

WATER, SANITATION, ENVIRONMENT and DEVELOPMENT

Water defluoridation with modified ion exchange

Veli Aalto, J Omwenga, and G Lengube

Introduction

WHO guideline for maximum fluoride concentration in drinking water is 1.5 ppm (1). Higher concentrations can cause mottling of tooth enamel and even crippling skeletal fluorosis. In Kenya there are several large areas where groundwater fluoride concentration exceeds guideline value. The situation can be serious, if fluoride concentrations are really high and no alternative surface water sources with low fluoride contents are available. Such a situation exists in many places in the arid and semi-arid areas of Rift Valley. Those high fluoride waters have low hardness and high alkalinity (2). An example is the Lobo spring by a tourist lodge near Lake Bogoria. The lodge had problems in securing drinking water with acceptable fluoride concentration.

A small research group was formed to develop suitable defluoridation technology. Lobo spring water was chosen as test water. Several defluoridation technologies were reviewed. Activated alumina, regenerated with NaOH and excess alkali washed with sulphuric acid, is a known method (3). One kg of alum can adsorb 1 g of fluoride ions. Defluoron 2 developed by NEERI in India is prepared by charring organic material, coconut shells, with concentrated sulphuric acid. When loaded with aluminium ions it can remove fluoride from water. Being mechanically weak, high attrition of Defluoron 2 in ion-exchange column forced its inventors to abandon this technology (4). One member of the research group had done in Tanzania promising defluoridation tests with strong cation exchange resin loaded with aluminium ions. The group decided to study this technology further.

Materials and methods

A local firm kindly donated Amberlite IR-120 resin in Na⁺ form. The resin was transformed to H⁺ form with acid and then charged with Al³⁺ ions. One litre of IR-120 had 2 eq of sodium ions and took 1.95 eq aluminium ions. The test columns were made of 25 ml burettes with a small glass wool plug in the bottom to protect the valve. The cross sectional area was 0.72 cm². The depths of resin beds varied from 18 to 30 cm and corresponding volumes from 15 to 21.5 ml. Deeper bed depths gave better results. The recommended minimum bed depth in ion exchange is 60 cm but for practical reasons bed depth 30 cm and volume 21.5 ml were chosen as standard.

Analytical grade Al-sulphate was used at first. After four defluoridation/regeneration cycles technical Al-sulphate was used. Technical alum solutions usually had a heavy precipitate of undissolved Al₂O₃ that was partly removed by decantation. The solutions had pH between 3.0 and 3.3 depending on alum quality and concentration of the solution. Lime, NaF, and NaHCO₃ were of analytical grade.

Fluoride concentration was measured with ion-specific meter and later by visual colorimetry. Al³⁺ was determined by EDTA back-titration or with visual colorimetry. Possible mutual masking Al³⁺ and F⁻ was checked by making analysis with different dilutions. Standard water analysis methods were used for other determinations.

Several test waters were used. Nairobi tap-water with added NaF to reach fluoride concentration 4.2 ppm was the first test water. This had low alkalinity 18 ppm and low conductivity μS/cm. Samples were taken from Lobo spring and nearby Lorwai stream with F⁻ 4.5 to 5.3 ppm, alkalinity 240 to 280 ppm, TH 22 to 34 ppm, Na⁺ 130 ppm, K⁺ 18 ppm, Cl⁻ 13 ppm, sulphate 13 ppm, pH 8.5, conductivity 606 to μS/cm. Both waters were similar and later only spring water was used. The first sample from Lobo spring was taken from a pool after the spring and had some algal growth. As algae seemed to clog the column, a new sample was collected from the eye of the spring. This sample, although with some milky turbidity, did not clog the column. The turbidity was not reduced in ion exchange column. Synthetic samples were done by adding NaF and bicarbonate to Nairobi tap water to reach F⁻ concentrations 5 and 8 ppm and alkalinity 250 ppm. One synthetic sample was prepared to mimic Maji ya Chai stream water with F⁻ 20 ppm and alkalinity 288 ppm.

Results and observations

Synthetic test water with low alkalinity was defluoridated successfully in the laboratory columns. Regeneration was done with alum solution without sulphuric acid. The performance of the columns deteriorated rapidly with successive regenerations. Based on these results, 30 cm bed depth and 21.5 ml bed volume was chosen as standard. Different flow rates were tested. One litre in 90 minutes was chosen as standard corresponding flow rate of 9 ml/hr.

When samples from the spring and the stream were defluoridated and regeneration was with alum alone the capacity deteriorated rapidly. In addition strong bubble formation on the resin reduce its efficiency. The bubbles

were removed after every one litre of eluate by inverting the column. No bubble formation was observed during regenerations.

Al-loaded resin was then equilibrated with 0.001 N or 0.01 N solutions of NaOH, NaCl, NaF, and NaHCO₃. The supernatant conductivity, pH, alkalinity and fluoride were reduced. Chloride concentration was not affected. Sodium concentration was reduced with F and OH⁻. Next some Al-loaded resin was filled with F and this resin was equilibrated with 0.001 N solutions of NaOH, NaCl, and HCl or 0.01 N NaHCO₃. All supernatants had F about 11 ppm. Chloride concentration did not change. Alkalinity and pH were reduced except in HCl solution.

From these results it was concluded, that Al-loaded cation exchange resin adsorbs F ions and even more so OH⁻ ions. To maintain electrical neutrality of the solution, equivalent amounts of cations are also adsorbed. Removal of OH⁻ ions will reduce pH and carbonic acid is formed from bicarbonate ions.

Alum regeneration could remove adsorbed F ions but was not effective in removing adsorbed OH⁻ ions. Some kind of acid regeneration might help.

When regeneration solution was sulphuric acid or alum acidified with sulphuric acid the regenerations were improved but not enough. Regeneration with acid followed with alum regeneration restored the original defluoridation capacity of the resin. Several tests were done to find optimum acid/alum regeneration conditions.

A good regeneration combination was 2.3 bed volumes sulphuric acid 16 g/l followed by 1.5 bed volumes rinsing, then 2.3 bed volumes technical alum 116 g/l and rinsing with 10 bed volumes of water. One litre of resin could then reduce F concentration from 5 ppm to 0.75 ppm in 232 litres of Loboï spring water. The consumption of regeneration chemicals for one litre of resin were 37 g of sulphuric acid and 267 g of technical alum. The fluoride removal capacity was about 1 g/l.

Regeneration effluent contained appreciable amounts of fluoride, aluminium, and sulphuric acid. Two tests were done whereby these effluents were neutralized with lime. The supernatant had acceptable concentrations of 0.2 to 0.3 ppm Al³⁺, 1.5 to 2.0 ppm F and pH between 6.3 and 6.4. Roughly 30 g or lime is needed to neutralize regeneration effluents and rinsings of one litre of resin.

According to the 1990 market prices of chemicals in Kenya, the cost of chemicals to defluoridate Loboï spring type water was 5 Sh/m³ or 0.24 USD/m³. At the same time, water rate in Nairobi was 6 Sh/m³ or 0.30 USD/m³.

The defluoridation eluent was collected in one litre portions. Fluoride concentrations increased in consecutive litres with about 2 ppm in the last litre. The average fluoride contents of eluents were calculated. The increase of fluoride leakage during defluoridation might be caused by the shallow bed depth. On some occasions pH, TA, Al³⁺, and conductivity were determined in eluents. In a typical

case the first litre had 0.2 ppm F, conductivity 62 µS/cm, and pH 5.7 while the 5th and last litre had 2.5 ppm F, conductivity 319 µS/cm, and pH 7.0. Aluminium in eluates of another test was between 0.06 and 0.2 ppm. Alkalinity in a third case rose during defluoridation from 10 ppm to 158 ppm while the test water had alkalinity 250 ppm and conductivity 550.

A synthetic sample similar to Maji ya Chai water was prepared to test the defluoridation method. One litre of Al-loaded resin could defluoridate 70 litres of such water. Fluoride retention capacity of resin was 1.35 g/l.

During all the experiments no formation of aluminium hydroxide nor aggregation of ion-exchange resin particles was observed.

Suggested reaction mechanism

Trivalent aluminium ion is adsorbed by three monovalent sulphonic acid groups of the strong cation-exchange resin. During defluoridation process, one bound aluminium ion in the resin can adsorb either one fluoride ion or one hydroxyl ion. In the same time one sulphonic acid site is freed to adsorb on cation, in this case Na⁺ ion. Removal of OH⁻ ions will reduce pH of the solution and carbonic acid is formed from bicarbonate. If pressure in the column is not high enough CO₂ bubbles are formed. In technical deionization process, where columns are operated under pressure, CO₂ bubble formation is not a problem.

According to the mechanism above, one litre of Al-loaded resin could adsorb 0.66 eq of F and OH⁻ ions. In these experiments it could adsorb 0.7 eq of those ions. As OH⁻ and F are competing from the same sites, increasing the ration of F to OH⁻ should improve the defluoridation capacity of the resin, as happened with Maji ya Chai type water. Operating the column under pressure should keep carbonic acid in solution and lower pH and the concentration OH⁻ ions and so improve defluoridation capacity of the resin.

Conclusions and proposals for further action

It is possible to defluoridate drinking water with Al-loaded strong cation-exchange resin regenerated with sulphuric acid and alum solutions. The method is technically feasible and economically interesting in places where drinking water with acceptable fluoride concentration is not available nearby. Further testing is necessary to investigate the process under normal technical ion-exchange conditions like pressure 1 to 2 atmospheres and bed depth 60 cm. Lack of available funds has prevented these pilot plant tests up to day.

References

1. WHO Guidelines for Drinking Water Quality Vol. 1 and 2, Geneva, Switzerland, 1984.

2. United Nations Environment Programme, Kenya National State of the Environment Report 2, Nairobi, 1987.
3. Rubel, F. and Woosley, R.P. 1978. "Removal of Excessive Fluoride from Drinking Water". EPA 570/9-78-001, Washington DC.
4. Majumder, N. 1973. "Defluoridation REvised", Central Public Health Engineering Research Institute, Nagpur, India.