content comparison of group means chart (JMP©) shows statistical difference across each variable.

With increasing amounts of certain minerals, such as MgCl_2 and CaCl_2 , the surface tension is expected to decrease, as theorized in the Hoffmeister series. Both salts are considered to be chaotropic molecules that destabilize hydrogen bonding and decrease the hydrophobic effect of the system (35). Normally this destabilizing is expected to decrease the nucleation rate, contrary to the results. But these effects have been mainly studied in water/air systems, so they may not apply in this case because the beverage system included emulsions. Systems containing emulsions react differently from water/air systems only. For example, CaCl_2 was observed to increase interfacial tension in systems containing emulsions (36). Emulsions may account for the differences from predicted results based on classical theories.

In all three sets of testing, first or second type of rapid de-carbonation described in the introduction of this thesis was observed. Salts used in these tests (CaCl_2 and MgCl_2) prevent

coalescence of bubbles, and thus, formation of foams. However, different salts potentially have the reverse effect. Only studied the effects of calcium chloride and magnesium chloride in these tests were studied. Another factor is that the initial batch water in the PepsiCo Valhalla Technical Center where all filling took place for testing has very low mineral content. This factor may account for the inability to replicate foaming in rapid de-carbonation examples that were experienced at some PepsiCo plant locations.

Another beverage ingredient that may contribute to rapid de-carbonation is antifoam agents. Antifoam agents have been historically used in the beverage industry. Although they are designed to prevent foaming during the mixing process prior to filling, it has been noted that they often cause foaming of the beverage post filling once the product is in the hands of the consumer. Foaming caused by this antifoam agent had been associated with the foaming type of rapid de-carbonation. Antifoam used in beverages is typically silicone based. The silicone in the antifoam often act as nucleating agents, potentially causing or exacerbating rapid de-carbonation in a beverage. Antifoam was not used in any of the tests. No foaming type of rapid de-carbonation was observed during testing.

5.4. Processing Conditions

The effect of fill height was studied in the first and third sets of testing. In the first set, sample cans were filled at three specific fill volumes representing low, medium, and high volumes found in commercial samples, as detailed in the materials and methods section. The samples were then tested for carbonation loss using the 10-minute gravimetric carbonation

loss method. In each test, the samples did not exhibit a statistical difference or trend in carbonation loss based on fill volume (Figure 18). Carbonation loss results were similar from the third round of testing when analyzed in relation to fill volume.

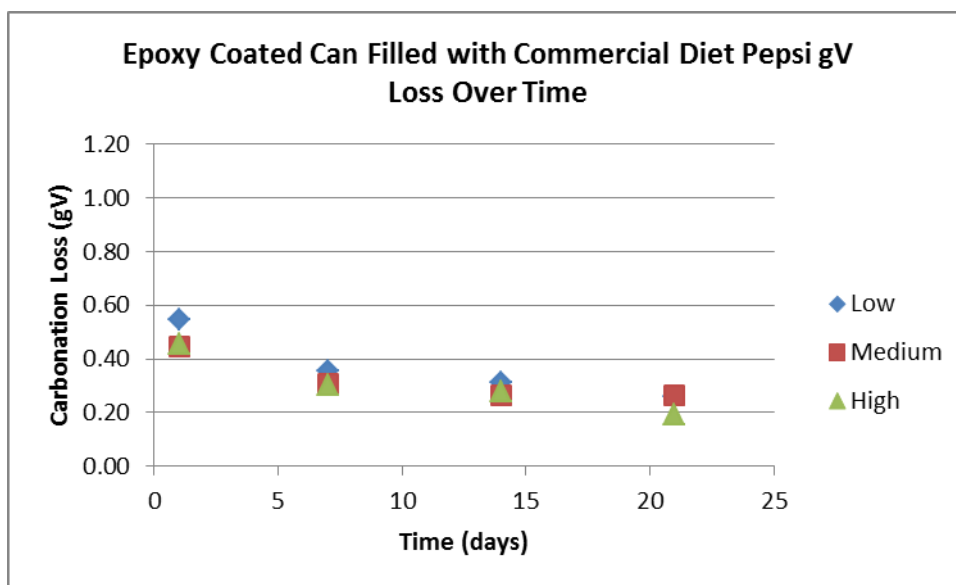


Figure 18 Carbonation loss of commercial formula Diet Pepsi filled in epoxy-based coated cans show no difference in loss related to low, medium, and high fill heights

Prior to testing, it was hypothesized that greater fill volumes would lead to higher carbonation loss. This hypothesis was based on basic thermodynamics: as the fill volume increases, pressure inside the beverage should also increase. The increase in pressure should push bubbles, or carbonation, more readily out of a supersaturated system. However, the data do not support this theory. The increase in pressure from the greater fill volumes may not be sufficient to drive a discernable difference in carbonation loss.

Another processing variable that was tested was initial carbonation level. Samples were filled with three specified levels of carbonation in-line during production. Samples were tested using the gravimetric test method for carbonation loss in the first 10 minutes after opening the can. Carbonation loss increased as the initial carbonation level increased (Figure 19).

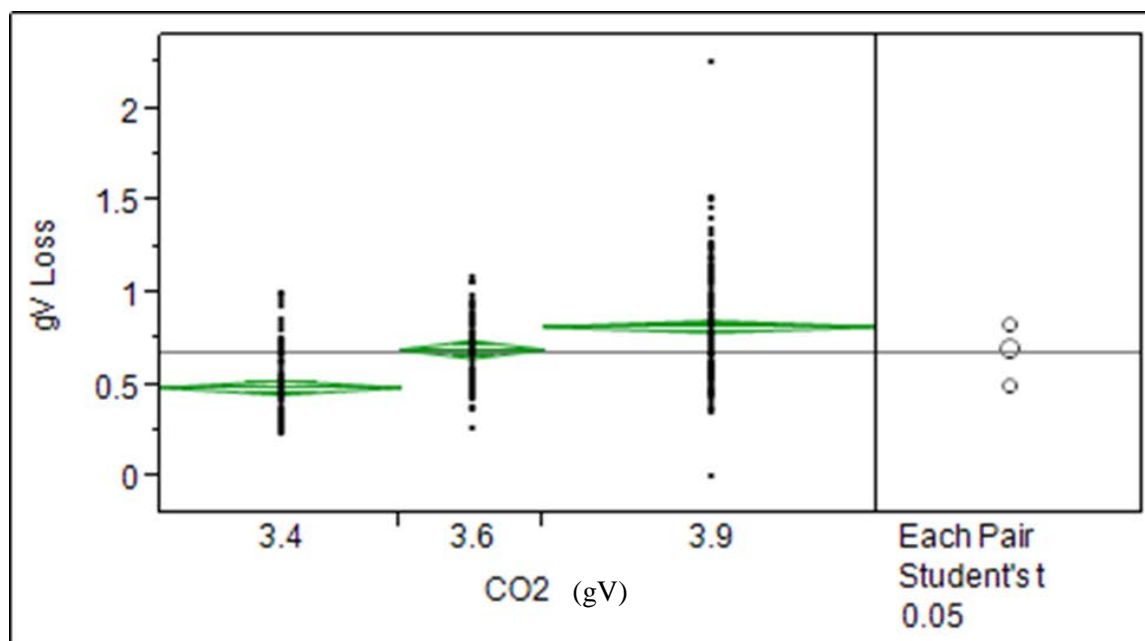


Figure 19 10-minute carbonation loss increases as initial carbonation content increase

The increased carbonation loss with increased initial carbonation can be explained in terms of pressure and concentration difference (Henry's Law). The amount of pressure in the can significantly increases as the level of carbonation increases. During filling, CO₂ is forced through the lines to carbonate the beverage. The beverage is chilled to close to freezing. CO₂ becomes more soluble at lower temperatures. By lowering the temperature, more CO₂ can be incorporated into the beverage with minimal loss to the ambient air. The beverage has

a high concentration of dissolved CO_2 when initially filled into the can. Once the can is filled and sealed, the system begins to achieve equilibrium. As the system warms, some of the dissolved CO_2 in the supersaturated liquid moves into the fill space over the liquid until equilibrium is established at a given temperature. In all systems, energy flows from high to low concentrations. When the can is opened, the high pressure CO_2 in the fill space is immediately vented. The CO_2 escapes from the supersaturated liquid over a short period of time, driven by the large delta in CO_2 concentration between the beverages to that of ambient air. The rate of loss in carbonation has a direct impact on the nature of CO_2 effervescence and on the taste of the product (7).

6. CONCLUSION

In this thesis the following factors were identified as having a significant effect on rapid de-carbonation in canned carbonated beverages: internal can coating morphology, beverage chemistry, and filling/processing conditions. The results from the experiments demonstrate the synergistic effect of these factors on the system. Independently each factor raised the carbonation rate loss; when analyzed separately, carbonation rate loss increased by approximately 15% when stress levels were maximized in factors. Independent of can coating, when initial carbonation and mineral content were raised simultaneously, the carbonation loss rate was increased by more than 80% at mid-range levels and more than 150% at high levels compared to low initial carbonation and low mineral content samples.

Initial 10-minute carbonation loss was greater in samples where the mineral content was increased versus the samples where the initial carbonation level was increased, when tested with the same internal coating. This is indicative that although the morphology of the coating is important to nucleation and the initial formation of the bubbles, the chemistry of the beverage plays a significant role. Changes in the beverage chemistry dictate the likelihood the bubble will be released after nucleation, the stability of the bubble, and the size of the bubble that are released. Varying bubble size will affect the amount of carbonation lost. Beverage chemistry coupled with pressure highly influence the rate of bubbles released.

Previously these factors have been studied separately within the can and beverage industry. However, the different factors were tested together in these experiments demonstrating that this rapid de-carbonation phenomenon is driven by multiple factors and the interactions between the separate factors. The carbonation loss rate increased as the

stress level of each factor was increased. Specific internal coating morphology, higher levels of mineral content and higher initial carbonation were all identified in the results section as key performance indicators. The results also support the effect of individual factors demonstrated in past internal studies that indicated higher levels of initial carbonation and different internal can coatings affect the carbonation loss rate in canned carbonated beverages.

Remarkable qualitative changes in the internal can coating were observed through the shelf life of the canned beverage. Can-coating surface roughness increases over time with the greatest increase in surface roughness observed from the time the can was empty to 24 hours after filling. Over time, deposits high in nitrogen content believed to come from the caramel colorant appeared on the can coating surfaces. The deposits were more pervasive on the epoxy-based coatings than the acrylic-based coatings. Both observations were surprising to find on coatings that are largely viewed to be inert by the industry. These findings highlight the importance of including the internal can coating and its interactions when studying can beverage systems. This variant has been often overlooked in the past.

The deposits may play a role in the evolution of the foaming de-carbonation phenomena. Around two weeks after filling, the foaming type of de-carbonation disappears at the same time pervasive deposits were observed on the epoxy-based coatings. These deposits may act as a barrier preventing interaction between the internal coating and beverage. The geometry of the coating surface is thus altered by the deposits and becomes unfavorable for nucleation.

Although the experiments demonstrated the individual and synergistic effects of several factors on the rate of carbonation loss in canned carbonated beverages, the foaming type of rapid de-carbonation was not reproduced during these experiments in the laboratory. The parameters used for the studies were not conducive to the formation and stabilization of foams. Further testing to characterize and measure surface topography of the internal coatings is recommended. Testing that will enable a quantitative analysis of surface defects that contribute to rapid de-carbonation is vital. Also further experiments of different types of beverage ingredients, including minerals found in water beyond calcium chloride and magnesium chloride would enable a better understanding of the effects of ingredients on the foaming type of rapid de-carbonation.

The phenomenon of rapid de-carbonation is currently not fully understood within the industry. The industry has attempted to control this problem by altering factors independently in isolation. The results from these experiments demonstrate that the industry will need to look at rapid de-carbonation holistically, rather than attempting to attribute the driving force to any one single factor. While each factor does have a significant effect on rapid de-carbonation, the combined effect of factors increased carbonation loss rate by more than 150% compared to samples with the lowest stress levels.

REFERENCES

1. S. Jones, G. Evans, K. Galvin, Bubble nucleation from gas cavities—a review. *Advances in colloid and interface science* **80**, 27-50 (1999).
2. G. Navascués, L. Mederos, Theoretical analysis of heterogeneous nucleation data: Effects of line tension. *Surface Technology* **17**, 79-84 (1982).
3. S. N. Leung, C. B. Park, A. Wong, Spe, Ed. (CANADA, 2007).
4. T. S. Coffey, Diet Coke and Mentos: What is really behind this physical reaction? *American Journal of Physics* **76**, 551-557 (2008).
5. M. J. Rosen, J. T. Kunjappu, *Surfactants and Interfacial Phenomena*. (John Wiley & Sons, Hoboken, 2012).
6. K. Koczó, L. A. Lobo, D. T. Wasan, Effect of oil on foam stability: Aqueous foams stabilized by emulsions. *Journal of Colloid and Interface Science* **150**, 492-506 (1992).
7. G. Liger-Belair, The Physics and Chemistry behind the Bubbling Properties of Champagne and Sparkling Wines: A State-of-the-Art Review. *Journal of Agricultural and Food Chemistry* **53**, 2788-2802 (2005).
8. M. Firouzi, T. Howes, A. V. Nguyen, A quantitative review of the transition salt concentration for inhibiting bubble coalescence. *Advances in colloid and interface science*, (2014).
9. S. Jones, K. Galvin, G. Evans, G. Jameson, Carbonated water: the physics of the cycle of bubble production. *Chemical engineering science* **53**, 169-173 (1998).
10. D. S. Lee, K. L. Yam, L. Piergiovanni, *Food Packaging Science and Technology*. (Taylor & Francis, 2008).
11. Cans for Fans – Production Process. Ball Can Corporation Europe, from http://www.ball-europe.com/382_791_ENG_PHP.html
12. Wootton, E., Deutschland GmbH, A., & Göttingen. (1994). *Case Study on Can Making* (Rep. No. TALAT Lecture 3710). Retrieved January 10, 2017, from <http://core.materials.ac.uk/repository/eaa/talat/3710.pdf>.
13. R. P. Singh, D. R. Heldman, in *Introduction to Food Engineering (Fifth Edition)*. (Academic Press, San Diego, 2014), pp. 617-644.
14. S. S. Zumdahl, *Chemistry*. (DC Health and Company, ed. 6th, 1986).
15. Z. W. Wicks, F. N. Jones, S. P. Pappas, D. A. Wicks, in *Organic Coatings*. (John Wiley & Sons, Inc, ed. 3rd, 2006), pp. 271-294.
16. E. F. Efsa Panel on Food Contact Materials, A. Processing, Scientific Opinion on the risks to public health related to the presence of bisphenol A (BPA) in foodstuffs. *EFSA Journal* **13**, (2015).

17. **Notice of Proposed Rulemaking and Announcement of Public Hearing Amendment to Section 25603.3, Title 27, California Code of Regulations, Warnings for Exposures to Bisphenol A from Canned and Bottled Foods and Beverages. (2016, December 01). Retrieved January 10, 2017, from <http://oehha.ca.gov/proposition-65/crn/notice-proposed-rulemaking-and-announcement-public-hearing-amendment-section>**
18. ASM Handbook Vol. 22A, Fundamentals of Modeling for Metals Processing D. U. Furrer and S. L. Semiatin (Eds.), pp. 203-219.
19. A. Puntis, *Introduction to Mineral Sciences*. (Cambridge University Press, 1992).
20. V. G. Dubrovskii. (Springer Berlin Heidelberg, 2014), Chapter 1, Fundamentals of Nucleation Theory.
21. M. A. Chappell, S. J. Payne, The effect of cavity geometry on the nucleation of bubbles from cavities. *The Journal of the Acoustical Society of America* **121**, 853-862 (2007).
22. B. Steer, B. Gorbunov, J. Rowles, D. Green, Surface area controlled heterogeneous nucleation. *The Journal of chemical physics* **136**, 054704 (2012).
23. S. N. Leung, A. Wong, C. B. Park, J. H. Zong, Ideal surface geometries of nucleating agents to enhance cell nucleation in polymeric foaming processes. *Journal of applied polymer science* **108**, 3997-4003 (2008).
24. A. Hienola *et al.*, Estimation of line tension and contact angle from heterogeneous nucleation experimental data. *The Journal of chemical physics* **126**, 094705 (2007).
25. R. D. Gretz, The line-tension effect in heterogeneous nucleation. *Surface Science* **5**, 239-251 (1966).
26. M. Lazaridis, M. Kulmala, B. Z. Gorbunov, Binary heterogeneous nucleation at a non-uniform surface. *Journal of Aerosol Science* **23**, 457-466 (1992).
27. W. Kamuf, A. Nixon, O. Parker, G. Barnum Jr, Overview of caramel colors. *Cereal foods world* **48**, 64 (2003).
28. H. D. Belitz, M. Burghagen, W. Grosch, P. Schieberle, *Food Chemistry*. (Springer Berlin Heidelberg, 2004).
29. B. H. Licht *et al.*, Characterization of Caramel Colour IV. *Food and Chemical Toxicology* **30**, 365-373 (1992).
30. G. Sengar, H. K. Sharma, in *Journal of Food Science and Technology*. (2014), vol. 51, pp. 1686-1696.
31. Trivett, B. (2003, December 10). *THE RIGHT WATER CHEMISTRY: UNDERSTANDING THE AQUEOUS INFLUENCE UPON METALWORKING FLUID PERFORMANCE* (Tech.). Retrieved January 10, 2017, from PICO Chemical 32. R. Battino, H. L. Clever, The solubility of gases in liquids. *Chemical Reviews* **66**, 395-463 (1966).

33. P. K. Weissenborn, R. J. Pugh, Surface Tension of Aqueous Solutions of Electrolytes: Relationship with Ion Hydration, Oxygen Solubility, and Bubble Coalescence. *Journal of Colloid and Interface Science* **184**, 550-563 (1996).
34. Y. Zhang, M. Wang, X. Lin, W. Huang, Effect of substrate surface microstructure on heterogeneous nucleation behavior. *Journal of Materials Science & Technology* **28**, 67-72 (2012).
35. A. Salis, B. W. Ninham, Models and mechanisms of Hofmeister effects in electrolyte solutions, and colloid and protein systems revisited. *Chemical Society Reviews* **43**, 7358-7377 (2014).
36. E. Lima, B. de Melo, L. Baptista, M. Paredes, Specific ion effects on the interfacial tension of water/hydrocarbon systems. *Brazilian Journal of Chemical Engineering* **30**, 55-62 (2013).