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Cause, Effect and Remedial Options for Fluoride in Drinking Water

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1. Introduction

Increasing population in developing countries and high industrialization of the advanced countries are creating environmental problems of enormous dimensions. Fluoride contamination of drinking water is one of such problems worldwide. At present, twenty nine countries, are reported to be affected with fluorosis, the fluoride related disease. The problem in India, too is known for quite a long time. Recently the fluoride concentration in the ground water of Rampurhat and Nalhati block of Birbhum district, West Bengal, is found much above the safe limit.

In the present communication the fluoride level in the drinking water of different parts of India with special emphasis on West Bengal is highlighted. The cause of elevated fluoride level in the ground water, its effect on the health status of the people in the affected area is presented. Moreover, the remedial options for reduction of fluoride from drinking water are discussed.

2. Status of fluoride in the ground water of India

Endemic fluorosis related to the presence of fluoride in water is a public health problem in most of the Indian states. More than 90% of the rural population uses ground water for domestic purposes. Major problems are being faced by the country due to the presence of excess fluoride, arsenic and nitrate in ground water in certain parts of India. Seventeen of fifteen states and the Union Territory of Delhi are reported with dental, skeletal and skeletal forms of flourosis and associated health complaints [1÷3]. Keeping in view the fact that fluorosis is an emerging public health problem in India, and in order to mitigate the fluorosis problem, the ground water study indicates the occurrence of fluoride [4] in the different states of India (Table 1).

Table 1. Ground water fluoride pollution in India
Tabela 1. Zanieczyszczenie wód gruntowych fluorem w Indiach

State	Places of occurance
Kerala	Palaghat Krishna, Ananipur, Nellor, Chittoor
Andhra Pradesh	Cuddapah, Guntur and Nalgonda
Gujrat	Banskanta, Kachch & Amreli
Haryana	Hissar, Kaithan & Gurgaon
Orissa	Bolangir, Bijapur, Bhubaneswar and Kalahandi
Punjab	Amiritsar, Bhatinda, Faridkot, Ludhina & Sangrur
Rajasthan	Nagaur, Pali, sirohi, Ajmir & Bikaner
Tamil Nadu	Chengalput, Madurai
Uttar Pradesh	Unnao, Agra, Aligrah,Mathura, Ghazibad, Meerut & Rai Barrali

In order to predict the pattern or distribution of fluoride in the ground water the fluoride levels are categorized as, below 1.0 ppm, between 1.0 to 1.5 ppm and over 1.5 ppm together with the maximum fluoride concentration found (Table 2).

Table 2. Categorized distribution of fluoride
Tabela 2. Skategoryzowany rozkład fluoru

States	Amount of water samples	Fluoride	Fluoride	Fluoride	Max. Fluoride
		mg/l<1.0	mg/l 1.0÷1.5	mg/l >1.5	value, mg/l
Uttar Pradesh	502	95.7%	2.4%	1.9%	7.9 mg/l (Nalgonda district)
Rajasthan	780	51.7%	14.6%	33.7%	22.0 mg/l (Nagaur district)
Haryana	306	43.8%	15.7%	40.5%	21.0 mg/l (Hissar district)
Orissa	83	83.1%	6%	10.8%	11.0 mg/l (Balashar&Bolangir)
Tamil Nadu	464	85.8%	11.4%	2.8%	6.8 mg/l (Maduri district)
Gujrat	589	94.1%	2.5%	3.4%	11.0 mg/l (Amreli district)
Kerala	669	99.0%	0.4%	0.6%	4.6 mg/l (Trichur district)
Punjab	332	69.9%	13.9%	16.2%	11.7 mg/l (Bhandia District)

2. Toxicity of fluoride and health status of the people in Birbhum

The people continuously consuming fluoride-rich drinking water have several complaints bearing health and social implications. The health status of the people in the present study revealed a significant incidence of dental fluorosis among the children between age group of 5 to 16 years while skeletal fluorosis is prevailing among adults. The harmful effect of fluoride on health is believed to be cumulative with respect to duration, level of exposure to fluoride ions as well as the maturity stage of the teeth enamel [5]. Depending on the

extent of quality degradation several gradation from G0÷G4 are made as follows:

G0: normal, translucent, smooth and glossy,
G1: white opacities, faint yellow line,
G2: Brown strain,
G3: Pitting and chipped off edges,
G4: Brown black and falling.

About 90% of the children in Nashipur show prevailing symptom of dental fluorosis, in some form of other, among which 60% are severely affected with G2, G3 and G4 type and rest with G1 type lesion. Only 10% of subjects are detected free from dental problem.

Interestingly, we noted that the number of female child suffering from G2, G3 and G4 problem are more compared to male child. This is in accordance to with the report of Mizuno et al [6], that there is a sex related difference in salivary volumes in male and female; males having salivary volumes lesser than female. This eventually causes a difference in the retention time in the mouth and leads to more fluoride absorption by females. In contrast, there are also reports [7] which indicate more fluoride concentration in the teeth enamel of male children than the female. Further, it is found that the lesion is more pronounced in the age group of 11÷16 years for both male and female compared to the lower age group of 1÷10 years. Stanely and Pillai [8] claimed that number of victims due to fluoride toxicity in India is higher than in any other country and nearly 45% of drinking water source contain high level of fluoride, with a high probability of harmful, adverse effect on the habitats.

Other than prolonged intake of fluoride through drinking water fluorosis also results due to intake through food or use of fluoridated dental products like mouth rinse or toothpaste. But the rural people residing in Nashipur and suffering from fluorosis are very poor, and according to the data available from the questioners, supplied to them, shows that they do not use such fluoridated dental product. Other than dental fluorosis, fluoride damages the body system in many ways. Excess fluoride affects calcium functioning, which is most essential for bone formation, muscle movement, blood clotting and every muscular contraction. Constant disfunction leads to the typical knock knee system, excessive accumulation of calcium fluoride in the renal system and leading to stones formation in the kidney and eventual renal failure. Skeletal fluorosis involves excessive quantities of fluoride which, when deposited in the skeleton, increases bone densities and bone mass, causing pain. This is associated with rigidity and restricted movement of cervical and lumber joints, pelvis and shoulder. In severe cases there is complete rigidity resulting in a stiff spin. Moreover, fluoride is found to destroy the living mucosa of the gastrointestinal

system. Such health problems are known in fluoride prone areas also [9]. Research correlating health problem and fluoride is at very important stage. Complaints of the male infertility with an abnormality in sperm morphology and low testosteron levels are said to involve fluoride toxicity [10]. Recent reports also indicate an early development of cataract in human eyes due to excess consumption of fluoride [11]. Apart from the health aspect, the villagers are facing some aesthetic and social problem. No one is ready to make matrimonial relationship with the females (no symptom of fluorosis) of this area.

In Nashipur, almost 90% of the adults have identified to suffer from skeletal fluorosis and in sometimes severe osteosclerosis (abnormal increase bone density), spondylosis (degeneration of intervertibral disks), osteopertosis (bones become abnormally dense, splinter and fracture), arthritis. In early stage patient have shown symptomes of nausea, vomiting, abdominal cramps, muscular fibrillation and numbness of mouth. There are cases of allergic reactions in some individual with variations in susceptibility from patient to patient. The picture in Nashipur is really tragic. Many people become crippled, knock-kneed, fingers crumpled, teeth mottled. People at advanced stage of fluorosis even cannot pass urine and clean themselves. We identified a large number of cattle here consuming fluoride through water and cattle feed showing abnormality both in teeth and spine. The X-ray pictures revealed that at an early stage of fluorosis the lowest rib cannot be seen in the X-ray picture plate. This early detection method may save many from suffering from horrifying disfiguration afterwards.

3. Background of fluoride occurrence in some parts of India with special emphasis on Birbhum

There are various sources through which fluoride enters the groundwater. Mainly the anthropogenic activities (industrial operations, atmospheric deposition during coal burning or mining) or the natural sources (the dissolution of fluoride bearing minerals) are responsible for occurrence of fluoride in drinking water. During weathering and circulation of water in rocks and soil, fluorine is leached out and dissolved in ground water. The fluoride content of ground water varies greatly depending on the type of rocks from which they originate. Among the various minerals fluorapatite $Ca_3(PO_3)_2$,CaF_2; Sellaite MgF_2 and Fluorite CaF_2 are important. Fluorite is, however, most important and the leaching of fluoride for the metamorphic rocks hornblende gneiss of proterozoic age. An attempt has been made to trace the state wise geological reasons for high fluoride in ground water. In the state of Himachal Pradesh, geologically three district belts separated by major tectonic features are identified. The southern belt essentially consists of gneiss, schist, granite, lensold of proterozoic age and represents the Indian subducted plate. Several

phases of igneous intrusions have been identified in these rocks. Therefore, in all probabilities, the high concentration of fluoride could be due to the presence of metamorphic gneiss present in the region. The presence of Bundel gneiss complex appears to be the cause of high fluoride in ground water from the Bhilwara region in Rajasthan. Sohna, in the state of Haryana, the main rock types are quartzite, schist, siliceous limestone, slate and phyllite. In absence of hornblende gneiss in the region, fluoride concentration in groundwater is not high. In Bihar and West Bengal high fluoride in groundwater is supposed to be due to leaching of fluoride for the hornblende gneiss and granelites. The state Chattisgarh is covered by proterozoic and Gondwana group of rocks. The proterozoic comprises grey, pink gneiss and hornblende gneiss. Therefore, the leaching of fluoride from the hornblende gneiss of proteozoic age appears to be main source of fluoride in thermal water at Tattapari. In the state of Orissa, and Maharashtra volcanic rocks like Basal, Andesite and Dacite are present and high content of fluoride result due to the reaction of volcanic rocks and water and high temperature .

The village Nashipur lies on the Rajmahal trap consisting of volcanic eruption of basaltic composition. The basaltic rocks are exposed to surface. They are highly weathered, fractured and jointed. Fresh basalt exists at a depth about 20 to 30 m and is found in a nearby quarry. They are fine grained, hard and compact. Due to its interaction the fluoride is released into soil and ground water.

4. Remedial Options for Fluoride Reduction in Water

The widespread incidence of fluorosis in India bearing both health and social problem has now become a great concern nowadays. The experts and researchers working with fluoride problem in drinking water agree to overcome the problem of the need of fluoride free drinking water. As an immediate solution, to alleviate the human sufferings defluoridation of ground water and supply of safe drinking water is the only option. Although many attempts have been made still it remains a problem. The available defluoridation processes have their own limitations in terms of either the cost or technofeasibility.

Among the acceptable methods Nalgonda technique [12] is quite common. It is based on, in sequence addition of bleaching powder, lime and alum to water. The excess fluoride gets precipitated as AlF_6^{-3} and CaF_2. The technique is simple and can be adopted at domestic level. But the dangers of excess use of lime and problem of storage of bleaching powder (leakage of chlorine) can not be neglected. Ion exchange method [13] is proved to be a very effective removal process. Combination of cation and anion exchanger deionise the water completely. Then the required amount of desired salts are added to raise the quality of drinking water. The method is easy but high cost of installation, operation and handling of addition of external salts limit its use by

common people. Alumina based filters are suggested by the society affiliated to Research and Improvement of Tribal Area, Udaipur (SARITA), India. Venkatramanan et al. developed a technique using paddy husk carbon impregnated with alum. The process involved autoclaving paddy husk carbon by 1% sodium hydroxide and soaking overnight in 1% alum solution. Both the above techniques suggest the success but details are awaited. Reverse osmosis is another technique for large scale fluoride reduction in water. At high pressure, solvent is allowed to pass through a semi permeable membrane from concentrated solution to a dilute solute. The operation cost of the technique is very high and beyond the reach of rural people. Fluoride can be reduced from water by precipitation using $CaSO_4$ or $Fe_2(SO_4)_3$ solution. But elimination of excess of calcium is difficult and if iron is taken regularly, it will have adverse effect to the body because it does not have any metabolic exit (14). Distillation of water can effectively remove salts and hence fluoride from water. The later on requisite amount of salt is added as per mineral water standard. The advantage of the method is that it also disinfects the water simultaneously. But the method is the costlier even than ion exchange.

Considering the limitations and difficulties of the above processes we develop a simple, low cost and technofeasible method in our laboratory for removal of fluoride in drinking water. The locally available natural material Laterite (or red soil) is used as an adsorbent. The fluoride partitioning between Laterite-solution phases is determined by clay type and dominant cations of Laterite, total amount of fluoride in the solution and the pH and temperature of operation. The quick attainment (1 hr) of equilibrium makes the process technofeasible. The adsorption isotherm follows a favourable L-type nature. Either Langmuir or Freundlich adsorption isotherm can be applied changing particular range of fluoride concentration. The process is energetically favourable as indicated by negative free energy change of process. The process is aided by higher temperature and higher dose of Laterite. The kinetic consideration indicates that both surface adsorption and pore diffusion are operative and the process is favorable kinetically. The local abundance of Laterite as well as its easy regeneration makes the process quite cheap and acceptable by rural people.

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Przyczyna, skutek i opcje zaradcze dla fluoru w wodzie pitnej

Streszczenie

Celem obecnych badań przedstawionych w tym artykule jest przegląd miejsc występowania fluoru w różnych częściach Indii. Pomiary jakości wody wskazują, że niektóre części dzielnicy Birbhum w West Bengal są również dotknięte wysokim stężeniem fluoru w wodzie do picia. Mieszkańcy wsi, którzy są biedni i ze stosunkowo niską świadomością zdrowia, bardzo cierpią na fluorozę zębową, szkieletową i nie szkieletową.

Powaga problemu we wsi Nashipur w Birbhum jest taka, że zamieniła się ona teraz w wioskę „niepełnosprawnych". Ludzie spożywają wodę do picia o wysokiej zawartości fluoru (19 mg/l), gdy górna granica określana przez WHO wynosi 1,5 mg/l. Wysokie zawartość fluoru spowodowana jest budową geologiczną terenu. Możliwość pojawienia się fluoru w wodzie gruntowej w pobliskich dzielnicach jak Bankura i Purulia, mających podobną geologiczną budowę, nie może zostać odrzucona.

Aby złagodzić cierpienia miejscowych ludzi i dostarczyć bezpieczną wodę do picia zaproponowano prostą, tanią i wykonalną technicznie metodę oczyszczania wody. Lokalnie dostępny, naturalny minerał laterit (albo czerwona ziemia) został zastosowany jako substancja adsorbująca. Miejscowa obfitość lateritu, jak również jego łatwa regeneracja czyni proces całkiem tanim i do przyjęcia przez mieszkańców wsi.