

USE OF ACTIVATED CLAY FOR DEFLUORIDATION OF WATER

K Bjorvatn* and A Bårdsen*

SUMMARY: A number of studies have been made to assess the fluoride binding potential of fired clay. Most researchers have concluded that the processes involved are too slow, and the fluoride binding capacity is too low. Recently reported findings, however, indicate that clay calcined at temperatures < 800°C may be suited for practical defluoridation of potable water. The present study presents data obtained by the use of red soil (lateric clay), calcined at 570°C for three hours. Fluoride containing water, at concentrations from 5.50 and 7.75 mg-F/L (well water) to 12, 30 and 130 mg-F/L (NaF-solutions), were exposed to calcined laterite, w/v 1:10. Water samples were taken at 1, 2, 4, 12, 24, 48, 72 h and after one week and analysed for fluoride by the use of a fluoride selective electrode. Rapid reduction of the fluoride concentration in the water was observed during the first few hours. A steady state was in most cases reached in 48 hours. Best results were obtained by the use of laterite from Balang, Northern Cameroon: Here the fluoride concentration was reduced from 5.47 to 0.48 mg-F/L in two h, from 12.2 to 0.26 mg-F/L in 12 hours and from 31.2 to 0.76 mg-F/L in 12 h. Water with 132 mg-F/L had a fluoride concentration of only 4.58 mg-F/L after one week's exposure to calcined lateric clay. A "total" analysis (ICP/MS) of well water before and after defluoridation showed minor changes in most micro elements. No adverse changes in taste or smell were observed in defluoridated water.

Key words: Activated clay, defluoridation, fluoride, calcined clay.

INTRODUCTION

Fluoride may be found in all natural waters; even in precipitation. The fluoride content of creeks and rivers and most inland lakes is normally less than 0.3 mg-F/L¹; subsurface water has, on an average, slightly more fluoride², while wells and lakes in certain high-fluoride areas may contain very high fluoride concentrations. The maximum value reported for surface water seems to be 2.8 g-F/L, which was found in Lake Nakuru, Kenya³.

Fluoride in low-fluoride rivers and lakes may be derived from precipitation, while chemical weathering of fluoride-rich rocks in the drainage basin seem to provide fluoride for high-fluoride inland lakes⁴. The volcanic rocks of the rift zone of East Africa are richer in F than analogous rocks in other regions⁵. Consequently, rivers, lakes and boreholes in the African Rift Valley often provide water with exceptionally high fluoride content.

Fluoride in waters is of concern for public health officials as well as for hydrogeologists and geochemists. Prolonged intake of high-fluoride water may create problems such as dental and skeletal fluorosis in the human and also in the animal population. According to WHO, drinking water of adequate quality should contain max. 1.5 mg-F/L⁶. Where water intake is high, e.g. in tropical areas, the recommended fluoride concentration of drinking water should be substantially reduced. A formula has been proposed to calculate "optimum" fluoride concentration⁷:

$$\text{Optimum level} = \frac{0.34}{-0.038 + (0.0062 \cdot \text{mean max.temp.}(^{\circ}\text{F}))}$$

To avoid health problems, high-fluoride water should not be used for household purposes. In arid or semiarid areas, however, alternative, low-fluoride water sources may not be available, and defluoridation is needed to render the water potable⁸. Excessive fluoride may easily be removed by modern water treatment. For practical and financial reasons, however, high-technology water treatment is unavailable in rural East Africa. Priority, therefore, should be given to the development of simple devices for defluoridation of drinking water at a (preferentially) home based level. A number of methods have been proposed, see e.g. Hendrickson and Vik.⁹

Defluoridation devices should meet a number of the following requirements¹⁰:

- Modest investment
- Low maintenance cost
- Simple design
- Operable by villagers
- Able to reduce fluoride content, e.g. from 5 to 0.5 mg/L
- Improve water quality in general
- Ingredients maintainable for acceptable period

No single method seems to meet with all the requirements, but some techniques are more widely used than others. The so-called Nalgonda technique, which comprises addition to high-fluoride water of, in sequence, Na-aluminate or lime, bleaching powder and filter alum, is in frequent use in India¹¹. Likewise, the use of bone char has received much attention¹².

The aim of the present paper is to discuss a third possibility: the use of clay or soil for defluoridation of drinking water.

Clay consists of minute mineral particles which have precipitated under water. The main components of clay are *oxygen, silicon, and aluminium*. Smaller amounts of *iron, potassium, calcium, magnesium*, and other elements are also present. Most clays also contain *fluoride*; concentrations of 2 to 4 g-F/kg have been reported¹³. Also the physical composition of clay varies; several clay minerals, such as kaolinite, illite, bentonite, and montmorillonite, can be distinguished. The different clay minerals may have different fluoride-binding capacities¹⁴. Naturally occurring clays normally contain a mixture of clay minerals.

Simple, locally made pottery has been used for "water treatment" for thousands of years; especially for transportation and storage of water. Claypots have a cooling effect on the water, and may - possibly - also cause a reduction in the water's fluoride content¹⁵.

Various researchers have assessed the fluoride binding effect of simple pottery. Thus Ndegwa¹⁶ reported a fluoride binding capacity in clayware of 80 mg-F/kg, while Zewge & Moges¹⁷ found that pot chips were able to bind as much as 560 mg-F/kg. Hendrickson & Vik⁹, however, concluded that fluoride uptake in clayware is slow and of limited capacity.

In a more recent investigation Hauge et al (1994) assessed the effect of firing temperature on the fluoride binding capacity of clay¹⁸. They concluded that firing temperatures between 500 and 700°C produced clayware with optimal fluoride binding properties, while the fluoride binding processes were greatly reduced by firing above 800 degrees. A certain increase in the fluoride content could sometimes be seen when water was exposed to high-fired ceramics.

During the last few years the fluoride binding capacity of a series of different clays have been tested at the Inst. of Dental Research, Univ. of Bergen School of Dentistry¹⁹.

The aim of the present paper is to demonstrate defluoridation of water by the use of lateric red clay from Cameroon, West-Africa.

MATERIALS AND METHODS

Red top soil (laterite) was collected from two different sites, N'Gaoundéré and Balang, in the Adamoua province, North Cameroon. The material was dried, and subsequently fired at 570 °C for three hours. The fired clay was crunched, and 10 g samples were weighed up and placed in plastic bottles to which 100 ml aliquots of aqueous *fluoride solutions* were added, at concentrations ranging from 5.42 to 132 mg-F/L. All solutions above 10 mg-F/L were made by dissolving suitable amounts of NaF in de-ionized water, while solutions of less than 10 mg-F/L were taken from natural Norwegian ground water wells. Two parallel tests were performed for each of the laterite samples. Bottles were kept agitated during the test period.

At given time intervals (1h, 2h, 4h, 12h, 24h, 48h, 72h, 1 week) 5 ml liquid test samples were extracted. After the addition of TISAB III (1:10) the fluoride content of the samples was measured by the use of a fluoride selective combined electrode (Orion 96-09-00) connected to an Orion Ionalyzer 906 - according to standard procedure²⁰.

The elemental composition of the Balang clay was analysed by the use of a Philips SEM 515 scanning electron microscope combined with an EDAX PV 9900 energy dispersive x-ray analyser. KV = 20.0.

In order to assess possible changes in ionic composition of the waters, a total analysis of water from Well II was made by the use of ICP/MS - *before* and *after* defluoridation with lateric clay from Balang, Cameroon.

RESULTS

Upon exposure to fired clay a sharp reduction of fluoride concentration in the water was seen all solutions, especially during the first hour, see Table 1 and 2. The rapid initial fluoride binding process tapered off, in most cases reaching a plateau (steady state) in approximately 48 hours. During the agitation the fluoride containing water tended to become discoloured. The red soil, however, settled quickly when agitation stopped. The water tasted good, even after one week's defluoridation.

The main elements of the Balang-laterite were Al, Si and Fe. As compared to ordinary (grey) clay, the iron content of the red lateric clay was very high. The elemental set up, according to the EDAX analysis, is given in Table 3.

TABLE 1: Defluoridation of High-fluoride water by the use of (humus-containing) laterite from N'Gaoundéré, Cameroon. results in mg-F/L.

Water sample	Contact time:								
	Start	1h	2h	4h	12h	24h	48h	72h	1w
Well I	5.42	2.52	2.22	1.34	0.73	0.59	0.50	0.48	0.42
Well II	7.76	4.73	3.76	2.41	1.19	0.81	0.71	0.69	0.58
NaF I	12.1	7.28	5.96	4.27	1.43	0.84	0.67	0.65	0.55
NaF II	29.7	17.9	15.9	12.5	6.15	4.48	3.33	2.89	2.17
NaF III	120	82.5	78.0	68.2	60.8	54.1	48.7	46.0	42.4

TABLE 2. Defluoridation of high-fluoride water by the use of laterite from Balang, Cameroon. results in mg-F/L.

Water sample	Contact time:								
	Start	1h	2h	4h	12h	24h	48h	72h	1w
Well I	5.47	0.55	0.48	0.46	0.22	0.17	0.18	0.09	0.11
Well II	7.75	1.08	0.88	0.78	0.39	0.27	0.23	0.15	0.15
NaF I	12.2	2.44	1.94	1.36	0.26	0.17	0.13	0.11	0.11
NaF II	31.2	11.7	9.98	8.05	1.69	0.76	0.55	0.45	0.40
NaF III	132	73.2	64.1	55.4	27.5	18.5	11.4	8.62	4.58

The chemical profile of water from Well II, before and after defluoridation, is given in Table 4.

DISCUSSION

Fluoride is a natural constituency of soils. Most fluoride is firmly bound to minerals or other chemical compounds but may, over time, be washed out. Fluoride concentrations in soil tend to increase with depth. In high mountain areas, the fluoride content of the soil is usually low³. The clay samples used for the present experiments were taken from top soil in the savannah of Northern Cameroon, at approximately 1100 m above sea level. Laterite is a reddish ferruginous soil, which is formed in tropical regions by the decomposition of the underlying rocks.

As to the main components, laterite is similar to other clays. Table 3, however, demonstrates the high iron content of laterite. Lateric clays are widespread in Africa, and are frequently used for the production of bricks and simple clay ware. The fluoride content of the lateric clays used for the present experiments is not known. There seems to be, however, an inverse relationship between the soil's fluoride content, and its ability to absorb fluoride from water, and, consequently, low fluoride values in the relevant clays would be expected.

TABLE 3. Elemental composition of lateric clay from Balang, Cameroon according to EDAX analysis.

Element	Weight percent
Na	0.10
Mg	0.60
Al	30.50
Si	25.13
P	0.15
K	0.29
Ca	0.18
Ti	6.01
Fe	36.83
Ni	0.07
Cu	0.15

TABLE 4. Total analysis. Natural ground water before and after defluoridation with laterite from Balang, Cameroon.

Element	Before def. µg/g	After def. µg/g	Element	Before def. µg/g	After def. µg/g
F	7.76000	0.15000	Pr	0.00000	0.00004
Li	0.00111	0.00077	Nd	0.00000	0.00012
B	0.00643	0.00226	Sm	0.00000	0.00001
Na	18.00000	15.00000	Eu	0.00001	0.00002
Mg	0.88550	0.90000	Gd	0.00000	0.00002
Al	0.01328	0.03773	Ni	0.00000	0.00154
Si	1.34100	1.00200	Cu	0.00513	0.07573
Ca	9.70000	2.30000	Zn	0.00000	0.00987
Sc	0.00110	0.00075	Ga	0.00019	0.00005
Ti	0.00962	0.00451	As	0.00011	0.00019
V	0.00011	0.00526	Se	0.00086	0.00395
Cr	0.00500	3.50000	Br	0.10750	1.31100
Mn	0.00024	0.01681	Rb	0.00189	0.00078
Fe	0.00632	0.02452	Sr	0.20000	0.20000
Co	0.00001	0.00046	Y	0.00001	0.00005
Rh	0.00003	0.00004	Zr	0.00001	0.00016
Pd	0.00001	0.00000	Nb	0.00000	0.00004
Cd	0.00029	0.00745	Mo	0.00848	0.00518
Sn	0.00000	0.00004	W	0.00290	0.00004
Sb	0.00000	0.00003	Os	0.00000	0.00003
I	0.00049	0.00127	Au	0.00000	0.00003
Cs	0.00007	0.00002	Th	0.00000	0.00002
Ba	0.06042	0.10630	U	0.00029	0.00001
Ce	0.00002	0.00019			

The defluoridation kinetics in lateritic clays seemed to be in accordance with the model established by Bregnhøj and Dahi^{12,21}, and the results obtained were safely within the requirements put forward by Phantumvanit et al: fluoride reduction from 12 to ~ 0.25 mg-F/L within 24 h¹⁰. Water with more than 12 mg-F/L is rarely used for consumption, even in the Rift Valley area.

It is of interest to note that the fluoride concentrations finally obtained in the present experiments, were slightly higher for *natural spring water* which originally contained 7.75 (7.76) mg-F/L than for laboratory-produced water with 12.5 mg-F/L. This may be due to interference of "competing" anions (other than F⁻) in the well-water²¹.

More research is needed in order to establish the chemical processes responsible for the defluoridation of the water. For practical purposes, however, the important thing is to remove excessive fluoride, without introducing other noxious agents. According to the pilot study (total analysis) of ground water before and after defluoridation, fired laterite caused a relatively great decrease in the calcium concentration and a similar increase in the concentration of chromium. The increase in chromium is unwanted. Apart from Cr, however, all elemental concentrations in defluoridated water were safely within the limits accepted for good drinking water quality²². Due to the high iron content of the laterite, one might have expected an increase in the Fe content of defluoridated water. No such change was observed.

Large scale defluoridation tests with lateric clays from various parts of the world should be carried out. Likewise, further studies should be performed to decide the total composition of water before and after defluoridation.

REFERENCES

1. Livingstone DA. Chemical composition of rivers and lakes. In: Data of Geochemistry, chap. G (ed. Fleischer, M.) U.S. Geological Survey Prof. Pap. 1963.
2. White DE et al. Chemical composition of subsurface water. In: Data of Geochemistry, chap. F (ed. Fleischer, M.) U.S. Geological Survey Prof. Pap. 1963.
3. World Health Organization. Fluorides and oral health. WHO Technical Report Series 846. Geneva 1994.
4. Kilham P, Hecky RE. Fluoride: Geochemical and ecological significance in East African waters and sediments. Limnology and Oceanography 18 (6) 1973.
5. Gerasimovskiy, V.I.; Savinova Y.N. Fluorine contents of volcanic rocks in the rift zone of East Africa. Geochim. Int. 6 1124-1128 1969.
6. World Health Organization. Fluorides and human health. WHO Monograph series No. 59 Geneva, Switzerland, 1970.
7. Galagan DJ, Vermillion JR. Determining optimum fluoride concentrations. Public Health reports 72 491-493 1957.
8. World Health Organization. Fluoride and Fluorides. Environmental Health Criteria 36 14 WHO, Geneva, Switzerland, 1984.
9. Hendrickson K, Vik EA. Adsorption in water treatment. Fluoride removal. Norwegian Institute for Water Research (NIVA), Report No. FP-83828, Oslo Norway 1984.
10. Phantumvanit P, Songpaisan Y, Möller IJ. A defluoridator for individual households. World Health Forum 9 555-558 1988.
11. Nawlakhe WG, Kulkarni DN, Pathak BN, Bulusu KR. Defluoridation of water by Nalgonda technique. Indian Journal of Environmental Health. 17 (1) 26-65 1975.
12. Bregnhøj H. Processes and Kinetics of Defluoridation of Drinking Water Using Bone Char. Ph.D. Thesis, Department of Environmental Science and Engineering, Technical University of Denmark, 1995.
13. Day FH. The chemical elements in nature. Harrap p. 306 London England 1963.
14. Weiss A, Sextl E. Clay and clayminerals. In: Ion exchangers (ed. Dorfner, K.) Walter de Guyter, New York US 493-517 1991.
15. Manji F, Kapila S. Fluorides and fluorosis in Kenya. Part II: The occurrence of dental and skeletal fluorosis. Odontostomatol. Trop. 9 (2) 1986.
16. Ndegwa WM. Investigations leading to defluoridation of waters in Kenya. Thesis, University of Nairobi, Kenya 1980.
17. Zewge F, Moges G. Investigation of brick and pot chips as defluoridating media. Water supply and Sewerage Authority, Southern Regional Office, Awassa, and Department of Chemistry, Addis Ababa University, Addis Ababa, Ethiopia, 1990.
18. Hauge S, Østerberg R, Bjorvatn K, Selvig KA. Defluoridation of drinking water with pottery: effect of firing temperature. Scandinavian Journal of Dental Research 102 329-333 1994.

19. Østerberg R. Bruk av leirmaterialer til billig defluoridering av drikkevann. Thesis, 107 p. University of Bergen, Norway 1992.
20. ORION. Instruction manual, fluoride/combination fluoride electrodes. Orion research Inc. Boston, US, 1987.
21. Dahi E, Singano JJ, Nielsen JM. Defluoridation kinetics by means of magnesita and clay. Proceedings of the First International Workshop on Fluorosis and Defluoridation of Water, Ngurdoto, Tanzania 1995.
22. De Zuane J. Handbook of Drinking Water Quality. Standards and Controls. Van Nostrand Reinhold, New York, US 1990.