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A STUDY ON THE ELIMINATION OF FLUORIDE IN A HOT SPRING WATER

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Abstract : The hot spring water of the north Jeonla province such as Wanggung, Jookrim, Seokjung, and Hwasim, has fluoride concentration of 3.9 mg/L, 12.7 mg/L, 1.9 mg/L, and 6.3 mg/L, respectively. These figures fairly exceed the Korean and WHO standard for potable water, which is 1.5 mg/L. Therefore, in this study, research on elimination of fluoride in a hot spring water of Jookrim region, which has the highest level of fluoride concentration level in the north Jeonla province, was carried out. In analysis of Jookrim hot spring water according to the water quality standard for potable water, pH was very high at 9.25 and the concentration of fluoride was 10 times higher than the standard at 18.2 mg/L. Other measurements were within the standard or not detected. After injecting 10g of activated carbon for elimination of fluoride, the fluoride concentration was measured at 13.5 mg/L, and when 70mL or more of alum 10 g/L solution was injected, the concentration was measured at 2.8 mg/L, and injecting 3g of lime was measured at 9 mg/L. Alum showed the best elimination performance among all individual injections. Injection of 25 mL of activated carbon and 100 mL of alum solution together reduced the fluoride concentration down to 1.3 mg/L, which is under the potable standard. Injection of lime 1g and 75 mL of alum 10 g/L solution together reduced fluoride concentration to 4.1 mg/L. From the modifying HRT, by using ion exchange resin column, the pH was stabilized when HRT was 1min and showed range of 6.7~7.8. The fluoride concentration reduced gradually as the HRT increased, and satisfied the potable standard when HRT passed 6 min, and after 30 min HRT, the concentration of fluoride was 0.05 mg/L: almost eliminated.

Key Words : Hot spring water, Fluoride, Activated carbon, Alum, Lime, Ion exchange resin

INTRODUCTION

The underground water quality is determined mainly by the mineral compositions contained in natural water or the composition of aquifer. Accordingly, the overall quality is subject to significant influence from proximity to surface, earth composition in regions with high infiltration rate, and various minerals contained in the earth[1].

Fluorine is the most common element, and content in the crust is approximately 0.3 g/kg, existing in form of fluorides in fluorite, cryolite, or apatite.[2] Otherwise, it is derived from fluorine minerals included in granite, other fluorides, or volcano gas. In some cases, it may be contained in wells in mountains with plenty of granite or in spring water; yet, this is only limited to specific areas. The main component of formation distributed in nature is calcium fluoride, extensively dispersed throughout hot-spring areas. For this reason, the underground water of hot-spring areas, in general, contains abundance of fluoride.[3]

Small quantity of fluoride can be seen in most of waters, however, the higher concentrations can only be related to subsurface water source. In nature, where minerals containing fluoride are abundant, creatures may contain fluoride up to 10 mg/L or above.[4,5]

The hot spring water of South Korea is ample

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and of high quality; yet only a small portion of it is being used for health or medical purposes. In tourism attractions, it is being used not any differently from a public bath. In order to use such hot spring water as potable water source, the water must satisfy standards for potable water.

The hot spring water of the north Jeonla province such as Wanggung, Jookrim, Seokjung, and Hwasim, has fluoride concentration of 3.9 mg/L, 12.7 mg/L, 1.9 mg/L, and 6.3 mg/L respectively; these figures fairly exceed the Korean and WHO standard for potable water, which is 1.5 mg/L. Therefore, prolonged drinking of such water seems inappropriate due to excessive intake of fluoride.[6]

Fluoride, depending on its concentration, has various effects on the human body, animals, and plants, and intake of suitable amount of fluoride strengthens secretion of thyroid glând, thereby helping prevention of rickets and cavities. If the fluoride concentration is increased up to 1 mg/L, the cavities are reduced; however, if it is increased to 1.5~2.0 mg/L, spots(fluorosis) may form on teeth.

Specifically, patients with long history of chronic kidney disorders or polydipsia may form spots on their teeth, when drinking water with 1 mg/L fluoride concentration for a prolonged period, as mainly with the children 0~7 years old, whose teeth are proceeding mineralization.[7]

Drinking water with 3 mg/L or more of fluoride for a prolonged period will adversely damage the teeth, and be a cause of fluorosis, which leads to change in skeletons. Intake of fluoride in high levels will cause critical toxicity in human body. Moreover, fluoride brings about acute toxicity in high concentration. From the pathological changes, Hemorrhagic Gastritis or Acute Nephritis may occur, liver and myocardium may be damaged, or if severe, the thyroid gland may be affected.

Methods to dispose fluoride in wastewater studied are precipitation using $Ca(OH)_2$[8] or $CaCl_2$, absorption using gas concrete[9] or rare earth metal,[10] coagulation using alum,[11] use of ion exchange resin,[12] filtration using membrane, dialysis, etc.

Among these, the most commonly used treatment in processing fluoride acid wastewater is addition of lime($Ca(OH)_2$), and using the generated calcium salts: CaF_2 precipitation. This method can process large quantities of wastewater in a short time, and provides easy engineering; however, the solubility of lime is low, responsiveness is lowered, and due to the content of impurities interfering precipitation of CaF_2, the processing efficiency is low.

Therefore, in many cases, two-phase process of alum coagulation and precipitation or 3-phase process also including rare earth metal are widely used; the cost is heavy, and excessive injection of low-solubility lime leaves high level of calcium remnant and hinders reuse. Excessive production of sludge also leads to various problems due to scale.

Therefore, this study purports to research on characteristics and elimination of fluoride in hot spring water of Jookrim region, which has the highest level of fluoride concentration level in the north Jeonla province.

EXPERIMENTAL METHODS

Materials

The sample used in this study is hot spring water of Jookrim Spa, located in the north Jeonla province, Wanju-Gun, Sanggwan-Myun, Jookrim-Ri. After sampling, the samples were packed to prevent contact with air, and were transported to the laboratory for tests. The Analysis was done by KOWACO Water Quality Inspection Center in Gumgang/Seomjin River. As the result of analysis, pH was found very high at 9.25 and the concentration of fluoride was more than 10 times higher than the standard at 18.2 mg/L. Other measurements were within the standard or not detected.

Equipments

The batch reaction test for fluoride elimination implemented Jar-test equipment. In order to shift the response time and agitation solidity, a Jar-tester equipped with time controller and speed controller was used.

Moreover, for ion exchange, a reactor was created for column test, and experiments were done by shifting HRT for each reactor. The Jookrim hot spring water that contains fluoride (14~17 mg/L) was experimented with Jar-test by using alum ($Al_2(SO_4)_3$), activated carbon(Daelim), and lime ($Ca(OH)_2$). By using identical sample, the column filled with negative ion exchange resin(SA20AP) was passed through upflow to investigate the fluoride elimination rate. The diameter of column at this point was 30mm, and the filled layer 500 mm. Fluorine measurement was utilizing DR-2500 to investigate changes. The schematic diagram of column used in experiment is shown in Figure 1.

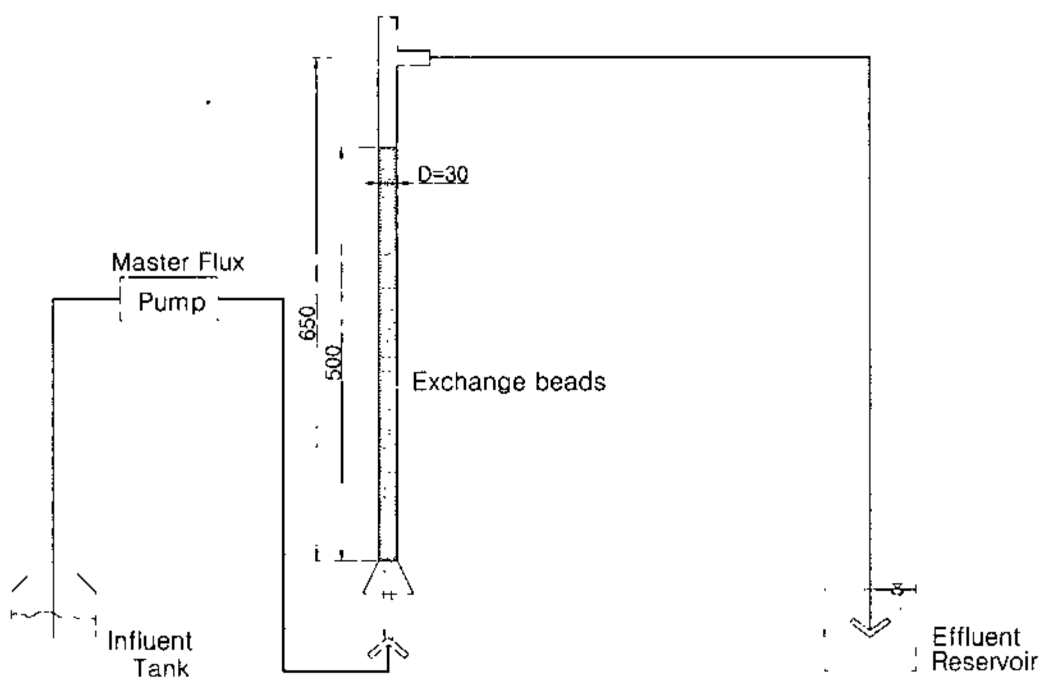

Figure 1. Schematic diagram of column used in experiment.

Method and measurement

1) Activated carbon absorption

Activated carbon absorption experiment was done for elimination of fluoride. Sample 1 L was filled in 1 L beaker, and the amount of activated carbon was shifted through 0 g, 1 g, 5 g, 10 g, 15 g, 20 g, respectively. The Jar-tester was adjusted to 150 rpm, and the change in fluoride and pH was measured as time passed by. Moreover, the 1 L beaker was filled with 50 mL, 100 mL, 200 mL, 300 mL, 400 mL, and 500 mL of activated carbon; the chronological changes of fluoride and pH were measured.

2) Alum coagulation

For alum coagulation, 10 g/L alum solution is produced, and injected from 0.5 mL to 90 mL, in 1 L beaker filled with sample. After 1 min of rapid agitation, 15 min of slow agitation, and 40 min of precipitation, fluoride and pH transition of each was measured.

3) Lime

1 L beaker is filled with sample, and lime is injected from 0.5 g to 7 g. After 1 min of rapid agitation, 15 min of slow agitation, and 40 min of precipitation, fluoride, pH, and TDS transition of each was measured.

4) Activated carbon + Alum

1L beaker is filled with sample and 25 mL of activated carbon. Alum solution is then injected in quantities of 25 mL, 50 mL, 75 mL, and 100 mL. After 1 min of rapid agitation, 15 min of slow agitation, and 40 min of precipitation, fluoride, pH, and TDS(Total Dissolved Solids) transition of each was measured.

5) Alum + Activated carbon

1 L beaker is filled with sample and 50 mL, 100 mL, 150 mL of activated carbon. Alum solution is then injected in quantities from 5 mL to 30 mL. After 1 min of rapid agitation, 15 min of slow agitation, and 40 min of precipitation, fluoride and pH transition of each was measured.

6) Powdered activated carbon

Mix 1 g of powdered activated carbon in 1 L of distilled water. Inject the solution in 1 L beaker filled with sample in quantities of 5 mL, 10 mL, 15 mL, 20 mL, 25 mL, and 30 mL. After 1 min of rapid agitation, 15 min of slow agitation, and 40 min of precipitation, 75 mL of alum solution is injected in each beaker. Then the cycle of 1 min of rapid agitation, 15 min of slow agitation, and 40 min of precipitation is repeated for measurement of fluoride, pH, and TDS transition.

7) Lime + Alum

After filling the 1 L beaker with sample, inject lime from 0.5 g to 7 g each. After 1 min of rapid agitation, 15 min of slow agitation, 75 mL of alum solution was injected. After another 1 min of rapid agitation, 15 min of slow agitation, and 40 min of precipitation, fluoride transition of each was measured.

8) Ion exchange resin

To identify the fluoride removal rate by using ion exchange resin, a column of 30 mm diameter and 650 mm height was produced. The sample was injected upflow, and the HRT at this point was shifted from 1 min to 50 min. The fluoride, pH, and TDS transitions in effluent of each column were measured.

RESULTS AND DISCUSSION

Activated carbon adsorption

As the amount of activated carbon was increased, the pH increased and fluoride decreased. The pH was highest at 9.46 when 15 g of activated carbon was injected, and fluoride was highest at 13.5 mg/L when 10 g of activated carbon was injected. There were no shifts according to time. The result is shown on Figure 2 and Figure 3.

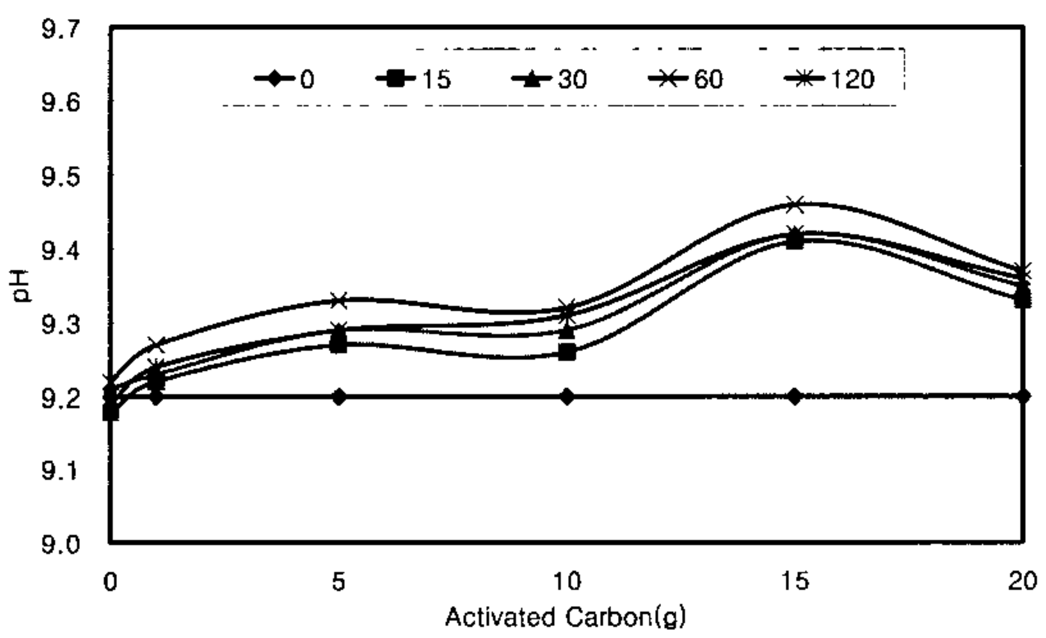

Figure 2. Change in pH according to amount of activated carbon injected.

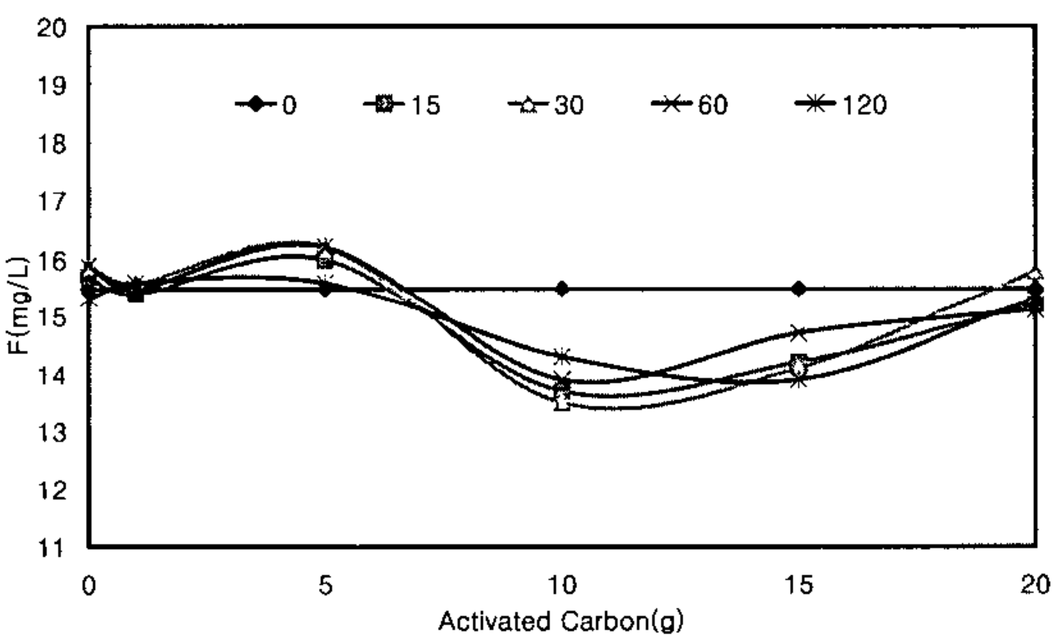

Figure 3. Change in fluoride concentration according to amount of activated carbon injected.

Figure 4 and Figure 5 measurements of pH and fluoride changes, as amount of activated carbon is shifted and the contact time with sample is increased. The pH in early stages, increases and gradually stabilizes; greater the injection amount

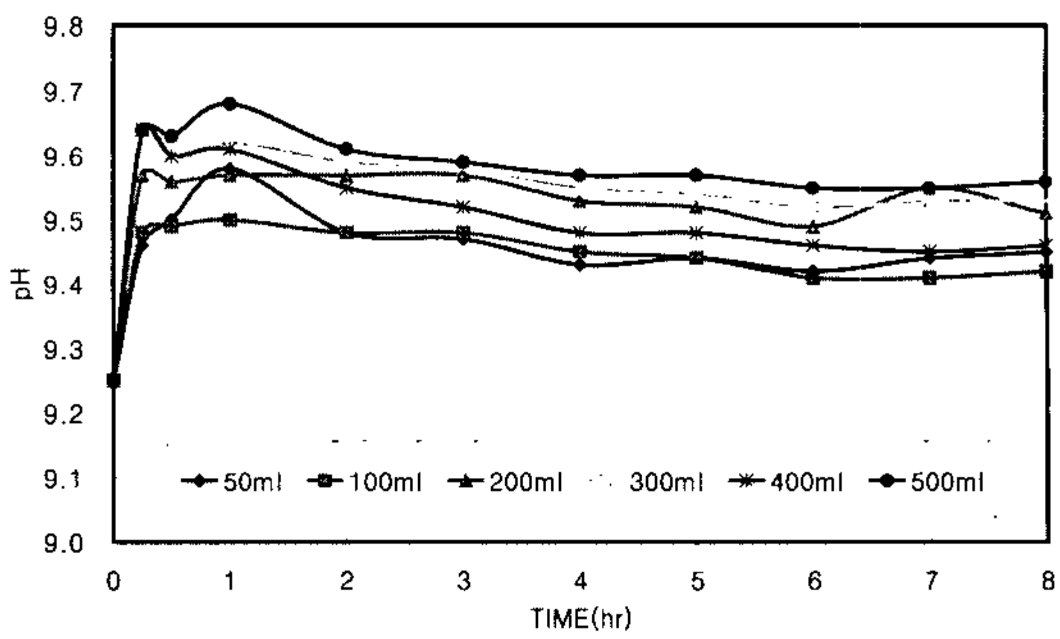

Figure 4. Change in pH according to time contacted to activated carbon injected.

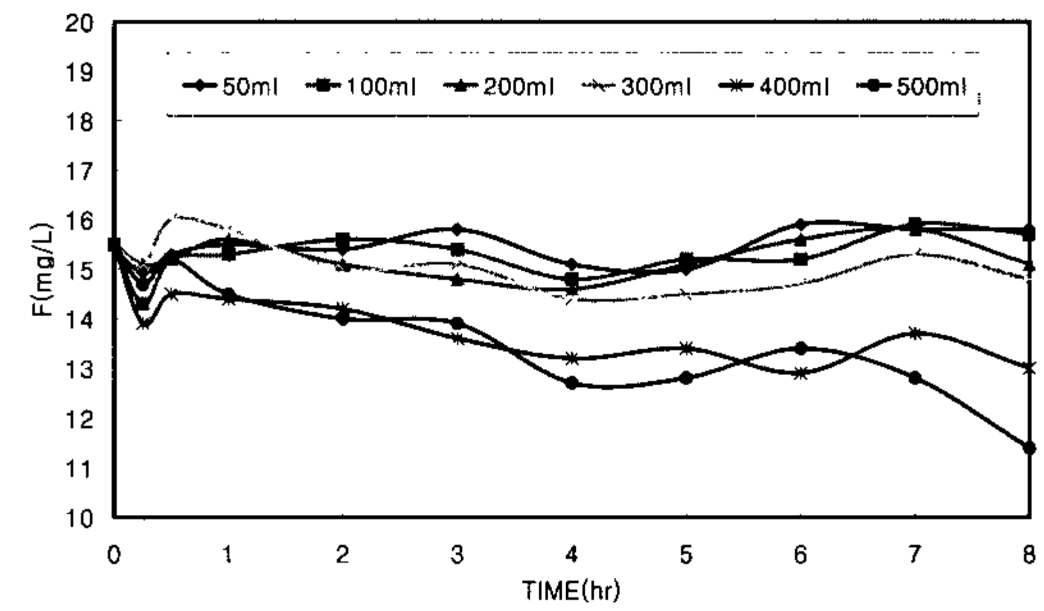

Figure 5. Change in fluoride concentration according to time contacted to activated carbon injected.

of activated carbon, higher the pH.

This is considered to be affected by the pH of activated carbon used in the study. Concentration of fluoride as well decreases as contact time increases, and as amount of carbon injected increases. When 500mL of activated carbon is injected and contacted for 8 hours, the concentration decreased to 11.4 mg/L. However, this still exceeds the potable standard of 1.5 mg/L, and therefore, activated carbon by itself is not a viable option for elimination of fluoride.

Alum coagulation

Figure 6 shows the measured result of the shifts in pH and fluoride concentration, when the amount of alum injection was changed.

As the injection amount of alum increases, the pH and fluoride concentration decrease; when more than 70 mL of 10 g/L alum solution is injected, the elimination was the most effective. The pH at this point was approximately 5, and the fluoride concentration 2.8 mg/L.

Although alum by itself showed some performance in elimination of fluoride, the processed water still did not satisfy the potable standard.

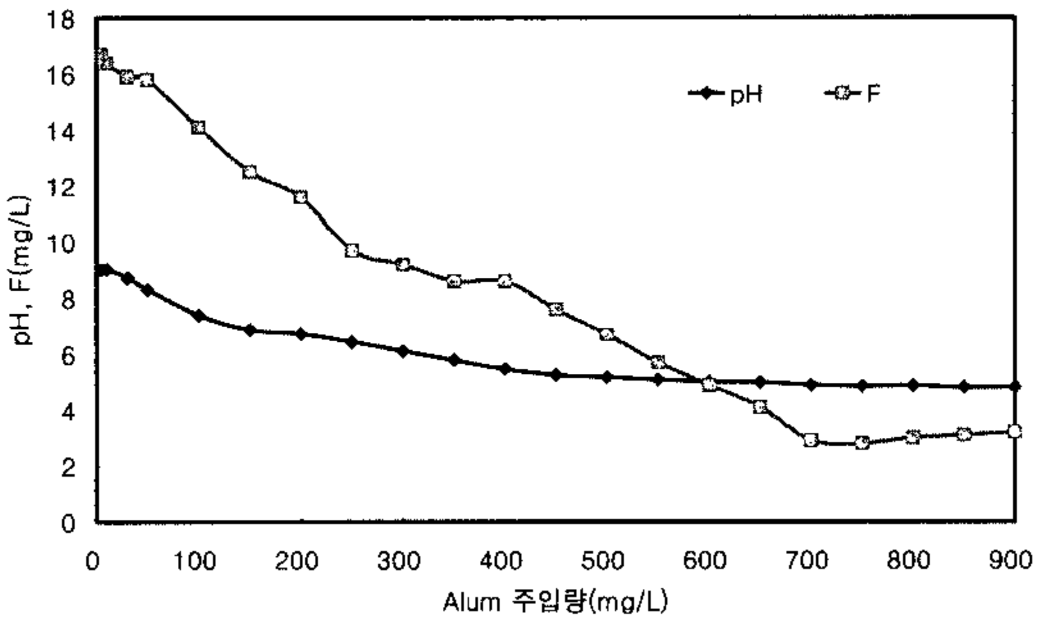

Figure 6. Shifts in pH and fluoride concentration according to the injection amount of alum.

Lime

When lime only was injected, pH and TDS increased and fluoride concentration gradually decreased. Injection of 3 g showed the most effective elimination at 9 mg/L fluoride concentration level, and addition of lime did not show any special changes. However, pH and concentration of TDS increased with the amount of lime. This is considered result from increased amount of remnant calcium, due to excessive input of lime. Such change is shown in Figure 7.

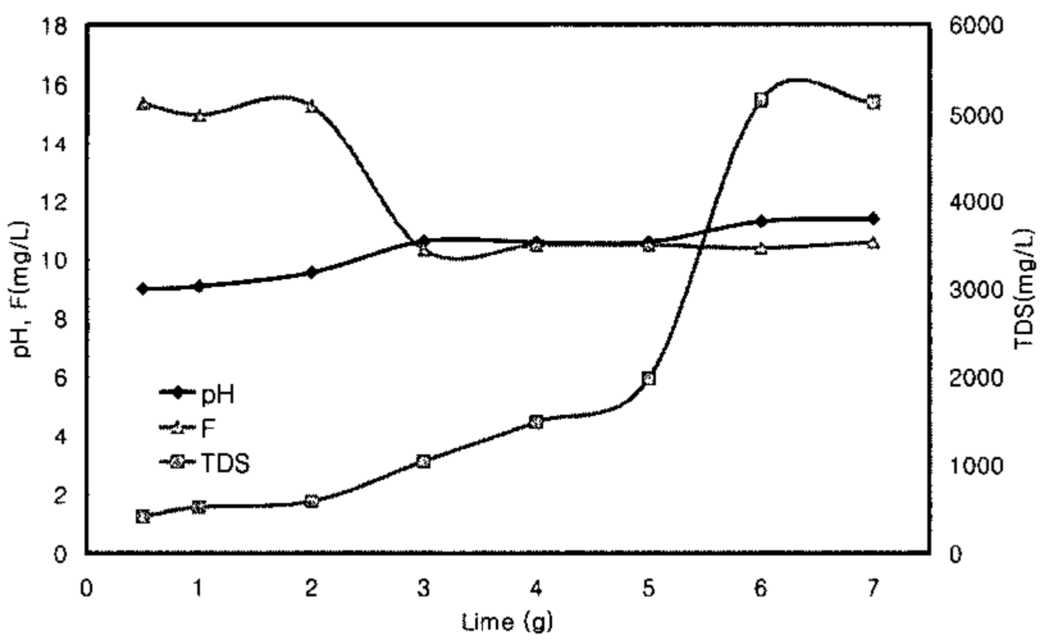

Figure. 7. Changes in pH, fluoride concentration, and TDS according to amount of lime injected.

Activated carbon + Alum

Figure 8 shows sample filled with 25mL of activated carbon and added with alum solution. By shifting the alum solution, the pH, fluoride concentration, and TDS concentration are measured. As the case of sole Alum injection, the pH and fluoride concentration decreased, and TDS concentration increased.

When alum solution 100mL was injected, the fluoride concentration was 1.3, within the potable standard, and showed significant improvement in performance of fluoride removal from sole injection of alum.

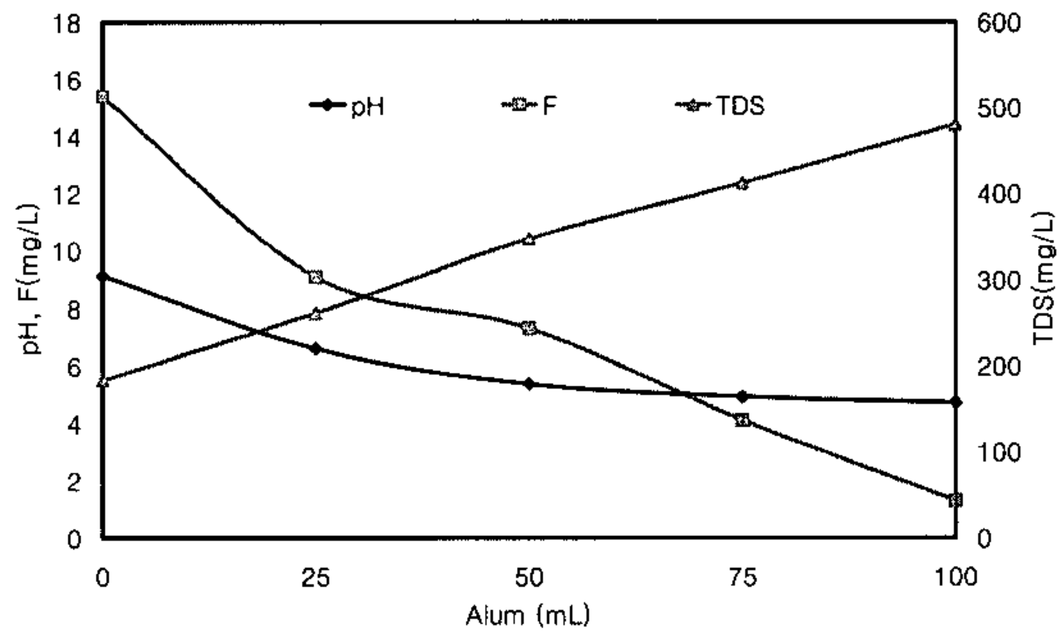

Figure 8. Changes in pH, fluoride concentration, and TDS concentration under fixed activated carbon and increase of alum injection.

Alum + Activated carbon

Figure 9 shows the changes in pH, fluoride concentration, and TDS concentration as amount of activated carbon and alum solution were shifted.

Greater amount of activated carbon showed greater pH, and greater amount of alum showed lower pH. Moreover, the fluoride concentration decreased as the amount of alum increased.

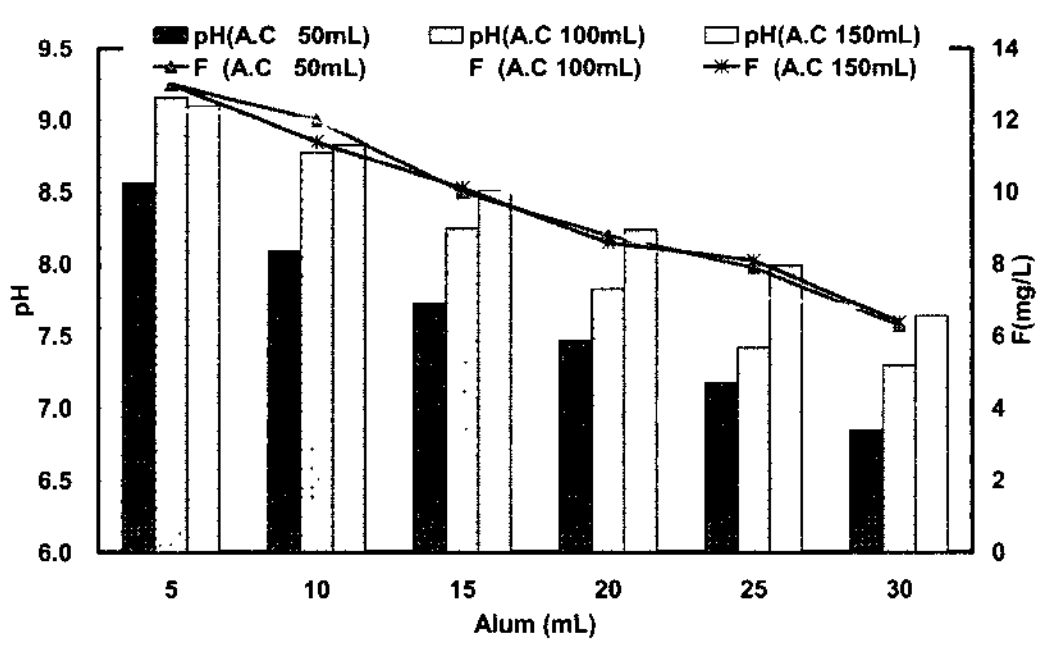

Figure 9. Changes in pH and fluoride concentration according to changes in activated carbon and alum.

Alum + Powdered activated carbon

Figure 10 is shows the measurement of changes in pH, fluoride concentration, and TDS concentration following increase of powdered activated carbon injected. When 20mL of powdered activated carbon was injected, the fluoride concentration was the lowest at 4.3 mg/L. The higher the concentration of powdered activated carbon slurry, the more likely the leak of powdered activated carbon. In case of leakage, blackening of water may occur; cautions must be taken on leakage of powdered activated carbon.

Alum + Lime

When lime and alum were injected, the fluoride concentration was the lowest at 4.1 mg/L with 1g, 2g of lime injection and alum solution fixed at 75mL. As the concentration of lime increased, the fluoride concentration tended to re-increase. This is considered to be a result from increase of remnant fluoride, due to ion exchange between fluoride elements in surface of calcium fluoride, for the Jookrim hot spring water is alkaline sodium bicarbonate.

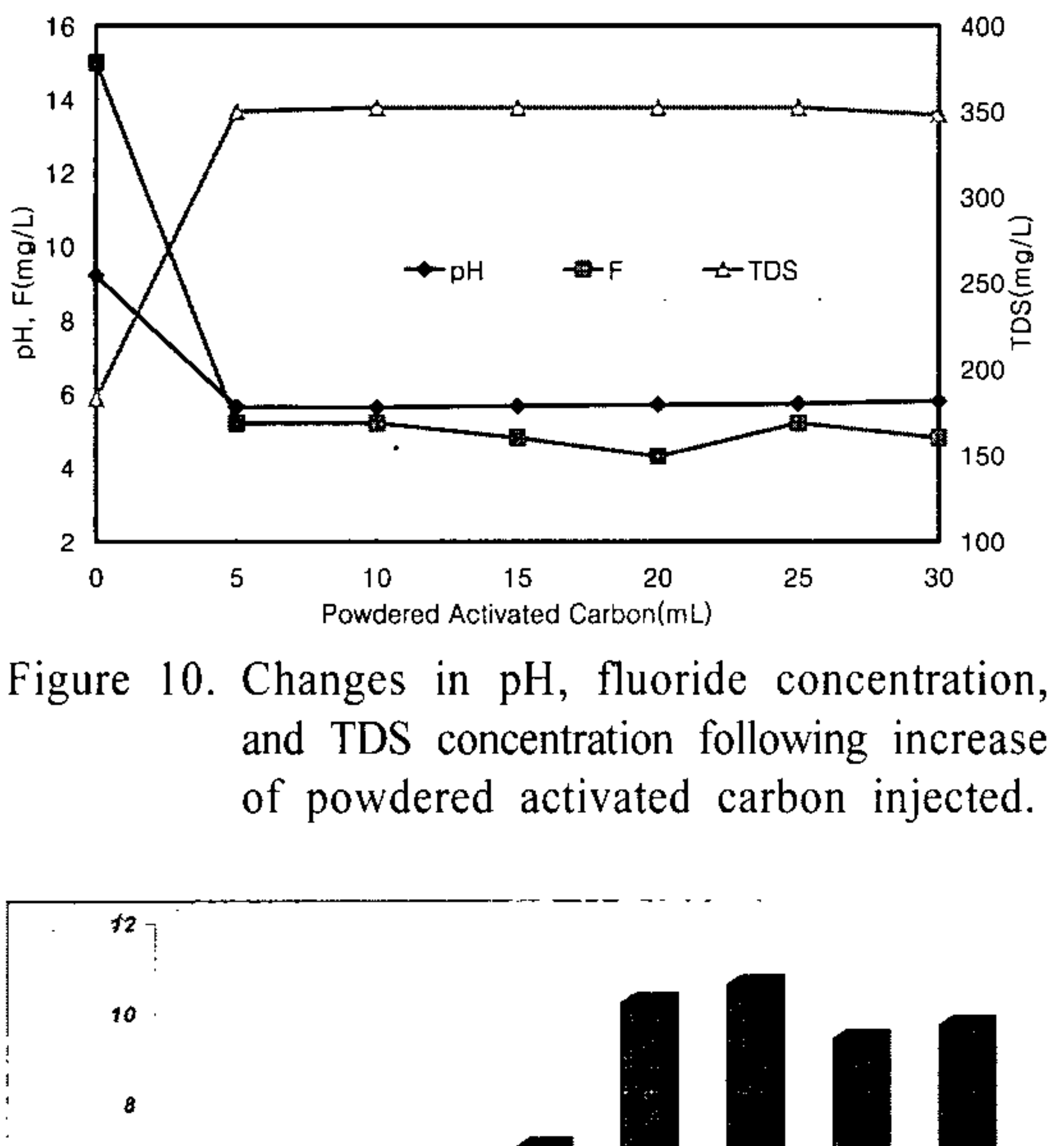

Figure 10. Changes in pH, fluoride concentration, and TDS concentration following increase of powdered activated carbon injected.

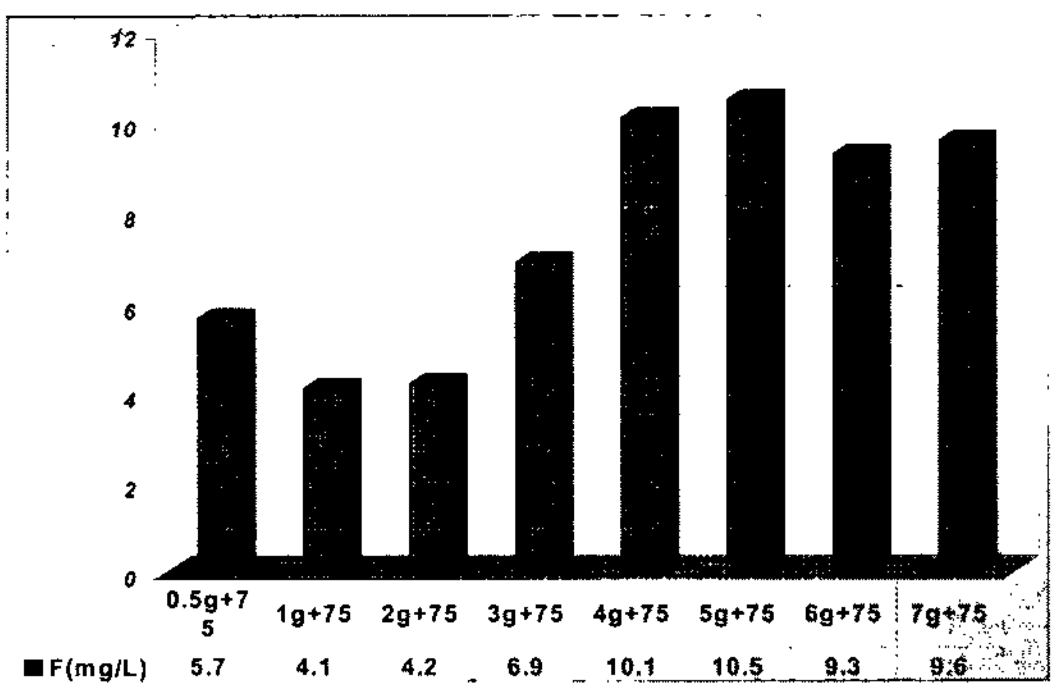

Figure 11. Changes in fluoride concentration when lime is injected and Alum is fixed.

Figure 11 shows changes in fluoride concentration when lime is increased and alum injection was fixed.

Ion exchange resin

pH, fluoride concentration, TDS concentration were measured using ion exchange resin column, by shifting HRT and contact time of sample and resin. As a result, the pH was stabilized between 6.7~7.8 from 1 min of HRT, and fluoride concentration gradually decreased as HRT increased, within the potable standard in 6 min of HRT. After 30 min of HRT, the fluoride concentration was 0.05 mg/L, almost removed. This is shown in Figure 12.

Analysis for composition of processed water at 20 min HRT, which was the most stable, was requested to the Korean Institute of Geoscience and Mineral Resources; the result is shown on Table 1.

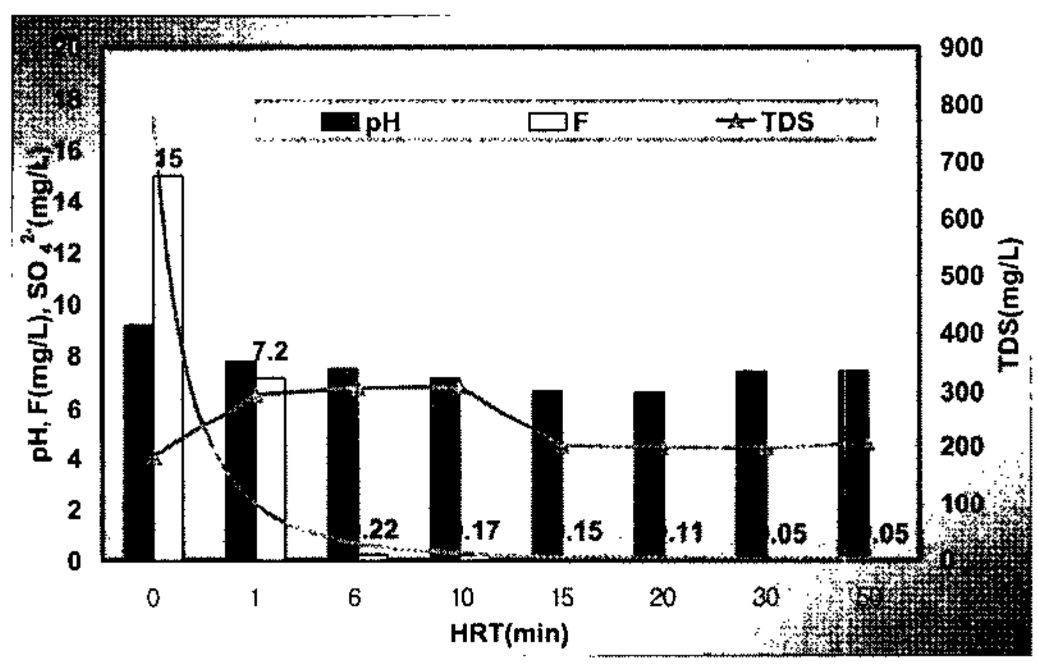

Figure 12. pH, fluoride concentration, TDS concentration were measured using ion exchange resin column, by shifting contact time of with resin.

Table 1. Composition analysis of hot spring water

unit : mg/L

	K	Na	Ca	Mg	SiO_2	Cl	SO_4	F	Li	Sr	Fe	Mn	Cu	Pb	Zn	T-Solids
INF	0.67	96.8	0.91	0.00	32.0	29.0	38.0	14.9	0.46	0.04	0.01	0.00	0.00	0.00	0.01	330
EFF	0.65	96.0	0.91	0.02	30.5	156	0.05	0.11	0.45	0.04	0.01	0.00	0.00	0.00	0.02	310

CONCLUSIONS

This study on elimination of fluoride in hot spring water of Jookrim region, which has the highest level of fluoride concentration level in the north Jeonla province, concludes the following.

1. In analysis of Jookrim hot spring water according to the water quality standard for potable water, pH was found very high at 9.25 and the concentration of fluoride was more than 10 times higher than the standard at 18.2 mg/L. Other measurements were lower than the standard level or not detected.
2. After injecting 10 g of activated carbon for elimination of fluoride, the fluoride concentration was measured at 13.5 mg/L. And when 70mL (or more) of alum 10 g/L solution was injected, the concentration was measured at 2.8 mg/L. And injecting 3 g of lime was measured at 9 mg/L. Alum showed the best elimination performance among all individual injections.
3. Injection of 25 mL of activated carbon and 100mL of alum solution together reduced the fluoride concentration below to 1.3 mg/L, which is under the potable standard. Injection of lime 1 g and alum 75 mL of alum 10 g/L solution together reduced fluoride concentration to 4.1 mg/L.
4. Modifying HRT and changing contact time of ion exchange resin column, the pH was stabilized when HRT was 1min and showed range of 6.7~7.8. The fluoride concentration reduced gradually as the HRT increased, and satisfied the potable standard when HRT passed 6min, and after 30 min HRT, the concentration of fluoride was 0.05 mg/L: almost eliminated.

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