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Removal of Fluoride from Mine Water via Adsorption for Land- Applied Soil Amendment

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Kevin Le
Honors Thesis Submission

Removal of Fluoride from Mine Water via Adsorption for Land-Applied Soil Amendment

During the Spring 2020 term, myself and 6 other team members worked on Task IV of the 30th WERC Environmental Design Contest. This task asked the team to research, evaluate, and design a treatment system to reduce total fluoride concentrations in mine water to below 2mg/L. The treatment goals of the designed system would be cost effectiveness, practicality, and ability to apply to large flows of 1000 to 14000 gallons per minute. The team was presented with a guide to create synthetic mine water that had the composition profile of 1.7 grams of gypsum, 22.1 mg of sodium fluoride, and dilute sulfuric acid or sodium hydroxide to adjust pH to 7.

Throughout the course of this project I was tasked with many responsibilities and entrusted to complete those in a thorough and adequate manner. These duties included: contacting the Fayetteville Water Quality Lab and coordinating testing details, contacting Freeport McMoRan to connect with Brett Waterman the author of Task IV, researching adsorption capacities and other parameters for the removal of fluoride by different sorbents, devising a white paper on reverse osmosis, developing procedures for the usage of a pyrolysis unit, testing the heating capacity of the pyrolysis unit, pyrolyzing rice hulls and orange peels for testing, performing and monitoring adsorption tests for all of the selected adsorbents, completing required documentation for the WERC competition, meeting with graduate civil engineering students to test activated alumina potential in concrete, obtaining auditors for the report, assisting in making sure the team was focused and on task, writing multiple sections in the report, and revising the overall report.

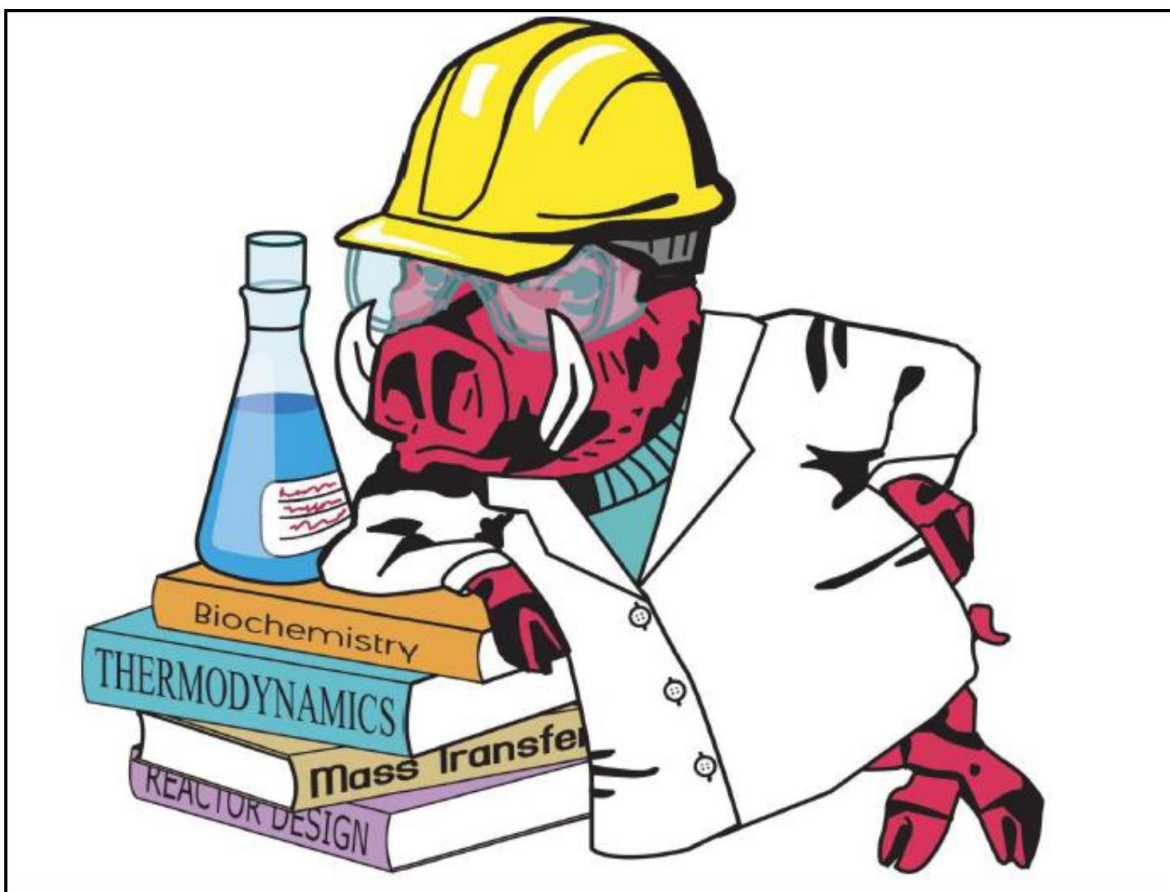
After a careful analysis of water treatment methods, adsorption media, and literature reviews, the team decided that bone char for the adsorption of fluoride was the most feasible secondary water treatment method. The adsorption properties were vastly affected by the presence of sulfate and other minerals and metals in the water, lowering the adsorption capacity of the chosen media. The size of the full-scale system designed must accommodate enough adsorbent that can remove the necessary amount of fluoride in the presence of competitive ions. The land application of spent bone char is cost effective and environmentally safe. Since the adsorbent loads sulfate as well as fluoride, the sulfate that will leech from the material can act as a soil amendment. Fluoride will be stripped in minimal and harmless amounts. The team believes this water treatment proposal will make a good candidate for the removal of fluoride in the discharged mine water and will allow mines to have a sustainable and environmentally friendly byproduct.

Removal of Fluoride from Mine Water via Adsorption for Land-Applied Soil Amendment

WERC 2020

Task #4

Moo Pig Sooie



Ralph E. Martin Department of Chemical Engineering
University of Arkansas
Fayetteville, AR

**Removal of Fluoride from Mine Water via Adsorption for Land-Applied Soil
Amendment**

WERC 2020

Task #4

April 1st, 2020

Moo Pig Sooie

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Executive Summary

The process of mining minerals and elements from ores and rocks creates acid rock drainage (ARD). This drainage is water that contains heavy metals and minerals that can be dangerous for human consumption or damaging to the environment. The mining industry has employed various water treatment methods to prevent these metals and minerals from being discharged into water sources such as ponds, lakes, and streams.

Currently, the most used treatment process in the mining industry is a cost-effective high-density sludge (HDS) process. This method reduces the concentration of metals and elements with the use of lime/limestone. However, the concentration of fluoride is not reduced to Environmental Protection Agency (EPA) standards, and so it is necessary to design a fluoride removal system. Reverse osmosis (RO) was considered as well as precipitation, ion exchange, and adsorption by media such as biochars, bone char, and activated alumina.

Although RO is perhaps the most obvious solution to reducing fluoride concentrations, this method was eliminated due to expensive overhead and maintenance costs. Many metals and compounds present in the mine water will lead to severe scaling and precipitates collecting in the membrane, requiring constant upkeep and high maintenance costs. Precipitation was eliminated because it produced a byproduct only suitable for landfilling, and ion exchange was eliminated due to its high cost and complications with competitive ions. Adsorption was chosen as a viable option for fluoride removal because of its low cost and environmentally friendly byproduct generation.

The adsorption media was chosen based on a ranking system designed by our team. This system provided a way for our team to compare the adsorption capacity, rate of adsorption, byproduct application, and price per ton for each adsorbent. From this ranking system, Moo Pig Soobie is presenting a solution of cow bone char as a fluoride adsorbent. This type of biochar can be bought pre-charred and can be land applied as a fertilizer once the char is spent.

A full-scale facility was designed to treat 1000 gallons per minute (GPM) of mine water 24 hours a day, seven days a week, for eight months out of the year. To achieve this flowrate and timeline, two packed beds with volumes of 8,900 ft³ each were designed to run in parallel to ensure loading does not occur until the 168-hour mark, the end of the work week. Once the bone char is loaded, the spent bone char will be hauled offsite to be land applied in soil that is

naturally slightly acidic. Our experimental results indicate that minimal amounts of fluoride are stripped from bone char in acidic environments. Applying spent bone char to soil presented a desirable environmentally friendly solution for our byproduct.

The overall capital cost of a full-scale facility is approximately \$750,894 with a yearly operating cost of \$4,778,840. Although this is high, the proposed solution will reduce the concentration of fluoride to EPA standards of 2ppm and the process will generate a land-applicable byproduct. Since consuming fluoride in excessive amounts can lead to health issues, public awareness is a necessary aspect of this solution. Citizens affected by the application of fluoride to their soil and water sources should be regularly involved in and aware of the fluoride levels in their environment.

From our analysis of bone char adsorption, Moo Pig Sooie believes this type of treatment is a beneficial, cost effective, and sustainable solution for mining facilities that generate high concentrations of fluoride in their water.

Background Research

Introduction

Fluorine is the 13th most abundant element in the world.¹ It is vastly dispersed throughout the environment in soil, water, rocks, and air. Water is the most common source of exposure to humans due to ingestion. According to the EPA, the primary standard for fluoride in drinking water is 4.0 mg/L or 4.0 parts per million (ppm), and the secondary standard is 2.0 mg/L.² While the secondary standard is not a federally backed concentration level, the EPA requires notice of discharged water with fluoride concentrations approaching the 2.0 ppm mark.

Fluoride can strengthen tooth enamel and prevent tooth decay. Many cities add fluoride to their municipal water, at concentrations of 2 ppm or lower. However, exposure to levels above 4 ppm can cause adverse health effects ranging from mild dental fluorosis to skeletal fluorosis. Mild dental fluorosis can result in tooth decay and tooth discoloration.³ Skeletal fluorosis is the buildup of fluoride on the bones, which can lead to weakened bones and joint immobility.⁴ To lower the likelihood of people experiencing these illnesses, fluoride is a highly regulated element in drinking waters.

A contributing factor to high concentrations of fluoride in water is the mining of certain minerals. Moo Pig Sooie focused on the Henderson mine Empire, Colorado, for our study. Henderson mines molybdenum ore that naturally contains fluoride. Fluoride dissolves from the ore during processes such as wet grinding and flotation, which concentrate molybdenum mineral from the ore. The rock that is not removed during these processes is sent to a tailings pond as a slurry, where the slurry separates from the water as a fine silt.⁵ This water, concentrated with many different elements and heavy metals, remains in the tailings pond.⁵ The tailings pond will continue to fill until discharge is necessary, typically during months of high precipitation and snow melt. The discharged water must undergo fluoride removal treatment before being released into the surrounding freshwater creeks; however, the current treatment process only reduces the concentration of fluoride in the water to 10 ppm, well above the EPA's secondary standard. Because of this, the Henderson mine is a good candidate for a study of post-HDS fluoride removal.

There is concern that the EPA standards for discharged water will be lowered within the next ten years. As of today, the state of Colorado requires a water discharge permit from mining sites but considers the addition of fluoride into water as a form of water fluoridation.⁶ The

Henderson mine is in the county of Clear Creek, which contains 10 water systems that support the 9,605 residents in the county.^{6,7} Currently, the mining process discharges 10 ppm fluoride, so it is important reduce this concentration and prevent nearby water systems from experiencing fluoride levels that exceed the EPA's standards.

Current Treatment Process

The current treatment process for the discharged mine water is a high-density sludge (HDS) process in Figure 1.

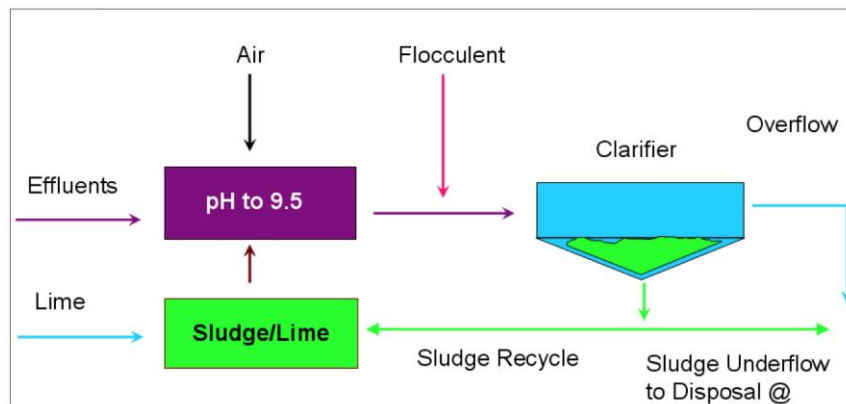


Figure 1: HDS Process⁷

The process uses lime to precipitate the dissolved ions present in the acid rock drainage (ARD), which contains dissolved metals. The process begins by mixing ARD with lime and recycled sludge and then transferred into a lime reactor where manganese is oxidized by aeration. A flocculent is added to the mixture, and the slurry then enters a clarifier to separate the treated effluent from the sludge. The treated effluent is pH neutralized and some of the sludge is recycled and the rest is sent off as waste.⁸

The HDS process can only reduce the calcium fluoride concentration to 10 ppm, because this is the solubility limit of calcium fluoride in water. Therefore, a second treatment step is needed to reduce the fluoride levels.

Task Overview

Synthetic water containing 10 ppm fluoride is to be reduced to 2 ppm. The fluoride source is 20 ppm of sodium fluoride. The synthetic water will also contain 1700 ppm of gypsum.

The process should produce a low-cost or marketable byproduct. The process should be scaled to treat 1000 gallons per minute (gpm) of water to support a full-scale water treatment plant.

Potential Treatment Methods

Precipitation

Precipitation is a treatment method that allows an insoluble product to settle out of solution by sedimentation.⁹ The fluoride compound with the lowest solubility in water is calcium fluoride, with a solubility limit of 0.016 ppm.⁹ When calcium sources such as lime or calcium chloride are added to a solution containing fluoride ions, calcium fluoride will form and precipitate out of the solution.

This method was not pursued by our team because the currently employed HDS method already uses lime to precipitate calcium fluoride. The resulting sludge has a water content of 60-80% and contains low-quality calcium fluoride at 20-40%.¹⁰ Additional precipitation would likely require dilution, and the resulting solids would be impure and only viable for landfilling. Precipitation was eliminated as a method for reducing fluoride concentration because it does not produce the environmentally friendly solution that Moo Pig Soovie would prefer.

Ion Exchange

Ion exchange (IE) is a chemical process that exchanges unwanted ions for more desirable ions with a similar charge. IE is an attractive water treatment method because the IE resin can be made highly selective towards fluoride ions, requires small volumes of resin, and can last up to five years.¹¹ However, the efficiency of ion exchange is greatly limited by mineral scaling and surface clogging, which cause resin fouling¹¹. This is problematic for mine water, which is saturated with many metals and minerals. The resins would require extra maintenance to control fouling, and the spent IE resin would need to be landfilled or incinerated.

Reverse Osmosis

Reverse osmosis (RO) is a common filtration system that can be used to remove ions or compounds from a solution through a pressure gradient within a membrane. It has the capability of recovering 85 to 95% of brackish or sea water running through a system and turning it into potable water, while only losing a small percentage to the retentate/concentrate.

According to a report released by R. Alan Shubert, City of El Paso Vice President of Operations and Technical Services, the Kay Bailey Hutchison Desalination Plant had a total capital cost of \$91 million.¹² This facility uses pre-treatment and post-treatment methods that costs close to \$1 million annually.¹³ The annual cost of labor for this facility is around \$400,000

and the annual cost of electricity is near \$1.5 million.¹³ This plant can treat 27.5 million gallons per day (MGD), but on average treats 4.2 MGD¹⁹. Since the startup of this desalination plant in 2007, it costs the facility on average \$7.83 per 1000 gallons. The cost of water per 1000 gallons in El Paso, Texas varies between \$3 to \$5, roughly half the production cost of 1000 gallons from the desalination plant.¹⁴

Brett Waterman, Manager of Environmental Projects at Freeport McMoran and creator of WERC Task 4, gave Moo Pig Soobie details about the approximate chemical composition of the mine water that this issue originated from, shown in Table 1. The amounts of sodium, potassium, and fluoride present in the mine water will not foul an RO membrane. However, the amount of calcium present in the mine water can result in scaling, which reduces the amount and quality of the membrane output.¹⁵ A sulfate concentration of 700 to 1500 ppm would not foul an RO membrane but causes the product to have a strong odor and bad taste, making it undesirable as drinking water.¹⁵ The phosphate in the mine water crystallize on the membrane and lead to poor performance.¹⁵

Table 1: Chemical Composition of Mine Water

Compound	Concentration Range (mg/L)
Sodium	10 — 150
Calcium	250 — 500
Sulfate	700 — 1500
Potassium	10 — 20
Phosphate	10 — 20
Fluoride	10

The high costs and concerns about the exposure of a RO system to certain compounds within the mine water caused Moo Pig Soobie to pursue a different method of reducing fluoride concentrations. Compared with adsorption, a full reverse osmosis system must address pretreatment, membrane fouling, and posttreatment of the feed and product streams, while adsorbents do not need these treatments to work effectively. Additionally, RO greatly exceeds the necessary purification standards for this task and does not yield an environmentally friendly byproduct.

Adsorption

Adsorption is a common fluoride removal method that can be accomplished by a variety of adsorbents. This method functions by pumping the contaminated water through a packed bed filled with an adsorbent. This process is appealing because it is relatively simple and there are a large variety of adsorbents available to choose from. Each adsorbent has a unique equilibrium loading capacity and rate of adsorption. These parameters, as well as cost and byproduct generation, are used to select the best adsorbent for a process. Moo Pig Sooie decided to use adsorption as the fluoride removal method because of the readily available variety of adsorbents, high fluoride removal capacity, environmentally friendly byproduct generation, and the simplicity of operation that we believe gives the best possible solution to this task.

Adsorbent Background and Proposed Solution

Activated Alumina

Activated Alumina (AA) is commonly used as an adsorbent for the removal of fluoride and arsenic from contaminated water. AA is made from treating bauxite, or aluminum ore, with heat and acid. The product is highly porous, contains no organics, and is mostly of the form Al_2O_3 .¹⁶ As an adsorbent, it is often sold in granular forms of 14 x 28 Tyler mesh size.¹⁷ Activated alumina, at ideal operating conditions, can have a fluoride adsorption capacity of 16 mg/g. It can be regenerated with a slightly basic solution.¹⁸

AA adsorption systems are available for domestic and commercial use. AA water filters for domestic use may be found in most local hardware stores.¹⁹ Larger units for commercial use are often installed in production plants, where the process wastewater contains high concentrations of fluoride. These systems usually involve two adsorption columns in parallel.²⁰

A properly designed AA system can easily reduce fluoride concentrations from 10 ppm to less than 2 ppm. However, there are some disadvantages to using activated alumina. Firstly, the adsorptive capacity of AA can decrease up to 30% after 5 regeneration cycles. Eventually the AA must be discarded and replaced with fresh AA. The spent AA has no known applications and, the EPA recommends it to be landfilled. Another disadvantage of using activated alumina is handling the regeneration solution that retains high concentrations of fluoride. Usually, this waste is sent to an evaporation pond.²¹

Despite its unfavorable byproduct generation, AA is an appealing adsorbent because it is inexpensive. A 2014 study by the EPA estimated the total operating costs of an AA unit treating 900 gpm of water with 8 ppm fluoride to be approximately \$1/1000 gallons.²¹

The Moo Pig Soobie team pursued activated alumina as a potential solution due to its known success and low operating costs. Moo Pig Soobie also investigated applications for spent AA that would avoid landfilling.

Biochar

Biochar is a potential adsorbent because of its availability, low cost, and low environmental impacts. Moo Pig Soobie felt that biochar adsorbents proposed a unique solution to this problem and decided to pursue orange peel char (OPC) and rice hull char (RHC).

OPC is a viable fluoride adsorbent because orange peels are biodegradable, inexpensive, and naturally contain high amounts of calcium.²² Fluoride has an affinity for calcium and will

readily adsorb onto the calcium in the orange peels. OPC is made by drying and then pyrolyzing orange peels. However, the cost to ship orange peels gets increasingly expensive since orange peels are water heavy. A second step of drying them before shipment would need to preferably be implemented.

Rice hull char (RHC) is also a viable adsorbent because contains carboxyl, hydroxyl, and amidogen groups, all of which increase adsorption capabilities. Rice hulls are also very inexpensive because they are one of the most readily available agricultural byproducts. Literature values report fluoride equilibrium loading capacity of RHC ranging from 2.91 mg/g to 8 mg/g.²³ Because the RHC yields lower capacities than the other adsorbents, it would take more in a column to get the desired results.

Bone Char

Bone char is a common adsorbent used for removing heavy metals and fluoride from water. The char is made by crushing and pyrolyzing animal bones, most of which come from cattle.²⁴ Bone char is a highly porous material that is suitable for adsorption and consists mostly of carbonates and calcium phosphate.²⁵ Under ideal conditions, bone char can have an adsorption capacity of 11 mg/g. It is a commonly used soil amendment, and sulfate-enhanced bone char can even be used as a substitute for phosphate fertilizer.²⁷ This appealed to our team, since our spent bone char would contain high amounts of sulfate and phosphates.

Bone char is generated in millions of tons each year. The agricultural outlook provided by the Organization for Economic Co-operation and Development (OECD) in 2018 predicted that the amount of meat production will increase by 40 million tons in ten years. There will be a corresponding increase in meat production waste, specifically animal bones.²⁶

The high adsorption capacities, environmentally friendly byproduct, and projected supply of bone char led Moo Pig Soovie to pursue bone char as a fluoride adsorbent.

Selected Adsorbent

To select an adsorbent, the adsorption capacity, rate of adsorption, byproduct product application, and costs of each adsorbent were evaluated. The adsorbents studied were activated alumina, orange peel char, rice hull char, and bone char. A scoring system was created to determine which adsorbent might be the best choice.

The adsorption capacity score was determined by the maximum adsorption capacities found in literature. The highest adsorption capacity received the highest ranking. Although we performed the batch experiments in our own lab to determine the adsorption capacities, the batch test results varied so greatly from literature values that we decided to only reference literature values. Discussion of batch testing and possible errors can be found in section 4.2.

The rate of adsorption scores was determined by the minimal contact time needed for the adsorbents to reach the max adsorption capacity. The least amount of time received the highest score. Byproduct application had two possible scores. If the solution resulted in landfilling the byproduct, this earned a score of 1. If the byproduct could be applied elsewhere, such as a fertilizer or benign soil amendment, this earned score of 4. The cost scores were determined by costs per ton of adsorbent. All the cost values were obtained from wholesale company Alibaba. If a price range was given, the lowest value was selected to represent cost per ton.

At the end of the ranking system evaluation, the results end up showing that activated alumina would be the least favorable option to pursue with a score of 9. The other three adsorbents ended up having very similar scores, so a definitive primary adsorbent was not determined. All adsorbents were batch tested to see if the test results would reflect literature results.

Table 3: Adsorbent Comparison Table

	Activated Alumina ²⁸	Orange Peel Char ²⁹	Rice Hull Char ³⁰	Bone Char ²⁴
Capacity (mg/g)	16.3	5.6	7.9	11.3
Score	4	1	2	3
Contact Time (min)	180	50	180	180
Score	3	4	3	3
By-Product Application	Landfill	Soil Amendment	Soil Amendment	Soil Amendment
Score	1	4	4	4
Cost (\$/ton)	500	25	20	60
Score	1	3	4	2
Total Score	9	12	13	12

Test Data

Preparation of Adsorbents

The Moo Pig Sooie team investigated five different adsorbents: 1/8" spherical AA, bone char, orange peel char, rice hull char, and 14 x 28 Tyler mesh AA. The activated alumina was purchased in its appropriate form. Bone char was purchased in 8 x 24 Tyler mesh size, and sieved to particle sizes greater than 1.4 mm. Orange peels and rice hulls were bought uncharred and were both pyrolyzed using the unit shown in Figure 2.

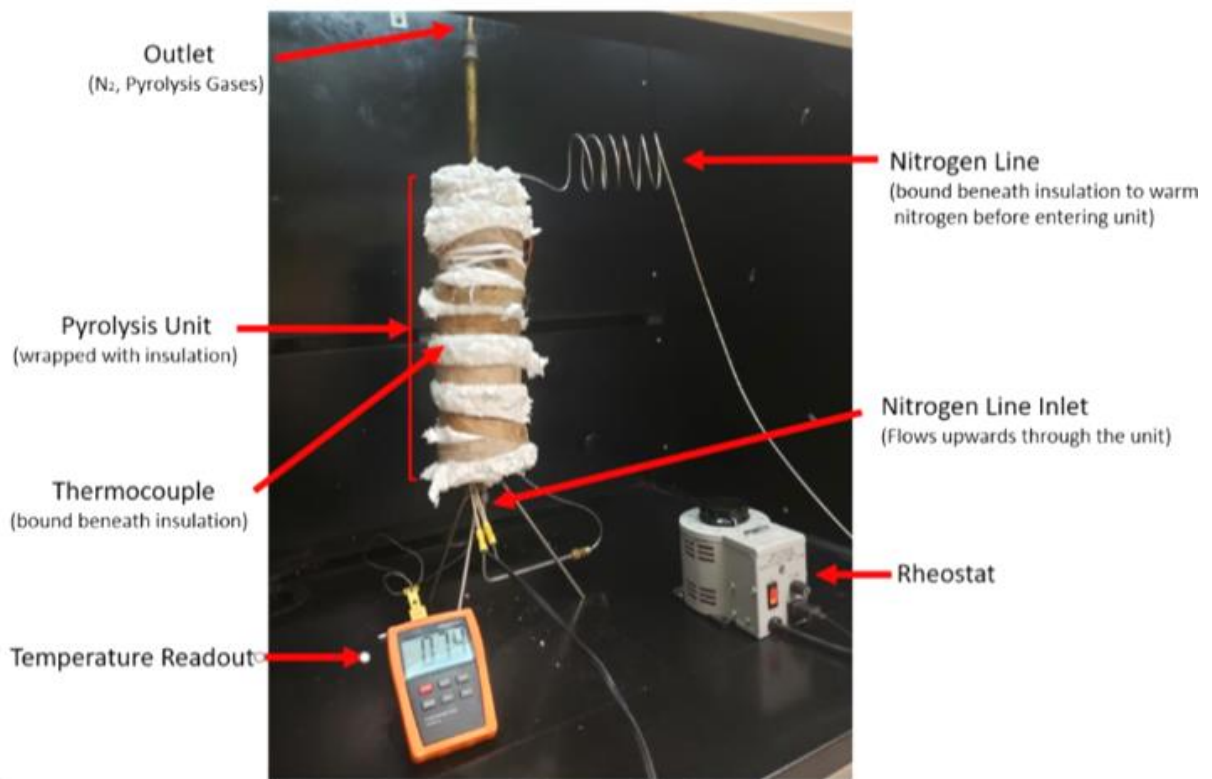


Figure 2: Pyrolysis Unit

The orange peels were dried in an oven at 190°F for three hours before pyrolysis to reduce the time required for pyrolysis and mitigate the accumulation of oils in the pyrolysis unit. Rice hulls were not dried beforehand because their moisture content was determined to be low enough that it would not affect the pyrolysis time or unit.

For each biochar, the pyrolysis unit was filled with the material to 80% of the unit's volume. The temperature was raised to 900°F, and then held constant for one hour before cooling. The charred products were sieved to sizes greater than 1.4 mm.

Batch Testing

Batch tests were performed for each of the five adsorbents to determine their adsorption capacities. First, one liter of synthetic water was prepared using 1.7 g/L of calcium sulfate, and 22.1 mg/L of sodium fluoride.

15g of the adsorbent was added to the solution and stirred with an impeller at 300 RPM and 20°C. A baffle was placed on the side of the beaker to promote the distribution of adsorbent during stirring. The stirring apparatus is shown in Figure 3.



Figure 3: Batch Testing Apparatus, Bone Char

Samples were analyzed by the Don Tyson for Agricultural Sciences Water Quality Lab at the University of Arkansas, using the EPA 300 method. Results are shown in Figure 4.

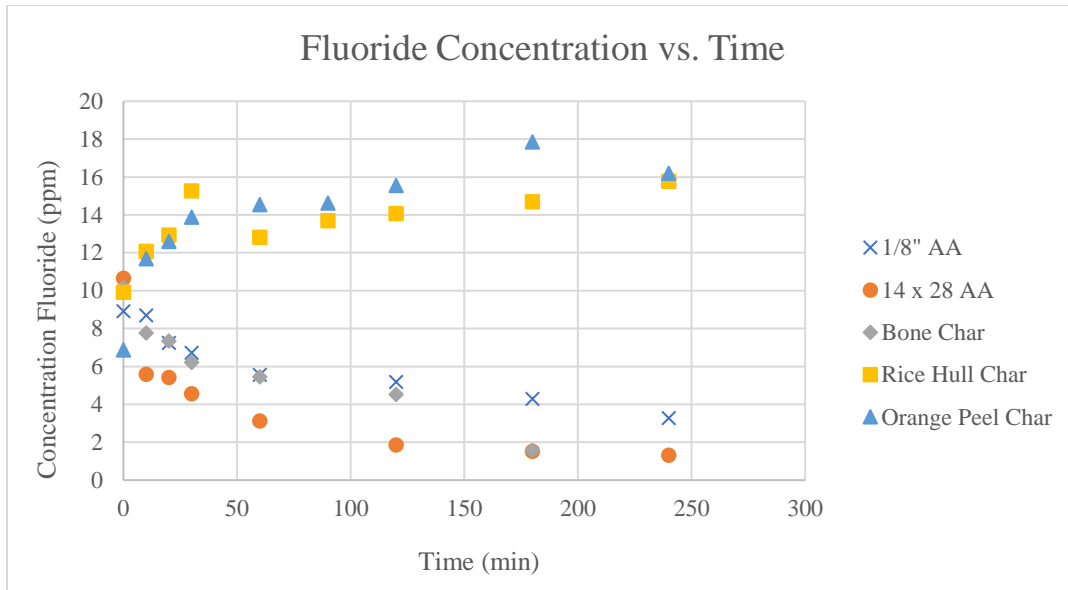


Figure 4: Fluoride Concentration vs Time for Batch Tests

Based on these data, Moo Pig Soovie eliminated the 1/8" AA as a potential adsorbent because the granular 14 x 28 AA adsorbed more fluoride and was made of the same material. If AA was chosen as the final adsorbent, the 14 x 28 mesh form would be preferred. These data also indicated that fluoride concentrations increased in biochar batches. Our team hypothesized that these chars must naturally contain fluoride. To test this, rice hull and orange peel chars were batch tested in solutions of pure deionized (DI) water. See Figure 5 for results.

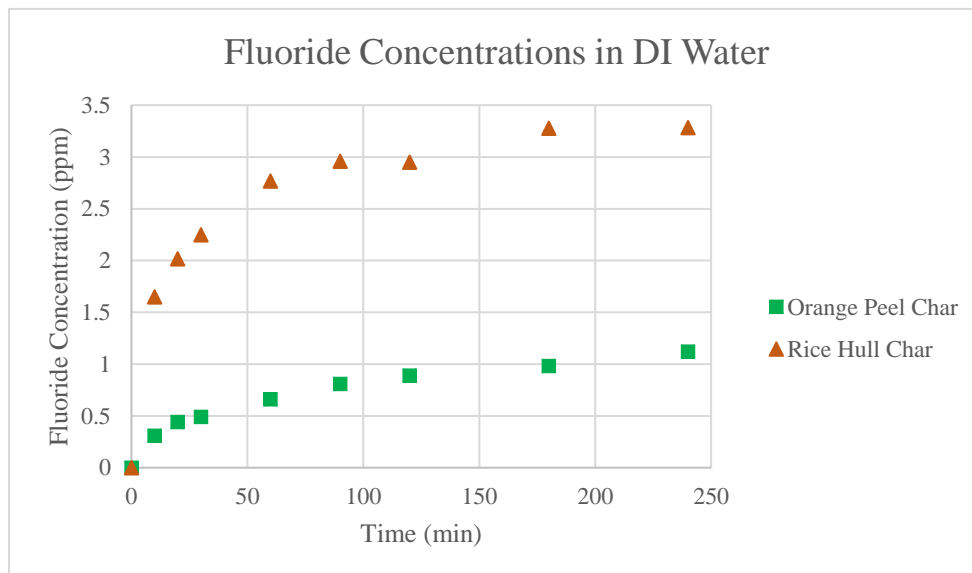


Figure 5: Fluoride Concentrations in DI water with Biochars

These results indicate that biochar solutions increase fluoride content in the water and therefore must naturally contain fluoride. Although these results contradicted literature, Moo Pig Soie concluded that rice hull and orange peel chars were not viable fluoride adsorbents.

With biochars eliminated, Moo Pig Soie continued testing only activated alumina and bone char. The Langmuir isotherms of these two adsorbents were determined by using a linear form of the Langmuir isotherm equation:

$$\frac{C_e}{Q_e} = \frac{1}{k_m Q_m} + \frac{C_e}{Q_m} \quad (1)$$

Where Q_e = amount of fluoride adsorbed at equilibrium (mg/g), C_e = amount of fluoride in the water at equilibrium (mg/L), and the slope of the line is the inverse of the maximum adsorption capacity, Q_m . The Langmuir adsorption constant is k_m , specific to each experiment.²⁷

The Langmuir isotherms of activated alumina and bone char, which were determined from batch testing at 20°C in 1 liter of synthetic water, are shown in Figure 6.

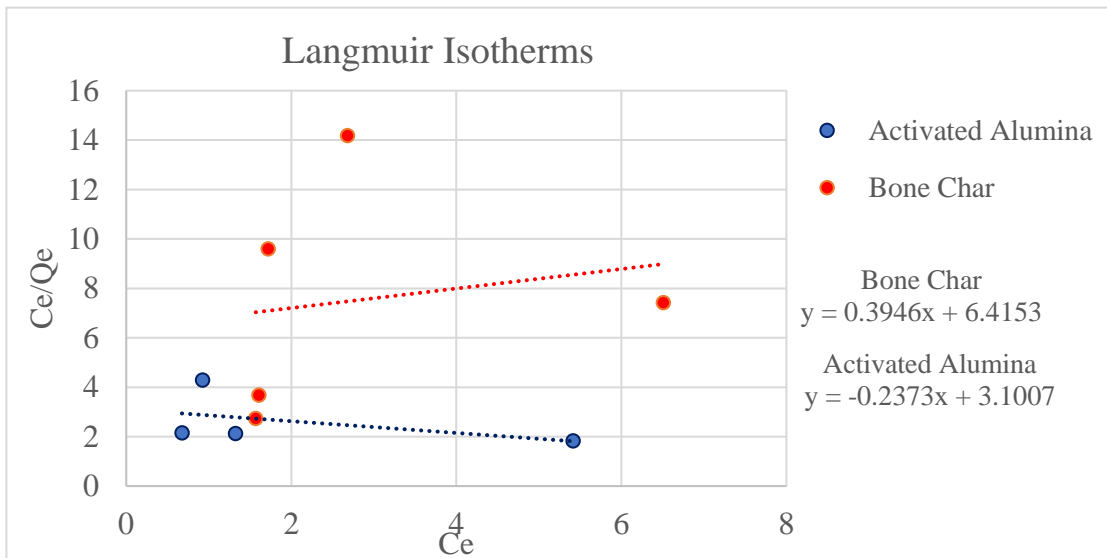


Figure 6: Langmuir Isotherms of Activated Alumina and Bone Char at 20°C

The maximum adsorption capacities determined from the linear trendlines of this figure are physically impossible since the isotherm for activated alumina shows a negative slope.

Our team chose to calculate the maximum adsorption capacity by calculating the adsorption capacities for each of our batch experiments and choosing the largest. The maximum

adsorption capacities for bone char and AA were determined to be .57 mg/g and .63 mg/g, respectively. Literature reports that, at a pH of 7 and at 20°C, AA and bone char should have a maximum adsorption capacity of 16 mg/g and 11 mg/g, respectively.^{24,31}

Moo Pig Sooi hypothesized two reasons for the large disparity between our results and literature values. The first hypothesis was that the high concentrations of other ions, specifically sulfate, were competing with fluoride for active sites on the adsorbent. Multiple studies have indicated that sulfate competes with fluoride during adsorption.^{9,18,24,28,30} Moo Pig Sooi tested this hypothesis by running batch experiments with water containing only fluoride, water with fluoride and sulfate, and water using the synthetic mine water recipe listed in Table 1 listed earlier. Our team predicted that the adsorbents would adsorb the most fluoride when only fluoride was present in the water, and that the least amount of fluoride would be adsorbed from the mine water, where multiple competitive ions were present.

The results of this experiment with bone char are shown in Figure 7. Adsorption of Fluoride was defined as the concentration of fluoride present in the water at the time of sample collection, divided by the initial concentration in the water, C_0 .

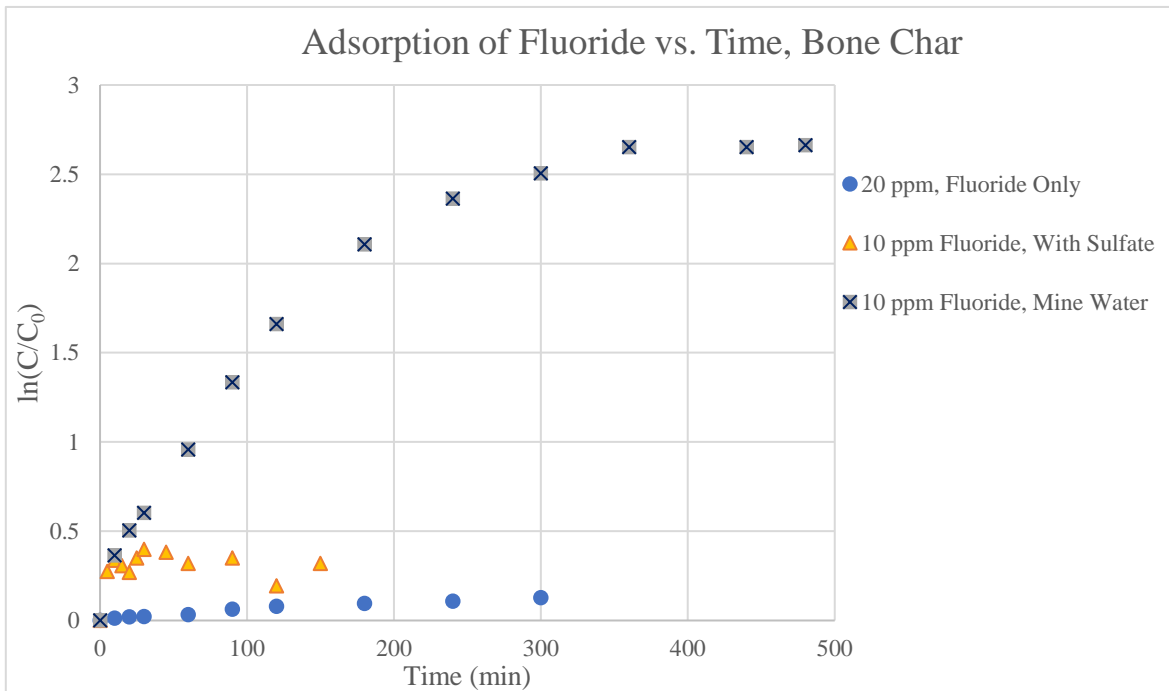


Figure 7: Adsorption of Fluoride with Competitive Ions, Bone Char

The same experiments were performed using activated alumina, with similar results. The results are shown in Figure 8.

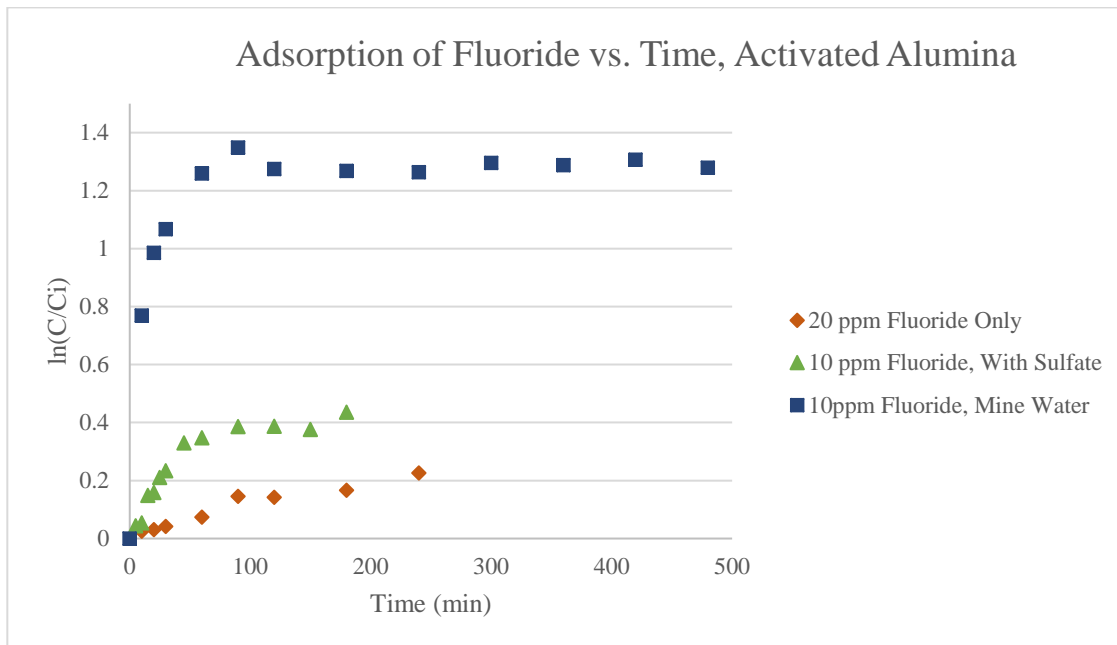


Figure 8: Adsorption of Fluoride with Competitive Ions, AA

Based on these results, Moo Pig Soocie reasoned that other ions may interfere with the adsorption of fluoride onto bone char. The most fluoride was adsorbed in solutions of pure DI water. The least fluoride was adsorbed using the synthetic mine water recipe that included sulfate and phosphate ions. This was consistent with Moo Pig Soocie's hypothesis.

Without any competitive ions in the water, bone char reached a maximum adsorption capacity of 1.66 mg/g. This is still well below the projected literature value of 11 mg/g. Similarly, activated alumina reached a maximum adsorption capacity of 5.05 mg/g, nearly three times less than the literature values of 16 mg/g.

Moo Pig Soocie hypothesized that our experiments had not reached equilibrium when the final samples were taken. This would mean that the linearized Langmuir isotherm equation would not have an accurate value for C_e . Other studies allowed several hours, sometimes even days, for their adsorption systems to reach equilibrium.^{18, 23, 29, 24} Moo Pie Soocie concluded that their final samples were not taken at equilibrium and that interference from competitive ions affected their adsorption data, resulting in unreliable maximum adsorption capacities and Langmuir isotherms. Despite these hypotheses, Moo Pig Soocie wanted to maintain a consistent

study derived from experimental results, and so used our experimental data to design a full-scale system.

Byproduct Studies

Moo Pig Sooie investigated possible byproduct solutions for the two adsorbents. BC is an appealing adsorbent due to its biocompatibility and potential agricultural applications. However, high fluoride concentrations can be harmful to some plants.³¹ If the adsorbed fluoride was stripped from the BC, it could enter the soil and damage the plants, and eventually could contaminate water sources. Common soil pH's in the United States range from 5 to 7 and, in some areas can be up to 7.8.³² The Moo Pig Sooie team tested if fluoride would strip from BC in pH's of 5, 6, and 8 by placing fluoride-saturated bone char in solutions of these different pH's. A pH of 7 was not tested, because all batch experiments determining adsorption capacities were performed at a pH of 7 and had shown that bone char would adsorb fluoride at this pH. Samples were taken daily and can be seen in Figure 9.

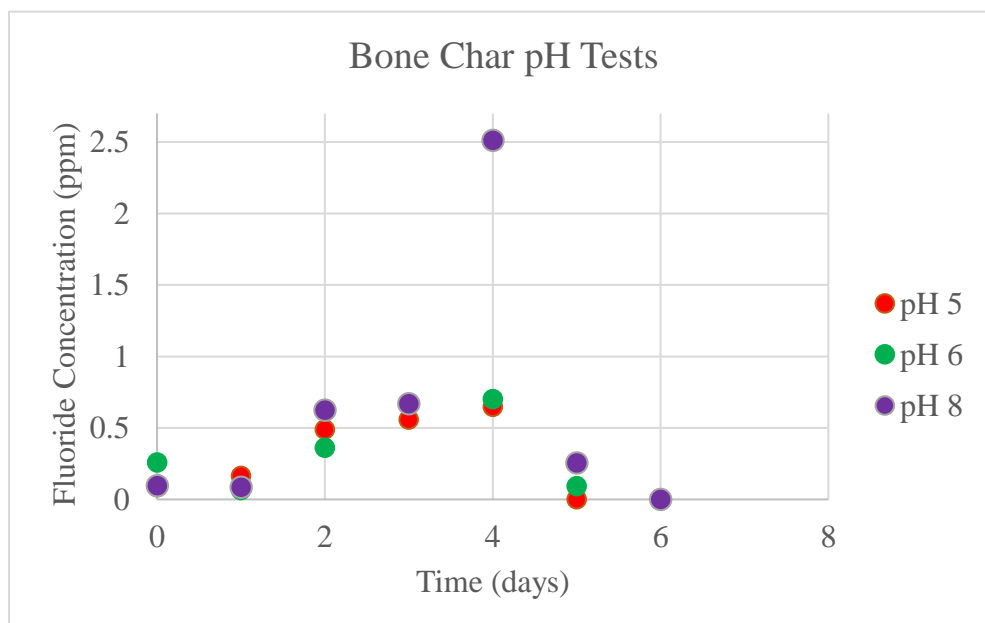


Figure 9: pH test results for Bone Char

These results indicate that bone char will initially slough fluoride ions, but over time will re-adsorb the ions. BC re-adsorbed the most fluoride all conditions. This good because this means the BC would not fully leech from the adsorbent into the soil, potentially harming the plant.

Moo Pig Sooie also explored alternative byproduct applications options for AA, since current AA treatment systems send the spent adsorbent to a landfill. Moo Pig Sooie pursued the

potential use of placing spent AA into concrete mixes. Concrete testing experiments were organized with Dr. Cameron Murray of the University of Arkansas Civil Engineering Department. These experiments involved replacing approximately 20% of the sand used in concrete with the mesh form or spherical form of activated alumina. The compositions are shown in Table 4.

Table 4: Composition of Control Mix, 14 x 28 Mesh, and 1/8" AA mixes

Mix	Composition (lbs/yd)						
	Cement	Rock	AA	Sand	Water	Air	Total
Control	611	1720	0	1087.97	305.5	0.06	3724.53
14 x 28 mesh AA	611	1720	289.57	870.38	305.5	0.06	3796.51
1/8" AA	611	1720	289.57	870.38	305.5	0.06	3796.51

These concrete mixes were subjected to slump tests and break tests. The slump test for concrete mix is done to determine the workability of the mix. If the mix is too viscous or not viscous enough, it is difficult to use the mix for projects. The slump test concluded that the 14 x 28 mesh AA had the lowest workability and slumped the most out of the three groups. The results of slump testing are shown in Table 5.

Table 5: Slump of Each Mix During Slump Test

Mix	Slump (inches)
Control	7
14 x 28 mesh AA	10
1/8" AA	8

Break tests are used to determine the compressive strength of the concrete. This involves applying a compressive force onto a cylinder of concrete until failure. These tests are performed after 1,7,14, and 28 days. After 28 days, it is assumed that the concrete has 95% of its maximum strength. The break tests of Moo Pig Soovie's concrete mixes are shown in Table 6.

Table 6: Average Strength of Each Mix During Break Test

Mix	Average Strength (psi)			
	Day 1	Day 7	Day 14	Day 28
Control	2,778	5,069	5,529	5,721
14 x 28 mesh AA	1,672	3,898	3,939	4,149
1/8" AA	2,294	4,168	4,452	5,268

The break tests showed that the 1/8" AA was stronger than the 14 x 28 mesh, but weaker than the control group. This leads to the possibility that AA decreases the strength of concrete by an unknown factor. These results indicated that AA might be used in concrete projects that require low strength performance, such as sidewalks. However, an AA-based concrete mixture has poor workability and further testing would be required to find an optimal AA to sand ratio that does not sacrifice strength and workability for landfill reduction. Moo Pig Sooie concluded that AA is not currently a desirable substitute for sand, and that AA-generated waste from an adsorption process is only fit for landfilling.

Bench Scale Design

The bench scale design consists of a clear PVC column, centrifugal pump, and tubing shown in in the Figure 10 schematic. Figure 11 is an image of the setup.

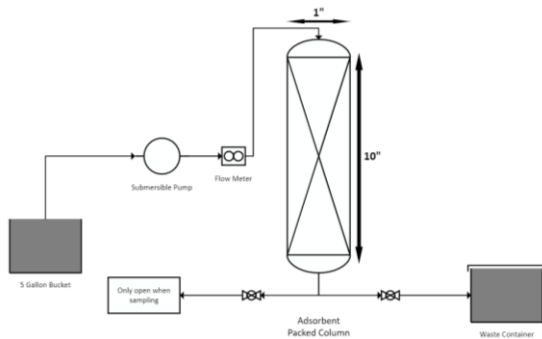


Figure 10: Bench Scale Adsorption Column

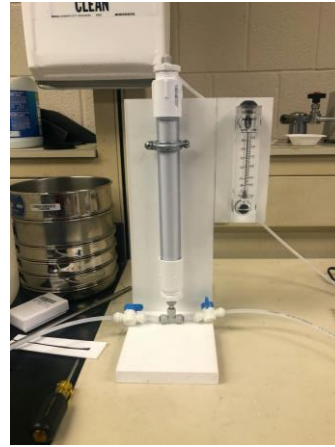


Figure 11: Bench Scale Column

The column is loaded with either 80.7 g of bone char or 83.7 g of AA. Once the column is packed, it is tightly sealed and reconnected to system. The submersible pump is started and introduces DI water to the column. Once the desired flow rate is achieved, the pump is transferred into a synthetic solution, and this solution is sent through the system.

Operating conditions were determined by varying the flowrate through the column and taking a sample once steady state was achieved. Tables 7 and 8 are the results for experiments.

Table 7: Bench Scale Adsorption Column Data for BC

Flow rate (mL/min)	Time for two bed volumes (min)	Residence time (min)	Concentration fluoride (ppm)	Fraction of Fluoride Adsorbed	Loading Capacity (mg Fluoride / g adsorbent)
0.00	0.000	0.00	8.99	0.00	0.00
9.25	24.86	12.4	0.215	0.98	1.89
13.0	17.69	8.85	0.11	0.99	1.91
14.4	15.97	7.99	0.117	0.99	1.91
16.3	14.11	7.06	0.149	0.98	1.90
19.0	12.11	6.05	0.147	0.98	1.90
20.1	11.44	5.72	0.221	0.98	1.90
23.3	9.870	4.94	0.256	0.97	1.89
30.1	7.640	3.82	0.427	0.95	1.88

Table 8: Bench Scale Adsorption Column Data for AA

Flow rate (mL/min)	Time for two bed volumes (min)	Residence time (min)	Concentration fluoride (ppm)	Fraction of Fluoride Adsorbed	Loading Capacity (mg Fluoride adsorbed/ g adsorbent)
0.00	0.000	0.00	8.716	0.0	0.00
8.65	29.83	14.9	0.000	1.0	1.94
13.0	19.85	9.92	0.228	0.97	1.89
15.0	17.20	8.60	0.000	1.0	1.94
16.5	15.64	7.82	0.483	0.94	1.84
18.8	13.76	6.88	0.100	0.99	1.92
22.0	12.29	6.14	0.490	0.94	1.83
22.4	11.52	5.76	0.900	0.90	1.74
25.0	10.32	5.16	0.416	0.95	1.85

Both adsorbents were tested at similar flowrates and initial fluoride concentrations in the solution. These adsorbents yielded similar fractions, with AA performing slightly better than the BC. Both columns were able to reduce solutions to less than 2ppm. The adsorbents yielded similar loading capacities, with average values of 1.84 mg/g and 1.87 mg/g for BC and AA,

respectively. These values are significantly skewed from literature values and our batch loading capacities. As discussed in our batch results, competitive sulfate ions may inhibit the adsorption of fluoride, and most literature studies were performed using solutions of only fluoride. The bench scale results may vary from the batch test results because the solutions experienced different contact times and adsorbent volumes in the column.

The bench scale results indicate that almost all the fluoride was adsorbed after passing through the column even at faster flow rates of 25 mL/min. The amount of fluoride adsorbed can be represented by fractional conversion of fluoride concentration in the solution. Figures 13 and 14 are the relationships between the fraction of fluoride adsorbed and residence time.

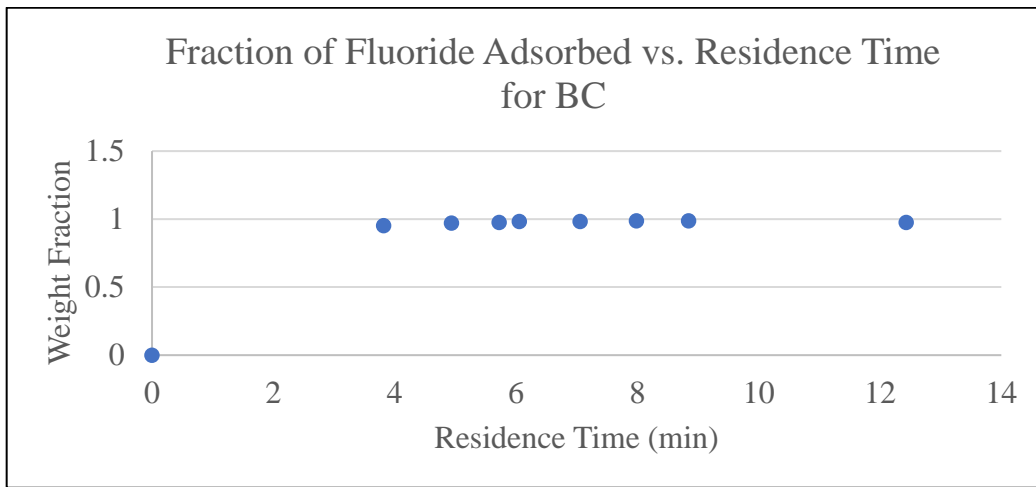


Figure 13: Fraction of Fluoride Adsorbed vs. Residence Time for BC

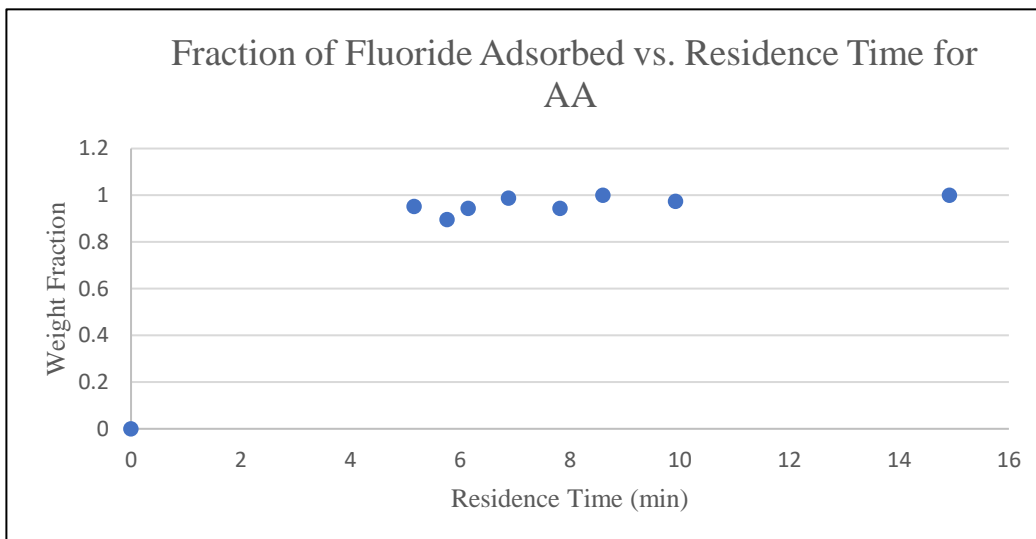


Figure 14: Fraction of Fluoride Adsorbed vs. Residence Time for AA

To reduce fluoride concentrations from 10 ppm fluoride to 2 ppm fluoride, 80% conversion is required. This criterion was met, with all flow rates achieving 89% conversion or better. From Figures 11 and 12, bone char has a more rounded curve as well as a shorter residence time than AA. This means that it will require less time and less material to achieve the adsorption needed. Additionally, less bone char will be needed since the column was initially loaded with less BC than AA.

Full-Scale Design

The full-scale design in Figure 15 consists of two treatment vessels in parallel using bone char adsorbent. The two vessels allow for one to be bypassed while the bone char is being replaced in the other. The basis of the design is that the packed beds will become fully loaded once a week, or every 168 hours, assuming the treatment facility runs 24 hours a day, 7 days a week. To determine the size of the full-scale packed beds, an equilibrium loading capacity of 1.89 mg/g was used. As a comparison, the size of packed beds needed for the literature equilibrium loading capacity of 7 mg/g is also shown. Based off the 168 hours, the fluoride flow rate and bone char loading capacity were used to calculate the total amount of bone char needed. For the measured loading capacity, 8,900 ft³ of bone char is needed, but for the literature loading capacity only 2,406 ft³ is needed. This is a large difference in volume which shows the importance of recognizing the decrease in bone char's equilibrium loading capacity due to the sulfate ions in the water.

The total volume of bone char needed is 8,900 ft³. The desired dimensions for these packed beds are a diameter of 11.5 ft and a height of 86 ft. These dimensions minimize the pressure drop throughout the bed to 11.4 psi. For the treatment vessel, an additional 2 ft should be added to the top to account for a flow distributor and an additional 5 ft should be added to be bottom for a level controller. This gives a total vessel height of 93 ft for each vessel. Based on this bed size and feed flow, the superficial residence time in the bed is 66 min. With a particle size of 2 mm, there is an actual residence time of 23 min because of a 0.35 void fraction. This residence time is adequate for the adsorption of fluoride.

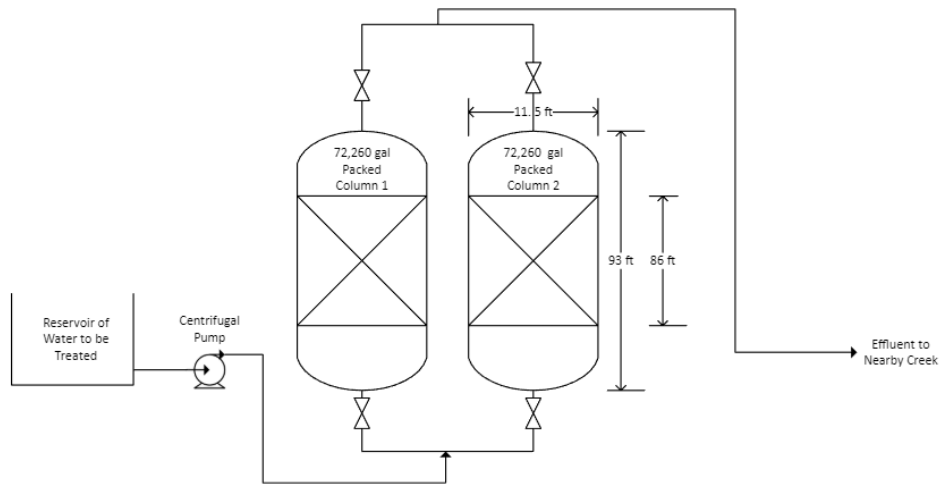


Figure 15: Process Schematic Diagram, Full Scale Industrial Design

Based on the literature equilibrium loading capacity values, the volume of bone char would require one vessel with a packed bed volume of $2,406 \text{ ft}^3$. The diameter of this packed bed would be 9.8 ft with a height of 31.6 ft. These dimensions would result in a pressure drop of 6.1 psi. This is drastically different than the vessel size calculated from real equilibrium loading capacity values, showing the importance of recognizing the competing ions in the water.

The beds are designed to treat an inlet concentration of 10 ppm fluoride. Figure 16 is the block flow diagram of the full-scale design depicting the mass of bone char that is required weekly and where the spent bone char will be moved. Once the water has run through the packed bed, the concentration of fluoride will be 2 ppm or lower. This water can be discarded to nearby creeks. The fluoride will eventually build up on the bone char and the bed will become fully loaded. This will occur after approximately 7 days or 168 hours of running the 1000 gpm feed water. At this time, the bone char will need to be replaced. The spent bone char can be land applied after it is removed from the columns. In this location, the pH of the soil is approximately 5.5. This pH will keep the fluoride attached to the bone char according to the pH experiments conducted with bone char, which was discussed earlier. The packed bed can then be filled with new bone char.

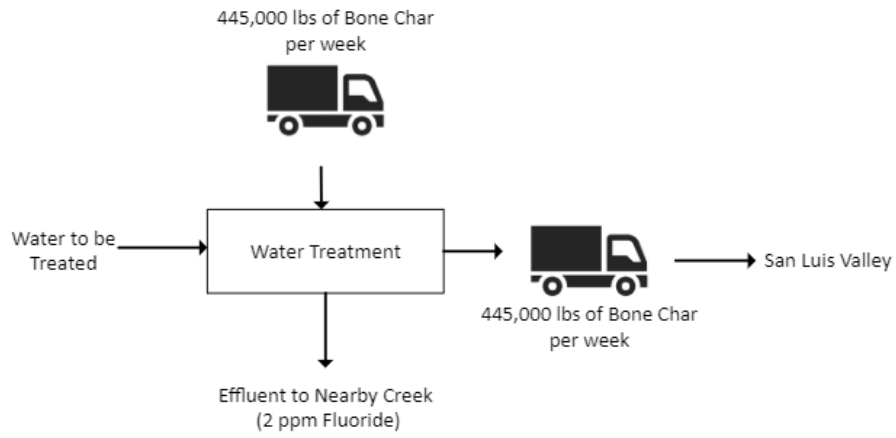


Figure 16: Block Flow Diagram for Full Scale Industrial Design

Bone Char Byproduct Application

The only byproduct generated from this process is spent bone char. The amount of spent bone char produced is approximately 8,900 ft³ per week. This bone char can be disposed of by land application because bone char is commonly used as fertilizer.³³ The main concern about land applying the spent bone char is whether or not the fluoride ions that are attached to the bone char will be released into the soil. As discussed in Section 4.3, Moo Pig Sooie determined that fully loaded bone char will retain almost all adsorbed fluoride in both acidic and basic conditions. Nearby cropland with any of these plants are a viable disposal site for the spent bone char. Additionally, the bone char naturally contains high amounts of phosphates and will have adsorbed sulfates from the water. Sulfates and phosphates are common soil amendments and would be beneficial for plant life.^{25,33,34}

Business Plan

The economic analysis for the full-scale bone char facility was done on a basis of adding this facility to already available land on the mine site as well as on the basis that it will not be operated for the entire year. The Henderson mine generates more water than the mine can handle eight months out of the year because of rainfall and snow melting. Figures B.2-4 show the average temperatures, rainfall, and snowfall in the area. This facility will be a 10-year project with a 2-year construction period. In order to generate revenue, the spent bone char after the adsorption process will be sold as a soil amendment to potato farms near the mine. Potato farms were chosen since potato plants have been known to handle higher concentrations of fluoride if needed. This analysis was done based on this facility operating only 8 months out of the year, as the winter months may cause the water to freeze. Currently, reverse osmosis is a very popular choice when it comes to water treatment, so our bone char facility was compared to a reverse osmosis facility as seen in Table 9.

Table 9: Bone Char vs. Reverse Osmosis Full Scale Facility Cost Breakdown

Bone Char Facility		Reverse Osmosis Facility	
Item	Cost	Item	Cost
2 Columns	\$133,512	Capital Cost	\$144,700,000
Pump	\$22,600	Yearly Operating Cost	\$8,145,000
Direct Costs	\$530,778	10-Year NPV	(\$38,180,000)
Indirect Costs	\$220,116	Cost per 1000 gal	\$15.50
Total Capital Cost	\$750,894		
Adsorbent Cost	\$3,110,000		
Utility Cost	\$13,600		
Operating Labor Cost	\$802,920		
Transportation Cost	\$865,920		
Yearly Operating Cost	\$4,792,440		
Revenue	\$2,592,000		
10-Year NPV	(\$10,944,505)		
Cost per 1000 gal	\$4.20		

The capital cost for the bone char facility was done by first determining the purchased cost of the equipment. A polyethylene column with a diameter like our design was found online and used as a basis for sizing it up to our desired capacity. This polyethylene column cost \$25,000 with a capacity of 13,000 gallons, and the six tenths rule was used for sizing.³⁶ The final cost is seen in Table 9 above. The total equipment purchased cost was then used to calculate the direct and indirect costs for the facility. Then the direct and indirect costs were added up to get the capital cost. The economics for the full-scale reverse osmosis facility was done by a report for the city of San Diego, which as show in Table 9, is a very expensive facility to construct.³⁷ The capital cost for the reverse osmosis is almost three orders of magnitude larger than the capital cost for the bone char facility, so it is more economical to construct a bone char facility.

The adsorbent cost for the bone char was determined by taking the market price of \$600/metric ton and multiplying it by the number of metric tons required for 8 months of operation per year.³⁸ The revenue generated from selling bone char as a soil amendment after adsorption was found by first finding the market price of bone char for soil amendment use which turned out to be \$750/metric ton.³⁹ This price was decreased to \$500/metric ton due to the bone char already being used and containing fluorine, and to make it a more attractive option. The transportation costs were determined by first calculating the amount of ocean containers required for international shipping from China to Los Angeles since the bone char is being purchased from China. Then the number of truckloads required to move the bone char from Los Angeles to Henderson, Colorado was calculated and added to the yearly transportation costs seen in Table 9. The net present value was calculated by doing a discounted cash flow analysis using a discount rate of 10% over a period of 10 years. As seen in Table 9, the NPV for the bone char facility is much lower than the reverse osmosis facility. Overall, Table 9 shows that the yearly operating cost for the reverse osmosis facility is almost twice as much as the yearly operating cost for the bone char facility. By taking the yearly operating cost and capital cost, the bone char facility is much cheaper and easier to construct and maintain than the reverse osmosis facility.

Health, Safety, and Environmental Regulations

One of the main concerns when working with fluoride is its ability to create hydrofluoric acid with water. The concentrations and temperatures used for the experiments were low enough that this did not pose a large threat, but all team members need to keep this in mind in case of spills. Proper PPE and housekeeping practices should always be followed. Any chemical containing fluorine, in our case sodium fluoride, should be stored and labeled properly. For bench scale experiments, the same precautions should be used as well as the additional concern of ensuring the discharge from the column feeds into the proper waste container. Because fluoride-concentrated water is regulated, a hazardous waste container large enough to accommodate multiple experiments must be kept in the lab. For the full-scale design, a hazardous waste container would only be needed in abnormal situations where the system was unable to discharge into the creek. Typical safety precautions such as PPE and housekeeping still need to be followed.

While the discharge for the Henderson mine flows into a creek that is not directly a source of drinking water, it is still necessary to consider health and environmental risks associated with waterways as they may lead to a drinking water source. Right now, the EPA has set an enforceable drinking water standard of 4 ppm, with a secondary, non-enforceable standard of 2 ppm. Reducing the fluoride concentration of the discharge from 10 ppm to 2 ppm will ensure the waterways are well within the enforceable drinking water standards.

Throughout the U.S., some locations add fluoride to their water supplies through a process called fluoridation. This act is not mandatory by the EPA and has been hit with some backlash as new risk assessments for fluoride evolve. Supporters of fluoridation, including the American Dental Association, argue that fluoride in water is beneficial for communities because it prevents tooth decay, protects against cavities, and saves money in dental care costs.⁴⁰ Opposing arguments claim that there is little to no regulation in personal intake when fluoride is added to water sources and cannot be safely monitored. Currently, Colorado does not mandate fluoridation of municipal water.⁴¹ Moo Pig Soobie's method to adsorb fluoride using bone char will ensure that the surrounding community is not exposed to a quality of water that could potentially be harmful to them, even though this monitoring is not required by the government.

Community Relations Plan and Public Acceptance

Having the community involved in the decisions regarding spent bone char land application is important for the success of the proposed system. Without the community's approval, the foreseen benefits would not outweigh the costs for the Henderson mine. The amount of fluoride in water, whether naturally occurring or added artificially, has been a controversial topic for many years.

Moo Pig Sooie's plan is to sample the affected communities to gather their thoughts on the addition of fluoride to the soil of their crops. During experimentation, it was found that fluoride was released from bone char most slowly in acidic conditions. Therefore, applying the spent bone char to potatoes or other crops that prefer acidic soil nearby the Henderson mine would be the optimal location to minimize the concern of the surrounding community. A public involvement plan is needed for the process to have the approval and enthusiasm from the community. This plan includes: first, keeping the public up to date on the information regarding the adsorption process so that they can be active participants; next, involving the community in decision making and actions to be taken, from the initial start-up to any amendments that may come up in the future; and lastly, making sure there is accountability on both sides to uphold the agreements put in place. This partnership between the Henderson Mine and the San Luis Valley community will ensure that all parties are satisfied with the conditions of their soil and will foster a mutually beneficial relationship that is dedicated to the progression of both the Henderson Mine's environmental regulations and the community's welfare.

Conclusion and Recommendations

After a careful analysis of water treatment methods, adsorption media, and literature reviews, Moo Pig Soobie decided the use of BC for the adsorption of fluoride was the most feasible secondary water treatment method.

The adsorption properties were vastly affected by the presence of sulfate in the water, lowering the adsorption capacity of the chosen media. Along with the sulfates in the water, other minerals and metals in the water affected the loading of fluoride onto the adsorbent. The size of the full-scale system designed must accommodate enough adsorbent that can remove the necessary amount of fluoride in the presence of competitive ions.

The land application of spent bone char is cost effective and environmentally safe. Since the adsorbent loads sulfate as well as fluoride, the sulfate that will leech from the material can act as a soil amendment. Fluoride will be stripped from the bone char in minimal and harmless amounts. This knowledge, as well as the plans to keep ongoing public updates on the fluoride content of the soil, will assist public acceptance of the process. Moo Pig Soobie believes this water treatment proposal will make a good candidate for the removal of fluoride in the discharged mine water and will allow mines to have a sustainable and environmentally friendly byproduct.

Acknowledgments

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Appendix

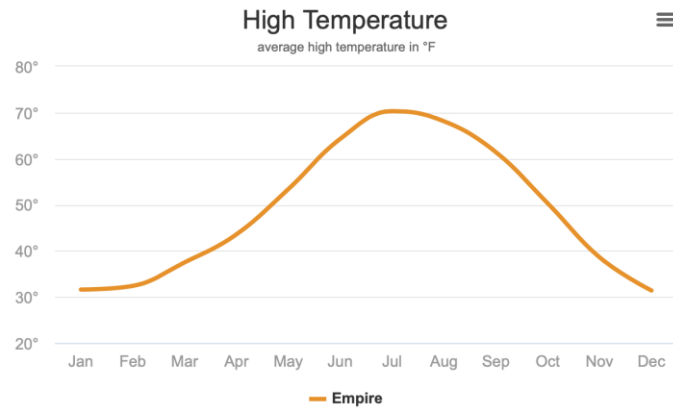


Figure A.1: High Temperature Graph for Empire, CO

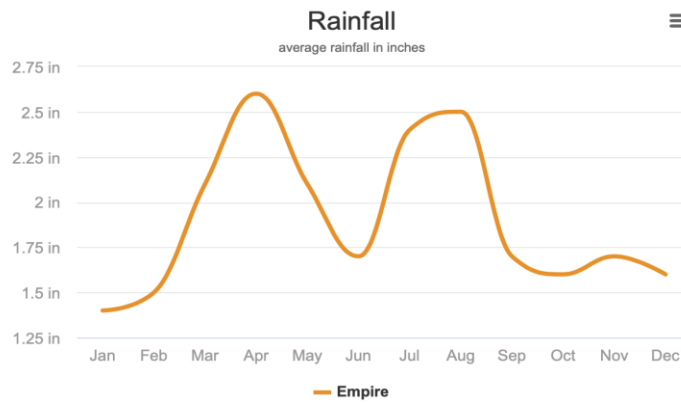


Figure A.2: Average Rainfall in Empire, CO

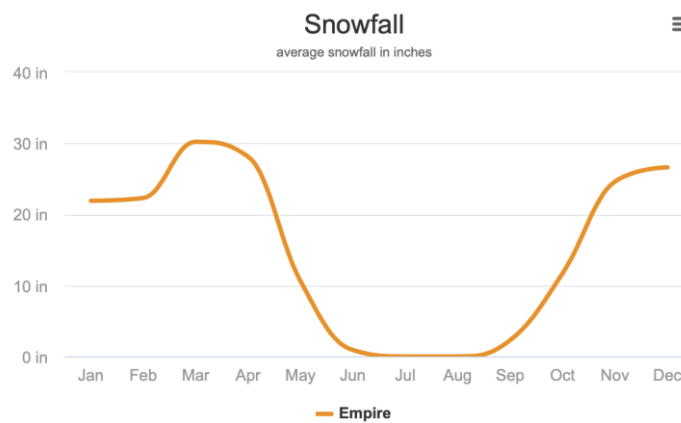


Figure A.3: Average Snowfall in Empire, CO