

CRC Report No. CM-136-15-1

**INVESTIGATION INTO
FILTER PLUGGING DUE TO
SULFATE SALT CONTAMINATION OF
ETHANOL, GASOLINE, AND
GASOLINE-ETHANOL BLENDS**

January 2018



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FINAL REPORT

Investigation into Filter Plugging Due to Sulfate Salt Contamination of Ethanol, Gasoline, and Gasoline-Ethanol Blends

CRC Project CM-136-15-1

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January 17, 2018

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1. Executive Summary

During the early- to mid-2000's, several reported instances of fuel injector deposit formation and filter plugging occurred with gasoline-ethanol fuel blends. Investigation of these problems revealed the presence of fuel-insoluble, inorganic sulfate salts, with sodium sulfate being most frequently identified. Although a clear understanding of sulfate sources was lacking, there was strong evidence that most of the sulfate contaminant originated in the ethanol component of the fuel blends. Based upon information available at the time, ASTM established a maximum limit of 4 ppm (by weight) of inorganic sulfate as part of the Standard Specifications for Denatured Fuel Ethanol (ASTM D4806). Following incorporation of this sulfate specification into ASTM D4806, field problems related to sulfate deposits disappeared.

These earlier field problems occurred primarily with gasoline blends containing 10 vol.% ethanol (E10). Current interest in using higher ethanol blend gasolines (e.g. E15-E30) has generated concerns that the earlier field problems with sulfate deposits could recur. Thus, this project was undertaken to gain a better understanding of sulfate contaminant issues in gasoline-ethanol fuel blends. A combination of literature review and experimental work was conducted to investigate possible sources of sulfate contaminants, solubilities of sulfates in ethanol and gasoline, and fuel factors that may contribute to formation of insoluble sulfate deposits.

A review of ethanol plant operations was conducted to identify possible sources of sulfate in the final, denatured ethanol product. Based upon literature information and personal conversations with plant operators, use of bisulfite within the plant's fermentation scrubber was identified as one possible source. Non-optimized operation of the scrubber system can result in the presence of solubilized, reduced forms of inorganic sulfur (SO_2 , bisulfite, and sulfite), which can distill with the ethanol. Other sources of volatile sulfur oxides within ethanol plants may also be involved. For instance, sulfurous acid (H_2SO_3 - which is chemically equivalent to SO_2 in water) is used in the steeping process in wet mill plants. Subsequently, such "potential sulfate" species can undergo oxidation to produce insoluble sulfate salts in fuel blends. The presence of such reduced sulfur species is not detected by the existent sulfate methods as usually employed to comply with the 4 ppm maximum standard in ASTM D4806.

A series of laboratory experiments was conducted to address three principal questions: (1) What is the solubility of selected sulfate salts in anhydrous, 200-proof ethanol containing varying amounts of water? (2) What is the solubility of selected sulfate salts in low- and high-aromatics gasolines containing various detergent additives? (3) What can be learned about the solubility and filter plugging potential of sulfate salts when added in low concentrations to gasoline-ethanol blends?

To determine the solubility of sulfate salts in ethanol and gasoline, solid anhydrous salts were vigorously stirred in the appropriate solution before filtering to remove the undissolved salt. The filtrates were analyzed by ion chromatography (IC) to measure the concentration of solubilized sulfate. Solubility/filtration experiments in 200 proof ethanol were conducted with four anhydrous sulfate salts (ammonium, calcium, potassium, and sodium), along with sodium bisulfite. In agreement with literature reports, the solubilities of calcium, potassium, and sodium sulfates were shown to be extremely low (<1 ppm), and unaffected by inclusion of 2 wt.% water in the ethanol.

The effect of temperature (5° vs. 25°C) on the solubility of sodium sulfate in ethanol was found to be negligible. The solubility of ammonium sulfate appeared to be an order of magnitude higher (~10 ppm), although high experimental variability creates some uncertainty about this conclusion.

The solubility of sodium bisulfite in ethanol was much higher than that of the sulfate salts, being at least 100 ppm at 25 °C. The solubility was slightly lower at 5 °C and slightly higher with addition of 2 wt.% water to the ethanol. As expected, much larger differences between existent and potential sulfate concentrations were observed in the sodium bisulfite solutions than in any of the sulfate salt solutions. Upon extended storage at room temperature (1-3 months), filtrate solutions from the sodium bisulfite experiments became noticeably cloudy, whereas filtrates from all sulfate salt experiments remained bright and clear. This cloudiness is thought to be due to the gradual oxidation of soluble bisulfite, to produce insoluble sulfate.

Particle number counts in discrete size ranges were measured in all ethanol/salt solutions using a Seta Analytics SA1000 automatic particle counter (APC). Although precise quantification of particle counts was difficult due to high experimental variability, useful semi-quantitative results were obtained. Before filtration, the ethanol solutions containing each of the five salts examined had particle counts in excess of 10^4 /mL, although they all appeared clear and bright to the human eye. Filtration reduced the number of particles by at least an order of magnitude. No substantial differences were seen among the five salts used, and no significant effects of temperature or water addition were found.

Solubility/filtration experiments in gasoline were conducted with two salts: sodium sulfate and sodium bisulfite. Two different non-oxygenated base gasolines were used: one having low aromatics content (1 vol.%); the other having high aromatics content (40 vol.%). Besides the base gasolines, samples were prepared containing two different detergent additives: one being a polyether amine (PEA); the other being a polyisobutyl amine (PIBA). Two additive dosage levels were used: one corresponding to fuel requirements of “lowest allowable concentration” (LAC); the other corresponding to the minimum requirements for TOP TIER™ Detergent Gasoline. Results showed the solubility of both sodium sulfate and sodium bisulfite in gasoline to be extremely low (< 1 ppm), with no large effects seen for aromatics level, additive type, or additive dosage.

An important observation is that the solubility of sodium bisulfite is at least 2-orders of magnitude higher in ethanol than in gasoline. This raises the possibility that blending of ethanol contaminated with solubilized sodium bisulfite into gasoline could result in de-solubilization of the salt, and formation of deposits in the gasoline-ethanol blend. This situation could be mitigated by limiting potential sulfate concentrations in ethanol, not just existent sulfate.

A series of experiments was planned in which ethanol containing low levels of sodium sulfate was used to produce E10, E15, and E30 fuels with various gasoline blendstocks. However, when preparing the sulfate-dosed ethanol by spiking with small amounts of a concentrated aqueous sulfate stock solution, the observed solubility of sodium sulfate was much higher than expected based upon previous solubility experiments using the anhydrous salt. It is hypothesized that this behavior resulted from conversion of anhydrous sodium sulfate to the hydrated form, sodium sulfate decahydrate, upon dissolution in water. The solubility of the decahydrate in both ethanol and

gasoline was shown to be considerably higher (by at least an order of magnitude) than that of the anhydrous form.

The large differences in solubility between hydrous and anhydrous forms of sulfate salts, and the possibility of converting from one form to another, make determination of solubility under real-world conditions quite difficult, and may contribute to the seemingly inconsistent and sporadic nature of the sulfate-related field problems originally reported. These complexities may also obscure any smaller solubility effects due to temperature, ethanol blending ratio, detergent additive, or other fuel factor.

The experimental efforts undertaken in this project to address the topic of sulfates in gasoline-ethanol fuel blends have proven to be more complex than originally thought. Despite great care taken in conducting the numerous laboratory experiments of this project, the results are unable to confirm (or refute) the suitability of the current ASTM sulfate specification for fuel ethanol. For further examination of this issue, it is recommended that larger-scale experiments be conducted, including filtration of realistic fuel blends under conditions that better represent real-world situations. A final recommendation is that monitoring of sulfate concentrations in ethanol for compliance with the current ASTM D4806 specification should include measurement of both existent and potential sulfate.

2. Introduction and Background

The use of ethanol as a transportation fuel has expanded greatly over the past two decades. Today, almost all U.S. gasoline contains 10 vol.% ethanol (E10), while small amounts of E15 are also used, as well as higher concentration ethanol blends such as flex fuel (E85). Nearly all fuel ethanol in the U.S. is produced by fermentation of corn starch, conducted in approximately 200 corn-ethanol biorefineries. Collectively, these biorefineries utilize 40-45% of the total U.S. corn crop and produce about 15 billion gallons/year of ethanol. The corn ethanol production trend over the past 35 years is shown below in Figure 1.

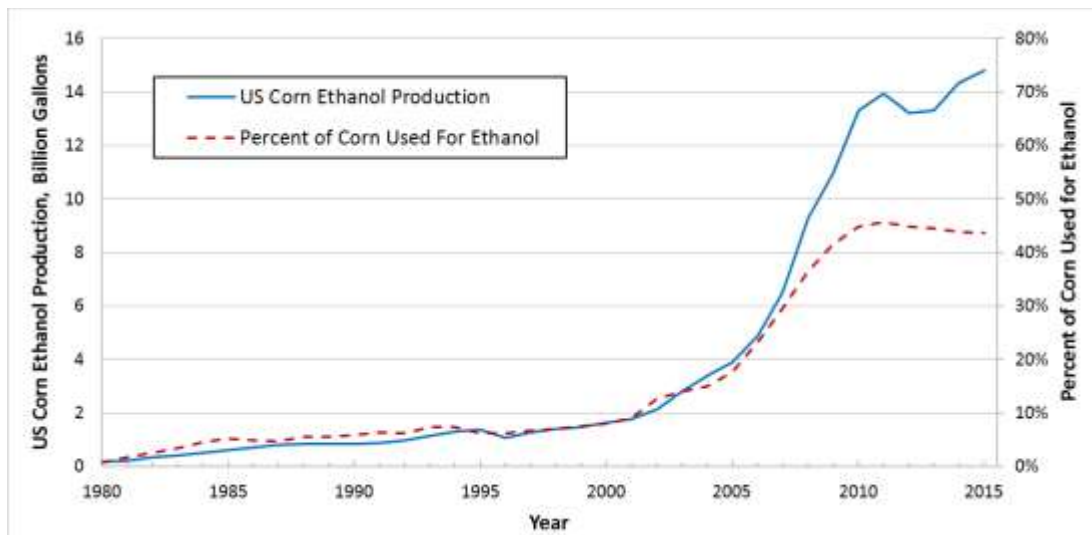


Figure 1. Corn ethanol production in the U.S.

Ethanol production data from RFA: <http://www.ethanolrfa.org/pages/statistics#>

Corn use data from USDA-ERS: <http://www.ers.usda.gov/topics/crops/corn/background.aspx>

2.1. Earlier sulfate problems

During the period of rapid expansion of U.S. ethanol production and use in the early- to mid-2000s, there were several reported instances of clogging/plugging of filters used in gasoline distribution and dispensing systems. In addition, sticky deposits were observed in fuel injectors and plugging of fuel filters in some vehicles. A recent report by NREL provides a more complete discussion of these field problems.¹ It is also understood that while the filter-plugging problems at fuel terminals and retail stations were a significant nuisance, formation of engine deposits and the resulting vehicle operational problems were the most significant issue. Although the causes of these problems were not determined unequivocally, evidence suggested that they were related to high levels of sulfate contamination in denatured ethanol that was blended into finished gasoline. In some cases, gelatinous or “gummy” deposits were reported. Other reports hypothesized that molecular complexes between gasoline detergent additives and sulfates may be involved. Several reported laboratory analyses of deposits were inconclusive as to the chemical composition of the filter-plugging deposits, although sulfates in general – and sodium- and ammonium-sulfate in particular – were identified. (See description of field problems documented below in Section 3.1.)

Based on information presented by various fuel producers, suppliers, and users, ASTM modified the Standard Specification for Denatured Fuel Ethanol (ASTM D4806²) in 2005 to include a maximum specification of 4 ppm (by mass) for “existent sulfate” in denatured fuel ethanol. Along with this new sulfate specification, the following language regarding the “Significance of Specified Properties” was added to D4806: “The presence of small amounts of inorganic sulfates in denatured fuel ethanol under the right conditions can contribute to turbine meter deposits and the premature plugging of fuel dispensing pump filters in the fuel distribution system. The sulfates also have been shown to cause fuel injector sticking resulting in engine misfiring and poor driveability in automobiles.”

Following modification of ASTM D4806, field problems in the U.S. involving filter plugging and injector deposits disappeared. This development reinforced the hypothesis that high levels of sulfate in denatured alcohol were responsible for the problems. It is also possible that the situation improved due to increased experience and maturity within the corn-ethanol industry. The observed field problems coincided with the early stages of a period of rapid increase in ethanol production, as shown in Figure 1. During this time, many new ethanol biorefineries were coming on-line, and many others were being expanded or operated more aggressively. While correlation does not imply causation, it is possible that initial, sub-optimal operation of some biorefineries led to high sulfate contaminant levels in ethanol. Other factors – including modifications to blending practices and changes in additive packages – may also have contributed to the disappearance of field problems.

Because implementation of the sulfate specification in ASTM D4806 appeared to solve the problem, further investigation into the sources of sulfates (and their associated cations) was not conducted, nor was any formal research program undertaken to define acceptable levels of sulfate salts in denatured ethanol. However, current interest in using higher ethanol blend gasolines has renewed awareness of these earlier problems, and raised concerns that they could re-appear. This has also created interest in developing a more complete mechanistic understanding of how these filter-plugging deposits form.

2.2. Project objectives

While this research project has several objectives, the principal one is to improve understanding of the formation of sulfate salt deposits in ethanol, and in fuels containing ethanol. Factors thought to be important in causing the formation of these deposits were investigated, including concentration of dissolved sulfate, cations associated with the sulfate, water content, ethanol blending ratios, temperature, gasoline detergent additives, and gasoline aromatics content. Another objective is to develop a better understanding of how these factors influence filterability of fuel, and to develop guidance to avoid plugging issues and vehicle performance problems in the field if higher ethanol blend fuels were to be used in the future. These objectives were met by a combination of two sets of activities: (1) literature research and review and (2) laboratory experiments. Both of these activity sets are described below.

3. Literature Research and Reviews

While sulfate salts are highly soluble in water, most are considered insoluble in ethanol and gasoline. Reported data regarding experimentally measured solubility of sulfate salts in organic solvents is sparse. One highly cited source of information regarding the solubility of sodium sulfate (Na_2SO_4) in ethanol comes from a compilation of data by Stephen and Stephen, who reported a molar solubility

of 0.00143% at 20 °C.³ This value translates to a solubility of ~44 ppm (w/w), which seems much too high (for anhydrous Na₂SO₄), considering other information sources, including measurements made as part of the present project. Within the same Stephen and Stephen source, the solubility of Na₂SO₄ in ethanol at 50 °C is reported as ~35 ppm (w/w) – a lower value than at 20 °C, which does not seem likely.

The presence of water in ethanol is known to increase the solubility of Na₂SO₄, although a rather large amount of water (several percent) is required before the effect is noticeable. Vener and Thompson reported that with 20% water in ethanol, the solubility of Na₂SO₄ at 25 °C was only ~20 ppm.⁴ Another historical compilation of data reports the solubility of Na₂SO₄ in ethanol containing 28% water to be 0 g/g.⁵ A more recent source reported the solubility of Na₂SO₄ in pure methanol at 20 °C to be 170 ppm.⁶ Other than the recent European information referenced later in this report, we are not aware of any published studies in which the solubility of Na₂SO₄ (or other sulfates) has been investigated in gasoline-ethanol fuel blends.

Literature research and reviews were conducted as part of the present study to gain a better understanding of reported field problems with sulfates in fuels, to identify potential sources of sulfates in commercially-produced ethanol, and to investigate other relevant studies pertaining to sulfates in fuels. Each of these areas is described below in further detail.

3.1. Documented field problems

Prior to establishment of the existent sulfate limit of 4 ppm in ASTM D4806, numerous reported field problems were attributed to sulfate contamination of ethanol that was blended into gasoline. During the ASTM ballot procedure that eventually led to this sulfate specification, several opportunities existed to share information regarding sulfate contamination problems and potential solutions. The presence of sulfates in fuels was quite surprising, as there are no obvious sources of such contaminants. However, because sulfate salts are virtually insoluble in ethanol and gasoline, the formation of harmful, solid deposits would be expected to occur at very low sulfate levels.

Some of the most comprehensive information sharing occurred during an open forum on “Sulfates in ethanol and their effects in the field,” which was held at the June 2005 meeting of ASTM Subcommittee D02.A (Gasoline and Oxygenated Fuel).⁷ During this open forum, five formal presentations were given by fuel suppliers, automakers, and representatives of the ethanol industry. These presentations were posted on the ASTM website, and may still be available for viewing and downloading by ASTM members. The following paragraphs summarize the main points from these five presentations:

- Fuel Supplier A reported fuel filter plugging problems in 2003 at service stations in the St. Louis, Chicago, and Los Angeles areas. Varying levels of sulfate were measured in several dozen ethanol shipments. Concentrations ranged from below 1 ppm to over 8 ppm, with a median value near 2 ppm. In contrast, nearly all gasoline samples (E0) had sulfate levels below detection limits. Sodium sulfate was determined to be the main constituent on several filters, and was detected in tank water bottoms. The problems with sulfate contamination were rather sporadic and unpredictable, and the sources of sulfate were not well understood, although there seemed to be an inverse correlation between pH_e level of the ethanol and

sulfate concentrations. [At lower pH_e levels (more acidic) higher sulfate concentrations in ethanol were observed.]

- Fuel Supplier B reported intermittent retail fuel filter plugging problems in Chicago, Milwaukee, and Minnesota in 2003-2004. While initial inspections of filters were inconclusive as to the cause of plugging, subsequent analyses implicated a combination of sodium sulfate and ammonium sulfate. Some individual customer complaints about poor vehicle driveability were shown to be due to fuel injector sticking. Like Fuel Supplier A, Supplier B also analyzed several dozen samples of ethanol and gasoline (E0). Sulfate levels in E0 were generally not detectable, while in ethanol they ranged from less than 1 ppm to more than 8 ppm, as shown in Figure 2, which comes from a data chart presented by Fuel Supplier B. It was also thought that gasoline detergent additives could be complexing with sulfate anions in the ethanol, resulting in deposition of sulfate salts. Fuel Supplier B developed an internal target specification limit for sulfate in ethanol, which helped to identify a high sulfate ethanol supplier in the Milwaukee area. Once this problem was corrected, sulfate levels were reduced significantly, and reported field problems disappeared.

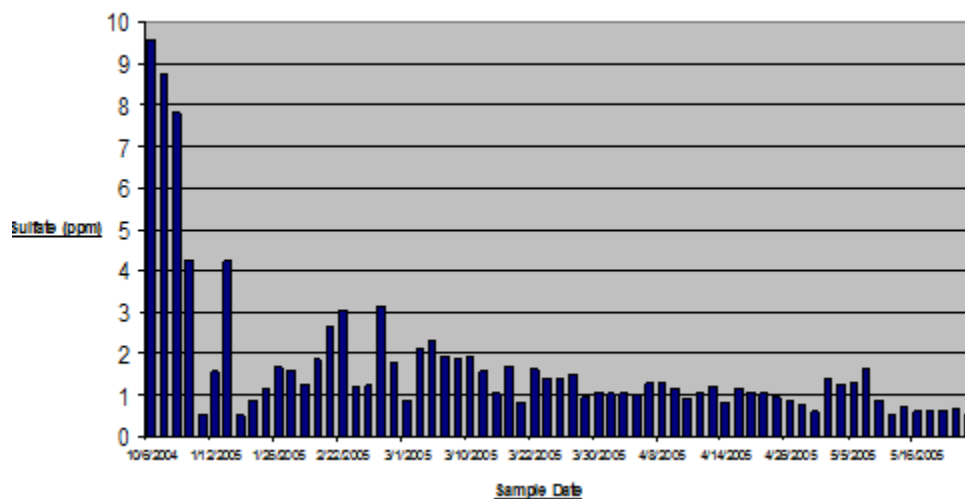


Figure 2. Sulfate concentrations measured in fuel ethanol during 2004-2005.

(Reported by Fuel Supplier B during Open Forum session at the June 2005 meeting of ASTM Subcommittee D02.A)

- Automaker A reported on their experiences with fuel injector performance problems, also in the Milwaukee area during the same time period (2004) as reported by the fuel suppliers. Injector sticking problems had led to numerous customer complaints involving several vehicle models and two types of port fuel injectors (PFIs). Inspection of stuck injectors revealed deposits on internal components, including the valve ball/seat area and the valve core area. Chemical analyses of these deposits showed the presence of sodium sulfate, and possibly calcium and ammonium sulfates. It was noted that following Fuel Supplier B's change in their Milwaukee ethanol policy, these injector-related service complaints largely disappeared.

- Automaker B reported that they had experienced a significant increase in fuel injector problems in the Phoenix area during the Fall of 2003, after introduction of ethanol-containing gasoline. Areas outside of Phoenix, which did not require ethanol fuels, did not experience the same level of problems. In some cases, Automaker B's injectors were found to be stuck in the closed position. Increased plugging of fuel filters was also noted, with "gummy" or "gelatinous" material being found in some cases. Based on their laboratory analyses, Automaker B believed that sulfate contamination was the primary contributor to these incidences of fuel injector sticking, filter plugging, and fuel pump failures.
- The Ethanol Industry stressed that the reported problems with filter plugging and injector fouling were very sporadic and difficult to attribute to specific causes. It was noted that ethanol had been blended into gasoline for over 25 years, without problems, until recently, and it was not clear what (if anything) had changed over time with ethanol, gasoline, engine hardware, or other factors that could lead to these reported field problems. It was pointed out that there were difficulties in analytical procedures for measuring sulfate in ethanol, and that a need existed to develop an appropriate ASTM test method. The ethanol industry also emphasized that before considering a specification for sulfate in ethanol, it was necessary to establish the level at which sulfate contaminants become a problem.

Subsequent to this open forum meeting, a normal ASTM ballot procedure was introduced to add a 1 ppm maximum limit on sulfate to D4806-04. In working through the ballot procedure, a consensus was reached by the auto, petroleum, and ethanol industries that the near-term sulfate limit should be 4 ppm. It should be mentioned that very little information was available upon which to define a specific sulfate level that would provide acceptable performance in the field. Based upon sulfate measurements of many batches of fuel ethanol (such as those shown in Figure 2) it was thought that 4 ppm was an achievable standard that would eliminate the few exceptionally high sulfate levels that were believed to have caused most of the field problems. Further discussion about these ASTM actions is provided in a recent NREL report.¹

The 4 ppm sulfate specification that was adopted is based on "existent sulfate," not "potential sulfate." Existent sulfate refers to inorganic sulfate anions (SO_4^{2-}) actually present in the sample at the time of analysis, with no oxidation treatment. Potential sulfate refers to total inorganic sulfate species present after the sample has been reacted with an oxidizing agent. Potential sulfate includes less highly oxidized forms of sulfur, such as SO_2 , HSO_3 , and SO_3 , which have the potential to oxidize into sulfate. It is important to note that the ion chromatographic (IC) methods used to characterize fuel ethanol (D7319⁸ and D7328⁹) are only able to quantify sulfate ions (SO_4^{2-}). Thus, existent sulfate is measured directly by IC. To determine potential sulfate, an extra oxidation step involving addition of hydrogen peroxide is included, such that SO_2 and SO_3 are converted to SO_4 prior to the IC analysis.

3.2. Potential sources of sulfates in fuels

Total sulfur levels in gasoline have been of concern for many years. EPA's Tier 2 gasoline specifications, which began in 2004, limited average gasoline sulfur levels to 30 ppm. Tier 3 gasoline specifications, which began in 2017, limit average gasoline sulfur levels to 10 ppm. Sulfur-containing compounds that are naturally present in petroleum product streams are almost entirely

organic, such as thiols, organosulfides, and thiophenes. These compounds are stable in the fuels, and do not readily oxidize to form sulfates. In fact, gasoline analyses that were conducted along with analyses of the ethanol batches described above demonstrated negligible sulfate levels in petroleum fuels. Thus, it is reasonable to assume that the dominant sources of sulfates observed in gasoline-ethanol blends originate from the ethanol component of the blend.

To investigate potential sources of sulfur in corn ethanol, a conventional search of the technical literature was conducted, utilizing the Web of Science (WOS) searching tools, as well as searching trade literature and websites. This approach was not very successful in obtaining the type of detailed information regarding facilities and processes that would be most useful in identifying potential sources of sulfate in ethanol production plants. Because of this, operators of 18 corn ethanol plants and 2 service providers to the bio-refinery industry were contacted (by phone) to gain further information. Taken together, these information sources have provided a much clearer picture of where sulfur-containing compounds appear within corn ethanol plants, and how sulfate contamination in gasoline-ethanol blends could result.

Due to concerns about total fuel sulfur levels, ASTM D4806 currently includes a maximum sulfur specification of 30 ppm for fuel ethanol. This limit may be reduced in the future, when Tier 3 gasoline specifications cap average total sulfur levels at 10 ppm. However, much of the total sulfur in ethanol occurs in organic form, similar to petroleum fuels, and thus is not believed to contribute significantly to sulfate formation. A significant source of total sulfur in ethanol can be from natural gasoline used as denaturant. Another external sulfur source can be corrosion inhibitors, which are usually added to fuel ethanol.

Corn kernels typically contain about 0.1 wt.% sulfur, mostly in the form of the amino acids cysteine and methionine, shown in Figure 3.¹⁰ This organic sulfur is concentrated by a factor of 2-3 during the ethanol-production process, but nearly all of it ends up in the distillers dried grains with solubles (DDGS) fraction, not in the ethanol product stream.

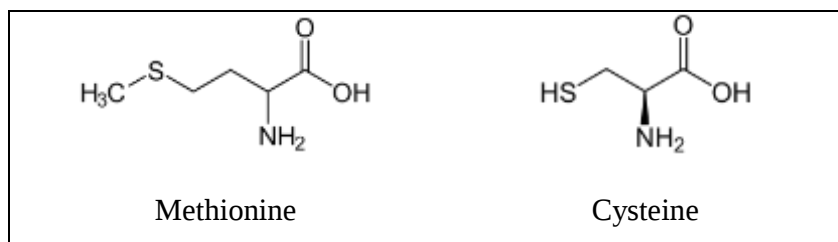


Figure 3. Forms of organic sulfur present in corn kernels

Corn ethanol in the U.S. is produced in two types of processing plants: wet mill and dry mill plants.¹¹ Rough schematics of these two processes are provided in Figure 4. From a sulfur standpoint, a significant difference between wet and dry mill plants is the use of sulfurous acid (H₂SO₃; also known as aqueous SO₂) in the steeping process used in wet milling operations.^{12,13,14} However, we are unaware of any identified pathway by which this sulfurous acid would carry over into the final ethanol product, although such a possibility cannot be ruled out.

Both types of corn ethanol plants use considerable amounts of sulfuric acid (H₂SO₄) – mainly employed for two purposes. First, it is used within the fermentation process to maintain proper pH

levels for optimum enzymatic performance and to minimize unwanted bacterial growth. If the pH varies too much from optimum levels, enzymatic activity will decrease, or even stop.^{11,15} Second, sulfuric acid is used within the distillation process to prevent occurrence of mineral deposits that form scale on heat exchangers.^{10,16} Without use of sulfuric acid, heat exchanger efficiency is reduced and more frequent cleaning is required. Although considerable amounts of sulfuric acid are used in these two applications, it is unlikely that these sources contribute significantly to sulfates in the final ethanol product. This is because sulfates are non-volatile and highly water-soluble, thus they end up in by-product streams, not in the volatile ethanol product stream. However, these sulfates could be of concern if excessive levels occur in the DDGS product that is used for animal feed.^{17,18}

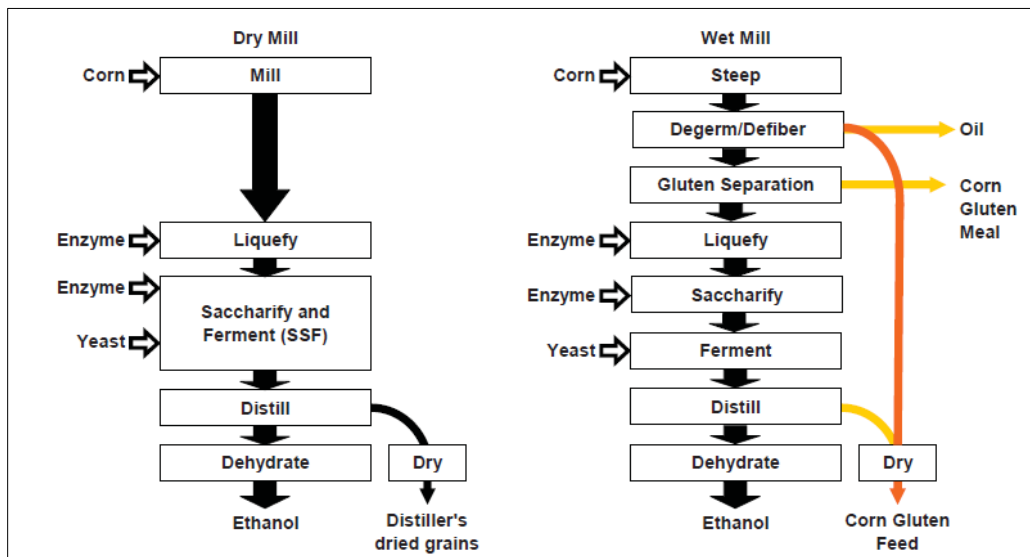


Figure 4. Schematics of dry (left) and wet (right) mill processes for ethanol production

A possible cause of sulfate contamination in the ethanol product could result from bisulfite (HSO_3^-) treatment within the ethanol plant's fermentation scrubber system. The primary purpose of this scrubber is to recover additional ethanol that would otherwise be vented along with the fermentation by-product, CO_2 . A schematic of the process water system for a typical corn ethanol plant is shown in Figure 5, where the location of the scrubber is highlighted with a red oval. Although not shown in this figure, the aqueous scrubber bottoms are usually routed to the front end cooking process, although historically, some plants may have routed them to the distillation process.

In addition to ethanol and CO_2 , small amounts of acetaldehyde and acrolein are also emitted from the fermentation process. These aldehydes are classified as hazardous air pollutants (HAPs), thus their emissions must be controlled. According to the sources we spoke with, the need to control these aldehyde emissions became critical in the mid- to late-2000's, as larger ethanol plants were being built and additional EPA emissions regulations were being introduced during this time. The preferred means of aldehyde control involves the well-known reaction with sodium bisulfite.¹⁹ In the case of acetaldehyde (CH_3CHO), reaction with sodium bisulfite (NaHSO_3) forms the adduct, 1-hydroxyethane sulfonic acid salt ($\text{CH}_3\text{CH}(\text{OH}) \text{SO}_3^- \text{Na}^+$), as shown below in Eq.1. An analogous reaction occurs with acrolein to produce another sulfonic acid salt.



Within an ethanol plant, a concentrated aqueous solution of sodium bisulfite is injected near the top of the fermentation scrubber. The fermentation gas enters the bottom of the scrubber, thus contacting the bisulfite in a counter-current fashion. Because the organo-sulfonic acid adduct products are water soluble and have much lower volatility than the original aldehydes, they are removed from the scrubber in the water bottoms. While sodium bisulfite was originally the reducing agent of choice, ammonium bisulfite (NH_4HSO_3) is more commonly used today.

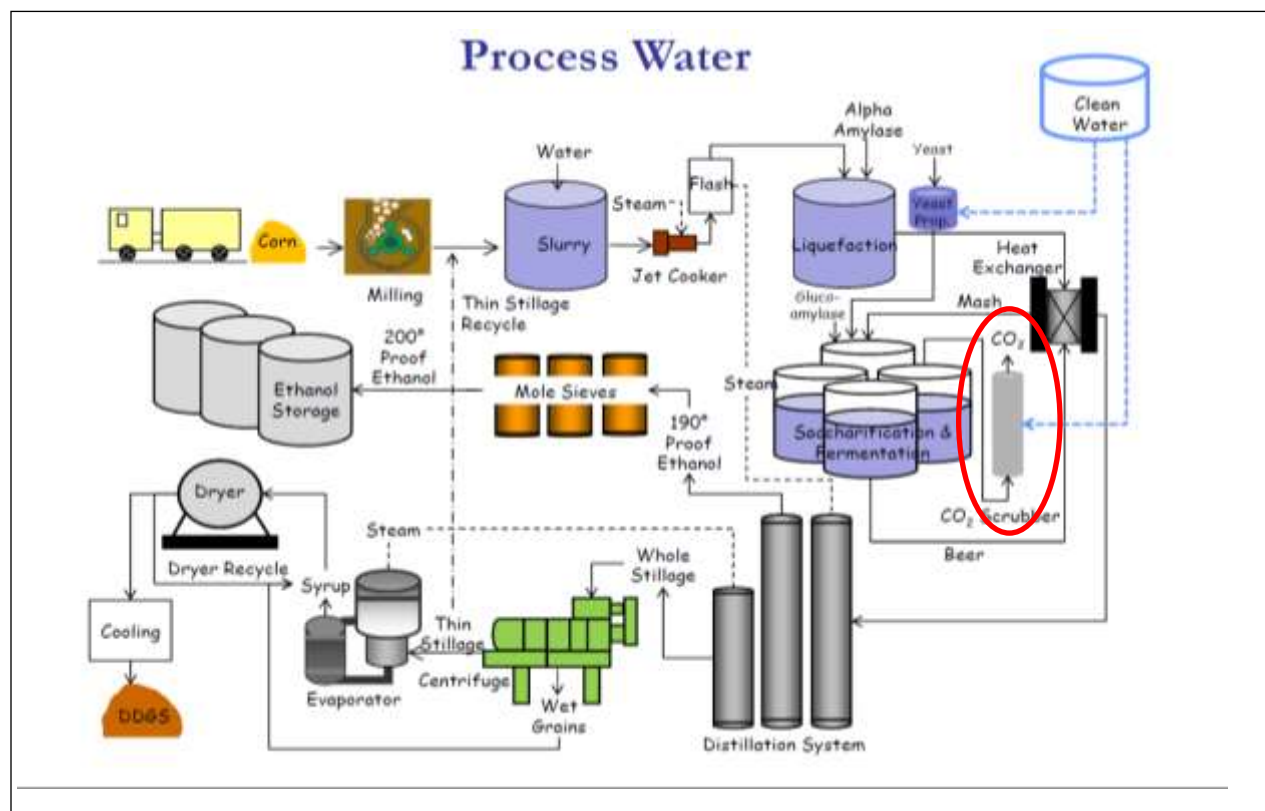


Figure 5. Schematic of process water system in a corn ethanol biorefinery.

(Taken from V. Singh, Illinois Water Conference, Oct. 2008.²⁰ Scrubber unit highlighted with red oval.)

To drive Equation 1 to the right, and minimize the amount of aldehydes escaping the scrubber, excess bisulfite is sometimes used. However, this can lead to problems, particularly at low pH levels. Under such conditions, excess bisulfite can produce sulfurous acid (H_2SO_3), which is chemically equivalent to sulfur dioxide (SO_2) in water. At low pH, the equilibrium shown in Equation 2 is shifted to the right, increasing the concentration of SO_2 .



Because SO_2 is extremely volatile, it can be retained in the ethanol product, even after distillation and dehydration steps. This creates the opportunity for subsequent oxidation of sulfites to insoluble sulfates, possibly leading to the types of field problems that have been documented in the past. It has been pointed out that widespread use of bisulfite scrubber systems in corn ethanol plants began after the 2004-2006 time period when sulfate salt contaminants in gasoline-ethanol blends led to the field problems documented above. Nevertheless, the same process by which soluble, potential sulfate

species are introduced into fuel ethanol could occur with other sources of SO₂/SO₃ within the ethanol plant. This situation is also discussed in a recent report by NREL.¹

The existent sulfate level in every batch of denatured fuel ethanol produced in a commercial plant is measured using ion chromatography to ensure compliance with the 4 ppm specification in ASTM D4806. However, based on our discussions with technical service providers for the ethanol industry, we've learned that there have been instances in which a product shipment leaves the plant "in spec," but arrives at its destination "out of spec." To help avoid this problem, some ethanol producers now conduct potential sulfate analyses in addition to the required existent sulfate test. The potential sulfate test is able to quantify reduced forms of sulfur (SO₂, bisulfite and sulfites) that can later oxidize to sulfates. We have also learned that as a product quality precaution, some ethanol buyers now impose their own potential sulfate specification on ethanol shipments that they receive.

3.3. Other studies of sulfates in ethanol-blended fuels

Field problems with sulfate contamination in gasoline-ethanol blends have also been of concern in Europe, particularly in E85 blends. Problems with filter plugging and fuel injector fouling have been well-documented in Sweden.²¹ This led to a Swedish voluntary sulfate maximum level in ethanol of 2 ppm in 2010, and a formal E85 standard of 1.7 ppm in 2012. Introduction of this new E85 standard appeared to reduce the sulfate deposit issues in the FFV fleet.

Analysis of deposits obtained from Swedish field cases indicated the presence of potassium and calcium cations. In some cases, gasoline detergent additives based on polyisobutylene (PIB) chemistries appeared to be associated with the deposits. However, no final root causes of these sulfate deposit problems have been identified.

Other research to address these problems has been coordinated by the E85 Deposit Task Force of the European Committee for Standardization, CEN/TC 19WG21 (Specification for Unleaded Petrol). Both laboratory and field experimental programs have been conducted to obtain technical information upon which to base a sulfate specification in a revised standard for E85 fuel (prEN 15293). Laboratory experiments were conducted by the Process Design Center (PDC) in the Netherlands to determine the solubility of sodium sulfate in E10, E25, and E85 fuels.²² As shown in Figure 6, sodium sulfate's solubility is very low in all three fuels, although it increased noticeably in E85 having water content above 2 vol.%. In E10 and E25 fuels, the solubility of sodium sulfate was less than 1 ppm, even when the water content of the ethanol component was as high as 7 vol.%.

The authors of this European report concluded that a fuel ethanol sulfate standard of 4 ppm is appropriate for E10 fuels, as a 10-fold dilution of this ethanol to produce E10 would reduce the final sulfate level in the gasoline-ethanol blended fuel to 0.4 ppm (or below). At this level, the sulfate is expected to remain solubilized in the fuel, and not contribute to deposit formation. However, for E25 fuels, sulfate levels could be as high as 1 ppm, if the ethanol component contained 4 ppm. This level would exceed the solubility level of sodium sulfate, and thus might be expected to cause deposit problems. For E85 fuels, it has been suggested that using hydrous ethanol (containing 4 vol.% water) would be an economical approach to avoiding precipitation of sulfate salts.²³

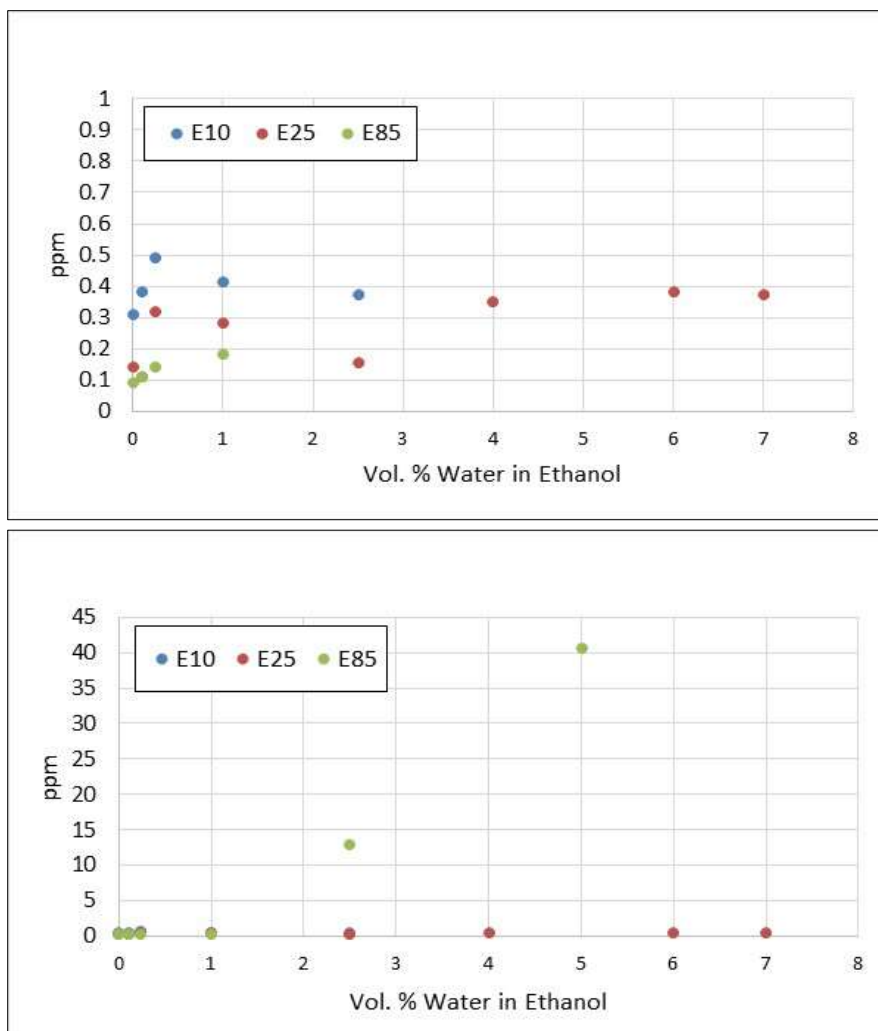


Figure 6. Solubility of Na_2SO_4 in E10, E25, and E85 fuels with various water contents.
(Top: expanded scale; Bottom: full scale. Data taken from Reference no. ²².)

4. Laboratory Experimental Program

To further explore issues related to sulfate solubility and formation of filter plugging solids, a laboratory-based experimental study was conducted at the Desert Research Institute (DRI). The main goal was to improve understanding of the factors that contribute to the formation of sulfate salts in ethanol and gasoline-ethanol blends. Specific objectives of this study include the following: (1) determine solubility of selected sulfate salts in anhydrous, 200-proof ethanol containing varying amounts of water; (2) determine solubility of selected sulfate salts in low- and high-aromatics gasoline containing various detergent additives; and (3) examine solubility and formation of solids in gasoline-ethanol blends that are spiked with low levels of sulfate salts.

4.1. Materials

The gasolines used in this study were supplied (in 1-gallon cans) by one of the CRC member companies. Five gallons each of a high aromatic (~40 vol.%) and a low aromatic (~1 vol.%) gasoline

were provided. These 1-gallon samples were additized with detergent additives of two types: polyether amine (PEA) and polyisobutyl amine (PIBA). Several additives of each type were supplied by commercial vendors, but selection of the specific additives used was done by the Fuel Additives Task Group (FATG) of the American Chemistry Council (ACC), using a ‘blind’ process, so that neither the vendors nor CRC was aware of the additive’s identities.

The detergent additives were dosed at two concentrations. The low dosage corresponds to the lowest allowable concentration (LAC) needed to satisfy the gasoline specifications for minimum level of intake valve deposits; the high dosage corresponds to the minimum concentration meeting TOP TIER™ Detergent Gasoline requirements. Information about the appropriate dosage levels was provided by the ACC. One gallon of each gasoline was left unadditized, to provide a baseline fuel for comparison. As shown in Table 1, the matrix of gasoline fuels consisted of 10 gasolines.

Table 1. Gasoline matrix used in laboratory experiments with sulfate salts

Low Aromatics Gasoline					High Aromatics Gasoline				
No Additive	PEA Additive		PIBA Additive		No Additive	PEA Additive		PIBA Additive	
	Low Conc.	High Conc.	Low Conc.	High Conc.		Low Conc.	High Conc.	Low Conc.	High Conc.
1	2	3	4	5	6	7	8	9	10

Anhydrous, 200-proof ethanol was obtained from Sigma-Aldrich and was additized with a corrosion inhibitor (at a level of ~50 ppm) provided by a commercial vendor. As with the detergent additives, the selection of the specific corrosion inhibitor used was made by ACC, using a similar blind process. Five anhydrous sulfate salts were purchased and used ‘as is’. These are identified below:

- Ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$ – VWR BDH9216 (>99.0%)
- Calcium sulfate (CaSO_4) – Alfa Aesar 40144 (99%)
- Potassium sulfate (K_2SO_4) – VWR 1B1106 (>99%)
- Sodium sulfate (Na_2SO_4) – VWR BDH9302 (>99.0%)
- Sodium bisulfite (NaHSO_3) – VWR N822

The purity level of sodium bisulfite was not specified. This material is known to be somewhat unstable with respect to oxidation; therefore, it is likely that some sulfate was also present in the sodium bisulfite used in this study.

4.2. Laboratory equipment and procedures

4.2.1. Water measurements by Karl Fischer titration

In this project, it was necessary to reliably measure water contents in the ethanol and gasoline solvents used to dissolve sulfate salts. Due to the tendency of ethanol-containing fuels to absorb water, it was important to conduct such water measurements on-site, rather than shipping the samples to outside labs for analysis. The accepted, standard method for water analysis in organic liquids involves Karl Fischer titration (ASTM E1064²⁴). To conduct such analyses, DRI acquired a used

Karl Fischer titrator (Metrohm 831 KF Coulometer), and set it up within one of its laboratories. A photo of this system is provided in Figure 7.



Figure 7. Metrohm Model 831 Karl Fischer Coulometer in DRI laboratory

The Karl Fischer (K-F) method was used to: (1) determine water content of the various fuel blends used in this project, and (2) monitor the gradual increase in water content of the anhydrous, 200-proof ethanol solvent. Throughout the course of the project, the same 2-L reagent bottle was repeatedly opened so that necessary quantities of ethanol could be removed and used in various experiments. Upon many of these bottle opening events, an aliquot was removed and analyzed by K-F titration. Results of these analyses over a 6-month period are illustrated in Figure 8. Although a gradual increase in water content is clearly seen, the total water levels remained very low throughout the project. A final K-F measurement made at the end of the project (approximately 1-year after the first measurement) showed a water content of ~400 ppm. These slight increases in water content throughout the project period are considered inconsequential with respect to dissolution or precipitation of sulfate salts in ethanol or fuels containing ethanol.

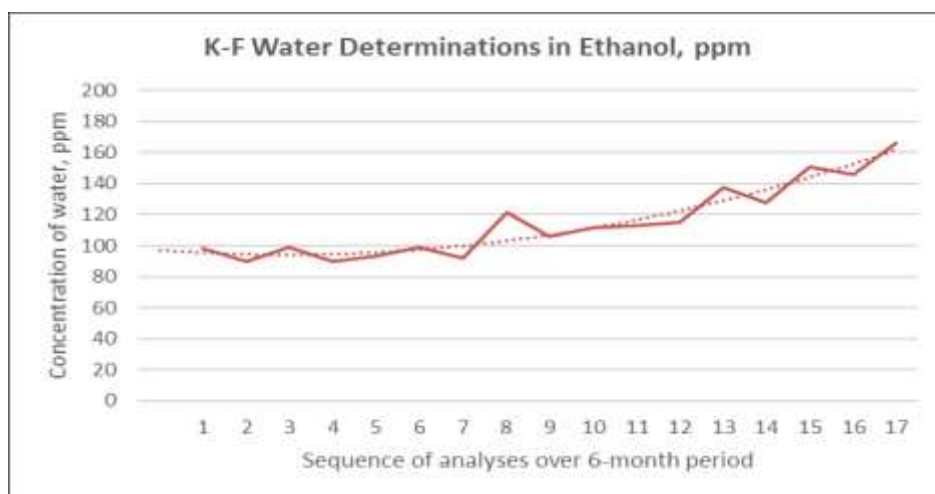


Figure 8. Karl-Fischer water measurements from repeated analyses of 200-proof ethanol reagent over a 6-month period.

4.2.2. Sulfate measurements by ion Chromatography (IC)

As specified in ASTM D4806, one of the approved methods for measuring sulfate in ethanol is ASTM D7328. In this project, ASTM D7328 was used to quantify both existent and potential sulfate in ethanol, gasoline, and gasoline-ethanol blends. Although the method has been standardized by ASTM only for use with fuel ethanol, there are no operational difficulties in also applying it to gasoline and gasoline-ethanol blends.

To determine existent sulfate, a small volume of sample is evaporated to dryness, then reconstituted to the initial volume with deionized water. A sample of this aqueous solution is then injected into an ion chromatograph consisting of appropriate ion exchange columns, suppressor, and conductivity detector. DRI uses a DIONEX ICS-5000+ system for this analysis. Although ASTM D7328 is said to be applicable over a sulfate concentration range of 0.55-20 ppm, DRI's application has demonstrated satisfactory performance over a much wider range, with a minimum detection limit (MDL) determined to be 0.01 ppm in aqueous solutions (from atmospheric samples collected on filters and extracted into water). For potential sulfate determination, after the ethanol solution is evaporated to dryness, it is reconstituted to the original sample volume using a dilute solution of hydrogen peroxide (~1 wt.%) in water. The hydrogen peroxide serves to oxidize reduced forms of sulfur (such as SO₂, sulfite, and bisulfite) to sulfate, which is then quantified using the same IC method as for existent sulfate. The difference between the potential and existent sulfate results provides an estimate of the oxidizable forms of sulfur present in the sample.

4.2.3. Filtration process

To determine the solubility of sulfate salts in ethanol, gasoline, and gasoline-ethanol blends, it was necessary to conduct a variety of filtration experiments. Due to the flammable nature of these materials, several precautions were taken to ensure safe laboratory operations. The vacuum-assisted filtration procedure used was based on ASTM D5452, "Standard Test Method for Particulate Contamination in Aviation Fuels by Laboratory Filtration."²⁵ The most important precautions involve adequate grounding of the entire filtration apparatus – including the metal filter funnel, the filtrate receiving flask, and the dry ice-cooled trap located between the filter flask and the house vacuum system. In addition, during filtration experiments, the laboratory technician wore an antistatic wrist strap. A photo of the entire filtration apparatus installed in a laboratory hood is shown in Figure 9.

Initial plans for determining the solubility of various sulfate salts in ethanol called for introducing known amounts of salts into 250-mL of 200 proof ethanol. After stirring the resultant slurries for 2-hours to dissolve the salts (using a magnetic stirrer), the solutions were to be rested for 24 hours and then filtered, using the method described in ASTM D5452. The mass of salts dissolved would then be calculated by the difference between the initial mass added and the undissolved mass recovered after filtration.

This approach of determining solubility of sulfate salts by a filter weight difference method proved to be quite problematic, and led to poor measurement reproducibility. Due to the extremely low solubility of most sulfate salts, this method relied on measuring small differences between two large values. For example, if 500 mg of sodium sulfate were added to 250-mL of ethanol, less than 1 mg

would be expected to dissolve, with 499 mg remaining undissolved. Given this, it is very difficult to reliably determine 1 mg as the difference between 500 and 499 mg.



Figure 9. Fuel filtration apparatus installed in laboratory hood

A second problem stems from difficulties in completely transferring materials from one vessel to another. Solubility experiments were conducted in 500-mL Erlenmeyer flasks, as shown in Figure 10. After stirring about 1 g of sodium sulfate in 250-mL of 200 proof ethanol for two hours, the solution was allowed to sit at room temperature for 24 hours. Immediately prior to filtering, the solution was swirled to suspend the solids. However, some solid particles strongly adhered to the walls of the flask, requiring extensive rinsing to completely remove them from the flask and transfer them into the filter assembly. Rinsing with hexane caused even greater adhesion of particles to the walls than did rinsing with ethanol. To completely remove these particles required a large volume (~200 mL) of rinse solution, which introduced the possibility of dissolving more sulfate salt and raised further doubts about the validity of the solubility results.

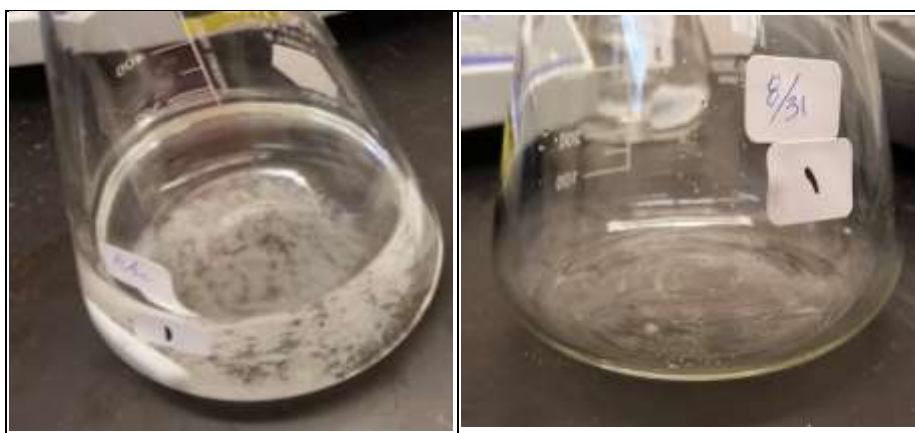


Figure 10. Sodium sulfate particles in Erlenmeyer flask.

(Left) Sodium sulfate in 250-mL of 200-proof ethanol. (Right) Some particles remain in the flask even after extensive rinsing with ethanol (right).

A third problem related to complete capture of all the undissolved sulfate salt on the filter for weighing. This proved to be quite challenging, as the wet filters were difficult to handle, and once dry, the powdery sulfate salts were difficult to keep on the filter. These problems were encountered when using either Nuclepore membrane or Teflon membrane filters. As shown in Figure 11, some sulfate ends up on the metal screen or outer rim of the filter apparatus. Failure to capture this material results in incorrect filter weights, and hence, invalid solubility results.



Figure 11. Collection of undissolved sodium sulfate on filter.

(Left) Particles spill over the sides of the filter upon removal of the filter funnel. (Middle) Removing the filter is difficult, as light particles “float off” and spill. (Right) Particles remain on base of filtration unit after removal of the filter.

Four preliminary filtration experiments were conducted using 1.0 g of sodium sulfate in 200-proof ethanol. Despite careful efforts to capture all undissolved salts by filtration, the highest recovery obtained was 97.1%. If all the remainder had truly dissolved, this would imply a solubility of approximately 94 ppm, which based on literature information, is too high by at least an order of magnitude.

Because of these filtration problems, it was decided to base all sulfate solubility results on direct measurement of dissolved sulfate in filtrate solutions using the IC method described in ASTM D7328. This also simplified the filtration experiments, as there was no longer any need to thoroughly rinse the sample flasks or completely recover undissolved sulfate salts on filters. Furthermore, the filtrate sample could be recovered and prepared for IC analysis without disassembling the filtration apparatus, thus avoiding potential contamination with the powdery sulfate salts collected on the filter.

With this change in methodology, we also changed the filter type to a smaller pore size. Rather than the 0.8 μm pore size called for in ASTM D5452 for filtering fuels, we used 0.4 μm Nuclepore filters, to ensure more complete removal of small particles, thereby improving reliability of the solubility determinations. Filtration of the salt solutions was done using 47 mm Whatman Nuclepore track-etched polycarbonate AOX filters, having a pore size of 0.4 μm (Whatman Product ID 111137). These filters were chosen because they are chemically inert, and can tolerate a wide variety of solvents (including ethanol and gasoline). Finally, Nuclepore filters have sharply defined pore sizes, as opposed to fibrous filters, thus providing a cleaner size cut of particles that can pass through the

filter. With a pore size as small as 0.4 μm , it was thought that almost all undissolved salt particles would be removed by filtration, leaving a filtrate solution with only dissolved sulfate, and thus allow for accurate determination of solubility, based on IC analysis of the filtrate.

4.2.4. Particle counts in fuel samples

In an effort to better understand the solubilization/precipitation of sulfate salts in ethanol, gasoline, and gasoline-ethanol blends, all experimental samples (both before and after filtration) underwent particle counting using a Seta Analytics SA1000 automatic particle counter (APC) instrument (Stanhope-Seta Company, UK). The APC method used was based on ASTM D7619, “Standard Test Method for Sizing and Counting Particles in Light and Middle Distillate Fuels, by Automatic Particle Counter.”²⁶ A photo of this APC instrument is shown in Figure 12. For each sample analyzed, the instrument provides triplicate measurements (and averages) of particle counts in six size band ranges: >4, >6, >14, >21, >38, and >70 μm .



Figure 12. Photo of Seta Analytics SA1000 automatic particle counter (APC).

This APC instrument operates with a built-in, microprocessor-controlled routine that pumps 10-mL of sample into a measurement cell where it is exposed to a laser light. Particles in the sample obscure this light and cast shadows on a calibrated sensor, which determines the size and number of the particles. In a single analysis routine, the APC instrument pumps and analyzes 3 separate 10-mL samples, and provides average particle count numbers for each size range. Including sample volume used for rinsing before and after each measurement, a total sample size of 80-mL is required for each analysis. Consistent sample handling techniques – including agitation of the sample during the analysis procedure – are necessary to obtain repeatable results, especially for samples that contain large numbers of particles.

4.3. Experiments using sulfate salts in ethanol

An initial set of experiments was conducted to investigate the solubility of sulfate salts in 200-proof ethanol, with and without addition of 2.0 wt.% water. In addition, particle counts were measured on

all samples, both before and after filtration. The five anhydrous salts identified in Section 4.1 were used: ammonium sulfate, calcium sulfate, potassium sulfate, sodium sulfate, and sodium bisulfite.

In each solubility/filtration experiment, approximately 1 g of salt was added to 250 mL of ethanol in a 500 mL Erlenmeyer flask. After stirring for 2 hours (using a magnetic stirring bar), the slurries were allowed to stand overnight at either room temperature (25 °C) or in a refrigerator (5 °C). In all cases, the undissolved salts quickly dropped to the bottom of the flask once stirring was stopped, and the solutions above the solids appeared clear and bright. The following day, an aliquot of the clear solution above the solids was decanted and retained for particle count measurements using the APC instrument. The remaining slurry samples were gently swirled to free the particles that had agglomerated upon standing, and were vacuum filtered through a 0.4 µm Nuclepore filter as described above. All samples filtered very quickly (<20 sec.) and all filtrate samples were clear and bright. The filtrates were analyzed by IC for both existent and potential sulfate. In addition, particle counts were determined for each filtrate sample. The total matrix of experiments in which solid sulfate salts were introduced into ethanol is shown below in Table 2.

Table 2. Sulfate solubility/filtration experiments conducted in 200-proof ethanol
(Number shown indicates replicate experiments)

Sulfate Salt	Room Temp. Storage, 25°C)		Refrigerator Storage, (5°C)		Total No. of Expt's
	0.0 wt.% Water	2.0 wt.% Water	0.0 wt.% Water	2.0 wt.% Water	
None (Baseline)	1	1	0	0	2
Ammonium Sulfate	2	1	0	0	3
Calcium Sulfate	1	1	0	0	2
Potassium Sulfate	1	1	0	0	2
Sodium Bisulfite	3	3	3	0	9
Sodium Sulfate	3	3	3	0	9
Total No. of Experiments					27

4.3.1. Sulfate solubility in ethanol

The filtrates obtained from the solubility/filtration experiments described above were analyzed for existent and potential sulfate concentrations using the IC method described in ASTM D7328. The numerical results are provided in Appendix Table I-1, and are summarized graphically in Figure 13. All results are expressed as solubility in units of ppm, or µg sulfate/g ethanol. Baseline results of ethanol without any added salt are not included in Figure 13, as these samples had undetectable levels of sulfate, which cannot be shown on the logarithmic scale.

The results displayed in Figure 13 confirm that calcium sulfate, potassium sulfate, and sodium sulfate all have extremely low solubility in ethanol – whether or not 2.0 wt.% water was included. In agreement with literature reports, inclusion of this small amount of water had no discernable effect on the sulfate solubilities. The solubility of ammonium sulfate was noticeably higher than that of calcium-, potassium-, or sodium sulfate – by approximately an order of magnitude. The apparent decrease in solubility of ammonium sulfate with addition of water is not significant when considering the high variability within these measurements. The solubility of sodium bisulfite in ethanol is clearly higher than that of any other salt used here. Addition of 2.0 wt.% water appeared to increase the

solubility of sodium bisulfite slightly (at 25 °C), although the high experimental variability makes this conclusion uncertain.

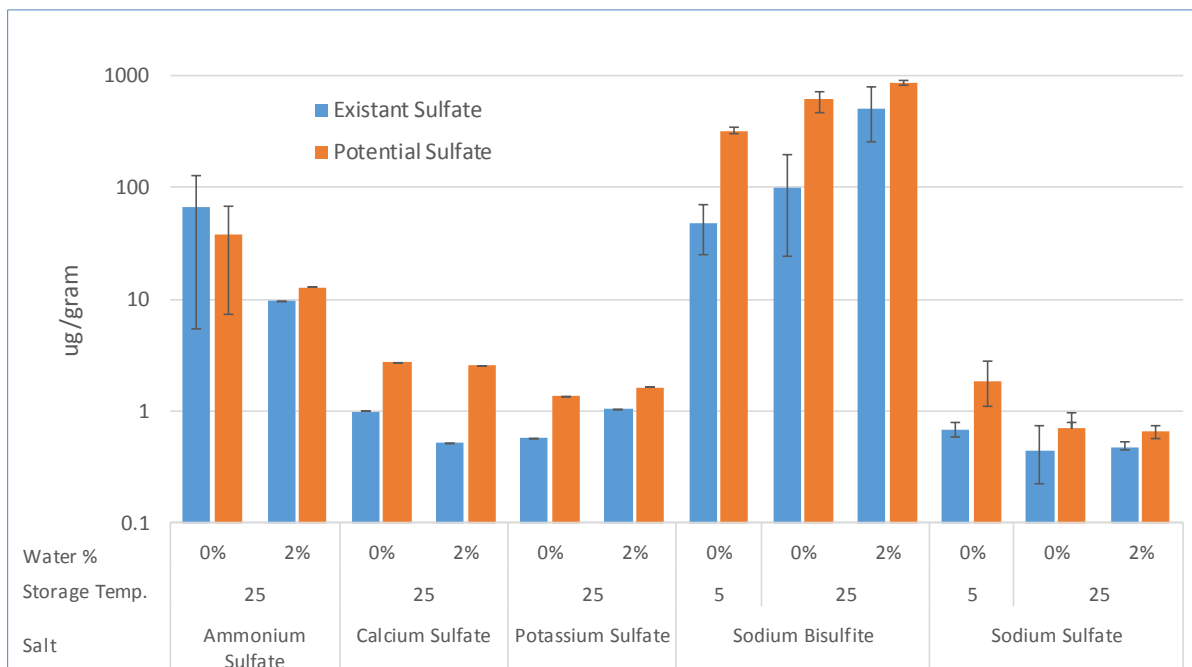


Figure 13. Existent and potential sulfate measurements by IC for 5 sulfate salts in pure ethanol. (Water content and storage temperature are indicated. Note the log scale in the y-axis. Error bars indicate the range of values in replicate experiments.)

These solubility results, including the effects of water addition, are largely consistent with literature reports and with recent results that were obtained from experimental studies conducted in Europe, as discussed in Section 3.3. This is illustrated in Figure 14, where data points from our experiments with sodium sulfate in E100 are included in the graph showing the earlier European results in E10, E25, and E85.

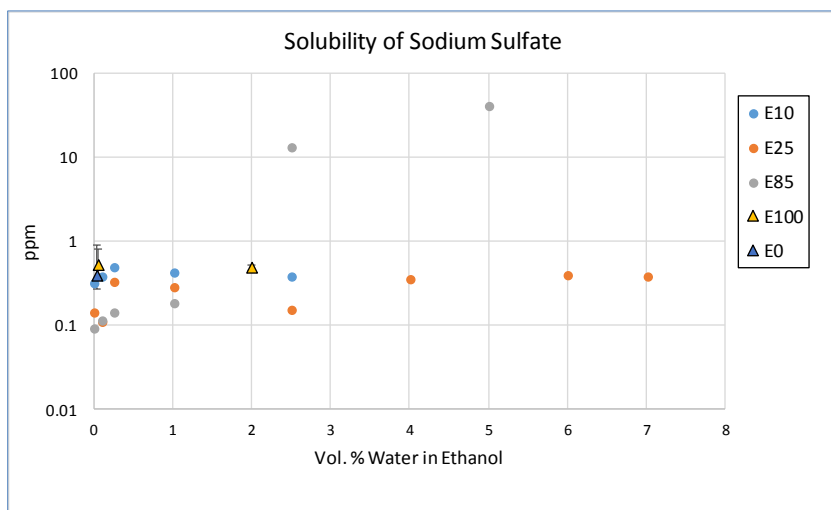


Figure 14. Solubility of sodium sulfate in gasoline-ethanol blends. Circles are from Keuken (2013). Triangles represent experiments from this CRC project.

Two sets of sulfate results are portrayed in Figure 13: blue bars represent existent sulfate results; orange bars represent potential sulfate results. When dealing with dissolution of pure sulfate salts, measured concentrations of existent and potential sulfate are expected to be the same. Yet, Figure 13 shows that potential sulfate results are higher than existent sulfate in most cases. A possible explanation for this is that impurities in the starting salt materials contribute to measurement of potential sulfate. Although each salt has a stated purity of >99% (except for sodium bisulfite), the presence of small amounts of oxidizable impurities could result in formation of sulfate during the potential sulfate test method.

The case of sodium bisulfite is particularly interesting. Because this is not a true sulfate salt, no significant amount of existent sulfate would be expected (other than from impurities that may be present). However, upon oxidation during the potential sulfate test method, the bisulfite would convert to sulfate, thereby resulting in a significant concentration of potential sulfate. As shown in Figure 13, potential sulfate is considerably higher than existent sulfate for the sodium bisulfite experiments conducted here (based on triplicate tests). Yet, the rather high levels of existent sulfate (about 100 ppm) suggests that substantial ethanol-soluble sulfate impurities were present in the starting salt material, and/or that oxidation of bisulfite to sulfate occurred during sample preparation, storage, and handling prior to conducting the IC sulfate measurements. Based on IC analysis of the starting sodium bisulfite sample, this reagent appeared to be contaminated with sodium sulfate. However, this alone cannot explain the high existent sulfate levels seen in Figure 13, since sodium sulfate has very limited solubility in ethanol (<1 ppm) and would be filtered out by our experimental methodology. We believe that due to the ease of oxidation, some unavoidable transformation of bisulfite to sulfate occurred during these solubility experiments.

Another interesting point about the sodium bisulfite results shown in Figure 13 is that the disparity between existent and potential sulfate measurements was much smaller in the case with 2 wt.% water. This suggests that the bisulfite may be more readily oxidized in the presence of water. These observations may have implications with respect to bisulfite usage within ethanol production plants, as discussed in Section 3.2. Although we are not aware of bisulfite itself coming into contact with finished ethanol (post-distillation), sporadic situations in which this did occur would likely cause significant problems due to the relatively high solubility of bisulfite in ethanol, and the oxidative instability of bisulfite, which leads to production of insoluble sulfate.

Some information about the influence of temperature upon salt solubilities is also illustrated in Figure 13. Solubility experiments were conducted at two temperatures (5 and 25 °C) for sodium bisulfite and sodium sulfate. In the case of sodium bisulfite, the solubility appeared to be about 2-fold higher at the higher temperature, while no effect of temperature was seen on the solubility of sodium sulfate. Given the variability of these solubility/filtration experiments, it appears that the effects of temperature on solubility are small, over the temperature range examined, which is consistent with the limited information available in the literature.

4.3.2. Particle counts in ethanol

A Seta Analytics SA1000 automatic particle counter (APC) instrument was used to measure the number of particles observed in these sulfate solutions before and after filtering through 0.4 µm Nuclepore filters. The “before filtration” sample was obtained by carefully decanting the clear

solution above the undissolved salts remaining in the Erlenmeyer flask after the slurry had sat overnight. The “after filtration” sample was obtained from filtrate in the vacuum filter flask, after the entire slurry had been filtered. The APC instrument was configured to conduct analyses of three sequential aliquots drawn from each sample. Appendix Table II-1 provides average particle count results from the three aliquots of each ethanol-based experiment.

Particle counts were also measured in the 200-proof baseline ethanol (additized with corrosion inhibitor) that was used in these experiments. The baseline ethanol was filtered using the same methodology as with the sulfate salts, thus “before filtration” and “after filtration” particle counts were also obtained for the baseline ethanol. These baseline particle counts are shown in Figure 15. Interestingly, slightly higher particle counts were observed after filtration, in both the pure ethanol sample and the sample in which 2 wt.% water was added. While initially unexpected, we now believe these results are explainable. The pre-filtration samples were obtained directly from the reagent bottles of 200-proof ethanol, and underwent very little handling before being analyzed with the APC instrument. In contrast, the post-filtered samples underwent multiple handling steps before APC analysis, and are likely to have picked up small numbers of contaminant particles in the process. However, it should be pointed out that the total particle numbers shown in Figure 15 are very small ($<10^3$), and the differences between pre- and post-filtration are not consequential.

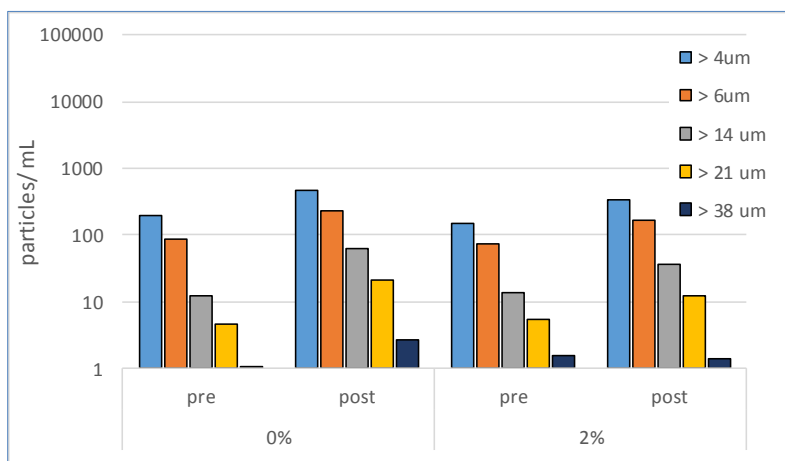


Figure 15. APC particle counts in baseline ethanol – with and without 2.0 wt.% water
(Average of three measurements, both before and after filtering through 0.4 µm Nuclepore filter. Ethanol contained 50 ppm corrosion inhibitor.)

The particle count results from the various sulfate salt experiments in pure ethanol (at room temp. storage) are shown in Figure 16. In nearly every case, these counts are over 2-orders of magnitude higher than the baseline ethanol counts shown in Figure 15. Because of this, no baseline corrections were made; thus the counts shown in Figure 16 are those directly measured by the APC instrument.

It is somewhat difficult to interpret the results shown in Figure 16. Clearly, large numbers of particles were introduced by addition of each salt to ethanol, despite the fact that all the samples appeared bright and clear with no particles visible to the human eye. In most cases, filtration of the salt solutions reduced the particle counts by about an order of magnitude. Nevertheless, significant particle numbers (around 10^4 per mL) still remained in the filtrate solutions, which is somewhat surprising, given the use of Nuclepore filters with 0.4 µm pore sizes. Although the particle numbers

were high, their cumulative mass is very low, as evidenced by the extremely low sulfate solubilities for most of the salts, as shown in Figure 13.

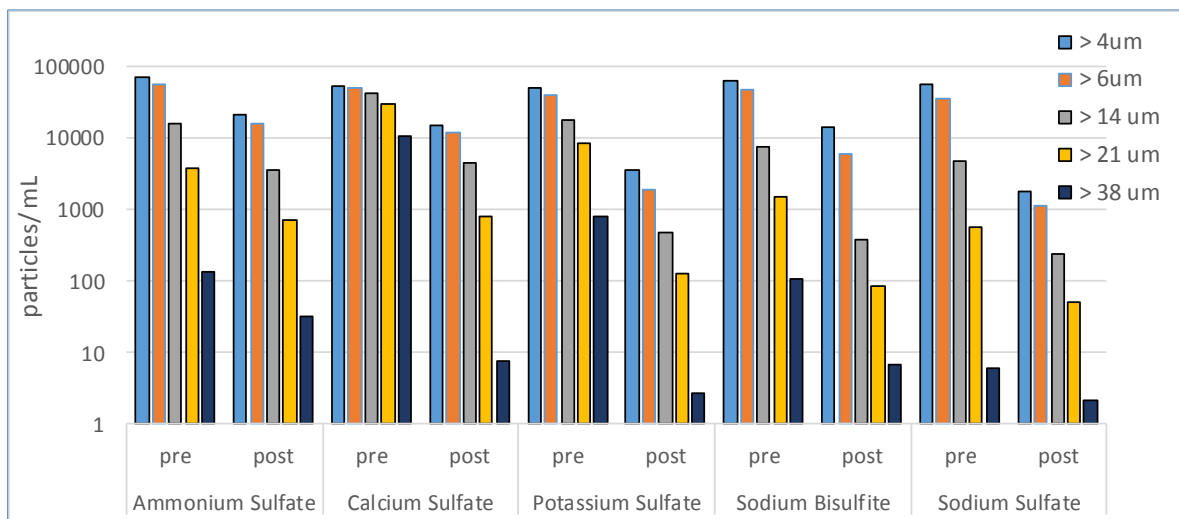


Figure 16. APC particle counts in ethanol containing anhydrous salts – avg. of three measurements. (All samples prepared at room temp. using anhydrous ethanol with 50 ppm corrosion inhibitor. Measurements were made before (pre) and after (post) filtering through 0.4 µm Nuclepore filters.)

While sodium bisulfite had much higher solubility than the other salts tested, no clear differences in particle numbers are seen for any of the salts included in Figure 16. However, it is of note that upon sitting in the laboratory for several months (in closed, glass bottles), the ethanol filtrate solutions containing sodium bisulfite became noticeably cloudy, whereas none of the other ethanol solutions did. A photo illustrating the cloudiness of the filtrates from sodium bisulfite experiments compared to all other salt filtration experiments is shown in Figure 17. We believe this resulted from gradual oxidation of the dissolved bisulfite to sulfate, which is insoluble and precipitated as white-colored, fine particles.



Figure 17. Photo of collected filtrates from experiments in which sulfate salts were added to ethanol. Samples were stored on a laboratory benchtop in the glass bottles shown for 1-3 months. Note cloudiness of filtrates from experiments using sodium bisulfite.

The effects of temperature and water addition upon APC counts in these ethanol-salt experiments are examined in Figure 18. The top panel shows results from sodium sulfate experiments, while the bottom panel shows results from sodium bisulfite experiments. Each bar cluster represents the average of triplicate experiments, with three aliquots from each experiment being analyzed.

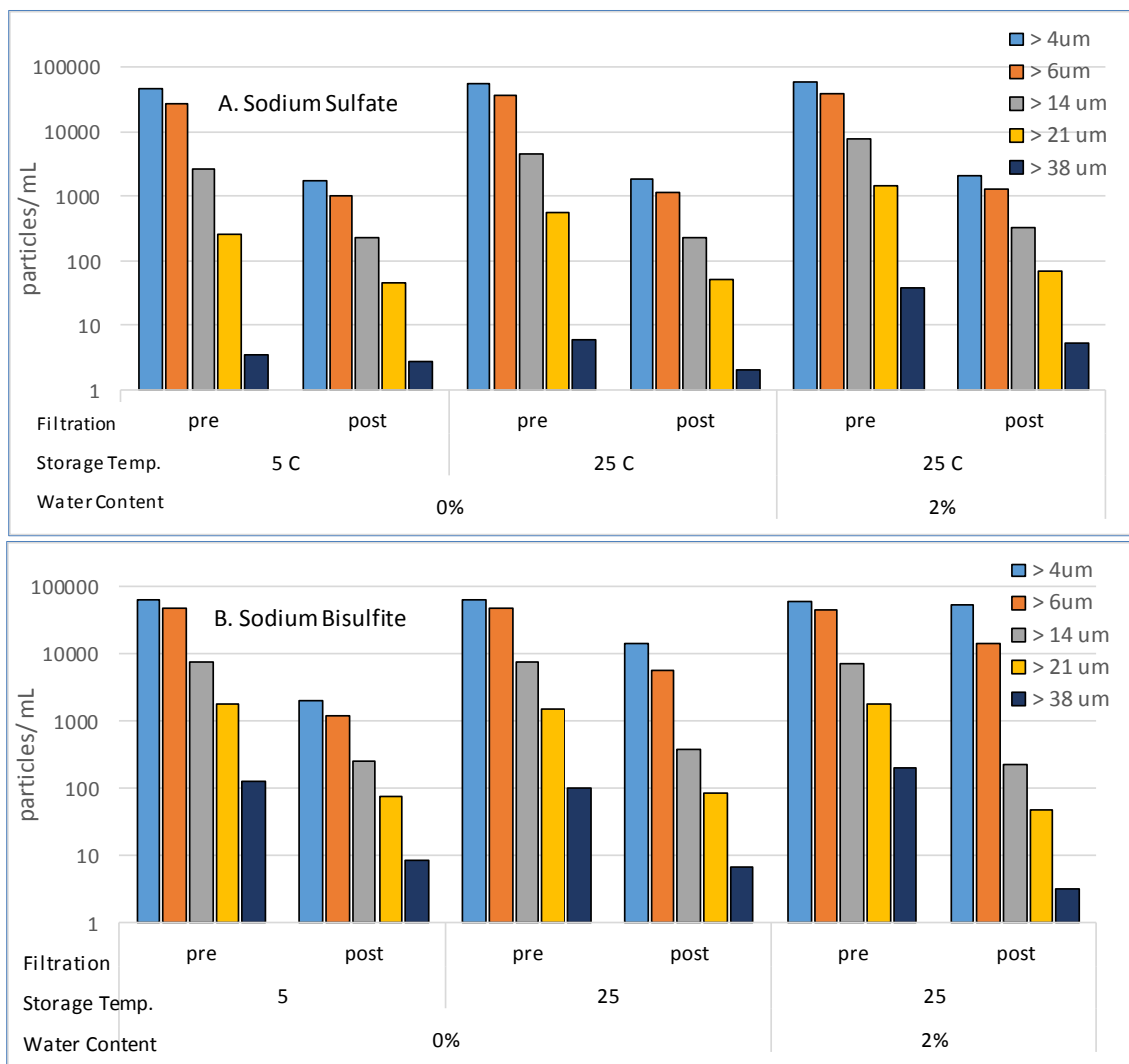


Figure 18. Effect of temp. and water content on APC particle counts of salt solutions in ethanol (Top – sodium sulfate; Bottom – sodium bisulfite. Measurements were made before and after filtering through 0.4 μm Nuclepore filters. Average results shown from triplicate experiments.)

The sodium sulfate experiments showed no effects of either temperature or water on particle counts. However, in the sodium bisulfite experiments, slight effects are seen for both temperature and water addition. For example, comparing the post-filtered sodium bisulfite samples at 5 °C and 25 °C shows higher particle counts under the higher temperature condition. (Note: overnight storage and filtration of these salt solutions were done at both 25 °C and 5 °C, but all APC measurements were done at 25 °C.) Similarly, slightly higher particle counts are seen in the post-filtered samples containing 2.0 wt.% water as compared to the water-free samples. However, these effects of temperature and water content appear to be very small, and probably inconsequential.

Based upon the information obtained from this entire set of experiments with ethanol, it is concluded that sodium bisulfite behaves somewhat differently from the other salts – both with respect to solubility and particle counts. Sodium sulfate appears to behave very similarly to calcium sulfate and potassium sulfate, and thus may be a good representative of all these salts. Ammonium sulfate appears to have intermediate behavior – at least in terms of solubility.

4.4. Experiments using sulfate salts in gasoline

A second set of laboratory experiments was conducted to investigate the solubility of two sulfate salts in gasoline: sodium sulfate and sodium bisulfite. Based upon the results described above in Section 4.3, the effects of temperature and water addition are quite small, so these parameters were not varied in the second set of experiments. (All experiments were conducted at room temperature, with no water added.) However, the effects of gasoline aromatic content and detergent additives were investigated. Two base gasolines were used: one with low aromatics (1 vol.%); the other with high aromatics (40 vol.%). Also, two detergent additives were used: one being a polyether amine (PEA); the other a polyisobutyl amine (PIBA). Each additive was dosed at low and high levels, corresponding to LAC and minimum TOP TIER™ Detergent Gasoline requirements. The complete experimental matrix of 42 samples is shown in Table 3.

Table 3. Sulfate solubility/filtration experiments conducted in gasoline
(Number shown indicates replicate experiments)

Sulfate Salt	Composition of Gasoline										Total No. of Expt's
	Low Aromatics					High Aromatics					
	No Additive	PEA Additive		PIBA Additive		No Additive	PEA Additive		PIBA Additive		
		Low Conc.	High Conc.	Low Conc.	High Conc.		Low Conc.	High Conc.	Low Conc.	High Conc.	
None (baseline)	1	1	1	1	1	1	1	1	1	1	10
Na ₂ SO ₄	2	2	2	2	2	1	1	1	1	1	15
NaHSO ₃	2	2	2	2	2	1	2	1	1	2	17
							Total No. of Experiments				42

To determine the solubility of sodium sulfate and sodium bisulfite, the same experimental methodology was used as described above for the ethanol experiments. This involved stirring excess amounts of the anhydrous salts in 250-mL of the appropriate gasoline sample for two hours, followed by filtration through a 0.4 µm Nuclepore filter. In all cases, the gasoline samples appeared clear and bright – both before and after filtering. Filtrates from the high aromatics gasoline were pale yellow color; those from the low aromatics gasoline were colorless. No differences in ease of filtration were observed among this set of experiments. As with the previous ethanol experiments, all samples were readily filtered within 20-sec.

4.4.1. Solubility in gasoline

The filtrates obtained from the gasoline solubility/filtration experiments with sodium sulfate and sodium bisulfite were analyzed for existent and potential sulfate by IC. In the sample work-up procedure prior to IC analysis, the gasolines were blown down to dryness under N₂, with the residue

then being taken up in water. Due to the presence of gasoline heavy ends and/or detergent additives, these aqueous solutions were quite cloudy with insoluble materials. However, this did not cause any apparent difficulty in the resulting IC analyses. (Note: Sulfate analyses were not conducted on the baseline gasoline samples that contained no salt.) The complete set of sulfate results are given in Appendix Table I-2. Average results of replicate experiments are shown in Figure 19, where sodium sulfate solubilities are represented in blue and sodium bisulfite solubilities are represented in orange. Note that most of the solubility results in the high aromatics gasoline are based on single determinations, while the results in the low aromatics gasoline are averages of duplicate experiments, with the range of values indicated by the error bars.

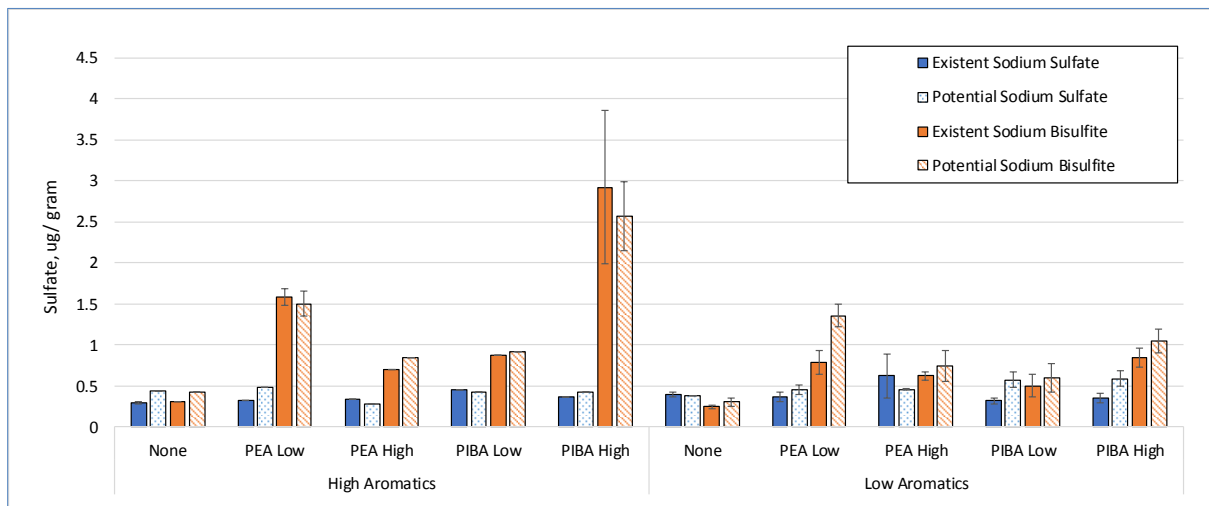


Figure 19. Effect of aromatics and detergent additives on existent and potential sulfate measurements by IC for sodium sulfate and sodium bisulfite in gasoline.
(Error bars indicate the range of values in duplicate experiments.)

Focusing first on the sodium sulfate experiments, very similar solubility results were obtained from all samples, regardless of aromatics level, additive type, or additive dosage. As was the case in the ethanol experiments (Figure 13), sodium sulfate exhibited very low solubility in gasoline – certainly <1 ppm. In fact, the solubilities (based on existent sulfate measurements) were all less than 0.5 ppm, except possibly in the low aromatics gasoline with a high concentration of PEA. However, this particular result was the average of two experiments that differed substantially, as seen by the large error bars.

The sodium bisulfite results are quite different, suggesting that the additive type and level may have small effects on solubility. Without any detergent additive present, the solubility of sodium bisulfite in gasoline is very low (<0.5 ppm). This contrasts sharply with the much higher solubility of sodium bisulfite in ethanol (~100 ppm; see Figure 13). The data in Figure 19 suggest that sodium bisulfite becomes slightly more soluble upon addition of either PEA or PIBA detergent additives. In the low aromatics gasoline experiments (which all had duplicates), this increasing solubility appears to be on the order of 2-4 fold. A similar, or larger increase may occur in the high aromatics gasoline, but this is difficult to confirm based on the few measurements made here. The differences in sodium bisulfite solubilities among the different additive types and dosages are small and inconsistent. Additional

replicate experiments would be necessary to determine with confidence whether real differences exist among additive type and dosage.

Another interesting observation is that the existent and potential sulfate results shown in Figure 19 are nearly identical in each of these gasoline samples – for both the sodium sulfate and the sodium bisulfite samples. This is in contrast to the ethanol experiments shown in Figure 13, where the potential sulfate levels were much higher than existent sulfate for the sodium bisulfite samples. These results are consistent with sodium bisulfite itself having very low solubility in gasoline, but higher solubility in ethanol.

Overall, these sulfate results show that both sodium sulfate and sodium bisulfite have very low solubility in gasoline. The addition of detergent additives does not seem to influence the solubility of sodium sulfate, but does slightly increase the solubility of sodium bisulfite, with the effect being larger – though somewhat inconsistent – in the high aromatics gasoline. The most significant conclusion is that sodium bisulfite has much lower solubility in gasoline than in ethanol. This raises the question of whether the blending of ethanol containing high levels of sodium bisulfite with gasoline would de-solubilize the salt, resulting in formation of deposits in the blended fuel.

4.4.2. Particle count results in gasoline

Particle counts of “before” and “after” gasoline filtration samples were obtained using the APC instrument and procedures as described above for the ethanol experiments. Numerical results from all the APC measurements of gasoline samples are provided in Appendix Table II-2. Figure 20 graphically summarizes particle counts from the 10 baseline gasoline samples: 5 with low aromatics and 5 with high aromatics. Close inspection of these results reveals several interesting features. First, although these gasoline samples appeared to be clear and bright, they all contained over 10^3 particles/ml, before filtration. These numbers are roughly an order of magnitude higher than the baseline numbers measured in the 200-proof ethanol (see Figure 15). A second observation is that filtration of the low aromatics gasolines noticeably reduced the particle counts in every case, while filtration of the high aromatics gasolines resulted in little, if any, reduction in particle counts. Third, addition of the two detergents (PEA and PIBA) to the low aromatics gasoline resulted in increased particle counts in the post-filtration samples, although these increases were small and inconsistent with additive dosage. In contrast, addition of the detergents to the high aromatics gasoline had very little impact on particle counts.

Particle count results for the gasoline solubility/filtration experiments with sodium sulfate are depicted in Figure 21. Clearly, addition of sodium sulfate increased the number of particles in the pre-filtration samples – by about an order of magnitude over the baseline levels shown in Figure 20. However, filtration was effective in reducing the particle counts substantially in every case, although the reductions were larger in the low aromatics gasoline (top panel of Figure 21) than in the high aromatics gasoline (bottom panel of Figure 21).

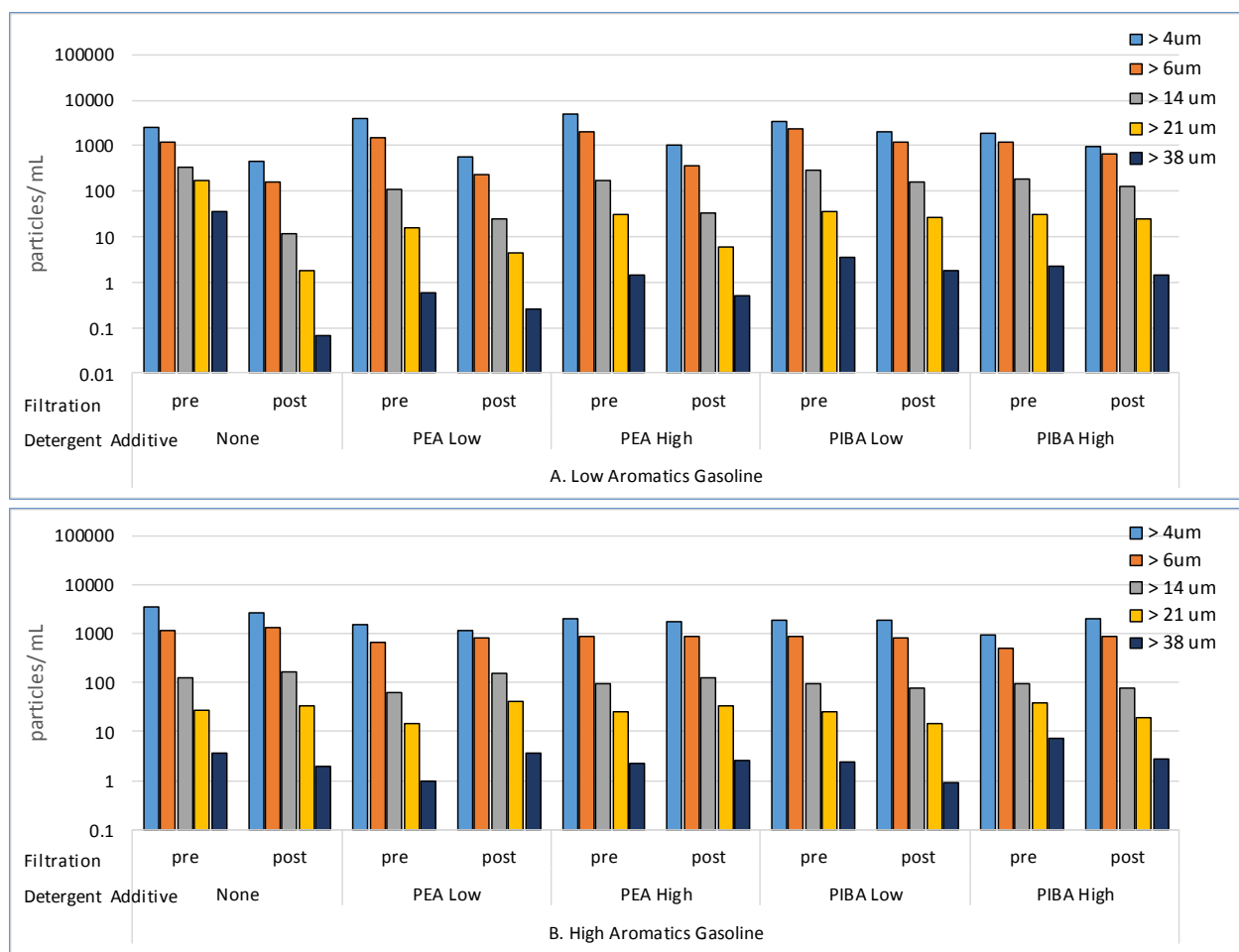


Figure 20. APC particle counts in baseline gasolines (no added salts) before and after filtering through 0.4 μm Nuclepore filters. (Top: low aromatics gasoline. Bottom: high aromatics gasoline. Results are average of three measurements from a single experiment.)

Note that all results shown in Figure 21 are based on raw particle counts, with no adjustments for baseline particle counts. Determining baseline-corrected particle counts proved to be complex and confusing. As shown in Figure 20, there are 10 different baseline levels to consider, each of which was determined only once. Applying these baselines to the gasoline-salt samples led to unstable results in some cases, including negative values for a few post-filtered samples.

Addition of detergent additives had only small effects on particle counts in these sodium sulfate experiments. In the low aromatics gasoline, particle counts in post-filtration samples were increased slightly with addition of PEA or PIBA, although no significant differences were seen between the two additives, and no consistent effects of additive dosage were apparent. In the high aromatics gasoline, addition of the detergents gave even smaller effects.

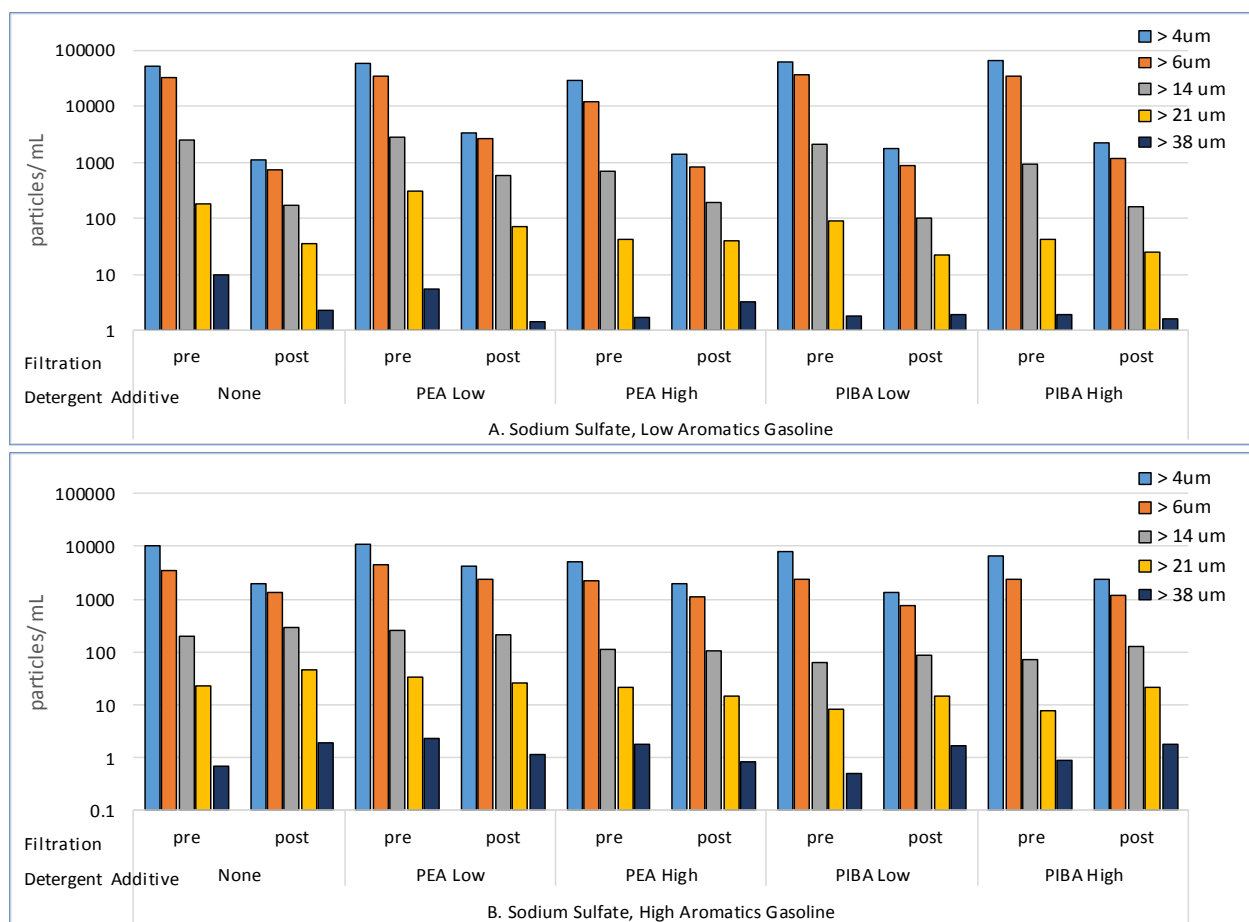


Figure 21. APC particle counts in gasolines with sodium sulfate - before and after filtering through 0.4 μm Nuclepore filters. (Top: Low aromatics gasoline. Bottom: High aromatics gasoline. Raw counts are presented – not background corrected. Results are average of 3 measurements from a single experiment.)

Particle count results for the gasoline solubility/filtration experiments with sodium bisulfite are depicted in Figure 22. Overall, these results are quite similar to the sodium sulfate results discussed above, although the particle counts are somewhat higher in the case of sodium bisulfite, particularly in the high aromatics gasoline. One noticeable difference is that in the high aromatics gasoline, the pre-filtration particle counts are higher with sodium bisulfite as compared to sodium sulfate. The effects of detergent additives in the sodium bisulfite experiments are similar to those seen with sodium sulfate. In both cases, addition of detergents slightly increased post-filtration particle counts in the low aromatics gasoline, but not in the high aromatics gasoline.

Based on the information obtained from this entire set of experiments with gasoline, we conclude that sodium sulfate and sodium bisulfite behave similarly – both with respect to solubility and particle counts. This is in contrast to the ethanol experiments, where these two salts differed dramatically in their solubility behavior. The addition of detergent additives appears to have small effects with respect to solubility and particle counts in low aromatics gasoline, but not in high aromatics gasoline. Differences between detergent additive types (PEA and PIBA) and dosage levels do not appear to be significant.

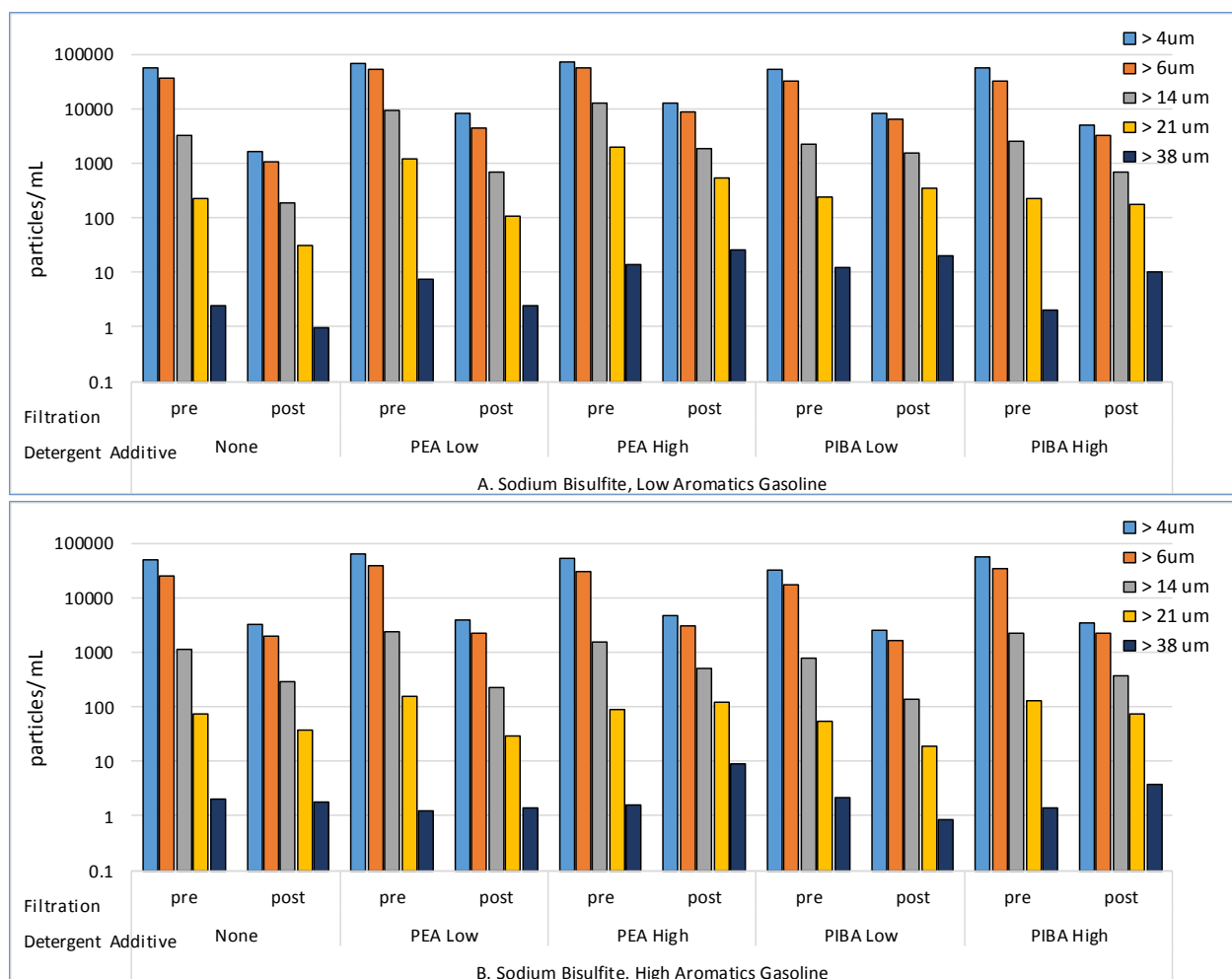


Figure 22. APC particle counts in gasolines with sodium bisulfite - before and after filtering through 0.4 µm Nuclepore filters. (Top - Low aromatics gasoline; bottom - high aromatics gasoline. Raw counts are presented – not background corrected. Results are average of 3 measurements from a single experiment.)

4.5. Sodium sulfate behavior in gasoline-ethanol blends

To investigate the formation of sulfate deposits under more realistic conditions, a series of gasoline-ethanol blends, spiked with low levels of sodium sulfate, were prepared. It was originally planned to produce E10, E15, and E30 blends, in which the ethanol component of the blend contained 0, 2, 4, and 8 ppm of sodium sulfate. These concentrations were selected to encompass a range from one-half to twice the current sulfate standard for fuel ethanol. The sulfate-spiked solutions would then be added to gasolines (both low and high aromatics) with and without inclusion of the PEA detergent additive. To observe particle behaviors in these fuel blends, the APC instrument was planned to be used to determine the particle count profile of each sample. The entire planned experimental matrix of samples is shown in Table 4.

Table 4. Planned experimental Matrix of Sodium Sulfate Dosed into Gasoline-Ethanol Blends
(single sample of each blend – total of 48 samples)

Conc. of Na ₂ SO ₄ in Ethanol	E10				E15				E30			
	Low Aromatics		High Aromatics		Low Aromatics		High aromatics		Low Aromatics		High aromatics	
	No PEA	High PEA	No PEA	High PEA	No PEA	High PEA	No PEA	High PEA	No PEA	High PEA	No PEA	High PEA
0 ppm	x	x	x	x	x	x	x	x	x	x	x	x
2 ppm	x	x	x	x	x	x	x	x	x	x	x	x
4 ppm	x	x	x	x	x	x	x	x	x	x	x	x
8 ppm	x	x	x	x	x	x	x	x	x	x	x	x

4.5.1. Preparation of sulfate-spiked ethanol solutions

To produce the gasoline-ethanol fuel blends described above, it was necessary to first prepare 200 proof ethanol solutions containing 0, 2, 4, and 8 ppm of sodium sulfate. (Note: the sulfate concentrations will be somewhat lower than these target values, as sulfate comprises only 68% of the mass of sodium sulfate.) Because of anticipated difficulties in directly adding small quantities of solid Na₂SO₄ into ethanol, it was decided to first prepare a concentrated aqueous stock solution of Na₂SO₄, then add prescribed volumes of this stock solution into ethanol to achieve the desired final concentrations. Although this method would also introduce low levels of water, this was not expected to be a problem, since earlier experiments had shown that the solubility of Na₂SO₄ in ethanol was unaffected when 2.0 wt.% water was included.

A 1000 ppm aqueous stock solution of Na₂SO₄ was prepared by adding 0.500 g of solid to 500 mL of deionized water. Aliquots of this stock solution were then added to 600 mL (473.4 g) samples of 200 proof ethanol to produce the 2.0, 4.0, and 8.0 ppm target levels of Na₂SO₄ in ethanol. This required addition of 0.95 g, 1.89 g, and 3.79 g of the aqueous stock solution to each 600 mL sample of ethanol. As previous experiments had shown the sulfate solubility in ethanol to be only about 1 ppm, we expected to observe cloudy solutions in the 4 and 8 ppm samples, and possibly in the 2 ppm sample. However, all the sulfate-spiked ethanol solutions were completely clear, with no visual appearance of undissolved solids. To verify the absence of solid particles in these solutions, they were analyzed by the APC instrument. In all cases, the particle counts were very low – generally between 100 and 200 per mL – consistent with the baseline ethanol results reported in earlier (see Figure 15).

To further investigate these puzzling results, a more concentrated aqueous stock solution was prepared, containing Na₂SO₄, at 10,000 ppm. Aliquots of this stock solution were spiked into ethanol to prepare solutions containing 20, 40, and 80 ppm of Na₂SO₄. Visual inspection indicated the 20 ppm solution to be completely clear, the 40 ppm solution was slightly cloudy, and 80 ppm solution was extremely cloudy. This is illustrated in Figure 23.



Figure 23. Ethanol spiked with aqueous stock solution containing 10,000 ppm of Na_2SO_4 .
(From left to right, solutions contain 20, 40, and 80 ppm Na_2SO_4 .)

APC measurements showed much greater particle counts in these three higher concentration solutions, as compared to the solutions containing 2, 4, and 8 ppm Na_2SO_4 . APC results from both the low and high concentration solutions are shown graphically in Figure 24, where they are presented using a logarithmic scale. Clearly, a dramatic change in particle counts occurred between the 8 ppm and 20 ppm samples; yet, both of these samples appeared clear and bright, with no insoluble material being visible to the human eye. At 40 ppm, the solution was slightly cloudy, suggesting that particles formed from precipitation of Na_2SO_4 in ethanol become visible to the human eye only when they exceed about $10^4/\text{mL}$. These results also suggest that when added to ethanol in the form of an aqueous solution, the solubility of sodium sulfate is at least an order of magnitude higher than when added in solid, anhydrous form.

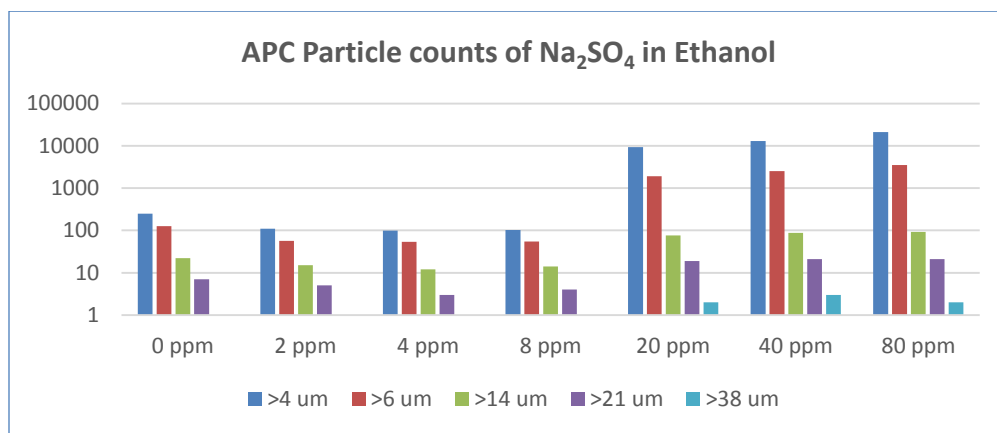


Figure 24. APC particle counts of ethanol spiked with aqueous solutions of Na_2SO_4 .
(The 2, 4, and 8 ppm solutions were prepared using a 1000 ppm aqueous Na_2SO_4 stock solution; the 20, 40, and 80 ppm solutions were prepared using a 10,000 ppm aqueous Na_2SO_4 stock solution. Average of triplicate measurements.)

Table 5 provides a summary of information from these Na₂SO₄ spiking experiments in ethanol. Water measurements by the Karl-Fischer method were conducted on the baseline ethanol and the solutions prepared with the 1000 ppm aqueous stock solution. These measurements showed good agreement with the expected results based on calculated amounts of water added with each spiking experiment. The sulfate concentrations measured by IC also agreed well with the calculated amounts added in the spiking experiments.

Table 5. Sodium Sulfate-Spiked Ethanol Solutions

Na ₂ SO ₄ Conc. in aqueous stock solution	Na ₂ SO ₄ Conc. In Ethanol	Visual Appearance	Water Content, wt.%		Sulfate Conc., ppm		APC Particle Counts >4 μm
			Calculated	Measured by KF	Calculated	Measured by IC	
none	0 ppm	Clear	0.00	0.04	0.0	0.22	247
1000 ppm	2 ppm	Clear	0.20	0.23	1.4	1.45	109
	4 ppm	Clear	0.40	0.43	2.7	2.78	99
	8 ppm	Clear	0.80	0.81	5.4	5.66	103
10,000 ppm	20 ppm	Clear	0.20	-	13.6		9328
	40 ppm	Slight Cloudiness	0.40	-	27.2		12,955
	80 ppm	Heavy Cloudiness	0.80	-	54.4		21,184

4.5.2. Explanations for high sodium sulfate solubility in spiked ethanol solutions

The experiments described above suggest that the solubility of sodium sulfate in ethanol is much higher when the salt is added as an aqueous solution as compared to direct dissolution of anhydrous solid. One possible explanation is that upon addition of a concentrated aqueous solution, Na₂SO₄ remains dissolved in a super-saturated solution, until the concentration reaches such a high level that precipitation is forced.

Another important factor may be that the form of sodium sulfate is different when added as an anhydrous solid vs. addition as an aqueous solution. In all previous solubility experiments, the anhydrous form of sodium sulfate was used. However, in the presence of excess water, sodium sulfate exists primarily in the form of a decahydrate (Na₂SO₄·10H₂O). (In nature, sodium sulfate most commonly occurs as the decahydrate, in a mineral called mirabilite, also known as Glauber's salt.) Thus, when anhydrous sodium sulfate is first dissolved in water, and then spiked into ethanol, it is actually a solution of the decahydrate that is being added. The solubility of the decahydrate in ethanol may well be different than the solubility of anhydrous sodium sulfate.

We examined this issue by purchasing a sample of sodium sulfate decahydrate and conducting simple experiments in which small increments of the solid decahydrate were added to 200 g of 200-proof ethanol and to 200 g of low aromatics gasoline. The smallest increment that we could reliably add was 0.002 g, which corresponds to addition of 10 ppm of the decahydrate, but only 3 ppm of sulfate. Following addition of each increment, the solutions were vigorously stirred for several hours. After this time, if no undissolved solids or cloudiness could be seen, another 0.002 g increment of the decahydrate was added. This process was repeated until cloudiness was observed, indicating that some of the decahydrate remained undissolved. Based upon these simple experiments, we estimated

that the solubility of the decahydrate in both ethanol and gasoline (at room temperature) is approximately 20-30 ppm, expressed on a sulfate basis. Clearly, this is much higher than the measured solubilities of anhydrous sodium sulfate in ethanol and gasoline. These observations cause us to question whether some of the higher ethanol solubilities of sodium sulfate reported in the literature were derived from using hydrated forms of the salt. In addition, the high sulfate levels reported in some marketplace gasoline-ethanol blends (such as those shown in Figure 2) may have been due to hydrated forms of sulfate salts, as the fuels probably would have appeared cloudy if they had contained such high levels of anhydrous sulfate.

In solution, conversion between anhydrous salts and hydrated forms is possible. This conversion influences the precipitation/crystallization process, and the apparent solubility of the salt. These effects are dependent upon the solvent in which the salt is placed, as well as the temperature of the system. Nordhoff and Ulrich investigated solvent-induced phase transformation of several salt hydrates, including sodium sulfate decahydrate.²⁷ They showed that when added to anhydrous methanol, hydrated salts lost some of their water of hydration and converted to their anhydrous pseudopolymorphs. (The term “pseudopolymorph” is used in referring to an anhydrous salt and its various hydrated forms.) This raises the possibility of a fully dissolved hydrated salt in a given fuel blend becoming dehydrated (and insoluble) when mixed with another fuel having lower water content. These authors also pointed out the difficulties of experimentally determining the solubilities of salts in such metastable situations.

More recently, Toro et al. investigated the solubility of sodium sulfate in a mixed solvent of water and ethanol.²⁸ Ethanol concentrations were varied over a range of 0-50%; temperatures of 25 °C and 35°C were used. In saturated solutions, the composition of the precipitated/crystallized salt varied with temperature. At 25 °C, the precipitated salt was sodium sulfate decahydrate; at 35 °C, the precipitated salt was anhydrous sodium sulfate. This literature information further confirms that determining the solubilities of sulfate salts in mixed solvents is quite difficult, and helps explain the complex nature of the field problems with marketplace gasoline-ethanol fuel blends.

4.5.3. Preparation of gasoline-ethanol blends

The observation that sodium sulfate’s solubility in ethanol appears to depend upon the method of addition introduces complexities into the experimental plan that was originally laid out. In actual field situations, water is often present, perhaps resulting in sodium sulfate (and other sulfates) being present in hydrated form, or allowing for interconversion among different pseudopolymorphs. It is also possible that these complexities contribute to the apparent inconsistencies and sporadic nature of the field problems as originally reported upon blending of ethanol with gasoline in the early-mid 2000’s.

To address the situation of sodium sulfate’s higher solubility when added to ethanol as an aqueous solution, the experimental matrix was modified from the original plans shown in Table 4. Due to limitations of time, materials, personnel, and funding, we decided to examine E10, E15, and E30 blends using only a single low aromatics gasoline (without detergent additive) and a single high aromatics gasoline (containing PEA detergent additive). However, the concentration range of sodium sulfate in these gasoline-ethanol blends was expanded beyond the original plan to include much higher levels of sodium sulfate. The entire experimental matrix is shown in Table 6.

Table 6. Experimental Matrix of Sodium Sulfate Dosed into Gasoline-Ethanol Blends

Conc. of Na ₂ SO ₄ in Ethanol	Added Water Content in EtOH, wt. %	E10		E15		E30	
		Low Aromatics	High Aromatics	Low Aromatics	High Aromatics	Low Aromatics	High Aromatics
		No PEA	High PEA	No PEA	High PEA	No PEA	High PEA
0 ppm	0.00	x		x		x	
2 ppm	0.16	x	x	x	x	x	x
4 ppm	0.32	x		x		x	
8 ppm	0.63	x		x		x	
12 ppm	0.95	x		x		x	
16 ppm	1.26	x	x	x	x	x	x
24 ppm	1.89	x	x	x	x	x	x
32 ppm	2.52	x	x	x	x	x	x

All the sulfate-dosed ethanol solutions used to produce these fuel blends were prepared by spiking 200-proof ethanol with an aqueous solution of 1000 ppm sodium sulfate. The amount of water that was added to each ethanol solution by this spiking method is also shown in Table 6. Blends containing the high aromatics gasoline were pale yellow in color; those containing low aromatics gasoline were colorless. All blends appeared clear and bright, with no cloudiness or particulate matter being seen, even at the highest concentration sample containing 32 ppm of Na₂SO₄.

4.5.4. Particle counts in gasoline-ethanol blends

Particle counts were measured for each of the gasoline-ethanol blends shown in Table 6 using the APC instrument and procedures as described previously. Numerical results are provided in Appendix Table II-3, with graphical summaries being shown in Figure 25. All the fuel blends were observed to have similar, relatively low numbers of particles, with no clear effects seen for ethanol blending ratio, aromatics content, or sulfate content. These results confirm that the hydrated form of sodium sulfate has very different solubility behavior compared to the anhydrous form.

Earlier experiments in which an aqueous solution of Na₂SO₄ was added to ethanol to produce a range of concentrations from 2 to 80 ppm (shown in Figure 24), revealed a sharp jump in particle numbers between the 8 ppm and 20 ppm samples. A similar increase in particle numbers with increasing sulfate concentration is not seen in the results of Figure 25. One key difference is that the samples shown in Figure 24 were produced using two different aqueous stock solutions of Na₂SO₄: samples with concentrations up to 8 ppm were prepared with a 1000 ppm stock solution, while those with concentration of 20 ppm and higher were prepared with a 10,000 ppm stock solution. In contrast, all samples shown in Figure 24 were prepared using the 1000 ppm stock solution. Consequently, the samples containing sodium sulfate at levels of 12 ppm and above all had higher water contents than any of the samples shown in Figure 24.

To investigate whether the additional amount of water included in the gasoline-ethanol fuel blends may be responsible for the apparent complete dissolution of sodium sulfate even at these higher concentrations, additional samples of the 24 ppm and 32 ppm E10 blends shown in Table 6 were prepared using the 10,000 ppm aqueous stock solution rather than the 1000 ppm stock solution.

Although these solutions also appeared clear and bright, the APC particle counts were about 2-3 times higher than in the blends prepared using the 1000 ppm stock solution. These results further illustrate the complex nature of sulfate solubilities in multi-component solutions, and the important roles that water and order of addition can play.

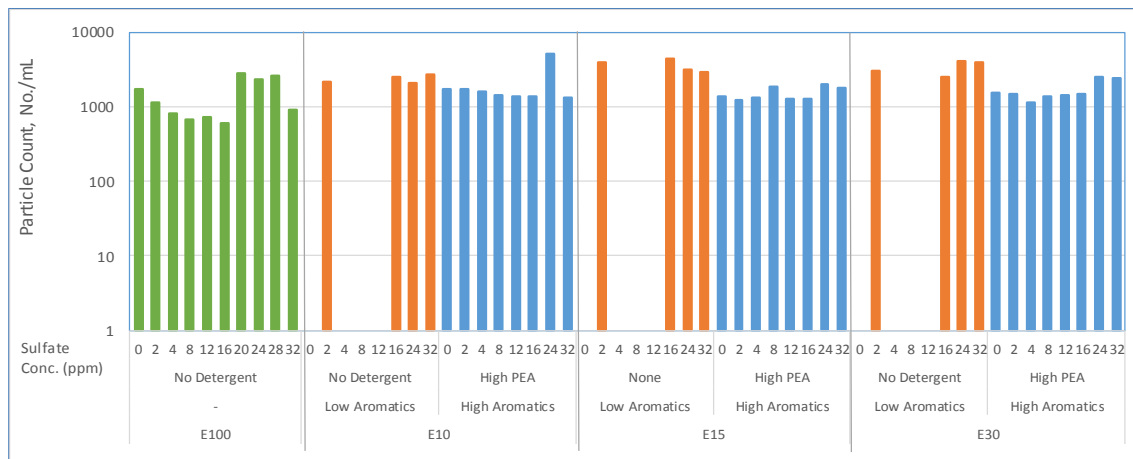


Figure 25. APC particle counts (>4 μm) in gasoline-ethanol blends spiked with Na_2SO_4 .

(Numbers along x-axis indicate concentration (ppm) of Na_2SO_4 in the ethanol blend component. Orange bars are low aromatics blends; blue bars are high aromatics blends. An aqueous solution of 1000 ppm Na_2SO_4 was used to dose each ethanol solution at the indicated sulfate concentration.)

5. Summary and Conclusions

Through a combination of literature reviews and experimental work, issues related to inorganic sulfate contamination in gasoline-ethanol fuel blends were examined. Information collected during the mid-2000's (when documented field problems were experienced with sulfate-contaminated fuels) indicated that the non-oxygenated gasoline components being used contained negligible levels of inorganic sulfate. Therefore, the contamination observed in marketplace fuels at that time was thought to originate from the ethanol blending component.

A possible cause of sulfate contamination in fuel ethanol arises from improper operation of bisulfite scrubber systems used to control air emissions of aldehydes from ethanol production plants. Use of excessive bisulfite can lead to contamination of the ethanol product with sulfurous acid (H_2SO_3), also known as aqueous SO_2 . Other sources of SO_2 or bisulfite within ethanol plants could be contributing factors. These ethanol-soluble, but volatile forms of potential sulfate can be distilled with the ethanol, thereby being present in the final fuel ethanol product. Subsequent oxidation to sulfate during fuel transport, storage and use could contribute to the deposit formation and filter plugging problems that were observed in the past. Importantly, the current ASTM sulfate specification may not be fully protective against these sulfate field problems, as it is based on measurement of existent sulfate, but does not include forms of potential sulfate such as sulfurous acid.

The solubilities of anhydrous calcium, potassium, and sodium sulfate salts in 200-proof ethanol are very low (<1 ppm) and are not significantly affected by addition of small amounts of water (2 wt.%) to the ethanol. Ammonium sulfate appears to be slightly more soluble in ethanol (~10 ppm), while sodium bisulfite has much greater solubility (>100 ppm). In non-oxygenated gasoline, sodium sulfate

and sodium bisulfite were both shown to have negligible solubility (~1 ppm). The solubility of sodium sulfate in gasoline was not affected by aromatics content, type of detergent additive used, or concentration of detergent additive. Additive type and concentration may have slight effects on the solubility of sodium bisulfite in gasoline, although additional work is necessary to confirm this.

We are not aware of any evidence that sodium bisulfite is a common contaminant in fuel ethanol. However, should this occur, it would likely contribute to fuel filter plugging and deposit problems due to two different mechanisms: (1) solubilized sodium bisulfite in neat ethanol would de-solubilize upon blending the ethanol into gasoline, and (2) bisulfite in the blended fuel would gradually oxidize to form insoluble sulfate.

Particle number counts determined using a Seta Analytics SA1000 automatic particle counter (APC) were of moderate use in assessing inorganic sulfate contamination issues, as high experimental variability limited quantitative reliability of the measurements. Solutions of both ethanol and gasoline having excess amounts of sulfate salts were found to contain large numbers of particles >4 μm in size (typically 10^4 - 10^5 particles/mL), although these solutions appeared clear and bright to the human eye. Filtration of these sulfate-containing solutions through 0.4 μm Nuclepore filters reduced the number of particles by about an order of magnitude. [As a point of reference, the base ethanol and gasoline samples that were used (without any added sulfate salts) contained 10^2 - 10^3 particles/mL.] Changes in the many experimental parameters that were examined (e.g., addition of 2 wt.% water to ethanol, high vs. low aromatics content of gasoline, type and dosage of detergent additive) had minimal effects on particle number counts.

Finally, the behavior of sodium sulfate at low concentrations was investigated in E10, E15, and E30 fuel blends. To produce ethanol blending components containing low levels of sulfate (2-32 ppm), appropriate amounts of a concentrated aqueous stock solution of sodium sulfate were spiked into the ethanol. This led to the surprising observation that the solubility of sodium sulfate in ethanol is much higher when the salt is added in its hydrated form, as opposed to its anhydrous form. Simple experiments were conducted to confirm that sodium sulfate decahydrate is more soluble in both ethanol and gasoline (by at least an order of magnitude) as compared to its anhydrous form.

These extreme differences in solubility between hydrous and anhydrous forms of sulfate salts, and the possibility of converting from one form to the other, greatly complicate efforts to ascertain sulfate solubilities and deposit formation under real-world field conditions. Also, the major effect of hydrous vs. anhydrous sulfate likely obscures any minor effects that may exist due to temperature, aromatics content, detergent type, etc. Such complexities may also help explain the apparent inconsistencies and sporadic nature of the field problems that were investigated in the early-mid 2000's.

Based upon the work conducted in this project, we are unable to confirm the suitability of the existing 4 ppm sulfate specification for fuel ethanol. However, it should be pointed out that a 4 ppm level of anhydrous sulfate exceeds the solubility limit in neat ethanol. Using ethanol containing 4 ppm sulfate to produce E10 would dilute the sulfate to a level that is likely to be completely soluble. This may not be the case if the ethanol were used to produce E20 or E30 fuel blends. However, a more significant concern with increasing ethanol content may be exacerbation of water contamination issues in marketplace fuels. As shown in this work, the manner in which sulfate salts

are exposed to water greatly affects their solubility in fuel blends, and likely their propensity to cause filter plugging deposits.

6. Recommendations

The topic of inorganic sulfate in gasoline-ethanol blends has proven to be more complex than originally thought. Despite great care taken in the laboratory, the extremely low solubilities of the anhydrous sulfate materials, and their conversion to hydrated pseudopolymorphs in the presence of water, make accurate determination of sulfate solubilities very challenging. Consequently, this work is unable to confirm or refute the suitability of the current ASTM 4 ppm max. sulfate specification for fuel ethanol. To examine this issue further, it is recommended that additional testing conditions be used, that would be more representative of actual field situations. For example, continuous filtration tests could be conducted to assess filter-plugging tendencies of different fuel blends. Such tests could be performed using a range of fuel blends and sulfate levels, both with and without exposures to water bottoms.

It is also recommended that any further experiments be conducted on a larger scale than was used in this project. Conducting small, laboratory bench top experiments requires extremely small quantities of sulfate salts, which are difficult to handle and measure with high precision. For example, producing a 1-L fuel sample containing 1 ppm of sulfate requires addition of 0.0011g of anhydrous sodium sulfate. Scaling this up to 1 barrel of fuel would increase the required amount of sodium sulfate to 0.176g, which would be much easier to handle.

A final recommendation is that when monitoring the concentration of inorganic sulfate in fuel ethanol for compliance with the ASTM D4806 standard, both existent and potential sulfate should be measured. This would provide protection against the possibility of unacceptably high levels of oxidizable forms of inorganic sulfur being present, which could contribute to enhanced levels of sulfate resulting from subsequent oxidation throughout the fuel distribution and storage system.

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Appendix I

Sulfate Solubility in Ethanol and Gasoline

Determined by ion chromatographic measurements of filtrate solutions

Table I-1: Sulfate solubility in ethanol

Table I-2: Sulfate solubility in gasoline

Table I-1: Sulfate Solubility in Ethanol

Sulfate concentration in filtrate determined by ion chromatography (IC) using ASTM D7328

Sulfate Salt	Water Content, wt. %	Temp., °C	Rep. No.	Sulfate Conc. in Filtrate, ppm	
				Existent	Potential
Ammonium Sulfate	0.0	25	1	127.24	68.73
	0.0	25	2	5.35	7.39
	2.0	25	1	9.64	12.84
Calcium Sulfate	0.0	25	1	1.00	2.75
	2.0	25	1	0.52	2.56
Potassium Sulfate	0.0	25	1	0.57	1.36
	2.0	25	1	1.04	1.63
Sodium Sulfate	0.0	25	1	0.36	0.84
	0.0	25	2	0.74	0.98
	0.0	25	3	-	0.79
	0.0	5	1	0.62	1.74
	0.0	5	2	0.60	1.12
	0.0	5	3	0.80	2.75
	2.0	25	1	0.46	0.56
	2.0	25	2	0.45	0.71
	2.0	25	3	0.52	0.73
Sodium Bisulfite	0.0	25	1	194.33	651.68
	0.0	25	2	24.13	721.18
	0.0	25	3	76.67	470.38
	0.0	5	1	49.41	342.83
	0.0	5	2	70.52	301.02
	0.0	5	3	25.34	317.40
	2.0	25	1	782.26	880.16
	2.0	25	2	493.00	895.99
	2.0	25	3	259.06	826.73

Table I-2: Sulfate Solubility in Gasoline

Sulfate concentration in filtrate determined by ion chromatography (IC) using ASTM D7328

Sulfate Salt	Aromatic Content, vol. %	Detergent Type	Detergent Level	Replicate No.	Sulfate Conc. in Filtrate, ppm	
					Existent	Potential
Sodium Bisulfite	1	None	none	1	0.27	0.35
		None	none	2	0.22	0.25
		PEA	low	1	0.93	1.50
		PEA	low	2	0.64	1.22
		PEA	high	1	0.67	0.56
		PEA	high	2	0.57	0.93
		PIBA	low	1	0.65	0.77
		PIBA	low	2	0.36	0.42
	40	PIBA	high	1	0.96	0.91
		PIBA	high	2	0.73	1.19
		None	none	1	0.30	0.42
		PEA	low	1	1.68	1.66
		PEA	low	2	1.48	1.35
		PEA	high	1	0.70	0.85
		PIBA	low	1	0.87	0.92
		PIBA	high	1	1.99	2.15
		PIBA	high	2	3.86	2.99
Sodium Sulfate	1	None	none	1	0.42	0.38
		None	none	2	0.36	4.13
		PEA	low	1	0.43	0.40
		PEA	low	2	0.30	0.50
		PEA	high	1	0.35	0.47
		PEA	high	2	0.89	0.45
		PIBA	low	1	0.28	0.66
		PIBA	low	2	0.35	0.48
	40	PIBA	high	1	0.40	0.68
		PIBA	high	2	0.29	0.49
		None	none	1	0.30	0.44
		None	none	2	0.27	8.24
		PEA	low	1	0.32	0.48
		PEA	high	1	0.34	0.28
	40	PIBA	low	1	0.46	0.42
		PIBA	high	1	0.36	0.42

Appendix II

Particle Counts of Sulfate Salt Solutions in Ethanol, Gasoline, and Gasoline-Ethanol Blends

Table II-1: Particle counts of sulfate salts in ethanol solutions

Table II-2: Particle counts of sulfate salts in gasoline solutions

Table II-3: Particle counts of sodium sulfate in gasoline-ethanol blends

Table II-1: Particle Counts of Sulfate Salts in Ethanol Solutions

Sulfate Salt	Water Content, wt. %	Temp., °C	APC Particle Counts/mL									
			Pre-Filter					Post-Filter				
			>4 µm	>6 µm	>14 µm	>21 µm	>38 µm	>4 µm	>6 µm	>14 µm	>21 µm	>38 µm
none	0.0	25	136	87	33	15	3	2173	1095	210	59	7
	0.0	25	196	89	12	4	1	462	234	61	21	3
	2.0	25	145	72	14	5	2	327	166	37	12	1
Ammonium Sulfate	0.0	25	69379	55749	15244	3710	134	21461	15800	3450	700	31
	2.0	25	26053	19479	6252	2272	165	1761	1006	164	44	5
Calcium Sulfate	0.0	25	51142	50143	40724	29684	10558	14544	11862	4386	779	7
	2.0	25	65201	64048	53180	41102	16949	17618	14357	4623	803	19
Potassium Sulfate	0.0	25	48783	39569	17567	8508	793	3583	1848	477	123	3
	2.0	25	58730	51614	26055	13720	2379	6355	3410	814	264	13
Sodium Bisulfite	0.0	25	61781	45286	6920	1530	181	34483	13945	617	144	12
	0.0	25	67516	52755	9380	1769	67	3646	1556	241	53	4
	0.0	25	62636	46271	6359	1126	62	4038	1992	278	60	4
	0.0	5	63618	47009	7563	1884	139	903	603	162	48	4
	0.0	5	64286	47242	7012	1636	153	3537	2051	366	121	17
	0.0	5	64573	48801	8400	1900	81	1627	1015	236	60	4
	2.0	25	61033	46205	7956	1995	233	52500	17851	350	69	4
	2.0	25	61851	46354	7823	1974	216	59110	13763	178	42	3
	2.0	25	61171	43872	6108	1409	145	49178	12153	151	30	2
Sodium Sulfate	0.0	25	38556	18397	1601	167	2	1391	906	187	40	2
	0.0	25	66649	46769	7535	1090	14	2035	1252	273	64	2
	0.0	25	63335	41291	4577	404	3	1959	1193	236	47	2
	0.0	5	40768	21170	1925	201	2	1822	1119	265	55	3
	0.0	5	54646	30882	3292	325	6	2033	1083	238	50	3
	0.0	5	47203	26667	2626	241	3	1504	806	188	34	2
	2.0	25	59209	44611	10627	2425	76	2780	1636	279	60	6
	2.0	25	57133	37195	4897	605	10	1493	957	288	48	3
	2.0	25	55443	37623	7269	1429	30	1814	1291	422	98	7

Table II-2: Particle Counts of Sulfate Salts in Gasoline

Sulfate Salt	Arom., Vol. %	Detergent Type	Detergent Level	APC Particle Counts/mL									
				Pre-Filter					Post-Filter				
				>4 µm	>6 µm	>14 µm	>21 µm	>38 µm	>4 µm	>6 µm	>14 µm	>21 µm	>38 µm
None	1	None	none	2449	1171	346	168	36	448	158	12	2	0
		PIBA	low	3511	2259	288	36	4	2003	1170	155	27	2
		PIBA	high	1899	1182	189	31	2	943	679	123	24	1
		PEA	low	3892	1488	108	16	1	561	230	25	4	0
		PEA	high	4797	1979	169	31	1	1004	370	33	6	1
	40	None	none	3478	1189	122	28	4	2666	1297	165	34	2
		PIBA	low	1807	858	92	26	2	1912	792	78	15	1
		PIBA	high	936	507	98	39	7	1999	853	78	19	3
		PEA	low	1479	671	65	14	1	1179	798	153	41	4
		PEA	high	2011	862	96	25	2	1776	864	128	34	3
Sodium Bisulfite	1	None	none	38461	22917	1628	132	3	1463	829	118	20	1
		None	none	70141	49293	4671	329	2	1845	1272	250	43	1
		PIBA	low	50214	27923	1820	206	4	12110	9678	2509	593	34
		PIBA	low	58049	35863	2567	267	21	4780	3105	544	95	5
		PIBA	high	48836	27695	2236	224	2	5219	3281	635	130	6
		PIBA	high	61131	36566	2700	226	2	4820	3013	746	217	14
		PEA	low	69879	53437	9256	1186	7	7706	4139	477	67	2
		PEA	low	68141	52078	9798	1256	7	8203	4878	886	147	3
		PEA	high	70812	57662	13780	2196	14	15452	10949	2749	861	41
		PEA	high	70170	55775	11800	1721	14	9839	6020	954	218	11
	40	None	none	50143	25555	1104	73	2	3229	1942	292	38	2
		PIBA	low	32032	16858	781	54	2	2545	1634	139	19	1
		PIBA	high	55933	34294	2282	132	1	3457	2170	367	73	4
		PEA	low	64927	39444	2386	153	1	3957	2278	220	29	1
		PEA	high	53712	29775	1547	90	2	4663	2984	516	124	9
Sodium Sulfate	1	None	none	65193	42571	3043	222	17	617	394	108	19	1
		None	none	36770	21172	1772	132	2	1542	1027	224	51	4
		PIBA	low	52439	26559	776	26	1	1416	716	105	25	3
		PIBA	low	71250	47407	3314	157	2	2094	1007	101	18	1
		PIBA	high	67713	38134	973	40	2	2634	1331	130	23	2
		PIBA	high	59439	29826	816	45	2	1843	1030	193	26	1
		PEA	low	52733	29931	2905	389	8	1656	1287	398	43	1
		PEA	low	61697	37190	2737	208	3	4997	4008	741	101	2
		PEA	high	22985	8083	415	21	0	1347	868	259	55	5
		PEA	high	35845	16419	951	63	3	1377	755	133	26	2
	40	None	none	13305	4147	278	36	1	1818	1256	251	27	1
		None	none	7824	2748	107	10	0	2184	1452	315	66	3
		PIBA	low	7810	2332	61	8	1	1375	756	85	15	2
		PIBA	high	6795	2319	74	8	1	2412	1181	127	21	2
		PEA	low	10752	4565	250	33	2	4229	2382	210	26	1
		PEA	high	5153	2207	115	21	2	1926	1096	104	15	1

Table II-3: Particle Counts of Sodium Sulfate in Gasoline-Ethanol Blends

Fuel Blend	Arom., Vol. %	Detergent Type	Conc. of Na ₂ SO ₄ in EtOH, ppm	>4 µm	>6 µm	>14 µm	>21 µm	>38 µm
E100	None	None	0	1714	739	100	20	1
			2	1125	546	106	24	2
			4	803	276	86	26	2
			8	669	293	64	17	2
			12	736	322	63	17	2
			16	603	272	61	17	2
			20	2827	1120	198	45	4
			24	2310	1086	210	54	6
			28	2630	1151	205	50	5
			32	911	440	107	29	3
E10	1	None	2	2132	868	46	5	0
			16	2513	1076	71	6	0
			24	2048	799	61	10	1
			32	2658	1570	188	27	1
	40	PEA	0	1713	709	54	6	0
			2	1712	729	52	5	0
			4	1622	645	44	5	0
			8	1433	572	44	5	0
			12	1375	556	40	6	0
			16	1369	541	34	3	0
			24	5066	2288	245	32	1
			32	1306	740	173	37	1
E15	1	None	2	3917	1885	148	14	1
			16	4433	2163	157	18	1
			24	3138	1636	127	16	1
			32	2857	1548	161	24	1
	40	PEA	0	1372	565	43	5	0
			2	1208	542	45	5	0
			4	1296	597	56	7	0
			8	1835	825	73	6	0
			12	1280	534	44	5	0
			16	1261	527	47	6	0
			24	1990	987	149	23	1
			32	1782	914	150	23	1
E30	1	None	2	2968	1415	169	28	2
			16	2517	1200	141	20	1
			24	4150	2134	226	35	2
			32	3977	2087	231	36	2
	40	PEA	0	1531	679	73	10	1
			2	1500	748	109	19	1
			4	1134	585	88	14	1
			8	1394	685	97	16	1
			12	1427	712	110	20	2
			16	1468	733	109	20	1
			24	2480	1211	176	31	1
			32	2448	1165	168	30	1