THESIS

PRECIPITATION AND REMOVAL OF IONIC COMPOUNDS FROM PRODUCED WATER: OBSERVED VERSUS MODELED RESULTS

Submitted by

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ABSTRACT

PRECIPITATION AND REMOVAL OF IONIC COMPOUNDS FROM PRODUCED WATER OBSERVED VERSUS MODELED RESULTS

Produced water is generated during the hydraulic fracturing and drilling process, and is regarded as the largest byproduct associated with oil and gas industrial development. Samples of produced water from wells near Greeley, Colorado, were collected from February - July 2013. Commercial produced water treatment at the laboratory scale was conducted and the results compared to computer-based software modeling predictions. Different parameters, such as pH and temperature, are adjusted in order to test how these parameters could affect the treatment for produced water softening. The study shows that removal treatment performance could be related to pH adjustment of coagulation process, temperature and to the size of the filtration membrane.

Comparison between different membrane filtration size (2.5 micron and 0.2 micron) apparently shows finer membrane (0.2 micron) improves the removal treatment performance. The results indicate that precipitation is not the limiter to divalent cation removal. During the research, OLI Chemical Analyst, the computer based modeling program, analyzed the precipitation performance of water samples under different temperature (-15 °C - 25 °C) and pH (9.0 – 10.2) conditions. The OLI Chemical Analyst shows that lower temperature could precipitate out different species. Sodium ions get separated (as $NaAl(OH)_2CO_3$, aluminum di-hydroxide carbonate) from the inflow when temperature is lower than 10°C, while other metal ions, such as calcium ions, barium ions, cannot get removed efficiently. However, the modeling results of pH adjustments demonstrate that lower pH would not obviously affect the scaling tendency of the target salts. The results show magnesium ions can only get removed when pH is higher than 11.0, the pH adjustment for softening can be optimized.

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CHAPTER 1

INTRODUCTION

1.1 Origin of the research

Produced water is generated during the hydraulic fracturing and drilling process, and is regarded as the largest byproduct associated with oil and gas industrial development. [1] The produced water that is pumped out of the ground and comes to the surface along with oil production dissolves large amounts of salts and some oil and gas. For example, produced water can contain high concentrations of total dissolved solids (TDS) and high silica. Waters with total hardness of 1,000-2,300 ppm as $CaCO_3$ and 10,000 -28,000 ppm of TDS were treated with conventional acid softeners. [2]

Currently, the amount of produced water generated along with oil and gas can be 14 -18 billion barrels each year in the U.S.[3] Sixty percent of produced water is recycled and re-injected in the oil and gas field. Reuse of the produced water can benefit those water-stressed countries. [3][4] For the oil and gas industry, produced water reinjection can be a more economic method for managing the waste stream. During the oil and gas development process, hardness in produced water could harm the drilling equipment and also scale the pipeline system for drilling wells. If increasing amounts of produced water are reused for fracturing, high hardness levels scale and block the fractures affecting the production efficiency directly. In order to avoid high damage costs on equipment and well fractures, the softening of produced water becomes a necessary part of the treatment. [5]

The Colorado Oil and Gas Conservation Commission has announced a disposal water quality standard in Colorado and therefore the treatment of produced water becomes necessary and essential.[1] Because of the high salinity and TDS in the produced stream liquid phase, the softening process results in a high cost of chemicals and energy used for treatment. [4][5] Because of the unstable produced water quality, the treatment process needs improvement and optimization. On one hand, higher treatment efficiency and maximum energy and chemical utility efficiency is needed; on the other hand, relative efficiency improvements mean lower costs.

1.2 Structure of the research

One commercially available treatment process uses a composite system that includes electrocoagulation (EC) and chemical coagulation for the treatment of produced water from oil and gas fields in the Denver-Julesburg basin. The purpose of this treatment system is meant to lower the scale of the metal ions and soften the produced water. Also, the benefit could be to reuse and recycle this large quantity of produced water. With the reuse ratio improvement, this treatment could lower the disposal cost and save on fresh water used for hydraulic fracturing.
In the simulated treatment process, the produced water stream comes up from the ground, and the pH of these produced water streams is adjusted to pH 7.0 making it ready for further treatment. The raw water is used as the input for electrocoagulation treatment. After EC, the pH is adjusted to 10.2 with sodium hydroxide and then filtered. Then the pH is then dropped back to 7.0 with hydrochloric acid.

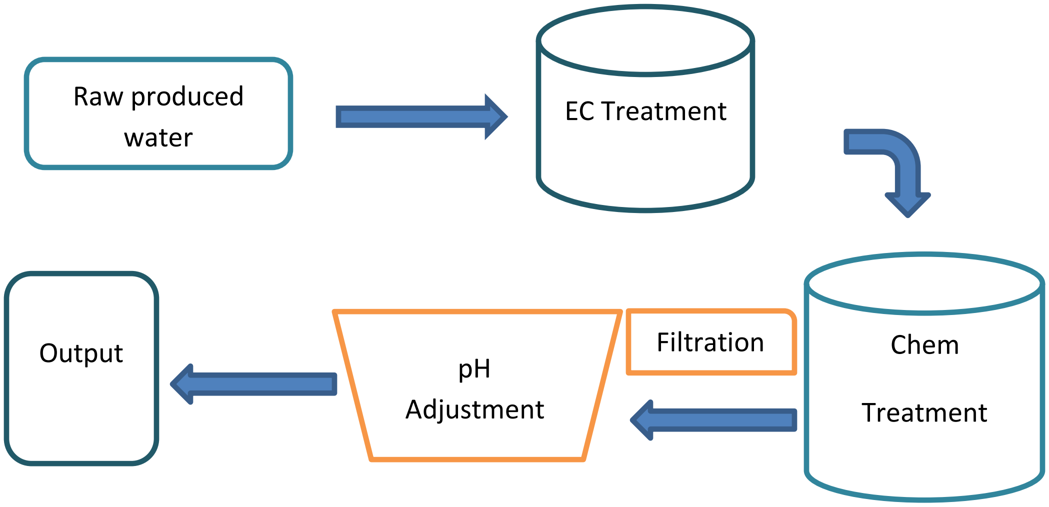


Figure 1.1. Overview of the produced water softening process.

In order to achieve the purpose of optimizing the treatment process, the bench-scale experimental results are compared to OLI Chemical Analyst modeling results. According to the results of simulation and OLI modeling of simulated treatment research, the treatment performance does not adequately reduce the metal ions scale with high cost acid for treatment. Considering the low efficiency of removing the hardness and TDS in the produced water, this research focuses on defining the parameters that could affect the treatment performance and optimizing the treatment process of produced water.

In order to identify the EC and chemical coagulation, EC only and chemical coagulation only treatment processes are used as parallel processes to indicate how the single treatment methods could affect the treatment process. OLI Analyst is used to model the pH adjustment process after EC and Chem flocculation, and in the modeling process, relative inflow will be used as input of the OLI modeling process. The modeling process could demonstrate both the expectation of the removal ratio under ideal conditions and what can be expected from the treatment facility.

The simulated treatment process uses sand bed filtration for removing the solid species and the bench scale testing used a 2.5 micron membrane for the filtration. The OLI chemical analyst modeling process is assumed to be ideal conditions. During the process, filtration will be 100% removed each time and the settlement will be totally removed after the filtration process.

Just as the acid and base are used to adjust the pH in the treatment process, the OLI will be used to predict the trends of target species of scaling tendency with different pH adjustment. This prediction could also make it more cost effective. The commercial treatment process adjusts the pH to 10.2, and based on the previous research, most of the target species would precipitate out at this pH. OLI Chemical Analyst software could predict how the scaling tendency would vary under different pH values. Observation of individual ions could indicate the different ions' removal efficiency, though some ions (such as barium and strontium) are not affected by pH adjustment. Magnesium and calcium salt would require a pH condition to precipitate out for the stream's aqueous phase.

With further research, wells No. 16-68 (24hours and 48hours samples) and No. 16-69 show abnormal precipitation compounds appearing in the OLI modeling results in the stream after pH adjustment. According to the sampling records, the temperature of No. 16-68 and No. 16-69 is below freezing. Considering the salinity of the produced water, the stream might not freeze because of the high concentration of salts and the velocity of the streams flow. In this situation, the OLI modeling would assume that the produced water would not freeze when the temperature is below -25oC. Modeling of the treatment under different temperatures would indicate how the temperature could affect the precipitation compounds.

According to the comparisons between OLI modeling results and laboratory scale results, the comparisons would indicate what we could expect from the treatment and what the goal is. This research focuses on improving the commercial process treatment efficiency by identifying the parameters that could affect the precipitation of produced water.

1.3 Research Objectives

1. Compare the bench scale treatment process data and OLI modeling results.
2. Optimize the filtration process with finer membrane, 0.2 micron instead of 2.5 micron.
3. Estimate how the precipitate changes as temperature decreases.
4. Estimate the optimized pH value for removal of individual ions.

CHAPTER 2

BACKGROUND

2.1 Produced Water

Geologically, the oil/gas-bearing rock underground is believed to be saturated with water, which functions to trap petroleum and natural gas. [7] These rock traps contain both hydrocarbons and water, creating reservoirs of saturated rocks. The trapped water in the reservoir comes out gradually during the drilling, hydraulic fracturing, and production process. [7][8]

The produced water is brought to the surface mixing with oil, gas, dissolved or suspended solids and injection additives for hydraulic fracturing. During the process of oil and gas generation, the water usage for drilling and hydraulic fracturing is significant. On average, the volume of water usage of drilling a well is 5.5 million gallon (19 million liters) on average, which needs 1,000 truck volumes to transport it. Ninety percent of the water is used for hydraulic fracturing. [7] [9] For every barrel of oil produced, three barrels of water can be generated with conventional production techniques. Global produced water production is estimated to be 250 million barrels per day compared with around 80 million barrels per day of oil. As a result, the water to oil ratio is about 3:1. [9] [10]

The produced water is composed of complex organic and inorganic compounds. As the production of gas and oil throughout the world increases, so does the volume of produced water [11]. As a result, the impact of disposing and discharging produced water into the environment has been noted as a serious issue and an potential ecosystem risk [12]. Table 2.1 - Table 2.4 indicates that the water quality varies according to the production of oil or gas.

Table 2.1. Water quality of gas wells [13].

Parameter	Value
Conductivity, umhos/cm	4200-180000
TDS, mg/L	2600-310000
TSS, mg/L	14-800
BOD_5, mg/L	75-2870
COD, mg/L	2600-120000
TOC, mg/L	67-38000
Benzene, mg/L	1.8-6.9
Toluene, mg/L	0.875-3.37

Table 2.2. Overview of concentration range of the contaminations in the produced water from the gas wells [14].

Metal Species	Values, mg/L	Metal Species	Values, mg/L
Aluminum	<0.4	Iron	<1100
Barium	<26	Magnesium	0.9-4300
Boron	<56	Manganese	0.045-6.5
Calcium	<25000	Sodium	520-45000
Chloride	1400-190000	Strontium	<6200
Copper	<0.02	Sulfate	0.1-47

Table 2.3. Water quality of oil wells [13].

Parameter	Values
TOC, mg/L	0-1500
COD, mg/L	1220
TSS, mg/L	1.2-1000
Total Oil, mg/L	2-565
Volatile(BTEX), mg/L	0.39-35

Table 2.4 . The overview of concentration range of the contaminations in the produced water from the oil wells [14].

Metal Species	Values, mg/L	Metal Species	Values, mg/L
Chloride	80-200000	Iron	<0.1-100
Bicarbonate	77-3990	Aluminum	310-400
Sulfate	<2-1650	Boron	5-95
Calcium	13-25800	Barium	1.3-650
Sodium	132-97000	Copper	<0.002-1.5
Potassium	24-4300	Manganese	<0.004-175
Magnesium	8-6000	Strontium	0.02-1000

2.2 Review of Produced Water Softening Methods

As visibility of the potential impact of drilling processes on environment increases, several states have implemented more stringent regulations and standards for discharging oil and gas produced water. Based on the U.S. Environmental Protection Agency regulations, the daily maximum limit for oil and grease is 42mg/L, and the monthly average limit is 29mg/L [1][16] Because of the large volume of produced water being generated, states that are water-stressed need to find a more efficient and cost-effective treatment approaches to supply their limited fresh water resources. Treatment of produced water from the oil and gas industry commonly involves physical, chemical and biological methods. As the quality of produced water is always high hardness, high TDS and poor biodegradability, the cost of the chemical treatments are high and could produce a large volume of hazardous sludge.[13] [15] The general reviews of techniques of produced water softening are shown in the Table 2.5.

Table 2.5. Overview of produced water treatment techniques.

[13][16][17][19][21][22][23][24][25]

Treatment Method	Description	Application
Corrugated Plate Separator	Separate free oil from water under gravity effects enhanced by flocculation on the surface of corrugated plate	Separation of dissolved/free oil and suspended solids. Water may contain oil & grease in excess of 1000 mg/L.
Centrifuge	Separate oil from water by centrifugal force	
Hydroclone	Oil and Grease removal tangential force generated by pressure	
Gas Floatation	Clarity oil and solids by floating the particles attached induced gas bubbles	
Extraction	Removal of free or dissolved oil soluble in lighter hydrocarbon solvent	Oil removal from water with low oil and grease content (< 1000 mg/L)
Ozone[8]	Oxidize the contaminations as precipitation	

Adsorption	Adsorbs contaminants by using porous media	
Lime softening	Removal of carbonate, bicarbonate, hardness by adding lime	Softening Suitable produced waters will have TDS values between 10,000 and 1,000 mg/L.
Ion exchange	Removal of dissolve salts and minerals by ion exchange equipment	
Treatment Method	Description	Application
Rapid spray evaporation	Injecting water at high velocity in heated air evaporates the water which can be condensed to obtained treated water	Softening. Suitable produced waters will have TDS values between 10,000 and 1,000 mg/L.
Ultrafiltration	Removal ultra-particles by membrane under the applied pressure	Removal of trace oil and grease, microbial, soluble organics, divalent salts, acids, and trace solids.
Reverse Osmosis	Purify fluids by R.O membrane with concentration difference	
Acivated Sludge	Using oil degrading microorganisms to degrade contaminants within water	

When produced water is generated and pumped up from the ground, the stream includes organic compounds, dissolved salts and solids. The water quality is tested for salinity, TDS, and hardness. In produced water, TDS could vary from 2,000 ppm to 150,000 ppm. [26][27][31]

Hard water typically contains high concentration of calcium and magnesium ions and removal of the hardness is often one of the most important parts of water treatment systems. [29][30]

The cause of hardness is the presence of divalent metal ions, such as Ca2+ and Mg2+, which could lead to the scaling of pipes and reduced performance of drilling equipment. [31][32] If increasing amounts of produced water are reused for fracturing, high hardness levels could scale and block the fracture significantly affecting the production efficiency. In order to avoid high damage costs on equipment and well fractures, the softening of produced water becomes necessary in the treatment.

2.2.1 Chemical Precipitation

Chemical precipitation softening is a process for removing the contaminants by coagulation with chemical additives. [33] Solubility is a factor that determines the removal performance of target contaminants in the water that varies as complex conditions, such as temperature and solution ionic strength. Metal ions that are dissolved in the water can potentially precipitate as insoluble hydroxide and carbonates. [34][35] The most common chemical precipitation processes are: lime softening, lime-soda ash softening, and caustic softening. [36] Three precipitation methods are selected based on the water quality shown in Table 2.6.

Table 2.6. Chemical coagulation softening processes.

Softening Process	Applicable Condition
Lime Softening	Low concentration of non-carbonate hardness
Lime-soda Softening	High concentration of non-carbonate hardness
Caustic Soda Softening	Inadequate carbonate hardness to react with lime

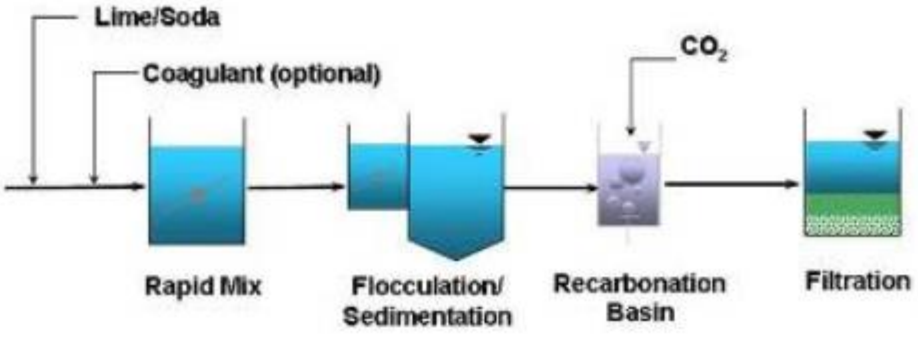


Figure 2.1. The overview of chemical coagulation treatment process.[37]

Figure 2.1 indicates the chemical coagulation precipitation treatment process. A chemical precipitation softening process contains several parts: rapid mix, sedimentation, re-carbonation, and filtration. [37][38] Rapid mix combines the coagulants with the inflow water, the sedimentation process functions to lower the turbidity through settling and re-carbonation adds alkalinity that has been removed. In the process of precipitative softening, calcium contaminants are removed in the form of calcium carbonate (CaCO3) and magnesium is removed as magnesium hydroxide Mg(OH)2. [38] In this precipitation reaction, solution pH would be the most important factor that affects the precipitation.

2.2.2 Ion Exchange

Ions in the water under equilibrium status obey charge balance rules. The ion exchange treatment functions to removes heavy metals, salts, radium, and other ions from the produced water. [39] Ion exchange is a reversible electro-chemistry treatment process, in which target contaminations and ions are replaced by the same amount charge of ions present within the resins. The brief structure of ion exchange process is shown in figure 2.2.

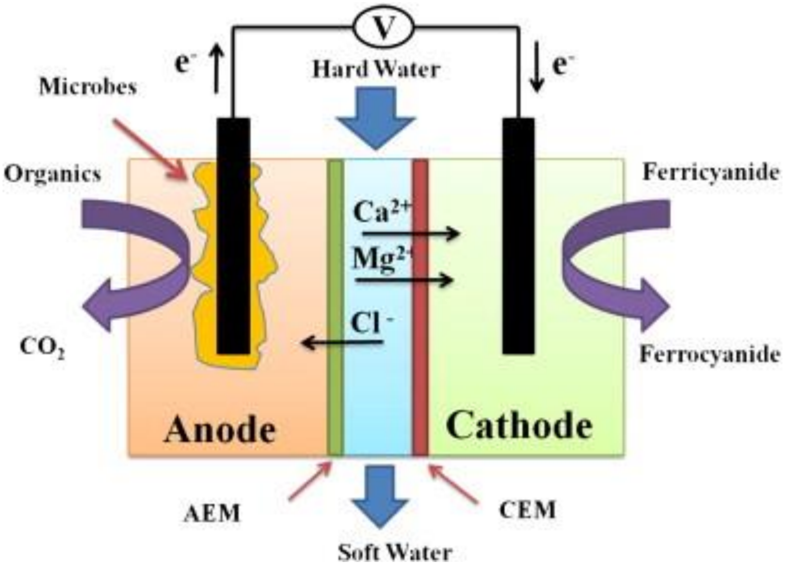


Figure 2.2. Overview of ion exchange process. [41]

The system performs well on inflow with TDS of lower than 5,000 ppm.When the TDS of inflow gets higher, the sodium ions in the produced water would compete with the target ions for sites on the resin and therefore it is difficult to achieve a hardness lower than 1-ppm. [42] [43] While ion exchange treatment functions to remove the calcium and magnesium ions from the aqueous phase, neither strong-acid nor weak-acid resins have any obvious effect on sillica removal.

2.2.3 Electrodialysis (ED) and Electrodialysis Reversal (EDR)

Most salts dissolve in the aqueous phase as the ionic form, existing as cations or anions. These ions are attracted to electrodes with the opposite electric charge. In ED process, membranes are used to seperate the resin into two sections. The membrane allows either cations or anions to migrate and reach the opposite electric charge electrodes. [44] [45] During migration, the charged ions can not pass through the same charged membranes. In one ED process, there contains numerous continuous units to improve the treatment efficiency. As a result, water within one unit gets concentrated and leaves desalted water within the next unit. And this inflow could get treated and concentrated continuously in the following units. The concentrated and desalted water are continuously removed in the following unit. [44]

The EDR process obeys the same general ED principle as well, except the polarity of the electrodes swiched periodcally. [46] At a particular frequency, the polarity of the electrodes switches. The flows changes along with the switching electrodes, which leads to switches between brine channel and the product water channel. [44][46]

The treatment result is that those ions are attacted by the opposite charge electrodes across the membrane. The brine channel and product channel switches perodically as the electrode polarity changes. [13] The concentrated water is disposed of until the membrane stack and lines are flushed, and the target water quality is restored. This period lasts 1 or 2 minutes, and then the unit resumes producing water.[44] [46] [47] This reversal process could clean the scale and deposits in the treatment cell, which could improve the treatment efficiency. The flushing step functions to reduce the pre-treatment chemicals and decrease the membrane fouling.[44] [49] According to the different target components in the aqueous phase, different membranes are selected in order to achieve better treatment performance. Figure 2.3 shows how different membranes suit different inflow and different targent components.

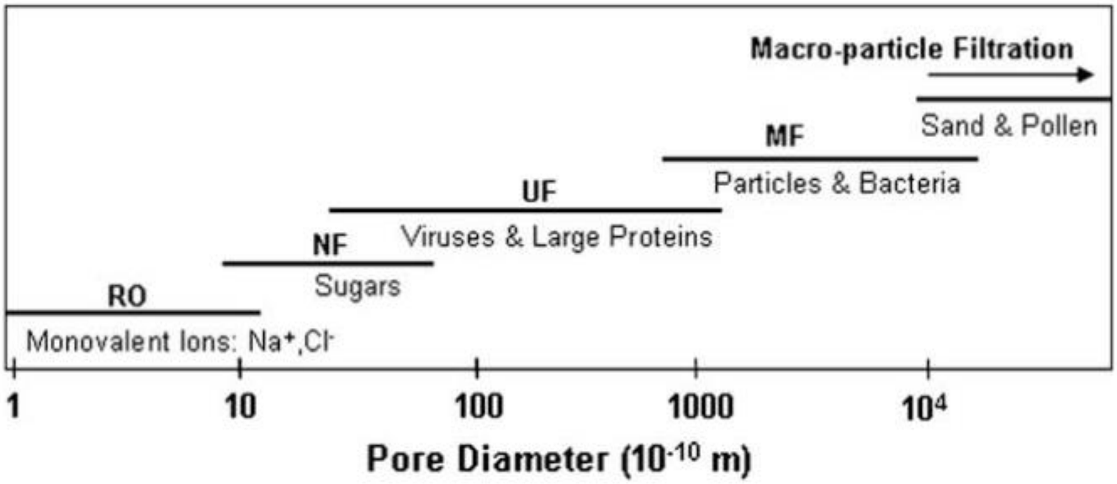


Figure 2.3. The applicable situation for different membranes. [48]

2.2.4 Evaporation

Evaporation is one of the common methods of water desalination, commonly used for inland domestic water supply. [50][51] The basis of this treatment method is to heat the inflow water so that vapor can be generated. Then the vapor can be collected and condensed as pure water. The remaining stream contains concentrated salt and high TDS which are disposal wastes.

Falling film vertical tube evaporators can have high heat transfer coefficients because of the character of the evaporator, which is considered energy-saving. The chance of fouling is minimized in the evaporator by wetting the tubing surface during operations. [53] After the produced de-oiled and pH adjustment, the pre-heater process increases the inflow temperature.

The de-aerator removes the dissolve gas in the heated inflow brine. And the de-aerated brine goes into the evaporator sump cell, in which the recirculating brine slurry is combined with the de-aerated inflows. The brine slurry is pumped up to the heat transfer tubes and then distributed into each tube. As Figure 2.4 shows, most of the the brine flows at the bottom of the tubes for recirculating, and only a small portion evaporates. [52] [16]

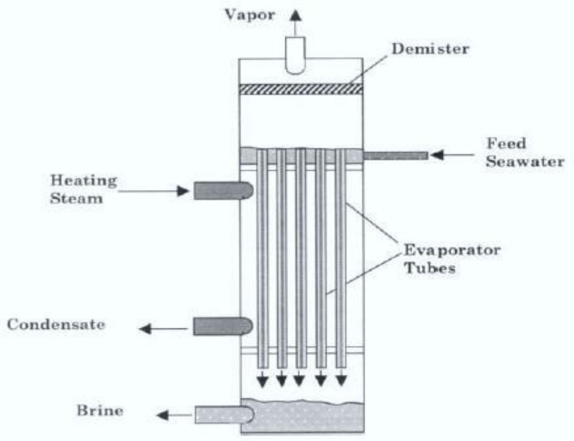


Figure 2.4. The process of falling film vertical tube evaporator has the highest heat transfer coefficient which is required to save energy. [53]

As Figure 2.4 shows, most of the the brine flows at the bottom of the tubes for recirculating, and only a small portion evaporates. [54][55] Then the vapor enters a compressor. The compressed vapor goes out of the heat transfer tubes and transfers into the cooler brine. As a result, the vapor is condensed into pure water . And the condensed water is pumped back through the heat transfer, in which the sensible heat is given to the inflow.

According to the review of produced water softening techniques, the treatment methods of the produced water are well developed and used by oil and gas industry. In this research, the OLI chemical analyst program are used to model and analyze the commercial company's produced water treatment. The company uses chemical precipitation and EC for produced water softening. Because of the high hardness in the produced water, the scaling potential could lead to damages on pipelines and drilling equipment. This research focuses on produced water softening and identifying the factors that could affect treatment performance.

CHAPTER 3

METHODS

3.1 Introduction

The commercial water treatment company that we worked with uses a composite system that includes EC and chemical coagulation for the treatment of produced water. In the treatment process, the produced water streams are pumped up from the ground, and the pH of these produced water streams are adjusted to pH 7.0, which makes them ready for further treatment. After the pH adjustment, the produced water is pre-filtered to remove the settlement and lower the turbidity in the streams. Then, the filtered raw water is used as the input of EC treatment. After the filtration, the post EC output water are processed with chemical coagulation and filtered after that. According to research results, most of the metal ions get precipitated after the pH is adjusted 10.2 with sodium hydroxide. The pH is then reduced to 7.0 with hydrochloric acid.

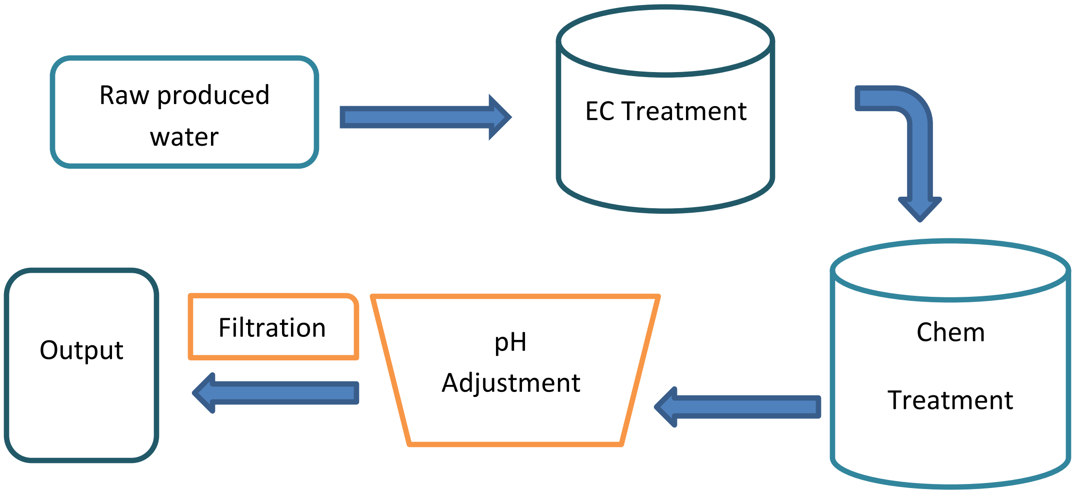


Figure 3.1. Brief view of the produced water treatment process.

3.2 Electrocoagulation (EC)

The treatment process uses electricity to treat flow back and produced water. This process neutralizes the aqueous charge and makes collision and attachment of particles easier, which allows the flocculation of suspended solids to happen. The theory of EC has been discussed by a number of authors [6] [32].

It is general, the EC process involves three successive stages: (a) formation of coagulants by electrolytic oxidation of the sacrificial electrode; (b) destabilization of the contaminants, particulate suspension, and breaking of emulsions; and (c) aggregation of the destabilized phases to form floc. [58]

3.3 Chemical Coagulation

An alternative approach for coagulating and adjusting the particle surface charge, the industry uses various polymer blends to flocculate the suspend solids. Hydrogen chloride (HCl) is used to adjust the pH of produced water below 6.0 and a dose of the coagulant blend PACl/ACH (5 parts per liter) for the sampling water and set up the flocculation time as 5 minutes in order to settle the solids.

Polyaluminium coagulants are commonly used in drinking water treatment softening. Chemical precipitation starts with adding chemical addtives such as polyaluminium chloride (PACl) and sodium hydroxide (NaOH) at the inflow. PACl is a synthetic polymer dissolved in water. The amount of polyaluminium chloride is defined with regard to the turbidity of the raw water.[56] To function as an effective flocculant, PACl concentration must be controlled to be higher than 10 %. [57] Polyaluminium chloride would tend to be unstable and precipitate out from the aqueous phase after a period of standing. Figure 3.2 shows the overview of the chemical coagulation treatment.

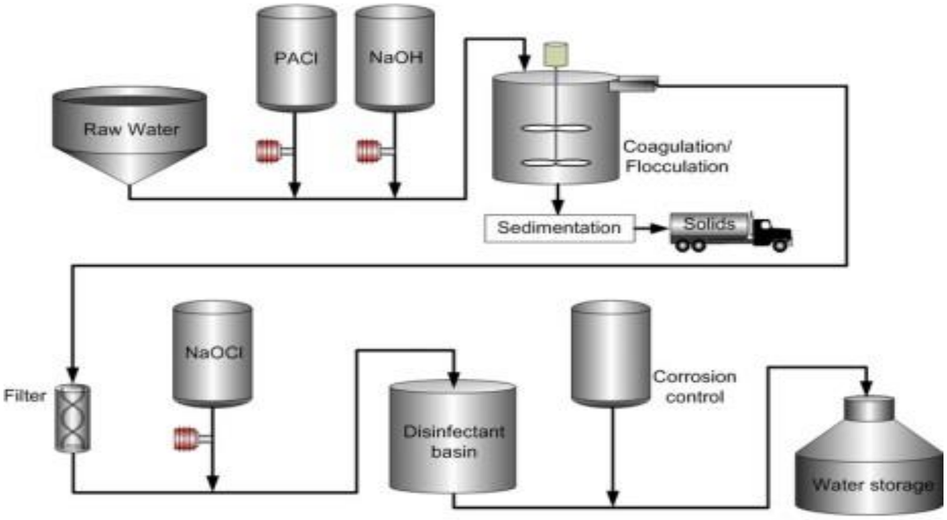


Figure 3.2. The overview of the chemical coagulation treatment. [56].

3.4 OLI Chemical Analyst system

OLI Chemical Analyst, developed by OLI Systems, Inc.,[57] is a predictive thermodynamic framework that is used for simulating physical and chemical properties of multi-phase systems. Prediction on chemical equilibrium and scaling tendencies based on the data developed during the bench scale testing are organized in the order of the age of the well.

The raw water samples were collected from wells in Weld County, CO and used for both bench scale experiments (EC and chemical coagulation treatment) and the OLI Analyst modeling process. The membrane used for filtration is 2.5 micron (sand bed filtration is used in the commercial treatment process and the size of filtration is uncertain), while the filtration removal effectiveness was assumed to be 100% for the OLI Analyst Modeling. In this study, the OLI modeling process results are compared to experimental bench scale testing using both EC and chemical coagulation. The OLI modeling process is based on the hypothesis that the entire coagulation and filtration process is effective enough to remove all the suspended solids in the aqueous phase. The comparison between OLI chemistry modeling and bench scale testing results will be used to indicate the performance of the solid-liquid separation process. These results may be useful for coagulation and/or filter process effectiveness.

Another main objective of the research is to understand how pH adjustment would affect the performance of the softening process. OLI software is used to model how the scaling tendency of different contaminants would change at different pH values, results that could benefit the industry by saving costs on chemicals and solids handling.

EC and chemical coagulation processes were run in parallel to indicate how the single treatment methods could affect the treatment process. OLI analyst is used to model the pH adjustment process after the coagulation processes; in the modeling process, relative inflow will be used as input of OLI Modeling process. The modeling process could demonstrate the expectation of removal ratio under ideal condition, as well as what we can expect from the treatment facility. The modeling process is shown in Figure 3.3.

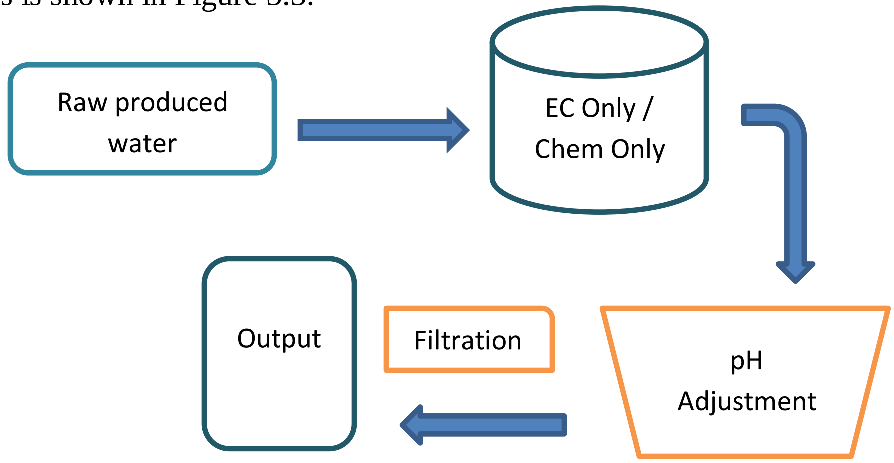


Figure 3.3.Two parallel bench scale experiment.

CHAPTER 4

RESULTS

4.1 Comparison between Softening and OLI Modeling

Two liters of water for each well were brought back to the lab and stored in a refrigerator. All of the raw samples were measured before and after primary filtration (2.5 micron) and measurements of water quality were taken at the CSU Environmental Engineering Labs shown in Table 4.1.

Table 4.1. The inflow water quality of all the wells

Ions, mg/L	NO.14-63	No.16-68 48(hours)	No. 16-68 24(hours)	No. 14-66	No.06 -63	No. 16-69
Na(+1)	12240	3482	2912	13456	12984	4529
K(+1)	152	62.3	73.5	1005	215	150
Mg(+2)	46.7	15.9	19.2	52.6	47.4	16.2
Ca(+2)	272	117	132	290	267	86.5
Sr(+2)	49.1	13.2	13.9	51.4	46.8	13.1
Ba(+2)	27.4	3.12	3.44	29.2	13.2	3.47
Fe(+2)	88.4	33.5	30	166	19.9	12.4
Cu(+2)	0.475	(Null)	(Null)	0.563	0.476	(Null)
Mn(+2)	1.77	(Null)	(Null)	2.39	0.813	(Null)
Al(+3)	1.45	4.51	3.67	1.09	1.63	0.899
Cl(-1)	20280	5080	4620	20412	19560	6780
SO4(-2)	0.05	189	376	106	13.5	113
HCO3(-1)	459	1020	1170	816	369	1044
B(-1)	14.8	10.2	12.2	11.6	20.5	11.4

According to the measurement of the water quality shown above, the ion concentration varies from well to well and temporally with individual wells. No.16-68 well samples were taken at 24 hours and 48 hours after drilling. Sodium ion concentration varied from 2912mg/L to 3482mg/L.

Bicarbonate ion concentration decreased from 1170 mg/L to 1020mg/L. Those differences are consistent within the estimation of former research as shown in the Table 4.2.

Table 4.2. Concentration range of different ions in produced water.

Metal Species	Values, mg/L	Metal Species	Values, mg/L
Aluminum	<0.4	Iron	<1100
Barium	<26	Magnesium	0.9-4300
Boron	<56	Manganese	0.045-6.5
Calcium	<25000	Sodium	520-45000
Chloride	1400-190000	Strontium	<6200
Copper	<0.02	Sulfate	0.1-47

Based on the statistical analysis, all the ion concentrations vary within a range as shown in Table 4.2. Excluding the wells that have a lack of copper and manganese ion concentration are wells No. 16-68 and No. 16-69, and well No. 14-66 are chosen as the representative of all 6 wells for OLI modeling as Figure 4.1 shows below.

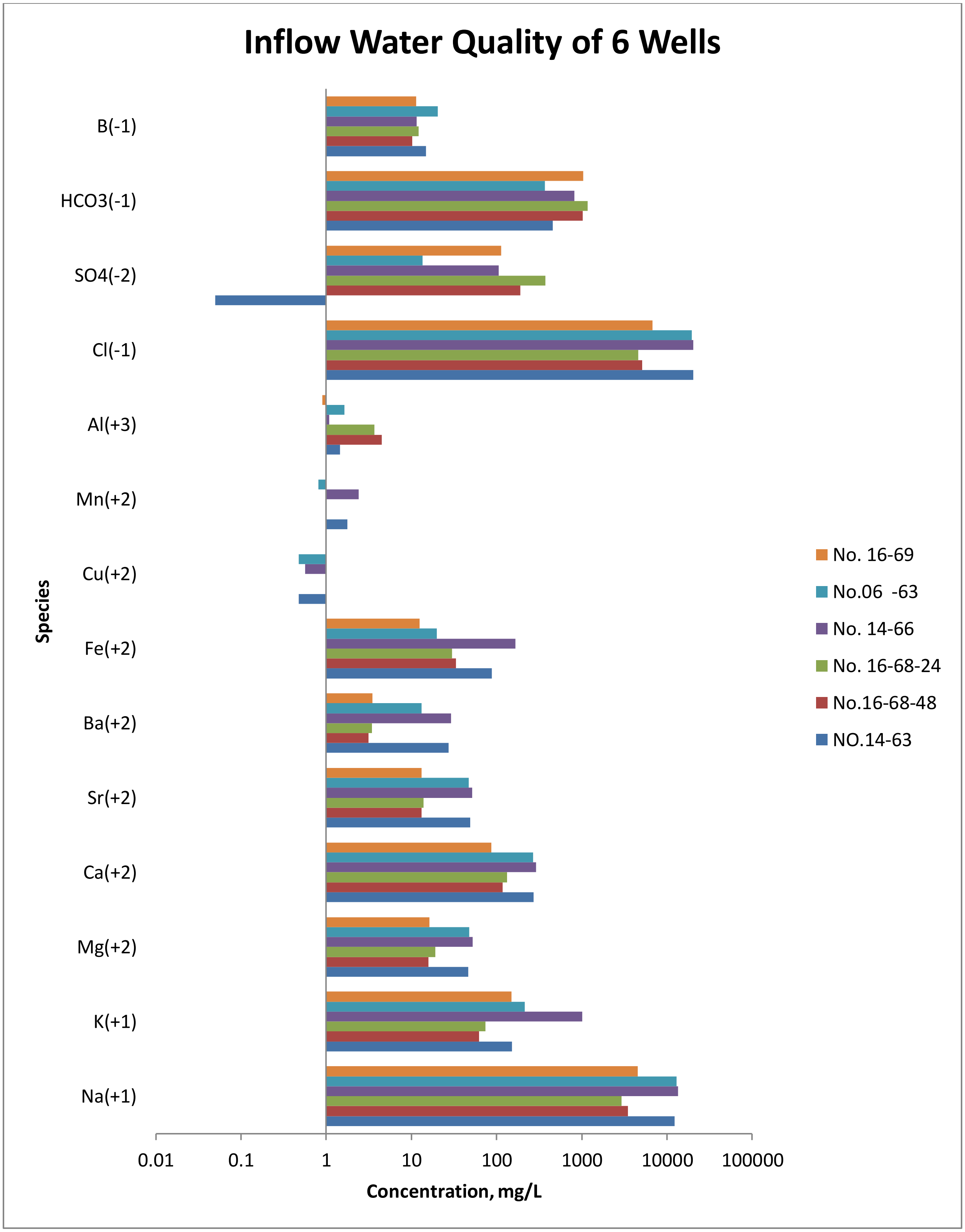


Figure 4.1. Inflow water qualities of six wells.

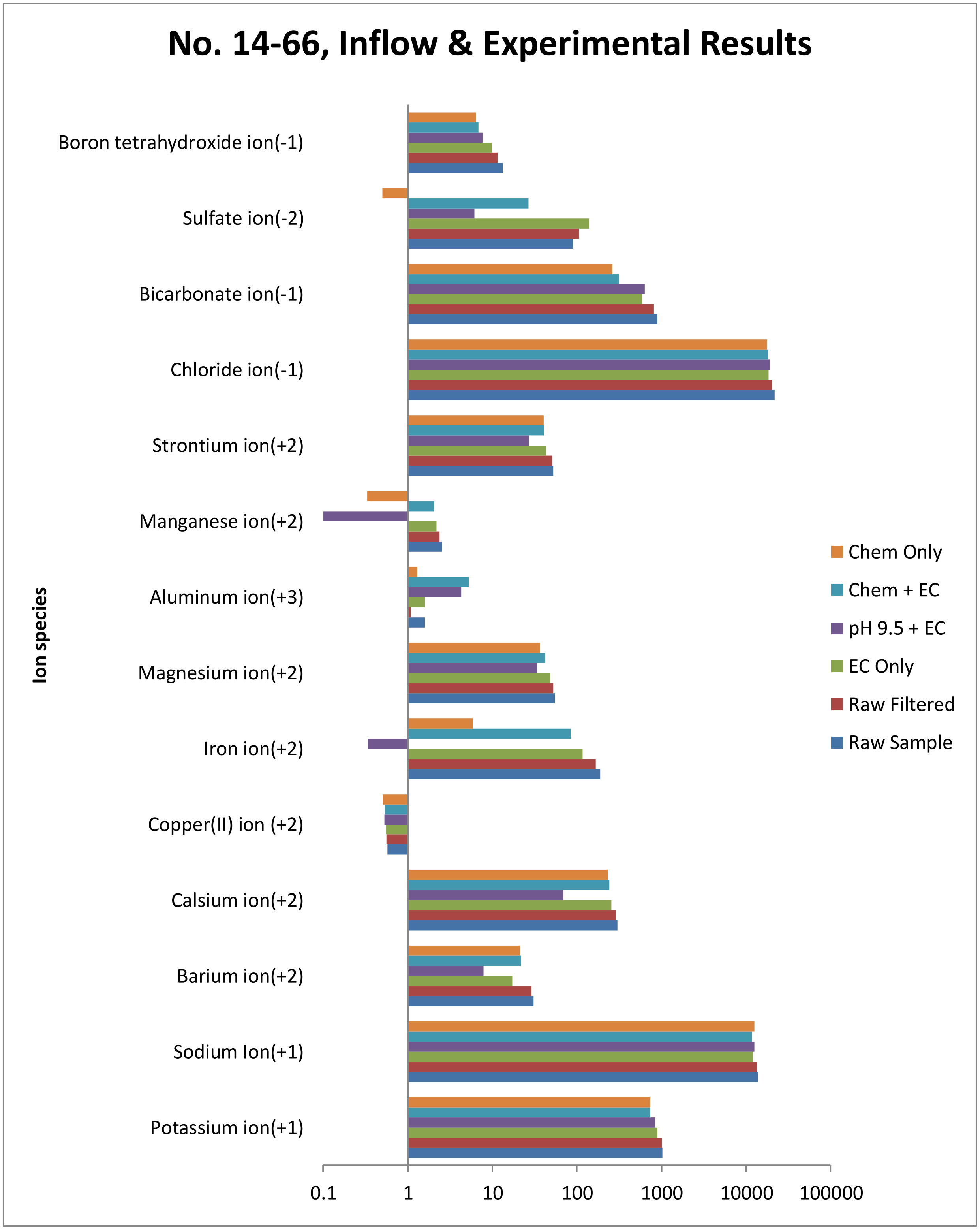
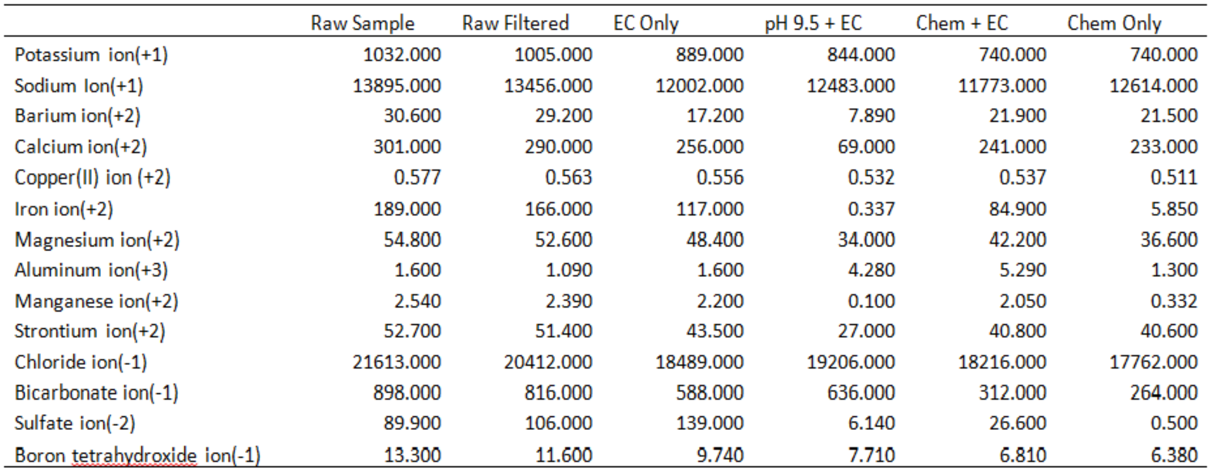


Figure 4.2. Comparison between inflow and experimental water quality of well No.14-66.

Figure 4.2 shows the water quality comparisons between raw inflow and each treatment method. The treated water quality outputs are from CSU Energy and Water Sustainability Group. The results demonstrate that the bench scale treatment methods did not function well in target compounds removal. The dark red bar is the raw water sample which gets physical filtration and then used as inflow of the bench scale experiment. Comparisons between raw filtered inflow water quality and each treatment method demonstrate that the simulation experimental results did not match the expectation of the hardness and metal ions. This outcome did not match the expectation of the hardness and metal ions removal. In order to figure out the reasons, OLI chemical analyst program is used to model the precipitation equilibrium with pH value changed. The data is shown in Table 4.3 as follow.

Table 4.3 Comparison between inflow and experimental water quality of well No.14-66.



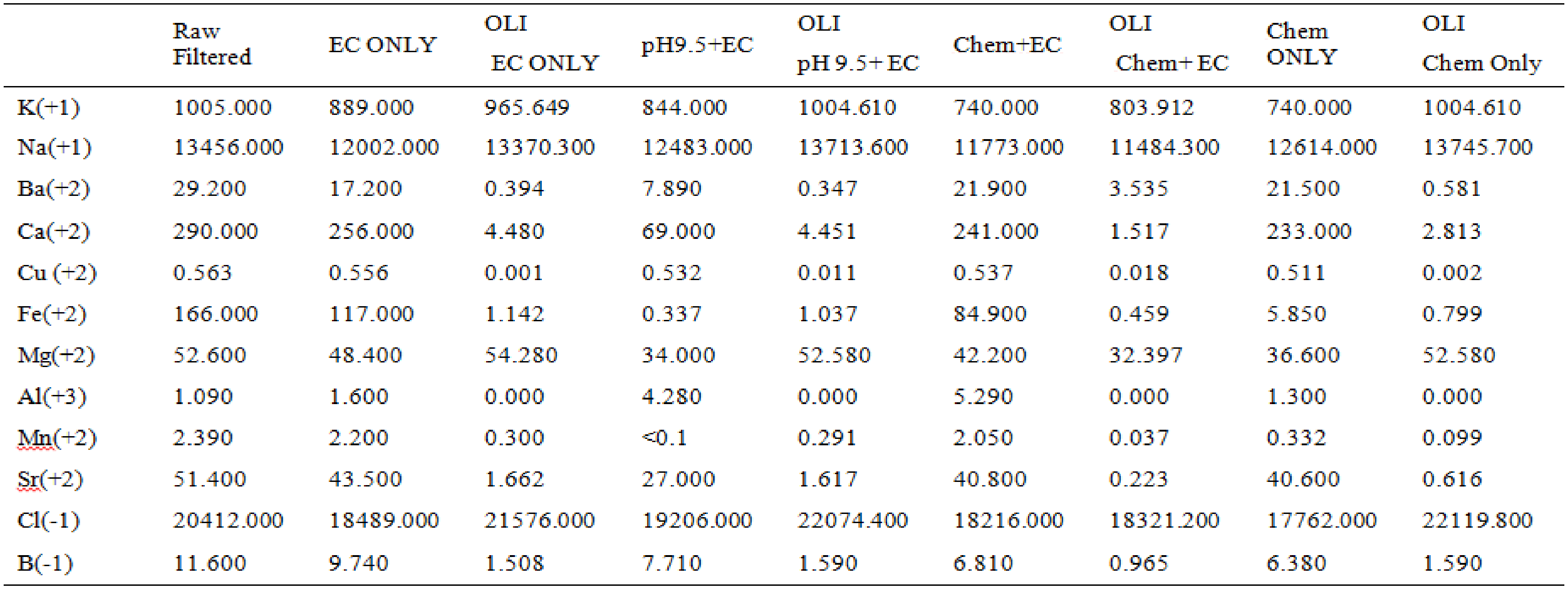
	Raw Sample	Raw Filtered	EC Only	pH 9.5 + EC	Chem + EC	Chem Only
Potassium ion(+1)	1032.000	1005.000	889.000	844.000	740.000	740.000
Sodium Ion(+1)	13895.000	13456.000	12002.000	12483.000	11773.000	12614.000
Barium ion(+2)	30.600	29.200	17.200	7.890	21.900	21.500
Calcium ion(+2)	301.000	290.000	256.000	69.000	241.000	233.000
Copper(II) ion (+2)	0.577	0.563	0.556	0.532	0.537	0.511
Iron ion(+2)	189.000	166.000	117.000	0.337	84.900	5.850
Magnesium ion(+2)	54.800	52.600	48.400	34.000	42.200	36.600
Aluminum ion(+3)	1.600	1.090	1.600	4.280	5.290	1.300
Manganese ion(+2)	2.540	2.390	2.200	0.100	2.050	0.332
Strontium ion(+2)	52.700	51.400	43.500	27.000	40.800	40.600
Chloride ion(-1)	21613.000	20412.000	18489.000	19206.000	18216.000	17762.000
Bicarbonate ion(-1)	898.000	816.000	588.000	636.000	312.000	264.000
Sulfate ion(-2)	89.900	106.000	139.000	6.140	26.600	0.500
Boron tetrahydroxide ion(-1)	13.300	11.600	9.740	7.710	6.810	6.380

In the modeling process, the effects of EC and chemical precipitation are ignored. And the removal ratio is assumed as 100% removal which means the settlements would get completely filtered and removed from the liquid phase. Removal ratio us decided by the filtration process. Membrane size of 2.5 micron is used as filtration process in the bench scale experiments

4.2 OLI Modeling vs. Experimental Results

In the analysis, OLI Chemical Analyst is used to model and assess the performance of the lab-scale produced water treatment process. Parallel experiments of EC and Chemical coagulation only are used to indicate how these two processes affect the precipitation and metal ion removal. This result is able to identify the performance that we can expect from the Produced Water Treatment Facilities. The comparisons between OLI modeling and experimental results are shown in Table 4.4.

Table 4.4. Well No. 14-66 comparisons between OLI modeling results and experimental results.



	Raw Filtered	EC ONLY	OLI EC ONLY	pH9.5+EC	OLI pH 9.5+ EC	Chem+EC	OLI Chem+ EC	Chem ONLY	OLI Chem Only
K(+1)	1005.000	889.000	965.649	844.000	1004.610	740.000	803.912	740.000	1004.610
Na(+1)	13456.000	12002.000	13370.300	12483.000	13713.600	11773.000	11484.300	12614.000	13745.700
Ba(+2)	29.200	17.200	0.394	7.890	0.347	21.900	3.535	21.500	0.581
Ca(+2)	290.000	256.000	4.480	69.000	4.451	241.000	1.517	233.000	2.813
Cu (+2)	0.563	0.556	0.001	0.532	0.011	0.537	0.018	0.511	0.002
Fe(+2)	166.000	117.000	1.142	0.337	1.037	84.900	0.459	5.850	0.799
Mg(+2)	52.600	48.400	54.280	34.000	52.580	42.200	32.397	36.600	52.580
Al(+3)	1.090	1.600	0.000	4.280	0.000	5.290	0.000	1.300	0.000
Mn(+2)	2.390	2.200	0.300	<0.1	0.291	2.050	0.037	0.332	0.099
Sr(+2)	51.400	43.500	1.662	27.000	1.617	40.800	0.223	40.600	0.616
Cl(-1)	20412.000	18489.000	21576.000	19206.000	22074.400	18216.000	18321.200	17762.000	22119.800
B(-1)	11.600	9.740	1.508	7.710	1.590	6.810	0.965	6.380	1.590

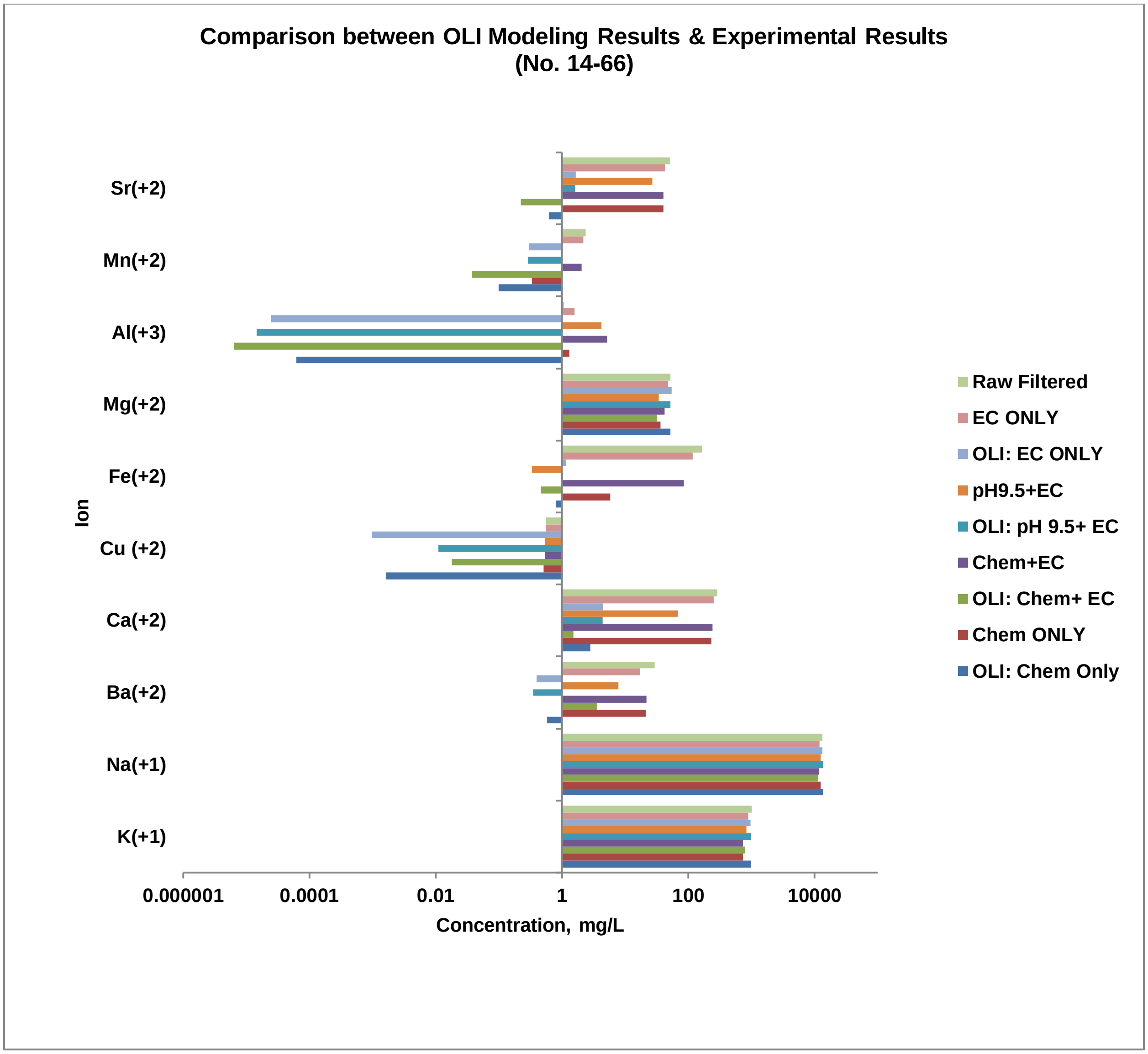


Figure 4.3. Comparison between OLI modeling results & experimental results of well No. 14-66.

In figure 4.3, EC only refers to electrocoagulation, and EC only is the lab process that is used to show how EC affects the whole situation. The post EC water flow is adjusted to pH 10.2, the filtered water flow is brought down to pH 7.0 again, and then measured. With the same purpose, Chem Only means the process shows how chemical coagulation will affect the whole treatment.

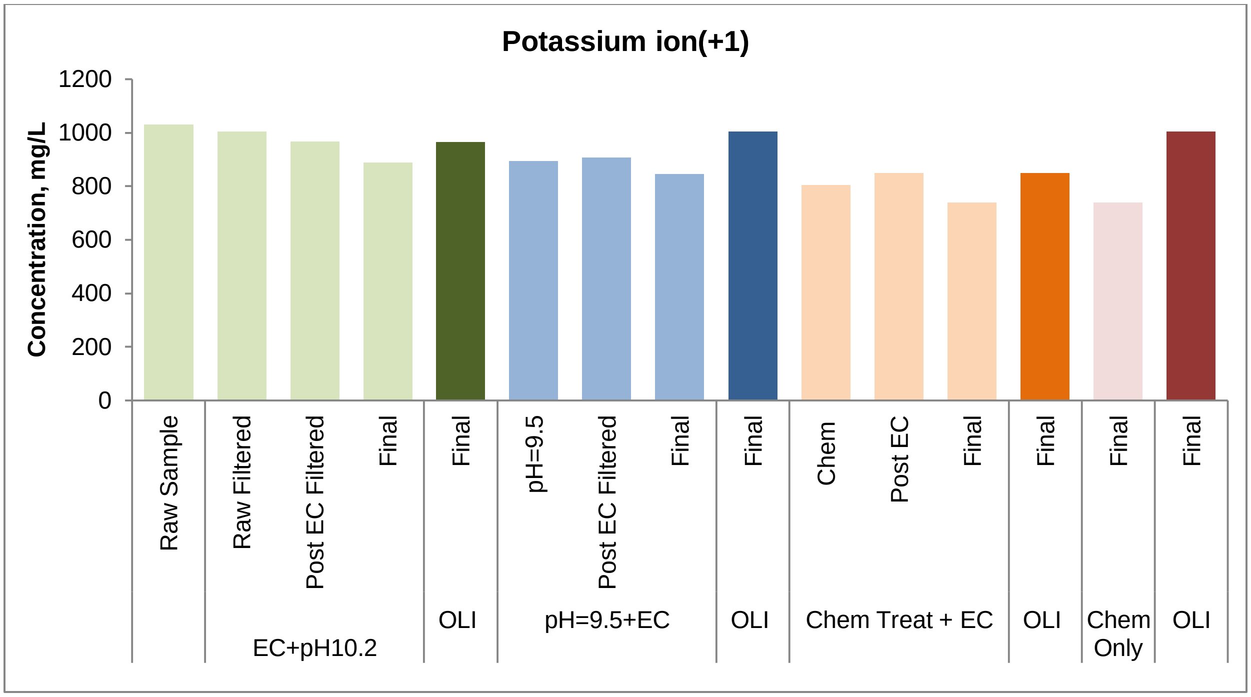


Figure 4.4. Element potassium, comparison between experimental results and OLI Analyst modeling results.

In figure 4.4, the potassium concentration values for different treatments are identified with different colors and compared to the modeled results. According to the output of OLI Analyst, potassium exists in the aqueous phase as four species: potassium chloride, potassium bisulfate (VI), potassium ion (+1), and potassium sulfate (VI) ion (-1), which formations are all soluble in the aqueous phase. Because of the high solubility of the species, potassium ion concentration remains around 1000 mg/L. The potassium species removal ability of the treatment facilities is predicted to be low.

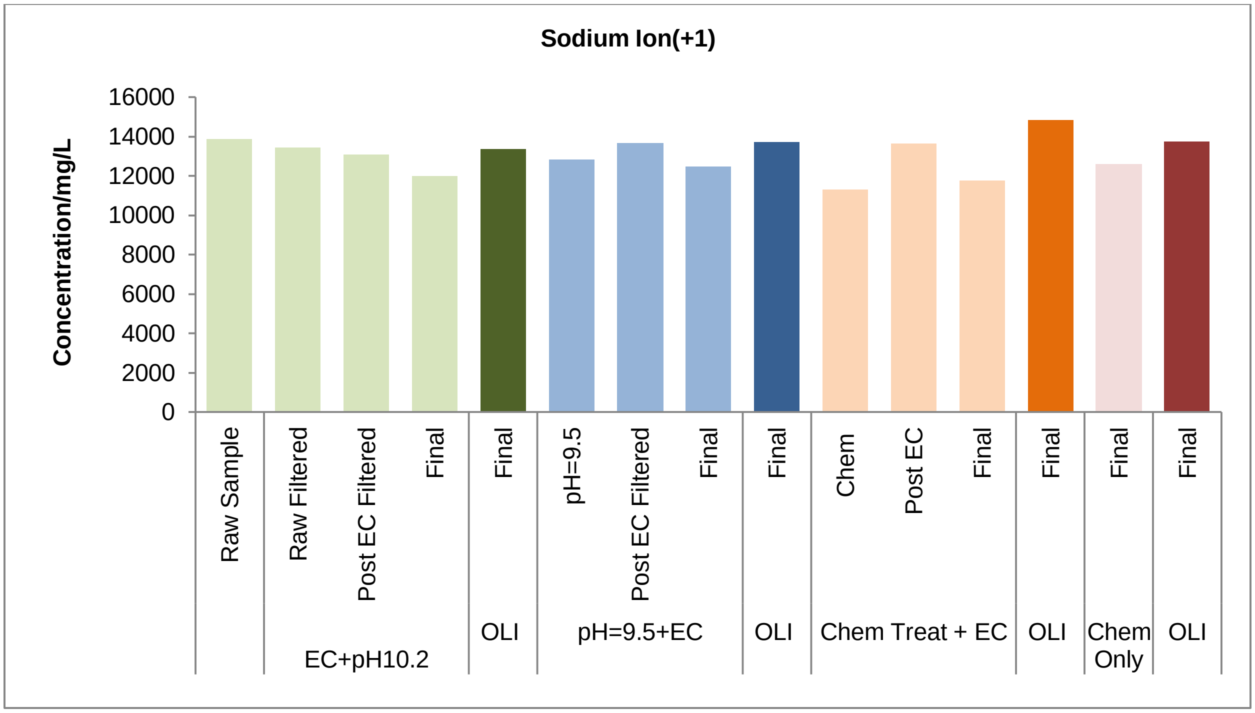


Figure 4.5. Element sodium_ comparison of experimental results and OLI Analyst modeling results.

In figure 4.5, sodium concentration values have been identified with different colors. The x-axis has been divided into several sections, similar to potassium. Experimental results are followed by OLl modeling results. The process of EC+ 10.2 stands for the experimental process of EC treatment. For well No. 14-66, the sodium compounds dissolve in the fluids as several species: sodium boron hydroxide, sodium carbonate ion (-1), sodium bicarbonate, sodium ion (+1), and sodium sulfate ion (-1). These formations of sodium can be soluble and hard to precipitate. In other conditions, such as low temperature, for example well No.16-68-48hours, at -8.5 ^{0}C, the scaling tendency of sodium aluminum dihydroxide carbonate (AlCH2NaO5) can be above 1, meaning that the solid phase will precipitate out from the system as equilibrium is approached. The data presented indicates that sodium and potassium ions cannot be removed during the simulated experimental process since the solubility of the solid species is high. Since these ions are not amenable to precipitation and solid/liquid separation as a removal process, more expensive techniques such as reverse osmosis will need to be used if concentrations are to be reduced.

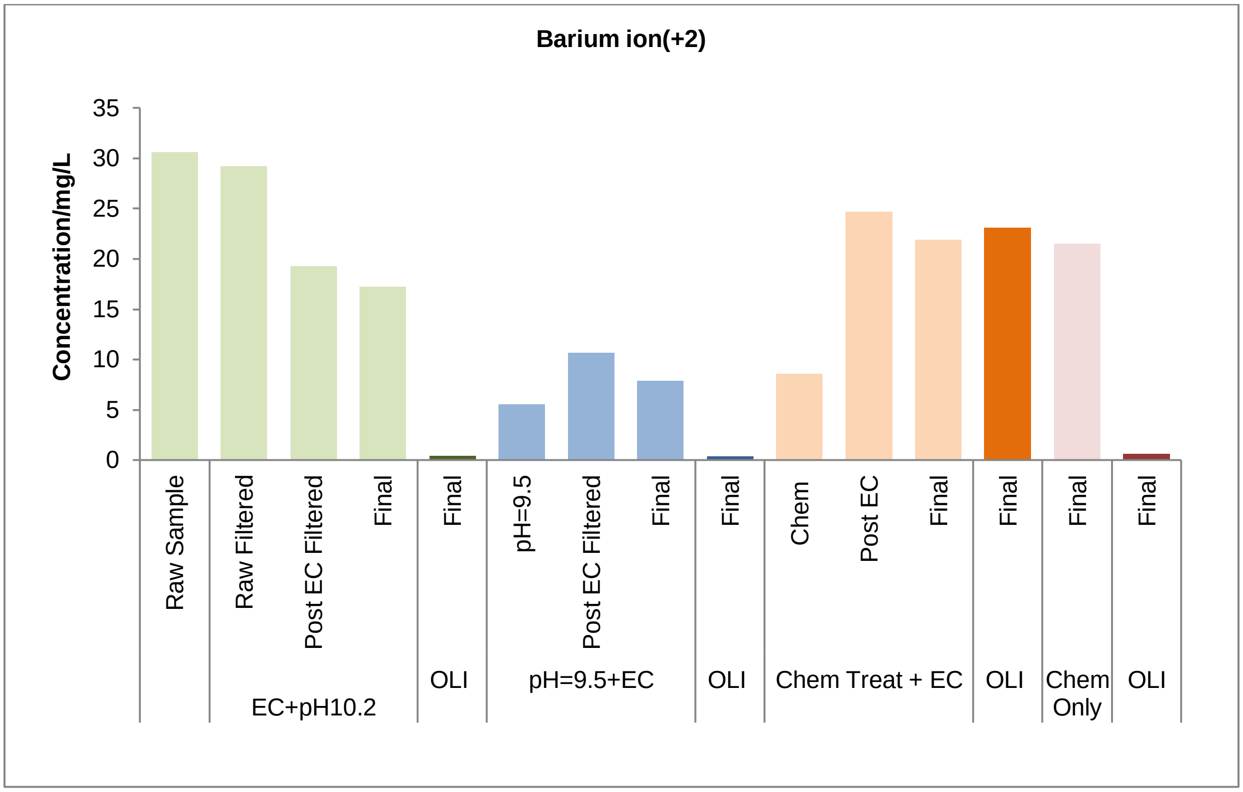


Figure 4.6. Element barium_ comparison between experimental results and OLI Analyst modeling results.

In figure 4.6, the barium concentration value after different treatment processes is shown along with corresponding modeling predictions. The OLI Analyst modeling results indicate that the experimental barium ion removal is significantly less efficient than predicted assuming chemical equilibrium. Since the solubility of barium sulfate is not significantly affected by temperature, the solubility products constant remains at approximately 1.1×10-10 even under water temperatures of 25℃. The barium species that exist in the aqueous phase are: barium chloride ion (+1), barium carbonate, barium bicarbonate ion (+1), barium ion (+2), and barium hydroxide ion (+1). As the OLI Chemical Analyst results show, the removal ratio of barium can be more than 90% with barium sulfate the primary solid phase that needs to be separated. The removal ratio of Barium can be more than 90%, and barium sulfate precipitates from the stream as settlement as shown in Table 4.5.

Table 4.5. Barium species at pH 10.2.

Species	Total (mg/L)	Liquid (mg/L)	Solid (mg/L)
Barium chloride ion (+1)	0.086968	0.086999	0
Barium carbonate	1.34E-03	1.34E-03	0
Barium bicarbonate ion(+1)	1.30E-04	1.30E-04	0
Barium ion(+2)	0.324614	0.324732	0
Barium hydroxide ion(+1)	9.00E-07	9.00E-07	0
Barium sulfate	32.1177	0	32.1294

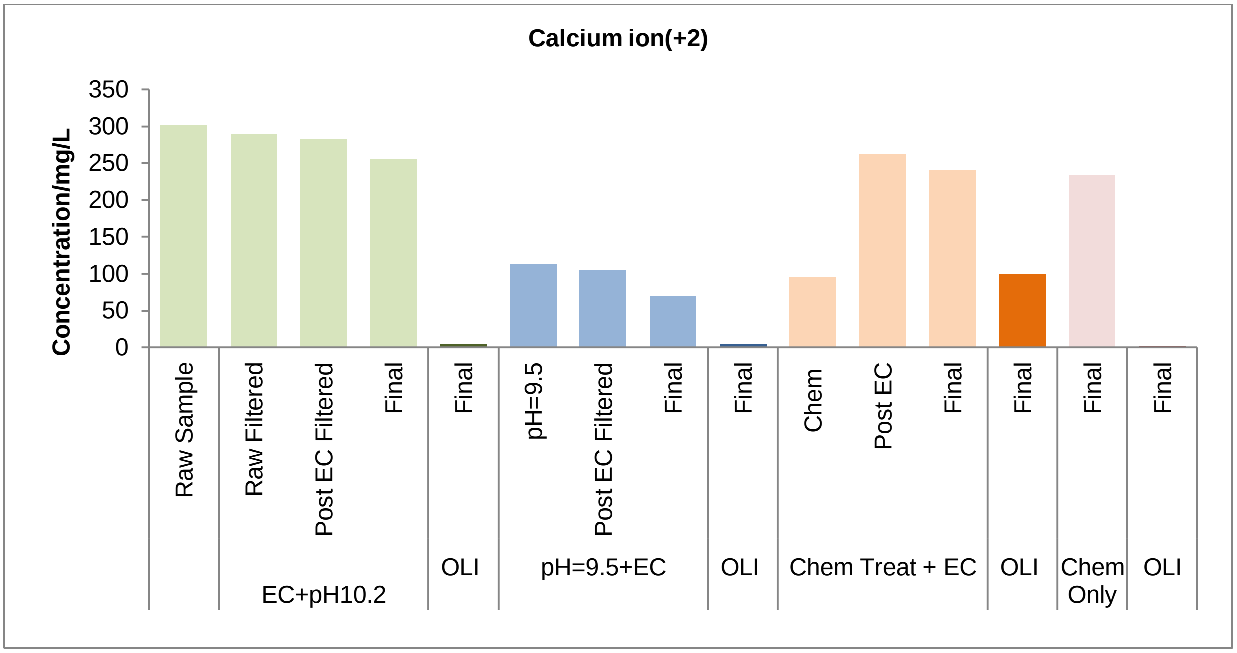


Figure 4.7. Element calcium_ comparison between experimental results and OLI Analyst modeling results.

Calcium concentration experimental results are compared OLI-model predictions in Figure 4.7. The model predictions are consistently less than the observed results from the lab scale testing, potentially indicating that calcium is precipitated but nit removed during the subsequent filtration process (2.5 μm filters were used in the bench scale tests to simulate full scale solid-liquid separation). The model predicts calcium species in the influent stream to include calcium chloride, calcium monochloride ion (+1), calcium dihydrogen borate ion (+1), calcium bicarbonate ion (+1), calcium ion (+2), calcium hydroxide ion (+1), calcium sulfate, and calcium carbonate (calcite). as shown in Table 4.6.

Table 4.6. Calcium species at pH 10.2.

Species	Total (mg/L)	Liquid (mg/L)	Solid (mg/L)
Calcium chloride	4.12E-23	4.12E-23	0
Calcium monochloride ion(+1)	5.18E-07	5.18E-07	0
Calcium carbonate (calcite)	697.806	1.25491	696.804
Calcium dihydrogen borate ion(+1)	0.023145	0.023154	0
Calcium bicarbonate ion(+1)	0.044353	0.04437	0
Calcium ion(+2)	3.44523	3.44648	0
Calcium hydroxide ion(+1)	6.62E-04	6.62E-04	0
Calcium sulfate	7.59E-03	7.59E-03	0

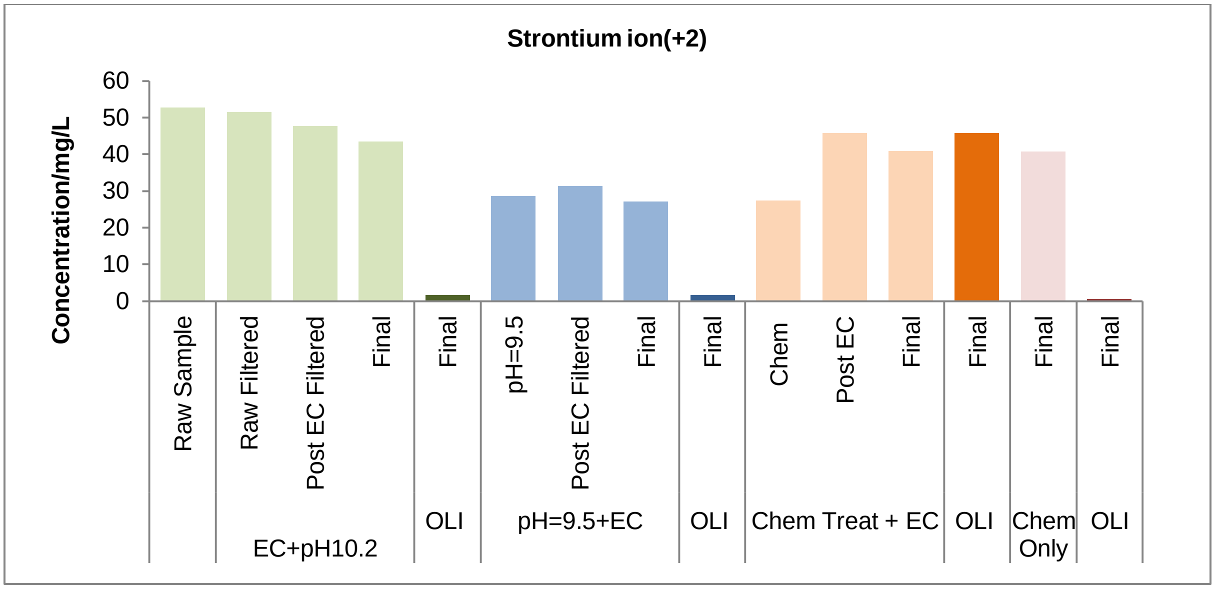


Figure 4.8. Element strontium_ comparison between experimental results and OLI Analyst modeling results.

In figure 4.8, the strontium concentration is shown for the different treatment stages and compared with modeled predictions. Like calcium, strontium precipitates as the metal carbonate, Sr(CO3) and the results shown in Figure 4.8 are similar to those shown in Figure 4.7. Again, the predicted removal assuming 100% solid separation is much less than the observed values indicating that pH is not the limiting factor in the removal of this metal. Most strontium ions precipitate out from the system as strontium carbonate as shown in Table 4.7.

Table 4.7. Strontium species at pH 10.2.

Species	Total (mg/L)	Liquid (mg/L)	Solid (mg/L)
Strontium ion(+2)	1.658	1.658	0
Strontium monohydroxide ion(+1)	6.43E-05	6.43E-05	0
Strontium sulfate	8.80E-03	8.81E-03	0
Strontium carbonate	77.539	0	77.5676

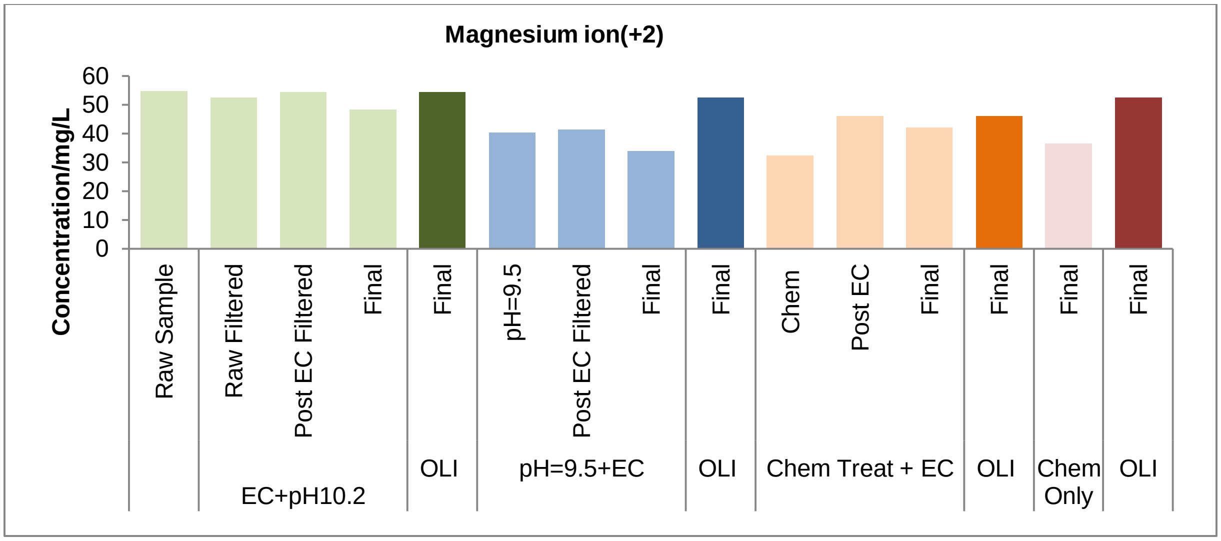


Figure 4.9.Magnesium_ comparison between experimental results and OLI Analyst modeling results.

Modeled and experimental removals of magnesium with various stages of treatment are shown in Figure 4.9. In contrast to barium, calcium and strontium, the predicted concentrations of magnesium is much greater and in general agreement with observed results. This is due to the pH at which magnesium is expected to precipitate as $Mg(OH)_2$ being greater than that used in the experiments (9.5 and 10.2). Chemical softening processes that are targeting magnesium are typically operated at a minimum pH of 11.0. [58] These results support the hypothesis that the model values are accurate and the assumption of 100% solids removal after precipitation is incorrect.The magnesium species are shown in the Table 4.8 as follow.

Table 4.8. Strontium species at pH 10.2.

Species	Total (mg/L)	Liquid (mg/L)	Solid (mg/L)
Magnesium carbonate	2.20627	2.20707	0
Magnesium bicarbonate ion(+1)	0.615867	0.616091	0
Magnesium ion(+2)	53.3682	53.3876	0
Magnesium hydroxide ion(+1)	0.130225	0.130272	0
Magnesium sulfate	0.119047	0.11909	0

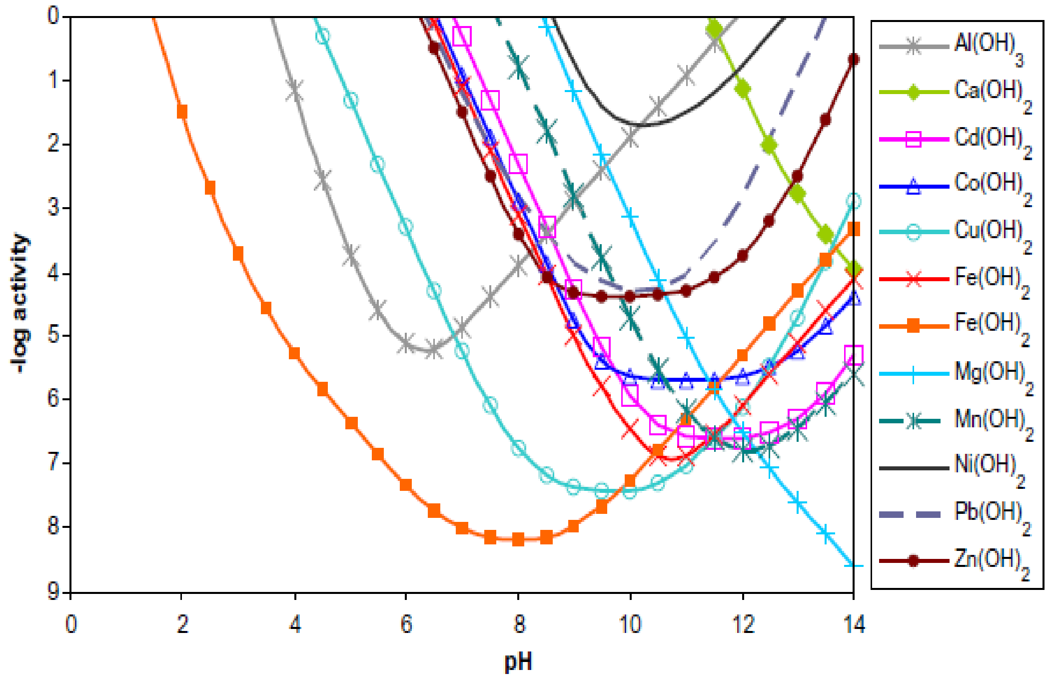


Figure 4.10. Hydroxide metal salt precipitation varies with pH.[59]

According to the comparison results, magnesium ions do not get removed when the streams go through the treatment. Based on the research, magnesium hydroxide starts to precipitate out from the system when pH is above 10 as shown in the following figure 4.10. The formation of settlement is magnesium hydroxide $Mg(OH)_2$ which is affected by pH easily.

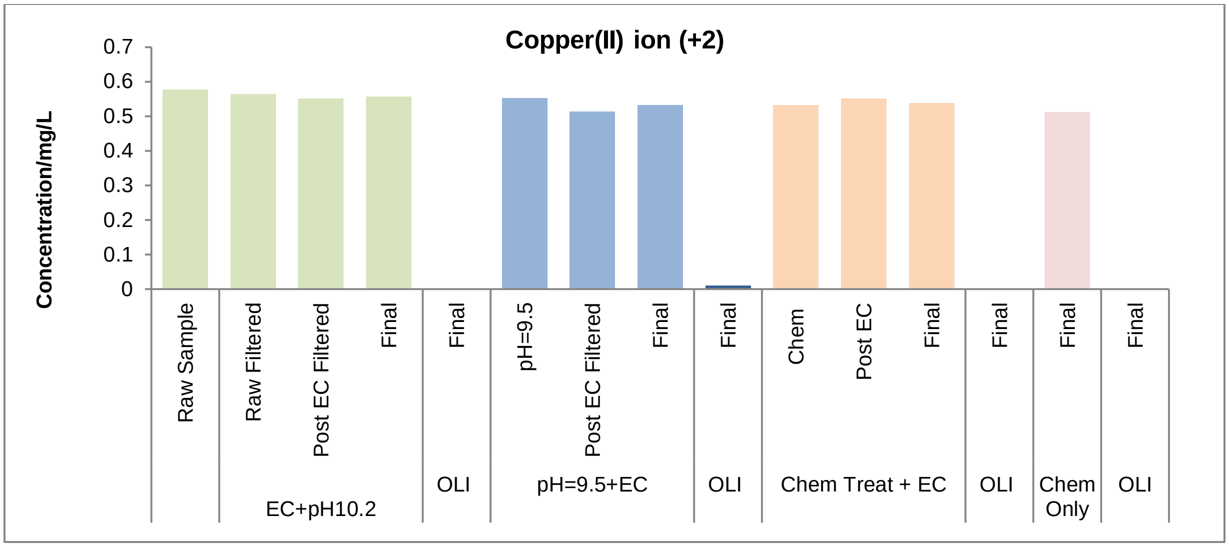


Figure 4.11. Copper_ comparison between experimental results and OLI Analyst modeling results.

In figure 4.11, bars of copper concentration value have been identified with different colors. The X-dimension has been divided into several sections. Experimental results are followed by OLI modeling results. The process of EC+ 10.2 stands for the experimental process of EC treatment. The following OLI final bar represents the modeling results as the EC only process. Most of copper ions get removed in the OLI modeling process. In the output table, the copper species would precipitate out as copper hydoxide shown as Table 4.9.

Table 4.9. Copper species at pH 10.2.

Species	Total (mg/L)	Liquid (mg/L)	Solid (mg/L)
Copper(II) chloride	6.38E-07	6.39E-07	0
Copper(II) trichloride ion(-1)	1.72E-09	1.72E-09	0
Copper(II) monochloride ion(+1)	2.65E-06	2.65E-06	0
Copper(II) dicarbonate ion(-2)	1.00E-03	1.00E-03	0
Copper(II) carbonate	9.33E-05	9.34E-05	0
Copper(II) hydroxide	0.844272	6.87E-05	0.845
Copper(II) trihydroxide ion(-1)	8.68E-04	8.68E-04	0
Copper(II) tetrahydroxide ion(-2)	6.04E-08	6.04E-08	0
Copper(II) monohydroxide ion(+1)	4.76E-06	4.77E-06	0

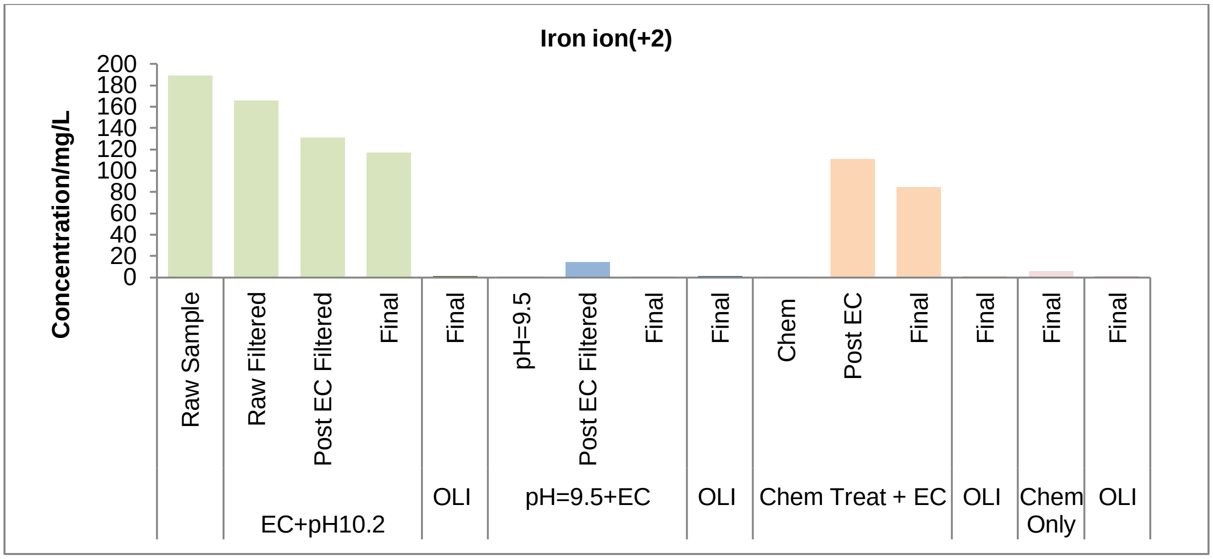


Figure 4.12. Iron_ comparison between experimental results and OLI Analyst modeling results.

In figure 4.12, bars of iron concentration value have been identified with different colors. The X-dimension has been divided into several sections. Experimental results are followed by OLI modeling results. The process of EC+ 10.2 stands for the experimental process of EC treatment. The following OLI final bar represents the modeling results as the EC only process. Iron ions get completely removed in the OLI modeling process In the output table, the iron species would precipitate out as iron carbonate shown as Table 4.10.

Table 4.10. Iron species at pH 10.2.

Species	Total (mg/L)	Liquid (mg/L)	Solids (mg/L)
Iron(II) chloride	3.13E-08	3.13E-08	0
Iron(II) monochloride ion(+1)	2.59E-05	2.59E-05	0
Iron(II) dicarbonate ion(-2)	0.016988	0.016994	0
Iron(II) carbonate	270.981	0.842287	270.237
Iron(II) bicarbonate ion(+1)	3.37E-06	3.38E-06	0
Iron ion(+2)	0.205463	0.205537	0
Iron(II) monohydroxide ion(+1)	0.153709	0.153764	0
Iron(II) oxide	1.25E-03	1.25E-03	0

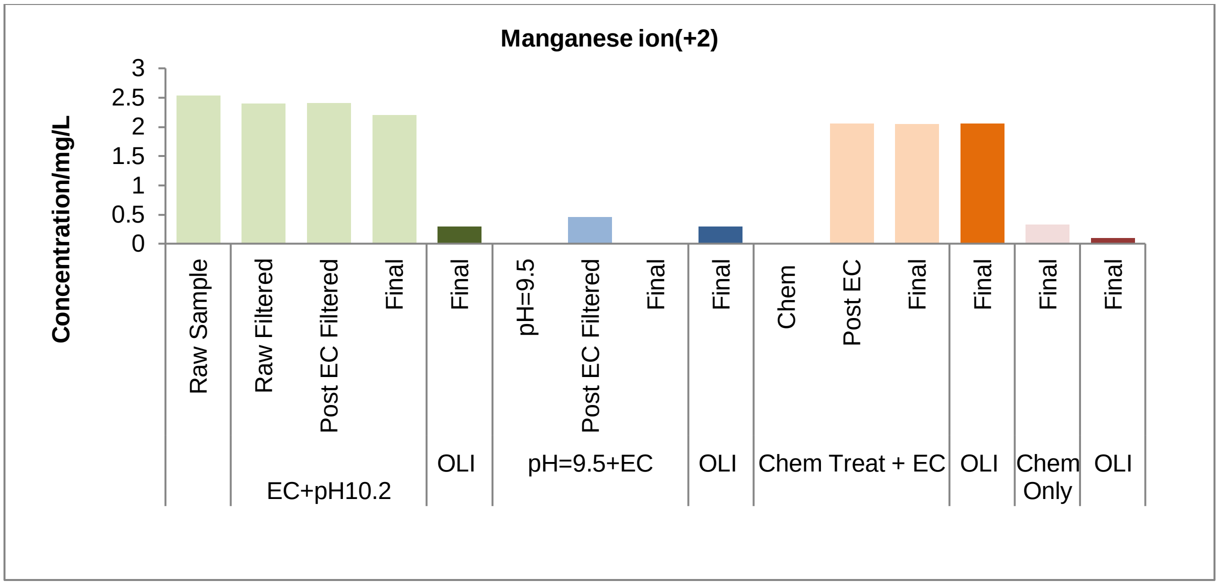


Figure 4.13. Manganese_ comparison between experimental results and OLI Analyst modeling results.

In figure 4.13, bars of manganese concentration value have been identified with different colors. The X-dimension has been divided into several sections. Experimental results are followed by OLI modeling results. The process of EC+ 10.2 stands for the experimental process of EC treatment. The following OLI final bar represents the modeling results as the EC only process. Maganese ions get completely removed in the OLI modeling process In the output table, the maganese species would precipitate out as manganese carbonate shown as Table 4.11.

Table 4.11. Maganese species at pH 10.2.

Species	Total (mg/L)	Liquid (mg/L)	Solid (mg/L)
Manganese(II) hydroxide	2.05E-05	2.05E-05	0
Manganese(II) trihydroxide ion(-1)	4.13E-08	4.13E-08	0
Manganese(II) tetrahydroxide ion(-2)	3.35E-11	3.35E-11	0
Manganese(II) monohydroxide ion (+1)	7.41E-03	7.41E-03	0
Manganese(II) sulfate	9.41E-04	9.42E-04	0
Manganese(II) carbonate	4.41365	0	4.41525

The comparisons indicate that there exist differences on the metal ions in aqueous phase. The removal ratio in the lab experiments is distinguished from the results of OLI chemical analyst Modeling Process under ideal conditions. According to the OLI chemical analyst results, most of the target species could be removed efficiently, such as barium, calcium, copper, iron, manganese, strontium.

4.3 Comparison between 0.2 Micron and 2.5 Micron Membrane Filter

When a comparison is done between the bench scale experiments and OLI modeling, significant differences are observed with some of the cations. The hypothesis is that the metals are being precipitated but not being removed due to insufficient coagulation, flocculation and subsequent solid-liquid separation. To test this theory, additional tests were conducted by filtering the treatment effluent with two filters sizes, 0.2 and 2.5 μm. The purpose of the smaller filter size is to remove smaller solids that may not be aggregating to larger sizes.

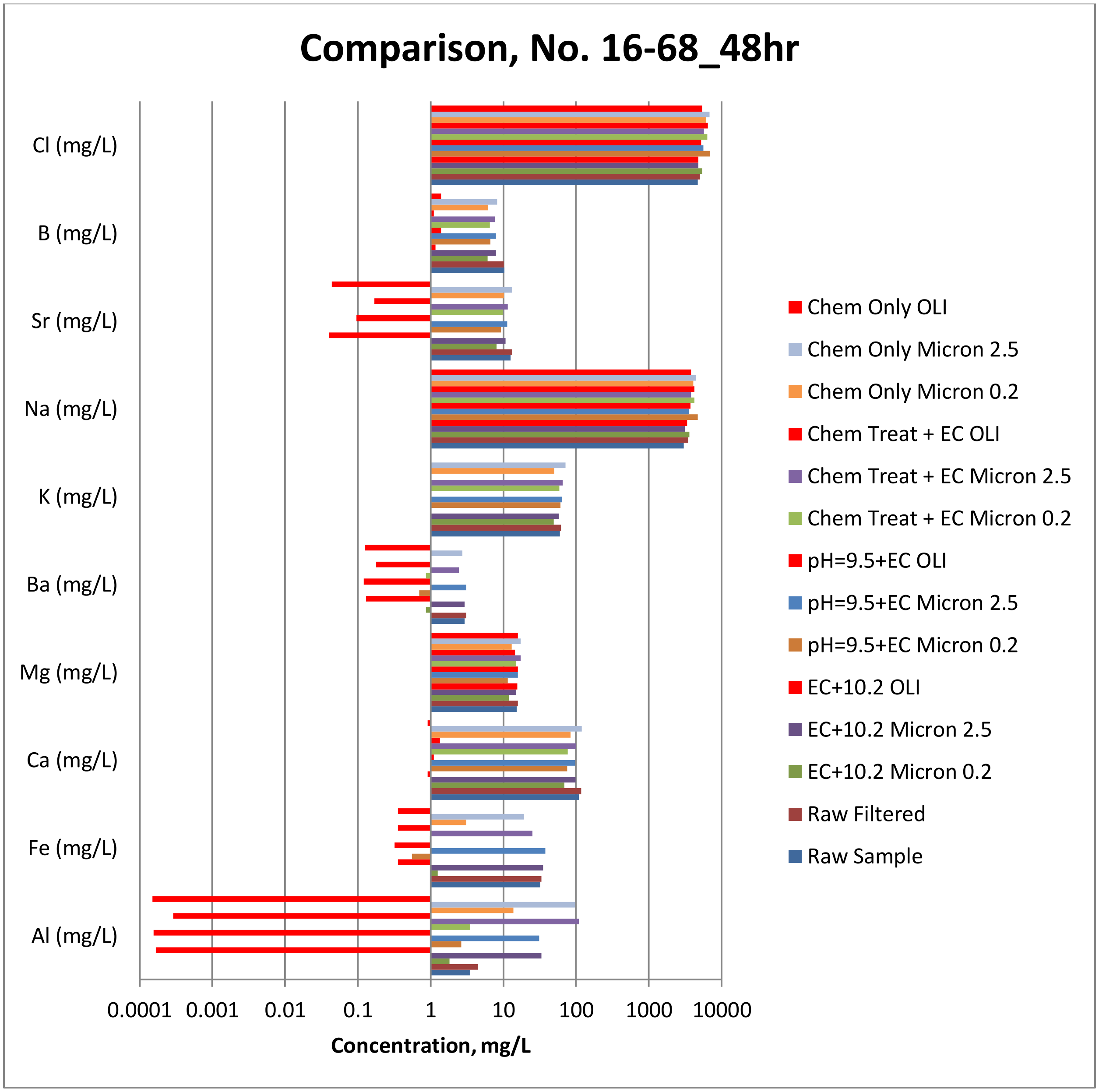


Figure 4.14. Comparison between filtration membrane size 2.5 micron and 0.2 micron.

As shown in Figure 4.14, some of the ions are predicted to precipitate completely but the observed removal results indicate that the solids have not been removed effectively. The commercial treatment process that is being simulated uses pressure sand filters that are effective with adequate coagulation and flocculation.

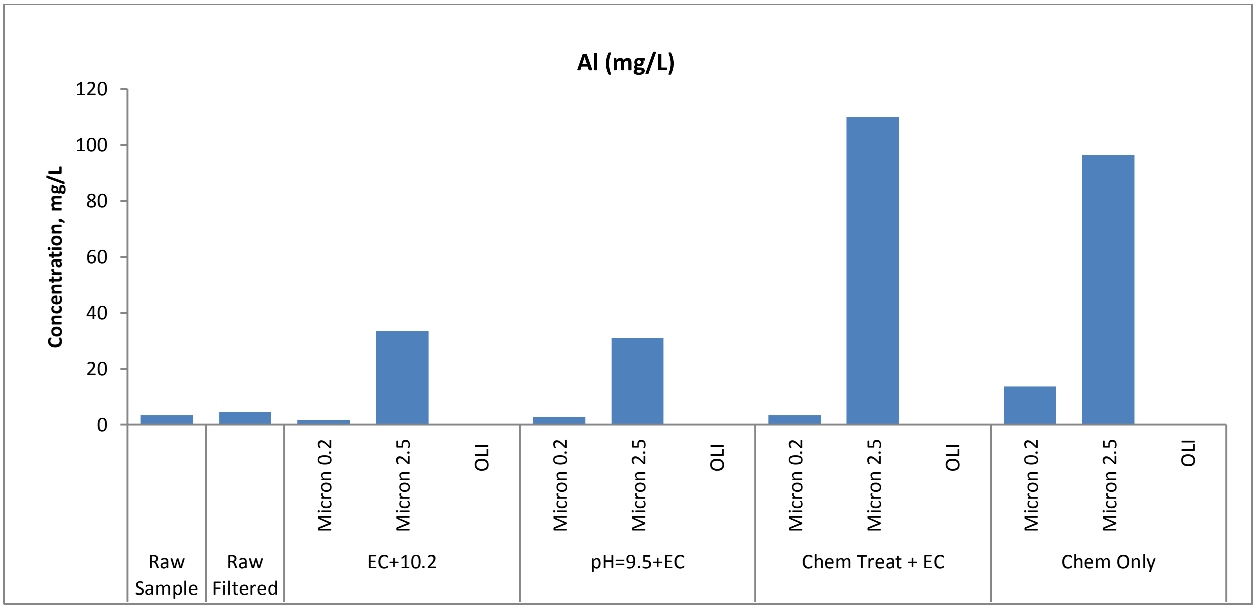


Figure 4.15. Aluminum_filtration performance: the comparison between 0.2 micron and 2.5 micron of well No.16-68.

The aluminum removal with varying filter sizes is shown in Figure 4.15. The data is not clear but in general colloidal Al less than 0.2 μm appears to be constant at about 1.0-1.5 mg/L.

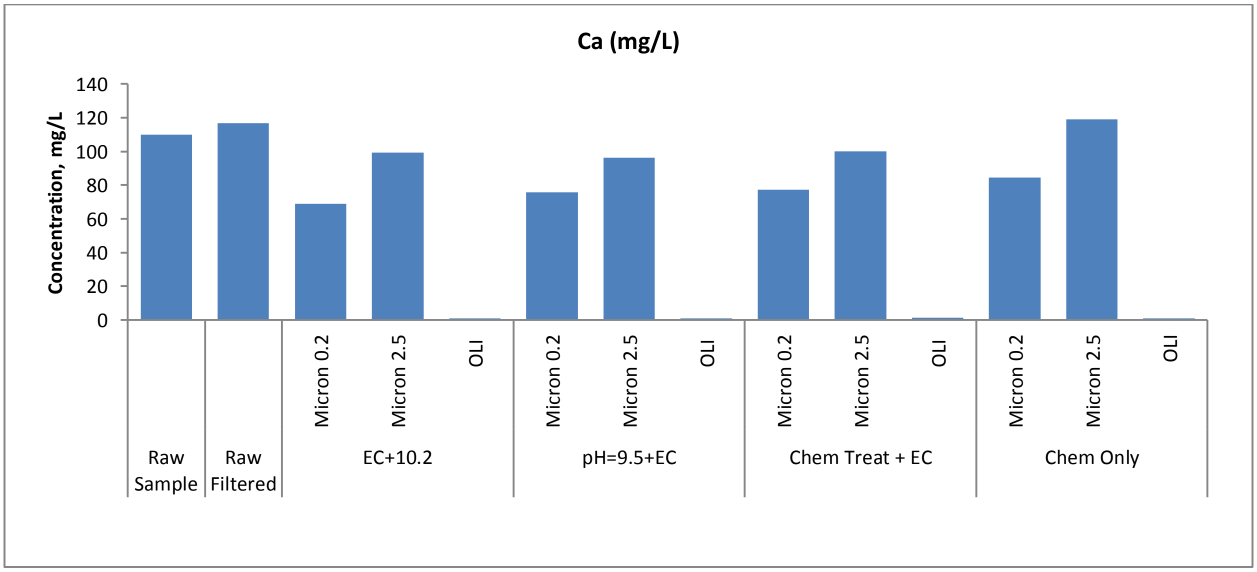


Figure 4.16. Calcium_filtration performance: comparison between 0.2 micron and 2.5 micron of well No.16-68.

Figure 4.16 shows that calcium ions removal is slightly improved with finer membrane size of 0.2 micron membrane filtration. OLI prediction is based on the hypothesis of 100% solids removal. The treatment performance is optimized with a finer filtration process.

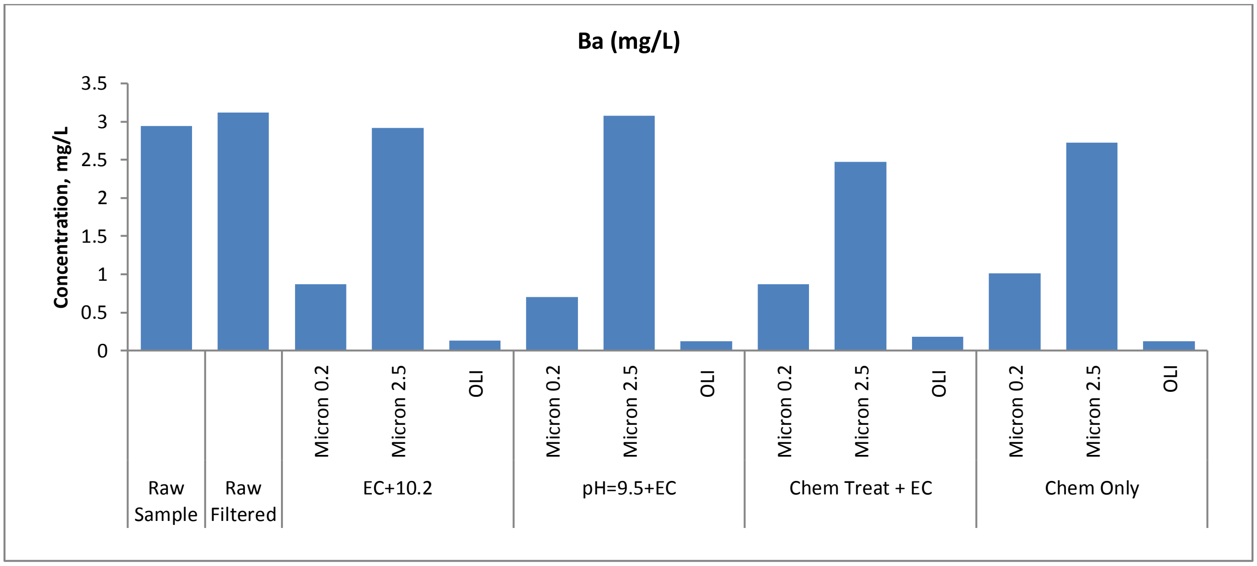


Figure 4.17. Barium _filtration performance: the comparison between 0.2 micron and 2.5 micron of well No.16-68.

Figure 4.17 shows that barium ions removal is slightly improved with finer membrane size of 0.2 micron membrane filtration. The treatment performance is optimized with a finer filtration process. Barium sulfate removal performance gets improved in each treatment methods. In the precipitants, barium sulfate is the specie that does not get affected by pH adjustment. In the following research, the results also show barium ions are also not affected by temperature adjustment.

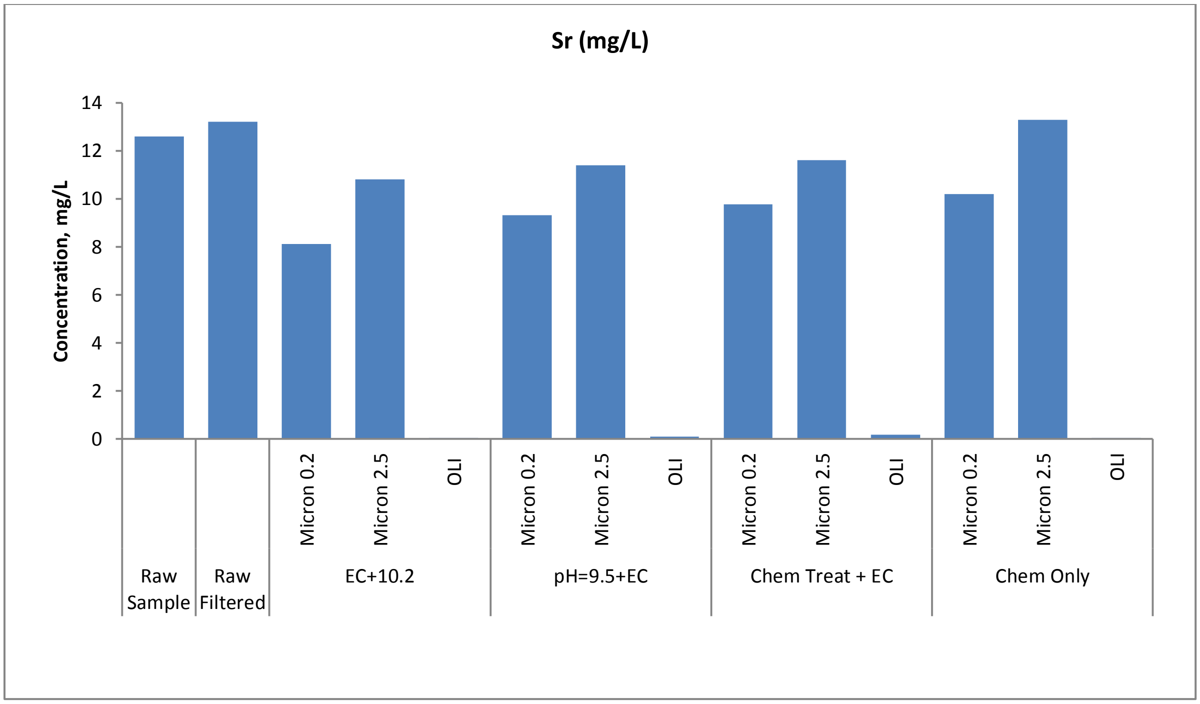


Figure 4.18. Strontium _filtration performance: the comparison between 0.2 micron and 2.5 micron of well No.16-68.

Figure 4.18 shows that strontium ions removal is slightly improved with finer membrane size of 0.2 micron membrane filtration. OLI prediction is based on the hypothesis of 100% solids removal. The treatment performance is optimized with a finer filtration process.

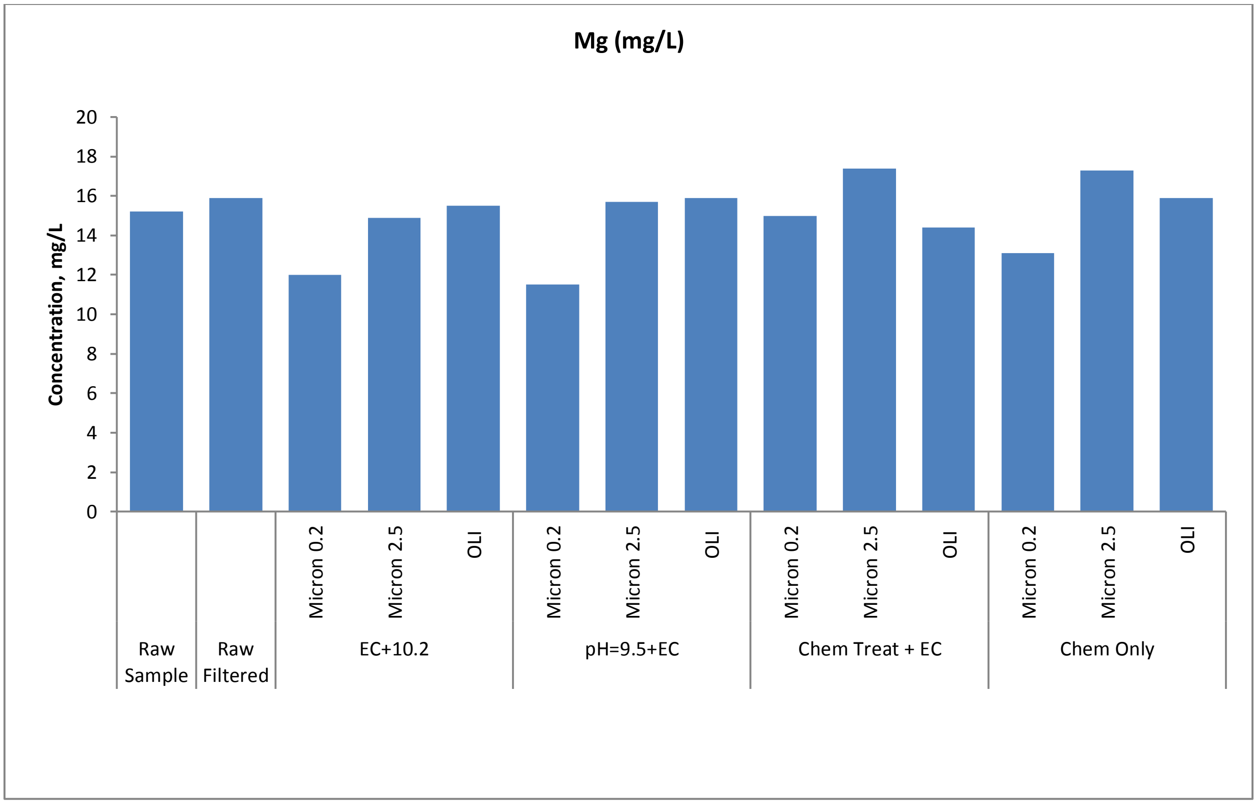


Figure 4.19. Magnesium _filtration performance: the comparison between 0.2 micron and 2.5 micron.

Figure 4.19 shows that magnesium ions removal is not improved with finer membrane size of 0.2 micron membrane filtration. According to the comparison results, magnesium ions do not get removed when the streams go through the treatment. Based on the research, magnesium hydroxide starts to precipitate out from the system when pH is above 10.

The finer filtration membrane cannot improve the removal efficiency of magnesium ions. OLI predictions still much less than 0.2um filter. Smaller filter size is more effective with EC+10.2 indicating that this treatment may result in a greater fraction of solids that between 0.2 and 2.5 um. Chem only seems to be less effective at removing particles of all sizes with filtration.

The pH 9.5/EC process seems to always be better than the EC+10.2 when using a filter size of 2.5 um but they are approximately the same with a filter size of 9.5. Magnesium removal is not impacted by filter size and in general is less because of the lack of precipitation at the lower pH values.

Commonly, industry use sand bed process to filter the precipitants and the settlements that formed in the softening treatments. Because the filtration efficiency cannot be estimated precisely, CSU Energy and Water Sustainability Group uses 2.5 micron membrane as the filtration process in the bench scale experiments. According to the laboratory observations, the softening performance of the bench scale experiments cannot meet the OLI chemical analyst modeling expectations. Finer membrane of size 0.2 micron is used. And the test results demonstrate that finer membrane can improve the target compounds removal efficiency. And the performance of the treatment is optimized.

4.4 Temperature – Precipitation

According to observation on wells No. 16-68 and No.16-69, the output of OLI chemical analyst modeling shows the different precipitants are generated and most of the ions cannot be removed efficiently, such as calcium and iron. These produced water samples are collected in the winter; the temperature is below the freezing point. Figure 4.20 shows the modeling results of well No. 16-68 at 16.7 ^{o}F.

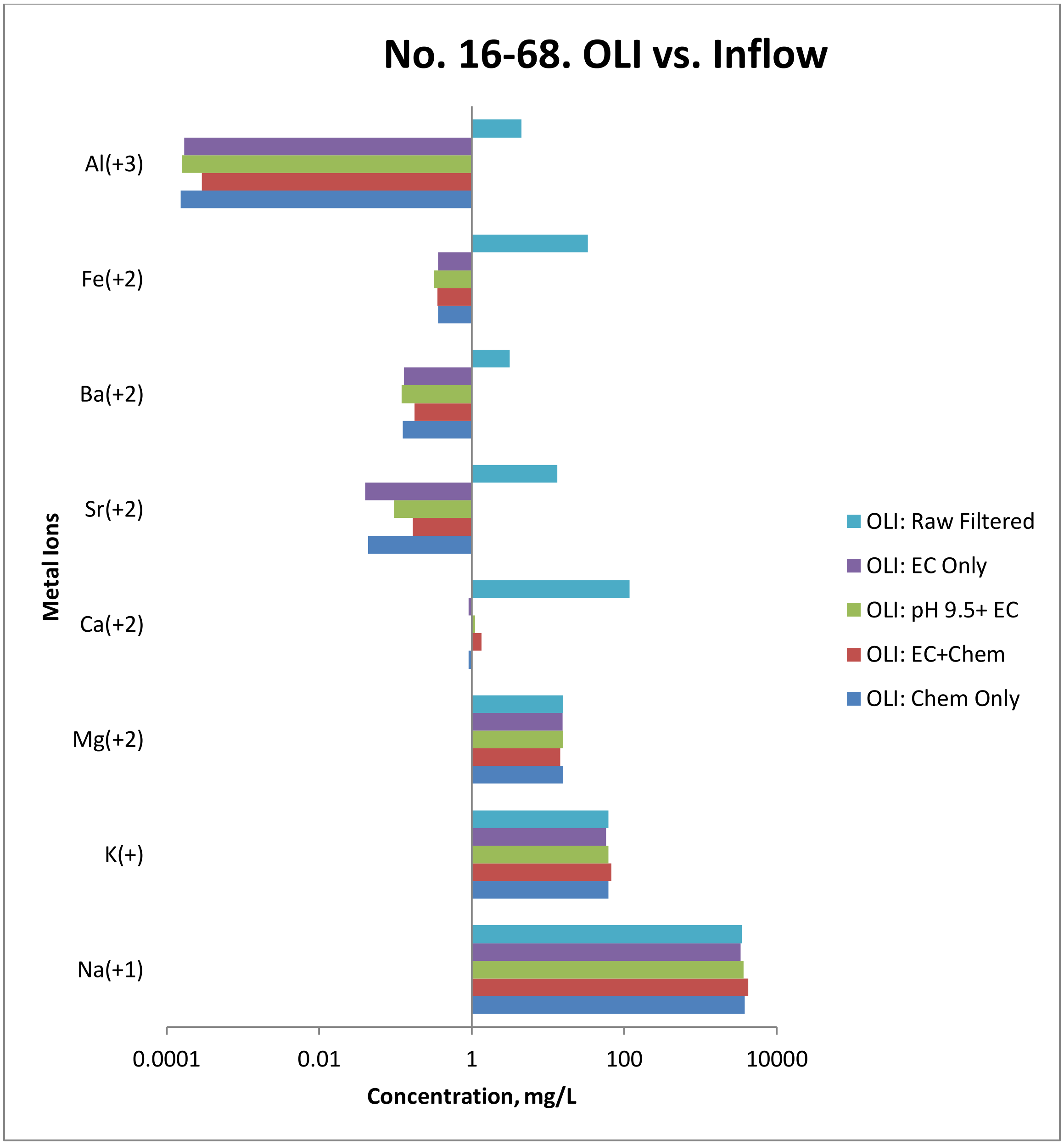


Figure 4.20. Well No.16-68_This well operated at the temperature of -8.5 ^{o}C.

According to figure 4.20, the results from OLI indicate that aluminum, barium, and strontium ions can be efficiently removed. According to the comparisons, OLI analyst prediction is based on 100% solids removal ratio in the filtration process. Ions, such as calcium and iron, are supposed to precipitate more from the system.

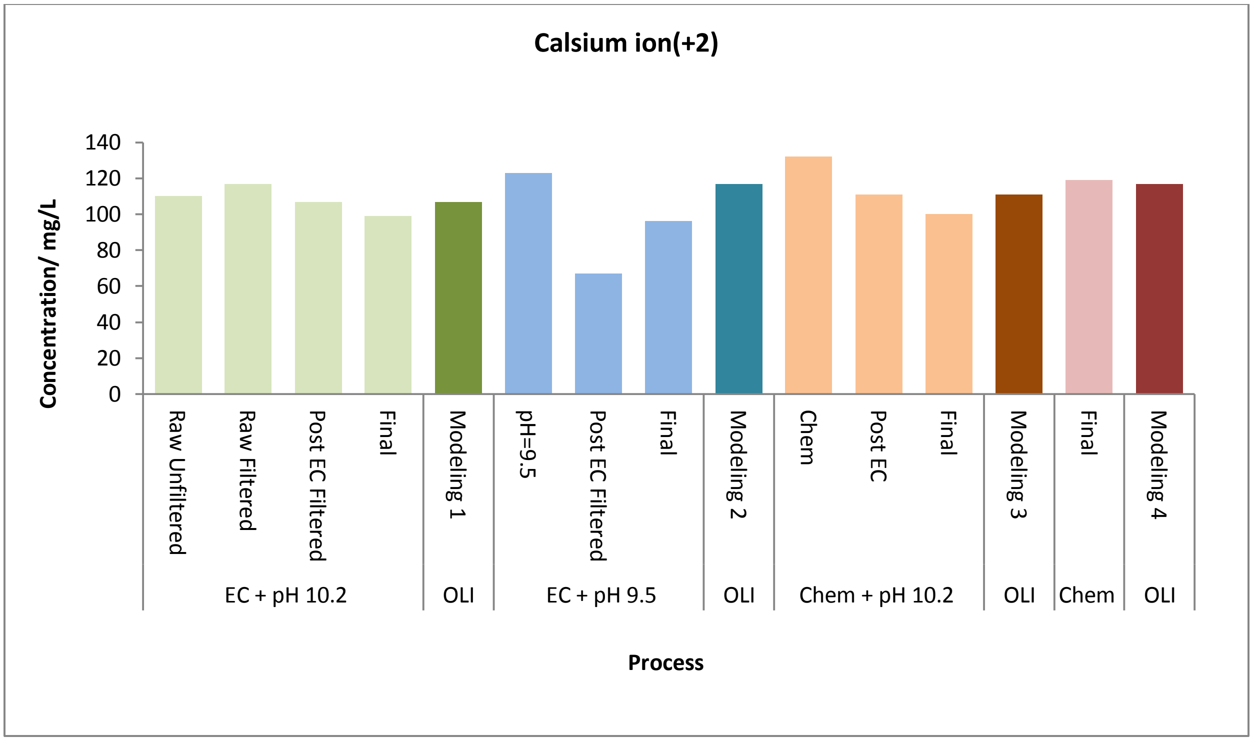


Figure 4.21. Calcium_ comparison between experimental results and OLI analyst modeling results -8.5 °C.

In figure 4.21, bars of calcium concentration value have been identified with different colors. The X-axis has been divided into several sections. Experimental results are followed by OLI modeling results. The process of EC+ 10.2 stands for the experimental process of EC treatment. The following OLI final bar represents the modeling results as the EC only process. Figure 4.21 indicates that calcium ions existing in the liquid phase does not get removed efficiently as other wells. The concentration of calcium ions stays same as the inflow water samples. According to the output of the OLI chemical analyst modeling, calcium carbonate dissoves in the liquid phase rather than precipitate out from the system.

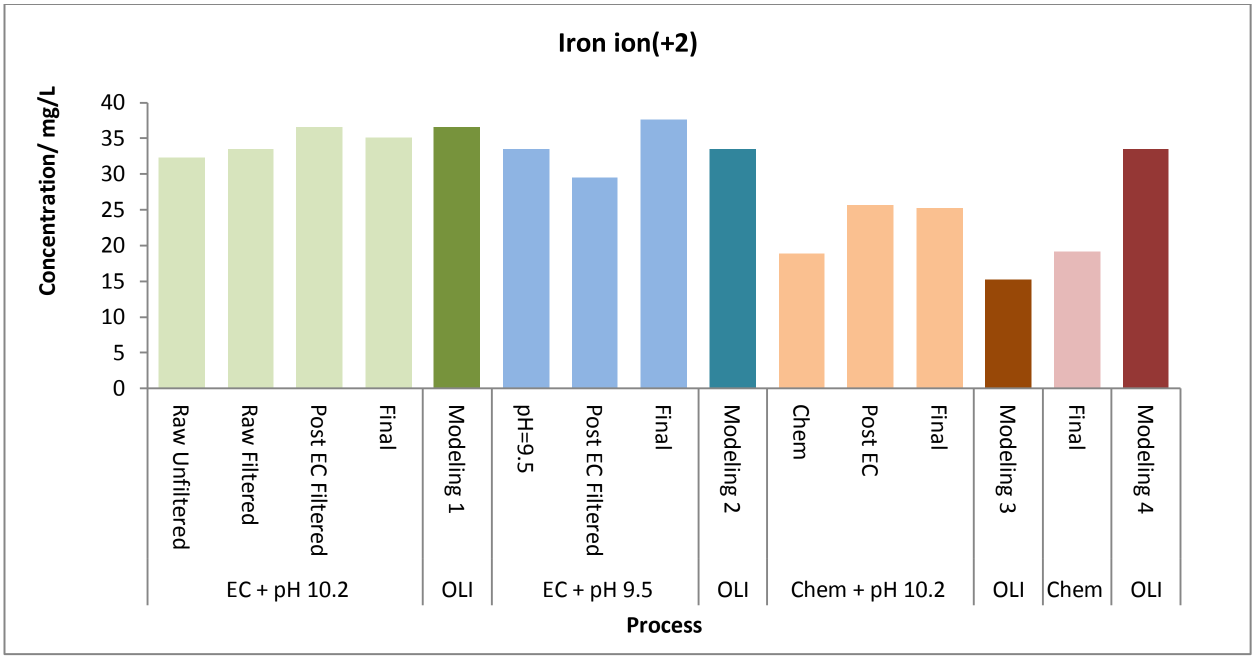


Figure 4.22. Iron_ comparison between experimental results and OLI analyst modeling results - 8.5 ^{o}C.

In figure 4.22, bars of iron concentration value have been identified with different colors. The X-dimension has been divided into several sections. Experimental results are followed by OLI modeling results. The process of EC+ 10.2 stands for the experimental process of EC treatment. The following OLI final bar represents the modeling results as the EC only process. Iron ions cannot get removed at temperature -8.5 ^{o}C.

Compared to the experimental results, the OLI prediction on metal ions removal is different from the lab. The experimental results that took in the lab show, that with 2.5 micron membrane filtration, the calcium and iron ions have not been removed as efficiently as expected. OLI modeling for the EC only process shows that the calcium was not reduced as ferrous ions were reduced. As the temperature outside can be less than 0 degree C, the solubility of salts in aqueous phase obeys the rules below:

$$\Delta G^0_{\mathrm{so\ In}} = -\mathrm{RTln}\left(\mathrm{K_{sp}}\right) = \Delta H^0_{\mathrm{soln}} - \mathrm{T}\Delta S^0_{\mathrm{soln}} \qquad (1)$$

According to this equation 1, temperature (T) can be one parameter that affects precipitation in the treatment system. The solubility decreases under the lower temperature. Since field treatment units operate outdoors, the temperature can potentially impact precipitation. Apparently, the treatment processes are always affected by temperature, especially when the winter temperatures in Colorado can be as low as -20 ^{o}C. In order to identify how the temperature would affect the treatment, OLI analyst is used to predict No. 16-68 work under different temperatures.

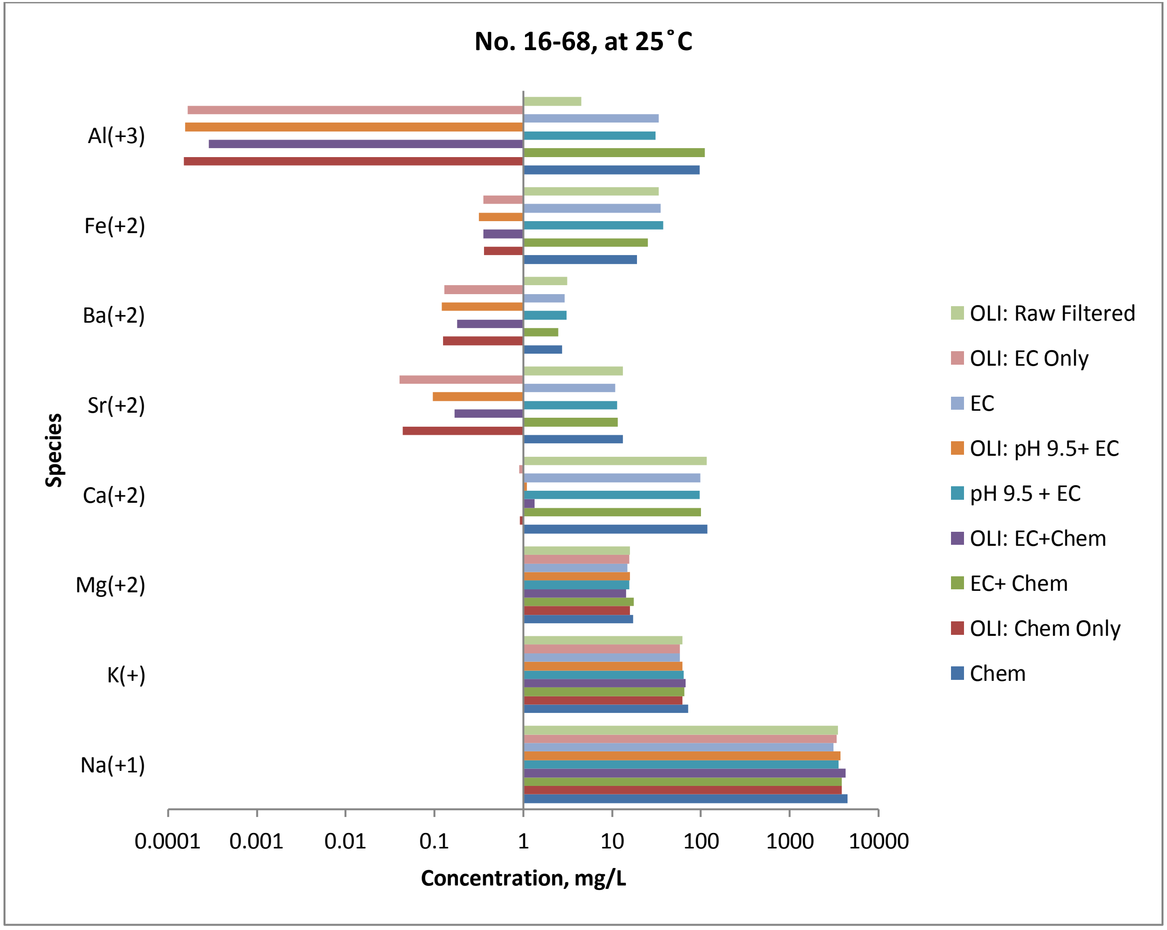


Figure 4.23. OLI modeling results of well No.16-68 at 25^{o}C.

Figure 4.23 shows that iron and calcium ions are precipitated out from the system more than the other. The OLI analyst prediction demonstrates that the treatments are more efficient when the temperature is adjusted to 25°C. Besides sodium ions, the sodium does not get removed as much as under lower temperatures. Figure 4.24 demonstrates comparisons between inflow water quality and OLI output results at 25°C of well No. 16-68 as following.

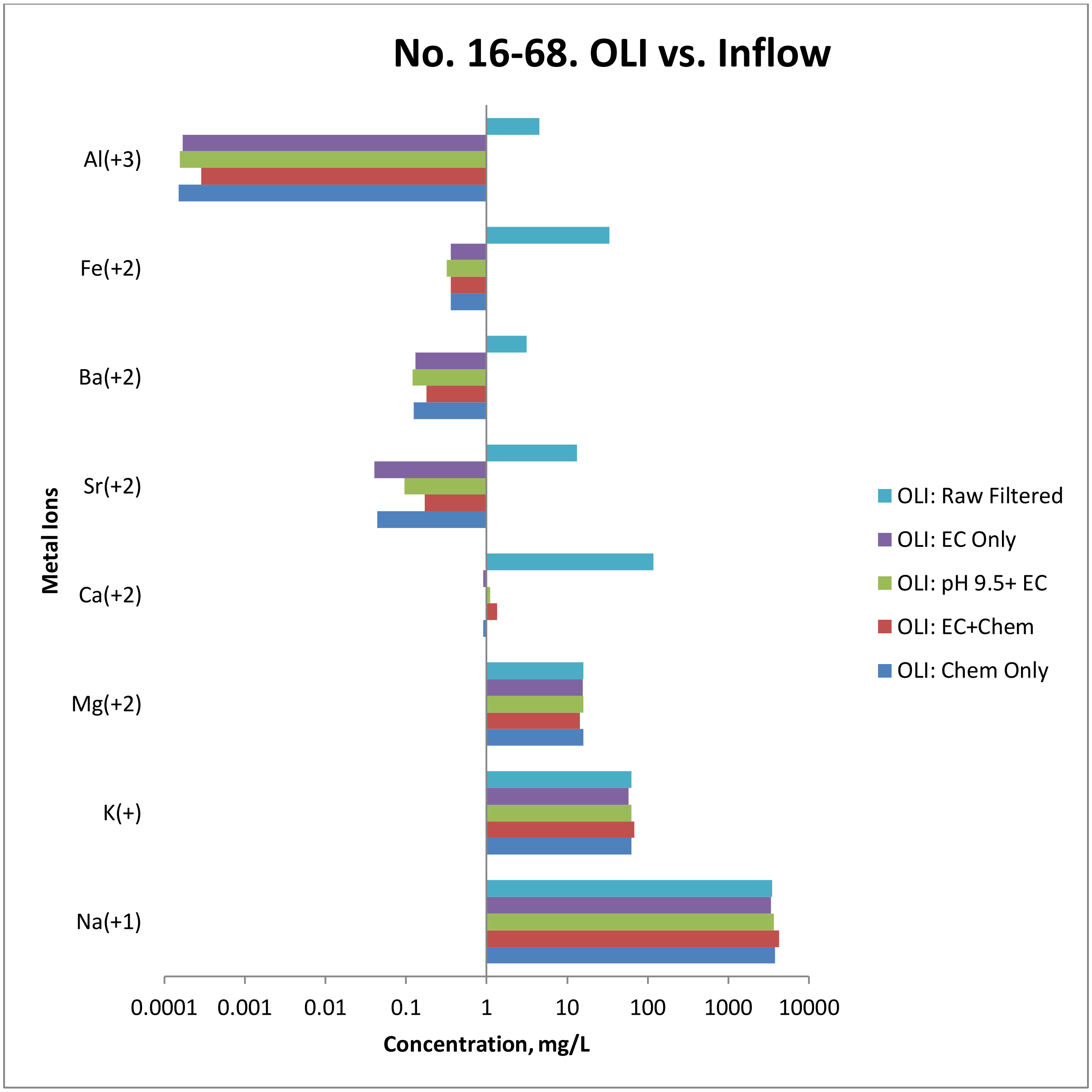


Figure 4.24. No. 16-68 comparisons between inflow water quality and OLI output results at 25°C.

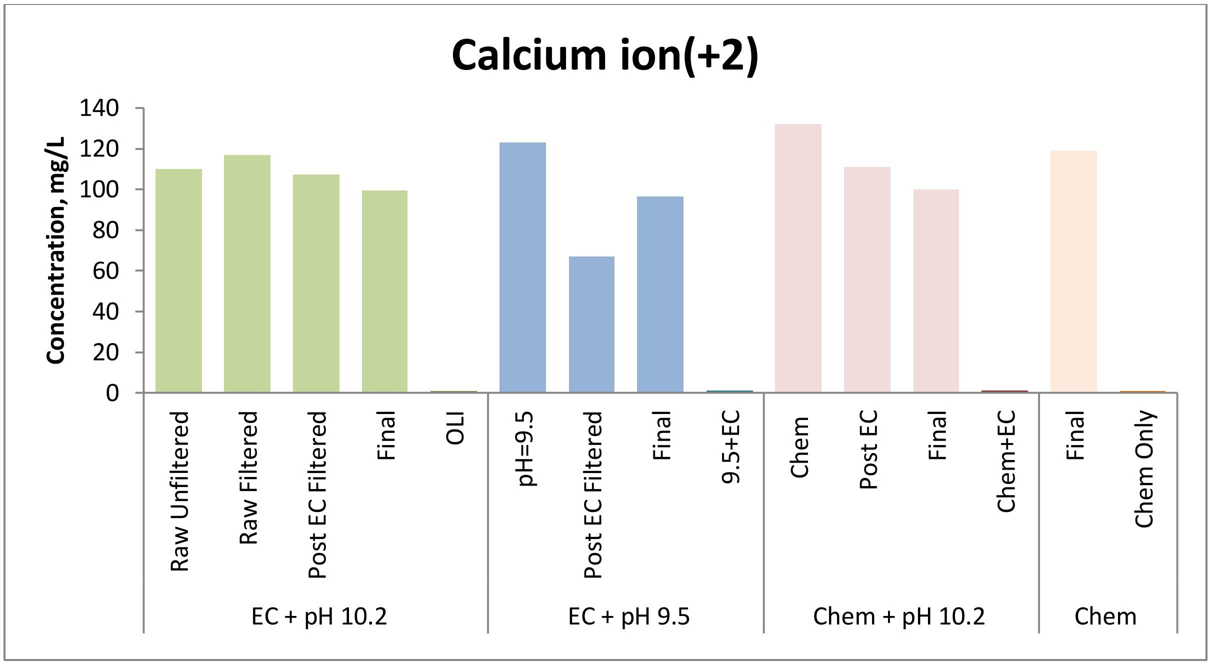


Figure 4.25. Calcium_ comparison between experimental results and OLI analyst modeling results at 25°C.

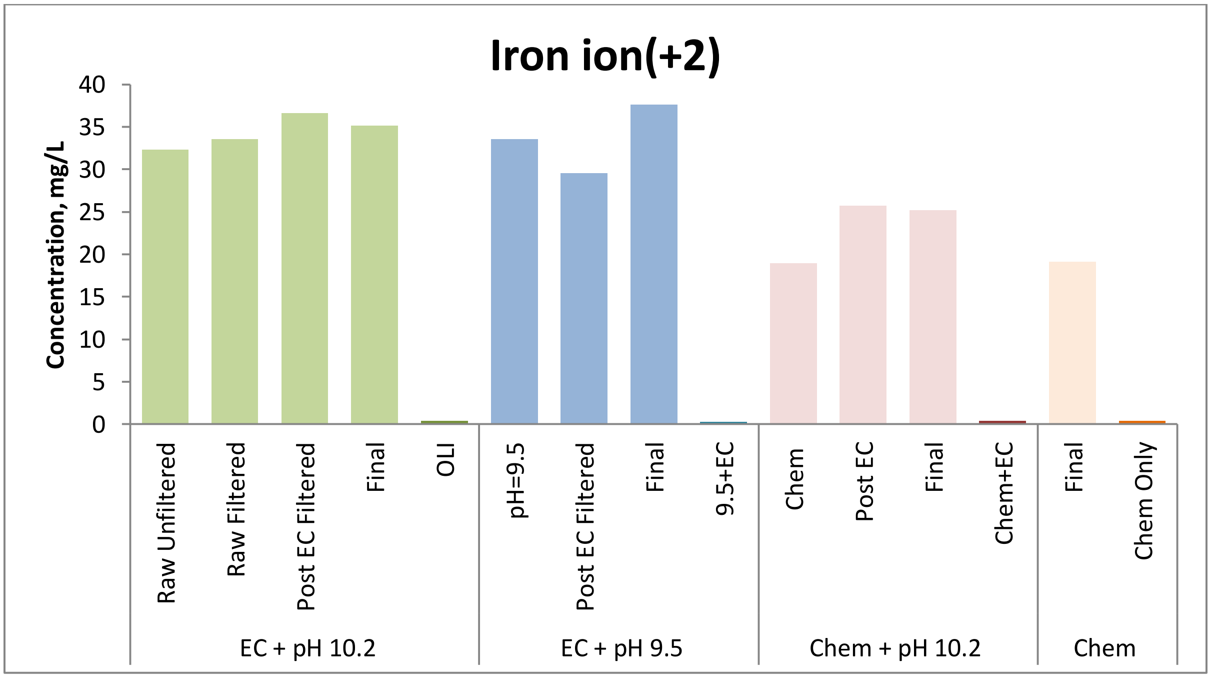


Figure 4.26. Iron_ comparison between experimental results and OLI analyst modeling results at 25°C.

Figure 4.25 and figure 4.26 shows the performance of Calcium and iron ions removal individually, when the temperature is adjusted to 25 °C. These results indicate that the removal treatment can be optimized if the temperature is increased.

The results show that, at 25 °C, the removal of Calcium ions and ferrous ions changed according to the equation prediction. Temperature could be a factor that affects solubility constant of species that exist in the stream. In order to figure out how the temperature would affect precipitation in the treatment, OLI analyst adjusted the temperature from -15 °C to 30 °C in the analysis.

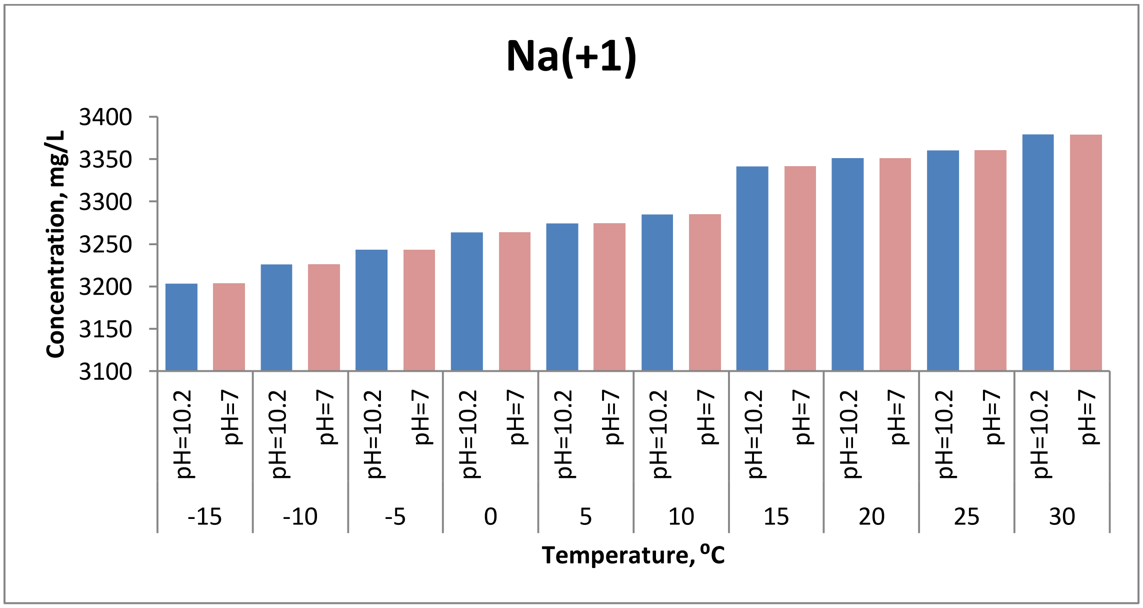


Figure 4.27. Sodium ions OLI modeling concentration – temperature adjustment.

When the temperature increases, the concentration of sodium ions existing in the aqueous phase also increases. The reason for the increasing concentration is related to the salts that sodium forms. When the temperature is above 15°C, the sodium salts are all soluble in the aqueous phase. Consider the species that contain sodium as follow:

Table 4.12. The species of sodium form in the aqueous phase above 15°C.

Species	Phase
Sodium boron hydroxide	Liquid
Sodium carbonate ion(-1)	Liquid
Sodium bicarbonate	Liquid
Sodium ion(+1)	Liquid
Sodium sulfate ion(-1)	Liquid

When the temperature is below 10 °C, the sodium would precipitate similar to the salt of sodium aluminum di-hydroxide carbonate. And sodium aluminum di-hydroxide carbonate would precipitate out from the aqueous phase.

Table 4.13. The species of sodium form in the aqueous phase below 10°C.

Species	Phase
Sodium boron hydroxide	Liquid
Sodium carbonate ion(-1)	Liquid
Sodium bicarbonate	Liquid
Sodium ion(+1)	Liquid
Sodium sulfate ion(-1)	Liquid

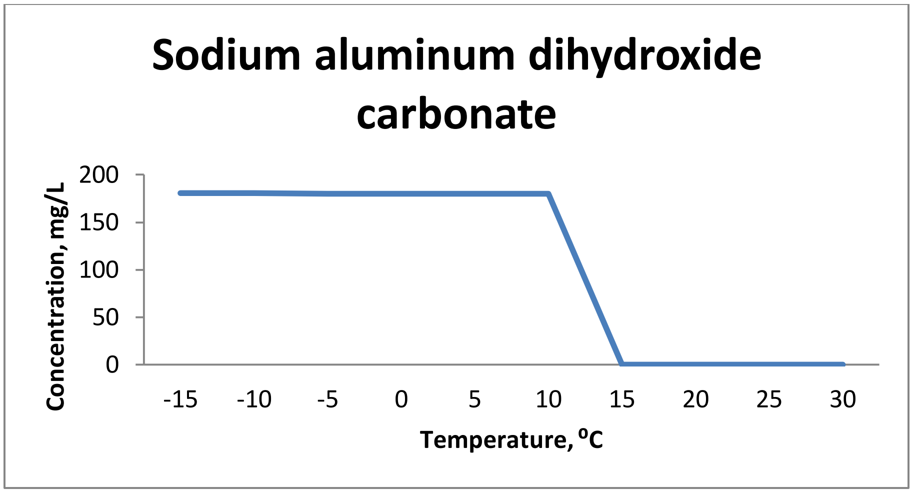


Figure 4.28. Sodium aluminum dihydroxide carbonate precipitation – temperature adjustment.

According to figure 4.28 of sodium ions, the low temperature would be a factor that affects the sodium precipitating from the system. Sodium aluminum di-hydroxide carbonate can only form below 10°C. During Colorado winter, the cold weather could lead to more sodium precipitating from the system.

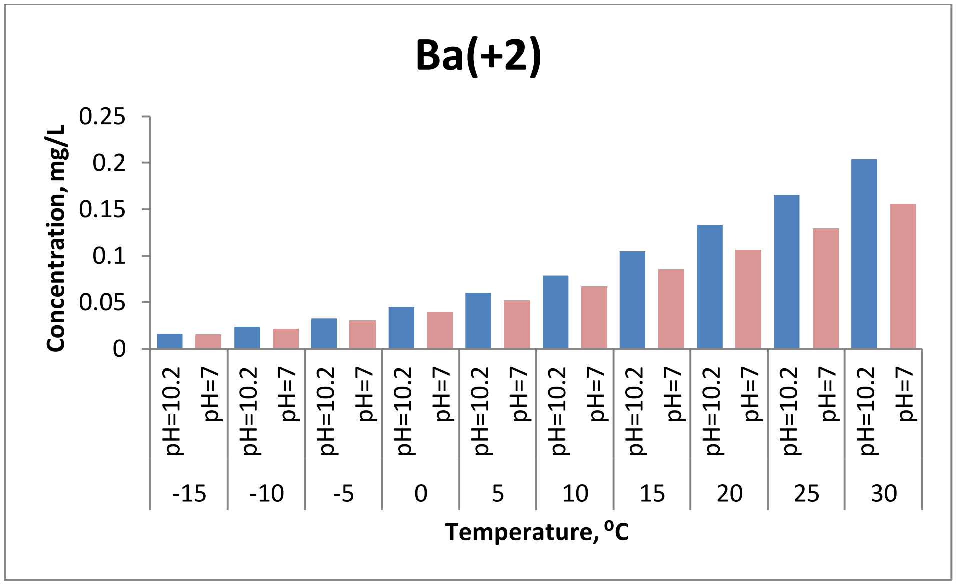


Figure 4.29. Barium ions OLI modeling concentration – temperature adjustment.

The amount of precipitated barium salt decreases as temperature increases. Most of the barium salts are dissolved in the stream. Barium sulfate is the main form that precipitates from the aqueous phase. The species that contain barium are shown below.

Table 4.14. The species of barium form in the stream.

Species	Phase
Barium chloride ion (+1)	Liquid
Barium carbonate	Liquid
Barium bicarbonate ion(+1)	Liquid
Barium ion(+2)	Liquid
Barium hydroxide ion(+1)	Liquid
Barium sulfate	Solids

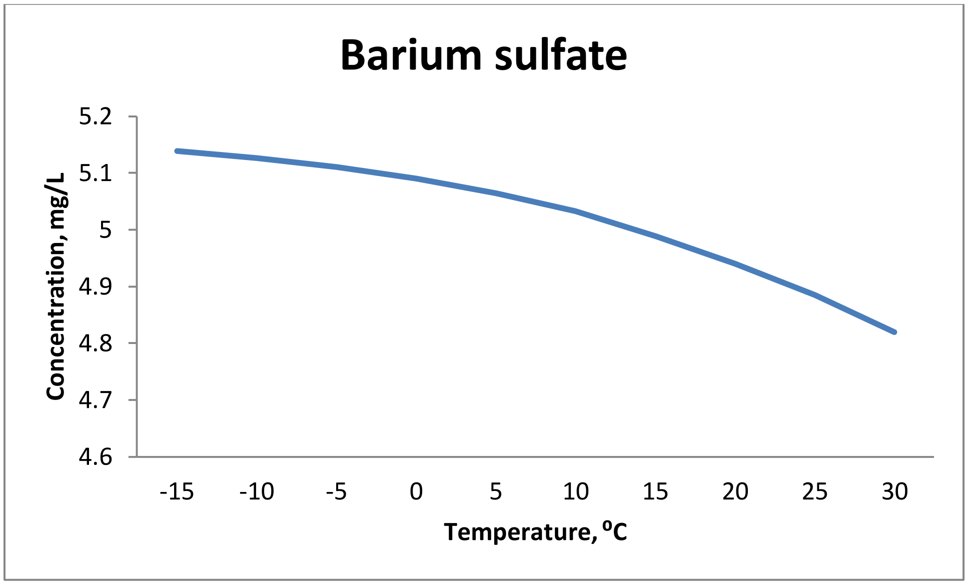


Figure 4.30. Barium sulfate precipitation – temperature adjustment.

Figure 4.30 indicates that, the amount of barium sulfate settlements decrease as the temperature increases. The high temperature can be one factor that limits the barium ions precipitation from the aqueous phase. The temperature in summer can be as high as 37 °C in Colorado, which could lead to a less efficient treatment for barium removal.

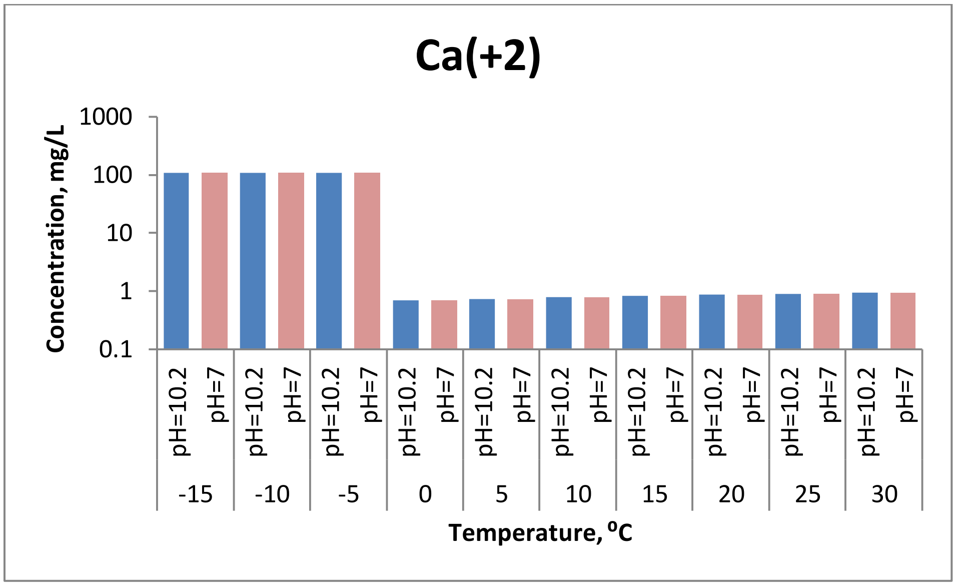


Figure 4.31. Calcium ions OLI modeling concentration – temperature adjustment.

Figure 4.31 indicates what happens to most of the calcium ions when temperature is adjusted above 0°C. Because the prediction is based on the hypothesis that the stream will not freeze, the OLI analyst modeling demonstrates that there is calcium carbonate forming in the aqueous phase. And the calcium carbonate is soluble in the aqueous phase. The species that existing in the aqueous phase, are as shown in Table 4.15.

Table 4.15. The species of calcium form in the stream.

Species	Phase
Calcium chloride	Liquid
Calcium monochloride ion(+1)	Liquid
Calcium carbonate (calcite)	Liquid/solids
Calcium dihydrogen borate ion(+1)	Liquid
Calcium bicarbonate ion(+1)	Liquid
Calcium ion(+2)	Liquid
Calcium hydroxide ion(+1)	Liquid
Calcium sulfate	Liquid

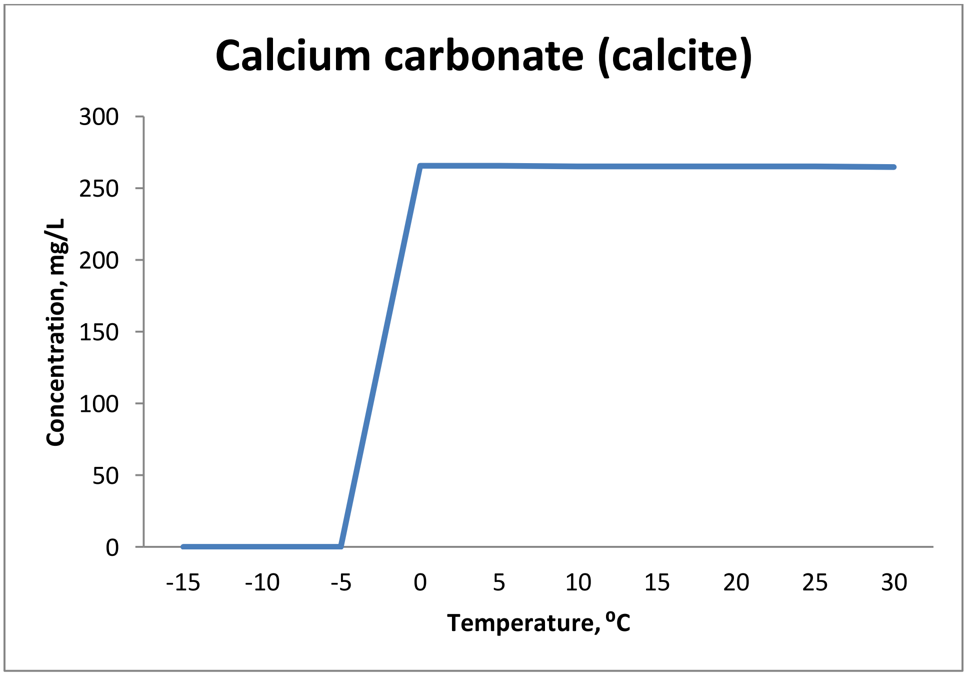


Figure 4.32. Calcite precipitation – temperature adjustment.

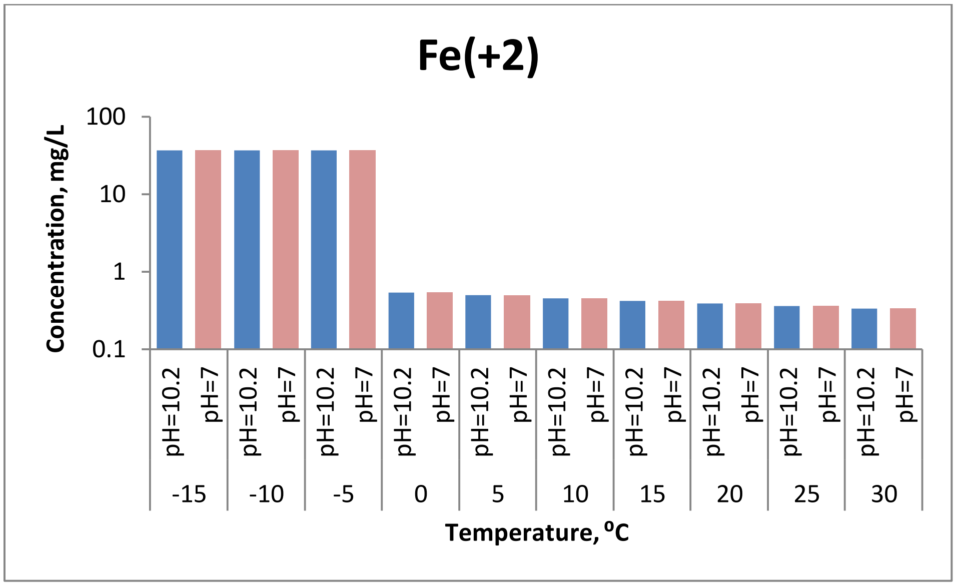


Figure 4.33. Calcium ions OLI modeling concentration – temperature adjustment**.**

The results of ferrous irons are predicted to be the same as calcium ions. The iron carbonate is the main settlement that precipitates iron ions from the aqueous.

Table 4.16. The species of iron salts in the stream.

Species	Phase
Iron(II) chloride	Liquid
Iron(II) monochloride ion(+1)	Liquid
Iron(II) dicarbonate ion(-2)	Liquid
Iron(II) carbonate	Liquid/Solids
Iron(II) bicarbonate ion(+1)	Liquid
Iron(II) monohydroxide ion(+1)	Liquid
Iron(II) oxide	Liquid

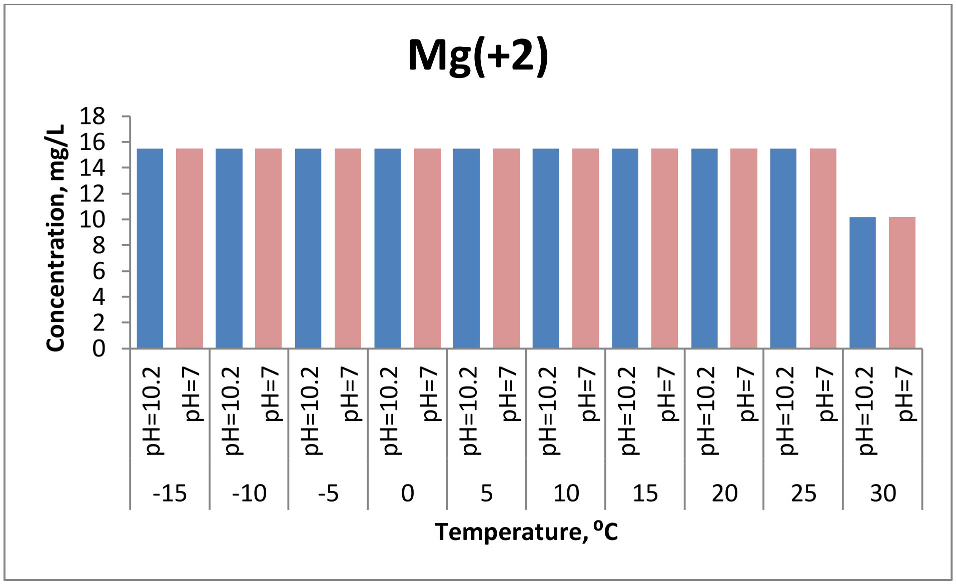


Figure 4.34. Magnesium ions OLI modeling concentration – temperature adjustment.

The magnesium ions are clearly affected by pH. When pH is adjusted to 12, the magnesium precipitates out from the stream. The OLI analyst prediction indicates that if the temperature is over 30°C, the magnesium ions would precipitate as the form of Magnesium hydroxide.

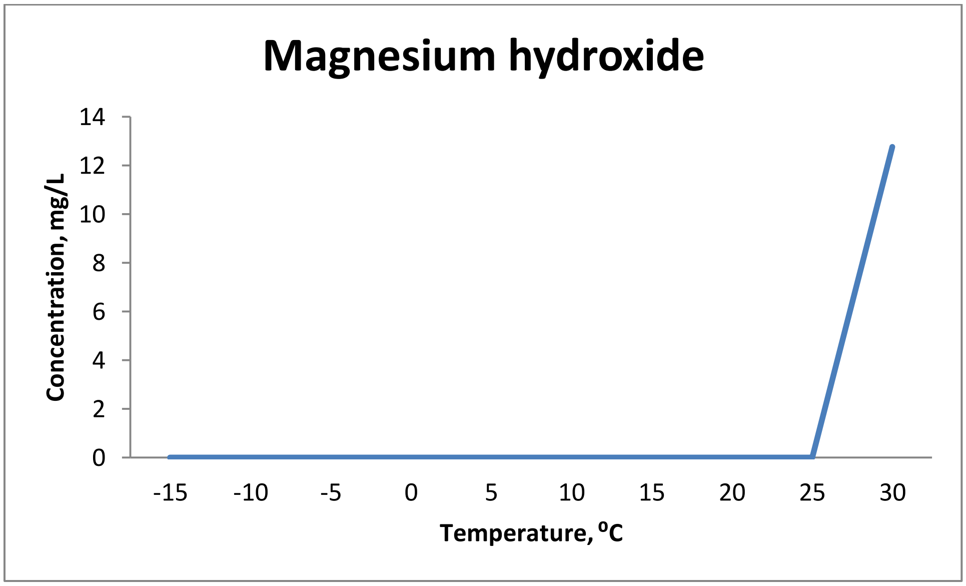


Figure 4.35. Magnesium hydroxide precipitation – temperature adjustment.

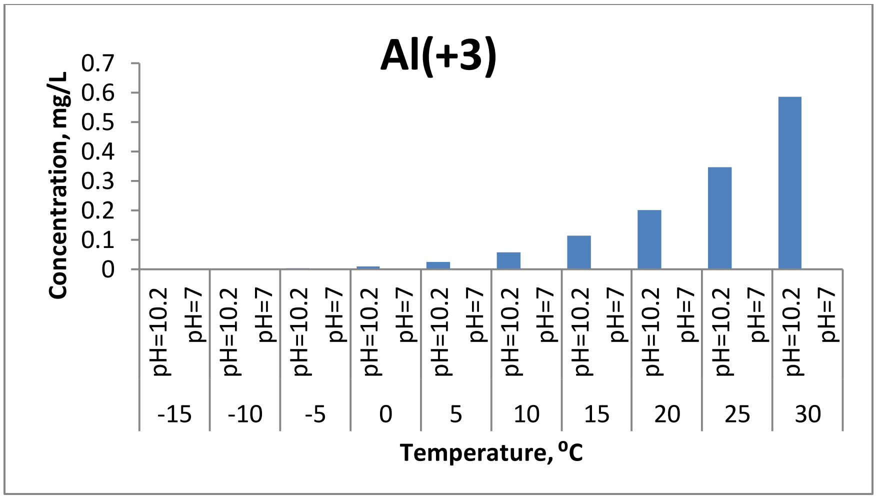


Figure 4.36. Aluminum ions OLI modeling concentration – temperature adjustment.

There are two species, aluminum hydroxide and sodium aluminum di-hydroxide carbonate, that precipitate out aluminum ions from the aqueous phase. With temperature increasing, the amount of sodium aluminum di-hydroxide carbonate decreases and the aluminum hydroxide increases. According to figure 4.36, the total removal ratio of aluminum decreases as the temperature increases. The higher temperature would lead to form more aluminum hydroxide and less sodium aluminum di-hydroxide carbonate.

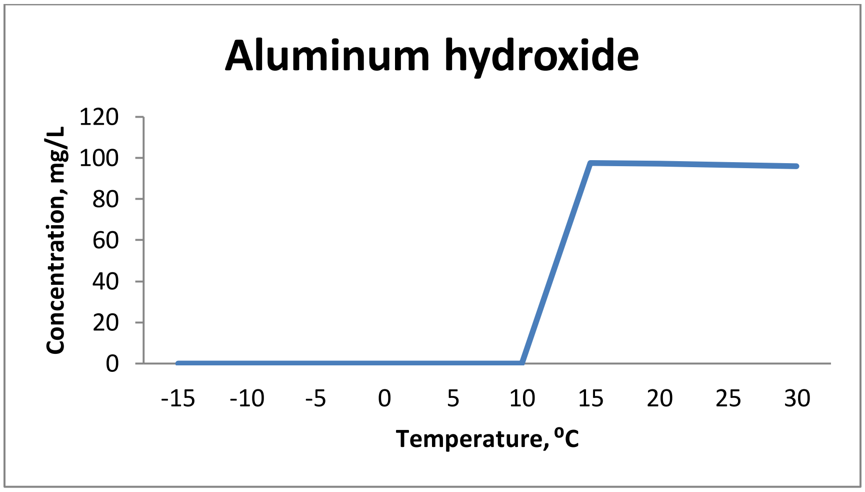


Figure 4.37. Aluminum hydroxide precipitation – temperature adjustment.

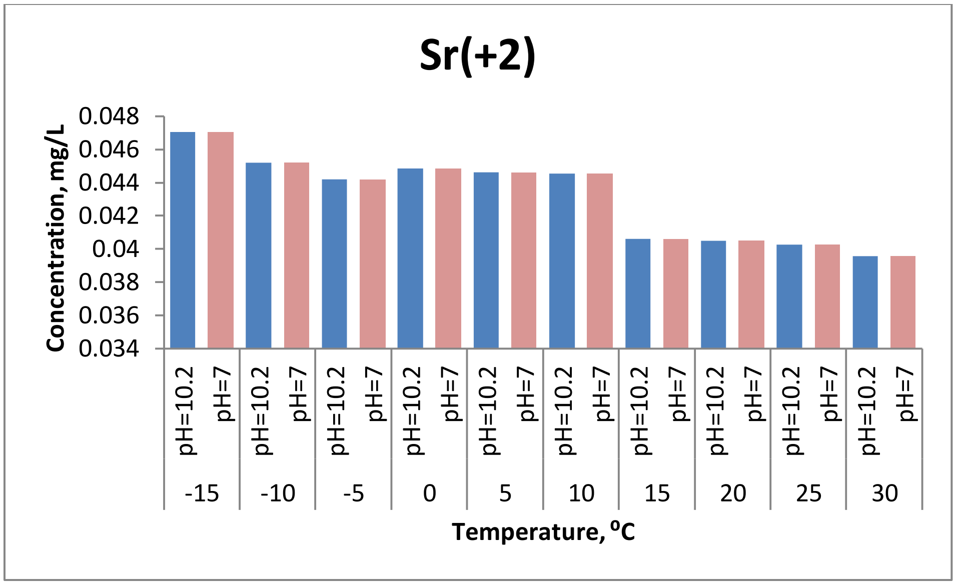


Figure 4.38. Strontium ions OLI modeling concentration – temperature adjustment.

According to the results of OLI prediction, the strontium ions precipitate more as the temperature increases. The increasing is especially obvious when the temperature is above 15 ^{0}C. The main salt that precipitates strontium ions out from the aqueous phase is strontium carbonate.

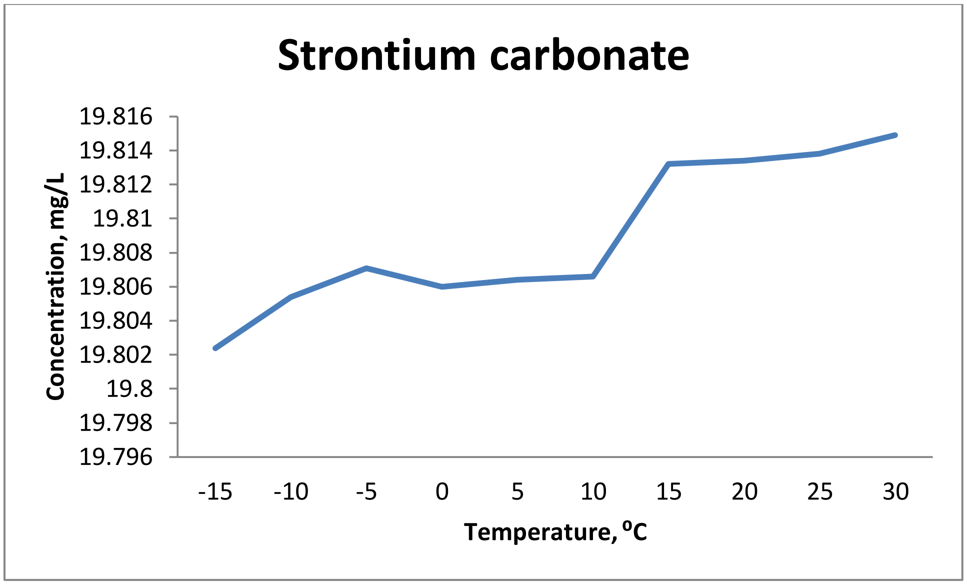


Figure 4.39. Strontium carbonate precipitation – temperature adjustment.

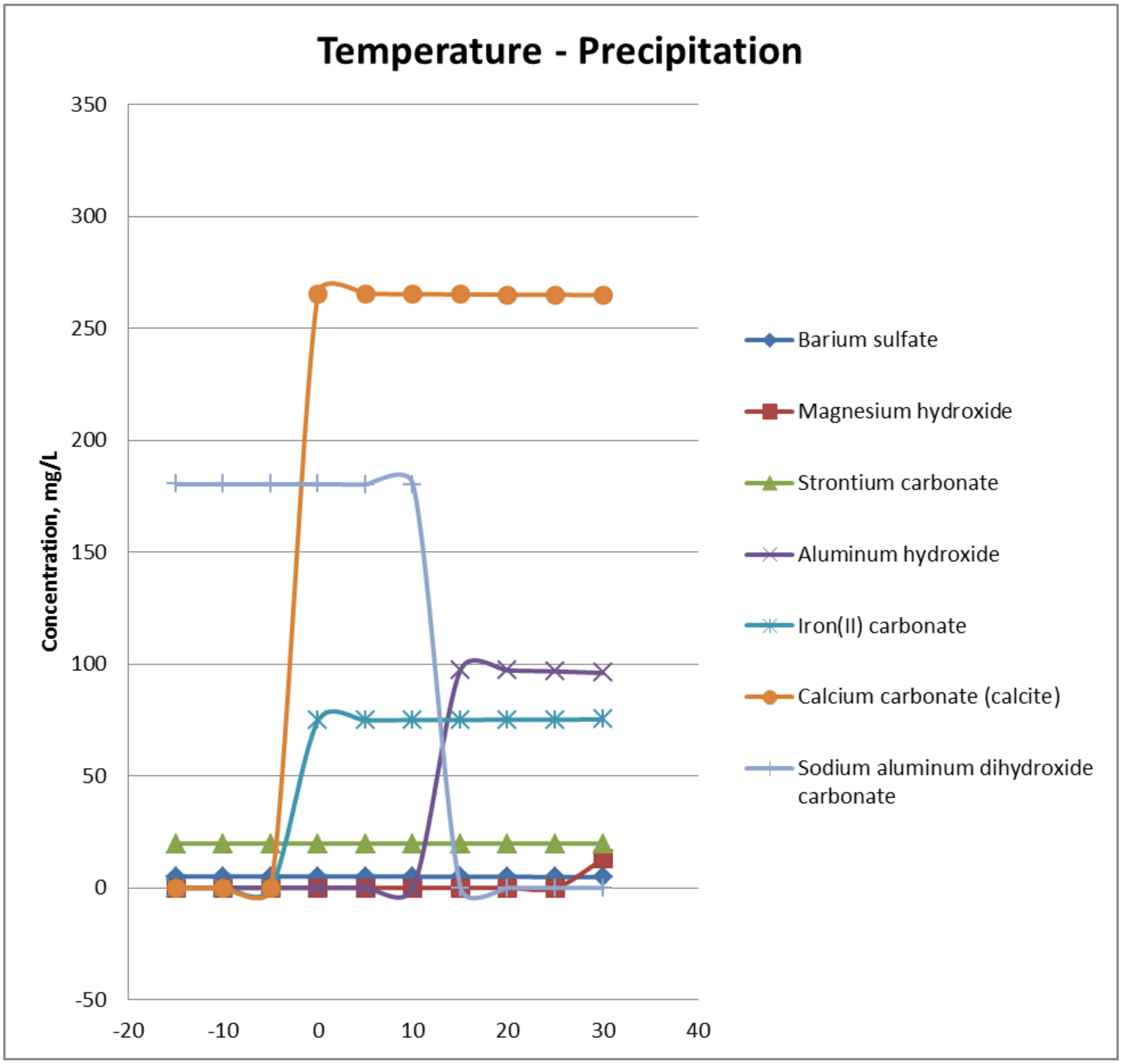


Figure 4.40. Precipitation- temperature adjustment.

Figure 4.40 show the impact of the temperate on the precipitants. According to the OLI Analyst prediction, in the range of -15°C to 30°C, almost all the ions precipitation increase as the temperature gets higher. In Colorado, the temperature difference between winter and summer can be as high as 60°C. For industry, the temperature should be taken into considerations.

4.5 pH – Scaling Tendency

The commercial waste water treatment company adjusts pH to 10.2 to precipitate most of the target compounds. Because pH is one of the most important factor that could affect the performance of precipitation, the following research focuses on optimizing the pH adjustment value, which could lower the cost on chemicals for coagulation precipitation. According to OLI chemical analyst prediction, figure 4.41 shows the results of how scaling tendency of the precipitants changes as pH adjustment.

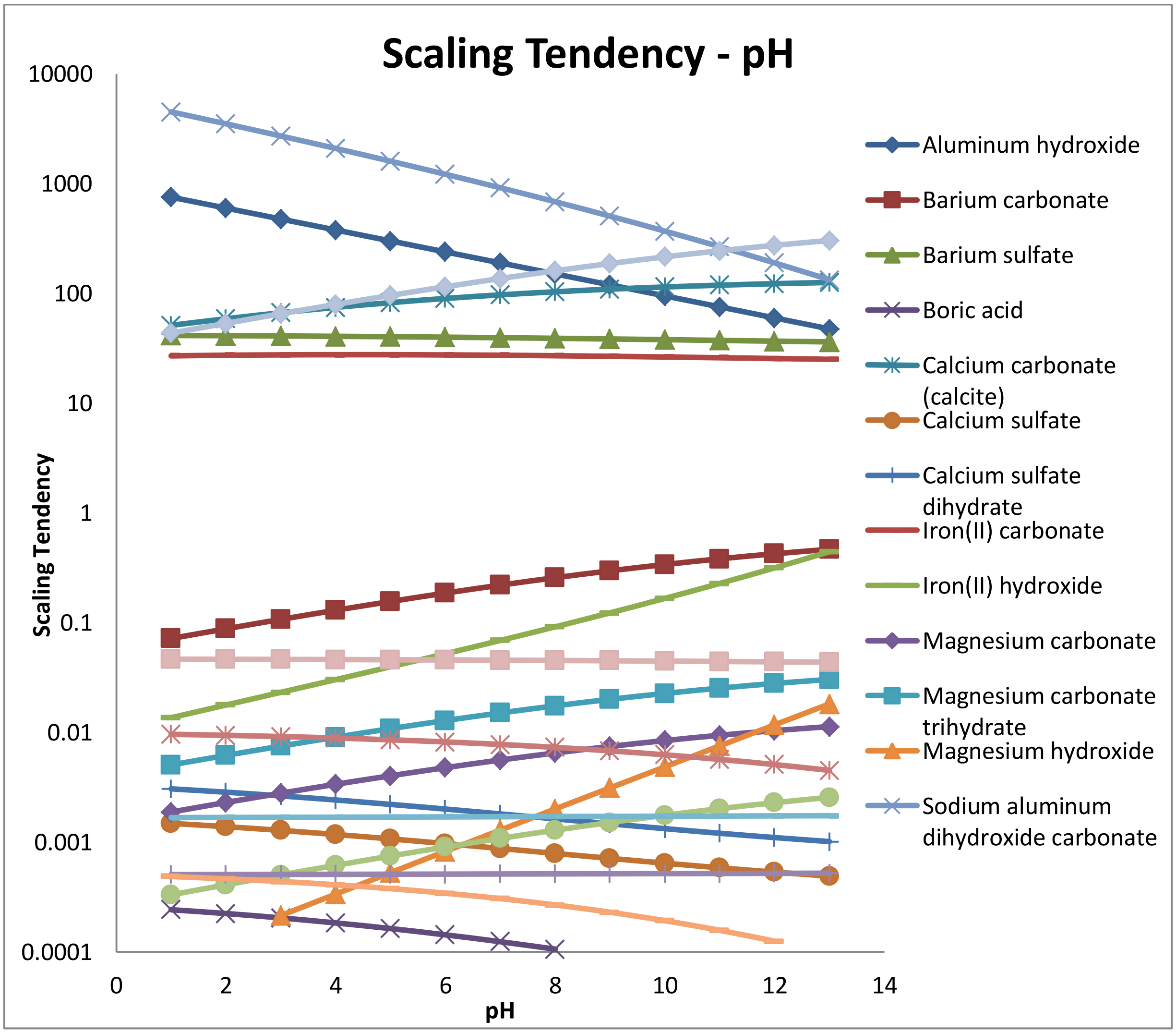


Figure 4.41. Scaling tendency – pH.

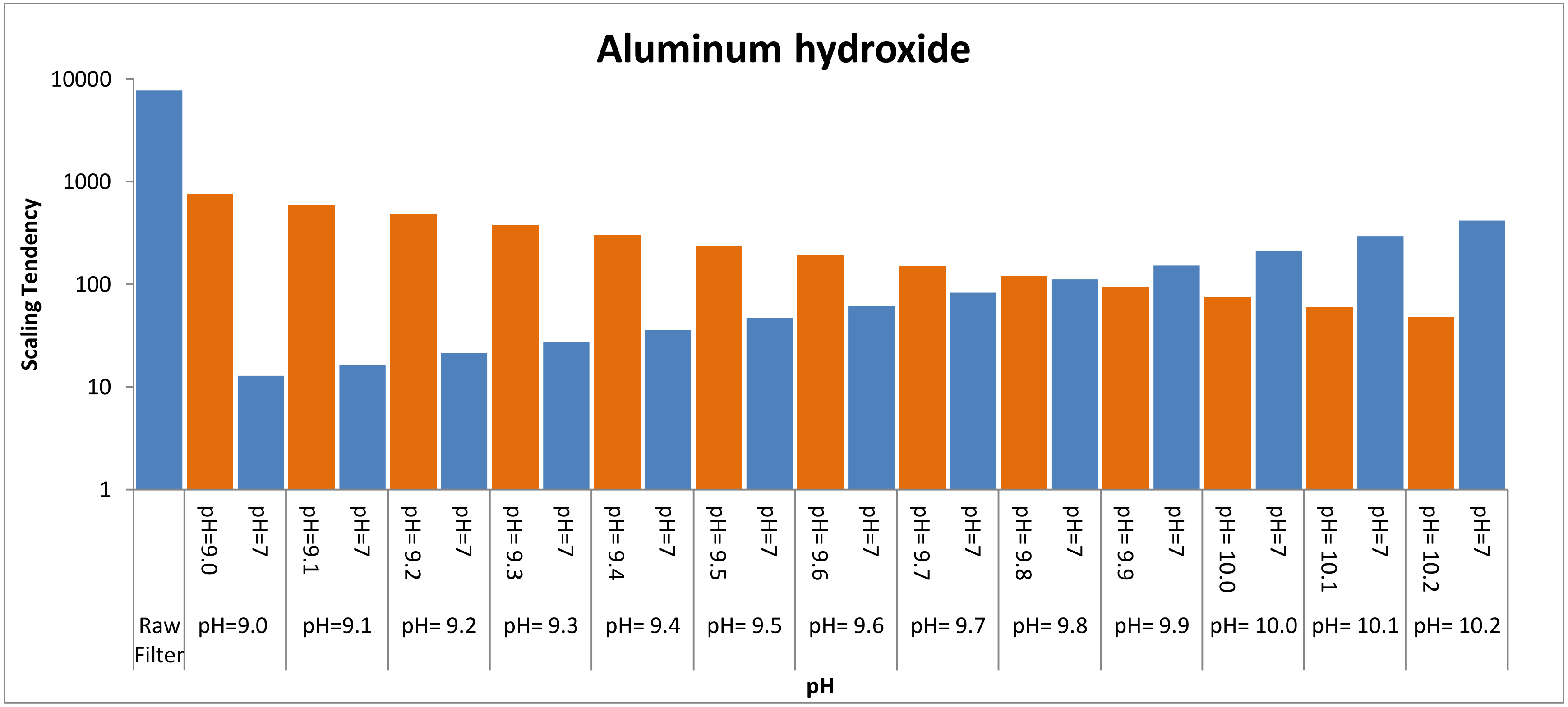


Figure 4.42. Aluminum hydroxide scaling tendency – pH adjustment.

Figure 4.42 shows the scaling tendency trends of aluminum hydroxide changes varies pH adjustment. The orange bars stand for the scaling tendency when pH is adjusted to target value (from pH 9.0 to pH 10.2) According to figure 4.42, the scaling tendency of aluminum hydroxide decreases as the pH increasing (orange bars). And the scaling tendency varies from 750 to 47. In order to remove the aluminum hydroxide in the produced water, pH value of the aqueous phase should be decreased.

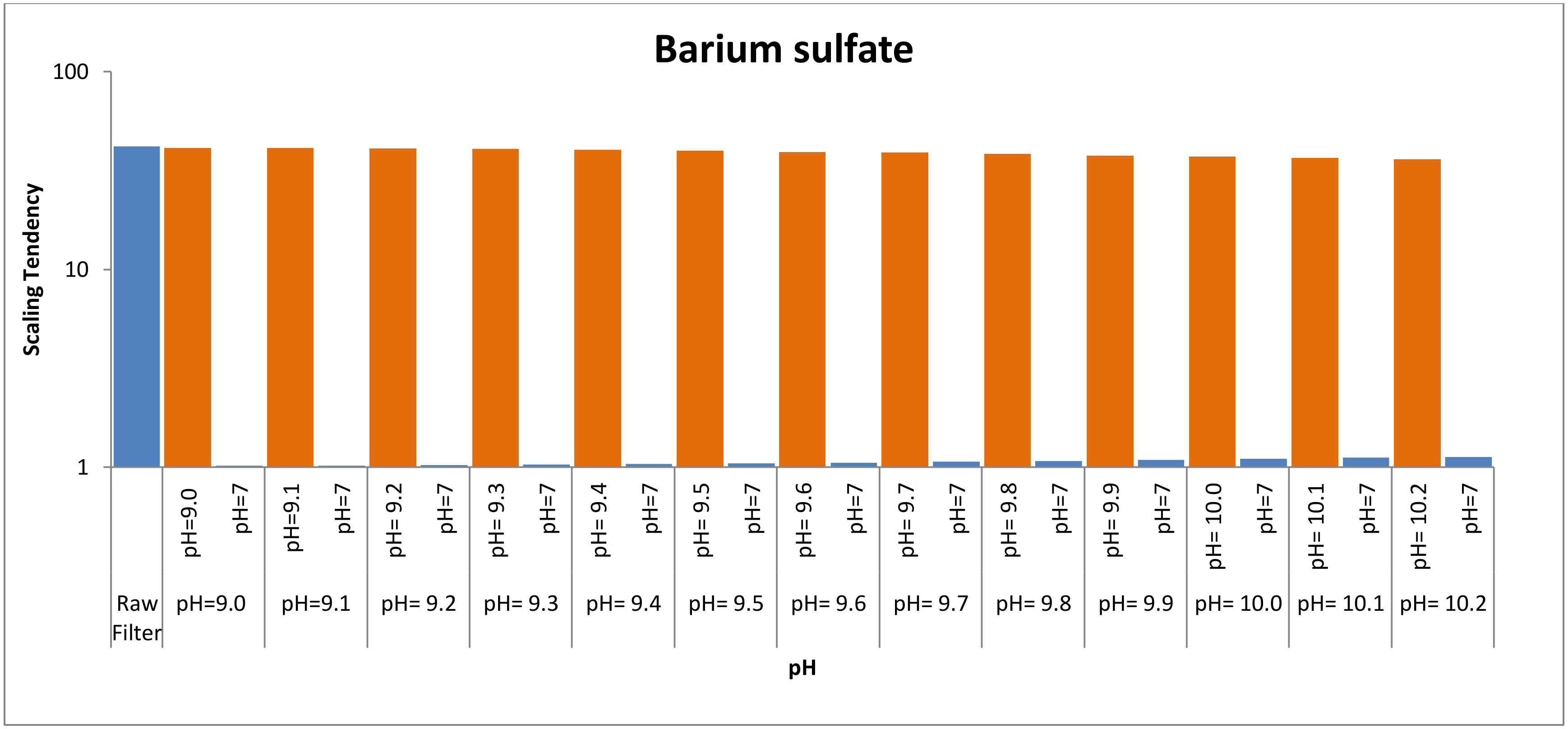


Figure 4.43. Barium sulfate scaling tendency – pH adjustment.

Figure 4.43 shows the scaling tendency trends of barium sulfate changes varies pH adjustment. The orange bars stand for the scaling tendency when pH is adjusted to target value (from pH 9.0 to pH 10.2) According to figure 4.43, the scaling tendency of barium sulfate stays the same and does not get affected by pH adjustment (orange bars).Barium sulfate is the main salt that precipitates barium ions out from the stream. And barium sulfate cannot be affected by pH value. The scaling tendency remains the same, as the pH value increases.

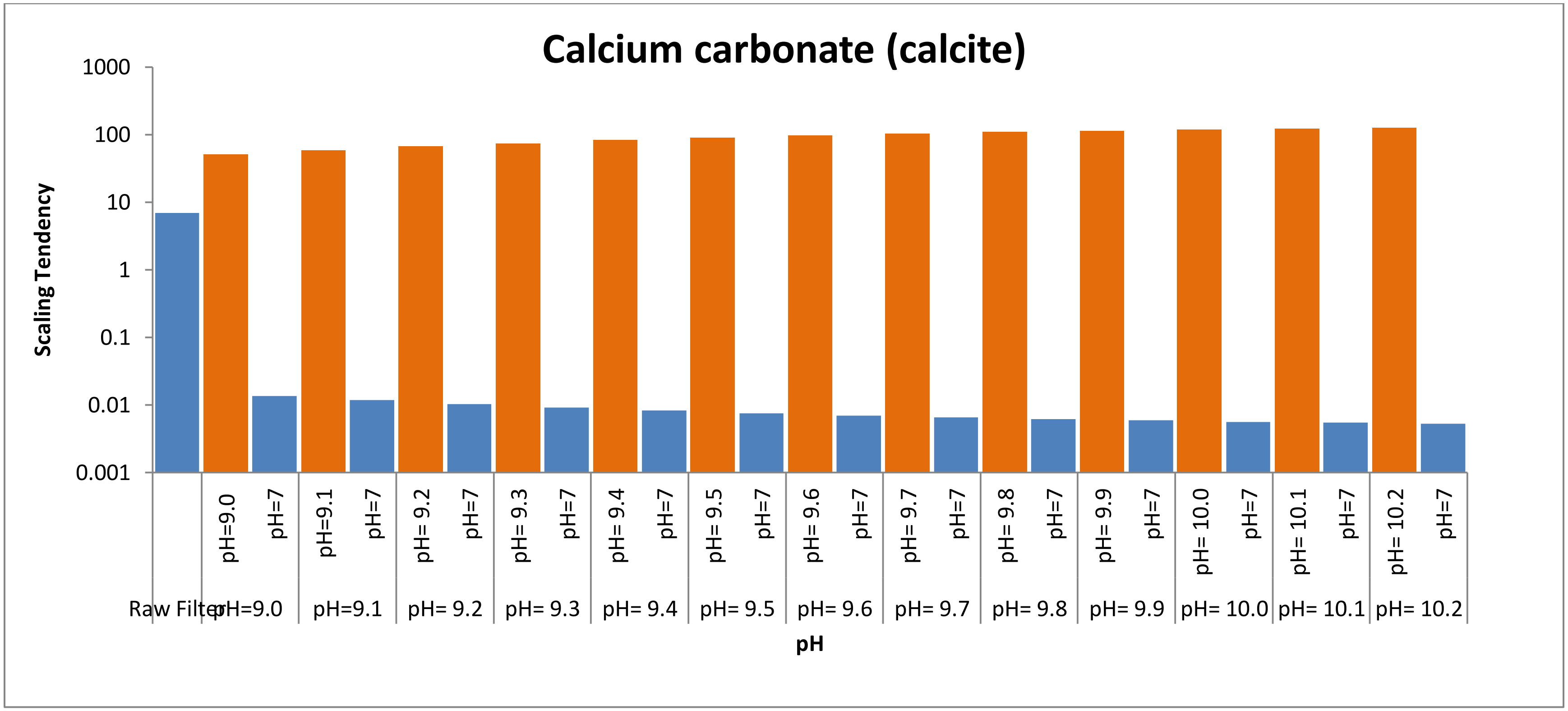


Figure 4.44. Calcite scaling tendency – pH adjustment.

Figure 4.44 shows the scaling tendency trends of calcium carbonate changes varies pH adjustment. The orange bars stand for the scaling tendency when pH is adjusted to target value (from pH 9.0 to pH 10.2). According to figure 4.44, the scaling tendency of calcium carbonate increases as the pH increasing (orange bars). The scaling tendency of calcium carbonate varies from 51 at pH 9.0 to 125.0 at pH 10.2. As the pH increases, the bicarbonate ions are converted to carbonate ions. The process increases the production of calcium carbonate. And calcium carbonate precipitates more when pH is higher.

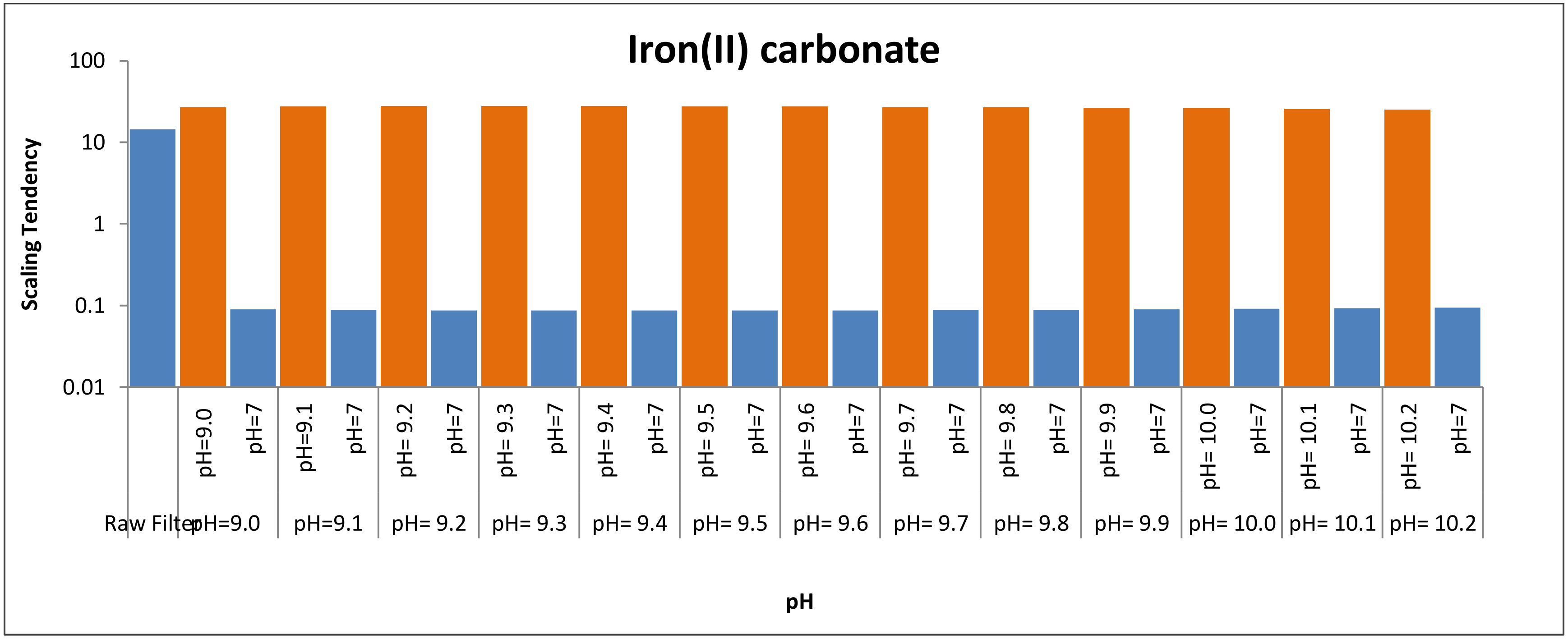


Figure 4.45. Iron carbonate scaling tendency – pH adjustment.

Figure 4.45 shows the scaling tendency trends of calcium carbonate changes varies pH adjustment. The orange bars stand for the scaling tendency when pH is adjusted to target value (from pH 9.0 to pH 10.2). According to figure 4.45, the scaling tendency of Iron carbonate remains the same and does not change as the pH increasing (orange bars).

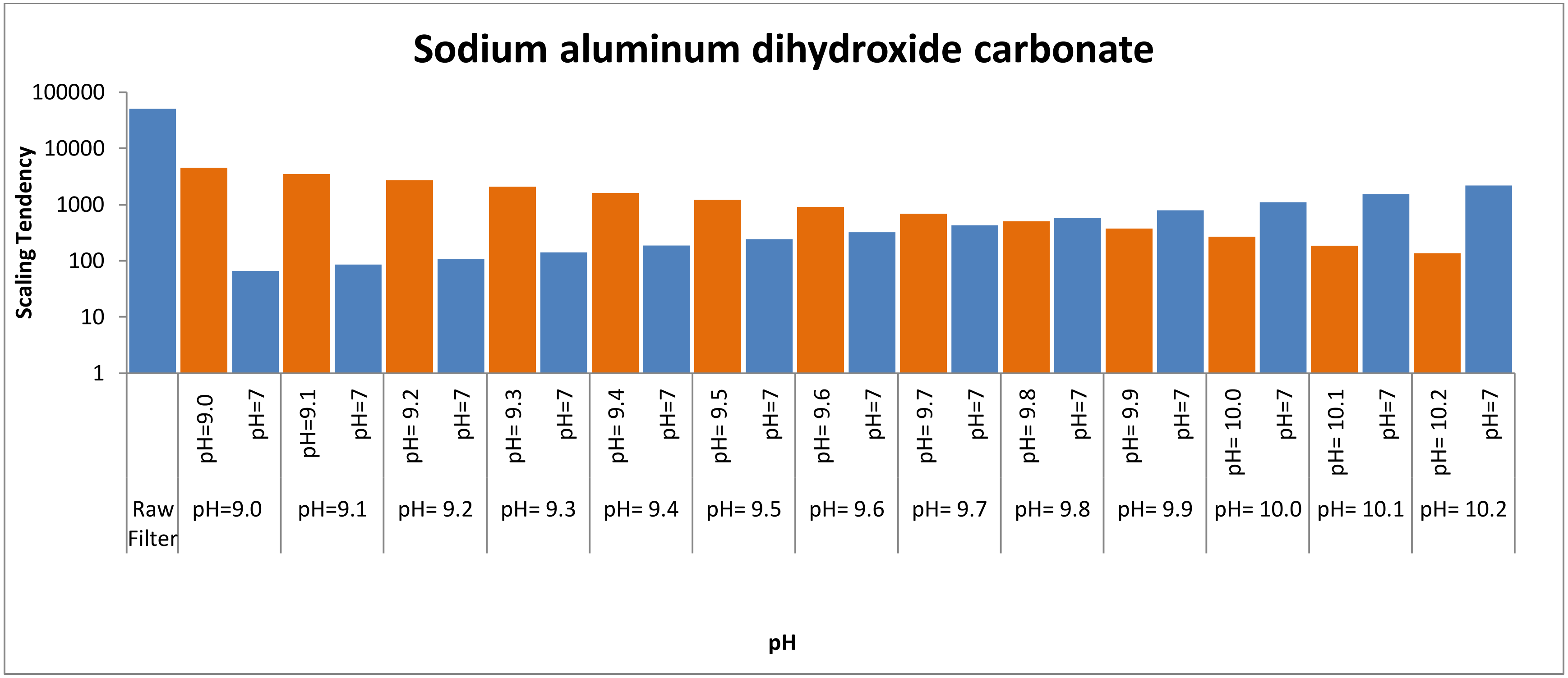


Figure 4.46. Sodium aluminum dihydroxide scaling tendency – pH adjustment.

Figure 4.46 shows the scaling tendency trends of sodium aluminum dihydroxide changes varies pH adjustment. The orange bars stand for the scaling tendency when pH is adjusted to target value (from pH 9.0 to pH 10.2) According to figure 4.46, the scaling tendency of sodium aluminum dihydroxide decrease as pH (orange bars).When pH is adjusted back to 7.0, the scaling tendency will increases back. According to the trends, sodium aluminum dihydroxide can be removed more efficiently when pH is lower than 9.7.

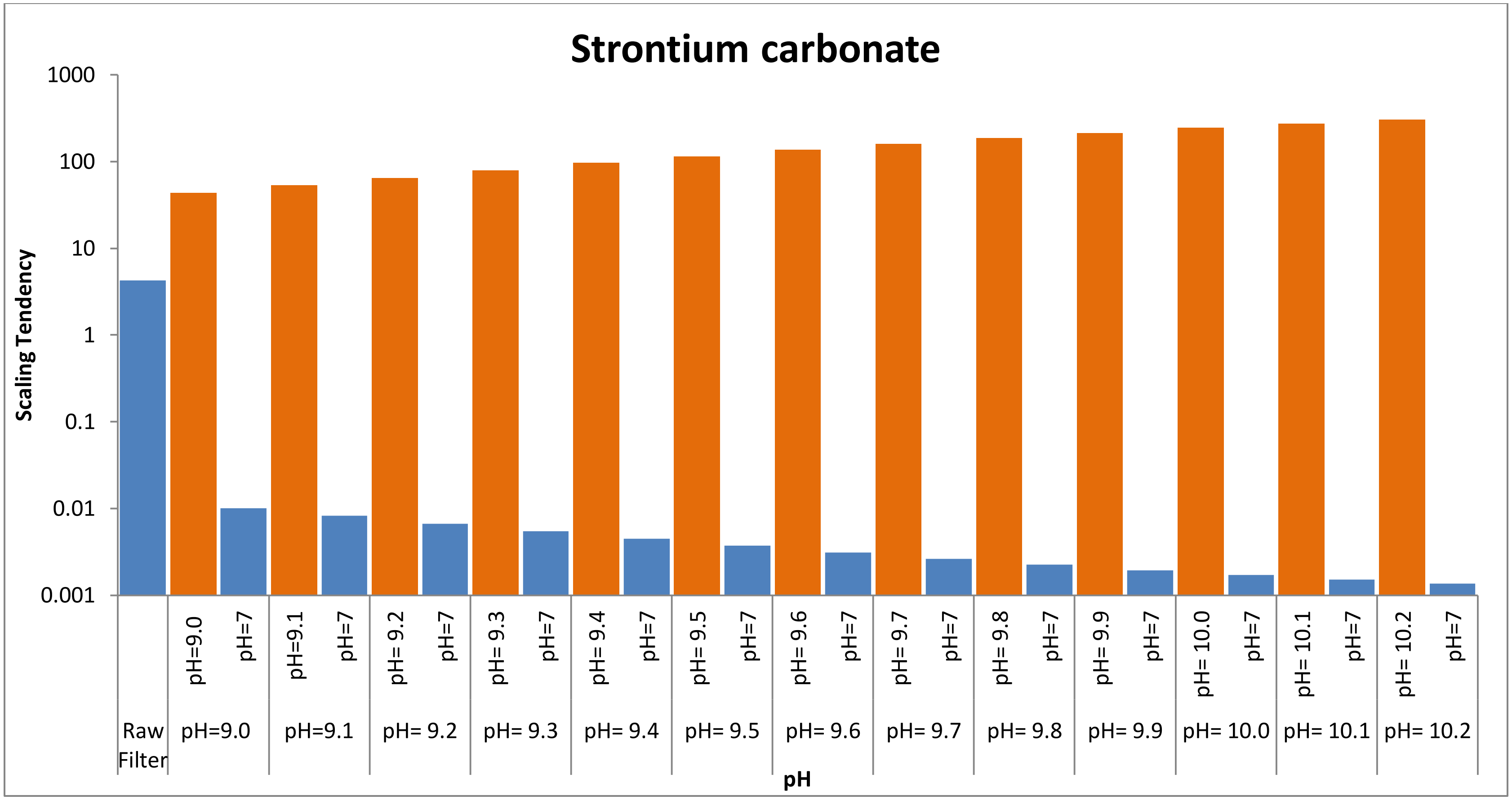


Figure 4.47. Strontium carbonate scaling tendency – pH adjustment.

Figure 4.47 shows the scaling tendency trends of strontium carbonate changes varies pH adjustment. The orange bars stand for the scaling tendency when pH is adjusted to target value (from pH 9.0 to pH 10.2) According to figure 4.47, the scaling tendency of strontium carbonate increase as pH (orange bars).When pH is adjusted back to 7.0, the scaling tendency will slightly decreases. According to the trends, strontium carbonate can be removed more efficiently when pH is adjusted higher..

CHAPTER 5

CONCLUSION

Conclusion

This research focused on optimizing a commercial produced water treatment process, which includes lowering the cost and improving the performance of the softening or metal precipitation process. The process studied uses a composite system that includes EC, chemical coagulation, and pH adjustment processes for the treatment of produced water from oil and gas field in the Denver-Julesburg basin. Raw and treated water samples were analyzed and compared with results from a chemical equilibrium model, OLI Analyst. To optimize the softening treatment process, the water samples were used as the input of OLI modeling. OLI Chemical Analyst built different models for water treatment under different conditions, such as pH, and temperature.

The comparison between laboratory and modeling results indicated that metal precipitation should be effective if 100% solid-liquid separation is assumed. However, several metals that were expected to precipitate and be effectively removed were not (e.g. calcium and strontium) leading to the conclusion that coagulation and flocculation were not producing a floc that was easily filtered. In order to verify the precipitation removal performance, a finer filtration membrane (0.2 micron) was used and compared to the former membrane (2.5 micron). With 0.2 micron filtration membrane, the removal ratio does improve and efficiency of the treatment also increases, although there is still significant difference between model and actual results.

Using laboratory scale simulation, the pH was adjusted to 9.5 to verify if there is a better pH for softening the produced water one that also costs less. The results from the laboratory showed slight differences on pH 10.2 and pH 9.5. As one of the target ions, magnesium, was not affected by pH adjustment when the pH was below12.0 (as shown in figure 12), the pH impacts on precipitation need re-evaluated. OLI chemicals analyst was used to verify that the settlements removal performance varies according to the different pH adjustments. While doing the OLI modeling, wells No. 16-68 and No. 16-69 did not precipitate as others did. The temperature of these two wells was below freezing point. In order to test if temperature could impacts on precipitation, OLI was used to adjust the temperature from -15°C to 25°C. Based on OLI modeling results, the low temperature could precipitate more sodium ions. In the range from -15°C to 25°C, target compounds, calcium and iron, get removed more efficiently when temperature gets above 0°C.

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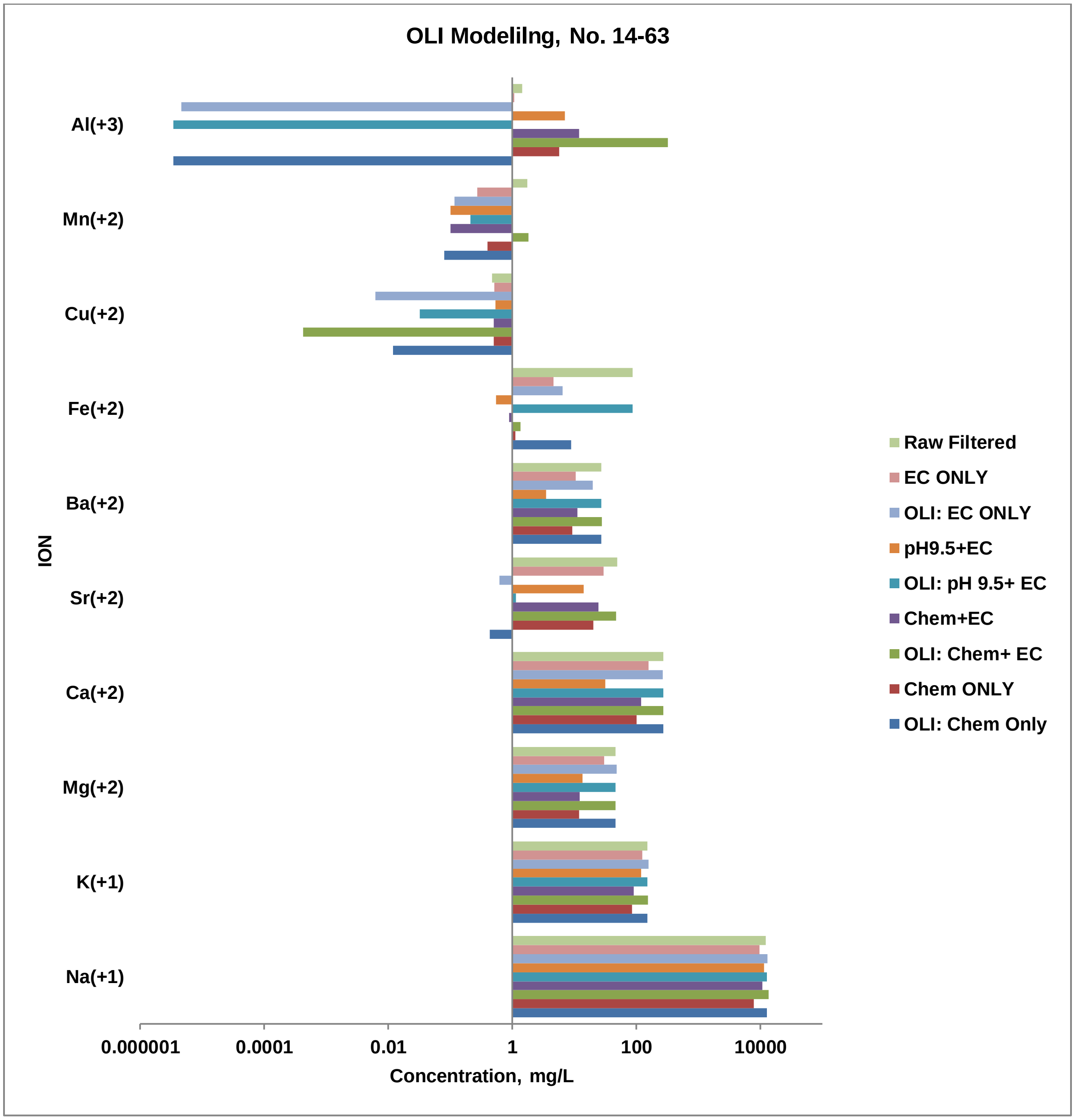
Well No. 14-63



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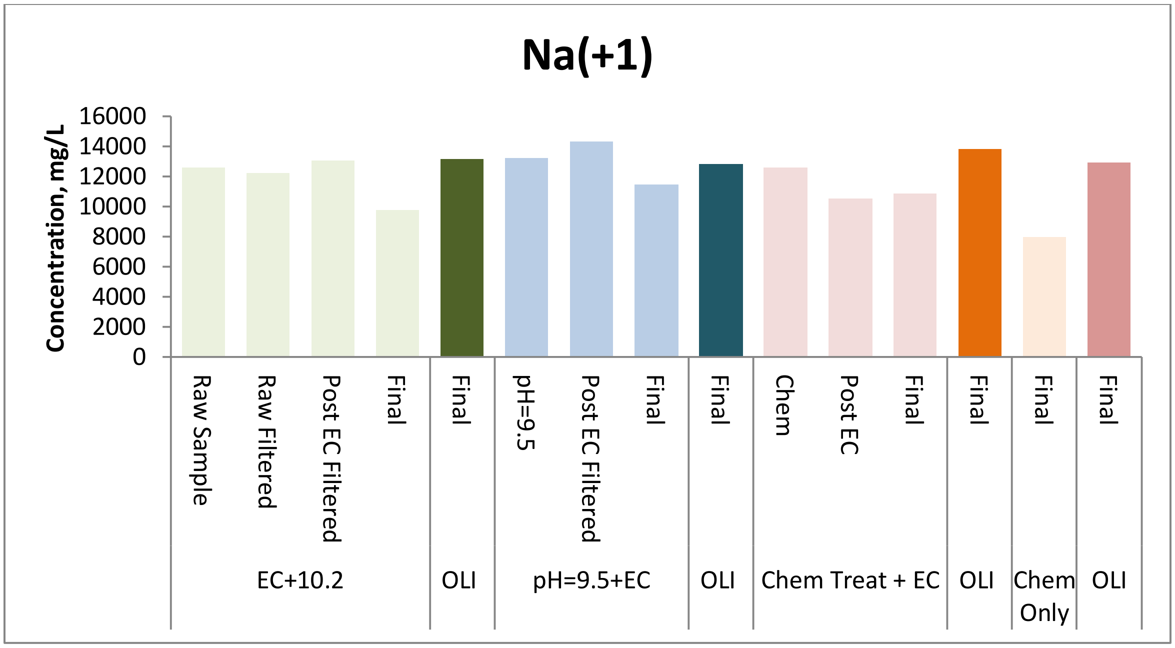

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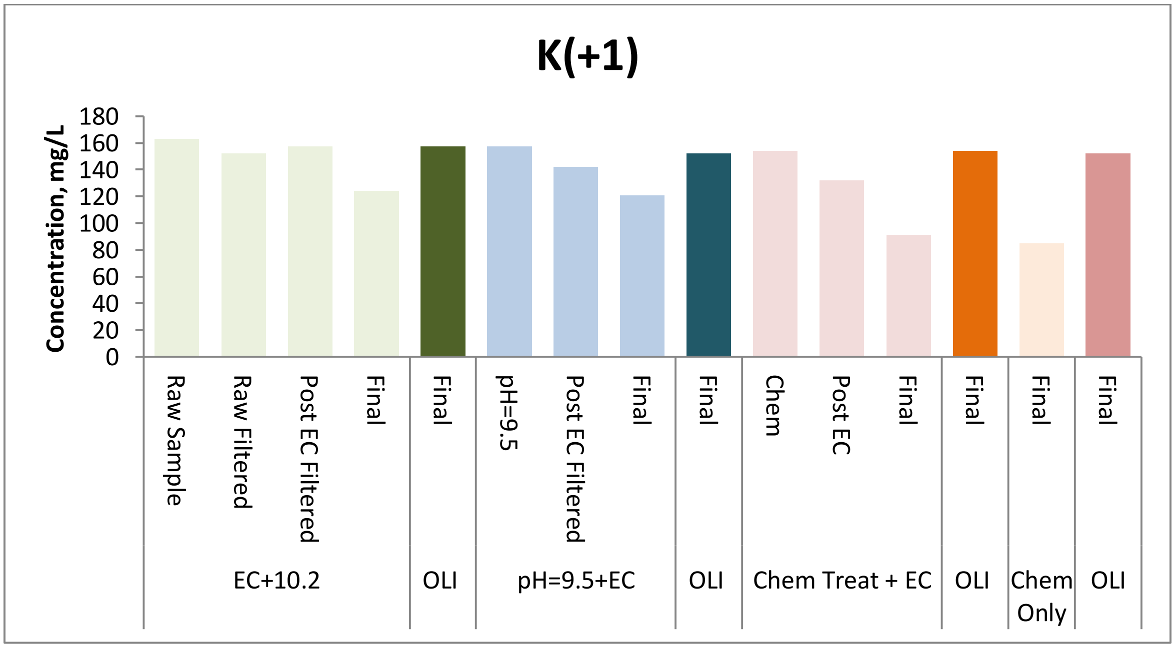

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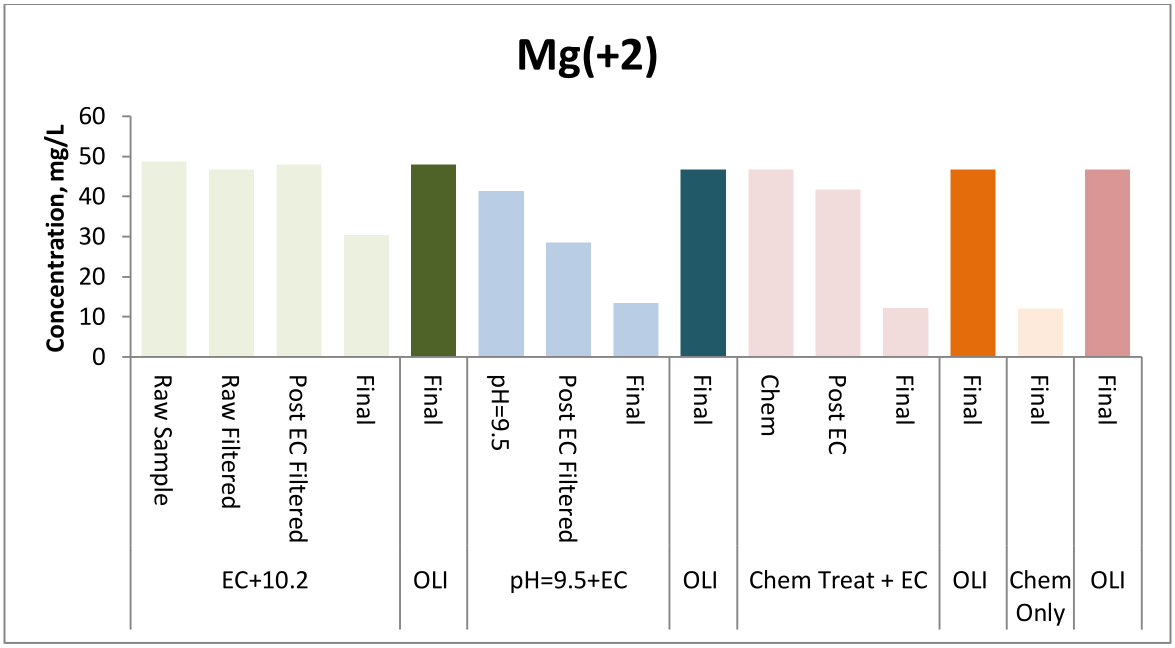

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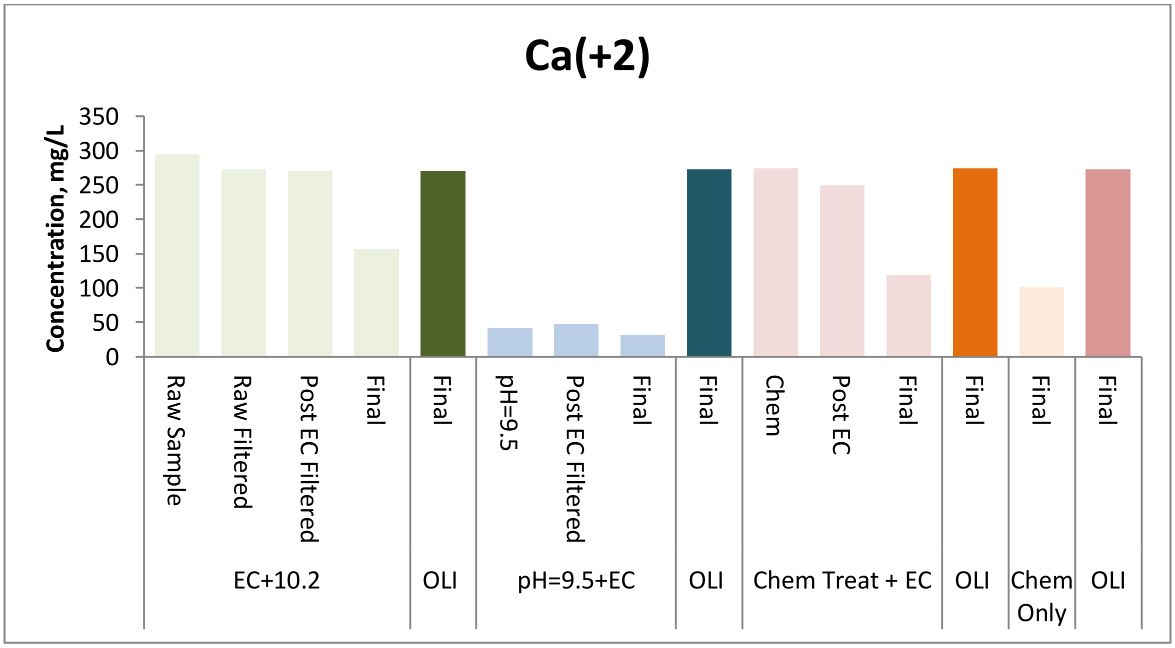

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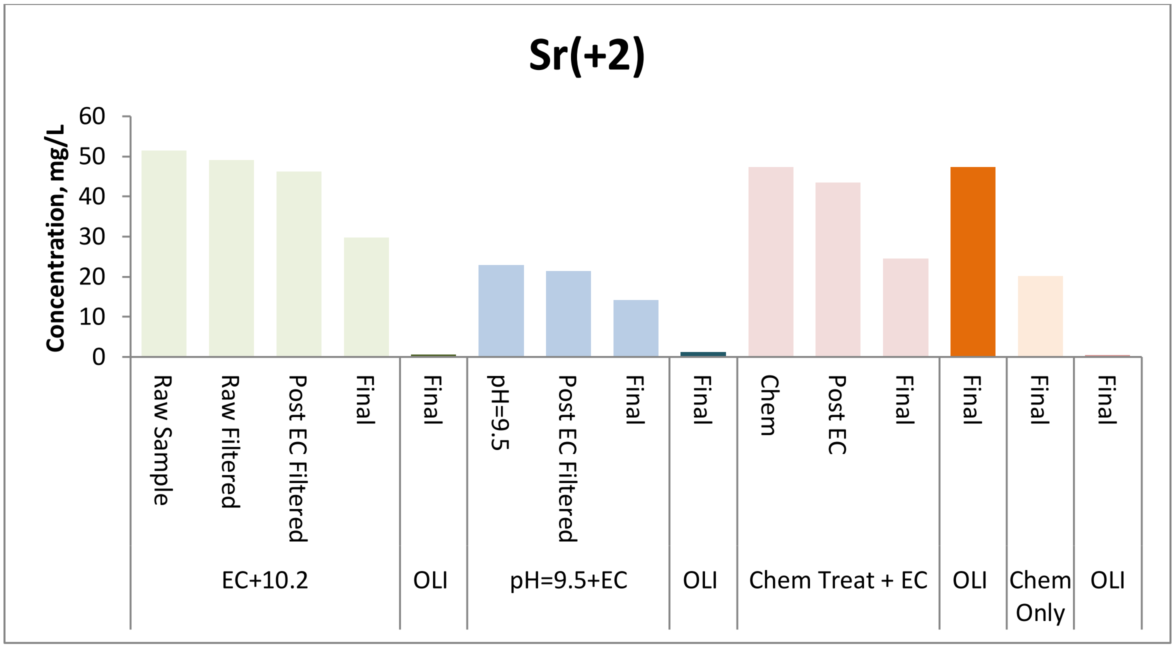

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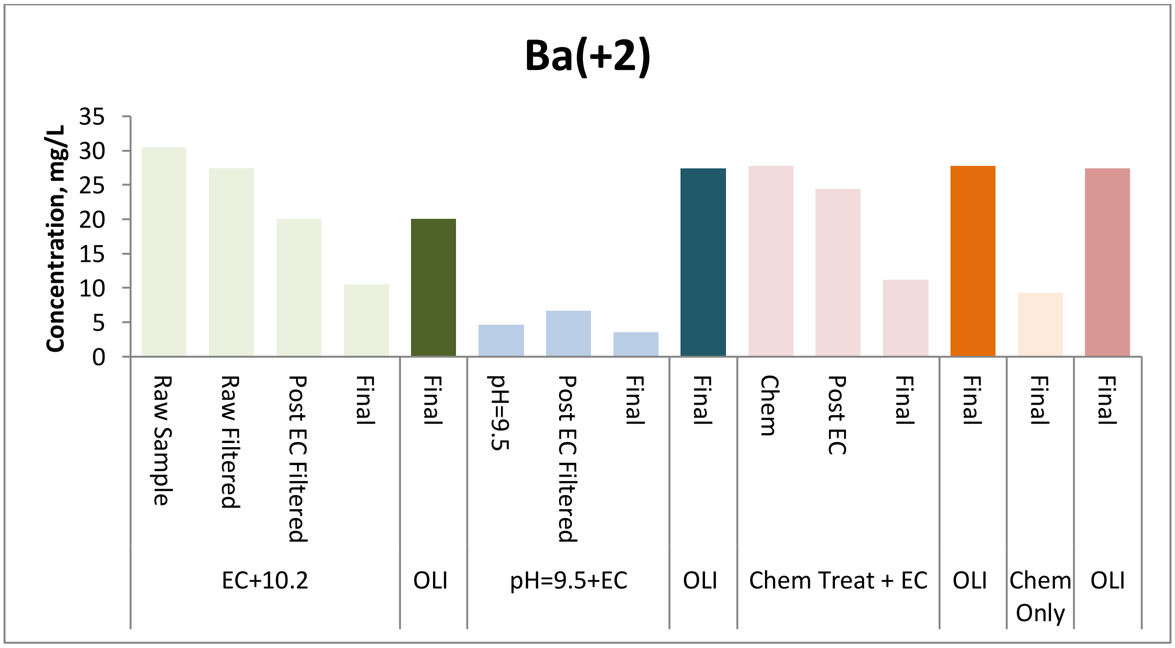

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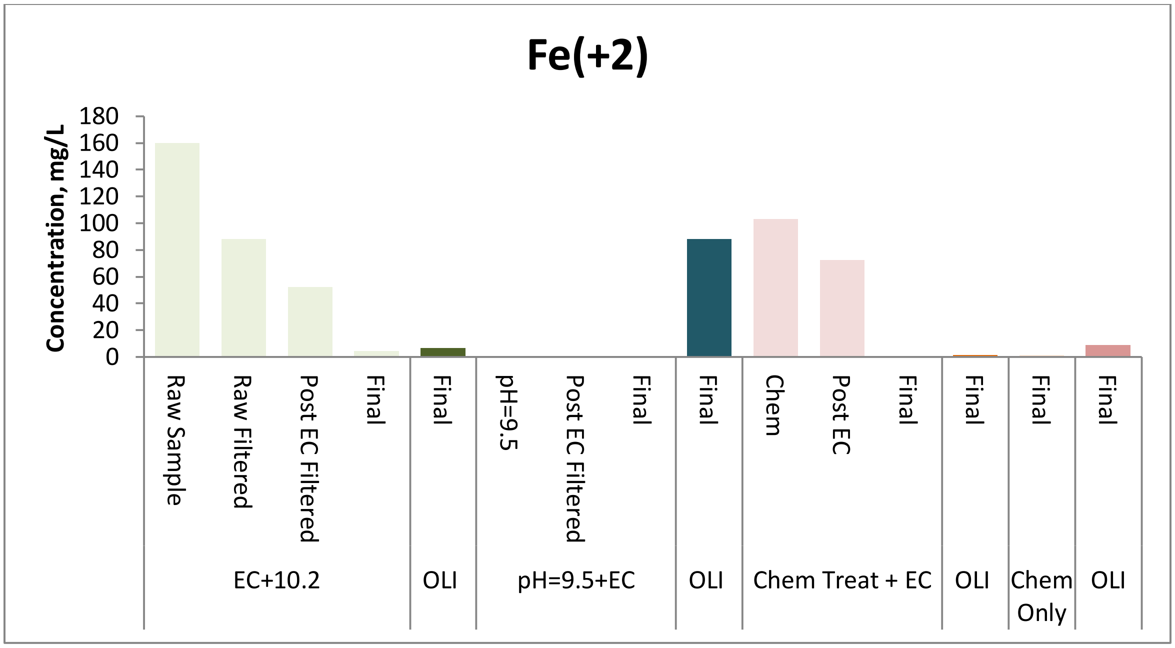

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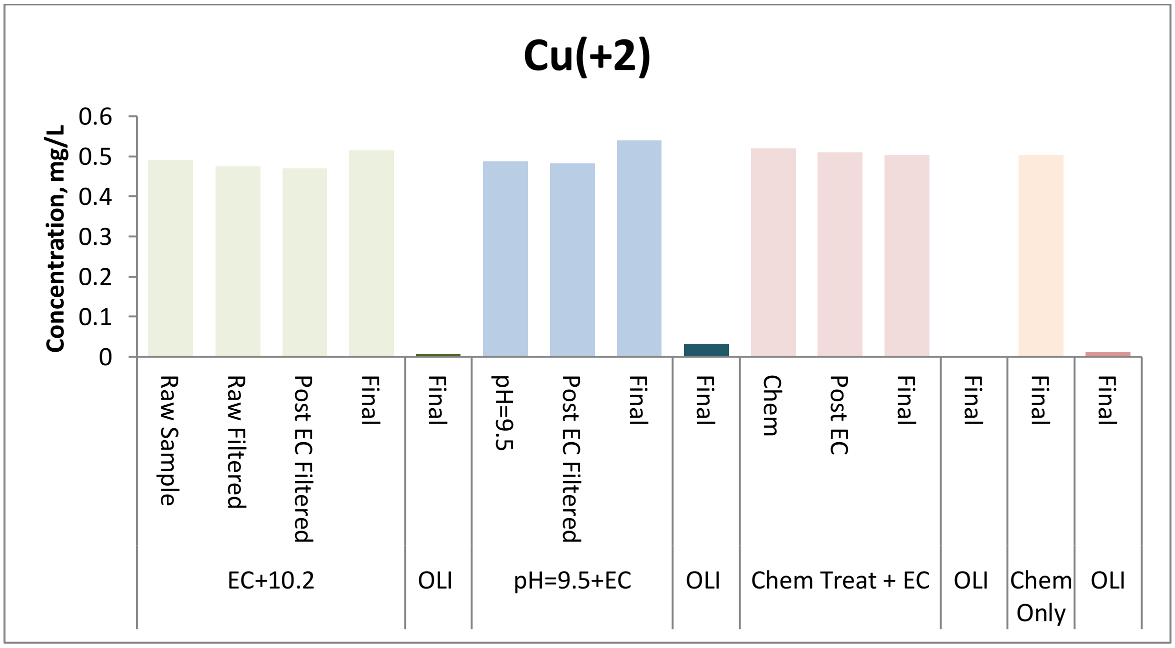

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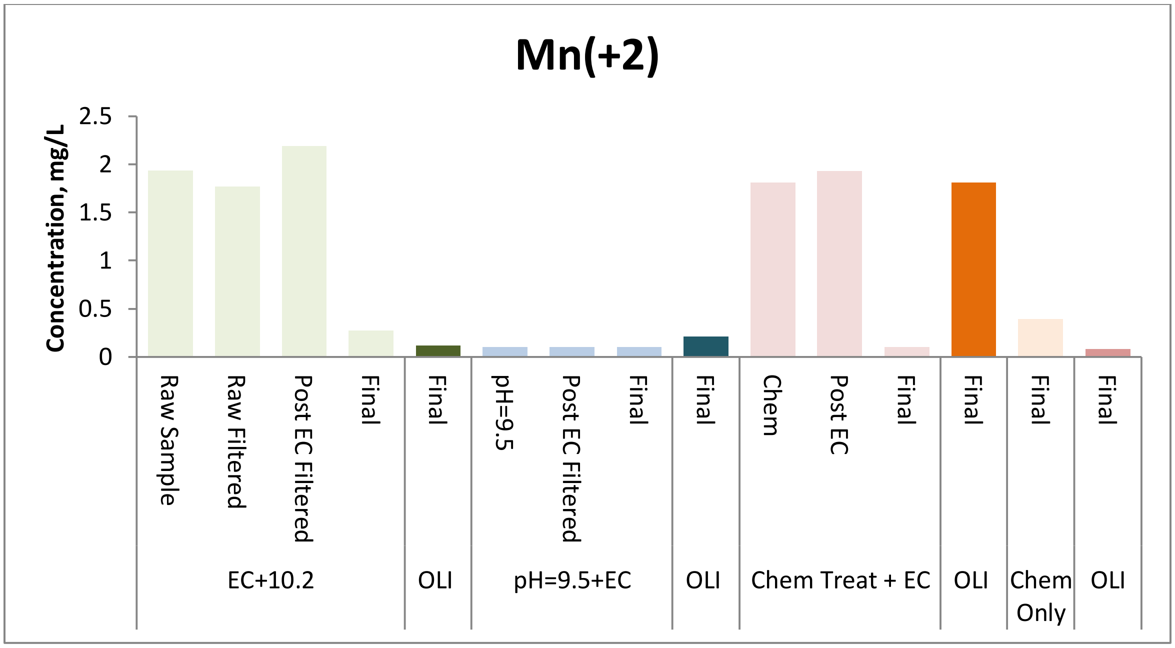

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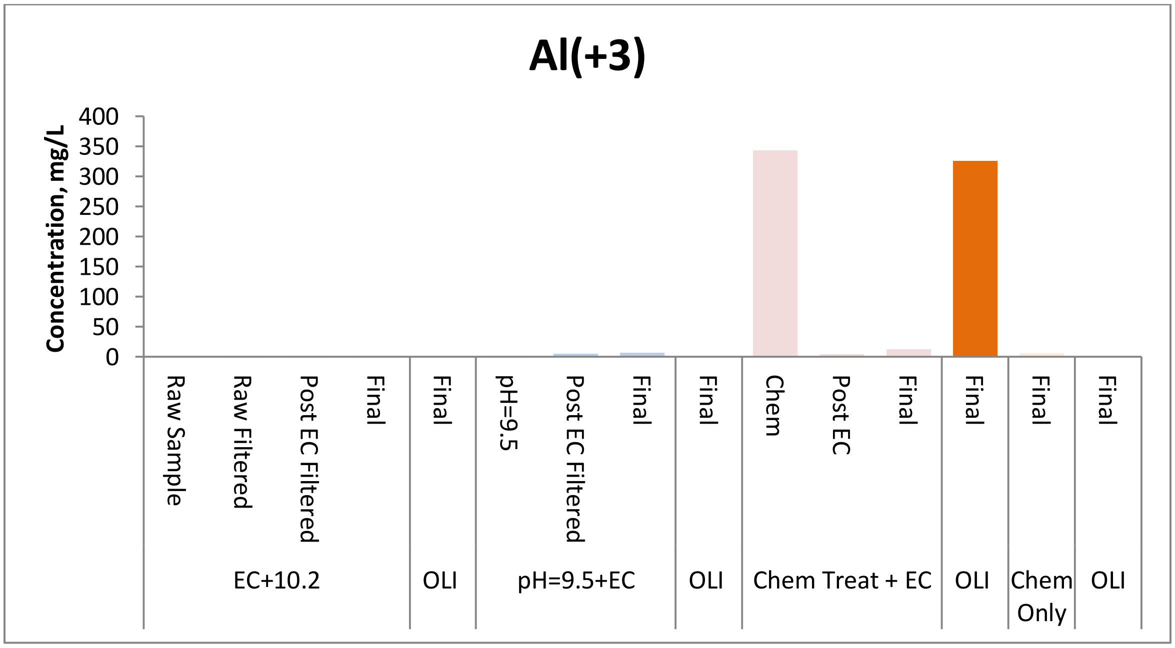
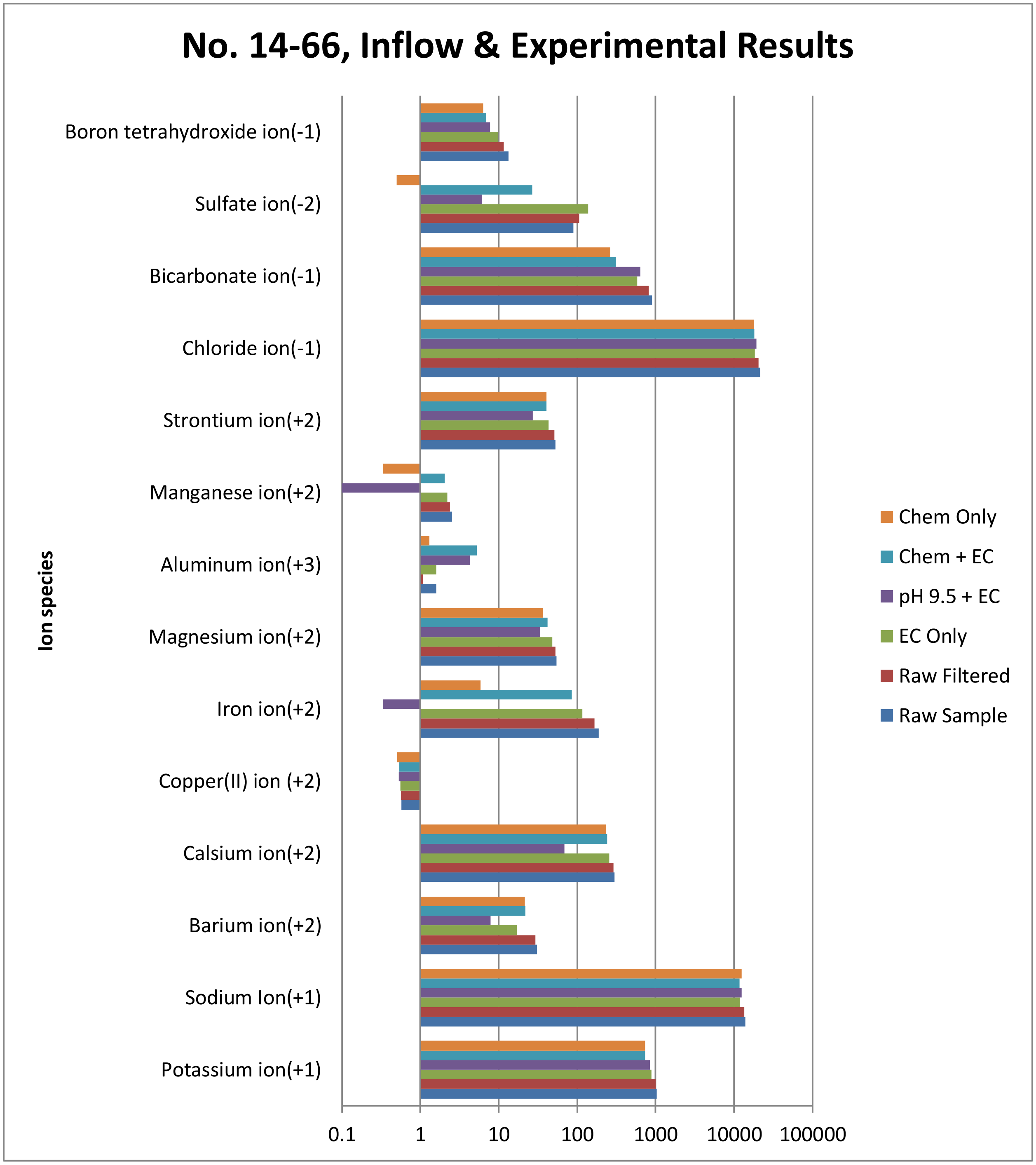


Figure 6.11. Well No. 14-63_Al

Well No. 14-66



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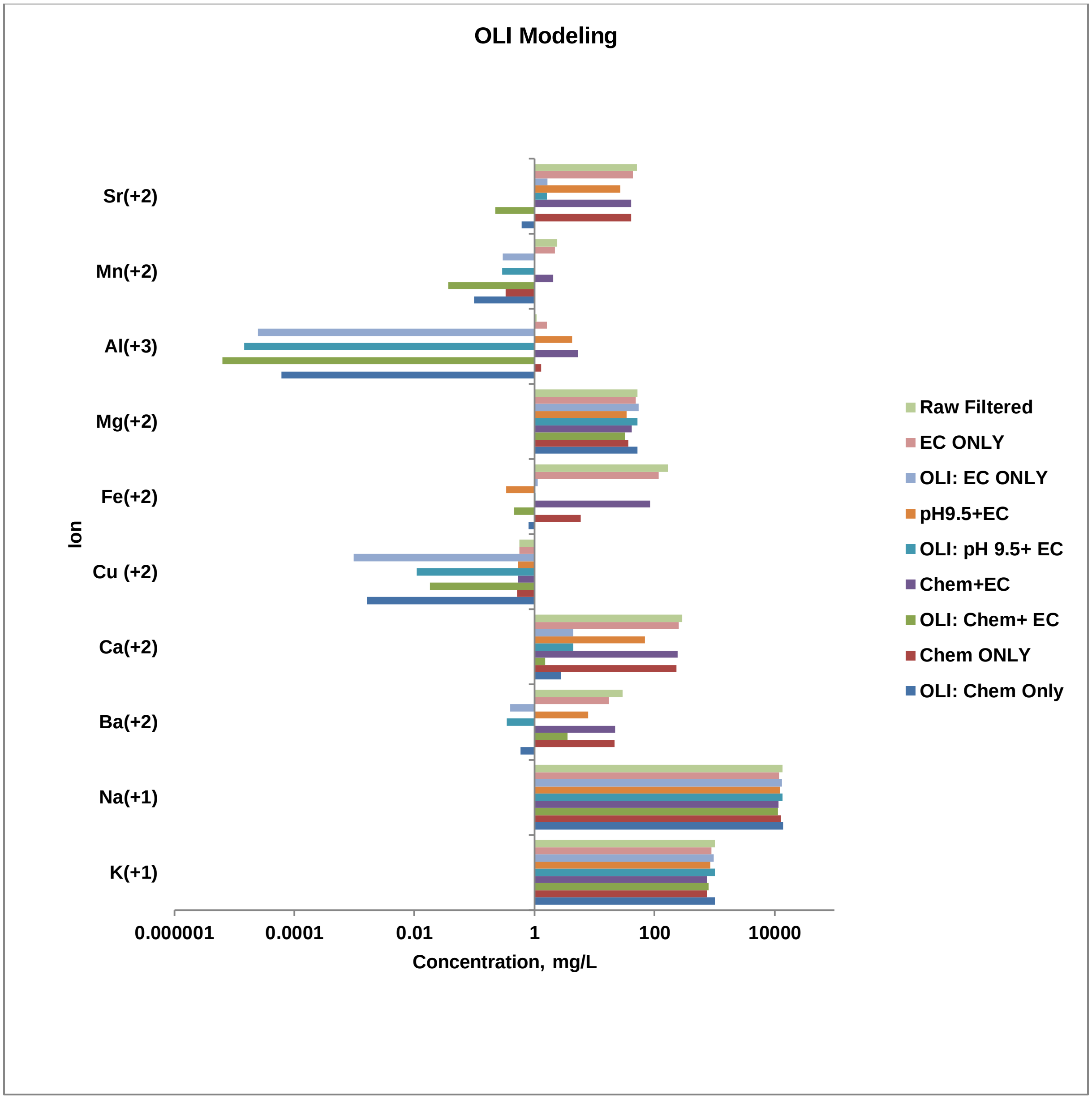

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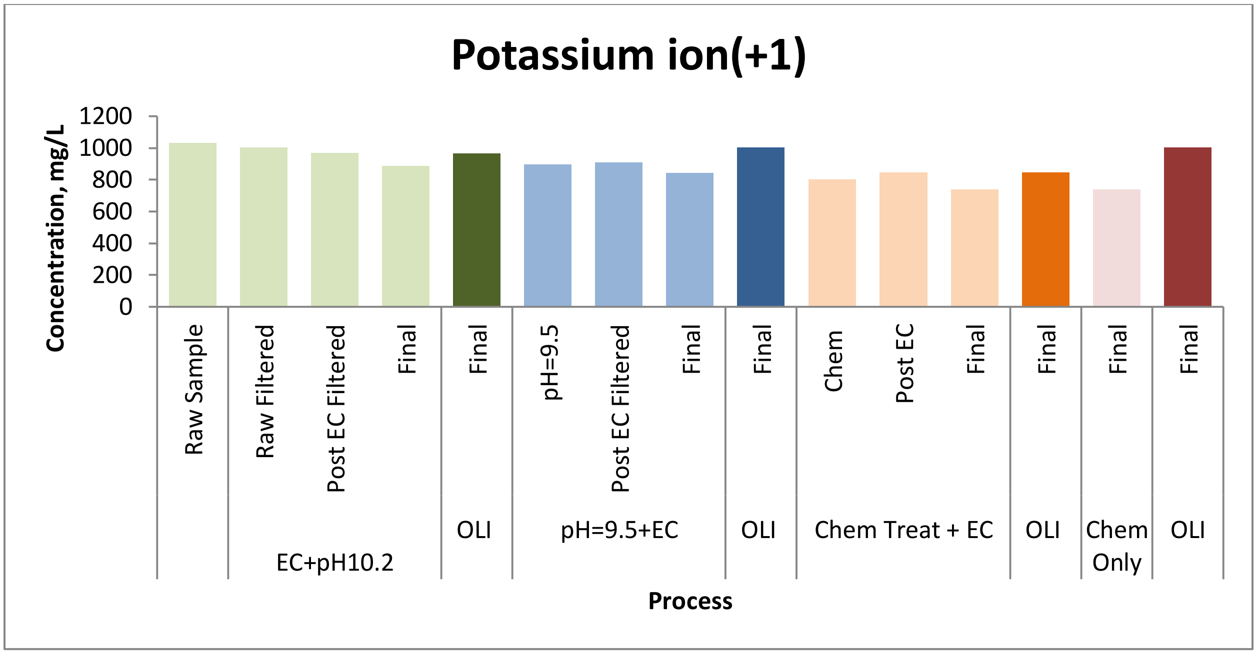

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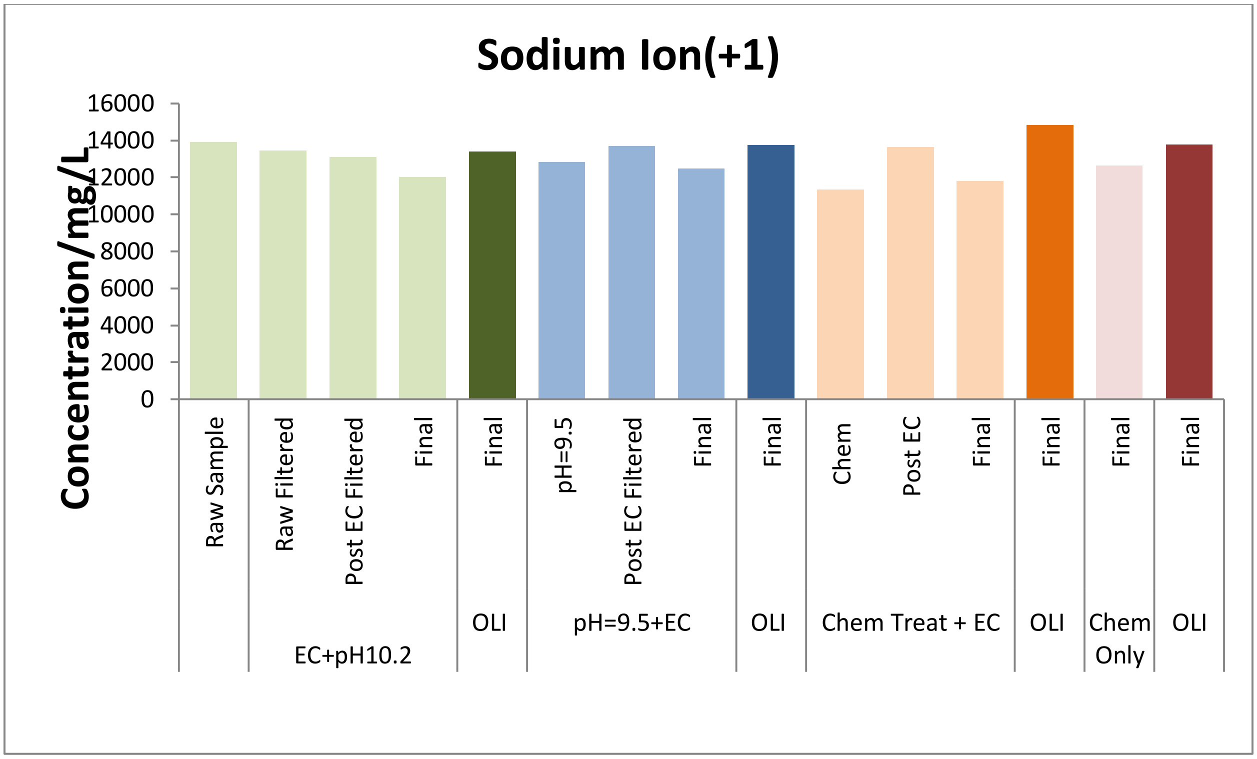

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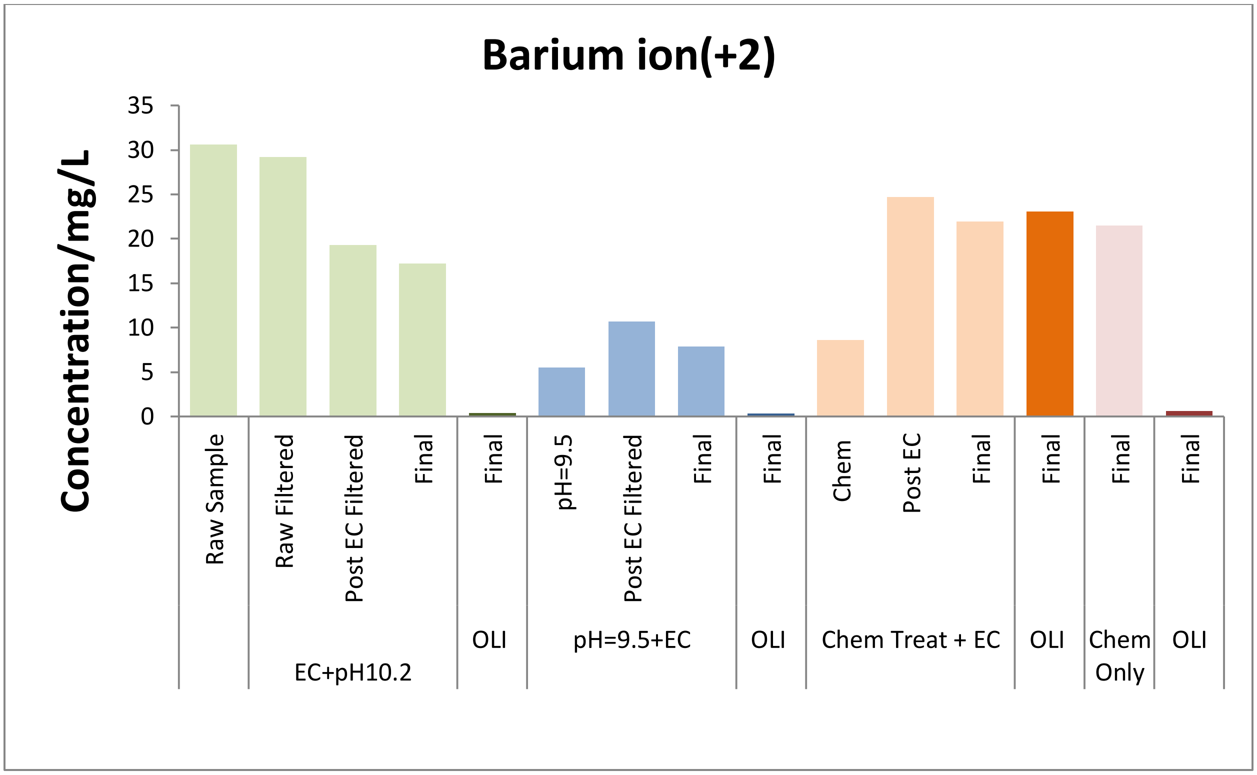

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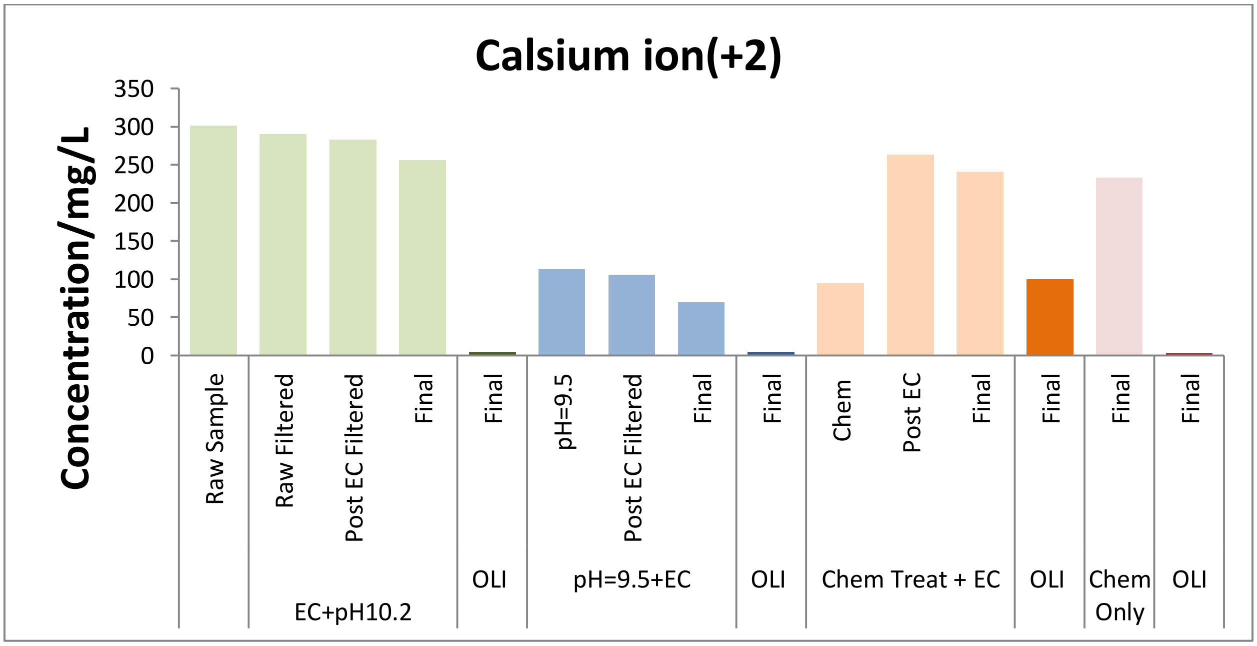

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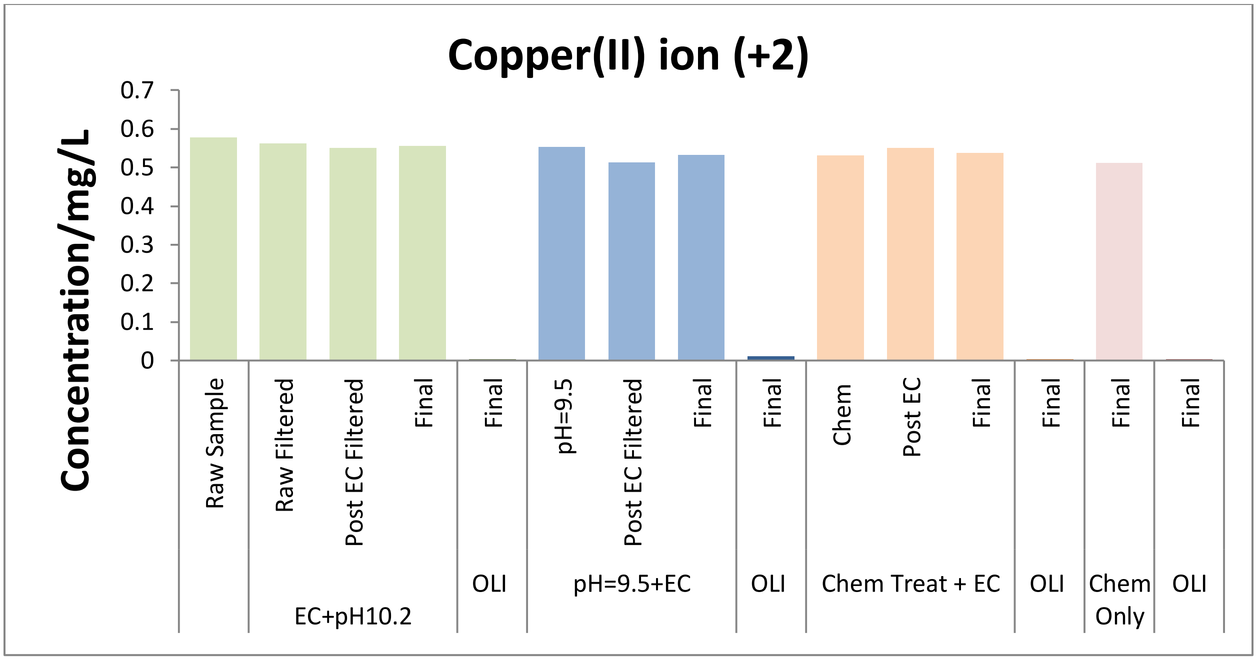

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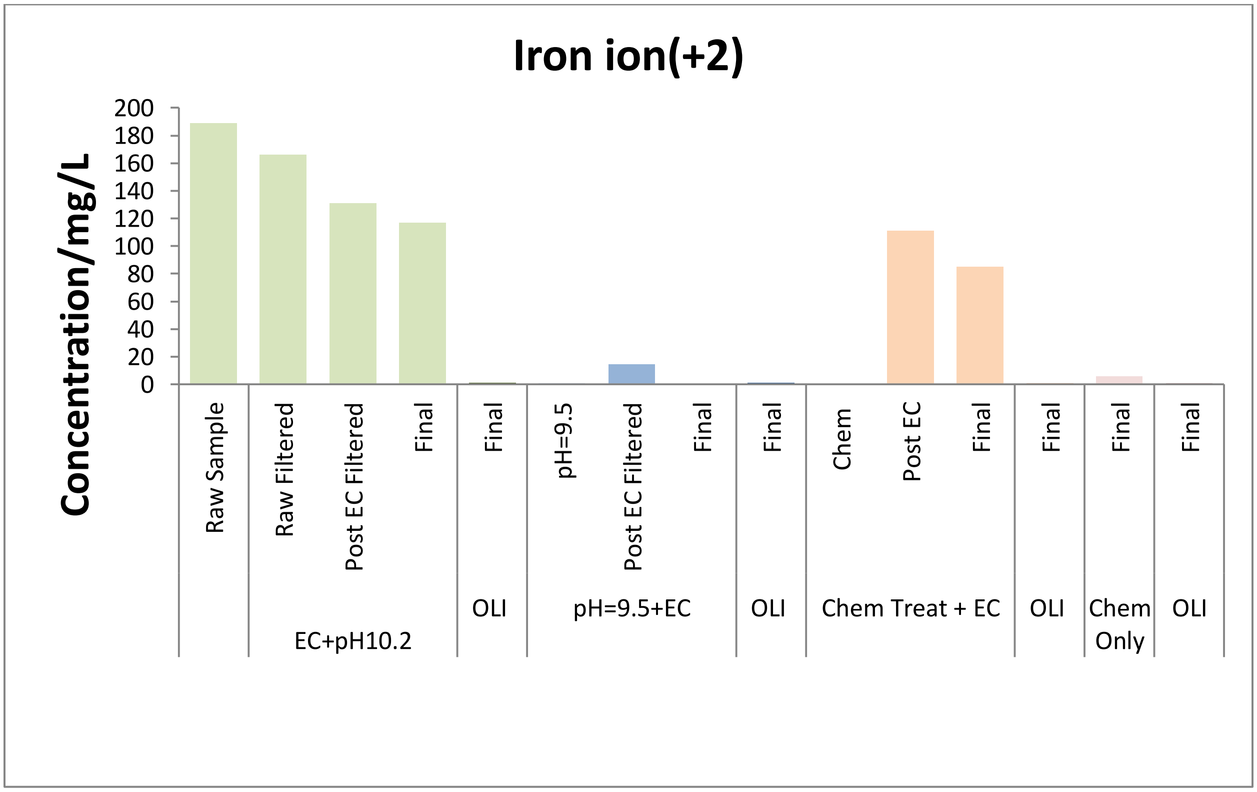

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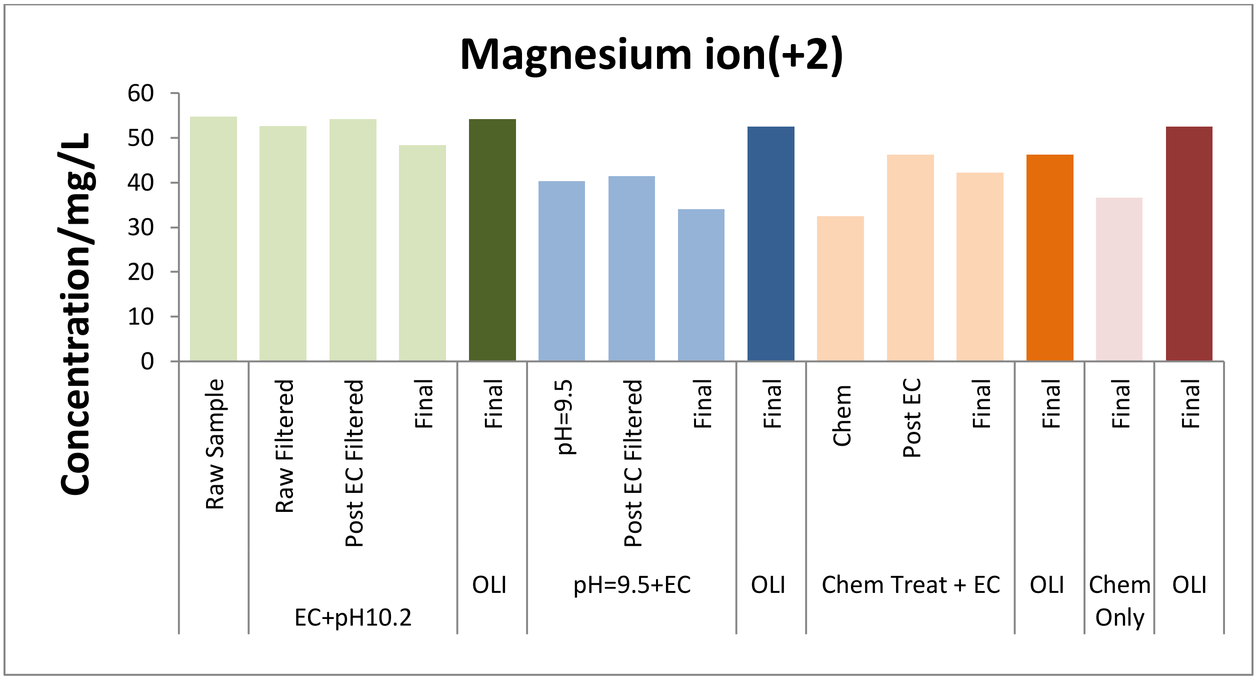

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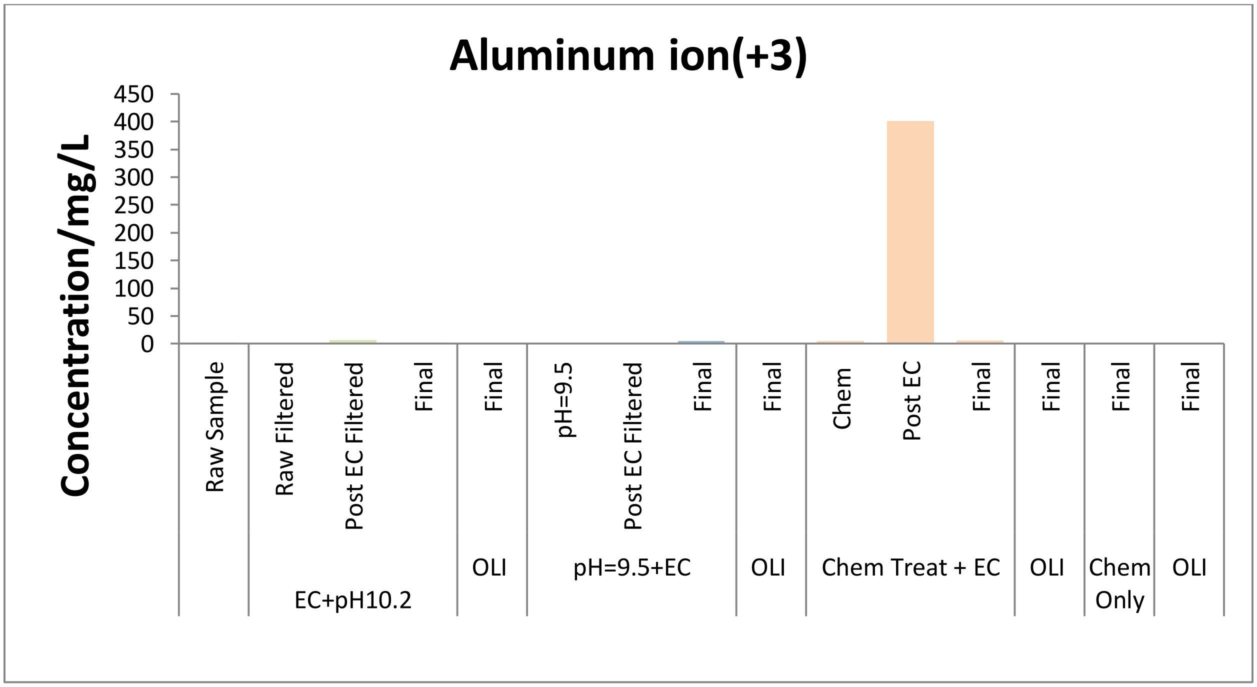
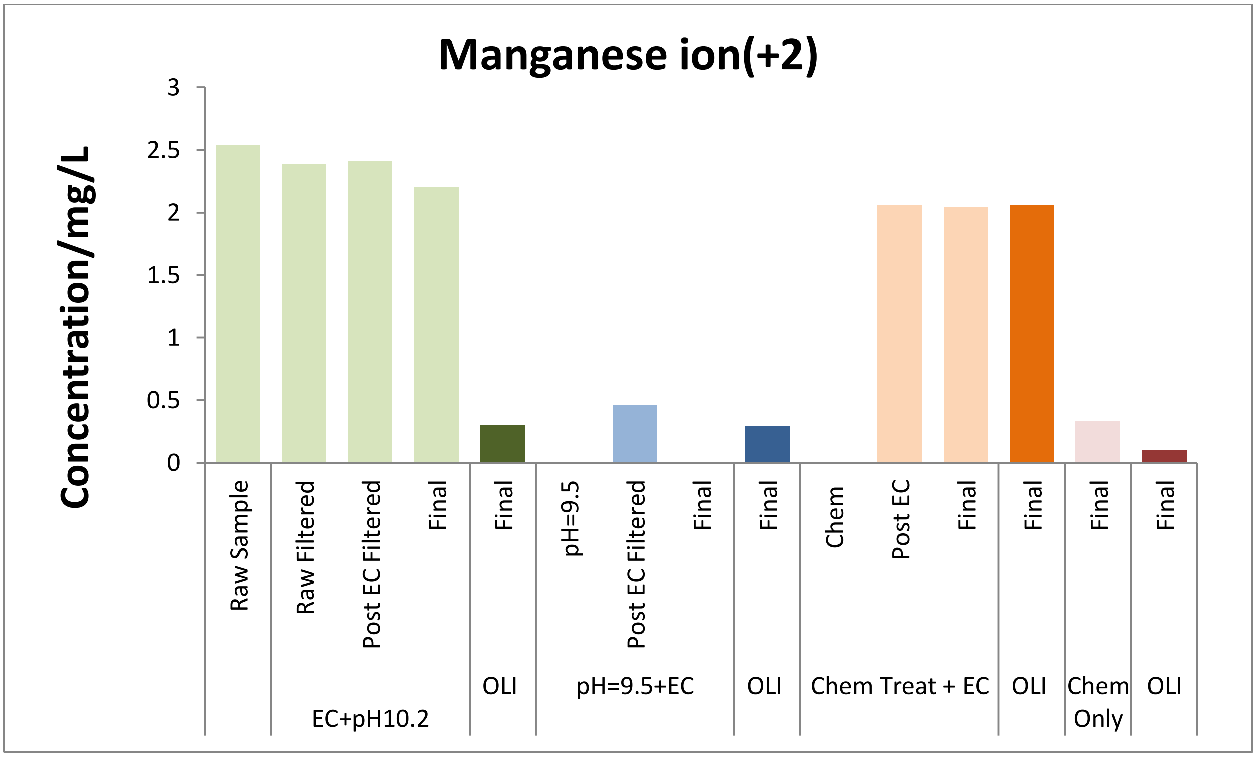


Figure 6.21. Well No. 14-63_Al



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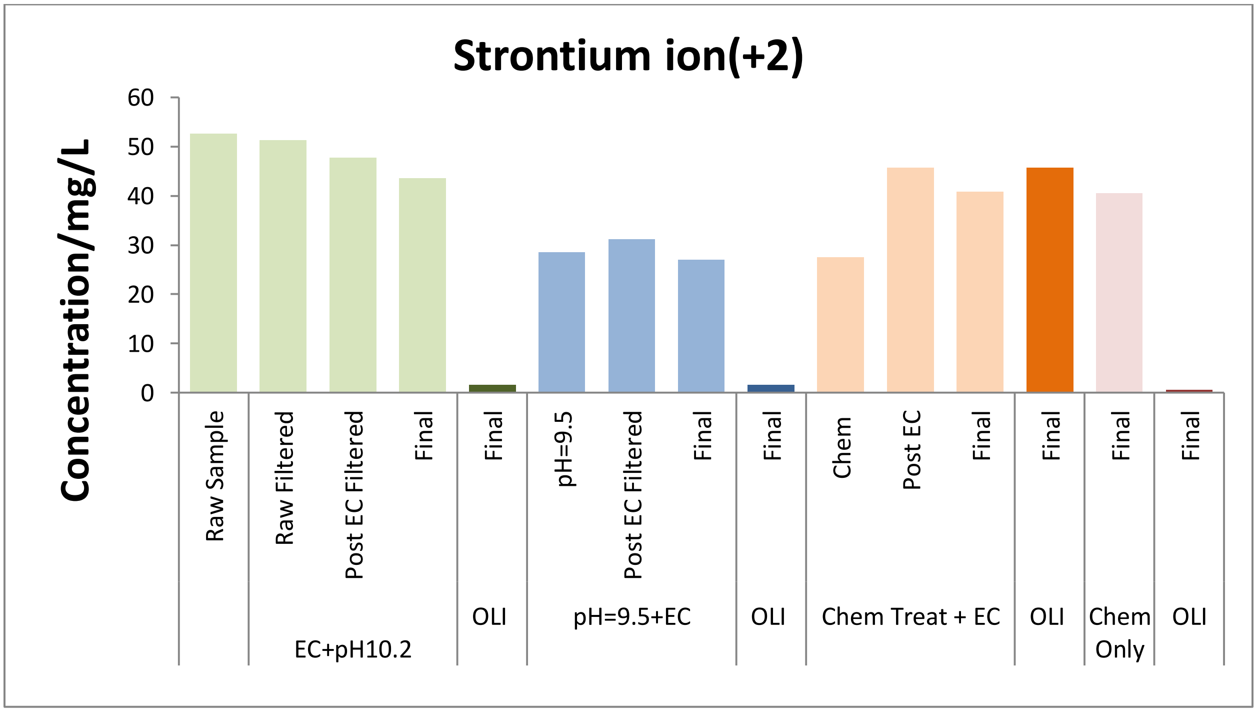

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Well No. 06-63

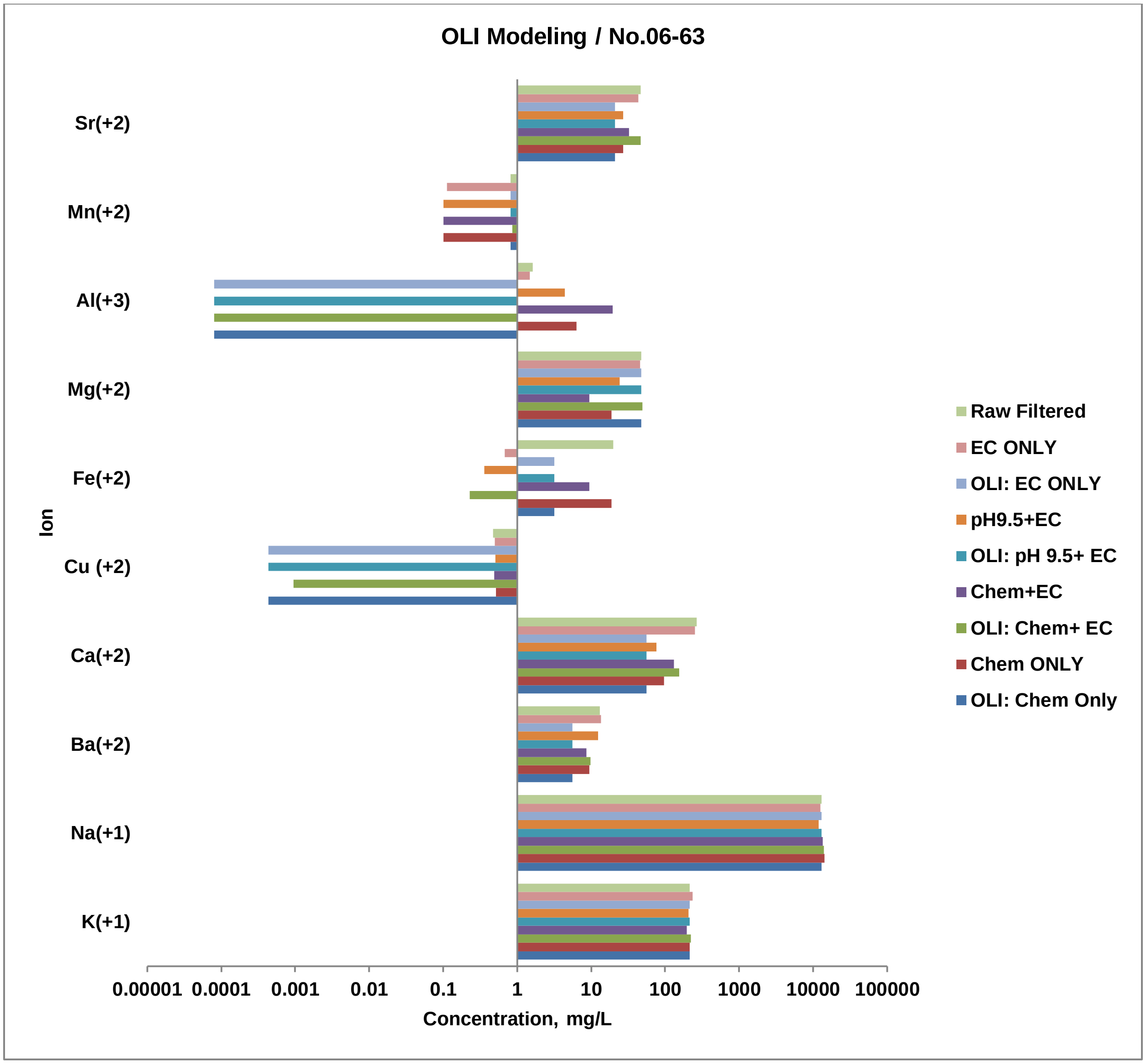
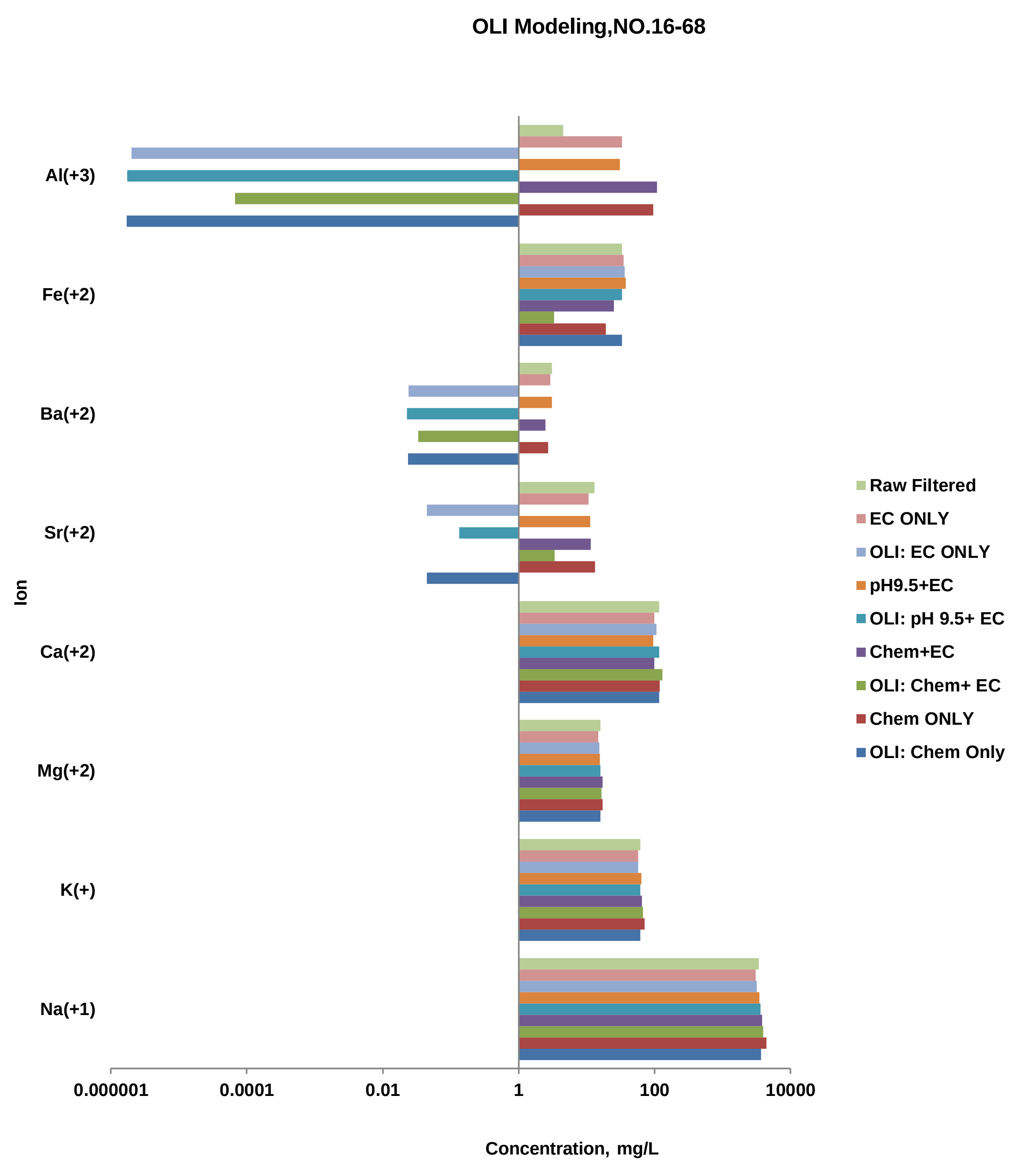


Figure 6.24. Well No. 06-63

Well No. 16-68



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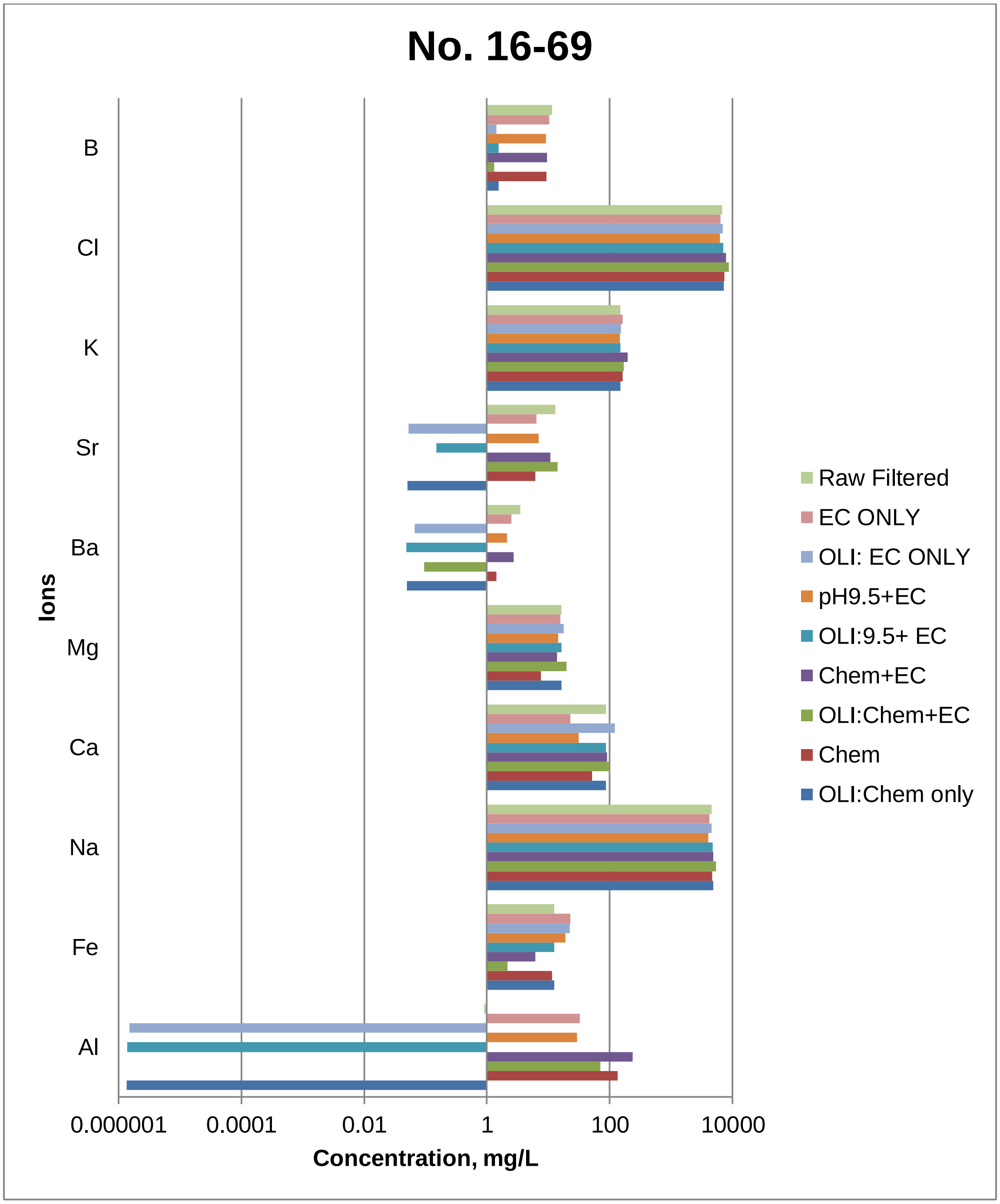
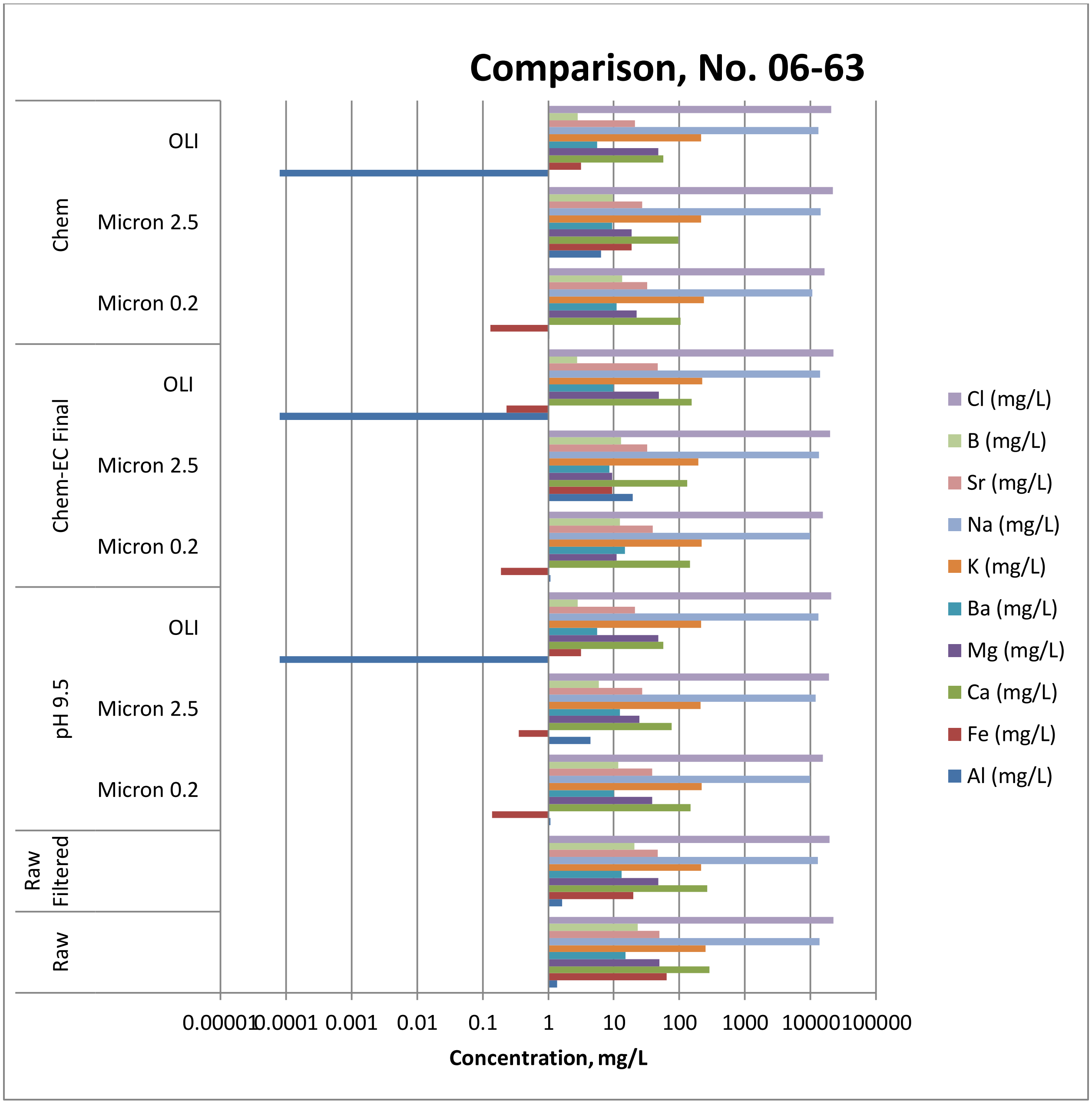


Figure 6.26. Well No. 16-69

Comparisons between Micron 2.5 and Micron 0.2



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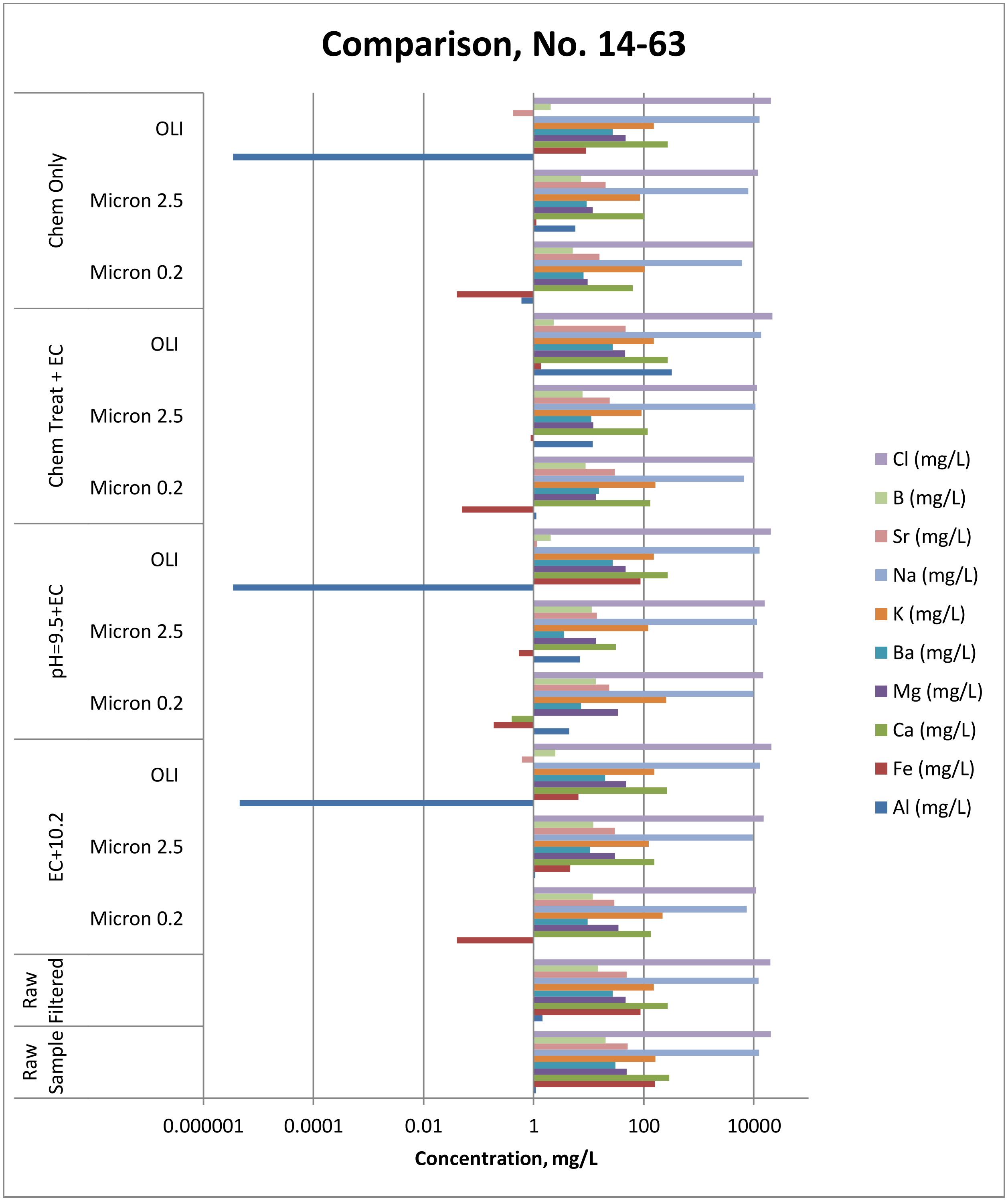

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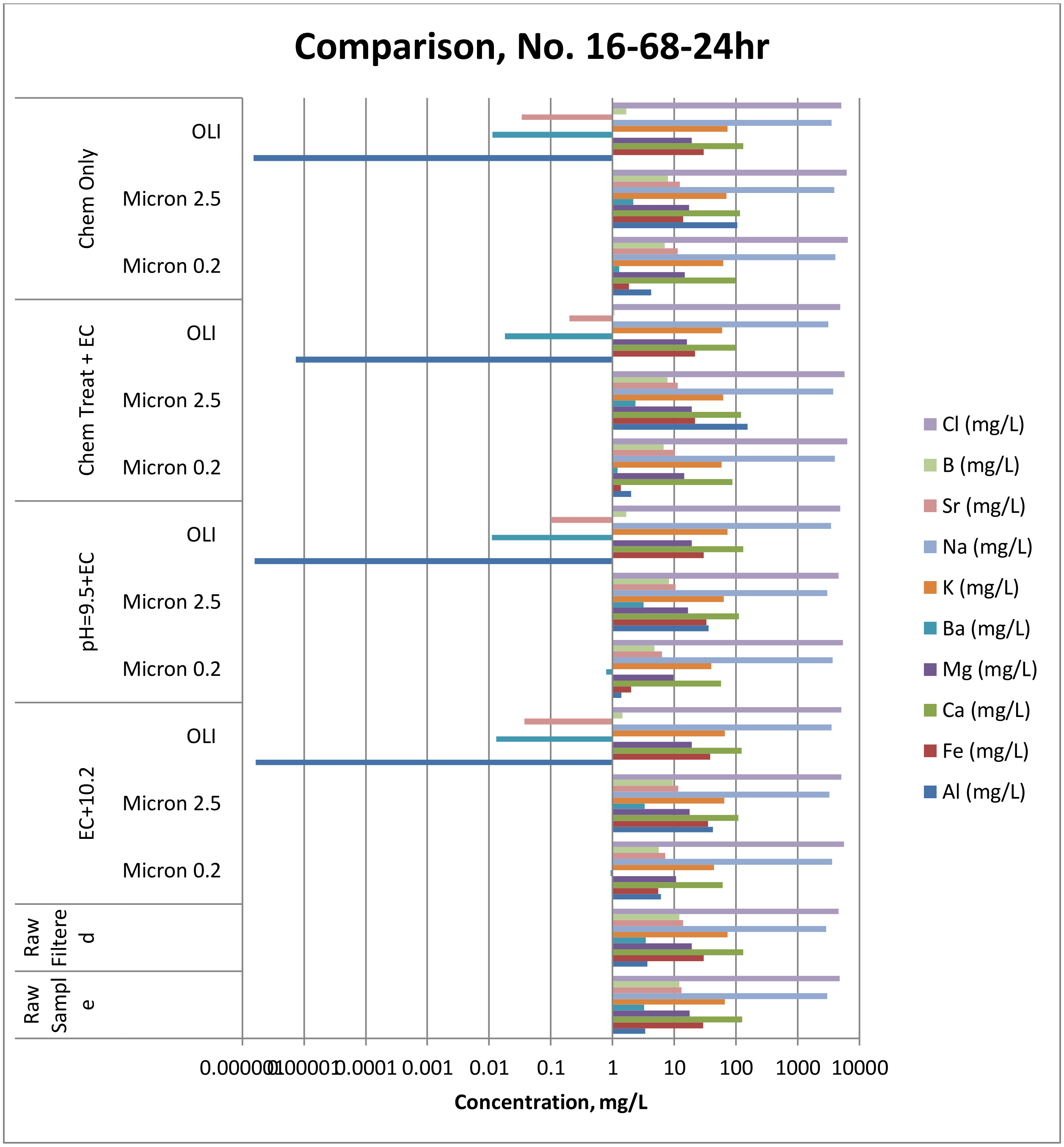

Figure 6.29. Well No. 16-68-24hr

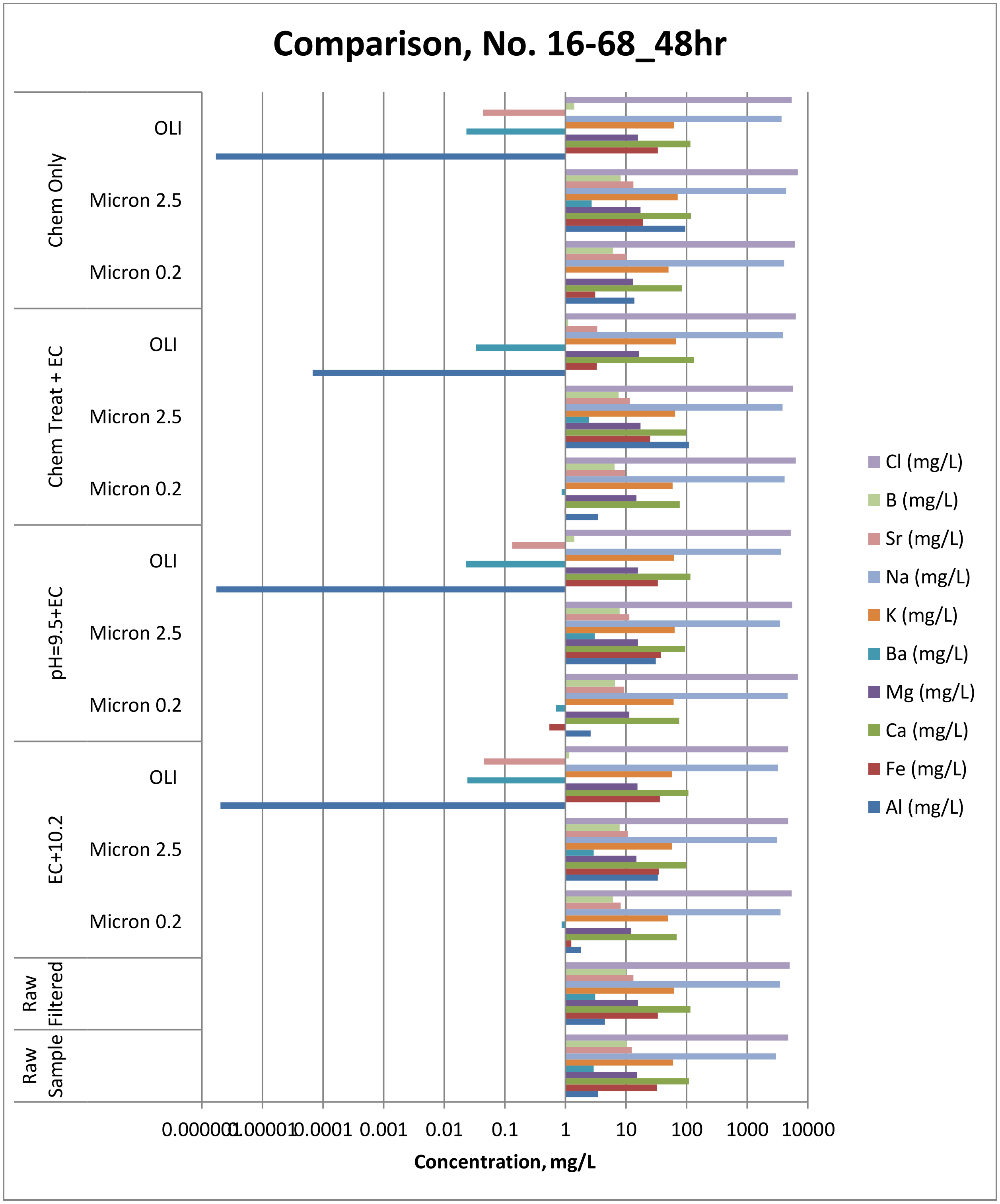

Figure 6.30. Well No. 16-68-48hr

Table Temperature - Precipitation

	-15		-10		-5		0		5		10		15		20		25		30	
	pH=10.2	pH=7	pH=10.2	pH=7	pH=10.2	pH=7	pH=10.2	pH=7	pH=10.2	pH=7	pH=10.2	pH=7	pH=10.2	pH=7	pH=10.2	pH=7	pH=10.2	pH=7	pH=10.2	pH=7
K(+1)	57.4	57.4	57.4	57.4	57.4	57.4	57.4	57.4	57.4	57.4	57.4	57.4	57.4	57.4	57.4	57.4	57.4	57.4	57.4	57.4
Na(+1)	3203.41	3203.41	3225.85	3225.84	3243.24	3243.24	3263.35	3263.34	3274.44	3274.42	3284.76	3284.71	3341.34	3341.24	3351.11	3350.94	3360.37	3360.07	3378.9	3378.4
Ba(+2)	0.0162756	0.0153457	0.0234156	0.0218241	0.032882	0.0302874	0.0446469	0.0393786	0.0598809	0.0518162	0.0787117	0.066798	0.104624	0.0856467	0.132803	0.106385	0.165779	0.129892	0.204125	0.155857
Ca(+2)	107	107	107	107	107	107	0.68829	0.688289	0.737152	0.737152	0.787562	0.787562	0.82279	0.82279	0.865675	0.865676	0.90278	0.90278	0.932383	0.932383
Fe(+2)	36.6	36.6	36.6	36.6	36.6	36.6	0.539803	0.539803	0.49543	0.49543	0.454555	0.454555	0.422993	0.422993	0.388765	0.388766	0.358072	0.358072	0.331288	0.331288
Mg(+2)	15.5	15.5	15.5	15.5	15.5	15.5	15.5	15.5	15.5	15.5	15.5	15.5	15.5	15.5	15.5	15.5	15.5	15.5	10.1813	10.1813
Al(+3)	0.000665711	1.23905E-06	0.00167813	1.74819E-06	0.00416968	2.98056E-06	0.0104407	6.64219E-06	0.0249433	0.000013045	0.0582371	2.57173E-05	0.115556	4.51046E-05	0.202476	8.74673E-05	0.348037	0.00016753	0.587373	0.000315096

Cl(-1)	4383.12	4721.82	4383.12	4750.35	4383.12	4771.94	4383.12	4668.85
	4383.12	4680.98	4383.12	4692.68	4383.12	4737.87	4383.12	4749.76
	4383.12	4761.46	4383.11	4772.55				
Sr(+2)	0.047034	0.047034	0.0452074	0.0452074	0.0442032	0.0442031	0.0448587	0.0448586
	0.0446252	0.0446251	0.0445238	0.0445238	0.0406191	0.0406191	0.0404983	0.0404983
	0.0402444	0.0402444	0.0395549	0.0395549				
B(+3)	1.16273	1.16273	1.16273	1.16273	1.16273	1.16273	1.16273	1.16273
	1.16273	1.16273	1.16273	1.16273	1.16273	1.16273	1.16273	1.16273
	1.16273	1.16273	1.16273	1.16273				

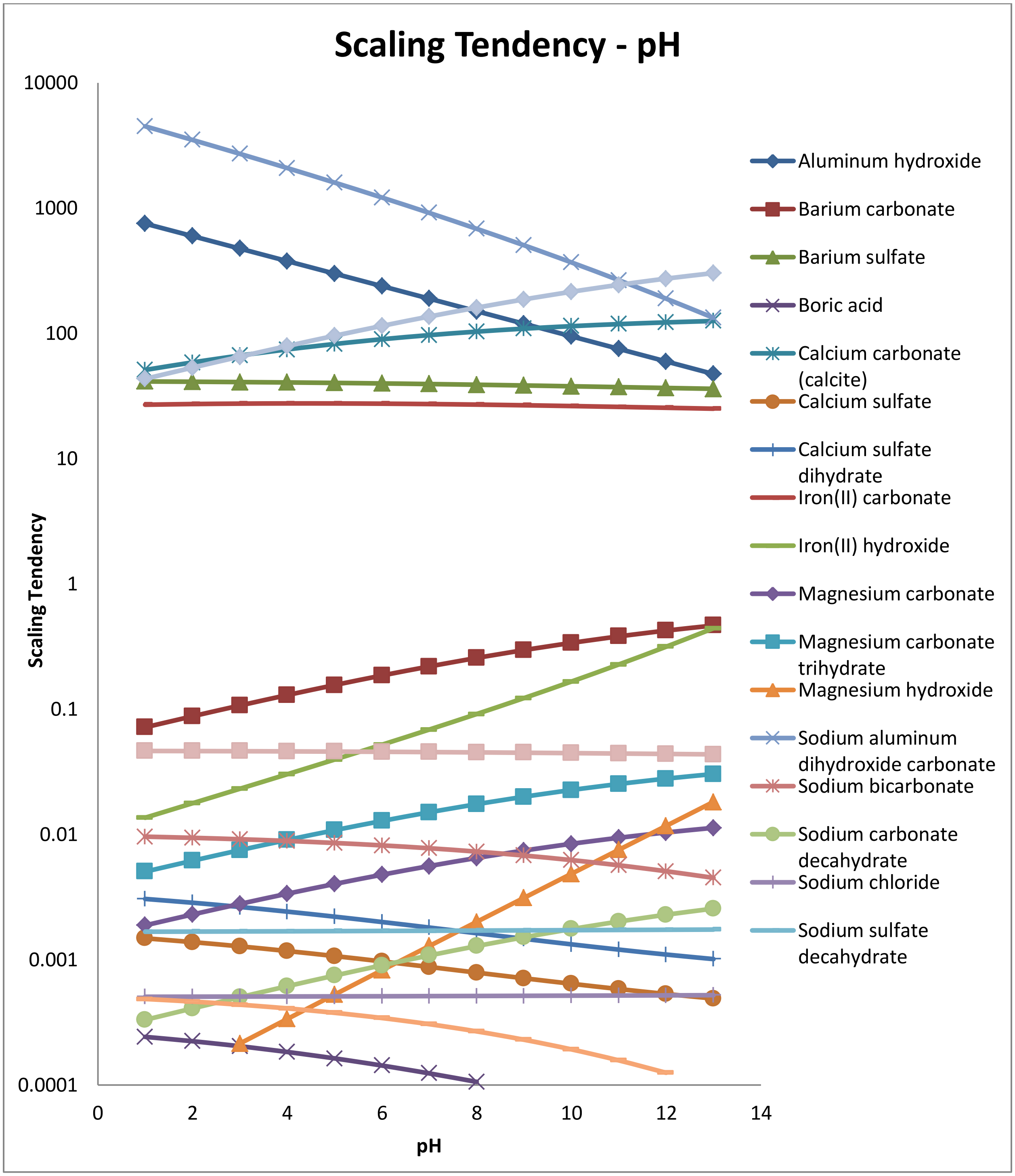

Figure 6.31. The pH vs. Scaling Tendency