

# **Colin's Incredibly Safe and Beginner Friendly Fireworks Manufacturing Facility**

Wastewater Treatment Plant Plans

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## Background

My name is Colin, and I own “Colin’s Incredibly Safe and Beginner Friendly Fireworks Manufacturing Facility”. I manufacture about 1000 fireworks a day: 250 red, 250 white, 250 green, and 250 blue. I secretly will sell fireworks to anyone who asks, without checking for proper identification or credentials. To combat the large amount of fires caused by idiots using my fireworks, I am designing a wastewater treatment plant to take the wastewater from my fireworks production and supply local firefighters and wildfire fighting agencies with clean water, safe for the environment.

To begin, we must first look at how my fireworks work and are manufactured.<sup>1,2</sup> In the eyes of the public, I only manufacture the most average fireworks, and I have kindly taken the time to draw a diagram of my fireworks below, which I will reference while explaining (Figure 1). Each of my fireworks are 3 inch (~8cm) chrysanthemum shell fireworks. To say upfront, at each stage of the manufacturing process, I lose about 2% of all ingredients I use, and they are washed into the wastewater. All ratios are in mass.

1. Paper shells and mortar:

My fireworks are created using #60 Kraft paper. Kraft paper is the name of common brown paper, similar to what is used for Trader Joe’s bags. The “#60” refers to the thickness of the paper. Anything higher becomes difficult to work with. #60 paper is about 100 grams per square meter, and each firework uses **0.1m<sup>2</sup> of the paper**. This is because the paper is triple layered, there are two shells, and the lift charge as well is encased in paper. The glue I will use is referred to as wheat paste among us pyrotechnics, and it’s simply a mixture of a specially processed flour and some water. The ratio I use is 4:1 water and dextrin (not flour), and I use about **5g of the substance per firework**.

2. Fuse:

The fuse is essentially black powder wrapped in paper. Black powder is the explosive I use in all parts of my firework to propel the firework and cause the big burst. Two kinds of black powder are used in my fireworks. The fuse and the lift use **a 1:2 ratio of potassium nitrate and charcoal**. The fuse uses **3g of this black powder**. (4 cm long for a 3 second delay after igniting lift charge).

3. Lift charge:

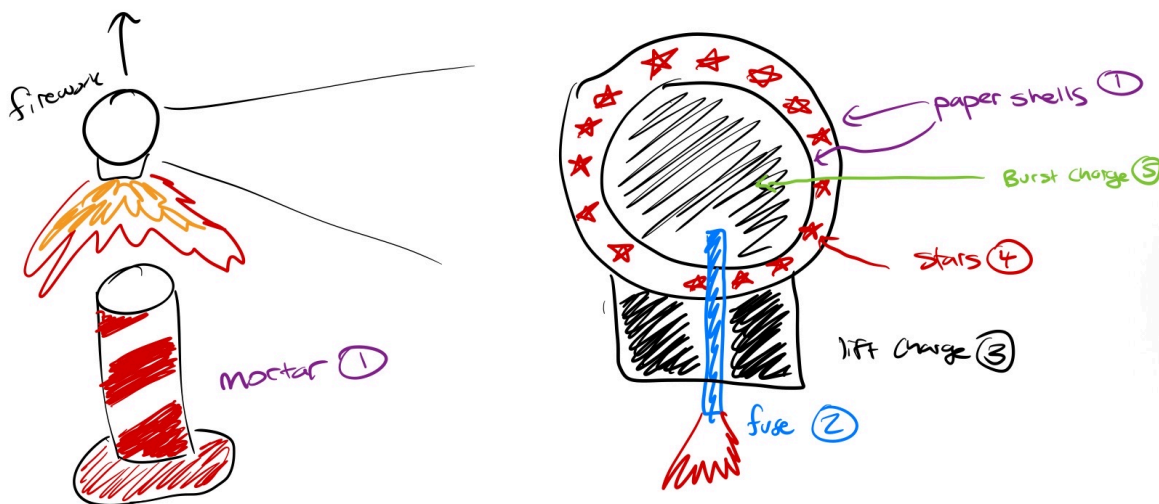
The lift charge is **15g of the 1:2 potassium nitrate/charcoal black powder**. The lift charge is what is ignited to launch the firework into the air.

4. Stars:

The stars are where things get mildly complicated. The ingredients depend on the desired colour and effect, and will be split into the four different colours below. The ingredients are mixed together and compressed into small balls, with each firework having **100 21g “stars.”** Stars themselves can be difficult to ignite, so each of the stars are coated with a “prime.” Specifically, a primer created by a famous pyrotechnician, Dr Takeo Shimizu, which is known to work well on stars containing ammonium perchlorate. Normal primer, similar to our black powder, uses potassium nitrate. However, ammonium perchlorate and

potassium nitrate can form ammonium nitrate, which is susceptible to degradation from humidity. For longevity, I make sure to use Shimizu's recipe, which is **1 gram per star of 80:15:5 sodium nitrate, charcoal, and sulphur (100g per rocket)**. Also, dextrin is basically a thick, processed cornstarch, and thus will be treated as such, being 162 g/mol of  $C_6H_{10}O_5$ . Magnalium is 50:50 aluminum and magnesium. Finally, each of these are combined with a mixture of **25% isopropyl alcohol and 75% water (10g per firework?)**.

- a. Green stars powder (100g)  
56g barium nitrate, 7g red gum (acaroid resin), 17g mangalium, 15g polyvinyl chloride (PVC), 5g dextrin
  - b. Blue stars powder (100g)  
39g potassium perchlorate, 29g ammonium perchlorate, 14g copper carbonate, 14g red gum, 4g dextrin
  - c. White stars powder (100g)  
60g potassium nitrate, 16g antimony trisulfide, 20g sulfur, 4g dextrin
  - d. Red stars powder (100g)  
35g potassium perchlorate, 25g strontium perchlorate, 14g magnalium, 13g parlon ( $C_4H_6Cl_2$ , chlorinated rubber), 5g dextrin
5. Burst charge:  
The burst charge will use a special kind of black powder, abbreviated KP, also created by Dr. Takeo Shimizu. KP is used instead of H3 (another burst charge black powder) because H3 is sensitive to accidental ignition with both sulfur and perchlorates. KP is a mixture of **70:18:10:2 potassium perchlorate, charcoal, sulfur, and dextrin**, and we will be using **15g per rocket**.



**Figure 1:** Firework diagram.

## Feed

**Table 1:**

Component	Formula	Molar Mass (g/mol)	Total g per 1000 rockets	Total g in wastewater (2 percent)	Moles in wastewater
#60 Kraft Paper (cellulose)	$(C_6H_{10}O_5)_n$	162	10,000	200	1.24
Dextrin (corn starch)	$(C_6H_{10}O_5)_n$	162	94,300	1,886	11.64
Potassium nitrate	$KNO_3$	101.1	312,000	6,240	61.7
Charcoal	C	12	23,700	474	39.5
Sulfur	S	32.1	106,500	2,130	66.4
Sodium nitrate	$NaNO_3$	85	80,000	1,600	18.8
Isopropyl alcohol	$C_3H_8O$	60.1	2,500	50	0.83
Potassium perchlorate	$KClO_4$	138.5	380,500	7,610	54.9
Polyvinyl chloride (PVC)	$(C_2H_3Cl)_n$	62.5	75,000	1,500	-
Magnesium (Mg)	Mg	24.3	77,500	1,550	63.7
Aluminum (Mg)	Al	27	77,500	1,550	57.4
Red gum (acaroid resin)	-	-	105,000	2,100	-
Barium nitrate	$Ba(NO_3)_2$	261.3	28,000	560	2.14
Ammonium perchlorate	$NH_4ClO_4$	117.5	145,000	2,900	24.7

Copper carbonate	$\text{CuCO}_3$	123.5	70,000	1,400	11.3
Antimony trisulfide	$\text{Sb}_2\text{S}_3$	339.7	80,000	1,600	4.71
Strontium perchlorate	$\text{Sr}(\text{ClO}_4)_2$	286.5	125,000	2,500	8.73
Parlon <sup>3</sup>	$(\text{C}_4\text{H}_6\text{Cl}_2)_n$	125	65,000	1,300	10.4

All compounds being used in the production of the 1,000 fireworks daily, and the amount that is washed away in the wastewater.

Next, I want my perchlorate concentration in my wastewater to equal the standard recorded in a recent paper testing firework manufacturing runoff in China (280mg/L). Doing the calculation, I need to use around **30,000 L/day or 30m<sup>3</sup> d<sup>-1</sup>** of water to make sure that my wastewater is comparable to other factories.

To better organize and tabulate the wastewater, I can organize based on several things. If a part of my wastewater is soluble in water, **I will assume that it completely dissolves into its respective ions** and group those ions according to industry standards. The solids like the PVC, charcoal, cellulose, parlon, magnesium powder, aluminum powder, and sulfur powder can all be grouped together as total suspended solids (TSS<sup>4</sup>) as they don't dissolve and the EPA has regulations on them.<sup>5</sup> UGA explains that the classification depends on the size of the particle, so in this case I am **assuming that the plastics do not break down past 1 micrometer**, and thus can be filtered and treated as TSS. The dextrin and red gum can be grouped together as chemical oxygen demand (COD) which is essentially a measure of dissolved starches and such, and is an indicator of organic pollution. EPA has a limit on these as well.

Next, for the soluble components, I can track their ion counterparts and group them according to EPA regulations as well, and use molar ratios to find the current mg/L of each, and then the desired amount for each group (Table 2). I am also including a column on generally how I might remove the substance. Desired amounts read from "Environmental Reuse" maximum contaminant level (MCL) regulations when available, otherwise drinking water standards.

**Table 2:**

<b>Group</b>	<b>Sources</b>	<b>Amount (mg/L)</b>	<b>Desired (mg/L)</b>	<b>Daily Load (g/d)</b>	<b>How to remove</b>
TSS	Parlon, PVC, cellulose, charcoal, sulfur	168.8	0.03 <sup>5</sup>	8704	
COD	Dextrin, red gum	132.9	20 <sup>5</sup>	3987	
Perchlorates (ClO <sub>4</sub> <sup>1-</sup> )	KClO <sub>4</sub> , NH <sub>4</sub> ClO <sub>4</sub> , Sr(ClO <sub>4</sub> ) <sub>2</sub>	305.56	0.056 <sup>6</sup>	9167	
Nitrates (NO <sub>3</sub> <sup>1-</sup> )	Ba(NO <sub>3</sub> ) <sub>2</sub> , NaNO <sub>3</sub> , KNO <sub>3</sub>	175.21	10 <sup>5</sup>	5256	
Antimony trisulfide (Sb <sub>2</sub> S <sub>3</sub> )	Sb <sub>2</sub> S <sub>3</sub>	5.33	0.006 <sup>7</sup>	160	(Amount for pure antimony, so maybe 0.003mg/L)
Strontium (Sr <sup>2+</sup> )	Sr(ClO <sub>4</sub> ) <sub>2</sub>	25.5	4 <sup>8</sup>	765	
Copper (Cu <sup>2+</sup> )	CuCO <sub>3</sub>	23.9	1.3	717	
Carbonate (CO <sub>3</sub> <sup>2-</sup> )	CuCO <sub>3</sub>	22.6	-	678	Not specifically regulated, but maintain proper pH
Barium (Ba <sup>2+</sup> )	Ba(NO <sub>3</sub> ) <sub>2</sub>	9.79	2	294	
Magnesium (Mg <sup>2+</sup> )	Magnalium (50:50, MgAl)	51.67	- <sup>9</sup>	1550	Maintain neutral pH so remains insoluble
Aluminum (Al)	Magnalium (50:50, MgAl)	51.67	- <sup>10</sup>	1550	Maintain neutral pH so remains insoluble
Sulfur (S)	S	71	-	2130	
Isopropyl alcohol	C <sub>3</sub> H <sub>8</sub> O	1.667	-	-	Already at an OK level and miscible with water
Ammonium (NH <sub>4</sub> <sup>+</sup> )	NH <sub>4</sub> ClO <sub>4</sub>	15.1	0.5 <sup>11</sup>	453	

Potassium (K <sup>+</sup> )	KNO <sub>3</sub> , KClO <sub>4</sub>	151.6	-	4548	Already at an OK level
Sodium (Na <sup>+</sup> )	NaNO <sub>3</sub>	14.35	- <sup>12</sup>	431	Already at an OK level

Grouped ions and other products that are inside the wastewater from the firework manufacturing.

**Table 3:**

Property	EPA Range
pH	6.0-9.0
Turbidity	Clear

Other characteristics of the wastewater that need to be managed according to EPA regulations before being ready for wildfires.

## Assumptions

**Table 4:**

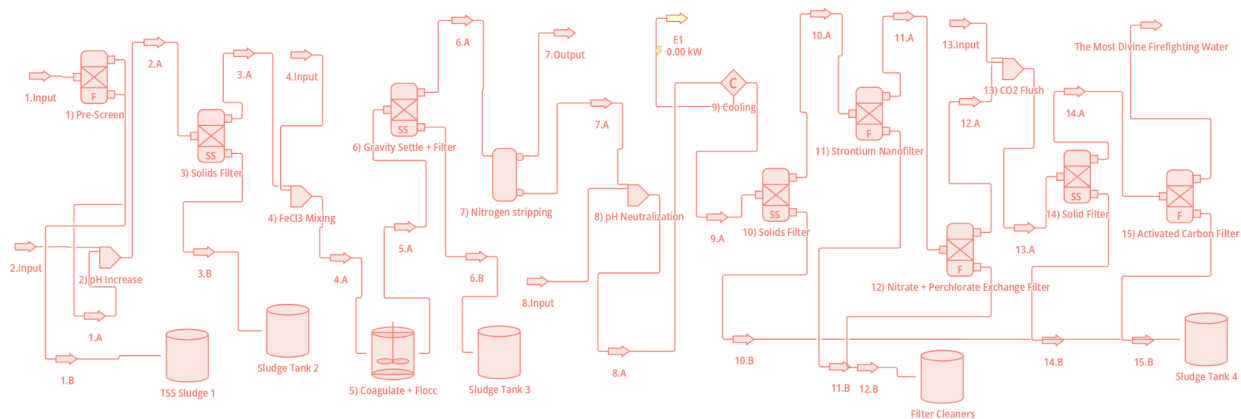
#	Assumption
A.1	Constant volumetric flow (30000L/day) (no recycle streams, no evaporation, 100% drying of solid waste, all streams have same flow rate, and additions of components like H <sub>2</sub> SO <sub>4</sub> do not significantly alter flow rate)
A.2	Instantaneous, well-mixed equilibriums in mixers, and no significant temperature change except for one unit process (detailed below).
A.3	Ideal-solution activity coefficients
A.4	All feed is ionic form if soluble
A.5	A large excess of OH <sup>-</sup> and SO <sub>4</sub> <sup>2-</sup> set by pH control such that the ions are not measurably depleted by any single metal-ion reaction. Therefore, each solubility product can be evaluated independently.
A.6	No side reactions at any step of the process
A.7	Magnesium completely dissolves into Mg <sup>2+</sup> , and the H <sub>2</sub> is just released into the air before entering the treatment facility
A.8	With instructor permission, assuming that all processes produced minimal energy except for the pH neutralization with H <sub>2</sub> SO <sub>4</sub>

Key **overall** assumptions for the wastewater treatment process: individual assumptions may be made and discussed in sections pertaining to individual unit processes.



## Process

### Overall



**Figure 2:** Schematic of the entire wastewater treatment process from start to finish, each of the streams are described below (Table 5) (Enlarged photo on last page of report).

It should be noted that any “B” stream, i.e. 2.B, represents solid byproducts that are 100% dried (A.1) and hand-removed (no power usage) to a storage tank around the clock by well-paid employees. Streams labeled “Input” include something being added to the system.

**Table 5:**

Stream	Components (mg/L)				Destination + pH + temp when not 25C
1.Input	TSS 168.8	COD 132.9	$\text{ClO}_4^-$ 305.56	$\text{NO}_3^-$ 175.21	1) Pre-screen
	$\text{S}_3\text{Sb}_2$ 5.3	$\text{Sr}^{2+}$ 25.5	$\text{Cu}^{2+}$ 23.9	$\text{CO}_3^{2-}$ 22.6	
	$\text{Ba}^{2+}$ 9.79	$\text{Mg}^{2+}$ 51.67	Al 51.67	S 71	pH 7
	IPA 1.667	$\text{NH}_4^+$ 15.1	$\text{K}^+$ 151.6	$\text{Na}^+$ 14.35	
1.A	TSS 151.92	COD 132.9	$\text{ClO}_4^-$ 305.56	$\text{NO}_3^-$ 175.21	2) pH Increase
	$\text{S}_3\text{Sb}_2$ 5.3	$\text{Sr}^{2+}$ 25.5	$\text{Cu}^{2+}$ 23.9	$\text{CO}_3^{2-}$ 22.6	
	$\text{Ba}^{2+}$ 9.79	$\text{Mg}^{2+}$ 51.67	Al 51.67	S 71	pH 7
	IPA 1.667	$\text{NH}_4^+$ 15.1	$\text{K}^+$ 151.6	$\text{Na}^+$ 14.35	
1.B	TSS (Cellulose) 16.88				TSS Sludge 1

2.Input	Ca <sup>2+</sup> 258.07		OH <sup>-</sup> 218.9		2) pH Increase
2.A	TSS 151.92	COD 132.9	ClO <sub>4</sub> <sup>-</sup> 305.56	NO <sub>3</sub> <sup>-</sup> 175.21	3) Solids Filter
	S <sub>3</sub> Sb <sub>2</sub> 5.3	Sr <sup>2+</sup> 25.5	Cu <sup>2+</sup> 2*10 <sup>-11</sup>	CO <sub>3</sub> <sup>2-</sup> 0.028	
	Ba <sup>2+</sup> 9.79	Mg <sup>2+</sup> 0.002	Al 51.67	S 71	
	IPA 1.667	NH <sub>3</sub> 14.435	K <sup>+</sup> 151.6	Na <sup>+</sup> 14.35	pH 12+
	Cu(OH) <sub>2</sub> 36.7	Mg(OH) <sub>2</sub> 124	Ca(CO <sub>3</sub> ) 36.9	OH <sup>-</sup> 134	
	Ca <sup>2+</sup> 243				
3.A	TSS 151.92	COD 132.9	ClO <sub>4</sub> <sup>-</sup> 305.56	NO <sub>3</sub> <sup>-</sup> 175.21	4) FeCl <sub>3</sub> Mixing
	S <sub>3</sub> Sb <sub>2</sub> 5.3	Sr <sup>2+</sup> 25.5	Cu <sup>2+</sup> 2*10 <sup>-11</sup>	CO <sub>3</sub> <sup>2-</sup> 0.028	
	Ba <sup>2+</sup> 9.79	Mg <sup>2+</sup> 0.002	Al 51.67	S 71	
	IPA 1.667	NH <sub>3</sub> 14.435	K <sup>+</sup> 151.6	Na <sup>+</sup> 14.35	pH 12
	Ca <sup>2+</sup> 243	OH <sup>-</sup> 134			
3.B	Cu(OH) <sub>2</sub> 34.9		Mg(OH) <sub>2</sub> 118	CaCO <sub>3</sub> 36.9	Sludge Tank 2
4.Input	FeCl <sub>3</sub> (Coagulant) 60		NaOH 39.997		4) FeCl3 Mixing
4.A	TSS 151.92	COD 132.9	ClO <sub>4</sub> <sup>-</sup> 305.56	NO <sub>3</sub> <sup>-</sup> 175.21	5) Coagulate + Flocc
	S <sub>3</sub> Sb <sub>2</sub> 5.3	Sr <sup>2+</sup> 25.5	Cu <sup>2+</sup> 2*10 <sup>-11</sup>	CO <sub>3</sub> <sup>2-</sup> 0.028	
	Ba <sup>2+</sup> 9.79	Mg <sup>2+</sup> 0.002	Al 51.67	S 71	
	IPA 1.667	NH <sub>3</sub> 14.435	K <sup>+</sup> 151.6	Na <sup>+</sup> 37.25	pH 12
	Ca <sup>2+</sup> 243	OH <sup>-</sup> 151	FeCl <sub>3</sub> 60	Mg(OH) <sub>2</sub> 6	
	Cu(OH) <sub>2</sub> 1.8				
5.A	TSS 151.92	COD 132.9	ClO <sub>4</sub> <sup>-</sup> 305.56	NO <sub>3</sub> <sup>-</sup> 175.21	6) Gravity Filter (Assume flocc+microfilter was 100%)
	S <sub>3</sub> Sb <sub>2</sub> 5.3	Sr <sup>2+</sup> 25.5	Cu <sup>2+</sup> 2*10 <sup>-11</sup>	CO <sub>3</sub> <sup>2-</sup> 0.028	
	Ba <sup>2+</sup> 9.79	Mg <sup>2+</sup> 0.002	Al 51.67	S 71	
	IPA 1.667	NH <sub>3</sub> 14.435	K <sup>+</sup> 151.6	Na <sup>+</sup> 37.25	pH 12

	Ca <sup>2+</sup> 243	OH <sup>-</sup> 134	Fe(OH) <sub>3</sub> 39.6	Cl <sup>-</sup> 39.4		
	Cu(OH) <sub>2</sub> 1.8	Mg(OH) <sub>2</sub> 6				
6.A	COD 132.9	ClO <sub>4</sub> <sup>-</sup> 305.56	NO <sub>3</sub> <sup>-</sup> 175.21	Sr <sup>2+</sup> 25.5	7) Nitrogen Stripping	
	Cu <sup>2+</sup> 2*10 <sup>-11</sup>	CO <sub>3</sub> <sup>2-</sup> 0.028	Ba <sup>2+</sup> 9.79	Mg <sup>2+</sup> 0.002		
	IPA 1.667	NH <sub>3</sub> 14.435	K <sup>+</sup> 151.6	Na <sup>+</sup> 37.25	pH 12	
	Ca <sup>2+</sup> 243	OH <sup>-</sup> 134	Cl <sup>-</sup> 39.4			
6.B	TSS 151.92	S <sub>3</sub> Sb <sub>2</sub> 5.3	Fe(OH) <sub>3</sub> 39.6	S 71	Sludge Tank 3	
	Al 51.67	Cu(OH) <sub>2</sub> 1.8	Mg(OH) <sub>2</sub> 6			
7.Output	NH <sub>3</sub> 14.435				Air	
7.A	COD 132.9	ClO <sub>4</sub> <sup>-</sup> 305.56	NO <sub>3</sub> <sup>-</sup> 175.21	Sr <sup>2+</sup> 25.5	8) pH Neutralization	
	Cu <sup>2+</sup> 2*10 <sup>-11</sup>	CO <sub>3</sub> <sup>2-</sup> 0.028	Ba <sup>2+</sup> 9.79	Mg <sup>2+</sup> 0.002		
	IPA 1.667	K <sup>+</sup> 151.6	Na <sup>+</sup> 37.25	Ca <sup>2+</sup> 243	pH 12	
	OH <sup>-</sup> 134	Cl <sup>-</sup> 39.4				
8.Input	H <sub>2</sub> SO <sub>4</sub> 386.3 (6.57L/day of 18M H <sub>2</sub> SO <sub>4</sub> )				8) pH Neutralization	
8.A	COD 132.9	ClO <sub>4</sub> <sup>-</sup> 305.56	NO <sub>3</sub> <sup>-</sup> 175.21	Sr <sup>2+</sup> 16.9	9) Cooling	
	Cu <sup>2+</sup> 2*10 <sup>-11</sup>	CO <sub>3</sub> <sup>2-</sup> 0.028	Ba <sup>2+</sup> 0.0038	Mg <sup>2+</sup> 0.002		
	IPA 1.667	K <sup>+</sup> 151.6	Na <sup>+</sup> 37.25	Ca <sup>2+</sup> 243	pH 7	25.103C
	SO <sub>4</sub> <sup>-2</sup> 361	Cl <sup>-</sup> 39.4	SrSO <sub>4</sub> 18.1	BaSO <sub>4</sub> 16.6		
E.9	13500 kJ/day or 0.450 kJ/L				9) Cooling	
9.A	COD 132.9	ClO <sub>4</sub> <sup>-</sup> 305.56	NO <sub>3</sub> <sup>-</sup> 175.21	Sr <sup>2+</sup> 16.9	10) Solids Filter	
	Cu <sup>2+</sup> 2*10 <sup>-11</sup>	CO <sub>3</sub> <sup>2-</sup> 0.028	Ba <sup>2+</sup> 0.0038	Mg <sup>2+</sup> 0.002		
	IPA 1.667	K <sup>+</sup> 151.6	Na <sup>+</sup> 37.25	Ca <sup>2+</sup> 243	pH 7	
	SO <sub>4</sub> <sup>-2</sup> 361	Cl <sup>-</sup> 39.4	SrSO <sub>4</sub> 18.1	BaSO <sub>4</sub> 16.6		
10.A	COD 132.9	ClO <sub>4</sub> <sup>-</sup> 305.56	NO <sub>3</sub> <sup>-</sup> 175.21	Sr <sup>2+</sup> 16.9	11) Strontium Nanofilter	
	Cu <sup>2+</sup> 2*10 <sup>-11</sup>	CO <sub>3</sub> <sup>2-</sup> 0.028	Ba <sup>2+</sup> 0.0038	Mg <sup>2+</sup> 0.002		

	IPA 1.667	K <sup>+</sup> 151.6	Na <sup>+</sup> 37.25	Ca <sup>2+</sup> 243	pH 7
	SO <sub>4</sub> <sup>-2</sup> 361	Cl <sup>-</sup> 39.4	SrSO <sub>4</sub> 0.9	BaSO <sub>4</sub> 0.8	
10.B	SrSO <sub>4</sub> 17.2	BaSO <sub>4</sub> 15.8	H <sub>2</sub> O 142 *		Sludge Tank 4
11.A	COD 132.9	ClO <sub>4</sub> <sup>-</sup> 305.56	NO <sub>3</sub> <sup>-</sup> 175.21	Sr <sup>2+</sup> 1.69	12) Nitrate + Perchlorate Exchange Filter
	Cu <sup>2+</sup> 2*10 <sup>-11</sup>	CO <sub>3</sub> <sup>2-</sup> 0.028	Ba <sup>2+</sup> 0.0038	Mg <sup>2+</sup> 0.002	
	IPA 1.667	K <sup>+</sup> 151.6	Na <sup>+</sup> 37.25	Ca <sup>2+</sup> 243	pH 7
	SO <sub>4</sub> <sup>-2</sup> 361	Cl <sup>-</sup> 39.4			
11.B	Sr 15.21				Sludge Tank 4
12.A	COD 132.9	SO <sub>4</sub> <sup>-2</sup> 361	Cl <sup>-</sup> 39.4	Sr <sup>2+</sup> 1.69	13) CO <sub>2</sub> Flush
	Cu <sup>2+</sup> 2*10 <sup>-11</sup>	CO <sub>3</sub> <sup>2-</sup> 0.028	Ba <sup>2+</sup> 0.0038	Mg <sup>2+</sup> 0.002	
	IPA 1.667	K <sup>+</sup> 151.6	Na <sup>+</sup> 37.25	Ca <sup>2+</sup> 243	pH 11.76
	OH <sup>-</sup> 103 **				
12.B	ClO <sub>4</sub> <sup>-</sup> 305.56		NO <sub>3</sub> <sup>-</sup> 175.21		Filter Cleaners
13.Input	CO <sub>2</sub> 252 (3.85 m <sup>3</sup> /day)				13) CO <sub>2</sub> Flush
13.A	COD 132.9	SO <sub>4</sub> <sup>-2</sup> 361	Cl <sup>-</sup> 39.4	Sr <sup>2+</sup> 1.69	14) Solid Filter
	Cu <sup>2+</sup> 2*10 <sup>-11</sup>	CO <sub>3</sub> <sup>2-</sup> 0.868	Ba <sup>2+</sup> 0.0038	Mg <sup>2+</sup> 0.002	
	IPA 1.667	K <sup>+</sup> 151.6	Na <sup>+</sup> 37.25	Ca <sup>2+</sup> 186	pH 7
	CaCO <sub>3</sub> 143	HCO <sub>3</sub> <sup>-</sup> 195.3	CO <sub>2</sub> 48.3		
14.A	COD 132.9	SO <sub>4</sub> <sup>-2</sup> 361	Cl <sup>-</sup> 39.4	Sr <sup>2+</sup> 1.69	15) Activated Carbon Filter
	Cu <sup>2+</sup> 2*10 <sup>-11</sup>	CO <sub>3</sub> <sup>2-</sup> 0.868	Ba <sup>2+</sup> 0.0038	Mg <sup>2+</sup> 0.002	
	IPA 1.667	K <sup>+</sup> 151.6	Na <sup>+</sup> 37.25	Ca <sup>2+</sup> 186	pH 7
	CaCO <sub>3</sub> 7.1	HCO <sub>3</sub> <sup>-</sup> 195.3			
14.B	CaCO <sub>3</sub> 135.9		CO <sub>2</sub> 48.3	H <sub>2</sub> O 25.73 **	Sludge Tank 4
15.B	COD 126.25				Filter Cleaners
Final Water	COD 6.65	SO <sub>4</sub> <sup>-2</sup> 361	Cl <sup>-</sup> 39.4	Sr <sup>2+</sup> 1.69	Wildfires

Output	$\text{Cu}^{2+}$ $2 \times 10^{-11}$	$\text{CO}_3^{2-}$ 0.868	$\text{Ba}^{2+}$ 0.0038	$\text{Mg}^{2+}$ 0.002	pH 7.3
	IPA 1.667	$\text{K}^+$ 151.6	$\text{Na}^+$ 37.25	$\text{Ca}^{2+}$ 186	
	$\text{CaCO}_3$ 7.1	$\text{HCO}_3^-$ 195.3			

\*read pH neutralization section

\*\*Read  $\text{CO}_2$  flush section

Stream compositions for the wastewater treatment process (Figure 2).

Above is the schematic of the firework wastewater treatment process using DWSIM modeling software (Figure 2). Key assumptions for this model to work are listed above in Table 4. Included below is a detailed walkthrough of each unit process. For each unit process, the feed will be considered individually as the components that will be included in the process itself, as the others are assumed nonreactive (A.6). Almost all Ksp values come from UMass.<sup>13</sup>

**Table 6:**

Group	Final Amount (mg/L)	Desired (mg/L)	Environmentally Safe?
TSS	0	0.03	Yes
COD	6.65	20	Yes
Perchlorates ( $\text{ClO}_4^{1-}$ )	0	0.056	Yes
Nitrates ( $\text{NO}_3^{1-}$ )	0	10	Yes
Antimony trisulfide ( $\text{Sb}_2\text{S}_3$ )	0	0.006	Yes
Strontium ( $\text{Sr}^{2+}$ )	1.69	4	Yes
Copper ( $\text{Cu}^{2+}$ )	$2 \times 10^{-11}$	1.3	Yes
Carbonate ( $\text{CO}_3^{2-}$ )	0.868	-	Yes
Barium ( $\text{Ba}^{2+}$ )	0.0038	2	Yes
Magnesium	0.002	-	Yes

(Mg <sup>2+</sup> )			
Aluminum (Al)	0	-	Yes
Sulfur (S)	0	-	Yes
Sulfate (SO <sub>4</sub> <sup>2-</sup> )	361	-	Yes (but will smell odd)
Isopropyl alcohol	1.667	-	Yes
Ammonium (NH <sub>4</sub> <sup>+</sup> )	0	0.5	Yes
Potassium (K <sup>+</sup> )	151.6	-	Yes
Sodium (Na <sup>+</sup> )	22.07	-	Yes
Calcium (Ca <sup>2+</sup> )	243	-	Yes (hard)
Calcium Carbonate (CaCO <sub>3</sub> )	7.1	-	Yes
Bicarbonate (HCO <sub>3</sub> <sup>-</sup> )	195.3	-	Yes
pH	7.0	6.0-9.0	Yes
Turbidity	No more remaining solids so clear	Clear	Yes

FINAL OUTPUT COMPOSITION. Table showing the new levels of all contaminants after going through the proposed wastewater treatment process pathways.

#### *Overall Mass Balances (Non-Reactive)*

Adding up the mg/L from all “input” streams, and then then adding up the mg/L of all “output” streams, or streams going to tanks, we get:

**mg/L going into the system: 2242.88**

**mg/L going out of the system: 2234.40**

#### *Overall Atom/Mol Balance*

**Table 7:**

Atom	In (mmol/L)	Out (mmol/L)	% accuracy (1-change/in)
Al	1.915	1.915	100%
Ba	0.0713	0.0693	97%
C	6.186	6.193	99.9%
Ca	6.439	6.438	99.9%
Cl	4.182	4.184	99.9%
Cu	3.761	3.761	100%
Fe	3.699	3.706	99.8%
H	31.36	30.70	97.9%
K	3.877	3.877	100%
Mg	2.126	2.126	100%
N	3.662	3.672	99.7%
Na	1.624	1.620	99.7%
O	69.04	68.80	99.6%
S	6.19	6.19	100%
Sb	0.03120	0.03120	100%
Sr	0.291	0.286	98.2%

Atom balance of the entire process (TSS and COD omitted). Conversion of mg/L of inputs and outputs to mmol/L of individual atoms was done using ChatGPT (I'm almost 23 hours deep at this point, I cannot be bothered).

All moles of atoms have been accounted for, and are within rounding error percentages.

### *Overall Energy Balance*

Thanks to assumption A.8, all processes except for the reactive process of neutralizing the pH with sulfuric acid have been assumed to be non-influential on the temperature.

The heat of reaction of a strong base and strong acid ( $\text{OH}^-$  and  $\text{H}_2\text{SO}_4$ ) is  $-57.1 \text{ kJ/mol}$  of  $\text{H}^+$ . We are reacting approximately 236.3 moles of H every day, so that's around  $13,500 \text{ kJ/day}$  of

energy produced by this reaction. This raised the temperature, with the heat capacity of water being 4.18 J/g C, by about 0.1C. This temperature increase is neutralized by a cooler.

Thus, the 13,500kJ/day of energy created is equally being output into the air, all kJ are accounted for.

## Sizes for Major Treatment Stages

Basing my estimates on the Google AI auto summary when Google searching and will attach sources as it gives me. Essentially, average plants produce about 1 kg/3.8m<sup>3</sup> of water or about 0.3kg/m<sup>3</sup> of water<sup>14</sup>. If we add up the total input minus the final stream output, we get that 1254.35 mg/L of byproduct is filtered off in this process, or 1254.35 kg/m<sup>3</sup>. It is at this point that I realize that assuming the things you filter off in wastewater treatment plants are 100% solid is a **bad assumption**. In a realistic plant in the future, I will assume that all solid is carried off as only 5-10% solid and the rest is water, and simply supplement extra water to keep a constant volumetric flow. But, my number still fits with a 100% dewatered sludge solution. Regardless, with 30 m<sup>3</sup> a day, that means I am producing about 37,620 kg/day of waste. Wastewater treatment plants for a city it says produces about 0.3kg/day per capita.<sup>15</sup> Thus, I will need to match the size of a wastewater treatment plant designed for 125400 people sized cities.

### *Sludge Tanks*

LeHigh County has about 377000 people and made a blog about the size of sludge tanks. Thus, if they have sludge tanks around 1 million gallons, which is about 4000 m<sup>3</sup>, then I will make sludge tanks half that size at 2000 m<sup>3</sup>.

### *Screening/Filtering Stages*

Once again, I am coming to a realization here. 0.2micrometer filters that I built my assumptions on after Googling what the strongest water filters are, AREN'T used. So, while this may invalidate my assumptions about how much solid I'm able to filter out, I found large pond filters for 30 m<sup>3</sup>/hour (once again realizing my low flow rate). Thus, my screens will be 110x40 cm, like these pond filters.<sup>16</sup>

### *Mixers*

With 30 minute retention time, and 30000L/day, the mixers need to be able to hold at least 600 liters, or be 0.6m<sup>3</sup> in size, so we will go with 1m<sup>3</sup> sized mixers.



## Modes of Failure

I'm just going for common modes of failure based on just common sense.

pH Control Failures: This can happen due to bad neutralization or maybe days where I have more of a particular substance than expected. This can be mitigated with pH control at multiple checkpoints throughout the process and fail safes accordingly.

Excessive sludge: This is likely to happen due to the unrealistic setup I'm now starting to realize I have with my system. The filters likely can't always handle the amount of sludge that will be produced, and thus clog the filters. This can be mitigated by simply using more water, but then the assumptions of sludge prevention are likely to be even less valid.

Resin saturation and fouling: I don't completely understand this one but it came up when searching resin modes of failure. Essentially, they decrease efficiency overtime and need to be regenerated using regeneration solutions.

Incomplete flocc + precipitation: The last one I can think of is that I assumed my flocc worked extremely well and was able to basically clean up anything that couldn't be removed in previous stages. In reality, maybe an 85% assumption would be better. The way to prevent this would be to just do more post-flocc processing, and the signs of failure would be high TSS and metal content in the effluent.

## Individual Unit Processes

### 1) Pre-Screen (0.5cm) (Non-Reactive)

A portion of influent is excess paper that was not used in the manufacturing of the shell of the firework. This paper can be **assumed to be entirely >0.5cm in size.**<sup>17</sup> Thus, when filtering off, the cellulose will be completely filtered, which is 16.88 mg/L of the entire TSS. Due to assumption A.1, the flow rate does not change at this step. The influent and effluent compositions in mass is shown below, and the total mass balance is below that (Table 8).

Table 8:

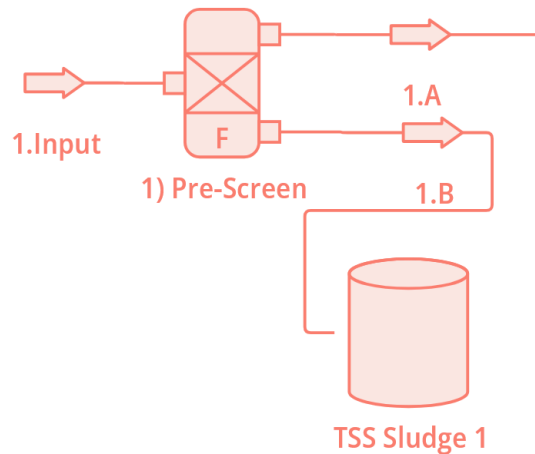
Input or Output	Components (mg/L)				
Input	TSS 168.8	COD 132.9	ClO <sub>4</sub> <sup>-</sup> 305.56	NO <sub>3</sub> <sup>-</sup> 175.21	
	S <sub>3</sub> Sb <sub>2</sub> 5.3	Sr <sup>2+</sup> 25.5	Cu <sup>2+</sup> 23.9	CO <sub>3</sub> <sup>2-</sup> 22.6	
	Ba <sup>2+</sup> 9.79	Mg <sup>2+</sup> 51.67	Al 51.67	S 71	
	IPA 1.667	NH <sub>4</sub> <sup>+</sup> 15.1	K <sup>+</sup> 151.6	Na <sup>+</sup> 14.35	

<b>Output</b>	TSS 151.92	COD 132.9	$\text{ClO}_4^-$ 305.56	$\text{NO}_3^-$ 175.21	
	$\text{S}_3\text{Sb}_2$ 5.3	$\text{Sr}^{2+}$ 25.5	$\text{Cu}^{2+}$ 23.9	$\text{CO}_3^{2-}$ 22.6	
	$\text{Ba}^{2+}$ 9.79	$\text{Mg}^{2+}$ 51.67	Al 51.67	S 71	
	IPA 1.667	$\text{NH}_4^+$ 15.1	$\text{K}^+$ 151.6	$\text{Na}^+$ 14.35	
<b>Output</b>	TSS (Cellulose) 16.88				

Mass in and mass out of compounds for this stage.

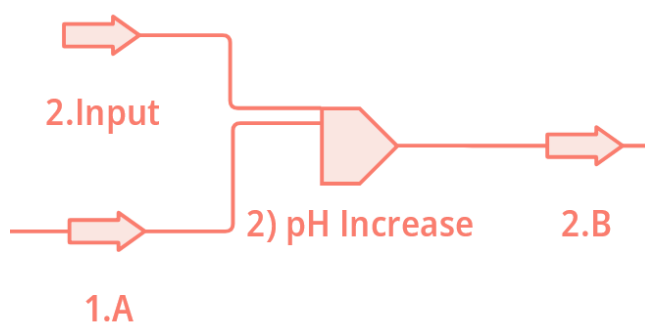
**Total mass in:** 1226.52 mg/L

**Total mass out:** 1226.52 mg/L



## 2) pH Increase (Reactive) (Atom Balance)

The thinking here was to increase the pH by also adding something to help crash the carbonate out of solution, which was  $\text{Ca}(\text{OH})_2$ . I did all of the math based on adding the right amount of moles for the significant crash to happen based on the ksp of  $\text{Ca}(\text{OH})_2$  and  $\text{CaCO}_3$ . Below is an atom balance (Table 9). The reason for the discrepancy in hydrogens is likely due to the fact that the addition of the  $(\text{OH}^-)$  in the  $\text{Ca}(\text{OH})_2$  produced some amount of water which has not been accounted for like it was in previous steps where more water was produced.



**Table 9:**

Atom	In (mmol/L)	Out (mmol/L)	% accuracy (1-change/in)
Al	1.915	1.915	100%
Ba	0.0719	0.0719	100%
C	4.598	4.524	98.4%
Ca	6.439	6.432	99.9%
Cl	4.182	4.184	100%
Cu	3.761	3.761	100%
H	16.4	15.6	95.2%
K	3.877	3.877	100%
Mg	2.126	2.126	100%
N	3.662	3.673	99.8%
Na	1.624	1.620	99.7%
O	34.79	34.786	99.97%
S	6.19	6.19	100%
Sb	0.03120	0.03120	100%
Sr	0.291	0.2910	100%

Atom balance of the pH increase step. NOT created using ChatGPT this time (I did this one first).

**Table 10:**

Input or Output	Components (mg/L)				
<b>Input</b>	TSS 151.92	COD 132.9	$\text{ClO}_4^-$ 305.56	$\text{NO}_3^-$ 175.21	$\text{Ca}^{2+}$ 258.07
	$\text{S}_3\text{Sb}_2$ 5.3	$\text{Sr}^{2+}$ 25.5	$\text{Cu}^{2+}$ 23.9	$\text{CO}_3^{2-}$ 22.6	$\text{OH}^-$ 218.9
	$\text{Ba}^{2+}$ 9.79	$\text{Mg}^{2+}$ 51.67	Al 51.67	S 71	
	IPA 1.667	$\text{NH}_4^+$ 15.1	$\text{K}^+$ 151.6	$\text{Na}^+$ 14.35	
<b>Output</b>	TSS 151.92	COD 132.9	$\text{ClO}_4^-$ 305.56	$\text{NO}_3^-$ 175.21	$\text{Cu}(\text{OH})_2$ 36.7
	$\text{S}_3\text{Sb}_2$ 5.3	$\text{Sr}^{2+}$ 25.5	$\text{Cu}^{2+}$ $2 \times 10^{-11}$	$\text{CO}_3^{2-}$ 0.028	$\text{Mg}(\text{OH})_2$ 124
	$\text{Ba}^{2+}$ 9.79	$\text{Mg}^{2+}$ 0.002	Al 51.67	S 71	$\text{Ca}(\text{CO}_3)$ 36.9
	IPA 1.667	$\text{NH}_3$ 14.435	$\text{K}^+$ 151.6	$\text{Na}^+$ 14.35	$\text{OH}^-$ 134
					$\text{Ca}^{2+}$ 243

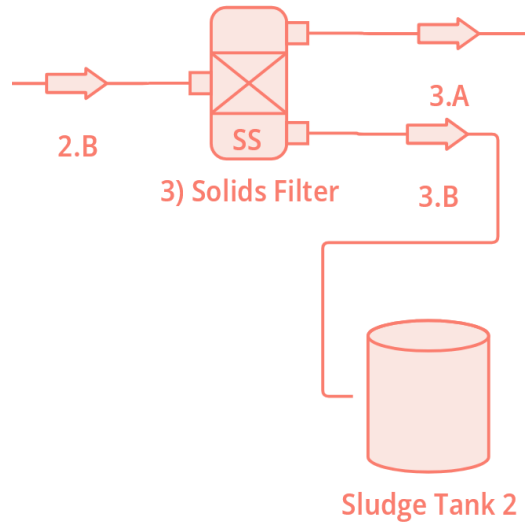
Mass in and mass out of compounds for this stage.

**Total mass in:** 1686.17 mg/L

**Total mass out:** 1685.53 mg/L

### 3) Solids Microfilter (Non-reactive)

For this stage, I am not assuming that 100% of the solids are filtered off. However, I will assume that 100% of the  $\text{CaCO}_3$  is filtered off. I will use a 1 micrometer filter, which will definitely get rid of a solid portion of things like the  $\text{Mg}(\text{OH})_2$  and  $\text{Cu}(\text{OH})_2$  which are both quite large. I assumed 95% would be filtered off, and all of the water– as per assumptions– is expertly removed by our dewaterers.



**Table 11:**

Input or Output	Components (mg/L)				
Input	TSS 151.92	COD 132.9	$\text{ClO}_4^-$ 305.56	$\text{NO}_3^-$ 175.21	$\text{Cu}(\text{OH})_2$ 36.7
	$\text{S}_3\text{Sb}_2$ 5.3	$\text{Sr}^{2+}$ 25.5	$\text{Cu}^{2+}$ $2 \times 10^{-11}$	$\text{CO}_3^{2-}$ 0.028	$\text{Mg}(\text{OH})_2$ 124
	$\text{Ba}^{2+}$ 9.79	$\text{Mg}^{2+}$ 0.002	Al 51.67	S 71	$\text{Ca}(\text{CO}_3)$ 36.9
	IPA 1.667	$\text{NH}_3$ 14.435	$\text{K}^+$ 151.6	$\text{Na}^+$ 14.35	$\text{OH}^-$ 134
					$\text{Ca}^{2+}$ 243
Output	TSS 151.92	COD 132.9	$\text{ClO}_4^-$ 305.56	$\text{NO}_3^-$ 175.21	$\text{Cu}(\text{OH})_2$ 34.9
	$\text{S}_3\text{Sb}_2$ 5.3	$\text{Sr}^{2+}$ 25.5	$\text{Cu}^{2+}$ $2 \times 10^{-11}$	$\text{CO}_3^{2-}$ 0.028	$\text{Mg}(\text{OH})_2$ 118
	$\text{Ba}^{2+}$ 9.79	$\text{Mg}^{2+}$ 0.002	Al 51.67	S 71	$\text{CaCO}_3$ 36.9
	IPA 1.667	$\text{NH}_3$ 14.435	$\text{K}^+$ 151.6	$\text{Na}^+$ 14.35	
	$\text{Ca}^{2+}$ 243	$\text{OH}^-$ 134			

Mass in and mass out of compounds for this stage. ChatGPT is used to sum up the inputs and outputs in the table from this point onwards (have done it once by hand for both a reactive and non-reactive process, this is just 2025's Microsoft Excel).

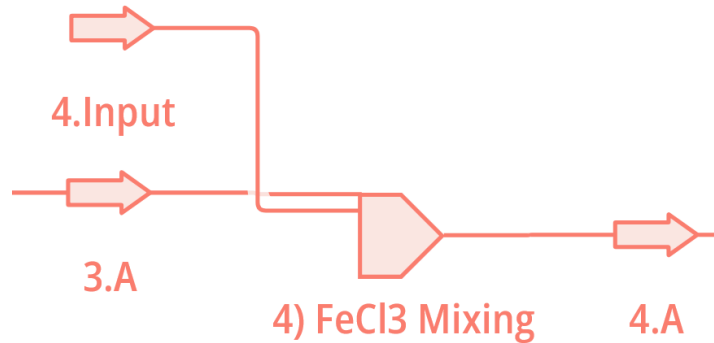
**Total mass in:** 1685.53 mg/L

**Total mass out:** 1677.73 mg/L

#### 4) $\text{FeCl}_3$ Mixing (Reactive)

I chose  $\text{FeCl}_3$  as a coagulant because it was reported to have both high performance with TSS<sup>18</sup> and also because it works well in high pH which we want so I can crash out more of the metals.<sup>19</sup> The amount I used was based on literature.<sup>20</sup>

I assumed the coagulant was so good, in fact, that this is the one stage where we have achieved 100% filtration thanks to the help of gravity settling.



**Table 12:**

Input or Output	Components (mg/L)				
<b>Input</b>	TSS 151.92	COD 132.9	$\text{ClO}_4^-$ 305.56	$\text{NO}_3^-$ 175.21	$\text{FeCl}_3$ (Coagulant) 60
	$\text{S}_3\text{Sb}_2$ 5.3	$\text{Sr}^{2+}$ 25.5	$\text{Cu}^{2+}$ $2 \times 10^{-11}$	$\text{CO}_3^{2-}$ 0.028	NaOH 39.997
	$\text{Ba}^{2+}$ 9.79	$\text{Mg}^{2+}$ 0.002	Al 51.67	S 71	
	IPA 1.667	$\text{NH}_3$ 14.435	$\text{K}^+$ 151.6	$\text{Na}^+$ 14.35	
	$\text{Ca}^{2+}$ 243	$\text{OH}^-$ 134			
<b>Output</b>	TSS 151.92	COD 132.9	$\text{ClO}_4^-$ 305.56	$\text{NO}_3^-$ 175.21	
	$\text{S}_3\text{Sb}_2$ 5.3	$\text{Sr}^{2+}$ 25.5	$\text{Cu}^{2+}$ $2 \times 10^{-11}$	$\text{CO}_3^{2-}$ 0.028	
	$\text{Ba}^{2+}$ 9.79	$\text{Mg}^{2+}$ 0.002	Al 51.67	S 71	$\text{Cu}(\text{OH})_2$ 1.8
	IPA 1.667	$\text{NH}_3$ 14.435	$\text{K}^+$ 151.6	$\text{Na}^+$ 37.25	
	$\text{Ca}^{2+}$ 243	$\text{OH}^-$ 151	$\text{FeCl}_3$ 60	$\text{Mg}(\text{OH})_2$ 6	

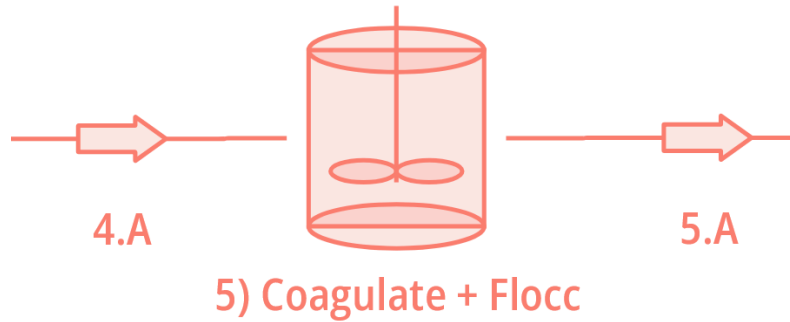
Mass in and mass out of compounds for this stage.

**Total mass in:** 1587.9

**Total mass out:** 1595.6

### 5) Coagulate + Flocc (Non-reactive (??))

This is just a batch stirrer to make sure that the coagulant gets mixed well with all of the contaminants in our flow.



**Table 13:**

Input or Output	Components (mg/L)				
<b>Input</b>	TSS 151.92	COD 132.9	$\text{ClO}_4^-$ 305.56	$\text{NO}_3^-$ 175.21	
	$\text{S}_3\text{Sb}_2$ 5.3	$\text{Sr}^{2+}$ 25.5	$\text{Cu}^{2+}$ $2 \cdot 10^{-11}$	$\text{CO}_3^{2-}$ 0.028	
	$\text{Ba}^{2+}$ 9.79	$\text{Mg}^{2+}$ 0.002	Al 51.67	S 71	$\text{Cu}(\text{OH})_2$ 1.8
	IPA 1.667	$\text{NH}_3$ 14.435	$\text{K}^+$ 151.6	$\text{Na}^+$ 37.25	
	$\text{Ca}^{2+}$ 243	$\text{OH}^-$ 151	$\text{FeCl}_3$ 60	$\text{Mg}(\text{OH})_2$ 6	
<b>Output</b>	TSS 151.92	COD 132.9	$\text{ClO}_4^-$ 305.56	$\text{NO}_3^-$ 175.21	
	$\text{S}_3\text{Sb}_2$ 5.3	$\text{Sr}^{2+}$ 25.5	$\text{Cu}^{2+}$ $2 \cdot 10^{-11}$	$\text{CO}_3^{2-}$ 0.028	
	$\text{Ba}^{2+}$ 9.79	$\text{Mg}^{2+}$ 0.002	Al 51.67	S 71	
	IPA 1.667	$\text{NH}_3$ 14.435	$\text{K}^+$ 151.6	$\text{Na}^+$ 37.25	
	$\text{Ca}^{2+}$ 243	$\text{OH}^-$ 134	$\text{Fe}(\text{OH})_3$ 39.6	$\text{Cl}^-$ 39.4	
	$\text{Cu}(\text{OH})_2$ 1.8	$\text{Mg}(\text{OH})_2$ 6			

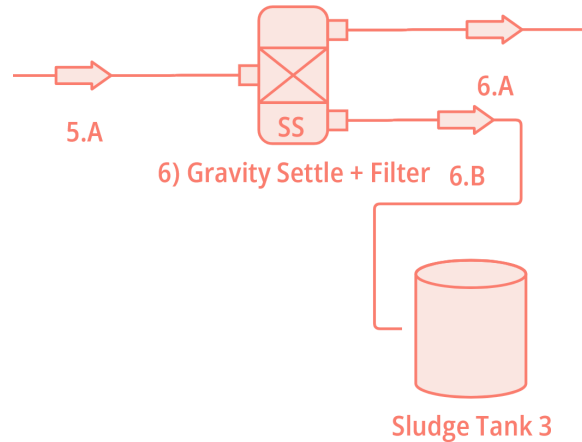
Mass in and mass out of compounds for this stage.

**Total mass in:** 1595.63 mg/L

**Total mass out:** 1597.63 mg/L

### 6) Gravity Filter (Non-reactive)

As mentioned above in the addition of the  $\text{FeCl}_3$  section, this is where we once again use a very small filter, around 1 micrometer, and let all of the big specks of coagulant and contaminant settle down to the bottom before decanting.



**Table 14:**

Input or Output	Components (mg/L)				
<b>Input</b>	TSS 151.92	COD 132.9	$\text{ClO}_4^-$ 305.56	$\text{NO}_3^-$ 175.21	
	$\text{S}_3\text{Sb}_2$ 5.3	$\text{Sr}^{2+}$ 25.5	$\text{Cu}^{2+}$ $2 \times 10^{-11}$	$\text{CO}_3^{2-}$ 0.028	
	$\text{Ba}^{2+}$ 9.79	$\text{Mg}^{2+}$ 0.002	Al 51.67	S 71	
	IPA 1.667	$\text{NH}_3$ 14.435	$\text{K}^+$ 151.6	$\text{Na}^+$ 37.25	
	$\text{Ca}^{2+}$ 243	$\text{OH}^-$ 134	$\text{Fe}(\text{OH})_3$ 39.6	$\text{Cl}^-$ 39.4	
	$\text{Cu}(\text{OH})_2$ 1.8	$\text{Mg}(\text{OH})_2$ 6			
<b>Output</b>	COD 132.9	$\text{ClO}_4^-$ 305.56	$\text{NO}_3^-$ 175.21	$\text{Sr}^{2+}$ 25.5	Al 51.67
	$\text{Cu}^{2+}$ $2 \times 10^{-11}$	$\text{CO}_3^{2-}$ 0.028	$\text{Ba}^{2+}$ 9.79	$\text{Mg}^{2+}$ 0.002	$\text{Cu}(\text{OH})_2$ 1.8
	IPA 1.667	$\text{NH}_3$ 14.435	$\text{K}^+$ 151.6	$\text{Na}^+$ 37.25	$\text{Mg}(\text{OH})_2$ 6
	TSS 151.92	$\text{S}_3\text{Sb}_2$ 5.3	$\text{Fe}(\text{OH})_3$ 39.6	S 71	
	$\text{Ca}^{2+}$ 243	$\text{OH}^-$ 134	$\text{Cl}^-$ 39.4		

Mass in and mass out of compounds for this stage.

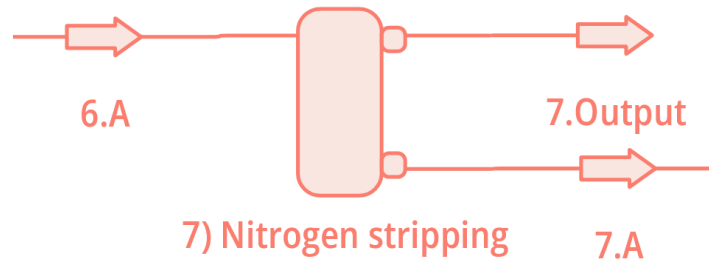
**Total mass in:** 1597.63 mg/L

**Total mass out:** 1597.63 mg/L



### 7) Nitrogen Stripping (Non-reactive for the purposes of this paper)

So due to the high pH of our solution right now, I have assumed that all of the ammonium has crashed out of its aqueous form and is appearing as pure ammonia gas. This ammonia gas, using a flow of air from the outside world, is just carried out of solution with 100% completion.<sup>21</sup> I am also assuming that 100% of the air that is injected is released back into the atmosphere. This takes place in a rather large, 1m<sup>3</sup> stripping tower.



**Table 15:**

Input or Output	Components (mg/L)				
<b>Input</b>	COD 132.9	ClO <sub>4</sub> <sup>-</sup> 305.56	NO <sub>3</sub> <sup>-</sup> 175.21	Sr <sup>2+</sup> 25.5	
	Cu <sup>2+</sup> 2*10 <sup>-11</sup>	CO <sub>3</sub> <sup>2-</sup> 0.028	Ba <sup>2+</sup> 9.79	Mg <sup>2+</sup> 0.002	
	IPA 1.667	NH <sub>3</sub> 14.435	K <sup>+</sup> 151.6	Na <sup>+</sup> 37.25	
	Ca <sup>2+</sup> 243	OH <sup>-</sup> 134	Cl <sup>-</sup> 39.4		
<b>Output</b>	COD 132.9	ClO <sub>4</sub> <sup>-</sup> 305.56	NO <sub>3</sub> <sup>-</sup> 175.21	Sr <sup>2+</sup> 25.5	
	Cu <sup>2+</sup> 2*10 <sup>-11</sup>	CO <sub>3</sub> <sup>2-</sup> 0.028	Ba <sup>2+</sup> 9.79	Mg <sup>2+</sup> 0.002	
	IPA 1.667	K <sup>+</sup> 151.6	Na <sup>+</sup> 37.25	Ca <sup>2+</sup> 243	
	OH <sup>-</sup> 134	Cl <sup>-</sup> 39.4			NH <sub>3</sub> 14.435

Mass in and mass out of compounds for this stage.

**Total mass in:** 1270.34 mg/L

**Total mass out:** 1270.34 mg/L

### 8) pH Neutralization (Reactive + ENERGY BALANCE)

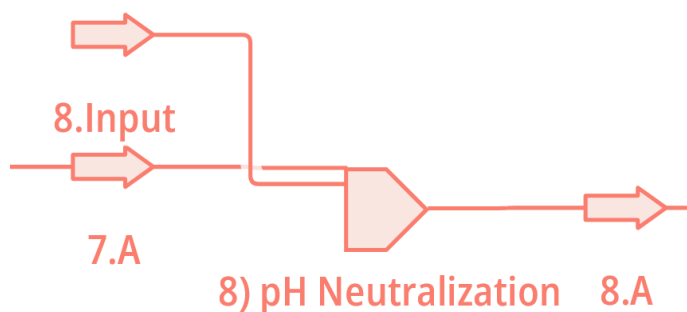
Rationale at this step was to put in an equal amount of H<sub>2</sub>SO<sub>4</sub> to bring the OH concentration down to a neutral level. I chose this as the place to do an energy balance as the reaction between a strong acid and strong base is very exothermic. I will paste the math I did

below. In addition, the introduction of sulfate allows me to crash the copper and a lot of the strontium out of solution. I tried to model this on DWSIM but it didn't work at all, so I just modeled something as equivalent as possible using just  $Mg^{2+}$  to represent both species.

The heat of reaction of a strong base and strong acid ( $OH^-$  and  $H_2SO_4$ ) is  $-57.1$  kJ/mol of  $H^+$ . We are reacting approximately 236.3 moles of  $H$  every day, so that's around 13,500kJ/day of energy produced by this reaction. This raised the temperature, with the heat capacity of water being  $4.18$  J/g C, by about  $0.1$  C.

The actual stream itself has a net zero change in energy due to the process below.

\*\*Water is created in this stage and output as being "filtered" off in a later stage, but not carried through the processes.



**Table 16:**

Input or Output	Components (mg/L)				
<b>Input</b>	COD 132.9	$ClO_4^-$ 305.56	$NO_3^-$ 175.21	$Sr^{2+}$ 25.5	
	$Cu^{2+}$ $2 \times 10^{-11}$	$CO_3^{2-}$ 0.028	$Ba^{2+}$ 9.79	$Mg^{2+}$ 0.002	
	IPA 1.667	$K^+$ 151.6	$Na^+$ 37.25	$Ca^{2+}$ 243	
	$OH^-$ 134	$Cl^-$ 39.4			$H_2SO_4$ 386.3
<b>Output</b>	COD 132.9	$ClO_4^-$ 305.56	$NO_3^-$ 175.21	$Sr^{2+}$ 16.9	
	$Cu^{2+}$ $2 \times 10^{-11}$	$CO_3^{2-}$ 0.028	$Ba^{2+}$ 0.0038	$Mg^{2+}$ 0.002	$H_2O$ 142 **
	IPA 1.667	$K^+$ 151.6	$Na^+$ 37.25	$Ca^{2+}$ 243	
	$SO_4^{2-}$ 361	$Cl^-$ 39.4	$SrSO_4$ 18.1	$BaSO_4$ 16.6	

Mass in and mass out of compounds for this stage.

**Total mass in:** 1642.21

**Total mass out:** 1642.21

9) Cooling (Non-reactive + ENERGY BALANCE)

13,500kJ/day of energy are removed from the stream so as to keep the temperature at 25C and all of the calculations done are valid. E1 = 13,500 kJ/day

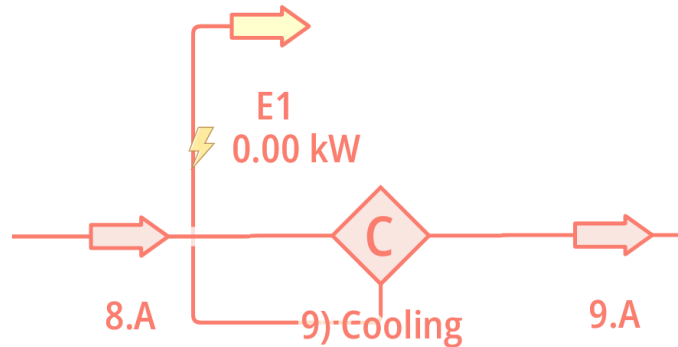


Table 17:

Input or Output	Components (mg/L)				
Input	COD 132.9	ClO <sub>4</sub> <sup>-</sup> 305.56	NO <sub>3</sub> <sup>-</sup> 175.21	Sr <sup>2+</sup> 16.9	
	Cu <sup>2+</sup> 2*10 <sup>-11</sup>	CO <sub>3</sub> <sup>2-</sup> 0.028	Ba <sup>2+</sup> 0.0038	Mg <sup>2+</sup> 0.002	
	IPA 1.667	K <sup>+</sup> 151.6	Na <sup>+</sup> 37.25	Ca <sup>2+</sup> 243	
	SO <sub>4</sub> <sup>-2</sup> 361	Cl <sup>-</sup> 39.4	SrSO <sub>4</sub> 18.1	BaSO <sub>4</sub> 16.6	
Output	COD 132.9	ClO <sub>4</sub> <sup>-</sup> 305.56	NO <sub>3</sub> <sup>-</sup> 175.21	Sr <sup>2+</sup> 16.9	
	Cu <sup>2+</sup> 2*10 <sup>-11</sup>	CO <sub>3</sub> <sup>2-</sup> 0.028	Ba <sup>2+</sup> 0.0038	Mg <sup>2+</sup> 0.002	
	IPA 1.667	K <sup>+</sup> 151.6	Na <sup>+</sup> 37.25	Ca <sup>2+</sup> 243	
	SO <sub>4</sub> <sup>-2</sup> 361	Cl <sup>-</sup> 39.4	SrSO <sub>4</sub> 18.1	BaSO <sub>4</sub> 16.6	

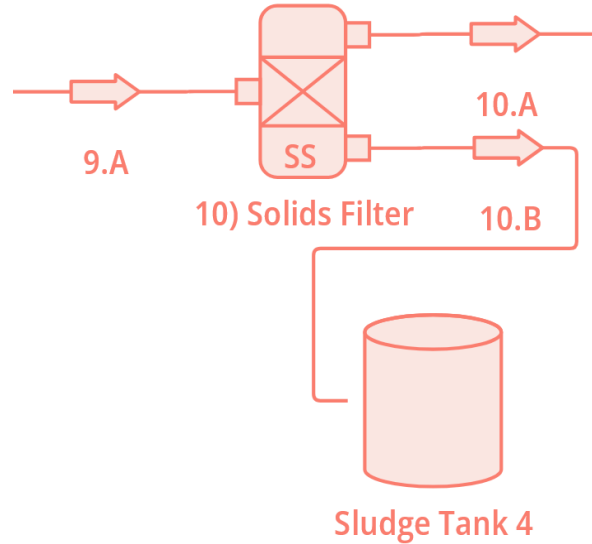
Mass in and mass out of compounds for this stage.

**Total mass in:** 1499.22 mg/L

**Total mass out:** 1499.22 mg/L

### 10) Solids Microfilter (Non-reactive)

As above, this is just another 1 micrometer filter where I am assuming that 95% of the solids are removed from the solution. The solids will then be dewatered (with the water returning to the flow) and taken to a sludge tank.



**Table 18:**

Input or Output	Components (mg/L)				
<b>Input</b>	COD 132.9	$\text{ClO}_4^-$ 305.56	$\text{NO}_3^-$ 175.21	$\text{Sr}^{2+}$ 16.9	$\text{H}_2\text{O}$ 142 *
	$\text{Cu}^{2+}$ $2 \times 10^{-11}$	$\text{CO}_3^{2-}$ 0.028	$\text{Ba}^{2+}$ 0.0038	$\text{Mg}^{2+}$ 0.002	
	IPA 1.667	$\text{K}^+$ 151.6	$\text{Na}^+$ 37.25	$\text{Ca}^{2+}$ 243	
	$\text{SO}_4^{2-}$ 361	$\text{Cl}^-$ 39.4	$\text{SrSO}_4$ 18.1	$\text{BaSO}_4$ 16.6	
<b>Output</b>	COD 132.9	$\text{ClO}_4^-$ 305.56	$\text{NO}_3^-$ 175.21	$\text{Sr}^{2+}$ 16.9	
	$\text{Cu}^{2+}$ $2 \times 10^{-11}$	$\text{CO}_3^{2-}$ 0.028	$\text{Ba}^{2+}$ 0.0038	$\text{Mg}^{2+}$ 0.002	
	IPA 1.667	$\text{K}^+$ 151.6	$\text{Na}^+$ 37.25	$\text{Ca}^{2+}$ 243	
	$\text{SO}_4^{2-}$ 361	$\text{Cl}^-$ 39.4	$\text{SrSO}_4$ 0.9	$\text{BaSO}_4$ 0.8	
	$\text{SrSO}_4$ 17.2	$\text{BaSO}_4$ 15.8	$\text{H}_2\text{O}$ 142 *		

\*See pH neutralization

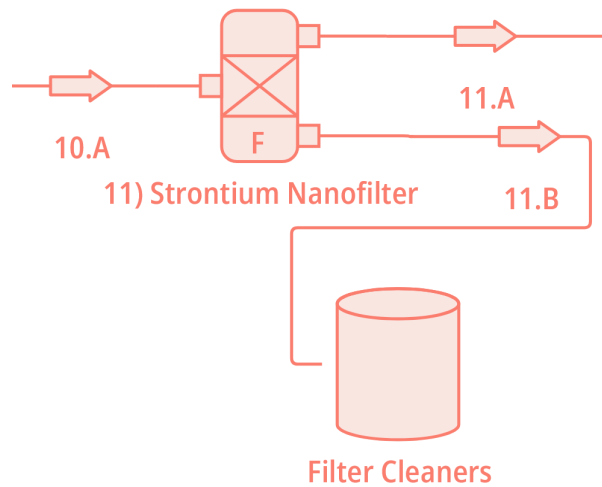
Mass in and mass out of compounds for this stage.

**Total mass in:** 1641.22 mg/L

**Total mass out:** 1639.52 mg/L

### 11) Strontium Nanofilter (Non-reactive)

The strontium-sulfate Ksp wasn't actually as high as I was hoping for so not all of the strontium ions crashed out of solution. According to the literature, there exist nanofilters that can be used to strip strontium ions out of solution, though the cleaning process is quite confusing.<sup>22</sup> Thus, I will pay professionals to clean the strontium from the filters on a regular basis. I assumed the strontium filter removed 90% of the remaining strontium with this.



**Table 19:**

Input or Output	Components (mg/L)				
<b>Input</b>	COD 132.9	ClO <sub>4</sub> <sup>-</sup> 305.56	NO <sub>3</sub> <sup>-</sup> 175.21	Sr <sup>2+</sup> 16.9	
	Cu <sup>2+</sup> 2*10 <sup>-11</sup>	CO <sub>3</sub> <sup>2-</sup> 0.028	Ba <sup>2+</sup> 0.0038	Mg <sup>2+</sup> 0.002	
	IPA 1.667	K <sup>+</sup> 151.6	Na <sup>+</sup> 37.25	Ca <sup>2+</sup> 243	
	SO <sub>4</sub> <sup>-2</sup> 361	Cl <sup>-</sup> 39.4	SrSO <sub>4</sub> 0.9	BaSO <sub>4</sub> 0.8	
<b>Output</b>	COD 132.9	ClO <sub>4</sub> <sup>-</sup> 305.56	NO <sub>3</sub> <sup>-</sup> 175.21	Sr <sup>2+</sup> 1.69	
	Cu <sup>2+</sup> 2*10 <sup>-11</sup>	CO <sub>3</sub> <sup>2-</sup> 0.028	Ba <sup>2+</sup> 0.0038	Mg <sup>2+</sup> 0.002	
	IPA 1.667	K <sup>+</sup> 151.6	Na <sup>+</sup> 37.25	Ca <sup>2+</sup> 243	
	SO <sub>4</sub> <sup>-2</sup> 361	Cl <sup>-</sup> 39.4	Sr 15.21		

Mass in and mass out of compounds for this stage.

**Total mass in:** 1466.22 mg/L

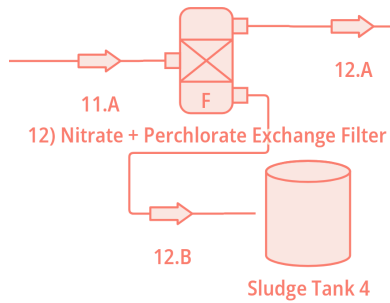
**Total mass out:** 1464.52 mg/L

### 12) Nitrate + Perchlorate Exchange Filter (Reactive)

At this point, in order to start removing some of these anions left in solution, we can use ion exchange resins.<sup>23</sup> These resins essentially swap anions in solution for an equivalent anion depending on the type of resin. It's super interesting but also confusing, so I suggest you read about it. In this case we are using hydroxide ones resins, which will exchange perchlorate and nitrates for hydroxides into solution.<sup>24</sup> We are assuming they work really well and thus will be taking 100% of the nitrate and perchlorates from solution, and replacing them with pure hydroxide.

This is a 1:1 molar process, and will make our solution basic.

In terms of filter maintenance, these also get washed with a regeneration solution which will replace the nitrates and perchlorates with fresh NaOH, we are going to use a 4% NaOH solution.<sup>25</sup>



**Table 20:**

Input or Output	Components (mg/L)				
<b>Input</b>	COD 132.9	ClO <sub>4</sub> <sup>-</sup> 305.56	NO <sub>3</sub> <sup>-</sup> 175.21	Sr <sup>2+</sup> 1.69	
	Cu <sup>2+</sup> 2*10 <sup>-11</sup>	CO <sub>3</sub> <sup>2-</sup> 0.028	Ba <sup>2+</sup> 0.0038	Mg <sup>2+</sup> 0.002	
	IPA 1.667	K <sup>+</sup> 151.6	Na <sup>+</sup> 37.25	Ca <sup>2+</sup> 243	
	SO <sub>4</sub> <sup>-2</sup> 361	Cl <sup>-</sup> 39.4			
<b>Output</b>	COD 132.9	SO <sub>4</sub> <sup>-2</sup> 361	Cl <sup>-</sup> 39.4	Sr <sup>2+</sup> 1.69	
	Cu <sup>2+</sup> 2*10 <sup>-11</sup>	CO <sub>3</sub> <sup>2-</sup> 0.028	Ba <sup>2+</sup> 0.0038	Mg <sup>2+</sup> 0.002	
	IPA 1.667	K <sup>+</sup> 151.6	Na <sup>+</sup> 37.25	Ca <sup>2+</sup> 243	
	OH <sup>-</sup> 103 **	ClO <sub>4</sub> <sup>-</sup> 305.56	NO <sub>3</sub> <sup>-</sup> 175.21		

\*\*See CO2 flush section

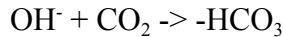
Mass in and mass out of compounds for this stage.

**Total mass in:** 1446.31 mg/L

**Total mass out:** 1552.31 mg/L (1446.31 without OH<sup>-</sup>, see section below)

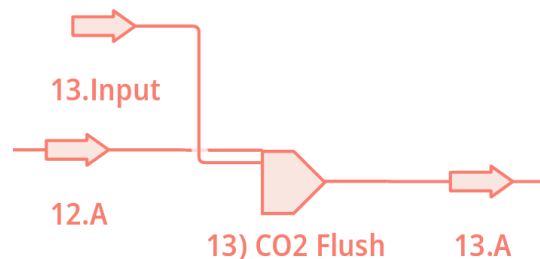
### 13) CO<sub>2</sub> Flush (Reactive)

A carbon dioxide flush is essentially pumping the solution with carbon dioxide air.<sup>26</sup> This is done expertly in my facility, as all of the carbon dioxide stays in solution and the apparatus doesn't blow up with the increasing pressure. The reaction is (to my understanding) as shown below:



There are many other side reactions and possible reactions to occur, like the HCO<sub>3</sub><sup>-</sup> being deprotonated and forming H<sub>2</sub>O. I created a system of equations for this with ksp values at pH 7 (Yes, I know that's not quite how it works), and that's how I got the values for the stream composition above.

In addition, as with other pH neutralization steps, it's difficult to carry the water mass that is created and doesn't fully make sense, but is needed to balance H and O. Thus, it is put into tables where necessary to balance mass. However, the large table at the top (Table 5) accurately records the stages where the excess H<sub>2</sub>O is removed from the main flow.



**Table 21:**

Input or Output	Components (mg/L)				
<b>Input</b>	COD 132.9	SO <sub>4</sub> <sup>-2</sup> 361	Cl <sup>-</sup> 39.4	Sr <sup>2+</sup> 1.69	CO <sub>2</sub> 252
	Cu <sup>2+</sup> 2*10 <sup>-11</sup>	CO <sub>3</sub> <sup>2-</sup> 0.028	Ba <sup>2+</sup> 0.0038	Mg <sup>2+</sup> 0.002	
	IPA 1.667	K <sup>+</sup> 151.6	Na <sup>+</sup> 37.25	Ca <sup>2+</sup> 243	
	OH <sup>-</sup> 103 **				
<b>Output</b>	COD 132.9	SO <sub>4</sub> <sup>-2</sup> 361	Cl <sup>-</sup> 39.4	Sr <sup>2+</sup> 1.69	
	Cu <sup>2+</sup> 2*10 <sup>-11</sup>	CO <sub>3</sub> <sup>2-</sup> 0.868	Ba <sup>2+</sup> 0.0038	Mg <sup>2+</sup> 0.002	
	IPA 1.667	K <sup>+</sup> 151.6	Na <sup>+</sup> 37.25	Ca <sup>2+</sup> 186	
	CaCO <sub>3</sub> 143	HCO <sub>3</sub> <sup>-</sup> 195.3	H <sub>2</sub> O 25.73 **	CO <sub>2</sub> 48.3	

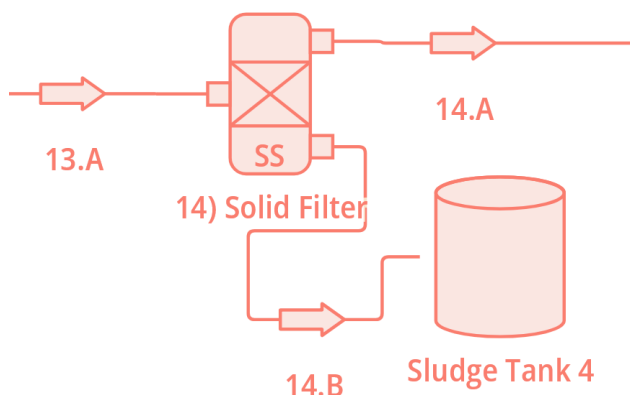
Mass in and mass out of compounds for this stage.

**Total mass in:** 1323.54 mg/L

**Total mass out:** 1324.71 mg/L

*14) Solid Filter (Non-reactive)*

As with previous stages, this is a 1 micrometer filter and we are assuming that it removes 90% of all solids in solution, and the solids are dewatered (all except the water that was produced during CO<sub>2</sub> flushing) and taken to sludge tank 4. It should also be noted that in this stage, the filtering somehow agitates all CO<sub>2</sub> in solution to leave solution.



**Table 22:**

Input or Output	Components (mg/L)				
<b>Input</b>	COD 132.9	SO <sub>4</sub> <sup>-2</sup> 361	Cl <sup>-</sup> 39.4	Sr <sup>2+</sup> 1.69	H <sub>2</sub> O 25.73 **
	Cu <sup>2+</sup> 2*10 <sup>-11</sup>	CO <sub>3</sub> <sup>2-</sup> 0.868	Ba <sup>2+</sup> 0.0038	Mg <sup>2+</sup> 0.002	
	IPA 1.667	K <sup>+</sup> 151.6	Na <sup>+</sup> 37.25	Ca <sup>2+</sup> 186	
	CaCO <sub>3</sub> 143	HCO <sub>3</sub> <sup>-</sup> 195.3	CO <sub>2</sub> 48.3		
<b>Output</b>	COD 132.9	SO <sub>4</sub> <sup>-2</sup> 361	Cl <sup>-</sup> 39.4	Sr <sup>2+</sup> 1.69	H <sub>2</sub> O 25.73 **
	Cu <sup>2+</sup> 2*10 <sup>-11</sup>	CO <sub>3</sub> <sup>2-</sup> 0.868	Ba <sup>2+</sup> 0.0038	Mg <sup>2+</sup> 0.002	CO <sub>2</sub> 48.3
	IPA 1.667	K <sup>+</sup> 151.6	Na <sup>+</sup> 37.25	Ca <sup>2+</sup> 186	CaCO <sub>3</sub> 135.9
	CaCO <sub>3</sub> 7.1	HCO <sub>3</sub> <sup>-</sup> 195.3			

Mass in and mass out of compounds for this stage.

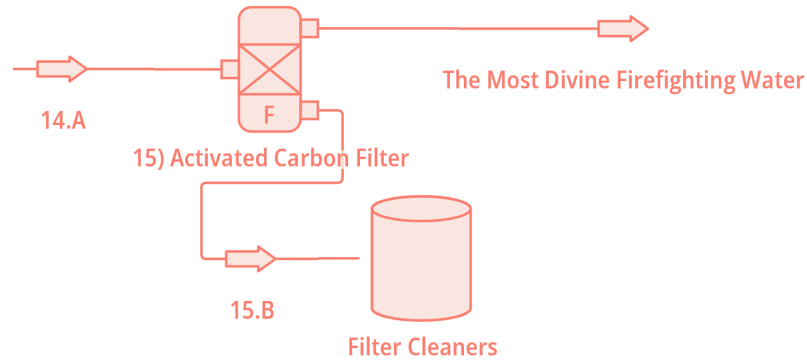
**Total mass in:** 1324.71 mg/L

**Total mass out:** 1324.71 mg/L



### 15) Activated Carbon Filter (Non-reactive (For the sake of this project))

The final stage here. An activated carbon filter is essentially what it sounds like, and I'm assuming it's non-reactive here. They work through a process called absorption, where molecules stick to the structure. They are highly porous and this is what facilitates the absorption of contaminants. Granulated activated carbon (GAC) which is what we plan to use here has been shown to remove up to 90% of COD.<sup>27</sup> That is why I assume 90% removal. Cleaning the GAC filters is quite difficult and complicated, and that's why we once again hire the professionals to come clean our filters and take away any filtered out contaminants.



**Table 23:**

Input or Output	Components (mg/L)				
<b>Input</b>	COD 132.9	SO <sub>4</sub> <sup>-2</sup> 361	Cl <sup>-</sup> 39.4	Sr <sup>2+</sup> 1.69	
	Cu <sup>2+</sup> 2*10 <sup>-11</sup>	CO <sub>3</sub> <sup>2-</sup> 0.868	Ba <sup>2+</sup> 0.0038	Mg <sup>2+</sup> 0.002	
	IPA 1.667	K <sup>+</sup> 151.6	Na <sup>+</sup> 37.25	Ca <sup>2+</sup> 186	
	CaCO <sub>3</sub> 7.1	HCO <sub>3</sub> <sup>-</sup> 195.3			
<b>Output</b>	COD 6.65	SO <sub>4</sub> <sup>-2</sup> 361	Cl <sup>-</sup> 39.4	Sr <sup>2+</sup> 1.69	COD 126.25
	Cu <sup>2+</sup> 2*10 <sup>-11</sup>	CO <sub>3</sub> <sup>2-</sup> 0.868	Ba <sup>2+</sup> 0.0038	Mg <sup>2+</sup> 0.002	
	IPA 1.667	K <sup>+</sup> 151.6	Na <sup>+</sup> 37.25	Ca <sup>2+</sup> 186	
	CaCO <sub>3</sub> 7.1	HCO <sub>3</sub> <sup>-</sup> 195.3			

Mass in and mass out of compounds for this stage.

**Total mass in:** 1114.78 mg/L

**Total mass out:** 1114.78 mg/L

27 hours later... my water is now ready to put out some forest fires.

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