Calcium Sulfate Precipitation in Biotrickling Filters Treating Hydrogen Sulfide

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Thesis submitted in partial
fulfillment of the requirements for the degree
of Master of Science in the Department of
Civil and Environmental Engineering in the Graduate School
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ABSTRACT

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Abstract

Hydrogen sulfide (H_2S) is a toxic gas and common odor nuisance produced in a variety of environmental processes. The biological oxidation of H_2S to sulfate/sulfuric acid in biofilters and biotrickling filters (BTFs) for air pollution control is an efficient and well-documented treatment method. Sulfate ions produced in a BTF can interact with various cations, specifically calcium, and form insoluble salts. Gypsum ($CaSO_4*2H_2O$) and other calcium sulfate minerals formed within a BTF can affect system performance by causing increased pressure and reducing pollutant mass transfer. An experimental approach was developed to quantify calcium sulfate precipitation in BTFs as a function of critical system parameters. Trickling liquid from one laboratory and four industrial BTFs was used to induce precipitation at various levels of pH, total sulfate concentration, calcium content, and ionic strength. A computer model was developed to predict calcium sulfate precipitation based on trickling liquid ionic composition. The results support the hypothesis that calcium sulfate precipitation in a BTF treating H_2S is a realistic concern for industrial systems. The computer model was able to successfully predict precipitation within a reasonable correction factor with respect to experimental data. The presence of calcium sulfate and elemental sulfur in solids collected from industrial BTFs illustrates the feasibility of mineral deposition in full-scale treatment systems. Ethylene diamine tetraacetic acid (EDTA) was shown to be a potentially effective additive for the prevention of calcium sulfate formation in a BTF treating H_2S.

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1. Introduction

1.1 Background Information and Theory

Hydrogen sulfide (H_2S) is a toxic, foul smelling gas that is a common odor nuisance in industrial and natural settings. It is produced as a result of many environmental and chemical processes including wastewater treatment, natural gas harvesting, and biogas production. H_2S emissions must to be controlled to avoid odor nuisances associated with the persistence of H_2S in the environment. It is well documented that the biological treatment of H_2S in biotrickling filters (BTFs) is a very effective remediation technique, both in efficiency and value (1-4). Treatment of H_2S in biotrickling filters relies on sulfide-oxidizing microorganisms for the conversion of absorbed aqueous H_2S to nonvolatile sulfate species (H_2SO_4, HSO_4^-, SO_4^{2-}), or elemental sulfur when oxygen availability is limited. Often times these microorganisms are made up of bacteria from the genus *Thiobacillus*, which are ubiquitous in the environment. These bacteria are especially prevalent in soils and sediments, making the establishment of an effective culture of sulfide-oxidizing bacteria in a biotrickling filter a relatively easy process.

The chemical processes associated with the biological treatment of H_2S are critical in understanding the value of a BTF system. The chemical reactions of significance are presented as Equations 1-6. Gaseous H_2S is absorbed into the aqueous phase as it contacts the reactor scrubbing solution and then trickles through a matrix of

packing material. The packing material generally consists of lava rocks or synthetic materials such as open-pore polyurethane foam, and is utilized to allow biofilm development within the packing pore space. As the aqueous H_2S comes in contact with the microbial biofilm, it is taken up by cells and oxidized to sulfate (SO_4^{2-}) as electrons are transferred from sulfide to molecular oxygen for energy generation. Under oxygen limiting conditions, sulfide is oxidized to elemental sulfur (S^0). Sulfate formed in biological sulfide oxidation is excreted from cells to the reactor trickling liquid, where it can exist as sulfate, HSO_4^-, and sulfuric acid (H_2SO_4).

$$H_2S_{(g)} \leftrightarrow H_2S_{(aq)} \qquad K^\circ_H = 1.0 \times 10^{-1}\ \text{M/atm} \qquad (1)$$

$$H_2S_{(aq)} \leftrightarrow H^+ + HS^-_{(aq)} \qquad pK_{a1} = 6.9 \qquad (2)$$

$$HS^-_{(aq)} \leftrightarrow H^+ + S^{2-}_{(aq)} \qquad pK_{a2} = 11.96 \qquad (3)$$

$$H_2S_{(aq)} + 2\,O_2 \xrightarrow{\text{bacteria}} SO_{4(aq)} + 2\,H^+ \qquad (4)$$

$$H_2SO_{4(aq)} \leftrightarrow H^+ + HSO^-_{4(aq)} \qquad pK_{a1} \sim -3 \qquad (5)$$

$$HSO^-_{4(aq)} \leftrightarrow H^+ + SO^{2-}_{4(aq)} \qquad pK_{a2} = 1.99 \qquad (6)$$

The waste products (H_2SO_4, HSO_4^-, SO_4^{2-}) are left to circulate in the reactor until they exit in the liquid outflow, where they can be used in further applications or be disposed of. Due to the production of sulfate/sulfuric acid during biological sulfide oxidation, the pH in a bioreactor, if not controlled, is acidic. pH values of 1.5 to 3 are commonly reported in biotrickling filters treating H_2S concentrations greater than 10

ppm (3, 11). As is apparent from the examination of the equations above, the pH of a BTF system has a major impact on the system characteristics in that it effectively governs H_2S absorption kinetics and sulfuric acid equilibrium.

The trickling liquid of a BTF treating even low levels of H_2S will contain a significant concentration of sulfate ions (SO_4^{2-}), as sulfate is one of the products of sulfide oxidation. Sulfate ions can form various low-solubility salts by reacting with certain metal cations, including calcium. Calcium is of special interest due to its natural presence in municipal, surface and ground waters. The chemical interaction between calcium and sulfate ions can result in the formation of gypsum ($CaSO_4*2H_2O$), a relatively insoluble crystalline mineral, and other calcium sulfate minerals. Gypsum has a solubility in water of 2.05 g L^{-1}. The formation of gypsum within a BTF can occur due to the relatively high concentration of sulfate ions and the presence of calcium in the reactor mineral nutrient feed and/or the water itself. Indeed, concentrations of sulfate ranging from 1000 mg L^{-1} to 4000 mg L^{-1} have commonly been reported in BTFs treating H_2S.

Calcium sulfate precipitation within a BTF can have detrimental effects on reactor performance due to plugging of the packing material, which can cause increased pressure and/or a significant loss of biofilm interfacial area, reducing mass transfer and biodegradation of the target pollutant. When gypsum is formed within a biotrickling filter, it will circulate in the trickling liquid and eventually adhere to the packing

material. An example of partially plugged BTF packing material can be seen in Figure 1. In this particular example, the actual deposit was not investigated and thus, it is not known whether it was indeed gypsum. It could other calcium sulfate minerals or elemental sulfur, which is frequently observed in highly loaded H_2S-degrading BTFs. operating under oxygen-limited conditions.

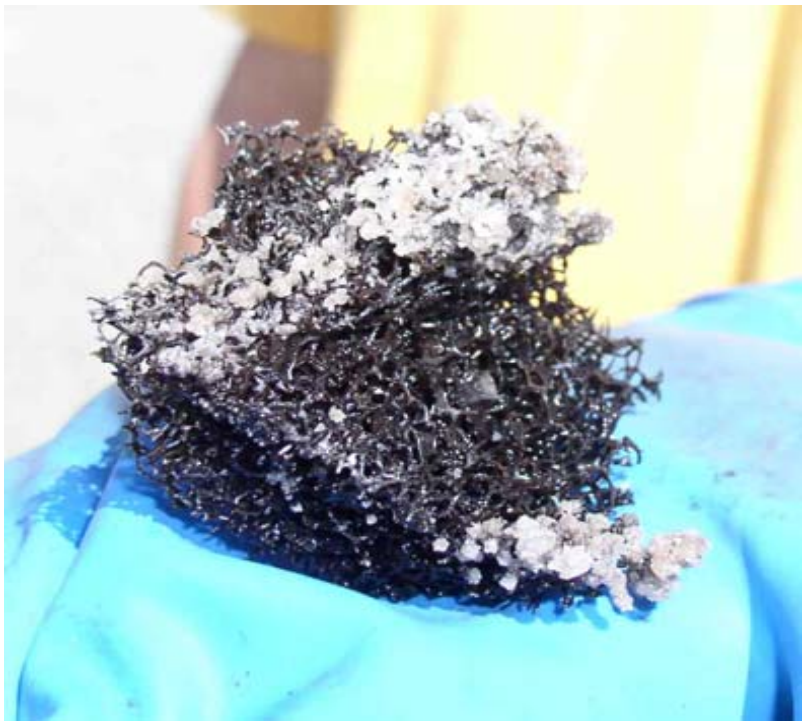


Figure 1: Mineral Deposit Attached to Biotrickling Filter Packing Material.

Gypsum formation in an aqueous solution is governed by its solubility reaction and solubility constant, or solubility product, K_{sp}. The chemical reactions and equations of significance are presented as Equations 7-9.

$$\mathrm{Ca}^{2+}_{(aq)} + \mathrm{SO}^{2-}_{4(aq)} + 2\,\mathrm{H_2O} \leftrightarrow \mathrm{CaSO_4} * 2\,\mathrm{H_2O}_{(s)} \tag{7}$$

$$\mathrm{K_{sp}} = \frac{\{\mathrm{Ca}^{2+}_{(aq)}\}\{\mathrm{SO}^{2-}_{4(aq)}\}}{\{\mathrm{CaSO_4}*2\,\mathrm{H_2O}_{(s)}\}} \tag{8}$$

$$\mathrm{K_{sp}} = \{\mathrm{Ca}^{2+}_{(aq)}\}\{\mathrm{SO}^{2-}_{4(aq)}\} \tag{9}$$

The solubility constant for gypsum is a product of the activity of sulfate ions and calcium ions in solution, divided by the activity of solid gypsum. By definition, the activity of a pure solid is equal to 1, thus the solid gypsum term in the denominator can be dropped from the equation. The solubility constant for gypsum formation is simplified to the product of the activity of sulfate ions and calcium ions in solution. The standard-state value for the gypsum solubility constant is equal to $10^{-4.62}$ mol^2 L^{-2} and corresponds to an ideal solution at standard temperature and pressure (25 °C, 1 bar) (13). Such a solution is considered ideal because its ionic strength does not affect the activity of its constituents and all activity coefficients can be assumed to equal 1, therefore equating species concentration to species activity. These assumptions are not valid for real systems and cannot be made in the analysis of effluent liquid from a BTF treating H_2S since this liquid has extremely high ionic content and numerous ions are present in significant concentrations. BTF effluent liquid can contain milli-molar concentrations of sulfate, carbonate, calcium, sodium, magnesium, and potassium. The

presence of these ions significantly impacts the activity of the various system constituents.

With the determination of the ionic strength of the trickling liquid of a BTF, appropriate activity coefficients for calcium, sulfate, and all other ionic constituents can be calculated along with the activities of each ion. With known activities for calcium and sulfate ions, a true solubility constant can be calculated for the desired BTF operating conditions and the likelihood of gypsum precipitation at these conditions can be determined. The equations used to determine ionic strength and activity coefficients are presented as Equations 10-11, where I is ionic strength, z_i is species charge, and f_i is species activity coefficient. Equation 11 is a version of the Davies Equation originally used in 1962 for the analysis of ionic associations (14). More information regarding the role of Equations 10 and 11 in this work can be found in Section 2.3.

$$I = \frac{1}{2}\sum_i [i] z_i^2 \tag{10}$$

$$\log_{10} f_i = -0.51\, z_i^2 \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I\right) \tag{11}$$

1.2 Research Objectives

The objectives of this work were to develop and demonstrate an experimental approach to quantify and validate calcium sulfate precipitation within a biotrickling filter treating hydrogen sulfide as a function of critical system parameters including reactor pH, calcium content, total sulfate concentration, and ionic strength; to develop a

fundamental understanding of the dynamic system characteristics that will promote calcium sulfate precipitation within a BTF; to investigate possible methods for the prevention of calcium sulfate precipitation; and to ultimately provide insight into safe operational and design conditions for biotrickling filters treating hydrogen sulfide for the purpose of avoiding solid formation and ensuring optimal reactor performance.

Supporting objectives to reach these goals were to:

1. Develop a rigorous and reliable method for the determination of calcium sulfate precipitation.
2. Develop a computer model to fit and/or predict the occurrence of calcium sulfate precipitation as a function of the reactor liquid pH and ionic composition.
3. Quantify calcium sulfate precipitation using samples collected from one laboratory and four industrial biotrickling filters.
4. Investigate and analyze solid formation within the laboratory and industrial BTFs.
5. Identify BTF system conditions that promote calcium sulfate precipitation.

1.3 Research Approach

The research objectives were addressed by developing an appropriate experimental approach that allowed for a rigorous and thorough investigation of the conditions that promote calcium sulfate precipitation within a biotrickling filter treating H_2S. A high-performance laboratory-scale BTF that could effectively treat low levels of

hydrogen sulfide was designed and maintained to provide well-defined samples for the systematic analysis of calcium sulfate precipitation. The trickling liquid collected from this BTF was studied and used in precipitation experiments, where it was combined with calcium ions and analyzed to determine the concentration of calcium needed to cause calcium sulfate precipitation. Trickling liquid from four industrial biotrickling filters located around the world was also used in similar precipitation experiments. Each of the five sets of samples contained a different concentration of total sulfate and a different ionic strength, allowing for a more complete range of analysis. The same six pH values (ranging from 1.25 to 3.0) were tested for each set of samples, allowing for comparison between very different systems. Ultimately, precipitation experiments and data from all sample sets were used to make firm conclusions about the conditions that are conducive to calcium sulfate mineral precipitation within a BTF treating H_2S.

The experimental and model data regarding the BTF reactor conditions that support calcium sulfate precipitation have been compared and presented in an attempt to provide information about safe operational and design parameters for the prevention of calcium sulfate mineral formation and its associated inhibitory effects.

2. Materials and Methods

2.1 Laboratory-Scale Biotrickling Filter

The laboratory-scale biotrickling filter used in the experimental approach (Figure 2) had an inner diameter of 10 cm and a bed height of 120 cm. The packing material was an open-pore polyurethane foam (PUF) with a density of 28 kg m^{-3} and a porosity of 0.90 to 0.95. The foam cubes (2 x 2 x 2 cm^3) were randomly dumped in the reactor. A mixture of humidified air and H_2S entered the biotrickling filter at the bottom of the reactor (upflow) and flowed countercurrently to the trickling liquid. Air sampling ports were located in the influent air stream before entry into the reactor and in the effluent air stream leaving the reactor. Four air sampling ports were also distributed along the height of the biotrickling filter.

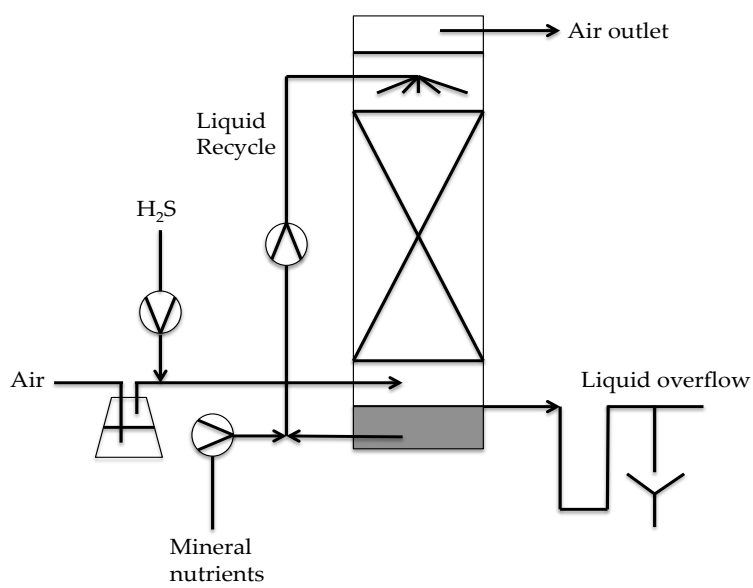


Figure 2: Schematic Representation of the Experimental Biotrickling Filter.

The mineral medium used as the biotrickling scrubbing liquid in the reactor consisted of (g L^{-1}) KNO_3 (0.05), $MgSO_4$*7 H_2O (0.05), K_2HPO_4 (0.05), NaCl (0.05), $NaHCO_3$ (0.05), $CaCO_3$ (0.02), $CaCl_2$*2 H_2O (1.0) and 1 mL L^{-1} of a trace elements solution derived from ATCC medium 1683. The mineral medium feed rate was 1.4 mL min^{-1}. The mineral medium entered the reactor at the bottom and was introduced into the trickling liquid sump. The sump liquid was pumped to the top of the reactor for recycling and dispersed evenly at a flow rate of 13 L h^{-1} over the packing material. The liquid volume (sump) in the reactor was approximately 1.5 L.

The air flow into the biotrickling filter was kept constant at 1.5 m^3 h^{-1} using a Porter mass flow controller and control module, corresponding to an empty bed residence time (EBRT) of 27 seconds. The air stream was mixed with pure (99.5%) H_2S supplied as a gas by a peristaltic pump from a 5 L Tedlar bag. The target concentration of H_2S in the influent air stream was 30 ppm (0.046 g m^{-3}). H_2S concentration measurements for the influent and effluent air streams were taken daily using a Jerome 631-X Hydrogen Sulfide analyzer (Arizona Instruments, Tempe, AZ). The daily H_2S loading rate for the biotrickling filter was 216 g m^{-3} d^{-1} (9 g m^{-3} h^{-1}). The conditions are representative of a conservatively designed biotrickling filter.

Due to the high levels of total sulfate (H_2SO_4 + HSO_4^- + SO_4^{2-}) produced in the biological oxidation of H_2S and the low flow rate of fresh medium, the biotrickling filter pH during operation reached an equilibrium value between 1.25 and 2. The main species

of sulfate under these operating conditions was HSO_4^-. Daily pH measurements were taken from the reactor effluent liquid to monitor natural pH fluctuations and reactor performance.

The biotrickling filter was operated at room temperature (20-25 °C). The reactor was inoculated with a mesophilic consortium of bacteria from soil located in Durham, North Carolina. The initial batch culture was prepared in a 250 mL flask and distributed throughout the reactor by recycling the liquid. Once the biotrickling filter was inoculated, the mineral medium feed and air/H_2S stream were applied. Both the mineral medium feed rate and H_2S loading were kept constant during reactor operation, including during the initial stages. The elimination capacity (EC) of the reactor was determined daily. The EC of a biotrickling filter is presented as Equation 12.

$$\mathrm{EC} = \frac{(\text{inlet}-\text{outlet concentration } (\mathrm{g\ m^{-3}}))}{\text{bed volume } (\mathrm{m^3})/\text{air flow } (\mathrm{m^3 h^{-1}})} \qquad (12)$$

2.2 Analytical Methods

2.2.1 Calcium Sulfate Precipitation Experimental Design

The trickling liquid from the laboratory biotrickling filter was used for calcium sulfate precipitation experiments. During reactor operation, the mineral medium feed rate was 1.4 mL min^{-1} (2 L day^{-1}) and the liquid sump volume was kept constant at approximately 1.5 L. The reactor effluent liquid flow rate was approximately 1.8 L day^{-1} due to some evaporative losses. The effluent liquid was collected in a 5-gallon plastic

carboy and used as needed. Excess reactor effluent liquid was stored in 2 L plastic bottles at room temperature (20-25 °C).

The biotrickling filter trickling liquid contained byproducts of H_2S oxidation (sulfate/sulfuric acid), minerals not utilized by microorganisms, and small concentrations of biomass. The concentration of total sulfate ($[SO_4]_T = [H_2SO_4] + [HSO_4^-] + [SO_4^{2-}]$) was determined semi-daily using a Hach sulfate kit (barium sulfate precipitation method, kit LR TNT+ 864) and a Hach DR/2500 spectrophotometer. The pH of the reactor effluent liquid was measured daily using a VWR SympHony pH electrode and an Oakton pH meter. The concentration of ionic calcium $[Ca^{2+}]$ in the effluent liquid was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Teledyne Leeman Labs High Dispersion Prism ICP.

Gypsum ($CaSO_4$*2 H_2O) and calcium sulfate mineral precipitation experiments were also carried out using biotrickling filter effluent liquid from four industrial biotrickling filters: Orange County Sanitation District in Fountain Valley, California, WeDoTech in Porto, Portugal, Cedar Rapids Water Pollution Control Facility in Cedar Rapids, Iowa, and a fourth confidential sample. In all cases, the BTF effluent liquid was filtered through a MF-Millipore VSWP 0.025 μm membrane filter and then mixed with a concentrated solution of calcium chloride dihydrate (2 M $CaCl_2$*2 H_2O). Filtered reactor effluent liquid with a known pH and $[SO_4]_T$ was placed into Hach vials (5 mL per vial) and a volume of 0 to 100 μL of concentrated calcium chloride solution was then added

to each vial. The vials were left in constant agitation on a mixing board for 6 to 8 days before further analysis was completed. After sufficient mixing, calcium sulfate precipitation was determined using dynamic light scattering (DLS). The instruments used for DLS analysis were an ALV/CGS-3 Compact Goniometer System and an ALV/LSE-5004 Light Scattering Electronics and Multiple Tau Digital Correlator.

2.2.2 Dynamic Light Scattering Analysis

For the dynamic light scattering (DLS) data processing, the photon count rate (kHz) was analyzed for filtered samples with $CaCl_2$ added and compared to a sample containing only filtered reactor effluent liquid. The photon count rate output is a measure of the light deflections caused by particles in solution, typically during a run time of 30 seconds. Large values in the photon count rate output correspond to the presence of large particles in solution (>1 μm). A large standard deviation in the photon count rate output provides information about the heterogeneity of the sample. The photon count rate of the filtered reactor effluent with no addition of $CaCl_2$ served as a baseline for comparison with the photon count rate of the samples with added $CaCl_2$.

The method for determining which Ca^{2+} concentrations yielded calcium sulfate precipitation in the samples consisted of three criteria: precipitation occurred when 1) the DLS particle count rate yielded a maximum value greater than the corresponding effluent baseline maximum value + 2 standard deviations, 2) the 10 highest values from the DLS output exceeded each of the respective 10 highest values from the effluent

baseline output, and 3) the standard deviation of the DLS output was greater than 2 times the standard deviation of the effluent baseline output. Here, the effluent baseline refers to the DLS output for the sample with no addition of $CaCl_2$. The concentrations of Ca^{2+} in the samples that met these criteria were determined, generating three values for each individual precipitation trial. The three values of $[Ca^{2+}]$ needed to cause precipitation at a specific pH and total sulfate concentration were then averaged and a definitive $[Ca^{2+}]$ value was generated for each unique pH value. This $[Ca^{2+}]$ value along with other system parameters (pH, total sulfate, ionic strength) was used to calculate a solubility product (K_{sp}) of gypsum for each set of conditions.

2.2.3 Mass Balances

Mass balances were performed on calcium and sulfur by measuring the amount of these elements entering and exiting the laboratory BTF system during a fixed period of time (24 hours) under steady operation. Mass balances for calcium and sulfur were performed during normal reactor operation and during a period of operation with an excess of calcium in the influent mineral feed. The amount of calcium entering the system over time was calculated from the concentration of calcium in the influent mineral feed and the daily influent flow rate. The amount of calcium leaving the system over time was determined by measuring the concentration of calcium in the effluent liquid using inductively coupled plasma optical emission spectroscopy (ICP-OES)

multiplied by the effluent liquid flow rate. The percent difference was calculated for balance closure.

The amount of sulfur entering the BTF system over time was determined by calculating the reactor H_2S elimination capacity (EC) and converting this value to moles of sulfur eliminated. Sulfur in the influent mineral feed was also included. Elimination capacity was determined by measuring the concentration of H_2S in the influent and effluent air streams using a Jerome 631-X hydrogen sulfide analyzer. H_2S concentrations were measured every 2 hours during mass balance data collection. The amount of sulfur leaving the system was determined by measuring the concentration of total sulfate in the effluent liquid using the Hach LR TNT$^+$ 864 sulfate kit and by measuring the effluent liquid flow rate. The percent difference was calculated for balance closure.

2.2.4 Solids Imaging and Analysis

Several methods were used to image and analyze solid samples for the determination of chemical composition and elemental bonding chemistry including scanning electron microscopy (SEM), dark-field microscopy, energy dispersive X-ray spectroscopy (EDX), and X-ray photoelectron spectroscopy (XPS). In total, five solid samples were analyzed. These samples consisted of solids collected from polyurethane (PUF) packing material sent from Orange County Sanitation District, California, Porto, Portugal, and the confidential sample, a gypsum sample that was precipitated and processed in distilled, deionized water, and a gypsum sample that was precipitated and

processed in BTF effluent liquid. The solid sample from Orange County Sanitation District was collected in March 2003. All other solid samples were collected recently.

The two solid samples collected from PUF packing material were processed as wet samples by spraying the packing material and collecting the liquid. The samples were centrifuged and the supernatant was drawn off. The remaining solid/liquid mixture was dried in a vacuum oven. Gypsum was precipitated by adding an excess of $CaCl_2$ and sodium sulfate to distilled, deionized water and by adding an excess of $CaCl_2$ to BTF effluent liquid, which contained high levels of sulfate. Once distinct solid precipitation was observed, the samples were centrifuged, the supernatant was drawn off, and the samples were dried in a vacuum oven.

The apparatus used for SEM imaging and EDX composition analysis was an FEI XL30 environmental scanning electron microscope. Electrons were concentrated on the samples using this instrument at 25 kV. The apparatus used for dark-field microscopy was an Optimus BX41 dark-field microscope. The software used for EDX analysis was developed by Bruker. The instrument used for X-ray photoelectron spectroscopy was a Kratos Analytical Axis Ultra XPS. Monochromated and charge-neutralized aluminum k-α X-rays were concentrated on the samples using this instrument at a pass energy of 160 eV for survey scanning and 20 eV for regional scanning. The pressure in the sample chamber was 5×10^{-7} Torr. XPS composition and bonding data was calibrated to carbon at 284.8 eV. The software used for XPS analysis was developed by CasaXPS.

2.3 Calcium Sulfate Precipitation Model Development

An iterative computer model was developed to predict calcium sulfate precipitation based on the ionic composition of each BTF effluent sample. Solubility constants (K_{sp} values) for gypsum are used to predict which Ca^{2+} and SO_4^{2-} concentrations are likely to cause precipitation. A standard-state K_{sp} value assumes ideal conditions (negligible ionic strength) and does not take into account that most natural systems are far from ideality. Thus, standard-state K_{sp} values must be adjusted for practical use to reflect non-ideal conditions by considering the effects of ionic strength. Because the ionic conditions in BTF effluent liquid are far from ideality, a model that can predict gypsum precipitation based on the ionic properties of the solution is essential. Ionic strength is calculated using Equation 10:

$$I = \frac{1}{2}\sum_i [i] z_i^2 \qquad (10)$$

The ionic strength calculations only include the concentration of charged ions. Ionic strength must be known to adjust the dissociation constants needed to calculate the ionic concentrations of interest. The method used for adjusting dissociation constants is the same as for adjusting K_{sp} values; ionic activity coefficients are calculated for each ion in equilibrium. Several models have been proposed for calculating ion activities. In this study, the Davies Equation (Equation 11) is used.

$$\log_{10} f_i = -0.51\, z_i^2 \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I\right) \qquad (11)$$

In Equations 10 and 11, I refers to ionic strength, z_i refers to ionic charge of species *i*, and f_i is the activity coefficient of species *i*. Species dissociation constants were determined by iteratively calculating $[H^+]$ from the hydrogen ion activity $\{H^+\}$ and the activity coefficient of H^+ (f_{H^+}) using the equation $[H^+] = \{H^+\}/f_{H^+}$, then adjusting the theoretical dissociation constants using the principle described in Equation 13 where K_A^T is the unadjusted thermodynamic dissociation constant and K_A^C the dissociation constant corrected for ionic strength. The corrected model K_{sp} values for each individual sample and precipitation trial are determined by the same approach as in Equation 13, where K_{sp}^T is the unadjusted thermodynamic solubility product of gypsum and K_{sp}^C is the solubility product corrected for ionic strength.

$$HA \underset{eq}{\Leftrightarrow} H^+ + A^- \; ; K_A^T = \frac{[H^+]f_+[A^-]f_-}{[HA]f_=} = \frac{[H^+][A^-]}{[HA]}\frac{f_+f_-}{f_=} = K_a^C\frac{f_+f_-}{f_=} \; ; \; K_a^C = K_A^T\frac{f_=}{f_+f_-} \qquad (13)$$

3. Results and Discussion

3.1 Laboratory Biotrickling Filter Performance

The experiments reported herein span over 15 months from November 2010 to February 2012 during which the laboratory-scale biotrickling filter was operated continuously. The BTF operating parameters can be seen in Table 1. After start-up of the reactor, H_2S removal started immediately and sulfate production was observed after 48 hours. The biotrickling filter reached a steady removal of H_2S after three weeks. During steady reactor operation, the target H_2S concentration in the influent stream was 30 ppm and the actual values ranged between 25 and 50 ppm. The outlet H_2S concentration did not exceed 1 ppm and the removal efficiency was consistently greater than 99%. The trickling liquid pH was between 1.25 and 2.

Table 1: Laboratory Biotrickling Filter Operational Parameters.

Parameter	Value
EBRT	27 s
$[H_2S]_{inlet}$	30 ppm
Average H_2S Removal	90%
Average H_2S Elimination	7.03 g m^3 h^{-1}
pH	1.25 – 2

3.2 Calcium Sulfate Precipitation Experimental Analysis

Dynamic light scattering (DLS) was used to determine the concentration of calcium needed to cause calcium sulfate precipitation in trickling liquid samples from one laboratory biotrickling filter (Duke University) and four industrial biotrickling filters. In DLS analysis, light deflections caused by particles in solution are measured and used to determine at what calcium concentration caused crystallization to begin to occur. Larger particles in solution cause more light deflections. For each sample set, light deflection signals were measured for a sample with no addition of concentrated $CaCl_2$ and compared to the light deflections measured for samples with incremental additions of $CaCl_2$. The light deflections significantly increased as the concentration of calcium added to the samples approached and exceeded the amount needed to cause calcium sulfate precipitation.

An example of the comparison between the DLS output for a sample with no addition of $CaCl_2$ and the DLS output for a sample with precipitation occurring can be seen in Figure 3. The "BTF Effluent" curve corresponds to a sample taken from the Duke laboratory BTF with no addition of $CaCl_2$. The oscillations are relatively consistent, typical of a baseline signal, and there is a small standard deviation of output values. The "Precipitation" curve corresponds to a sample taken from the Duke laboratory BTF with an addition of 16 μmol $CaCl_2$, sufficient to cause calcium sulfate precipitation. The signal is unsteady and there are several large peaks, which correspond to the detection of large

particles (>1 μm) in solution. Experiments like the one presented in Figure 3 were repeated with different concentrations of $CaCl_2$ and the five different trickling liquids. Once the differences in peak height and standard deviation between a sample with no addition of $CaCl_2$ and one with an addition of $CaCl_2$ were confirmed to be statistically significant according to the criteria presented in Materials and Methods, the minimum concentration of calcium needed to cause precipitation could be determined. The calcium sulfate precipitation experimental results determined by DLS can be found in Table 2.

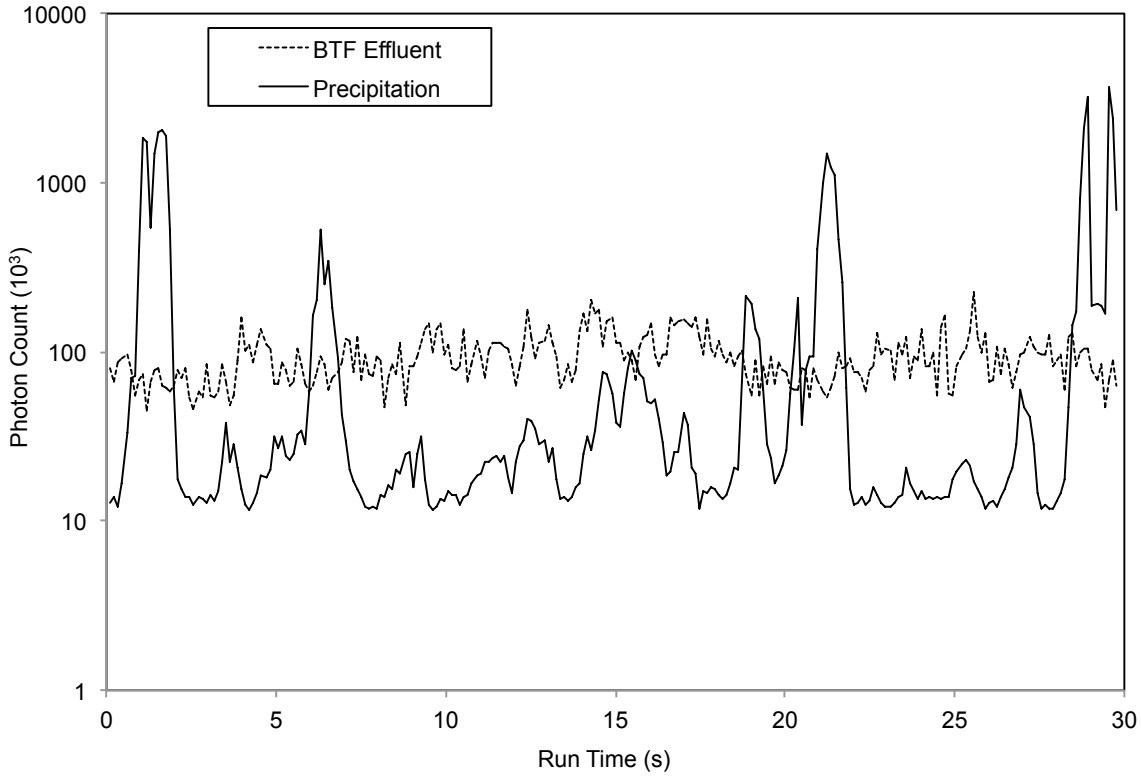


Figure 3: Particle Count Rate Output From Dynamic Light Scattering Analysis. BTF Effluent is Duke Reactor Liquid. Precipitation is After Addition of 16 μMol $CaCl_2$.

Table 2: Gypsum Precipitation Experimental Data.

pH	$[SO_4]_T$ * (mM)	$[Ca^{2+}]$** (mM)	K_{sp}^{exp} ***
Laboratory BTF, Durham, NC (Fed Synthetic Medium)			
1.25	23.8	27.8	$10^{-3.69}$
1.5	23.8	18.6	$10^{-3.68}$
1.75	27.4	16.0	$10^{-3.66}$
2.0	23.8	11.2	$10^{-3.62}$
2.5	19.0	18.0	$10^{-3.55}$
3.0	27.4	10.3	$10^{-3.43}$
Industrial BTF, Porto, Portugal (Fed Secondary Effluent)			
1.25	20.6	12.6	$10^{-4.18}$
1.5	20.6	12.6	$10^{-3.98}$
1.75	20.6	4.7	$10^{-4.23}$
2.0	20.6	2.7	$10^{-4.35}$
2.5	20.6	1.9	$10^{-4.35}$
3.0	20.6	1.5	$10^{-4.47}$
Industrial BTF, Orange County, California (Fed Secondary Effluent)			
1.25	12.2	37.1	$10^{-3.95}$
1.5	12.2	28.0	$10^{-3.94}$
1.75	12.2	25.4	$10^{-3.88}$
2.0	12.2	13.6	$10^{-4.02}$
2.5	12.2	11.6	$10^{-3.98}$
3.0	12.2	4.7	$10^{-4.19}$
Industrial BTF, Cedar Rapids, Iowa (Fed Secondary Effluent)			
1.25	11.5	39.2	$10^{-3.98}$
1.5	11.5	24.9	$10^{-4.01}$
1.75	11.5	21.0	$10^{-3.97}$
2.0	11.5	15.7	$10^{-3.98}$
2.5	11.5	10.5	$10^{-3.99}$
3.0	11.5	5.3	$10^{-4.13}$
Industrial BTF, Confidential (Fed Secondary Effluent)			
1.25	41.6	4.9	$10^{-4.14}$
1.5	41.6	8.9	$10^{-3.78}$
1.75	41.6	10.9	$10^{-3.61}$
2.0	41.6	2.2	$10^{-4.06}$
2.5	41.6	1.7	$10^{-4.03}$
3.0	41.6	1.6	$10^{-4.01}$

*$[SO_4]_T = [H_2SO_4] + [HSO_4^-] + [SO_4^{2-}]$

**$[Ca^{2+}]$ is the average minimum calcium concentration determined by DLS to cause gypsum precipitation. See Materials and Methods for details.

***$K_{sp}^{exp} = \{Ca^{2+}\}\{SO_4^{2-}\}$ at the point at which calcium sulfate precipitation is deemed to be occurring (DLS)

As the sample pH increases, the concentration of calcium needed to cause precipitation decreases significantly in the great majority of samples tested (Figure 4). This can be explained by the fact that as pH increases, the proportion of total sulfate existing as SO_4^{2-} increases, leaving more sulfate ions readily available to interact with calcium ions in solution. A few outliers to this trend can be seen in the results from the confidential sample. The outliers could perhaps be due to experimental errors, though it is more likely that they were due to the high ionic strength of this sample (0.198 M) which was the largest of all five liquid tested (Table 3). High ionic strength causes increased competition for ionic interactions and decreased ionic activity, but could also potentially result in greater variability in the DLS output.

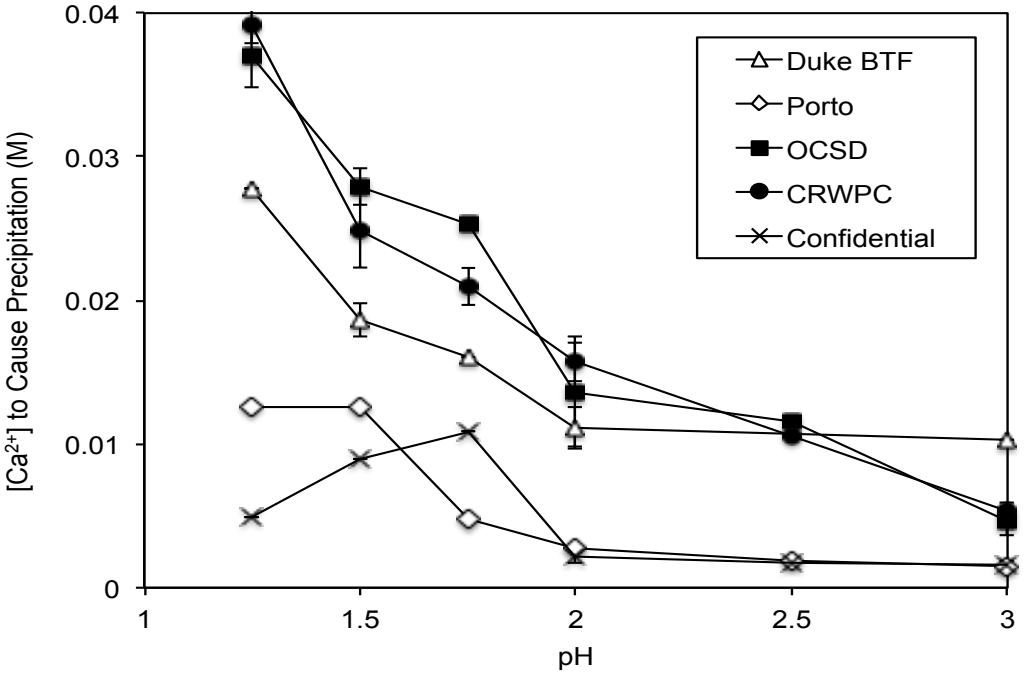


Figure 4: Minimum Calcium Concentration Needed to Cause Calcium Sulfate Precipitation as a Function of Liquid pH.

Less calcium was needed to induce precipitation in samples with a higher total sulfate concentration. The gypsum solubility product is a function of the activity of calcium and sulfate ions, so a larger value for the activity of sulfate will cause a decrease in the activity of calcium necessary for solid formation. The samples received from Orange County Sanitation District (OCSD) and Cedar Rapids Water Pollution Control Facility (CRWPC) had similarly low concentrations of total sulfate in the BTF effluent liquid, the lowest of all liquids tested. The concentration of calcium needed to cause calcium sulfate precipitation in these samples was generally higher than the other samples. Interestingly, the concentration of calcium needed to cause precipitation at the highest pH value tested (pH = 3.0) for the OCSD and CRWPC samples was less than the concentration of calcium needed to cause precipitation at pH = 3.0 for the Duke BTF sample. This is most likely attributed to the fact that the calcium content in the Duke BTF trickling liquid was much higher than the OCSD and CRWPC samples, and was over the threshold for calcium sulfate precipitation at high pH.

The confidential sample contained by far the highest total sulfate concentration (0.0416 M) of the samples tested. Very little calcium was needed to induce calcium sulfate precipitation in this sample. However, the calcium concentration data for the confidential sample is very similar to the calcium concentration data for the industrial BTF from Porto, Portugal even though the total sulfate concentration in the Porto sample (0.0206 M) is roughly half of the value for the confidential sample. This could be due to

the difference in ionic strength between these two samples. The confidential sample has a very high ionic strength, whereas the ionic strength of the Porto sample is slightly lower.

Figure 5 illustrates the dynamic relationship between sample total sulfate concentration, pH, and the concentration of calcium needed to cause calcium sulfate precipitation. As the total sulfate concentration increases, the concentration of calcium needed to cause precipitation significantly decreases. The six curves plotted correspond to each different pH value tested (between 1.25 and 3.0) and contain data from the various samples tested. As the pH increases, the curves shift downward, needing less and less calcium to induce precipitation.

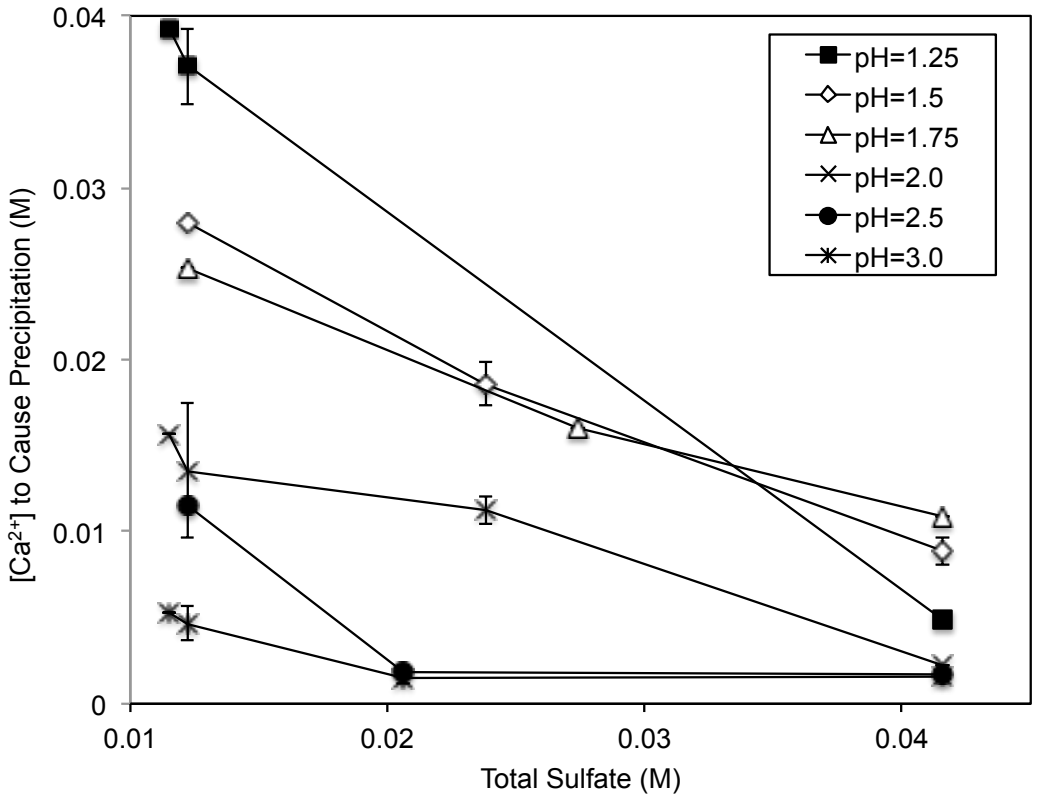


Figure 5: Minimum Concentration of Calcium Needed to Cause Calcium Sulfate Precipitation as a Function of Total Sulfate Concentration.

The relationship between ionic strength and calcium sulfate precipitation (Figure 6) is shown for each individual sample tested. Generally, as the ionic strength increases, the concentration of calcium needed to cause precipitation increases significantly as well. The samples with the highest ionic strength (Confidential and Porto) behave similarly with respect to ionic strength effects, i.e., with a leveling off or even decrease of the Ca^{2+} concentration needed for precipitation with increases of the ionic strength beyond about 0.1 M. The three remaining samples (Duke, OCSD, CRWPC) also seem to behave similarly. Ionic strength significantly affects calcium sulfate precipitation by

increasing ionic competition for molecular interaction. In this respect, increasing system ionic strength could be seen as a method for prevention of calcium sulfate precipitation. It is possible that the addition of bystander ions like sodium, potassium, and chloride could play a role in inhibiting mineral formation. This warrants further investigation. Importantly, the effects of ionic strength on gypsum precipitation are partially related to sample pH because as pH changes, so too does ionic strength.

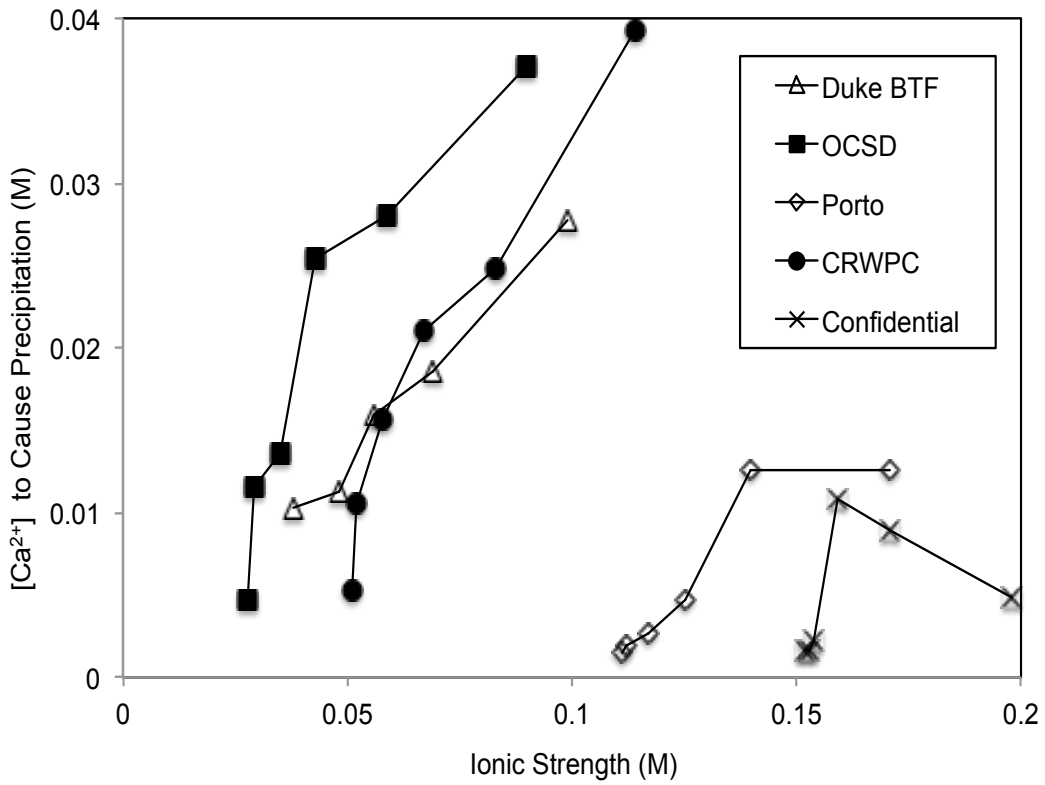


Figure 6: Minimum Concentration of Calcium Needed to Cause Calcium Sulfate Precipitation as a Function of Ionic Strength.

The effect of sulfate ion concentration on the concentration of calcium needed to cause calcium sulfate precipitation in samples is shown in Figure 7. Sulfate ion

concentration at equilibrium was determined using the total sulfate concentration and activity of hydrogen ion {H^+} for each sample. Overall, a good clustering of all experimental data is observed. The trend indicates that as the pH is increased for each precipitation trial, the concentration of sulfate ion relative to the total sulfate concentration increases and the concentration of calcium needed to cause calcium sulfate precipitation decreases. As [SO_4^{2-}] increases, the concentration of calcium needed to cause precipitation decreases greatly.

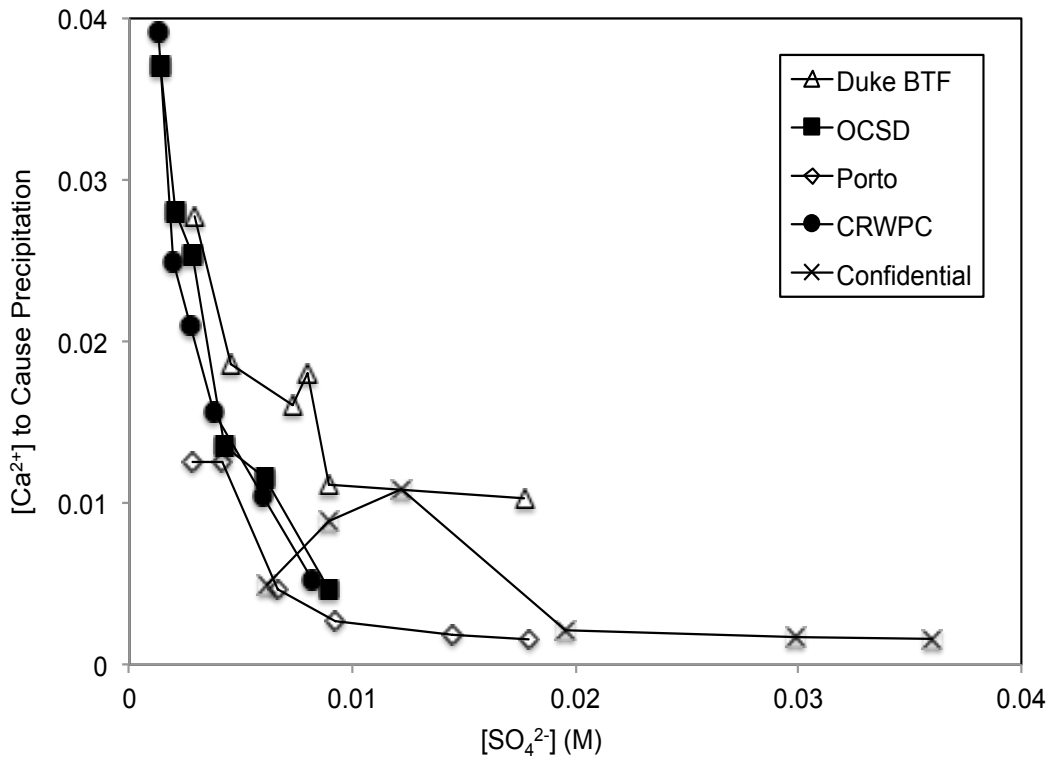


Figure 7: Minimum Concentration of Calcium Needed to Cause Calcium Sulfate Precipitation as a Function of Sulfate Ion Concentration.

Table 3: Sample Ionic Strength Data.

Sample	Ionic Strength (M)
OCSD Effluent	0.09
Duke BTF Effluent	0.099
CRWPC Effluent	0.114
Porto Effluent	0.171
Confidential Effluent	0.198

3.3 Calcium Sulfate Precipitation Model Analysis

A computer model was developed to predict calcium sulfate precipitation by considering the importance of ionic strength in affecting molecular interactions. The model returns the values for the solubility product of gypsum for each individual precipitation trial, corresponding to a single pH value. A comparison of the model, experimental, and standard-state precipitation results can be seen in Table 4. The results of the computer model appear to correlate strongly with the experimental results. On average, the solubility product of gypsum for the Duke BTF samples generated by the model differed from the experimental values by a factor of 0.78. For the industrial BTF samples, the solubility product of gypsum generated by the computer model differed from the experimental values by a factor of 1.7, 4.0, 1.6, and 2.2 for the OCSD, Porto, CRWPC, and confidential samples, respectfully, on average. In contrast, the solubility product of gypsum generated by the model differs from the standard-state values

calculated ignoring the effects of ionic strength by a factor of 8.2 on average for all samples tested.

The experimental values for the solubility product of gypsum for the Duke BTF samples differed from the standard-state value by a factor of 11 on average. This factor was 4.4, 2.5, 4.2, and 5.3 for the OCSD, Porto, CRWPC, and confidential samples, respectfully, on average. The experimental results fit more closely with the model results than the standard-state value for the solubility product of gypsum for all samples except those from Porto. Generally, the experimental results for the solubility product fell somewhere in between the values generated by the model and the standard-state value. The model tended to over-predict the amount of calcium needed to cause calcium sulfate precipitation relative to the experimental data. This is not true however for the Duke BTF samples. The experimental and model results generally agree within a correction factor of 2. The model demonstrates the ability to successfully predict the conditions in which gypsum and other calcium sulfate mineral precipitation will occur within a biotrickling filter treating H_2S within a reasonable correction factor.

Figure 8 illustrates the ability of the computer model to predict gypsum precipitation. Two data points from each sample set (corresponding to pH=1.75 and pH=2.5) are plotted with the ratio of the solubility product generated by the model to the solubility product from the experimental results (K_{sp}^{mod} / K_{sp}^{exp}) listed for each point. Two pH values were used from each sample to give a fair representation of the data set

while eliminating clutter in the figure. The difference factors shown are generally between 0.5 and 2, indicating the good agreement this model shows with the experimental data. These data points are representative of the entire data set, as seen in Table 4. The values larger than 2 correspond to data points from the Porto and confidential samples.

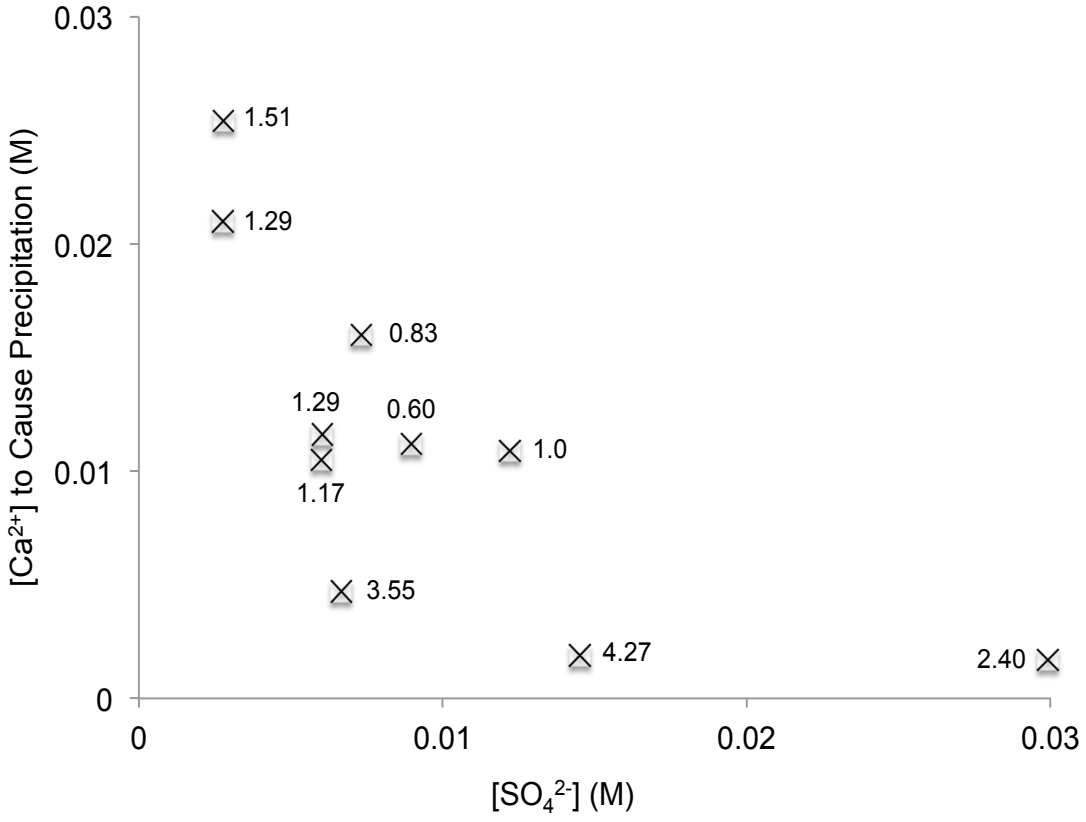


Figure 8: Calcium Sulfate Precipitation Data With Model-to-Experimental Index Values (pH=1.75 and 2.5). The Legend is the Ratio K_{sp}^{mod} / K_{sp}^{exp} for Each Point.

A direct comparison between the experimental and model K_{sp} values for gypsum precipitation can be seen in Figure 9. The solubility product of gypsum determined from experimental data is plotted on the x-axis, and the solubility product of gypsum generated by the computer model is plotted on the y-axis, with data points corresponding to each pH value tested in all five BTF samples. The horizontal dashed line in Figure 9 is the experimental K_{sp} values for each data point plotted against the standard-state value for the solubility product of gypsum. If the values for K_{so} determined by the experimental data and the computer model were identical, they would fall on a line with a slope of 1, shown in Figure 9 as m=1.

Overall, the data has good clustering around the line shown in Figure 9 with a slope of 2 (m=2), meaning that the model K_{sp} values tend to exceed the experimental K_{sp} values by a factor of 2. This figure illustrates the tendency of the computer model to over-predict the amount of calcium needed to cause precipitation, as most data points fall to the left of m=1. Interestingly, the data points from the Duke BTF sample are the only ones found to the right of m=1, meaning the experimental K_{sp} values are larger than the model K_{sp} values. Here, the difficulty in scaling a laboratory BTF system for mimicry of industrial systems is reflected in the data. All of the data points plotted fall to the left of the line corresponding to the standard-state value for the solubility product of gypsum, meaning more calcium is required to cause precipitation in the experimental and model results than the standard-state value would suggest. Figure 9 is a good

visualization of the general trends associated with the relationship between the solubility product of gypsum determined by experimental results, computer model output, and standard-state analysis. It also displays the room for improvement in the accuracy of the computer model and its agreement with experimental data.

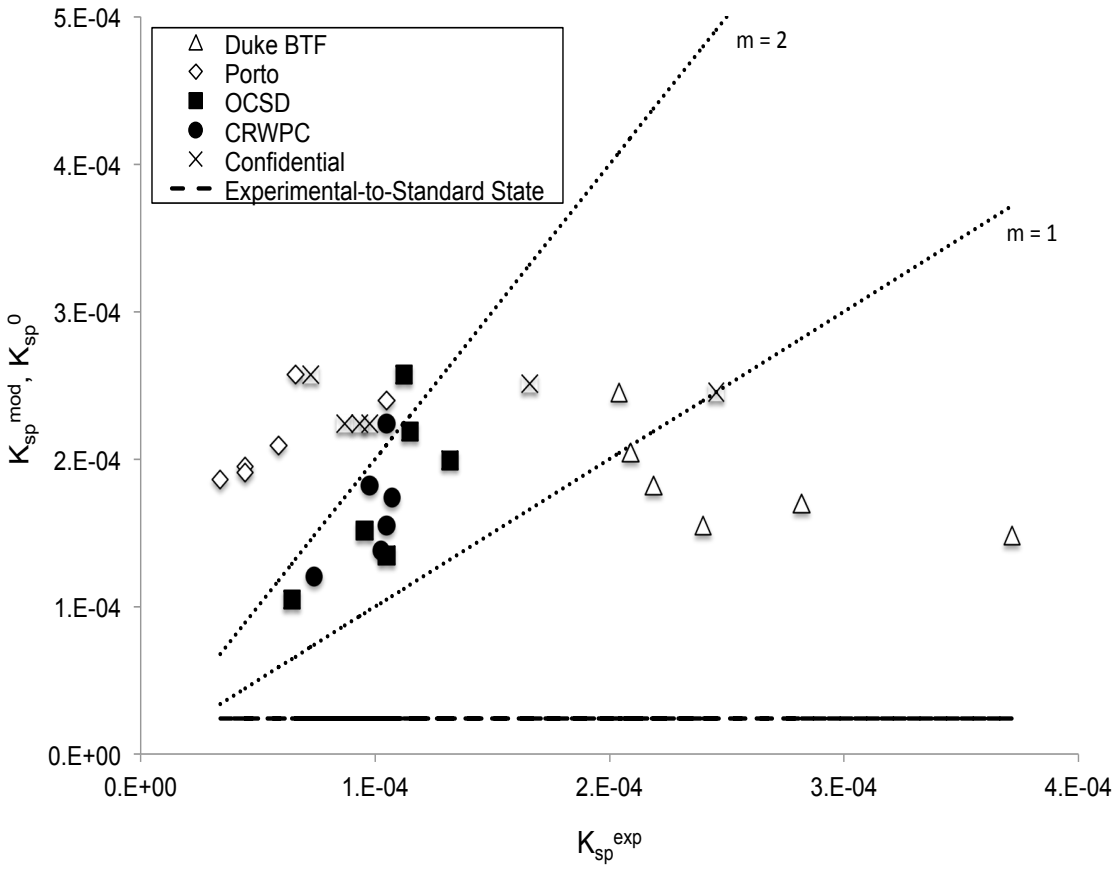


Figure 9: A Comparison of Experimental and Model K_{sp} Values for Data Points From Five BTF Samples.

Table 4: A Comparison of Experimental, Model, and Standard-State Gypsum Precipitation.

pH	K_{sp}^{exp}	K_{sp}^{mod}	K_{sp}^{0}	$K_{sp}^{mod}/K_{sp}^{exp}$	K_{sp}^{exp}/K_{sp}^{0}	K_{sp}^{mod}/K_{sp}^{0}
Laboratory BTF, Durham, NC						
1.25	$10^{-3.69}$	$10^{-3.61}$	$10^{-4.62}$	1.2	8.5	10.2
1.5	$10^{-3.68}$	$10^{-3.69}$	$10^{-4.62}$	0.97	8.5	8.7
1.75	$10^{-3.66}$	$10^{-3.74}$	$10^{-4.62}$	0.83	11.5	7.6
2.0	$10^{-3.62}$	$10^{-3.81}$	$10^{-4.62}$	0.65	10	6.5
2.5	$10^{-3.55}$	$10^{-3.77}$	$10^{-4.62}$	0.6	11.8	7.1
3.0	$10^{-3.43}$	$10^{-3.83}$	$10^{-4.62}$	0.4	15.5	6.2
Industrial BTF, Porto, Portugal						
1.25	$10^{-4.18}$	$10^{-3.59}$	$10^{-4.62}$	3.9	2.8	10.7
1.5	$10^{-3.98}$	$10^{-3.62}$	$10^{-4.62}$	2.3	4.4	10
1.75	$10^{-4.23}$	$10^{-3.68}$	$10^{-4.62}$	3.6	2.5	8.7
2.0	$10^{-4.35}$	$10^{-3.71}$	$10^{-4.62}$	4.4	1.9	8.1
2.5	$10^{-4.35}$	$10^{-3.72}$	$10^{-4.62}$	4.3	1.9	7.9
3.0	$10^{-4.47}$	$10^{-3.73}$	$10^{-4.62}$	5.5	1.4	7.8
Industrial BTF, Orange County, California						
1.25	$10^{-3.95}$	$10^{-3.59}$	$10^{-4.62}$	2.3	4.7	10.7
1.5	$10^{-3.94}$	$10^{-3.66}$	$10^{-4.62}$	1.9	4.8	9.1
1.75	$10^{-3.88}$	$10^{-3.70}$	$10^{-4.62}$	1.5	5.5	8.3
2.0	$10^{-4.02}$	$10^{-3.82}$	$10^{-4.62}$	1.6	4	6.3
2.5	$10^{-3.98}$	$10^{-3.87}$	$10^{-4.62}$	1.3	4.4	5.6
3.0	$10^{-4.19}$	$10^{-3.98}$	$10^{-4.62}$	1.6	2.7	4.4
Industrial BTF, Cedar Rapids, Iowa						
1.25	$10^{-3.98}$	$10^{-3.65}$	$10^{-4.62}$	2.1	4.4	9.3
1.5	$10^{-4.01}$	$10^{-3.74}$	$10^{-4.62}$	1.9	4.1	7.6
1.75	$10^{-3.97}$	$10^{-3.76}$	$10^{-4.62}$	1.3	4.5	7.2
2.0	$10^{-3.98}$	$10^{-3.81}$	$10^{-4.62}$	1.5	4.4	6.5
2.5	$10^{-3.99}$	$10^{-3.86}$	$10^{-4.62}$	1.2	4.6	5.8
3.0	$10^{-4.13}$	$10^{-3.92}$	$10^{-4.62}$	1.6	3.1	5.0
Industrial BTF, Confidential						
1.25	$10^{-4.14}$	$10^{-3.59}$	$10^{-4.62}$	3.6	3	10.7
1.5	$10^{-3.78}$	$10^{-3.60}$	$10^{-4.62}$	1.5	6.9	10.5
1.75	$10^{-3.61}$	$10^{-3.61}$	$10^{-4.62}$	1	10.2	10.2
2.0	$10^{-4.06}$	$10^{-3.65}$	$10^{-4.62}$	2.6	3.6	9.3
2.5	$10^{-4.03}$	$10^{-3.65}$	$10^{-4.62}$	2.4	4.1	9.3
3.0	$10^{-4.01}$	$10^{-3.65}$	$10^{-4.62}$	2.3	4.1	9.3

3.4 Calcium and Sulfur Balances

Calcium and sulfur balances were performed in an attempt to track the fate of degraded H_2S and to quantify any calcium sulfate precipitation within the laboratory biotrickling filter during normal operation and when an excess of calcium was fed the reactor. H_2S removal rates and sulfate production rates were subject to fluctuations due to H_2S loading variations and natural reactor performance variations, but precise mass balances were carried out over separate 24-hour periods during steady reactor operation. Mass balance data can be found in Table 5. During normal operation, the inlet and outlet hydrogen sulfide concentrations were 15 ppm and 0.05 ppm respectively, the influent medium flow rate was 1.73 L day^{-1}, and the effluent liquid flow rate was 1.63 L day^{-1}. The moles of calcium that entered and exited the system during this normal operation were within 7.5 percent, while those of sulfur were within 11.4 percent. It can be concluded from these results that very little or no calcium sulfate precipitation occurred within the reactor during normal operation.

A second calcium and sulfur balance was performed during reactor operation with an excess of calcium in the mineral feed. The concentration of $CaCl_2$ in the influent nutrient feed was increased from 1.0 g L^{-1} to 3.0 g L^{-1}. Calculations with the computer model and experimental data (see Table 4) indicate that this excess of calcium should result in calcium sulfate precipitation within the reactor. The inlet and outlet H_2S concentrations during this mass balance were 28 ppm and 0.05 ppm, respectively, the

influent medium flow rate was 1.70 L day^{-1}, and the effluent liquid flow rate was 1.41 L day^{-1}. The number of moles of calcium that entered the system during this mass balance was 75 percent larger than the number of moles of calcium that exited the system. The number of moles of sulfur that entered the system during this mass balance was 35 percent larger than the number of moles of sulfur that exited the system. These data suggest that calcium sulfate precipitation was indeed occurring within the reactor. The effluent liquid collected during this experiment was analyzed for total suspended solids by filtration and weighing. There were no detectable suspended solids in the effluent liquid during this mass balance, leading to the conclusion that gypsum and other calcium sulfate minerals were building up in the reactor.

The concentrations of calcium and sulfate in the industrial BTF samples (influent and effluent liquid) are listed in Table 6. Sulfate concentrations are much higher in the effluent liquid for all samples due to the biological oxidation of gaseous sulfide to sulfate in the BTF. The concentrations of calcium in the effluent liquid are higher than the influent liquid for all four samples except for the confidential sample. Calcium is increased in concentration in the effluent liquid of the OCSD, Porto, and CRWPC samples most likely due to moderate water evaporation in those systems. The lack of a decrease in the calcium content in the effluent liquid of these three samples indicates that calcium sulfate precipitation is probably not currently occurring within these systems. However, there is a distinct decrease in calcium concentration in the effluent

liquid of the confidential sample relative to the influent liquid. This could indeed be caused by calcium sulfate precipitation occurring within this system. A difference between the calcium content of the influent and effluent liquid of a BTF could be a useful indicator of precipitation taking place. Further analysis of solid samples collected from the OCSD, Porto, and confidential BTFs is presented in section 3.5.

Table 5: Calcium and Sulfur Mass Balance Data Collected Over 24 Hours (Duke BTF).

Calcium and Sulfur Balance – Normal Operation (7 mM)	
$Calcium_{in}$	0.0121 mol
$Calcium_{out}$	0.0130 ± 0.000052 mol
% Calcium Balance Closure	107.4%
$Sulfur_{in}$	0.0240 ± 0.0016 mol
$Sulfur_{out}$	0.0213 ± 0.00072 mol
% Sulfur Balance Closure	88.7%
Calcium and Sulfur Balance – Excess Calcium (21 mM)	
$Calcium_{in}$	0.0350 mol
$Calcium_{out}$	0.01995 ± 0.00008 mol
% Calcium Balance Closure	57%
$Sulfur_{in}$	0.0381 ± 0.0026 mol
$Sulfur_{out}$	0.0283 ± 0.00096 mol
% Sulfur Balance Closure	75.3%

Table 6: Calcium and Sulfate Data for Four Industrial BTF Systems.

Sample	$[Ca^{2+}]$ (M)	$[SO_4^{2-}]$ (M)
OCSD Influent	0.00154	0.0019
OCSD Effluent	0.00168	0.0122
Porto Influent	0.0003	0.00054
Porto Effluent	0.00071	0.0216
CRWPC Influent	0.00162	0.0029
CRWPC Effluent	0.00251	0.0115
Confidential Influent	0.00116	0.001
Confidential Effluent	0.00091	0.0416

3.5 Solids Imaging and Analysis

3.5.1 SEM-EDX Analysis and Dark-Field Microscopy

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) were used to visualize and analyze solid samples collected from industrial BTFs from Orange County Sanitation District, California, from Porto, Portugal, and from a confidential system, as well as solids generated by combining calcium and sulfate ions in distilled water and BTF reactor effluent in the laboratory. Dark-field microscopy was used to visualize experimental gypsum precipitation samples containing BTF effluent liquid from Duke University and $CaCl_2$. Selected dark-field microscopy pictures can be found in Appendix E.

SEM was used in combination with EDX for sample imaging and chemical composition analysis. SEM pictures of the solid sample collected from Orange County

Sanitation District and gypsum crystals precipitated in distilled water can be seen in Figures 10 and 11. Additional SEM pictures can be found in Appendix C. The solid sample from OCSD was collected in March 2003, and therefore is not a current representation of the state of this system. All other solid samples were collected recently. The presence of sulfur, oxygen, and carbon was detected in each of the solid samples collected from industrial BTFs using EDX, along with trace amounts of aluminum and silicon. The presence of calcium, sulfur, oxygen, and carbon was detected in the solid sample collected from Orange County Sanitation District, California using EDX, along with trace amounts of aluminum and silicon. Carbon is detected in all EDX trials due to the usage of carbon tape for sample securement. The presence of aluminum is likely to be from the aluminum trays used in sample drying.

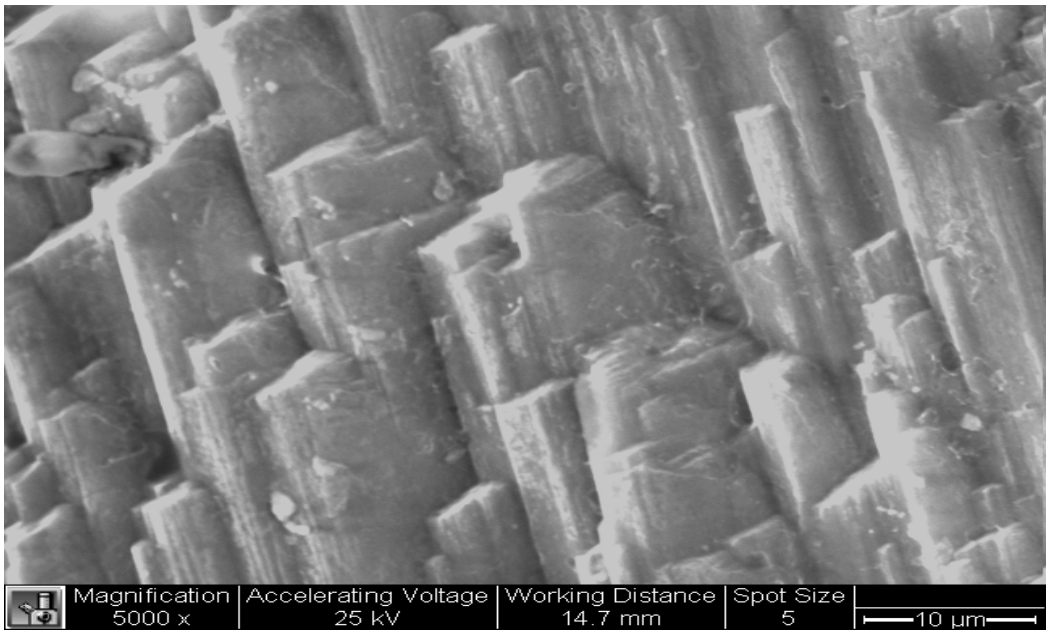


Figure 10: SEM Imaging of Solid Sample Collected From Orange County Sanitation District, California (2003).

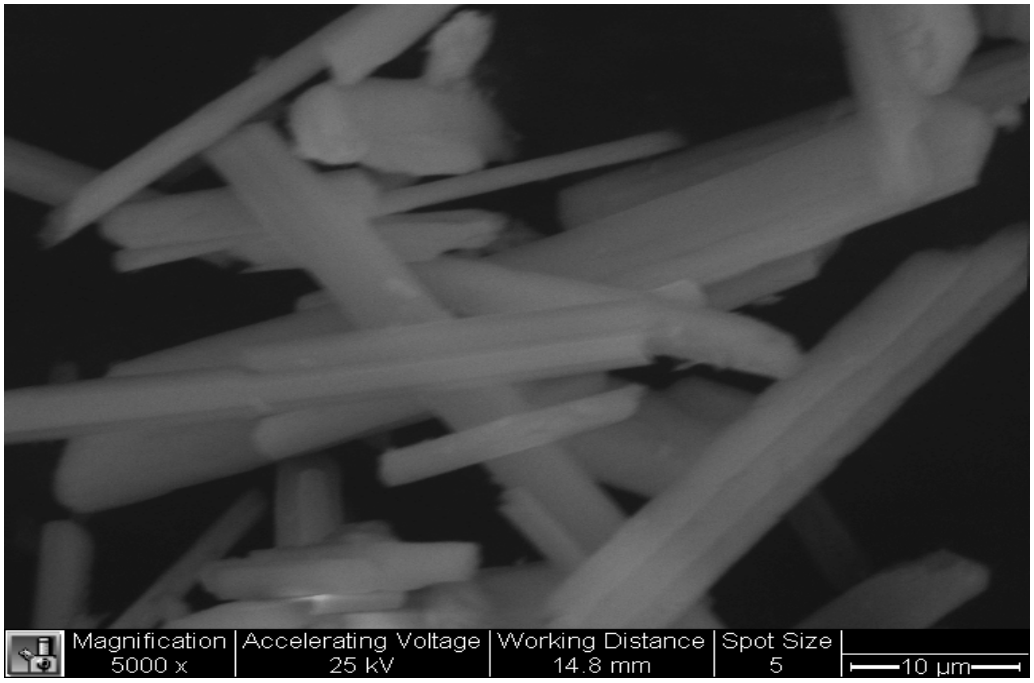


Figure 11: SEM Imaging of Gypsum Crystals Precipitated Distilled Water from Ca^{2+} and SO_4^{2-} in Distilled Water.

A comparison of the EDX spectra for the solid samples collected from Orange County Sanitation District, Porto, and the confidential sample (Figure 12) helps to illustrate the distinct similarities in the chemical composition of the Porto and confidential solids. Interestingly, there is no detectable presence of calcium in either of these samples, however sulfur and oxygen are present in significant amounts. The EDX spectrum for the solid sample collected from Orange County Sanitation District deviates in that it does indicate a significant presence of calcium. The detection of calcium, sulfur, and oxygen in significant quantities in the solid sample collected from Orange County Sanitation District allows for the conclusion that this solid is at least partly composed of gypsum and other calcium sulfate minerals.

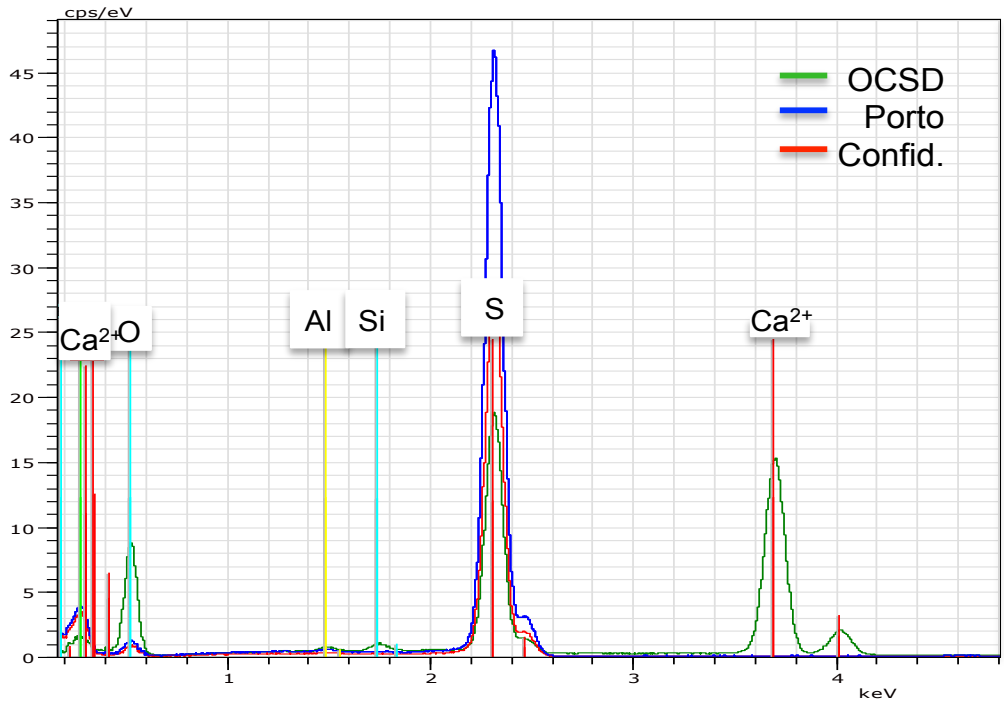


Figure 12: A Comparison of EDX Spectra for Three Solid Samples.

EDX was also used in the analysis of the gypsum samples precipitated with distilled water and Duke BTF effluent liquid. The presence of carbon, oxygen, calcium, and sulfur was detected in both gypsum samples. Chlorine was detected in the gypsum sample precipitated in Duke BTF effluent, possibly caused by dual solid phases of gypsum and calcium chloride. A comparison of the EDX spectra for the gypsum samples precipitated in distilled water and Duke BTF effluent liquid can be seen in Figure 13. The detection of calcium, sulfur, and oxygen in significant quantities in these samples support the notion that they are indeed composed of gypsum. Additional EDX spectra and associated data can be found in Appendix C.

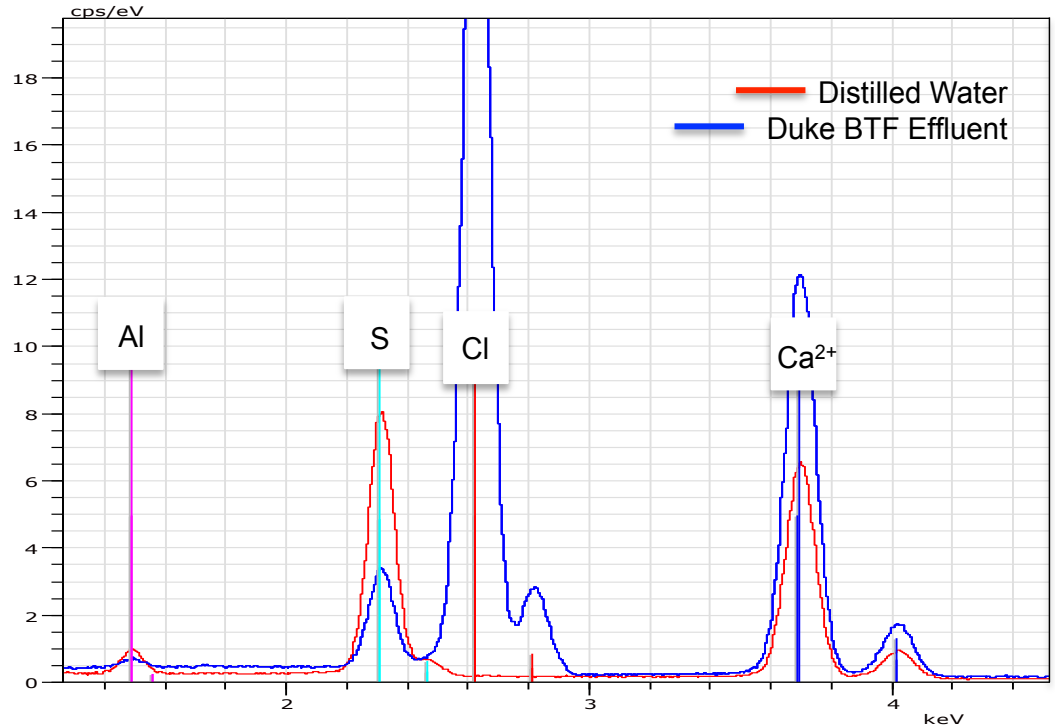


Figure 13: A Comparison of EDX Spectra for Gypsum Samples Precipitated in Distilled Water and Duke BTF Effluent Liquid.

3.5.2 XPS Analysis

X-ray photoelectron spectroscopy (XPS) was used for in-depth analysis of the chemical composition and elemental bonding chemistry of solid samples collected from Orange County Sanitation District, Porto, and the confidential sample, as well as gypsum precipitated in distilled water and Duke BTF effluent liquid. XPS survey scans were used to determine the chemical composition of the solid samples, and regional scans were used to examine the bonding characteristics of sulfur in the samples. The presence of sulfur, oxygen, carbon, and a trace amount of nitrogen were detected in each of the solid samples collected from industrial BTFs using XPS survey scanning. The atomic percentages for sulfur and oxygen were 17 and 72, 17.5 and 69, and 27.7 and 59 for the OCSD, Porto, and confidential solid samples, respectfully. These values exclude carbon, as it is inherently present in every sample tested. Calcium (3.8%) was detected in the solid sample collected from Orange County Sanitation District. The presence of calcium, sulfur, oxygen, and carbon was detected in both gypsum samples using XPS survey scanning. Chlorine was detected in the gypsum sample precipitated in Duke BTF effluent liquid as a result of dual solid phases of gypsum and calcium chloride. All solid sample XPS survey scans can be found in Appendix D.

XPS regional scanning was used to examine the bonding characteristics of sulfur in the solid samples. Specifically, regional scanning was able to determine to what atoms sulfur was bound to in the samples and what molecules these atoms formed. Consistent

with all of the solid samples, sulfur existed either as elemental sulfur via S-S bonding, or as sulfate via S-O bonding. In the XPS regional scan of the solid sample collected from Orange County Sanitation District, sulfur existed only as sulfate. Sulfur within the solid samples collected from Porto, Portugal and the confidential sample existed as both sulfate and elemental sulfur. In the solid sample collected from Porto, sulfate represented 62.4% of the sulfur and S^0 represented 37.6% (atomic percentage). In the solid sample collected from the confidential sample, sulfate represented 51.8% of the sulfur and S^0 represented 48.2%. Sulfur within the gypsum samples precipitated in distilled water and Duke BTF effluent liquid existed only as sulfate consistent with the fact that there is no mechanism for the reduction of sulfate to elemental sulfur. All XPS sulfur regional scans can be found in Appendix D.

The detection of calcium and sulfur as sulfate is concrete evidence to conclude the presence of calcium sulfate minerals like gypsum within a solid sample. The results from the XPS analysis confirm the presence of calcium sulfate in the solids collected from Orange County Sanitation District and confirm that the two calcium/sulfate samples precipitated in distilled water and Duke BTF effluent liquid are indeed composed of gypsum. Surprisingly, all results point to the fact that the solid samples collected from Porto and the confidential sample do not contain gypsum or any other calcium sulfate mineral. It is evident that both elemental sulfur and sulfate are present within the solids collected from these systems. It is unclear to what cation(s) the sulfate

in these two samples is bound to. The presence of elemental sulfur in the solids could be caused by BTF operation with locally limited oxygen availability, which can occur when the H_2S concentrations are high. Under these conditions, sulfide is oxidized to S^0 instead of a complete oxidation to sulfate. It is likely that H_2S concentrations fluctuated within these two reactors resulting in various degrees of dissolved oxygen limitation over time and within the depth of the biofilm, causing the presence of both elemental sulfur and sulfate.

More than likely, the BTF from Orange County Sanitation District did not operate with oxygen-limited conditions when the solid sample was collected, and sulfide was fully oxidized to sulfate. This is consistent with the relatively low H_2S concentrations treated and very high air flow rate in that biotrickling filter (2). The sulfate produced in the BTF subsequently interacted with calcium and calcium sulfate mineralization occurred. On the other hand, the PUF packing material from Porto and the confidential sample contained a deposit comprised of elemental sulfur and sulfate. The confidential biotrickling filter is reported to be exposed to relatively high H_2S concentrations (>50 ppm) and loadings, which are factors enhancing the probability of elemental sulfur formation. The BTF in Porto is reported to operate at moderate H_2S concentrations (25-40 ppm). The greater proportion of elemental sulfur in the mineral deposit from the confidential sample compared with the deposit from the Porto sample

could be caused by higher inlet H_2S concentrations and loadings in the confidential BTF system.

The fact that calcium was not detected in the solid sample from the confidential BTF is unexpected, especially given the presence of sulfate and the difference in calcium content of the influent and effluent streams (see Table 6). It is less unexpected in the Porto sample due to the lack of a significant difference in the calcium content in the influent and effluent streams for that system, although the packing from that reactor has visible deposits that did not resemble sulfur. It is highly improbable that calcium was present in the samples and undetected by XPS, hence it was probably just not there to begin with. It is possible that the sulfate detected in these solid samples was bound to ammonium. The sulfur regional spectrum for ammonium sulfate $(NH_4)_2SO_4$ is nearly indistinguishable from the sulfur regional spectrum for sulfate (20). Nitrogen was detected in both the Porto sample (4.2%) and the confidential sample (3.5%). While the presence of ammonium sulfate in the solid samples is a very real possibility, the results are not conclusive. Most likely, calcium sulfate was not detected in the solids from Porto and the confidential sample because there was not enough calcium present induce precipitation.

3.6 Calcium Sulfate Precipitation Prevention Using EDTA

Disodium ethylene diamine tetraacetate, a salt of ethylene diamine tetraacetic acid (EDTA), was used in an attempt to inhibit calcium sulfate precipitation within the

laboratory BTF. EDTA is a well-known chelating agent and is very effective at binding metal cations like calcium. EDTA can bind calcium ions in a 1-to-1 molar ratio (18). EDTA was added prior to precipitation experiments to determine its effectiveness at binding calcium ions and preventing gypsum from forming in solution. EDTA was added in a molar ratio with respect to the amount of calcium present in the samples (including the addition of $CaCl_2$). The experiments involving the addition of EDTA were performed using BTF effluent liquid from Duke University with a pH of 3 and a total sulfate concentration of 0.024 M. The results are presented in Figures 14 and 15.

The samples with an addition of EDTA of less than 1 mole EDTA per mole calcium in solution showed a decrease in the concentration of calcium needed to cause precipitation. This trend is obvious despite the relatively large error associated with these data points. A possible explanation to this phenomenon is that the addition of a small amount of disodium EDTA decreases the competition between hydrogen ions and calcium ions for interaction with sulfate by creating an interaction between hydrogen ions and EDTA. At low pH, EDTA becomes protonated and will not chelate very effectively (19). As hydrogen ions interact with and bind to EDTA, they are unable to compete with calcium for interaction with sulfate, allowing calcium sulfate precipitation to occur more efficiently. As EDTA is added in excess, it begins to overcome protonation and can interact with calcium more effectively.

The addition of 1 mole of EDTA per mole of calcium increased the calcium concentration needed to cause precipitation by approximately 12%, whereas the addition of 2 moles of EDTA per mole of calcium increased the calcium concentration needed to cause precipitation by approximately 26%. The addition of EDTA in excess of 2 moles EDTA per mole calcium yielded identical results.

The samples with an addition of EDTA between 1 and 2 moles EDTA per mole calcium showed a moderate increase in the concentration of calcium needed to cause precipitation, whereas the samples with an addition of greater than 2 moles EDTA per mole calcium showed the greatest increase in the concentration of calcium needed to cause precipitation. Thus, an excess of EDTA is needed to provide the greatest capacity for calcium sulfate precipitation prevention with EDTA. It can be concluded from these results that the addition of 2 moles of EDTA per mole of calcium in solution to the trickling liquid of a BTF where the possibility of calcium sulfate precipitation is a concern could be an effective preventative strategy.

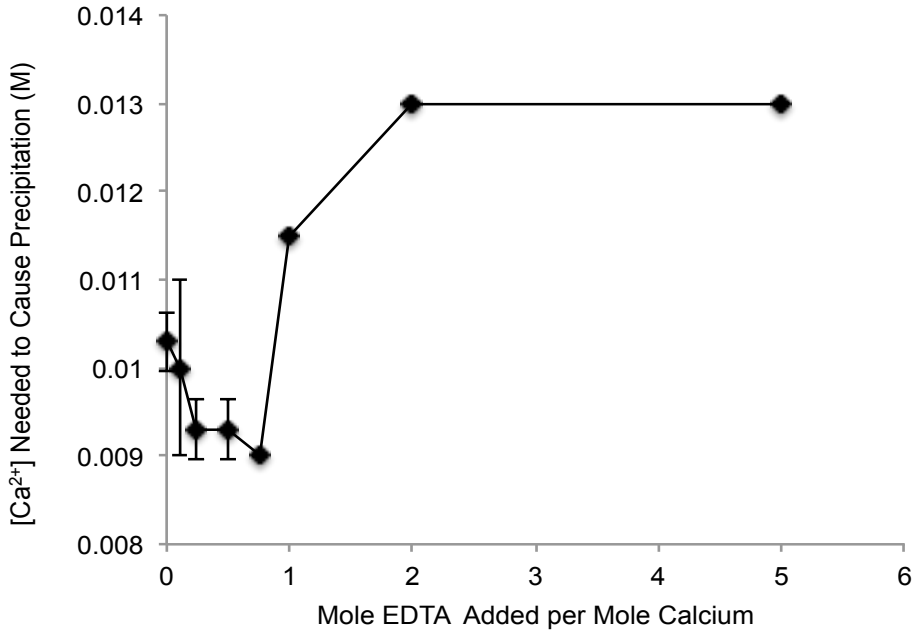


Figure 14: Calcium Concentration Needed to Cause Calcium Sulfate Precipitation as a Function of EDTA Added. 1 Mole EDTA per Mole Calcium Corresponds to 0.0105 M.

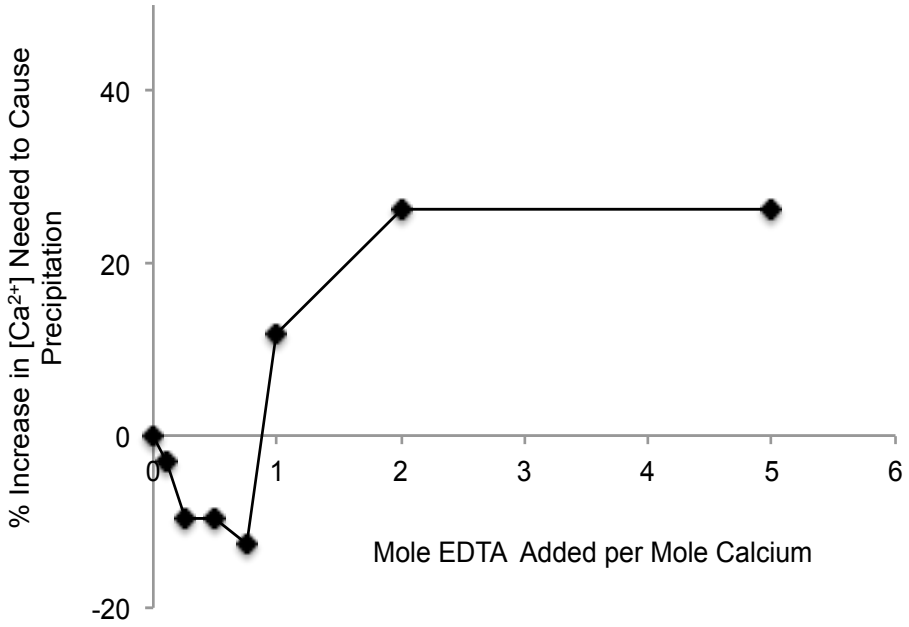


Figure 15: Percent Increase in Calcium Concentration Needed to Cause Calcium Sulfate Precipitation as a Function of EDTA Added.

4. Concluding Remarks

The results presented and discussed herein support the hypothesis that calcium sulfate precipitation within a biotrickling filter treating hydrogen sulfide is indeed a realistic concern for industrial systems. Calcium sulfate precipitation has been successfully quantified both experimentally and by computer model as a function of critical operational parameters including system pH, total sulfate concentration, calcium content, and ionic strength. With this work, a fundamental understanding of the effects of these parameters on the potential and conditions for calcium sulfate precipitation in a biotrickling filter has been developed and presented. This information can be used in safe reactor operation and design.

The computer model that has been developed shows the ability to successfully predict the conditions that will promote calcium sulfate precipitation based on the ionic composition of the trickling liquid within a BTF. The experimental and model data have a good correspondence with one another. These data demonstrate that calculating the standard-state solubility product of gypsum assuming a negligible ionic strength yielded greatly erroneous results. The experimental and model values for the solubility product of gypsum at various operational conditions generally agree within a correction factor of 2.

The presence of calcium and sulfate within a solid sample collected from an industrial BTF indicates that calcium sulfate precipitation can occur in full-scale

treatment systems. The existence of a mineral deposit consisting of elemental sulfur in two solid samples collected from industrial BTFs is an additional cause for concern for solid formation in parallel to calcium sulfate precipitation within these reactors. The availability of oxygen to microorganisms involved in the sulfide degradation process plays a major role in the chemical composition of mineral deposits that will occur. Calcium sulfate was not detected in two solid samples most likely because the concentration of calcium in the reactor trickling liquid was not sufficient to cause precipitation. Instead, a buildup of elemental sulfur occurred due to an oxygen limitation within the reactors.

EDTA shows the potential to be an effective additive for the prevention of calcium sulfate precipitation within a BTF. Specifically, the addition of an excess of EDTA (2 moles EDTA per mole Ca^{2+}) was shown to successfully chelate calcium ions and cause significant protection against solid formation. EDTA could be a relatively easy way to prevent a significant amount of calcium ions from interacting with sulfate within a BTF and causing unwanted calcium sulfate mineralization.

4.1 Recommendation

The results of this work provide the basis for some recommendations if concerns arise associated with the formation of mineral deposits within a biotrickling filter treating hydrogen sulfide or for information regarding preventative reactor operation and design. Operating conditions associated with a decreased risk of calcium sulfate

precipitation include a pH below 2.0, a total sulfate concentration of less than 0.02 M (20 mM), and a minimal amount of calcium in the mineral nutrient feed. Calcium sulfate precipitation is much more likely to occur in treatment systems with high pH, high total sulfate concentration, and/or high calcium content, so the avoidance of these conditions is essential.

4.2 Further Studies

This work is the first study focused on the quantification of calcium sulfate precipitation within biotrickling filters treating hydrogen sulfide. It is meant to provide a fundamental understanding of the ways in which critical system parameters including pH, total sulfate concentration, calcium content, and ionic strength affect the occurrence of calcium sulfate formation in a BTF and to propose a suitable model to predict when gypsum and other calcium sulfate minerals will precipitate. There are many ways in which this work can be expanded and provide greater depth of information on calcium sulfate precipitation in BTFs treating H_2S.

More sampling and quantification is needed to strengthen the results presented in this work. As more data is gathered from industrial systems around the world, the experimental results will gain reliability and value. A very interesting follow-up study would be the operation of a laboratory BTF for an extended amount of time under conditions known to promote calcium sulfate precipitation. As minerals build up in the reactor over time, the system performance (H_2S removal efficiency and elimination

capacity) could be monitored and compared statistically to a system without calcium sulfate mineral deposition. This would allow a full investigation of the possible inhibitory effects of calcium sulfate precipitation within a BTF.

In this work, the addition of EDTA has been proposed as a possible method for preventing calcium sulfate formation. The opportunity still exists to investigate other strategies associated with precipitation prevention. Two solid samples collected from industrial BTFs contained a mineral deposit consisting of elemental sulfur. An investigation of the chemical properties of this type of mineral deposit and the conditions that led to its formation could be useful in furthering the understanding of the conditions that promote mineral deposition, including gypsum precipitation, in biotreatment systems. While gypsum and other calcium sulfate mineralization is the result of chemical precipitation, elemental sulfur is most likely to be of biological origin. Hence, future studies will need to include detailed biological investigations, notably varying dissolved oxygen levels in H_2S-degrading biofilm, possibly with the use of microelectrodes in actual H_2S-degrading biofilms.

Finally, improvements can be made to the accuracy of the computer model that was developed to predict calcium sulfate precipitation in biotrickling filters as a function of system ionic composition and pH. The model proved to be very capable of predicting gypsum precipitation in agreement with experimental data within a reasonable correction factor. By altering the version of the Davies equation used in the model

algorithm and expanding the scope of analysis, the model output can continue to improve in accuracy and precision. A finely tuned computer model can be used to predict calcium sulfate precipitation in a biotrickling filter treating hydrogen sulfide with great confidence and help to avoid reactor operation under conditions that would promote solid formation and lead to reactor inefficiencies.

5. Supplementary Information

Appendix A – Sample Chemical Composition Data

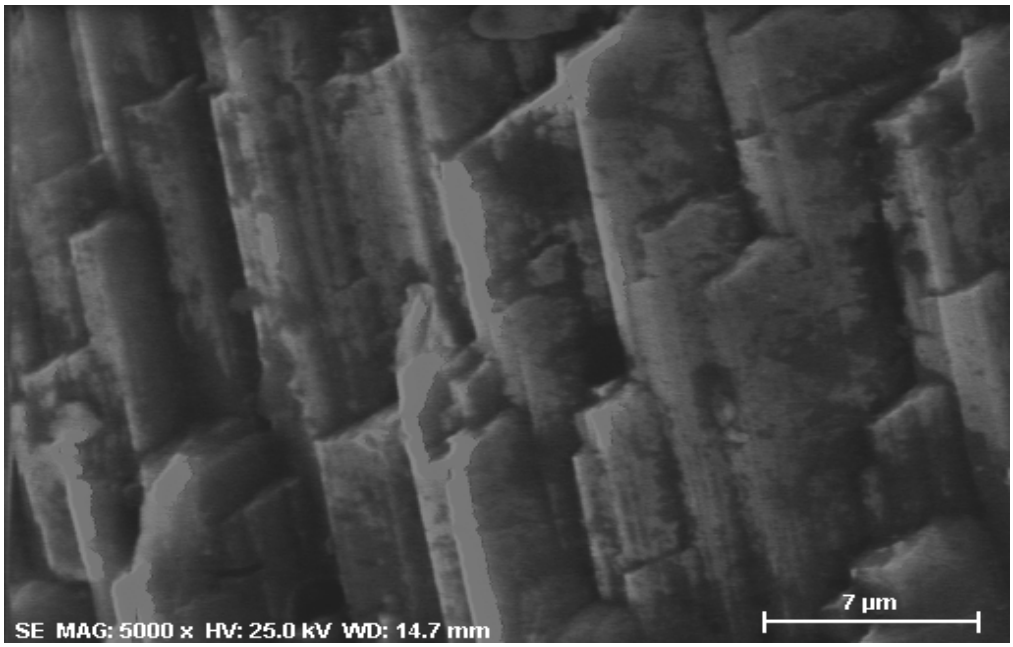
Sample	$[SO_4]_T$ (M)	[TIC] (M)	[TOC] (M)	$[Ca^{2+}]$ (M)	$[Mg^{2+}]$ (M)	$[Na^{=}]$ (M)	$[K^{+}]$ (M)
Duke BTF Influent	0.0002	7.4×10^{-4}	0	0.007	0.0002	0.00142	0.00156
Duke BTF Effluent	0.0238	N/A	N/A	0.007	N/A	N/A	N/A
OCSD Influent	0.0019	0	0.00156	0.00154	0.00134	0.01	5.8×10^{-4}
OCSD Effluent	0.0122	6.7×10^{-5}	8.1×10^{-4}	0.00168	9.6×10^{-4}	0.0081	3.9×10^{-4}
Porto Influent	0.0003	2.3×10^{-4}	0.00186	5.6×10^{-4}	1.2×10^{-4}	0.00117	6.0×10^{-5}
Porto Effluent	0.0206	2.3×10^{-4}	4.2×10^{-4}	7.1×10^{-4}	8.8×10^{-5}	0.0886	1.3×10^{-4}
CRWPC Influent	0.0029	0.0013	0.0112	0.00162	0.00119	0.0292	0.00127
CRWPC Effluent	0.0115	4.8×10^{-4}	0.00179	0.00251	0.00125	0.0275	0.00124
Confid. Influent	0.001	0.0022	0.00107	0.00116	6.3×10^{-4}	0.011	5.6×10^{-4}
Confid. Effluent	0.0416	8.8×10^{-4}	0.00258	9.1×10^{-4}	5.2×10^{-4}	0.108	5.1×10^{-4}

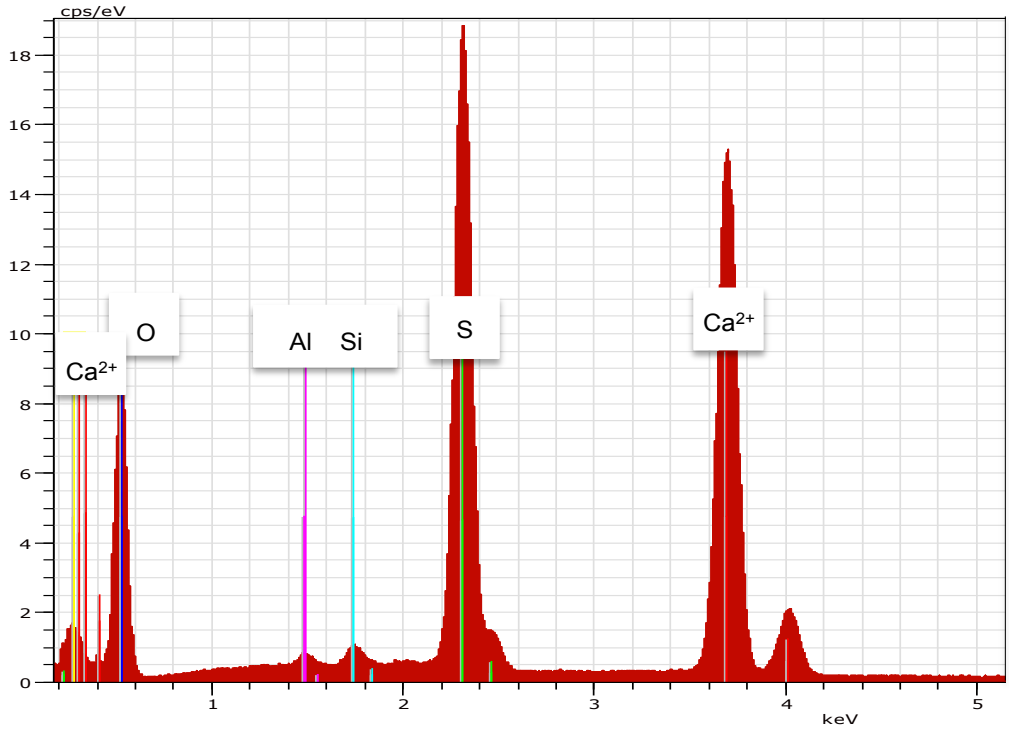
Appendix B – DLS Data

Calcium Sulfate Precipitation Data (DLS)						
Sample		Statistical Method of Analysis			Average	Std. Error
$[SO_4]_T$ (M)	pH	Method 1 (10 peaks)	Method 2 (Max peak)	Method 3 (Std. Dev.)		
Duke BTF		(Moles/L)	(Moles/L)	(Moles/L)	(M)	(M)
0.0238	1.25	0.0278	0.0278	0.0278	0.0278	0
0.0238	1.5	0.0199	0.018	0.018	0.0186	0.00066
0.0238	1.75	0.016	0.016	0.016	0.016	0
0.0199	1.75	0.018	0.018	0.018	0.018	0
0.0274	1.75	0.016	0.016	0.016	0.016	0
0.0141	1.9	0.0096	0.0096	0.0144	0.0112	0.0016
0.0238	2.0	0.0128	0.0104	0.0104	0.0112	0.0008
0.0190	2.5	0.018	0.018	0.018	0.018	0
0.0274	3.0	0.01	0.01	0.011	0.00103	0.00033
OCSD						
0.0122	1.25	0.0332	0.0371	0.0409	0.0371	0.00223
0.0122	1.5	0.0254	0.0293	0.0293	0.028	0.0013
0.0122	1.75	0.0254	0.0254	0.0254	0.0254	0
0.0122	2.0	0.0136	0.0136	0.0136	0.0136	0.00393
0.0122	2.5	0.0116	0.0116	0.01	0.0116	0
0.0122	3.0	0.0037	0.0037	0.0067	0.0047	0.001
Porto, Portugal						
0.0206	1.25	0.0126	0.0126	0.0126	0.0126	0
0.0206	1.5	0.0126	0.0126	0.0126	0.0126	0
0.0206	1.75	0.0047	0.0047	0.0047	0.0047	0
0.0206	2.0	0.0027	0.0027	0.0027	0.0027	0
0.0206	2.5	0.0019	0.0019	0.0019	0.0019	0
0.0206	3.0	0.0015	0.0015	0.0015	0.0015	0

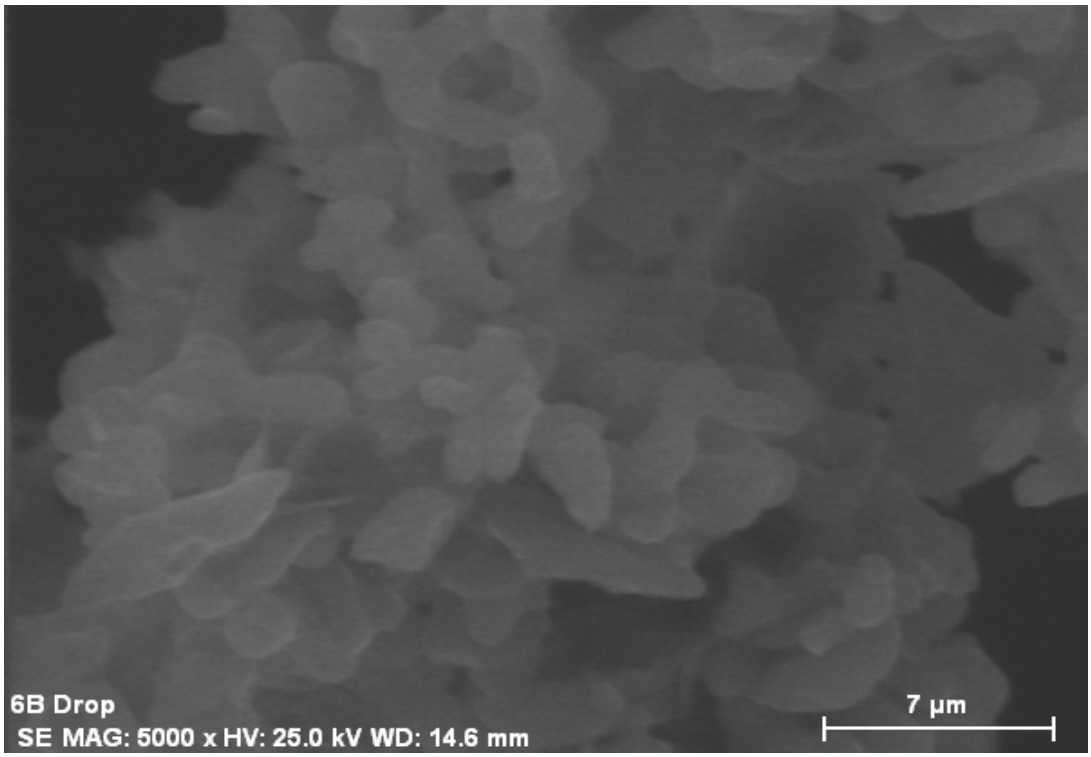
Calcium Sulfate Precipitation Data (DLS)						
Sample		Statistical Method of Analysis			Average	Std. Error
$[SO_4]_T$ (M)	pH	Method 1 (10 peaks)	Method 2 (Max peak)	Method 3 (Std. Dev.)		
CRWPC		**(Moles/L)**	**(Moles/L)**	**(Moles/L)**	**(M)**	**(M)**
0.0115	1.25	0.0379	0.0379	0.0417	0.0392	0.00129
0.0115	1.5	0.0223	0.0223	0.0301	0.0249	0.00261
0.0115	1.75	0.0223	0.0184	0.0223	0.021	0.00131
0.0115	2.0	0.0144	0.0144	0.0184	0.0157	0.00132
0.0115	2.5	0.0105	0.0105	0.0105	0.0105	0
0.0115	3.0	0.0045	0.0045	0.0065	0.0053	0.0007
Confidential						
0.0416	1.25	0.0049	0.0049	0.0049	0.0049	0
0.0416	1.5	0.0089	0.0089	0.0089	0.0089	0
0.0416	1.75	0.0109	0.0109	0.0109	0.0109	0
0.0416	2.0	0.0017	0.0017	0.0029	0.0022	0.00053
0.0416	2.5	0.0017	0.0017	0.0017	0.0017	0
0.0416	3.0	0.0013	0.0013	0.0019	0.0016	0.00027

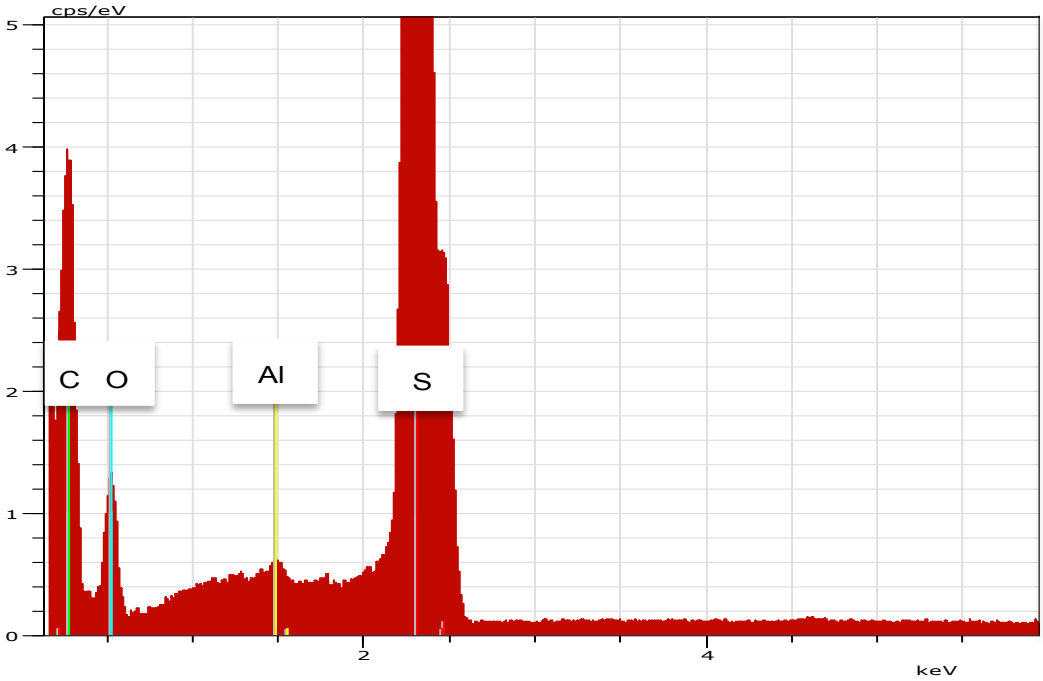
Appendix C – SEM and EDX Data



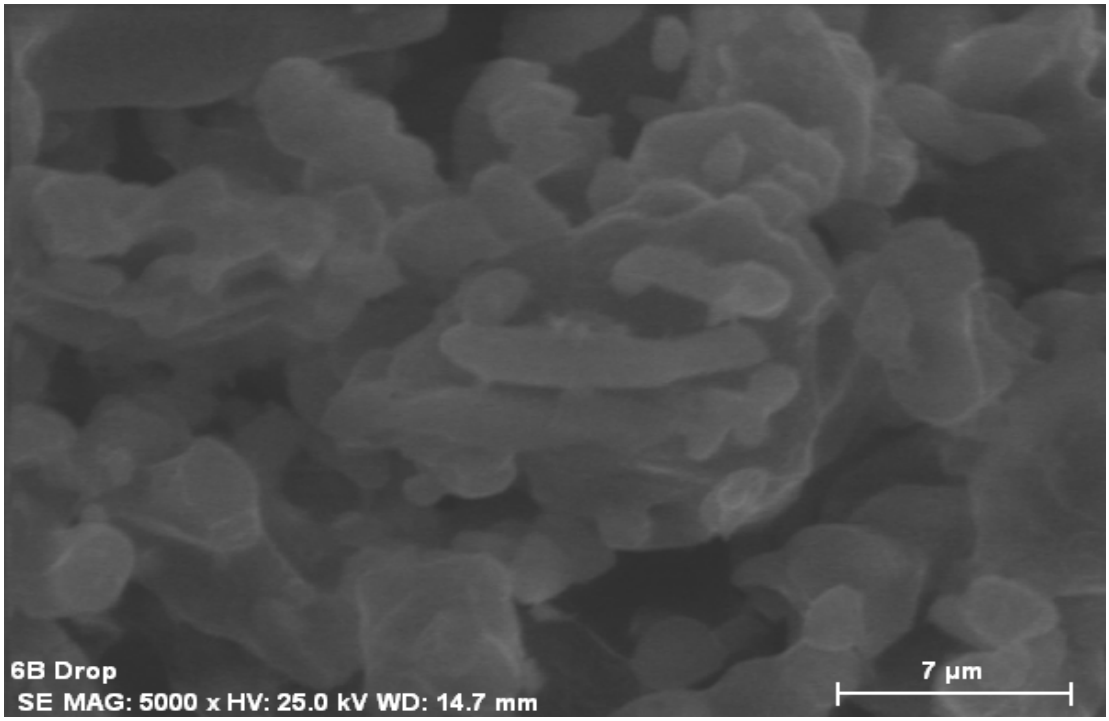


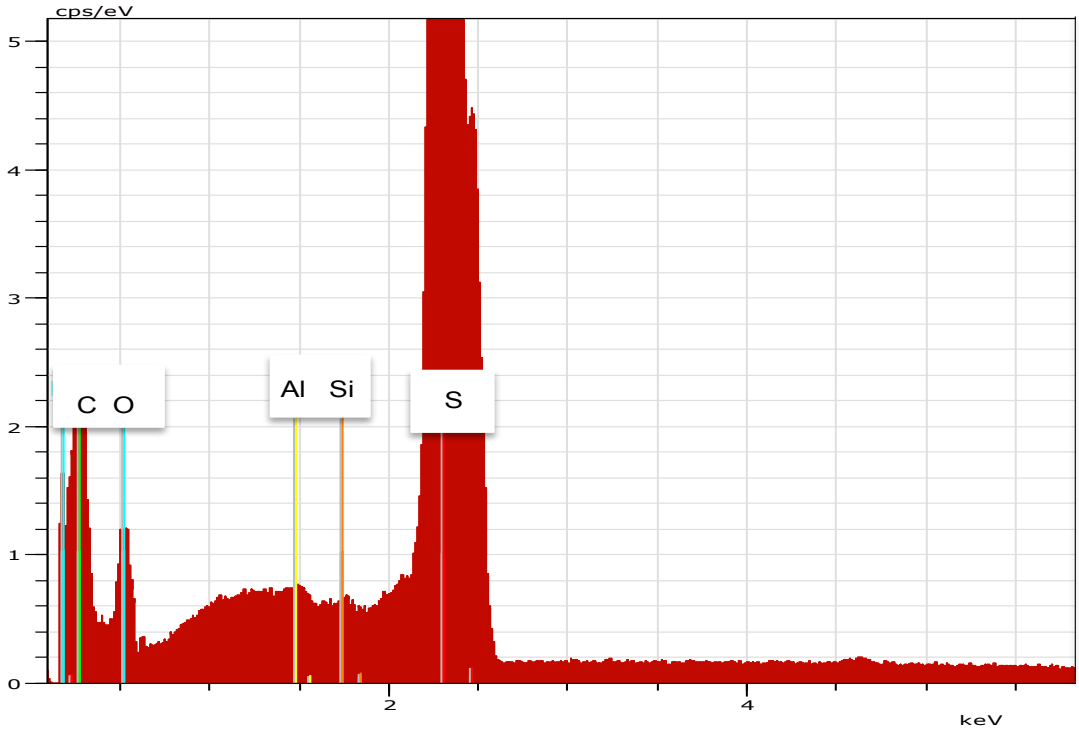
SEM-EDX Results for OCSD Solid Sample.



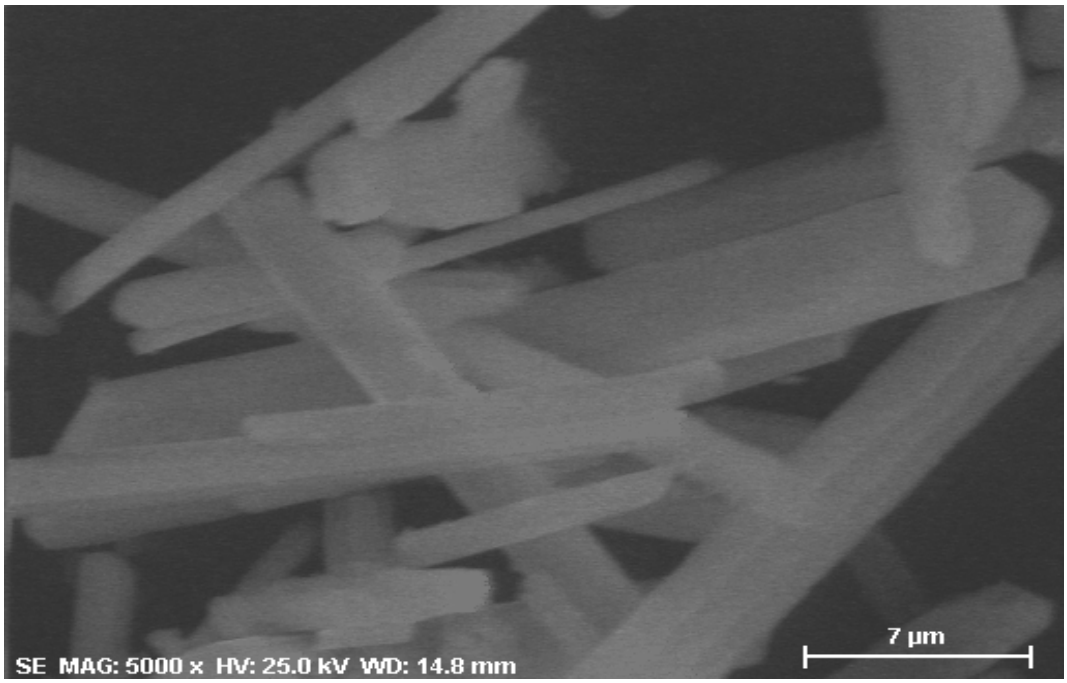


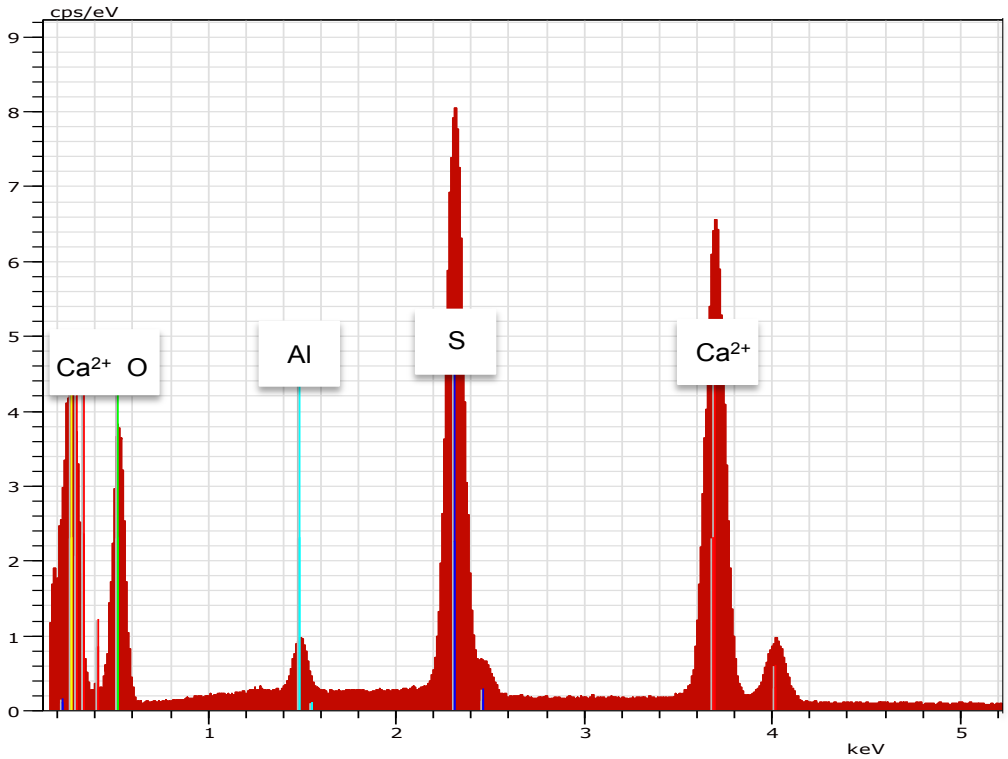
SEM-EDX Results for Porto Solid Sample.



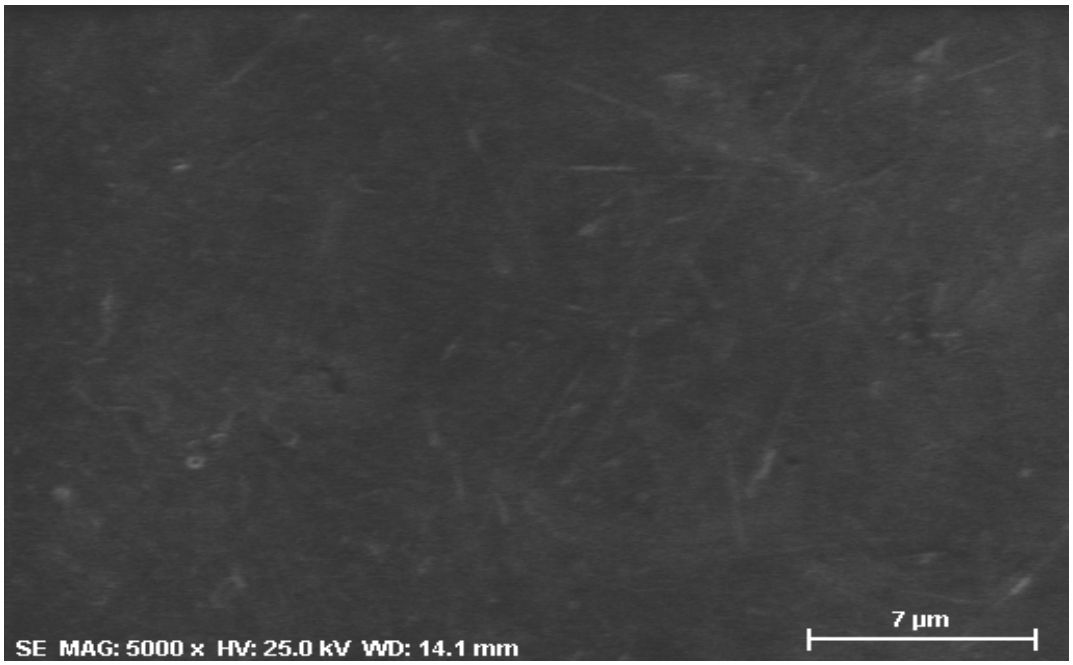


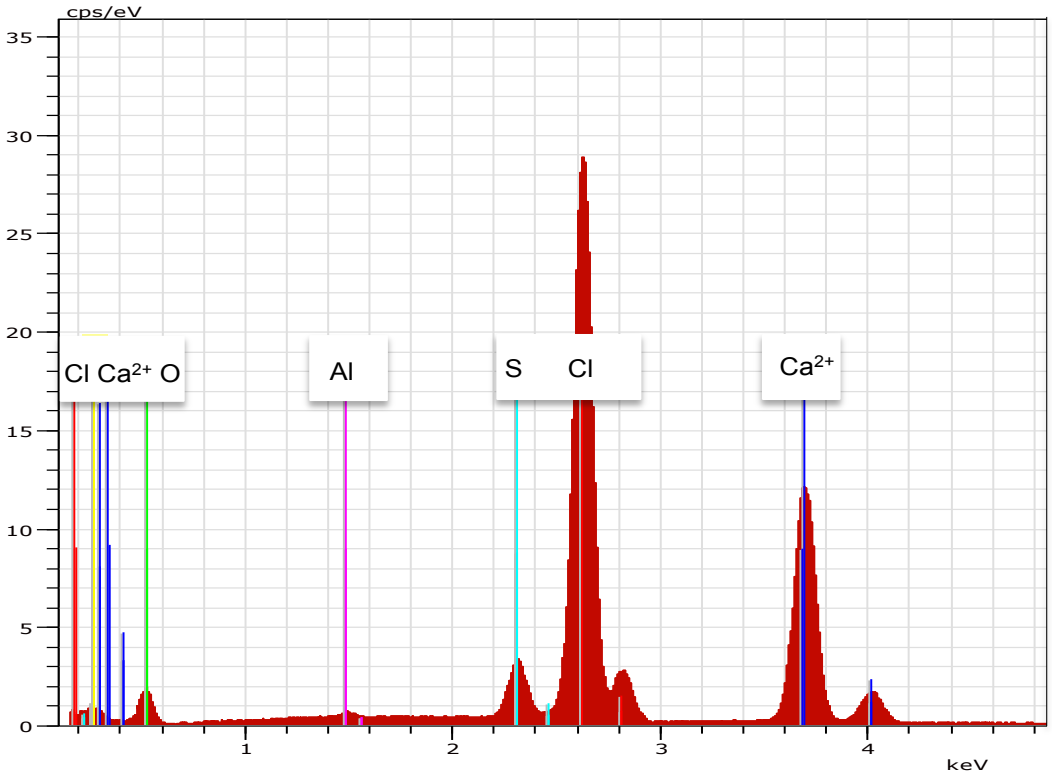
SEM-EDX Results for Confidential Solid Sample.





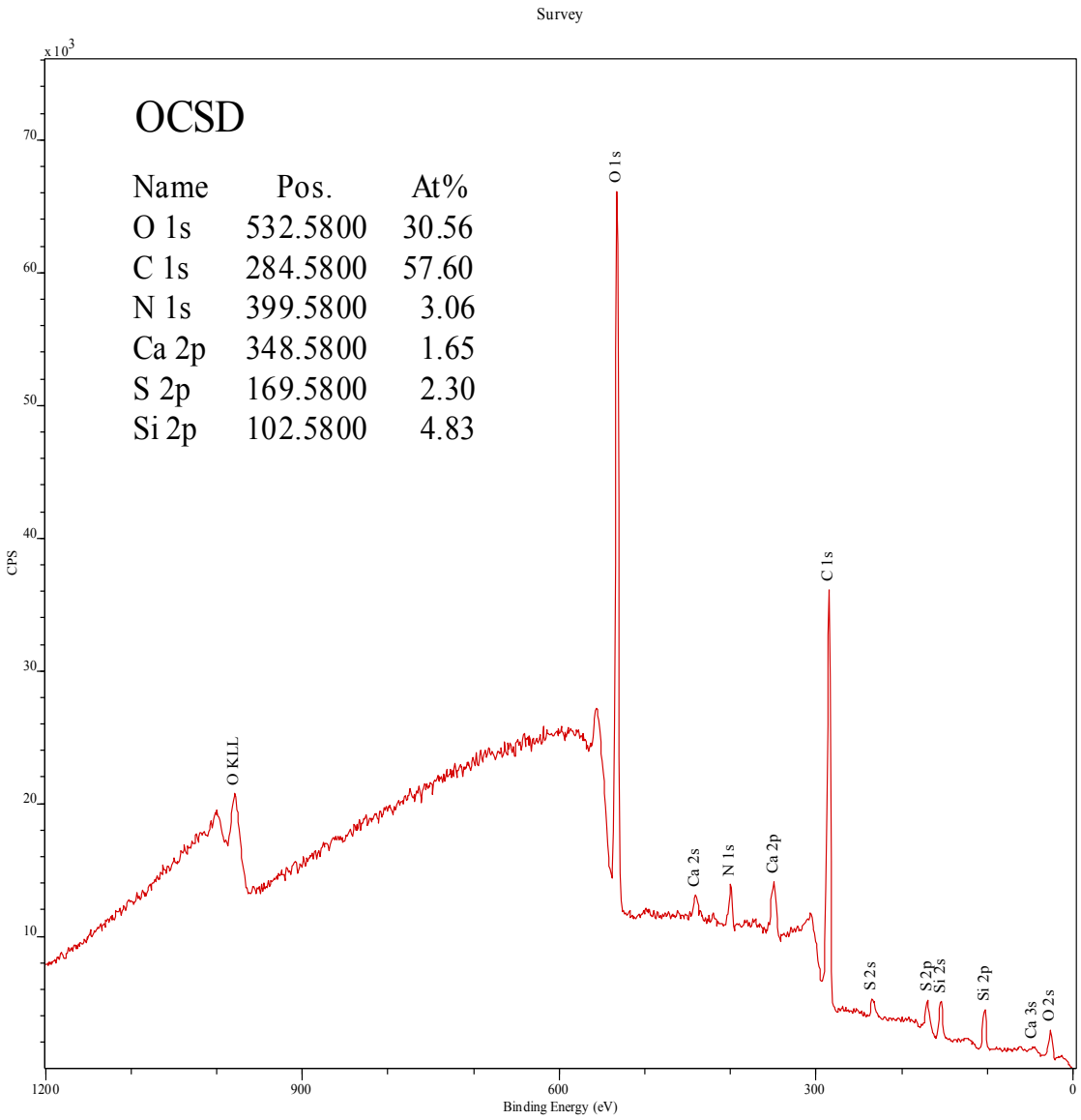
SEM-EDX Results for Gypsum Sample Precipitated in Distilled Water.



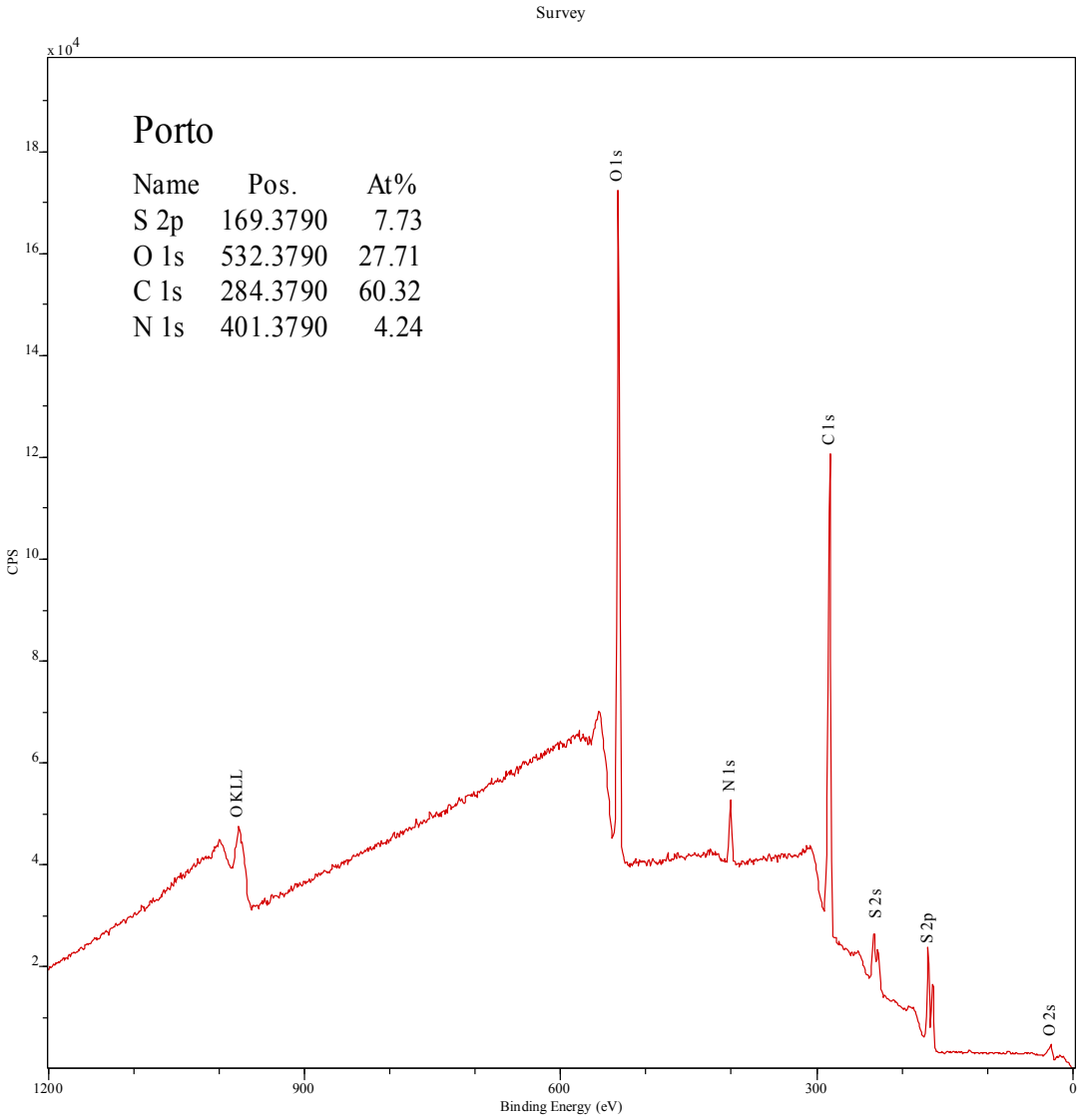


SEM-EDX Results for Gypsum Sample Precipitated in Duke BTF Effluent Liquid.

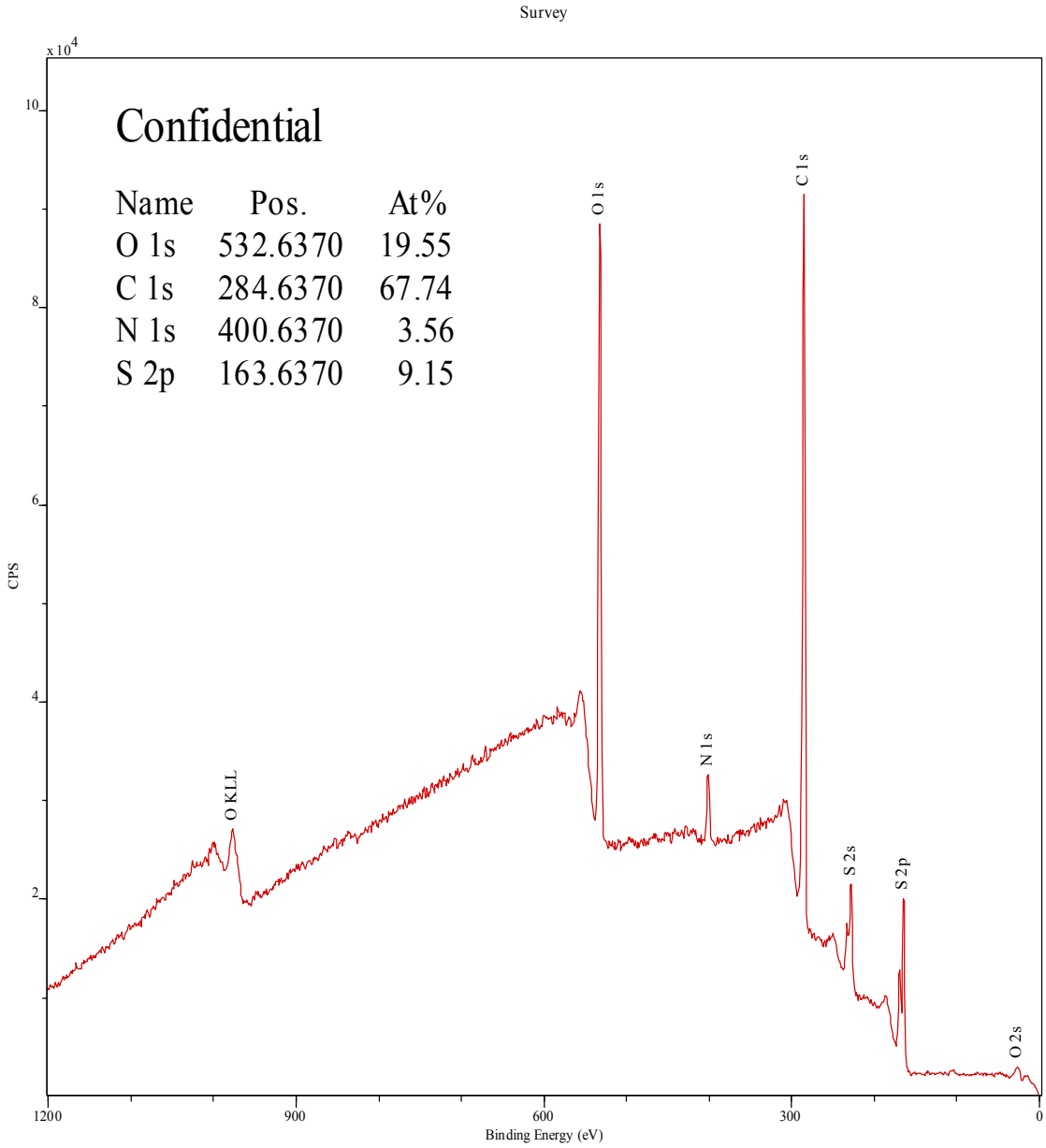
Appendix D – XPS Data



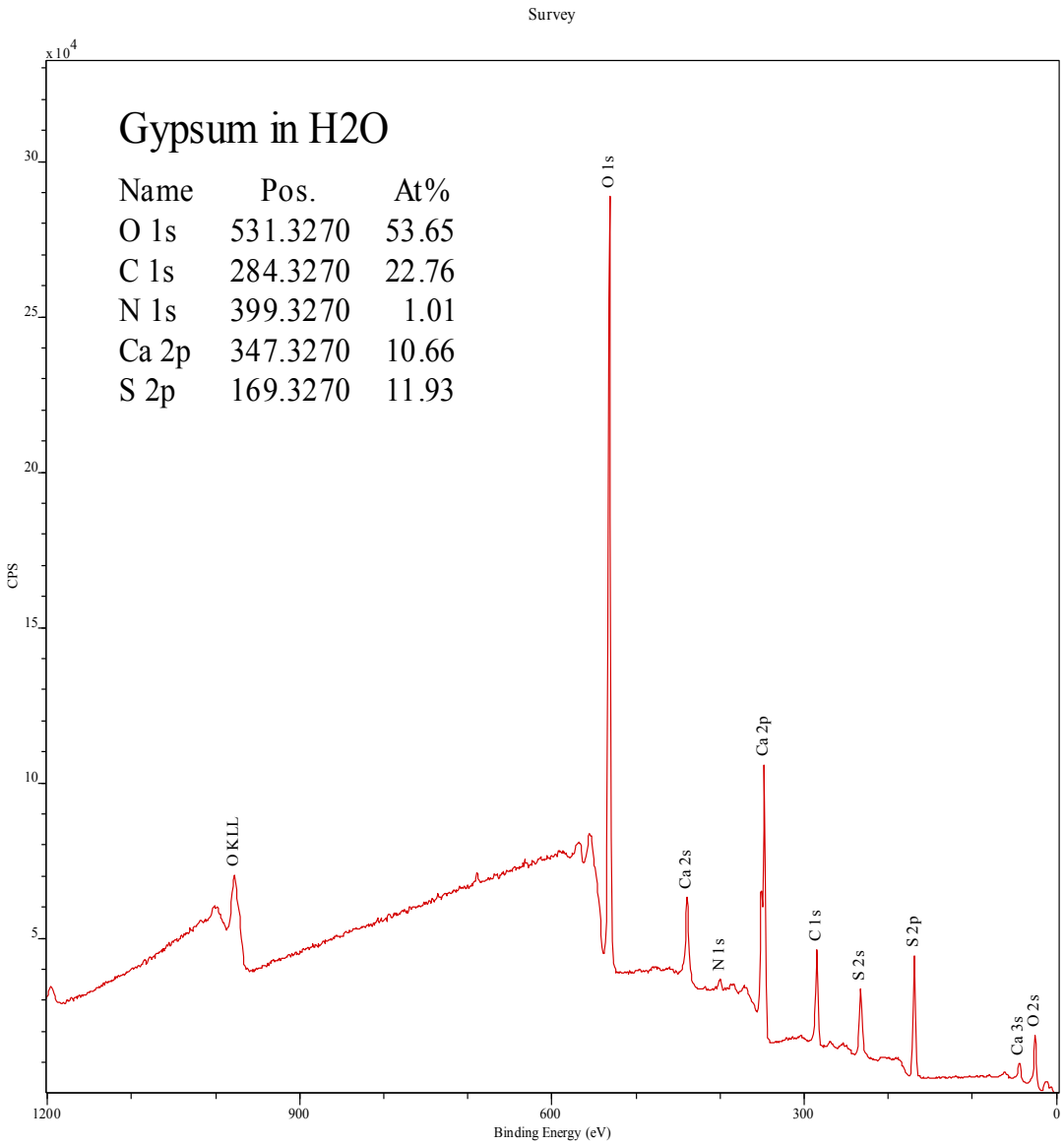
XPS Survey Scan of Solid Sample Collected From Orange County Sanitation District, California.



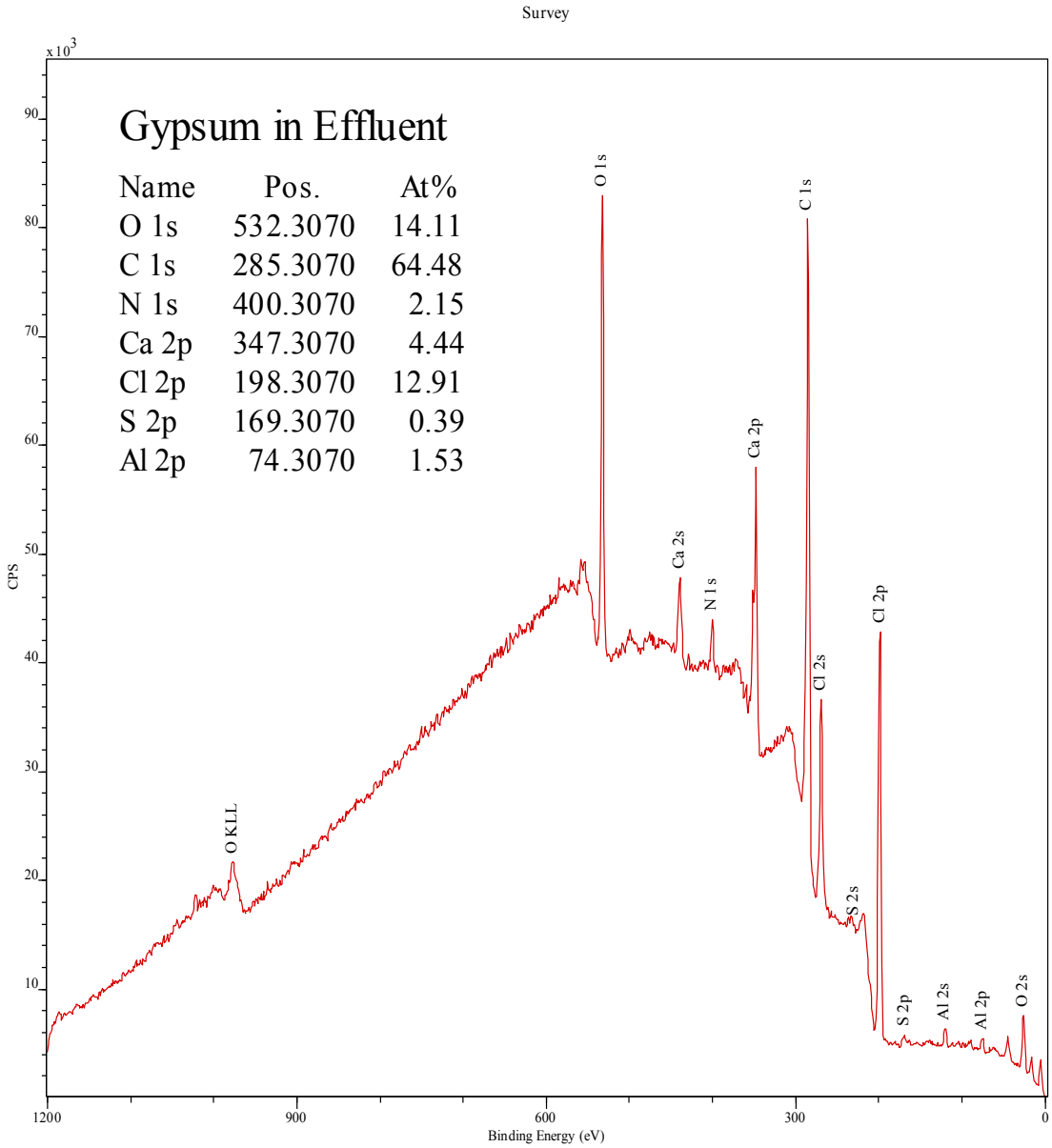
XPS Survey Scan of Solid Sample Collected From Porto, Portugal.



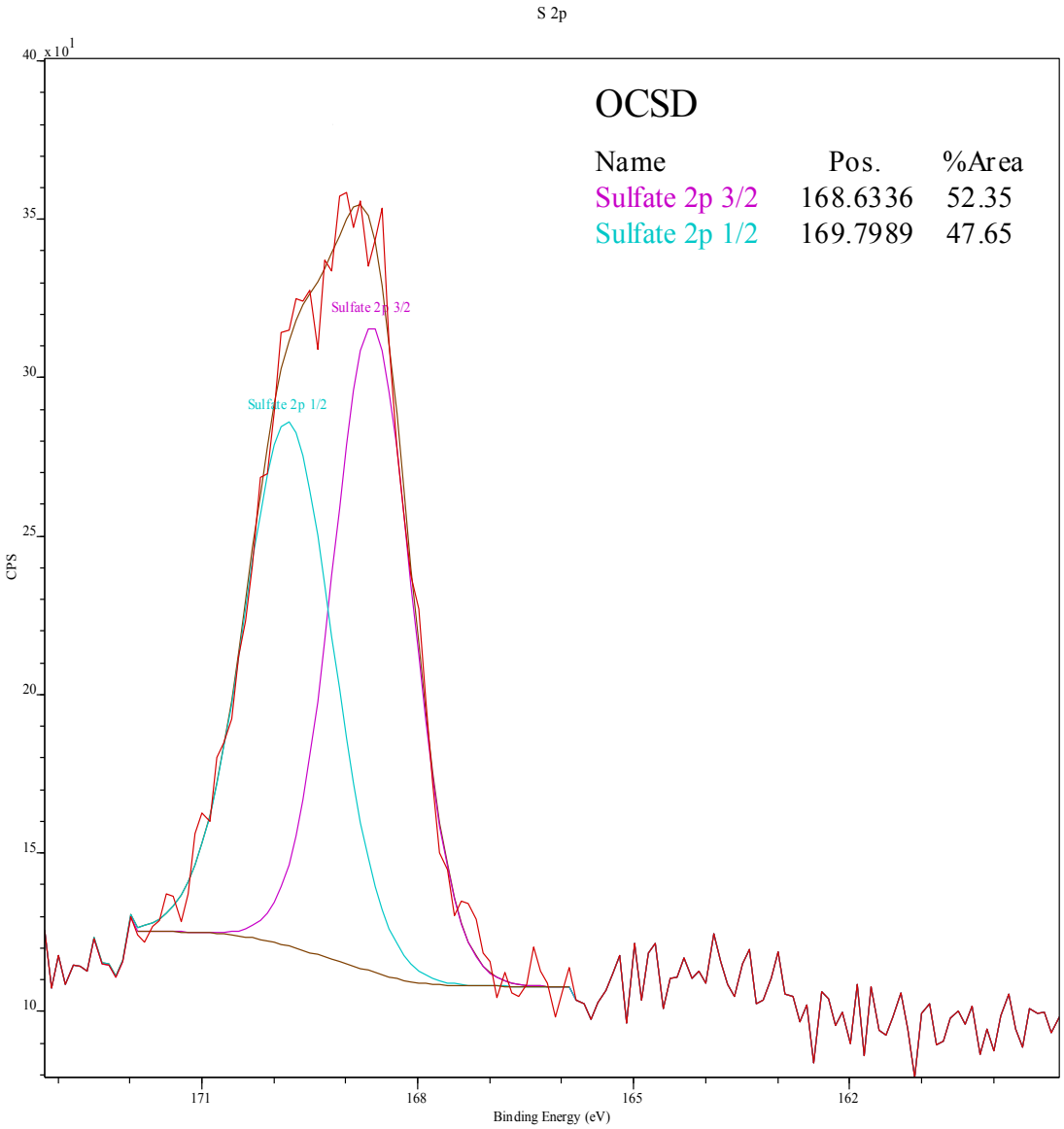
XPS Survey Scan of Solid Sample Collected from Confidential Sample.



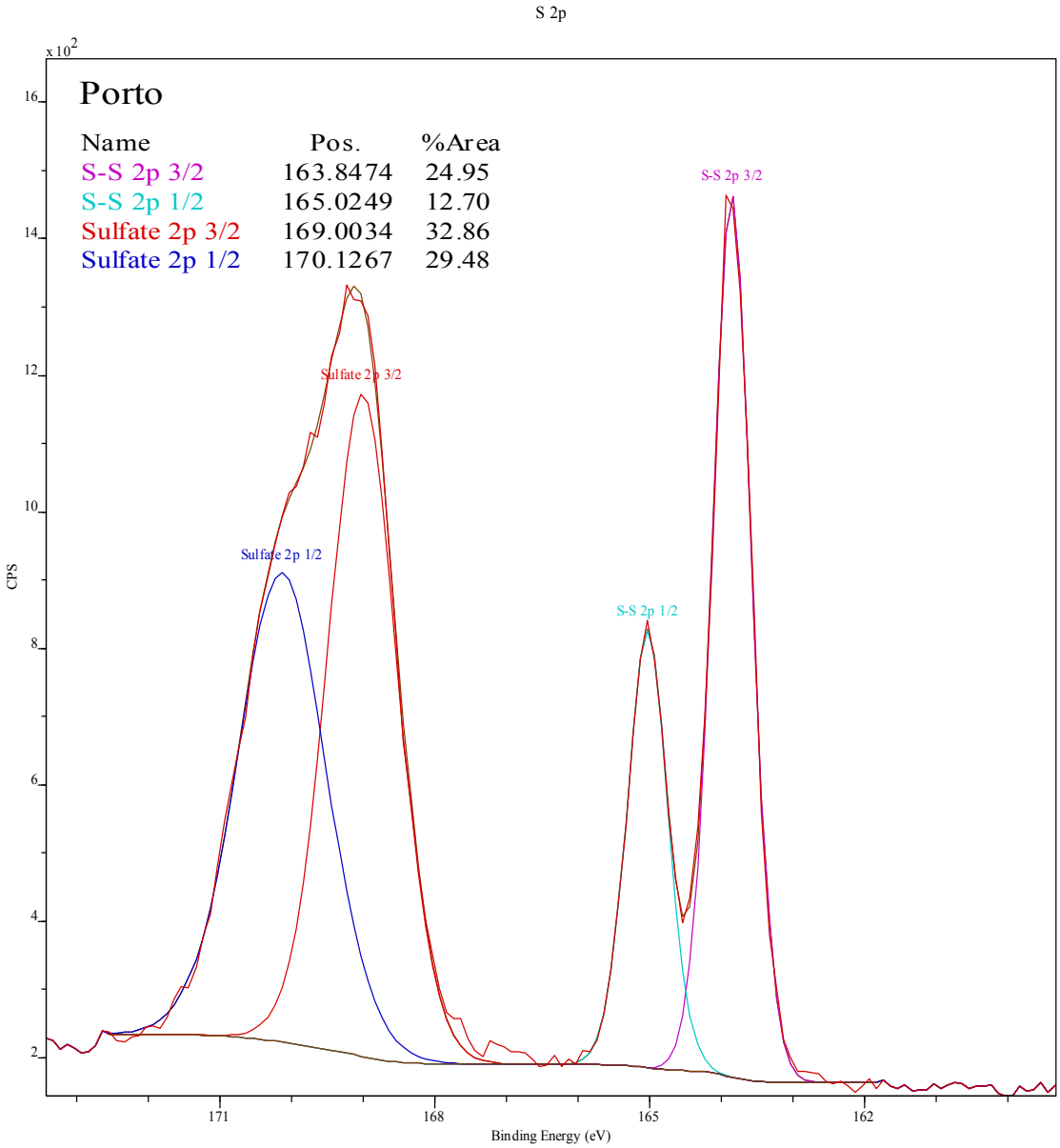
XPS Survey Scan of Gypsum Sample Precipitated in Distilled Water.



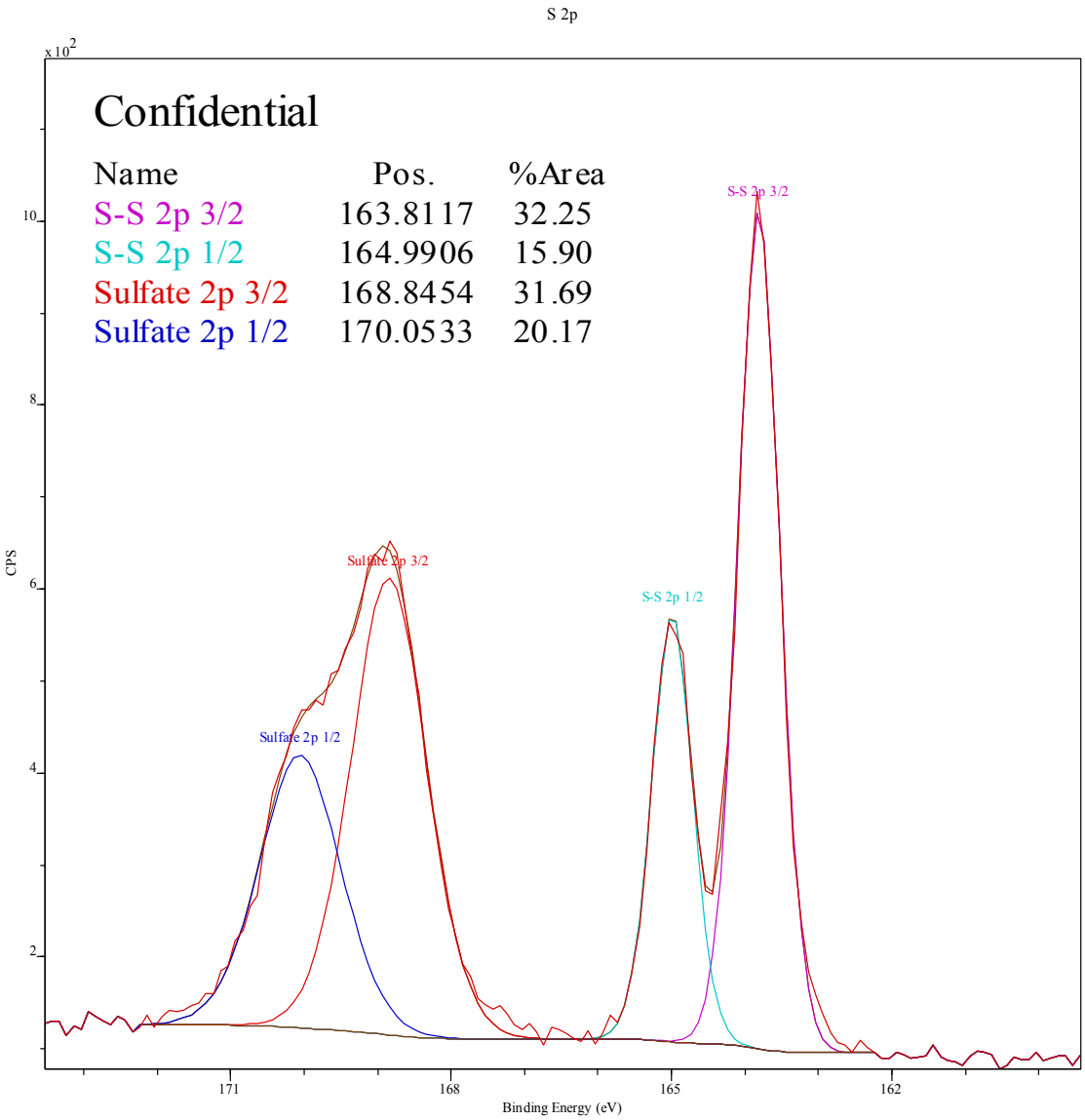
XPS Survey Scan of Gypsum Sample Precipitated in Duke BTF Effluent Liquid.



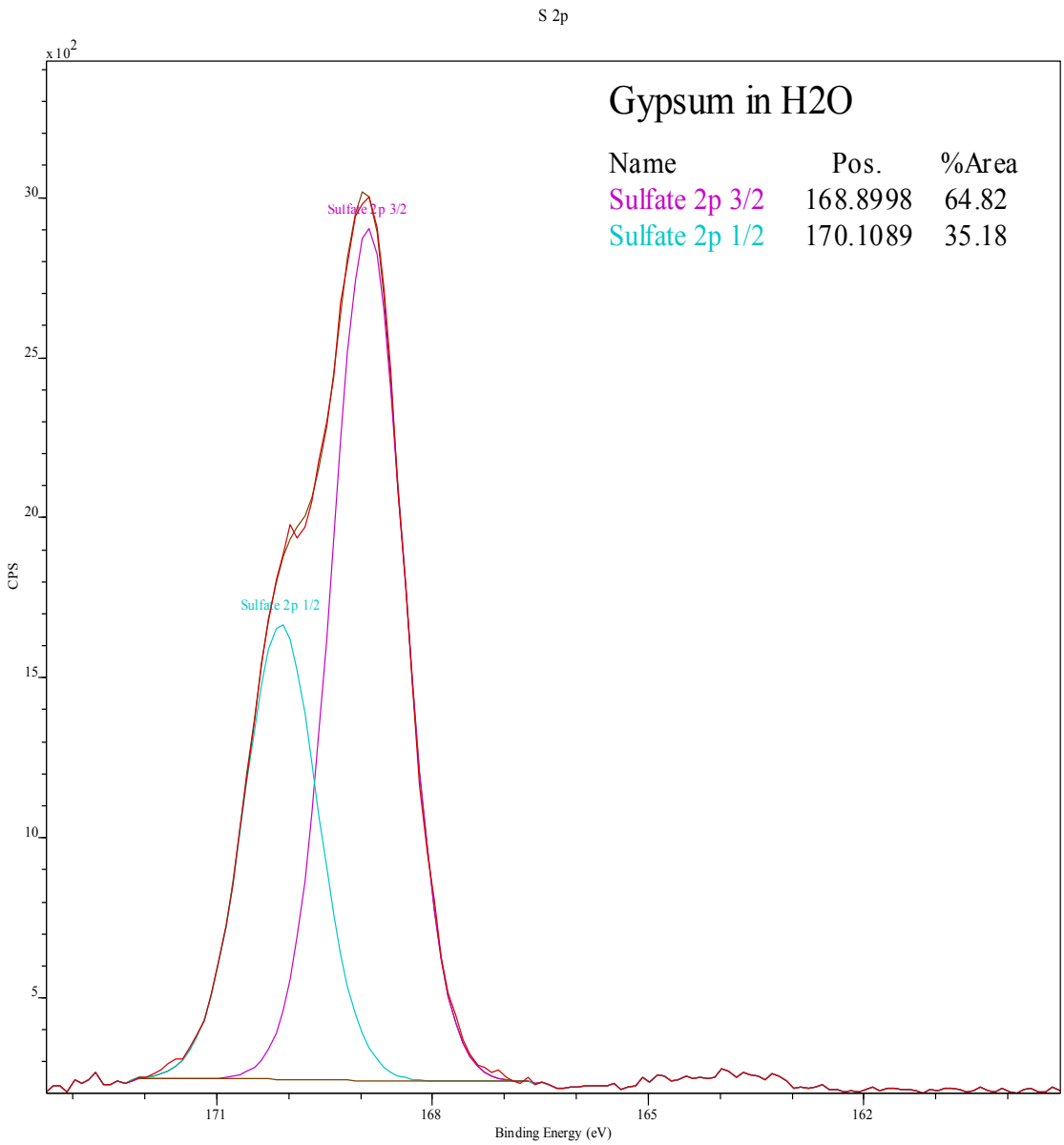
XPS Sulfur Regional Scan of Solid Sample Collected From Orange County Sanitation District, California.



XPS Sulfur Regional Scan of Solid Sample Collected From Porto, Portugal.



XPS Sulfur Regional Scan of Solid Sample Collected From Confidential Sample.

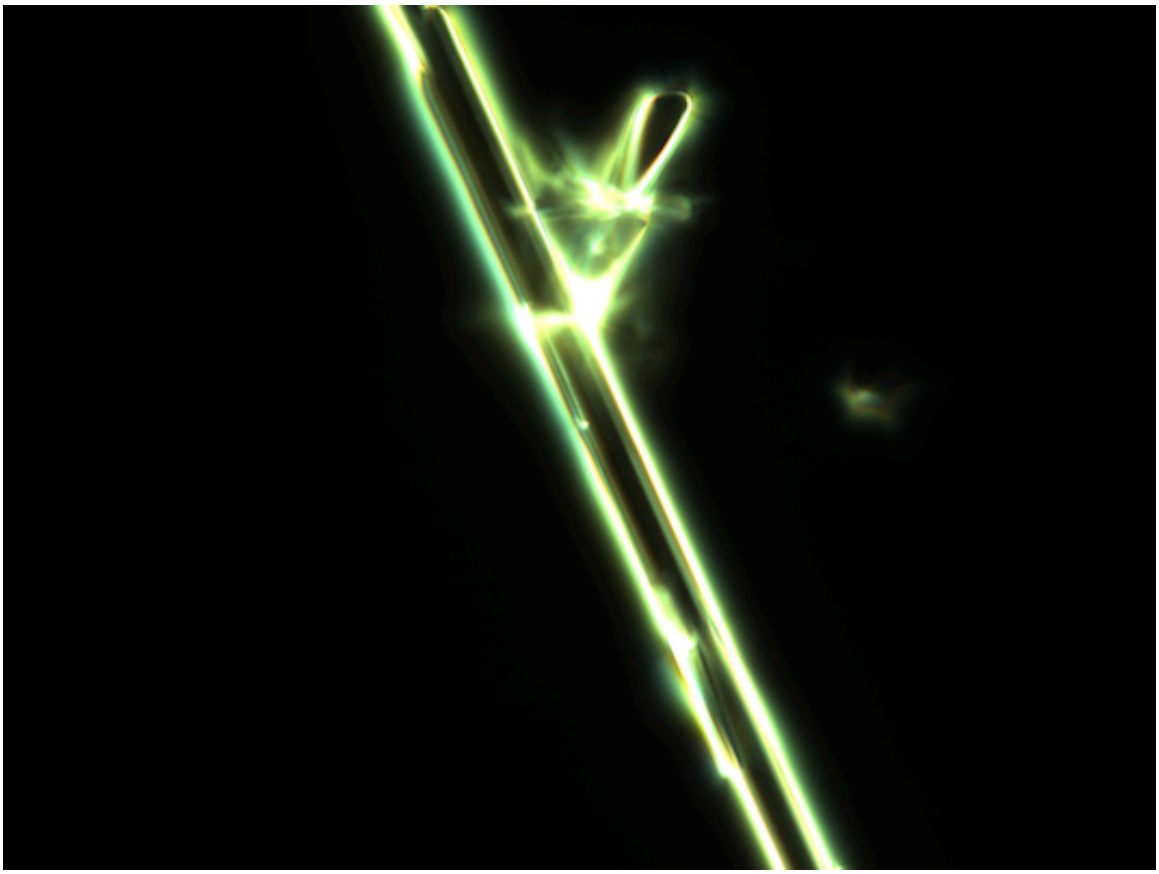


XPS Sulfur Regional Scan of Gypsum Sample Precipitated in Distilled Water.

Appendix E – Dark-Field Microscopy

Dark-Field Picture of Gypsum Crystals (65 μL $CaCl_2$ Added to Duke BTF Effluent Liquid) at 10x Magnification.

Dark-Field Picture of Gypsum Crystals (65 μL of $CaCl_2$ Added to Duke BTF Effluent Liquid) at 100x Magnification.



Dark-Field Picture of Gypsum Crystals (75 μL of $CaCl_2$ Added to Duke BTF Effluent Liquid) at 100x Magnification.

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