

## Fly ash Utilization as an Adsorbent for Removal of Fluoride

Dr. M.Husain<sup>1</sup>, F.I. Chavan<sup>2</sup>, Bhanudas Abhale<sup>3</sup>

<sup>1</sup>Professor, <sup>2</sup>Assistant Professor, <sup>3</sup>PG scholar,

<sup>1,2,3</sup> Department of Civil Engineering, SSBT College of Engineering and Technology,  
Bhambori, Jalgaon (MH) India.

**Abstract**— Fluorosis, a disease caused by exposure to elevated levels of fluoride in drinking water, impacts millions of people in both developed and developing countries. It is, therefore, important to improve existing methods of defluoridation. Fluoride is one of the very few chemicals that have been shown to cause significant effects in people through drinking-water. Fluoride has beneficial effects on teeth at low concentrations in drinking-water, but excessive exposure to fluoride in drinking-water, or in combination with exposure to fluoride from other sources, can give rise to a number of adverse effects. These range from mild dental fluorosis to crippling skeletal fluorosis as the level and period of exposure increases. Crippling skeletal fluorosis is a significant cause of morbidity in a number of regions of the world. Indian standards for drinking water recommended an acceptable fluoride concentration of 1.0 mg/l & an allowable fluoride concentration of 1.5 mg/l in potable water.

**Keywords**— fly ash, Fluorosis, Fluoride, DE fluoridation, drinking-water

### I. INTRODUCTION

Fluorine, a fairly common element of the earth's crust, is present in the form of fluorides in a number of minerals and in many rocks. Excess fluoride in drinking-water causes harmful effects such as dental fluorosis and skeletal fluorosis. The permissible limit of fluoride level is generally 1 mg/l. The high fluoride levels in drinking-water and its impact on human health in many parts of India have increased the importance of defluoridation studies. The fluoride-bearing minerals or fluoride-rich minerals in the rocks and soils are the cause of high fluoride content in the groundwater, which is the main source of drinking-water in India. Fluorine is the chemical element with atomic number 9, represented by the symbol 'F'. It is the lightest element of the halogen column of the periodic table and has a single stable isotope, fluorine-19. At standard pressure and temperature, fluorine is a pale yellow gas composed of diatomic molecules, F<sub>2</sub>. Fluorine is rare compared to other light elements. In Earth's crust, fluorine is more common, being the 13<sup>th</sup> most abundant element. Currently, a wide range of defluoridation methods exist. These methods can be divided into the following categories: sorption, chemical precipitation, removal by ion exchange, and membrane filtration. The most currently used method utilizes alumina sorbants to remove fluoride from drinking water. In developing countries there is also a growing movement towards the use of natural materials such as clays, ash, and bone char, which, when found in local communities, can significantly increase the cost efficiency of defluoridation methods.

*Table 1: Drinking water standards for fluoride*

Sr. No.	Authority	Permissible Limits (mg/l)
1	WHO (India Context)	1.5
	WHO (International Standard)	0.5
2	BIS(IS-10500)	1.0-1.5

3	ICMR	1.0-2.0
4	CPHEEO	1.0-1.5
5	US Public Health	0.7-1.2

## 1.1 CHARACTERISTICS

Fluorine forms diatomic molecules that are gaseous at room temperature. The density is about 1.3 times that of air. Though sometimes cited as yellow-green, fluorine gas is actually a very pale yellow. Its color can only be observed in concentrated fluorine gas when looking down the axis of long tubes. It appears transparent when observed from the side in normal glass tubes or if allowed to escape into the atmosphere. The element has a "pungent" characteristic odor that is noticeable in concentrations as low as 20 ppb.

Fluorine condenses to a bright yellow liquid at  $-188\text{ }^{\circ}\text{C}$  ( $-307\text{ }^{\circ}\text{F}$ ), close to the condensation temperatures of oxygen and nitrogen. Fluorine solidifies at  $-220\text{ }^{\circ}\text{C}$  ( $-363\text{ }^{\circ}\text{F}$ ) into a cubic structure, called beta-fluorine. This phase is transparent and soft, with significant disorder of the molecules. At  $-228\text{ }^{\circ}\text{C}$  ( $-378\text{ }^{\circ}\text{F}$ ) fluorine undergoes a solid–solid phase transition into a monoclinic structure called alpha-fluorine. This phase is opaque and hard with close-packed layers of molecules. The solid state phase change requires more energy than the melting point transition and can be violent, shattering samples and blowing out sample holder windows. In general, fluorine's solid state is more similar to oxygen than to the other halogens.

## 1.2 NEED FOR FLUORIDATION AND DEFLUORIDATION

Fluoride is one of the very few chemicals that have been shown to cause significant effects in people through drinking-water. Fluoride has beneficial effects on teeth at low concentrations in drinking-water, but excessive exposure to fluoride in drinking-water, or in combination with exposure to fluoride from other sources, can give rise to a number of adverse effects. These range from mild dental fluorosis to crippling skeletal fluorosis as the level and period of exposure increases. Crippling skeletal fluorosis is a significant cause of morbidity in a number of regions of the world. The high fluoride level in drinking water has become a critical health hazard of this century as it induces intense impact on human health including skeletal and dental fluorosis. Though fluoride is an essential constituent for both humans and animals, it can be either beneficial or detrimental to human health depending on the level of fluoride in drinking water. In India, this problem is common in places such as Andhra Pradesh, Tamilnadu, Karnataka, Kerala, Rajasthan, Gujarat, Uttar Pradesh, Punjab, Orissa and Jammu and Kashmir.

The free fluoride level in drinking water was identified at 3.02 mg/L in Kadayam block of Tamilnadu. A fluoride survey in Nilakottai block of Tamilnadu showed a positive correlation between the prevalence of dental fluorosis in children and levels of fluoride in portable water is 3.24 mg/L. Adsorption is one of the significant techniques in which fluoride is adsorbed onto a membrane, or a fixed bed packed with resin or other mineral particles. Many natural and low cost materials such as red mud, zirconium impregnated coconut shell carbon, cashew nut shell carbon, ground nut shell carbon and clays have been used as adsorbents for fluoride removal from drinking water. Recently, amorphous alumina supported on carbon nano tubes, aligned carbon nano tubes, ion exchange polymeric fiber, and an ion exchanger based on a double hydrous oxide of Al and Fe ( $\text{Fe}_2\text{O}_3\text{Al}_2\text{O}_3 \times \text{H}_2\text{O}$ ) have been assayed for removing fluoride from drinking water as well as industrial wastewater. Thus, it is important to develop or find cheaper adsorbents for fluoride removal from water that have greater fluoride adsorption capacities like the above said adsorbents.

## 1.3 FLUORIDE DISTRIBUTION IN WATER

Fluoride is found in all natural waters at some concentration. Seawater typically contains about 1mg /l, while rivers and lakes generally exhibit concentrations of less than 0.5 mg/l. In ground waters, however, low or high concentrations of fluoride can occur, depending on the nature of the rocks and the occurrence of fluoride-bearing minerals. Concentrations in water are limited by fluorite solubility, so that in the presence of 40 mg/l calcium it should be limited to 3.1 mg/l. It is the absence of calcium in solution which allows higher concentrations to be stable. High fluoride concentrations may therefore be expected in ground waters from calcium-poor aquifers and in areas where fluoride-bearing minerals are common. Fluoride concentrations may also increase in ground waters in which cation exchange of sodium for calcium occurs. Fluorosis has been described as an endemic disease of tropical climates, but this is not entirely the case. Waters with high fluoride concentrations occur in large and extensive geographical belts associated with a) sediments of marine origin in mountainous areas, b) volcanic rocks and c) granitic and gneissic rocks.

A typical example of the first extends from Iraq and Iran through Syria and Turkey to the Mediterranean region, and hence from Algeria to Morocco. Other important examples come from the southern parts of the USA, southern Europe and the southern parts of the former USSR. The most well-known and documented area associated with volcanic activity follows the East African Rift system from the Jordan valley down through Sudan, Ethiopia, Uganda, Kenya and the United Republic of Tanzania. Many of the lakes of the Rift Valley system, especially the soda lakes, have extremely high fluoride concentrations; 1,640 mg/l and 2,800 mg/l respectively, in the Kenyan Lakes Elmentaita and Nakuru (, and up to 690 mg/l in the Tanzanian Momella soda lakes. In Kenya, a detailed survey of fluoride in groundwater was undertaken [48]. Of over 1,000 groundwater samples taken nationally, 61 per cent exceeded 1 mg/l, almost 20 per cent exceeded 5 mg/l and 12 per cent exceeded 8 mg/l. The volcanic areas of the Nairobi, Rift Valley and Central Provinces had the highest concentrations, with maximum groundwater fluoride concentrations reaching 30–50 mg/l. A similar picture emerges for the United Republic of Tanzania, where 30 per cent of waters used for drinking exceeded 1.5 mg/l fluoride with concentrations in the Rift Valley of up to 45 mg/l.

High groundwater fluoride concentrations associated with igneous and metamorphic rocks such as granites and gneisses have been reported from India, Pakistan, West Africa, Thailand, China, Sri Lanka, and Southern Africa. In China, endemic fluorosis has been reported in all 28 provinces, autonomous regions and municipalities except Shanghai. Both shallow and deeper ground waters are affected; in general the deeper ground waters have the higher concentrations. In Sri Lanka[49], it was found that concentrations of up to 10 mg/l in ground waters in the Dry Zone, associated with dental and possibly skeletal fluorosis. In the Wet Zone, the intensive rainfall and long-term leaching of fluoride and other minerals from the crystalline bedrock are probably responsible for the much lower concentrations. Endemic fluorosis remains a challenging and extensively studied national health problem in India.

In 1991, 13 of India's 32 states and territories were reported to have naturally high concentrations of fluoride in water, but this had risen to 17 by 1999. The most seriously affected areas are Andhra Pradesh, Punjab, Haryana, Rajasthan, Gujarat, Tamil Nadu and Uttar Pradesh. The highest concentration observed to date in India is 48 mg/l in Rewari District of Haryana.

The high concentrations in groundwater are a result of dissolution of fluorite, apatite and topaz from the local bedrock, and noted the general negative correlation between fluoride and calcium concentrations in Indian groundwater. Efforts to address the problem of fluoride in rural water supplies in India have been led by the Rajiv Gandhi National Drinking Water Mission, with considerable support from external agencies, particularly UNICEF. However, even with the great interest in fluoride in India, it is not easy to arrive at an accurate or reliable estimate of the number of people at risk. This is because of the difficulty of sampling groundwater from India's many millions

of hand pumps. Existing sampling has been selective but unstructured, taking some villages from districts and some of the many pumps in each village.

Further, there have been no comprehensive health surveys for dental fluorosis from which the overall extent of the problem could be assessed. Nevertheless, in the most affected states listed above, half or more of the districts have some villages with groundwater supplies having high fluoride concentrations. In these states, 10 to 25 per cent of the rural population has been estimated to be at risk, and perhaps a total of 60–70 million people in India as a whole may be considered to be so. .

## II. FLY ASH

Fly ash is the major solid waste by-product from coal-fired power plants. It is produced as a fine residue carried off in the flue gases with relatively uniform particle size distribution in the 1 to 100  $\mu\text{m}$  range. The main components of fly ash are silica, alumina, iron oxides, calcium oxide, and residual carbon. The fineness of the fly ash particles and the inherent large surface area (1 to 6  $\text{m}^2 \text{g}^{-1}$ ), together with the content of unburnt carbon, make it a good candidate for utilization as an inexpensive sorbent.

A literature survey revealed that fly ash has been used for removing heavy metals and radionuclides from aqueous solutions, for treatment of wastewaters to remove organic compounds and color, as a coal desulphurization agent, and together with hydrated lime for  $\text{SO}_2$  removal from flue gases.

There is also evidence that the capital and operating costs of wastewater treatment by fly ash to remove turbidity, fluoride, and to reduce COD, are lower than those by conventional lime precipitation.

In view of the advantages of fly ash as a low-cost sorbent, it seemed worth-while to study its efficiency in removing fluoride ion from high-fluoride waters.

Two Different Types of flyash were used for the present study. One of the flyash named as Thermal power plant flyash (TPP flyash) was collected directly at the electrostatic precipitator of the Dirk India Pvt. Ltd., Nashik, Thermal Power Plant and the other as a residual Maize Husk flyash (MH flyash). The grain size of both the ash ranged between 1-90  $\mu\text{m}$  with a mean diameter of 20-30  $\mu\text{m}$ .

### **Method of Preparation of fly ash from Maize Husk is detailed as below:**

The method used to produce the corn ash started from the completion of the growing season, corn stalks were hand-harvested by cutting the stalk approximately 15 cm (6 inches) above ground level and then cleaned to remove soil particles. The corn biomass, termed corn husk, included the corn cobs and kernels in some amount. The corn husks were then air dried and coarsely chopped before shipment to the lab. The corn ashes were produced at temperatures below 700°C (1,292°F). Simple open burn procedures typically occur between 500°C (932°F) and 600°C (1,112°F) [50]. The dried corn husks were burned to 500°C (932°F) to obtain the fly ash. It was then passed through 60  $\mu\text{m}$  sieve, to obtain the required final MH flyash.



**Initial material (Maize husk)**



**Final material (Maize husk fly ash)**

**Figure 1: Image of Maize husk and Maize husk fly ash.**



**Figure 2: Image of Thermal power plant fly ash**

**Table 2: Chemical analysis of TPP fly ash and MH fly ash**

Constituent (Chemical characteristics)	TPP Fly ash	Maize Husk Fly ash
	Amount (%)	Amount (%)
SiO <sub>2</sub>	52.70	38.33
k <sub>2</sub> O	---	27.58
CaO	7.20	7.83
MgO	---	5.01
P <sub>2</sub> O <sub>5</sub>	---	4.53
Cl	---	3.02

SO <sub>3</sub>	---	1.72
Fe <sub>2</sub> O <sub>3</sub>	8.40	0.47
Al <sub>2</sub> O <sub>3</sub>	21.90	0.22
LOI	9.10	11.4

Source: Nair et al., 2006

## 2.1 SYNTHETIC FLUORIDE SOLUTION

a) The stock solution of 100 mg L<sup>-1</sup> fluoride was prepared by dissolving 221 mg of anhydrous NaF in 1 L of distilled water. This 1 ml of solution has 0.1mg of fluoride. Fluoride standard solution was prepared by diluting 100 ml of stock solution to 1000 ml distilled water. Test solution of 1, 3, 5,7,10 mg/l F<sup>-</sup> were prepared from fresh stock solution. A calibration curve was prepared using standard solutions.

b) SPAND solution

Dissolve 958mg of SPAND in 500ml of distilled water.

## 2.2 REAGENTS

### a) Zirconyl acid reagent

Dissolve 133 mg of zirconyl chloride octahydrate (ZrOCl<sub>2</sub>.8H<sub>2</sub>O) in about 25 ml distilled water. Add 350ml of concentrated HCl and dilute to 500ml with distilled water.

### b) Reference solution

Add 10ml of Spand solution to 100ml of distilled water. Dilute 7ml of concentrated HCl to 10ml of distilled water and add to diluted Spand solution.

## 2.3 METHODOLOGY

Experimental work of this study has been divided into following phases. They are

- Adsorbance procedure by Batch study.
  1. Effect of contact time on fluoride removal.
  2. Effect of p<sup>H</sup> on fluoride removal.
  3. Effect of Adsorbent dose on fluoride removal.
  4. Effect of stirring rate on fluoride removal.
  5. Effect of initial fluoride concentration (IFC) on fluoride removal.
- Validation of results through Modeling (Langmuir, Freundlich, Temkin, Redlich-perterson Models) for fluoride removal
- Infra Red (IR) Spectra Study to determine the presence of adsorption friendly functional groups in two adsorbents used.

## REFERENCES

- [1] Jones C.M and Worthington H., "Water fluoridation, poverty and tooth decay in 12-year-old children", The Journal of Dentistry, 2000, pp 389-393.
- [2] Marco Aurelio Peres, Liliane Simara Fernandes and Karen Glazer Peres "Inequality of water fluoridation in Southern Brazil—the inverse equity hypothesis revisited", The Social Science & Medicine, 2000, pp 1181-1189.
- [3] Bhaumik R, Mondal NK, Das B, Roy P, Pal KC, Das C, Banerjee A and Datta JK, "Eggshell Powder as an Adsorbent for Removal of Fluoride from Aqueous Solution: Equilibrium, Kinetic and Thermodynamic Studies", E-Journal of Chemistry, Vol. 9, No.3, 2011, pp 1457-1480.
- [4] Kaseva M. E., "Optimization of regenerated bone char for fluoride removal in drinking water: a case study in Tanzania", Journal of Water and Health, Vol. 4, No.1, 2011, pp 139-147.
- [5] Jamode A V., Sapkal V. S. and Jamode V. S., "Defluoridation of water using inexpensive adsorbents", The Journal of Indian Institute of Science, 84, 2004, pp 163-171.
- [6] Murugan M. and Subramanian E., "Studies on defluoridation of water by Tamarind seed, an unconventional biosorbent", The Journal of Water and Health, 2006, pp 453-461.

- [7] Shrivastava Brajesh K. and A. Vani, “Comparative Study of Defluoridation Technologies in India”, Asian J. Exp. Sci., Vol. 23, No.1, 2009, pp 269-274.
- [8] Ayamsegna J.A., Apambire W.B., Bakobie N and Minyila S.A., “Removal of Fluoride from rural drinking water sources using geomaterials from Ghana”, 33<sup>rd</sup> WEDC International Conference, Accra, Ghana, 2011, pp 441-446.
- [9] Srimurali M. and Karthikeyan J., “Activated Alumina: Defluoridation of Water and Household Application – A Study”, Twelfth International Water Technology Conference, IWTC12 2008, Alexandria, Egypt, 2008, pp 153-165.
- [10] Karthikeyan G, Apparao B V and Meenakshi S, “Defluoridation Properties of Activated Alumina”, the 2nd International Workshop on Fluorosis Prevention and Defluoridation of Water, pp 78-82

