

Fluoride, Spring 2015

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May 14th, 2015

Abstract

The goal of the Spring 2015 Fluoride team was to develop and create a system that effectively reduces the fluoride content in groundwater, allowing the water to be consumed without causing serious health concerns. Groundwater in developing countries contains high levels of fluoride, causing crippling fluorosis, calcification of the bones, and a number of other serious conditions. To reduce the amount of fluoride in water, a stacked sand filter was created. This, in conjunction with the coagulant polyaluminum chloride, absorbs the fluoride present in the groundwater - ultimately yielding safer, more “drinkable” water. This semester, the Fluoride team worked to create the stacked sand filter, set up the Process controller system, and begin trials to remove fluoride in groundwater.

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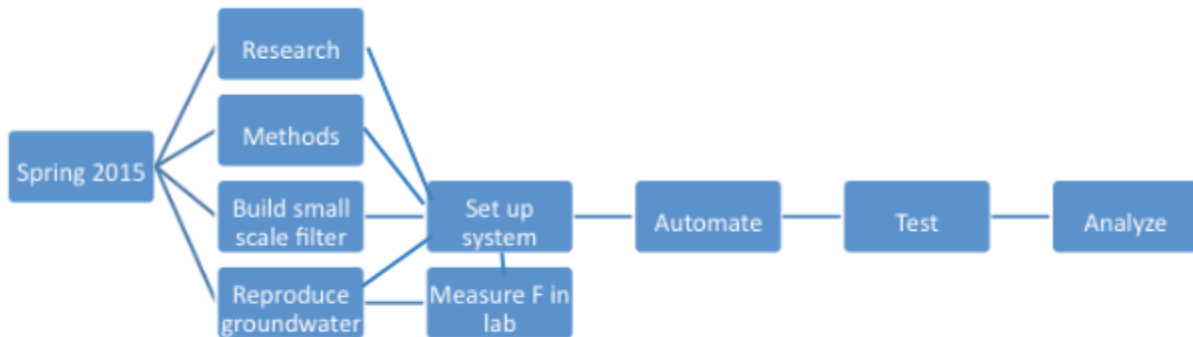
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Task List

Task Map



Task Details

- Research
 - Concentrations of F usually found in contaminated groundwater
 - Find a range of F concentrations to test
 - Recommended concentrations of F by WHO
 - Hazards of F and lethal/chronic doses
 - Create a consolidated list of hazards for working with Fluoride
- Determine method of cleansing water
 - Possible coagulant and filtration options include:
 - Calcium Carbonate
 - Aluminum Oxide
 - Polyaluminium Chloride
 - Aluminum sulfate
 - Iron Chloride
 - Bone Char
- Build a small scale filter
 - Using suggested size of tubing create a sand filter
 - Attach appropriate fittings
 - Choose a reasonable flow rate that correctly scales with the filter
- Set up our system
 - Connect raw water and coagulant with pumps
 - Then make and connect rapid mixer
 - Connect to sand filter
 - Create a way of collecting waste and samples
- Reproduce contaminated water
 - Purchase and dilute Sodium F

- Automate this process with ProCoDA
 - Calculate flow rates and rpms for coagulant and raw water
 - Using STAMP box run the pumps
 - Using the server box receive signals from the pressure and fluoride sensor
- Measuring F concentrations in lab
 - Options:
 - Ion selective probe
 - Fluoride Ion Selective Acquisition Electrode
 - Calibrate the probe and translate from probe output (volts) to a useful unit (mg/L)
- Test method of fluoride removal
 - Report and compare removal rates
- Analyze experimental data and determine ways to improve
 - Less leaky system
 - More tests
 - Different rates of coagulant
- Future research
 - Ensure byproducts don't react poorly with the other contaminants found in groundwater

Completion Dates

- Research - Completed
- Determine method - Completed
- Build a small scale filter - Completed
- Setup - Completed
- Reproduce contaminated water - Completed
- Automate - Completed
- Measuring F concentrations in lab - Completed
- Test method of fluoride removal
- Analyze experimental data and determine ways to improve
- Future research - Next semester

Introduction

In many developing countries, high levels of fluoride in groundwater have been found to have chronic effects on bone health. Though some countries intentionally add Fluoride to water in order to strengthen teeth, overexposure to fluoride has grown as a problem worldwide. With 85% of its drinking water sourced from groundwater, India is the largest user of groundwater in the world and is at a high risk of overexposure to over-consumption of fluoride (EPA, 2013).

Our team hopes to affordably, sustainably and reliably reduce fluoride levels in treated groundwater used for drinking water. Focusing on the groundwater used by the AguaClara plant in Jharkhand, India - we hope to develop a system that works efficiently with the

AguaClara plant and affordable technology to monitor and reduce fluoride levels. Ultimately, our goal is to provide safe drinking water on tap to villages and communities worldwide that are dependent on fluoride-rich water sources (EPA, 2013). Currently we are focusing our efforts on drinking systems in India. These systems only have filtration and then chlorination because the majority of the water they are distributing is ground water. Our system would have to work in this capacity.

Literature Review

Limitations and Hazards

Over-absorption of fluoride can interfere with bone formation, cause the calcification of ligaments, arthritis, dental fluorosis and crippling fluorosis among other conditions. Fluoride can cause irritation through inhalation, digestion, and touch and can cause damage to both eyes and exposed skin.

According to the National Research Council (NRC), the maximum contaminant level (MCL) of fluoride in drinking water is 4 mg/L. However, a secondary limit of 2 mg/L has been established to avoid potential cosmetic effects such as tooth and skin discoloration. The World Health Organization (WHO) established a safe limit of 1.5 mg/L to avoid all potential risks of fluoride consumption. We will be following the WHO guideline for fluoride levels for our research this semester.

Fluoride Removal Methods

A plethora of studies regarding methods for fluoride removal from groundwater have been previously conducted. Methods commonly cited include sorption media, co-precipitation chemicals, and contact precipitation chemicals. The sorption process, which uses either bone charcoal or activated alumina and clay, consists of the media being packed into columns that eventually reach saturation and must be renewed or regenerated (Bailey 46). Chemicals like polyaluminium chloride, aluminum sulfate and lime are used in the co-precipitation method. The chemicals are added in batches and used to precipitate out the fluoride. These processes often produce egregious waste sludge that needs to be properly disposed of (Bailey 46). The contact precipitation method inputs chemicals upstream of a catalytic filter bed which precipitates out the fluoride with no saturation of the filter bed or excess sludge. Chemicals used for this method include calcium and phosphate compounds (Bailey 45).

Each of these methods have benefits and pitfalls associated with them. Bone char used to be widely accessible, but in recent years has been limited in production. It can however, be generated within villages themselves for relatively low costs. Still, it is difficult to optimize bone char practice, and improper use leads to deteriorated water quality (Bailey 47). Water treated with poorly conditioned bone charcoal can have a smell similar to rotten meat and a displeasing appearance (Bailey 47). Another option similar to bone char is biochar, in which pine bark and different types of wood are used instead of bone char. Fluoride sorption by biochars has been found to be comparable to that of activated carbons (Mohan 909), but has only been proved efficient in acidic conditions (Oh 3737) .

The Nalgonda technique is a very popular way for developing countries to remove excess fluoride. A type of co-precipitation method, the overall process involves several steps, including rapid mixing, flocculation, sedimentation, filtration, and disinfection. In this method, alum and lime are used to create insoluble aluminium hydroxide that co-precipitates out the fluoride by settling towards the bottom of the tank. (Bhatnagar 812). The main advantage of this technique is that it uses materials that are easily accessible to developing regions (Bailey 64). The main disadvantage, however, is that the sludge containing the excess fluoride must be disposed of. Disposal is considered a serious environmental health problem, as the sludge contains highly concentrated fluoride. The sludge must be inaccessible to children and animals, and located nowhere near gardens or water sources (Bailey 65). Additionally, because the fluoride in the sludge is only loosely attached to the aluminium hydroxide flocs, water must be removed no later than a couple of hours after treatment (Bailey 64).

Contact precipitation with calcium and phosphate compounds is a theoretically plausible method, but nearly impossible in practice. Thus it is necessary to install a catalyst, namely bone char, in a contact bed that can act as a filter for the precipitate (Dahi). This leads to promising results, but still more research must be done to find the optimal time in which water contacts the catalyst. If more research is done, contact precipitation has the potential to be highly efficient and cost effective (Bailey 56).

This semester, we have decided to use the coagulant Polyaluminium Chloride to precipitate out the fluoride in solution. Traditionally, this chemical has been used in large quantities to encourage the precipitation with gravity. However, our group is exploring the possibility of pairing this process with a filter so less coagulant has to be added. If a coagulant is to be used, the coagulant must be mixed homogeneously into the solution. (Bailey 53). We plan to incorporate this into our design by rapidly mixing the two.

Methods

The apparatus used for experimentation is shown in Figure 1 below. To begin, a source of coagulant and a source of raw water were created. The raw water was created by diluting sodium fluoride, and the coagulant used to treat that water is Polyaluminium Chloride (PACl). Two pumps work to transport the two liquids from their respective containers, and a mixture is formed in the rapid mix piping. The diameter of the rapid mix tubing is small enough that the raw water and coagulant are sufficiently mixed. After the rapid mix, water is pumped up through a sand filter in order to remove the precipitate. Next, an ISE probe in conjunction with Process Controller measures and records the obtained values of fluoride.

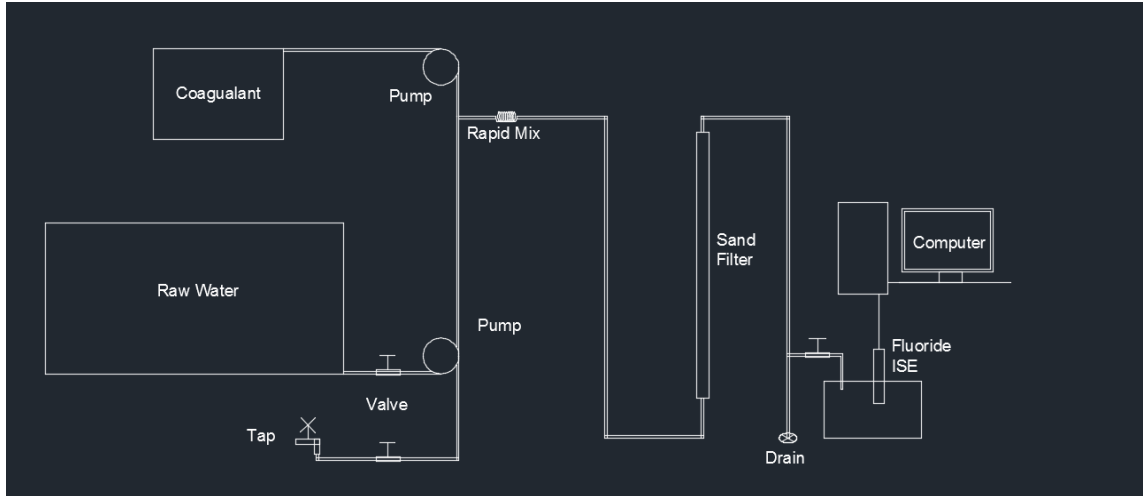


Fig 1. First draft diagram of the filtration system that will be used to both remove fluoride from raw water and record the obtained data values.

For the concentration of fluoride, the EPA states that the safe upper limit of fluoride is 4 mg/L. We planned to test various concentrations of fluoride starting with 10 mg/L, a concentration known to cause serious health concerns. However, problems with the system only allowed that one concentration be tested. We decided to use a higher concentration in the hopes that if the system worked that high, it could filter more realistic concentrations found in natural groundwater. To prepare the raw fluoride water, we used 45 mL of original NaF solution (2 mol/L) with 15 L raw water to obtain a concentration of 11.3 mg/L.

Preliminary Set -Up

At the start of the set-up, raw water is held in a large five gallon bucket and PACl is held in a two liter jar with a lid. Each of these fluids is added to the system by peristaltic pumps, from which they are combined together so that they can be rapidly mixed. To create the rapid mix we used a section of 1 inch piping and a ¼ inch tube wrapped around the pipe. These were secured together by zip ties. From there the water flows up through the bottom of the sand filter and out through the top. Once the water has exited the filter, it is ready to be tested. In the set-up we used a combination of ¼ inch and ⅜ inch tubes to connect each of our components.

To create the sand filter we used a combination of couplings and copper mesh. For the filter itself we are using a 1 inch pipe with one 1 inch coupling, a PVC compression pressure fitting and copper mesh. The mesh was cut to size so that it would fit into the compression pressure fitting, and the ledge on the fitting allowed the mesh to stay in place. The copper mesh was only attached to the bottom of the pipe so that sand can be taken out if necessary. Additionally, as the sand should not be fully fluidized to the length of the pipe, sand should not escape the system through the top of the filter. The filter was only filled halfway with sand to ensure that the sand would not fully fluidize. Lastly, a screen was attached to a compression fitted coupling in order to contain the sand.

Since the raw water for experiments and the tap water for backwash are to be controlled by the same pump, valves were added to the system. An additional T-fitting was added before the T-fitting connecting the coagulant and the water tubing, and tubing with a valve was then connected to each water source. Additionally, a T-fitting and a valve were added at the end of the system, where the effluent from the sand filter goes to a large collection bucket. The valve was added to a separate tube that does not lead to the bucket so that an effluent sample can be collected for ion testing. Water from this much shorter tube must first be emptied as to not test the water from the previous sampling cycle. This batch method was put in place to keep the ion probe from having water continuously run over it, so that unnecessary deterioration would be prevented.

Process Controller - System States

To control the pump speed and ultimately measure the concentration of fluoride, our system requires the use of Process Controller. In Process Controller, there are seven states that the system can be in: 10 rpm, 50 rpm, 90 rpm, Raw Water Pump, Coagulant Pump, System and OFF. The only three states used when running an experiment are System, Raw Water Pump and OFF, as the others were just created to troubleshoot problems that arose as we were setting up pumps and Process Controller itself. A description of the system states are as follows:

1. 10 rpm - Sets all pumps in ports 0, 1, 2 and 3 to 10 rpm. This state was created for pump calibration and was used when the lower limit of the pump needed to be set.
2. 50 rpm - Sets all pumps in ports 0, 1, 2 and 3 to 50 rpm. This state was created for pump calibration, but is not used in the calibration itself, but just to check the middle range of pump speeds.
3. 90 rpm - Sets all pumps in ports 0, 1, 2 and 3 to 90 rpm. This was created for pump calibration and was used when the upper limit needed to be set.
4. Raw Water Pump - Turns on the pump at port 2, which corresponds to the raw water pump. This state was created so that the System state would be easier to program, and also as the backwash state. Since our backwash is not a true backwash, water runs forwards through the system as it would normally, with the exception that the water source has changed from our raw water to tap water. This works to clear out all the stuck fluoride particles trapped within the sand filter, and should be done after experiments or when it seems that the fluoride is getting too stuck in the sand.
5. Coagulant Pump - Turns on the pump at pump port 3, which is our coagulant pump. This was done to help program the System state, so that the proper flow rate and pump speeds would be set.
6. System - Turns on the pumps at ports 2 and 3, which corresponds to the raw water pump and the coagulant pump. In System, the flow rates are set to the proper values in coordination with the Raw Water state and the Coagulant Pump state.

Calculating Flow Rate

Because we are basing our system primarily off of the previously created arsenic system, we decided that we should use similar flow velocities for the filtration and the backwash system. Because the arsenic system uses a ½ in diameter pipe and we are using 1 in diameter pipe, we needed to calculate a flow rate that corresponds to our system. The following are the calculations that were done to determine the system flow rate. The following table describes how we computed the flow rate for our system.

Table 1: Flow Rate Calculation

Calculation Corresponding to Filtration	US Units	SI Units
Hui's Flow Rate	0.702 in^3/min	191.7 mm^3/sec
Hui's Radius of Pipe	0.301 in	7.645 mm
Target Velocity	2.47 in/min	1.009 mm/sec
Radius of Pipe	1.029 in	26.14 mm
Target Flow Rate	8.2 in^3/min	2.18 mL/sec

Fig.2 Table of calculations done to determine the overall system flow rate based on Hui's arsenic system.

Though the arsenic system provided us with a backwash flow rate, more experiments will have to be done to see if it is effective for our set up. Since we are unsure if the sand in our system is similar to the sand used in the arsenic system, trial and error should be used to find the correct flow rate for our system to be fully fluidized.

Dilutions

To create our dilutions, we ordered a stock solution of 1,000 mg Fluoride/L. We created four standards to test with our probe in order to establish a relationship between the reported voltage and the concentration of fluoride in the water.

The 4 standards are as follows: 10 mg/L, 5 mg/L, 2.5 mg/L and 0 mg/L. To obtain the 10 mg/L standard, we combined one part fluoride stock solution to 99 parts water in a 100 mL volumetric flask. Some of this solution was set aside in a vial for later calibration of the probe, and the rest was used for the next round of dilutions. For the 5 mg/L equal parts of water and the 10 mg/L solution were added to a 100 mL volumetric flask. Again, some of this solution was set aside for calibration while the rest was used to make the 2.5 mg/L standard. The 0 mg/L standard was just deionized water.

Pressure

When running the system, it was difficult to tell when the filter was getting too clogged and needed to be cleaned out. To combat this, a pressure sensor was added to measure the change in pressure around the filter. With this mechanism and measurements of fluoride, we would be able to tell when the system needed backwash.

Problems

Throughout this semester there were several minor but critical problems that had to be addressed before the system could be run correctly. These ranged from the ProCoda box and system itself, to air bubbles in the filter.

First, there were substantial problems with the ProCODA boxes. At the beginning of the semester, a new ProCoDA box was used to connect the pumps to the computer. However, there was one port that was not functioning properly. After a few weeks, a new box was obtained which still had malfunctions with the sensor ports. After attempting to have someone fix resistors in the box, it was decided that the older, but more reliable STAMP boxes should be used to run the pumps. This meant that Process Controller and Data Acquisition would be used instead of ProCoda.

The next problem faced was that the fluoride probe was fluctuating and not stabilizing around one value. The probe was very sensitive, even to minor shakes and disruptions. To fix this problem, tape was used to keep the probe attached to the beaker when measuring ions. After that, the measured curve appeared like a sine wave which was caused by the impulse of peristaltic pump, and proper readings could be obtained.

Lastly, there have been many issues with air bubbles in the tubing. The connectors could not be perfectly sealed, sometimes allowing air into the system. The air bubbles would influence the head loss of the filter while constantly fluidizing sand. This problem has not been fully addressed, but is another issue that can be dealt with in the future.

Analysis

Before the system could be run, a calibration curve had to be created so that any data from the probe could be analyzed properly. Four fluoride standards of 0 mg/L, 2.5 mg/L, 5 mg/L and 10 mg/L were created and the corresponding voltage was read by the fluoride probe. The negative log of the fluoride concentration was then plot against the voltages to create a "p[F]" similar to how pH is obtained from the $-\log[H^+]$.

Graphing $-\log[F^-]$ against the voltage is expected to yield a linear function.

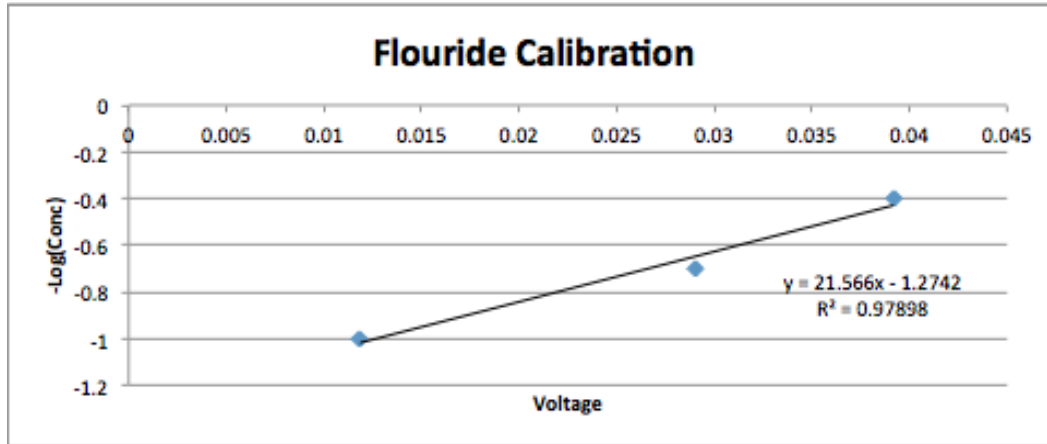


Fig 3. Semilog graph/ calibration curve of fluoride plotting the $-\log(F^-)$ against the probe voltage.

Three data points were plotted by calculating the mean voltage the probe yielded for the three concentrations, over a period of thirty seconds. Although only three points could be used, the data was fairly linear, demonstrating that as the concentration of fluoride increases, the voltage increases exponentially.

Next, by setting a best fit line for the data, an equation was obtained that would allow for the concentration of fluoride to be determined from a simple voltage measurement.

Due to time constraints, only one experiment was run, although it had promising results. The following is the data collected from this test (data collected on 5/14/2015):

Interaction	Time	Value (Volts)	Conc (mg/L)	%Removal	Pressure
	Hours	(Volts)	(mg/L)	%	(Volts)
Initial		0.01049	11.169		
0	0	0.02004	6.951	37.8	-0.0196
1	1	0.01945	7.158	35.9	-
2	1.5	0.02068	6.734	39.7	-0.0196

Fig 4. Data collected from initial test, showing approximately 40% fluoride removal.

It can be seen that there was a steady 35-40% removal rate, and the best removal had water that was only 2 mg/L over the WHO maximum chronic concentration level. This is impressive considering there were several issues that occurred during the trial. At the flow rate being used, the bed was fluidized, although only minutely, but enough to inhibit catching particles. This should be reevaluated and corrected to create a more docile flow. Additionally, only 10 mg/L of PACl were being added. This was at the lower edge of the desired range of PACl dosages, but it was chosen for several reasons. It was desired that the flocs would not get stuck in the tubing before entering the filter, as this would cause many issues with cleaning

the system. It was also considered that the small tubing size placed in the pump caused the pump to run close to capacity. This is likely due to the high overall flow rate. This trial was stopped because because the sand was fluidized, and because both the PACl and the raw water supplies were running out. In future trials there should be a substantial supply of both.

Conclusions

Despite a substantial amount of problems throughout this semester, the first semester of the Fluoride team has been fairly successful. Since the design of the fluoride system was based on that of the arsenic system, constructing the set-up did not involve any major setbacks. The main constraint of the semester was attempting to get the system to be functional, so that trials and experimentation could begin. There were many issues with trying to be one of the first teams to use ProCoda, as the ProCoDa box itself had many problems that could not be figured out. After attempting to make it work with the system, Process Controller was reverted to, and system states were designed. The mechanical problems with pumps not working properly and the probe not giving a linear calibration curve were dealt with after some time, but it caused difficulty with having the time to experiment.

After completing the first trial, it can be seen that the system is functional, it simply has to be optimized. This will be work for future Fluoride teams, but it is a promising sign that fluoride removal can be accomplished with this system design. Now that the system has no issues with functioning, there are a lot of different aspects of the removal process that need to be tested and optimized.

Future Work

As this was only the first semester of the fluoride subteam, there are several things that the team can expand on in the future. Most prominently, more trials need to be run since only one was completed this semester. With a greater number of trials, the coagulant dosage should first be run through a large range, and then narrowed down to a more optimal rate. Additionally, more points should be added to the fluoride probe calibration, since there are only three points in the range of testing. More points at a larger range would help to gauge if this system model can work for different concentrations.

Another important step would be to establish how often backwash should occur, and at what flow rate it should happen. Since only trial was able to be run, a lot more information on how the system should be cleaned would help to ensure that fluoride does not get stuck in the system and disrupt the readings. This can be done by measuring removal rates and the pressure of the system until removal drops and pressure increases.

Once a recommended coagulant dosage for this concentration of fluoride, it would be extremely beneficial to create a relationship between different fluoride concentrations and the recommended PACl dosage. This could help implement the system into areas where fluoride might be at concentrations that have not been tested yet. Similarly, it might be beneficial to testing different variations of sand filters by changing the dimensions to accommodate higher or lower fluoride concentrations.

Finally, a cost benefit analysis on the entire setup could be very helpful for different fluoride concentration. In conjunction with this, it might be worthwhile to try and reproduce a more realistic groundwater, with all the elements that are typically found in groundwater, instead of just fluoride. Other elements that are in actual groundwater might cause problems for the probe or even for the PACI and the sand filter, so it would be extremely beneficial to test these.

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