

The Significance of Fluorine Traces in Natural Waters and a Proposed Method to Effect their Removal.

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THE ENDEMIC HYPOPLASIA of the permanent teeth, known as chronic endemic dental fluorosis, was first described by Eager (1901). McKay (1916) established this defect of human dentition as a water borne disease. The causative etiological factor was proved beyond doubt by Smith (1931), Churchill (1931) and Velu (1931), as being associated with the continual ingestion of toxic amounts of fluorine in the water used for cooking and drinking purposes, during the period of calcification of the affected teeth. The permanent teeth in particular are affected, although in areas of marked severity, the high fluorine ingestion is manifested by permanent damage to the deciduous teeth. As the enamel-forming ameloblasts cease functioning at the time of the eruption of a tooth, this unsightly phenomenon is a permanent physical disfigurement.

Since 1931, when fluorine traces in the natural water were established by the American workers as the causative factor in the production of mottled enamel, fluorine toxicosis has been recognized in America as a public health problem.

A quantitative, epidemiological-chemical study was carried out by the American Public Health Service to determine the minimum threshold of toxicity, in other words the maximum amount of fluorine permissible in a domestic water supply.

In the light of present knowledge, it appears that mottling of the permanent teeth is caused by using water, containing fluorine in excess of one part per million, for both cooking and drinking purposes during the period of dental susceptibility.

In contrast to the findings of the American workers, Sugawa (1938), observed a high incidence of mottled teeth amongst the inhabitants of the island of Sakurasima, the fluorine content of the water ranging from 0.7 to 1.0 p.p.m. Even at a fluorine concentration of 0.3 p.p.m. this worker observed a dental fluorosis amongst the natives of the Kagosima prefecture in Japan.

Zelmanova (1937), examined the teeth of 4,000 children living on the shore of lake Immanda in Russia. The fluorine content of the drinking water ranging from 0.02 to 0.9 p.p.m. In approximately 6 per cent. of the children he observed curious nebulæ, accompanied by calcareous spots on the teeth. In conjunction with this slight defect, he frequently observed the occurrence on the teeth of these children of the Pristleaf Tarnish, a stain due to a chromogenic fungus. Zelmonova states that fluorine is not the causative factor in this defect, but that it is due to a decalcification of the dentine, a condition observed in areas where the mineral content of the water is low.

Dean (1938) observed that different individuals of even a homogeneous group are diversely affected by the same concentration of fluorine in the drinking water. He states that certain children have no mottled teeth, while others in the same family and using the same water are definitely affected. According to Dean this phenomenon is merely a normal manifestation of the operation of the law of normal biological variation. In the affected Amirillo area in Texas, Dean (1938) examined 289 children, all of whom continuously used the municipal water for both cooking and drinking purposes. Of the children examined the teeth of 9 were found to be normal, 19 questionable, 44 showed very mild, 81 mild, 98 moderate, 32 moderately severe and 6 showed severe mottling. These figures are based on the classification propounded by Dean (1934) for mottled enamel. It is at once evident, that this frequency distribution, represented graphically, roughly conforms to the characteristic monomodal curve of variation. The highest percentages being intermediate, with the initial and terminal ones the lowest.

The distribution of this disease is almost universal, Australia being the only continent from which dental fluorosis has not been reported. The reports by the various workers in the field of fluorine toxicosis, in America, Argentine, China, England, Spain, Italy, South Africa, etc., are to the effect, that the ingestion of fluorine in the drinking water in a concentration exceeding one part per million, manifests itself on the teeth calcifying during this period.

The characteristic features of dental fluorosis are not the same as those encountered in other disturbances, such as avitaminoses A (Wolbach, 1933), rickets (Erdheim, 1914), parathyroidectomy (Toyofuku, 1911), hyperthyroidism (Schour, 1934), and hypophysectomy (van Dyke, 1932). The most outstanding feature of fluorosis of the teeth, is the selective action of fluorine on the enamel, especially the primary accentuated incremental layers in the enamel. This selective action on the enamel is of special interest in the light of Erdheim's calcio protective law, stating that some tissues are more protected against disturbances in calcium metabolism than others. Thus as a rule enamel shows disturbances less frequently than does dentine.

Mottling of the teeth is chiefly characterized by chalky white patches distributed irregularly over the surface of the tooth. These chalky areas are as a rule well defined and may readily be differentiated from the rest of the tooth surface. In many instances the

whole tooth represents this dead white, turbid, unglazed appearance. As a result of the loss of their normal translucency the teeth glare unnaturally when the mouth is open.

In this country, especially in the rural areas of the North-Western Cape Province, dental fluorosis is chiefly characterized by marked parallel striations across the upper and lower central and lateral incisors, extending in many cases to the cuspids, the chalky areas being more or less confined to the molars and premolars. In the spaces between these striations the tooth surface retains its natural translucency and porcelain finish to a great extent. Sometimes the striations are very fine and irregular and can only be observed as fine intersecting lamellae. By force of circumstances the inhabitants of these affected areas are subjected to a more or less nomadic existence, which may to a certain extent account for the characteristic type of mottling encountered.

In the most severe forms of dental fluorosis, there is a marked loss of enamel, accompanied by pronounced pitting, both confluent and discrete, giving the tooth surface a corroded appearance. This marked influence of fluorine causes atrophy of the entire enamel organ, and may result in aseptic necrosis.

In the affected countries mentioned, no actual changes are observed in both size and shape of the affected teeth. The only other oral abnormality encountered is a tendency for the teeth to erupt somewhat later than in non-affected areas and a tendency towards gingivitis, in localities where the fluorine content of the water is excessively high.

As already pointed out, tooth fluorosis is a defect mainly of the permanent teeth. Deciduous teeth are also subject to fluorine damage, usually concomitant with the ingestion of large amounts of fluorine through the medium of the drinking water. Roholm (1937) observed mottling in the permanent teeth of children suckled by mothers working in cryolite factories. The deciduous teeth of these children are perfectly normal.

The fact that the temporary teeth are rarely affected, may be ascribed to a very rapid calcification and eruption. The calcification of the baby teeth is in process during early foetal life; thus, the enamel is protected from a fluorine interference by a nutritive supply dialyzed through placental osmosis.

In this country, Ockerse (1939) encountered 22 instances of a pronounced mottling of the deciduous teeth in the affected localities of the North Western Cape Province. The fluorine content of the respective waters is still pending analysis.

Mottled teeth may or may not become stained afterwards. The stain is frequently confused with the enamel defect itself, but is a secondary phenomenon. The stain which is presumably due to a secondary infiltration shows considerable variations in colour, ranging from almost black to yellow. As a rule the stain is not present in all the teeth, being more pronounced on the upper lateral and central incisors. The stained areas are mostly localized to the

labial surfaces of these teeth, and have a general tendency to follow the lip-line, thus suggesting that prolonged exposures to light may be a factor in its development. The behaviour of the stain during calcination suggests an organic nature. The stain generally deepens with age.

The enamel of adult teeth is unaffected by fluorine, the composition of the dentine, however, is liable to change and may thus be affected.

In the more advanced stages of dental fluorosis, severe pitting and loss of enamel may result in a general carious condition of the teeth. Isolated instances of such a condition were observed by Ockerse (1939) in this country in urban areas with a 100 per cent. incidence of mottled teeth amongst school children. This worker further reports, that the incidence of caries in the affected areas is exceedingly low.

Dean (1938, a) in America and Ainsworth (1933) in England, pointed out that the use of domestic waters in itself capable of producing mottled teeth, is concomitant with a lower incidence of caries.

The incidence of a pathological condition of the teeth of certain domestic animals, under natural conditions, has been reported from North Africa, Texas, and the Argentine Republic. Particularly those animals requiring several years for the calcification of their permanent teeth, are affected.

Van der Merwe and Malan (1939), observed in the Kenhardt-Upington districts that the ingestion of water containing up to 8 p.p.m. fluorine, has no visible effect on the calcification of the teeth of cows, goats, sheep and donkeys. Velu (1938), states that drinking water containing 7 p.p.m. fluorine as CaF_2 did not affect the teeth of animals. Steyn (1937) believes that a fluorine content of at least 4-6 p.p.m. in the drinking water is necessary to cause enamel defects in animals.

It seems fairly definite, that water containing fluorine in quantities sufficient to cause severe mottling in humans, will not affect the teeth of animals.

It has been known for a long time that the continual ingestion of large amounts of fluorine, adversely affects the calcium-phosphorus metabolism of animals.

Bartolucci (1912), described a disease amongst cattle on a farm in the environment of a superphosphate factory in Italy. Clinically this disease, which Bartolucci termed osteitis, conforms to the classical osteomalacia. Bartolucci associated this disease etiologically with the fluorine containing gases emanating from the factory. He states, that water, from a well sunk near the canal leading off the factory effluents, contains fluorine, and the interesting observation was further made, that the affection amongst the animals disappeared when the water from the town mains was used for drinking purposes.

Smith *et al* (1935) in America were unable to establish any impairment in the Calcium-phosphorus metabolism of young girls severely affected by tooth fluorosis. Their findings are based on balance trials. These workers state that the continual ingestion of fluorine through the medium of the drinking water in quantities sufficient to produce pronounced mottling of the teeth, in no way disturbs the body's ability to metabolize calcium and phosphorus.

In Texas, Lemmon (1934) observed that babies in the affected Amirillo area show greater tendency to bowing of the legs, even in the face of constant anti-rachitic therapy, thus supporting the theory that fluorine even in very small concentrations interfere with the general calcium and phosphorus metabolism.

In diametric opposition to the findings of the American workers, Shortt, McRobert and Barnard (1937), report the incidence of endemic fluorosis of a unique character, in the Madras Presidency. They state this condition to be prevalent in areas, amongst natives, who have been subjected for periods of forty years or more to the influence of drinking water, containing comparatively large quantities of fluorine. In the initial stages this disease is manifested by mottling of the permanent and sometimes the deciduous teeth. The affected teeth are in no way superior to or worse than the teeth of children in non-affected areas. Apart from the dental defect the children drinking these respective waters do not appear to suffer in any way. From birth until approximately thirty years a dormant period is observed, during which no ill effects are being encountered. At about thirty years of age the first symptoms of poisoning set in. This is manifested by a general recurrent tingling sensation in the limbs and sometimes in the entire body. Pain and stiffness next appear, especially in the lumbar region of the spine. The stiffness increases until the entire spine including the cervical region appears to be one continuous column of bone, producing a condition of poker back. Ultimately the spine loses its flexibility, accompanied by stiffness of various joints. The bony structure of the thorax is affected to a marked degree, the ribs become rigidly fixed at their junction with the spine, with the result that breathing becomes entirely abdominal. In the advanced stages of this disease, the victims exhibit a definite cachexia, loss of appetite and emaciation. Ultimately there is a loss of sphincter control and impotence is common. At this stage the patient is completely bed-ridden, death following, usually due to some intercurrent disease. Radiological findings show excessive calcification of tendons and ligaments, the presence of osteophytic outgrowths from various bones and almost complete synostosis of various joints. The biochemical estimation of serum calcium, phosphorus and phosphatase indicates a favourable condition for abnormal deposition of bone.

The clinical and radiological findings bear a close analogy to the observations of Flemming--Moller and Gudjonsson (1932), who encountered a marked osteosclerosis in workers in a cryolite factory in Denmark.

This report by Shortt, McRobert and Barnard is of great interest as it is the only one encountered in the literature, describing the devastating effect of water borne solute fluorides.

The nutritional aspect relevant to the above mentioned incidence of fluorosis, should, however, be considered. It has repeatedly been demonstrated that nutritional factors play an important part in the manifestation of symptoms of fluorine intoxication. Schlick (1911) reported that frogs receiving toxic doses of NaF may be protected by means of CaCl₂. Hauck, Steenbock and Parsons (1933), showed that the toxic effects of fluorine administration was less on a high calcium ration than on a low calcium ration. Elmslie (1936) pointed out that the addition of CaCO₃ to the ration of the rat, increased the level of toxicity of fluorine. Schulz (1938) found that the addition of cod liver oil to the diet of the rat, subjected to fluorine ingestion, tends to ameliorate the toxic effects of the fluorine. On the other hand, Phillips, English and Harts (1935), found that the toxicity of NaF to chicks, fed orally or injected intraperitoneally in water solution was much increased when desiccated thyroid was fed. They observed that non-toxic doses of thyroid became toxic when NaF was fed, and non-toxic doses of NaF became toxic when fed in conjunction with desiccated thyroid.

Chanelles (1928), found that when iodides are fed in conjunction with fluorides, the resultant fluorosis is much accentuated. This apparent relationship between fluorine and thyroxin in the animal body may be a factor governing chronic fluorosis.

A dental and mandible disease known as Darmous, occurs amongst herbivora in the phosphate zones of North Africa. This disease is a chronic fluorine intoxication affecting the general calcium-phosphorus metabolism. The form of Darmous occurring in man must be regarded as the most severe type of dental fluorosis, and is accompanied by pronounced developmental anomalies. The teeth may be delayed in eruption, and a marked dystrophy of the permanent teeth is observed, resulting in definite changes in the actual size and shape of the teeth. In both man and animal the terminal stages of this disease are accompanied by difficulties in mastication and increased sensitivity towards cold water. Inflammation of the gingiva often develops. Strictly speaking, however, Darmous is not a water borne disease. Roholm (1937) observed that the soluble fluorine fraction in the water of the endemic areas is comparatively low. Gaud and Charnot (1934) pointed out that the main factors involved in the production of Darmous is the drinking of water contaminated with phosphate suspensions, and chiefly the ingestion of vegetation covered with phosphate dust.

A dental and bone disease, termed Gaddur, is endemic in Iceland. Accounts of this strange disease are encountered in Icelandic literature dating back to the year 1,000 A.D. The natives found that domestic animals turned sick and died following eruptions of the volcanoes Hekla, Katla and Askja. The symptoms disappeared when the animals were taken indoors and fed hay reaped before the eruption. This disease which has played a great rôle in Iceland's economy, is encountered up to a period of twelve years following volcanic eruptions. The chief factor in the production of Gaddur is the ingestion of pasture contaminated by volcanic ash, intoxication through the medium of the drinking water being of secondary importance.

The true channels of the fluorine attack on the teeth are still rather obscure. It is a well known fact that dental fluorosis is accompanied by an increase in the fluorine content of the affected teeth. Whether the fluorine is deposited as the molecular CaF_2 or whether substitution of fluorine for the carbonate, chloride or hydroxyl radicles takes place in the isomorphous intermixtures of the various apatites comprising the bony matrix, is still a matter of conjecture.

Smith (1933) pointed out that in the teeth of rats fed NaF in the ration, the percentage of Ca, and the ratio of Ca to P as obtained by chemical analysis are remarkably similar to the calculated formula of the theoretical colophane, $3\text{Ca}_3(\text{PO}_4)_2 \cdot 2\text{CaX}$.

Rogers (1922) describes fossil bones, known for a long time to be high in fluorine content, as colophane, to which he assigns the following formula $3\text{Ca}_3(\text{PO}_4)_2 \cdot (1-2)\text{Ca}(\text{F}_2\text{CO}_3\text{SO}_1\text{O}) \cdot \text{XH}_2\text{O}$.

Reynolds and Corrigan (1938), by means of X-ray diffraction studies, observed that the teeth of rats fed fluorine were heterogeneous, being mixtures of normal apatite like materials and CaF_2 . The teeth are not uniformly orientated along the fibre axis, accompanied by an enlargement of the apatite crystals.

Bergara (1929), Chanelles (1929) and Pavlovic (1932), expressed the belief that the alterations observed in the teeth must be ascribed to endocrine factors. According to these workers, the fluorine acts directly on the parathyroid glands, and thus secondarily produces changes in the teeth. They base their claims on the fact that apparently similar changes are noted in the rat incisor in cases of fluorine feeding and parathyroidectomy.

This theory was, however, discredited by Hauck, Steenbock and Parsons (1933). Sutro (1935) found that parathyroid extract administered up to 700 units per day over a period of 2-3 months neither retarded nor prevented the appearance of striped enamel.

Schour (1934) pointed out that the amount of fluorine sufficient to cause dental changes is very small compared to the total ionized calcium content of the blood. It is, therefore, not likely that the calcio-prive effect of the fluorine would be sufficiently great to disturb the calcium-phosphorus metabolism appreciably. According to Schour's postulate, the fluorine has a very prompt and direct influence on the formation and calcification of enamel and dentine, particularly the enamel forming cells.

Fluorides and silico fluorides exhibit an amazing reactivity towards certain enzymatic processes, in some instances causing an almost complete inhibition and in others a pronounced stimulation. Ewig (1929) has shown that in isolated tissue both anaerobic and aerobic glycolysis is greatly inhibited by NaF. Fluorine has an inhibitory effect on the lactic acid synthesis occurring during muscle metabolism. On the other hand Doby (1914), found that the amylase of the potato was powerfully stimulated by NaF.

According to Smith (1935), fluorine does not exert its characteristic damage through its effect on the enzymatic phosphatase reaction concerned in tooth and bone formation. An increase in plasma phosphatase cannot be considered a criterion in fluorine toxicosis, as suggested by Phillips (1932).

The first report on the histology of this disease is that of Black (1916), who noted that the identifying characteristic was the absence of the interprismatic cementing substance between the enamel rods. Williams (1923), confirmed the observations of Black, but states that the enamel rods themselves are imperfectly calcified. He also observed the presence of imperfectly fused granules and some spherical globular masses which are identical with the calciospherites encountered in completely calcified forming enamel.

Beust (1925), called attention to the fact, that in addition to the enamel the dentine is likewise affected, a condition which he termed mottled dentine. Ainsworth (1933,a), confirmed the findings of Beust by reporting the occurrence of imperfectly calcified dentine with interglobular spaces such as may be encountered in ordinary cases of hypoplasia. Ainsworth (1933,a) noted that the pitting of the enamel surface may readily be explained as a breaking off of the ends of the enamel rods, weakened by the loss of the interprismatic substances.

Erausquin (1934), reports that the permeability of mottled enamel may be compared to that of immature, unerupted, normal enamel. The permeable zone characterizing mottled enamel is always the most external, its intensity diminishes from the outside inwards.

FLUORINE COMPOUNDS IN NATURAL WATERS AND THEIR ORIGIN.

The actual chemical nature of fluorine compounds present in drinking water is of some interest to the chemist, but apparently of no great practical significance.

In acute fluorine toxicosis studies in animals, various workers have observed that the attainment of gross symptoms of intoxication is definitely associated with the chemical nature of the fluorine compound used. Thus it was established that twenty times as much CaF_2 is needed to produce the same degree of severity of the symptoms caused by NaF , with NH_4F and Na_2SiF_6 being of the same order of toxicity as NaF during the same period.

Kempf and Nelson (1936), observed that CaSiF_6 and CuF_2 caused mottling of the rat incisor, whereas the ingestion of AlF_3 did not produce this defect. Similarly in the field of the organic fluorides, fluoro naphthalene produced mottling, the ingestion of p-p di-fluoro-biphenyl-p-fluoro-benzoic acid on the other hand has no effect of calcifying enamel.

In the light of present knowledge it appears that in dealing with the ingestion of small quantities of fluorine over extended periods of time, the actual chemical combination of the fluorine compound present is of secondary importance, whereas the physical state in which the fluorine is ingested is the primary factor governing the development of defective enamel.

Marcovitch (1938), established a marked difference in the accumulative effect of fluorine in rats subjected to a sodium fluoride intake equivalent to 4 p.p.m. of fluorine in the drinking water in one group and incorporated to the same fluorine equivalence as cryolite in the diet in a second group.

Bowes and Murray (1938), consider the fluorine contained in food supplies to be less dangerous than the fluorine derived from water origin.

Dean (1938, *b*), states that there is definite evidence implicating CaF_2 in solution as the sole factor in the production of mottled enamel in America. In America, however, fluorine concentrations in excess of 25 p.p.m. in the drinking water have been reported, a figure which cannot be explained when the solubility product of CaF_2 is taken into consideration. Assuming the postulate of Dean to be correct, then the high fluorine figures reported by the American workers must be considered a reflection of the pronounced disposition of fluorine compounds towards the formation of complexes.

In certain parts of Northern Africa, the natural waters contain fluorine due to percolation through or stagnation in the phosphate deposits, the fluorine in all probability passing into solution as CaF_2 .

In Iceland, the different volcano environs are subjected to fluorine contamination, with the result that both fluorides and silico fluorides may be expected in the natural waters.

Fluorine compounds are of comparatively common occurrence in the outer layers of the earth's crust, especially as minor constituents of eruptive rocks and in conjunction with the universal distribution of natural phosphate deposits.

In a computation of the average chemical composition of eruptive rocks, Clarke and Washington (1924), place fluorine in the twenty-second position in the order of the ranking of the elements. According to these workers, fluorine constitutes 0.03 per cent. of eruptive rocks. Amongst the numerous rock forming minerals containing fluorine the most common are, lepidolite zinnwaldite, two lithium micas containing up to 7 per cent. fluorine, fluor spar, tourmaline, fluo-apatite, topaz and cryolite.

If the igneous rocks are in an unaltered and preserved condition, leaching and consequently fluorine contamination of the ground water cannot take place. If the rocks are, however, highly weathered and disintegrated as is the case with the old Archean Zwasiland granites of the North Western Cape, ground water may be brought into intimate contact with fluorine bearing strata.

In contact zones surrounding great masses of eruptive rock, it is observed that migration of some of the constituents of the magma into the country rock takes place. In studies of contact metamorphism, fluorine was found to be one of the elements subjected to transference. Especially limestone contacts are ready recipients of fluorine due to the binding powers of the former. In the metamorphic limestone of Monte Somma in Italy, the following fluorine bearing minerals were found, apatite, chondrodite, clino-humite, cuspidine, fluor spar, humite, vesuvianite, tourmaline, koppite and topaz.

FLUORINE IN NATURAL WATERS.

Phosphorite and phosphatic limestone are two naturally occurring amorphous phosphates found in gigantic deposits in various parts of the world. The fluorine content ranging from 2-4 per cent. Water percolating through beds of phosphorite apparently exhibits no marked leaching properties as far as fluorides are concerned. Roholm (1937), pointed out that the fluorine figure of waters from the phosphate zones of North Africa ranges from 0.02-1.0 p.p.m. Of great importance however is the fluorine content of the suspended material in the water. That Dirmous is not primarily produced by solute fluorides in the drinking water may be deducted from a report by Gaud, Charmot and Langlais (1934), to the effect that Dirmous does not occur in areas where the fluorine content of the soil is less than 200 p.p.m.

Dean (1935) observed mottled enamel amongst cattle in Texas, where large phosphorite deposits are encountered.

That phosphorite may be instrumental in raising the fluorine content of ground water to a dangerous level, was demonstrated by Phillips and Hart (1934), who found a fluorine content of 1.7 p.p.m. in water draining from lands on which rock phosphate was used as fertilizer. Strangely enough, superphosphate, according to these workers, does not cause any significant increase in the fluorine content of drainage waters.

Thus far, no dental fluorosis has been reported from areas in South Africa where wavelite is found in vast deposits.

In areas of volcanic activity, the fluorine compounds present in the gas emanations may find their way into the natural waters of the volcanic environs. The presence of both HF and SiF_4 have repeatedly been demonstrated in volcanic exhalations, while the gas deposited incrustations about volcanic vents and fumaroles, contain up to 85 per cent. NH_4F .

In one locality in America, Mastodon bones from the Cenozoic era were suspected of contaminating the ground water with fluorine.

If the wide distribution of fluorine compounds in nature is taken into consideration it is only natural to assume the presence of traces of this element in many waters.

The formation of mottled enamel can readily be prevented, but there is no known cure once defective enamel sets in. The stain, due to its organic nature can temporarily be bleached by various oxidising agents, but the nebulae on the teeth and the general enamel defect is of a permanent nature.

Prior to the establishment of the etiological factor in this disease, prevention has been accomplished in America by simply changing the water supplies of the cities of Oakley (Idaho) and Bauxite (Ark.). A change of water supply is not always practical, but at the same time it is well to bear in mind that the only portion of the population in need of protection, is children from birth to eight years of age, and women during pregnancy—the latter precaution being necessary only in localities where the fluorine content of the water is excessively high.

The logical approach to the solution of this problem is to adopt a method of treating the affected waters by chemical or physical means to effect the removal of the toxic fluorides.

This problem has received the attention of the numerous workers and encouraging results have in many instances been attained. Various chemical compounds were investigated in regard to their mode of action towards solute fluorides. In the literature, the following attempts to defluorinize natural waters are mentioned. $\text{Al}_2(\text{SO}_4)_3$ (Boruff, 1934), Defluorite (Hess and Swopp, 1937), activated carbon (McKee and Johnson, 1934), activated alumina (Lindsay, 1936), activated MgO (Elvove, 1937) were used in filters.

The majority of these methods are costly and reliable results are not always obtained.

A more rational approach to the problem is to adopt as principle the great affinity exhibited by fluorine towards the tertiary phosphate complex. As far back as 1805, Morichini demonstrated this principle by reporting the very high fluorine content of a fossil elephant tooth found outside Rome, a phenomenon caused by the continual infiltration of fluorine from ground water origin. Margaret Smith (1938), working along these lines, advocates a method adopting a specially prepared bone product as a medium through which the fluorine contaminated water may be filtered. For limited supplies of water, low in total salt content, this method proved excellent in the hands of the author. The active principle is rapidly inactivated, and a constant check on the fluorine content of the filter effluent, is imperative, to ensure a safe water. On account of the fact that the active principle is poisoned in a comparatively short period of time, a continual regeneration of the bone product is necessary.

Adler, Klein and Lindsay (1938) found a tri-calcium phosphate used in conjunction with a filter bed, satisfactory for the removal of fluorine from water. Their product is essentially a mixture of hydroxy apatite and tri-calcium phosphate, and is prepared from high purity phosphoric acid and milk of lime. McIntire and Hammond (1938), stressed the possibility of exploiting baking powders and superphosphates as the calcium phosphate source to effect the removal of fluorides.

PROPOSED METHOD OF REMOVAL OF FLUORIDES FROM NATURAL WATERS.

In the determination of the titratable acidity of aqueous solutions of superphosphate, it was observed by the author that the soluble fluorine fraction suffers a reduction, presumably due to either a precipitation with the phosphate complex as an apatite or as a result of adsorption. The method advocated here to effect the removal of fluorine from water is based on this principle, which comes into operation when superphosphate in a modified form, is incorporated in the affected water and a tertiary phosphate is subsequently precipitated in the aqueous medium by the addition of a basic hydroxide.

FLUORINE IN NATURAL WATERS.

The products adopted in this investigation are the ordinary commercial superphosphates, comprising the 17, 19, 20 and 40 per cent. water soluble P_2O_5 varieties.

The water soluble selenium, boron and arsenic content of these products were found to be entirely negligible. Selenium and boron are both present in the mother rock from which the superphosphates are manufactured. The fate of these elements during the manufacturing process is still uncertain. Apparently they are partially expelled as their respective fluorides since these elements are only present in minute traces in the final product.

Superphosphate production by means of pyritic and lead chamber, volcanic sulphur-sulphuric acid, results in an arsenic containing final product. The use of sulphuric acid prepared from secondary sulphur in the contact process safeguards the superphosphates from an arsenic infiltration.

A sample of each respective superphosphate was ground to an impalpable powder to ensure a homogeneous product being obtained.

As a preliminary investigation the behaviour of the sulphate and fluorine compounds present in superphosphates was studied under the conditions prevailing in the proposed method.

Aqueous solutions (using distilled water) were prepared of double superphosphate (40 per cent. water soluble P_2O_5). The concentrations used are shown in Table I. Solid $Ca(OH)_2$ was added to these solutions in quantities just sufficient to develop the maximum colour of added phenolphthalein.

TABLE I.

Solution No.	Super-phosphate Gr.p.lit.	Ca (OH) ₂ Gr.p.lit.	Initial F. p.p.m.	Residual F. p.p.m.	Initial SO ₄ p.p.m.	Residual SO ₄ p.p.m.
A.....	10	4.03	34.3	0.75	410	88
B.....	10	4.03	34.3	0.28	410	51
C.....	2	0.81	12.8	0.34	113	30

Solutions A and C were allowed to stand for a period of 24 hours with occasional agitation.

Solution B was boiled for a period of 10 minutes and the precipitate allowed to settle.

From the table it is evident that both the solute fluoride and sulphate from superphosphate origin suffer a marked reduction. The results obtained for the 17, 19 and 20 per cent. varieties of superphosphate are less favourable. The results obtained for 17 per cent. superphosphate are tabulated in Table II. Analogous results being obtained in the case of the other two phosphates.

TABLE II.

Solution No.	Super-phosphate Gr.p.lit.	Ca (OH) ₂ Gr.p.lit.	Initial F. p.p.m.	Residual F. p.p.m.	Initial SO ₄ p.p.m.	Residual SO ₄ p.p.m.
A.....	10	3.9	24.7	0.82	1,284	860
B.....	10	3.8	24.7	0.56	1,284	834
C.....	2	0.77	10.3	0.93	711	419

Solutions A and C were allowed to stand for a period of 24 hours with occasional shaking.

Solution B was boiled for a period of 20 minutes and the precipitate allowed to settle.

It is observed from the table that the residual sulphate is unduly high, accompanied by an unsatisfactory reduction of the fluorine in solution.

It has been shown by the author, that in aqueous solutions, the solubility of the fluorine and sulphate compounds present in superphosphate, suffers a marked reduction, at high concentrations. By adopting this principle, a comparison was effected with the results obtained in Tables I and II, adopting the following procedure.

A highly concentrated solution of superphosphate was prepared, containing 70.5 grams P₂O₅ and 391 mgs. F₂ per litre. Volumes of this solution yielding the same gross P₂O₅ content per litre as in solutions A and B (Table I), were added to litre quantities of distilled water and the same procedure carried out as in the case of solutions A and B, Table I. The results obtained by means of this concentrate are tabulated in Table III.

TABLE III.

Solution No.	Concentrate c.c. p.lit.	Ca (OH) ₂ Gr.p.lit.	Initial F. p.p.m.	Residual F. p.p.m.	Initial SO ₄ p.p.m.	Residual SO ₄ p.p.m.
A.....	56	4.81	21.9	0.19	213	Trace.
B.....	56	4.81	21.9	0.02	213	Trace.

Solution A was allowed to stand for a period of 24 hours with occasional agitation.

Solution B was boiled for a period of 20 minutes and the precipitate allowed to settle.

FLUORINE IN NATURAL WATERS.

From Table III it is observed that as a result of the treatment the solute sulphate and fluoride derived from the concentrate suffer an almost complete removal.

Even more marked in comparison are the results obtained by using a concentrated solution of 17 per cent. phosphate, as indicated by the results in Table IV.

The solution adopted contained 62.5 grams P_2O_5 and 417 milligrams F₂ per litre. This solution is again added to litre quantities of distilled water, yielding equivalent P_2O_5 concentrations to solutions A and B (Table II).

TABLE IV.

Solution No.	Concentrate c.c. p.lit.	Ca (OH) ₂ Gr.p.lit.	Initial F. p.p.m.	Residual F. p.p.m.	Initial SO ₄ p.p.m.	Residual SO ₄ p.p.m.
A.....	26	3.4	10.84	0.45	155	Trace.
B.....	26	3.4	10.84	0.15	155	Trace.

Solution A was allowed to stand for a period of 24 hours with occasional agitation.

Solution B was boiled for 20 minutes and the precipitate allowed to settle.

A comparison of the results obtained in Tables II and IV reveals that a phenomenal reduction in the sulphate content of aqueous solutions of 17 per cent. superphosphate (Table IV), can be achieved by simple concentration. This finding proved of immense value in the project of this Institute to ameliorate the ill effects of aphosphorosis in this country by means of superphosphate as a water soluble phosphate.

A comparison of Tables III and IV shows that the two concentrated solutions have the same potential defluorinizing powers, both yielding a treated water containing a trace of sulphate.

The ability of both solid superphosphates and the concentrates to effect the removal of extraneous fluorine was investigated by treating along various lines a water containing 10 p.p.m. F₂ as NaF.

Solid double superphosphate was added in varying quantities to litre volumes of distilled water containing 10 p.p.m. F as NaF. The flasks were vigorously agitated to ensure maximal solution of the phosphate. Calcium hydroxide was added until the maximum colour of added phenolphthalein developed.

Solutions A, B and C were precipitated in the cold and then boiled for 20 minutes.

TABLE V.

Solution No.	Initial F. in Solution p.p.m.	Super-phosphate. Gr.p.lit.	Ca (OH) ₂ Gr.p.lit.	Residual F. p.p.m.	Residual SO ₄ p.p.m.
A.....	10	0.5	0.5	0.95	Trace.
B.....	10	1.0	1.0	0.60	16
C.....	10	2.0	1.85	0.45	27
D.....	10	2.0	1.85	0.20	19

Solution D was precipitated at boiling point and subsequently boiled for 20 minutes.

In the case of solutions C and D the fluorine is removed satisfactorily, the residual sulphate being of no significance.

The same procedure as adopted in Table V was carried out using 17 per cent. superphosphate. The results are tabulated in Table VI.

TABLE VI.

Solution No.	Initial F. in Solution p.p.m.	Super-phosphate. Gr.p.lit.	Ca (OH) ₂ Gr.p.lit.	Residual F. p.p.m.	Residual SO ₄ p.p.m.
A.....	10	0.5	0.15	5.5	192
B.....	10	1.0	0.3	3.1	374
C.....	10	1.5	0.45	2.4	485
D.....	10	2.0	0.6	1.8	536

Although a definite reduction in NaF concentration is achieved (Table VI), accompanied by a preclusion of the passing into solution of the fluorine contained in the superphosphate, the gross fluorine reduction is incomplete. Treatment by means of solid 19 and 20 per cent. superphosphates also resulted in incomplete removal of added fluorine and a high residual sulphate content of the treated water.

To effect a comparison with the results obtained in Tables V and VI the behaviour of the concentrates towards a water containing 10 p.p.m. F was investigated.

Water containing 10 p.p.m. added fluorine as NaF was saturated with Ca(OH)₂, filtered, and treated by means of double superphosphate concentrate as elucidated in Table VII.

TABLE VII.

Solution No.	Initial F. in Solution. p.p.m.	Concentrate e.c. p.lit.	Added F. p.p.m.	State of Neutralization.	Residual F. p.p.m.	Residual SO ₄ p.p.m.
A.	10	10·9	4·26	Half Neutralization...	0·35	Trace.
B.	10	21·8	8·52	Total Neutralization..	0·55	Trace.
C.	10	21·8	8·56	Total Neutralization..	0·15	Trace.
D.	10	10·9	4·26	Half Neutralization...	0·70	Trace.
E.	10	10·9	4·26	Half Neutralization...	0·25	Trace.
F.	10	10·9	4·26	Half Neutralization...	0·04	Trace.

Solution A.—Half neutralization and occasional thorough agitation through a period of 24 hours.

Solution B.—Total neutralization and subjected to the treatment of A.

Solution C.—Total neutralization and boiled for 15 minutes.

Solution D.—Half neutralized and a rapid airstream passed through for 30 minutes.

Solution E.—Half neutralized and boiled for 5 minutes.

Solution F.—Brought to boiling point, slowly half neutralized, boiling continued for 5 minutes.

Solutions A, B and D, precipitated in the cold, yielded precipitates of a gell structure. These precipitates settled very gradually, whereas the boiled suspensions settled readily.

The large volume of concentrate required to neutralize the Ca(OH)₂ solution of approximately 0·2 per cent. resulted in the formation of voluminous precipitates. In order to reduce the volume of concentrate, the process of precipitation was reversed, with the following results (Table VIII).

The solutions (Table VIII) were subjected to the following treatment:—

A.—The concentrate is added to the fluorine containing water (10 p.p.m.) and thoroughly agitated to effect mixing. The Ca(OH)₂ added and the suspension boiled for 15 minutes.

B.—The treatment of A.

C.—Concentrate added, shaken, followed by precipitation at boiling point, boiling continued for 15 minutes.

D.—Concentrate added, shaken, Ca(OH)₂ added and allowed to stand for 24 hours with occasional agitation.

E.—Concentrate added, shaken, Ca(OH)₂ added and boiled for 20 minutes.

F.—Concentrate added and mixture brought to boiling point, Ca(OH)₂ added, boiling continued for 10 minutes.

- G.—Concentrate added, shaken, $\text{Ca}(\text{OH})_2$ added and boiled for 10 minutes.
- H.—Concentrate added, shaken, thoroughly agitated for 30 seconds and precipitate allowed to settle.
- I.—Concentrate added, shaken, $\text{Ca}(\text{OH})_2$ added and allowed to stand for 24 hours with occasional shaking.
- J.—Concentrate added, shaken, mixture brought to boiling point, $\text{Ca}(\text{OH})_2$ added, boiling continued for a subsequent 10 minutes.
- K.—Treatment of D for a period of 72 hours.

TABLE VIII.

Solution No.	Initial F. in Solution.	Concentrate. c.c. p.lit.	Added F. p.p.m.	$\text{Ca}(\text{OH})_2$ Gr.p.lit.	Residual F. p.p.m.	Residual SO_4 p.p.m.
A.....	10	1.25	0.48	0.13	1.9	Trace.
B.....	10	2.5	0.97	0.28	1.1	Trace.
C.....	10	2.5	0.97	0.28	0.74	Trace.
D.....	10	5.0	1.94	0.50	0.60	Trace.
E.....	10	5.0	1.94	0.50	0.22	Trace.
F.....	10	6.25	2.44	0.65	0.05	Trace.
G.....	10	6.25	2.44	0.65	0.12	Trace.
H.....	10	10.0	3.91	0.98	1.4	Trace.
I.....	10	10.0	3.91	0.98	0.10	Trace.
J.....	10	12.5	4.88	1.29	0.04	Trace.
K.....	10	12.5	4.88	1.29	0.02	Trace.

The 17 per cent. concentrate proved to be equally effective as a defluorizing agent, when the different procedures outlined above are adopted.

The double superphosphate concentrate was evaporated to dryness, and the resultant greyish-brown was pulverized and mixed with the correct equivalent of $\text{Ca}(\text{OH})_2$. The incorporation of this product in boiling waters resulted in a very satisfactory removal of extraneous fluorine as elucidated by the results in Table IX.

TABLE IX.

Solution No.	Initial F. in Solution p.p.m.	Evaporated Concentrate Gr.p.lit.	$\text{Ca}(\text{OH})_2$ Gr.p.lit.	Residual F. p.p.m.	Residual SO_4 p.p.m.
A.....	10	0.25	0.3	1.6	Trace.
B.....	10	0.75	0.9	0.5	Trace.
C.....	10	1.0	1.2	0.35	Trace.
D.....	10	2.0	2.4	0.08	Trace.
E.....	10	2.5	3.0	0.05	Trace.

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Finally, the suitability of the concentrate method to reduce fluorides from waters very high in total salt content, was investigated. The water in question is one presently adopted in a study of salt water tolerance in sheep, conducted by the Section of Toxicology.

To a litre volume of the water, 5 c.c. of the double superphosphate concentrate was added, resulting in the formation of a slight opacity in the aqueous medium, presumably due to the precipitation of phosphates. $\text{Ca}(\text{OH})_2$ in slight excess was added, the mixture thoroughly shaken and boiled for 10 minutes. The results in Table X bear mute testimony as to the improved nature of the treated water.

TABLE X.

Initial Fixed Residue. p.p.m.	Initial SO_4 p.p.m.	Initial F_2 p.p.m.	Residual Fixed Residue. p.p.m.	Residual F_2 p.p.m.	Residual SO_4 p.p.m.
16405.....	1939	6	13670	0.45	1678

It is observed that the reduction in sulphate content (Table X) amounts to 261 p.p.m., being approximately equivalent to the sulphate present in the water as MgSO_4 . This is in line with the finding that the concentrate method of fluorine removal, reduces to a marked degree the sulphates of metals forming insoluble secondary and tertiary phosphates. The sulphates of the alkali metals hardly suffer any reduction.

In an attempt to exploit a possibly cheaper source of calcium phosphate than that of superphosphate origin, the naturally occurring wavelite was considered. This amorphous phosphate of iron and aluminium occurs in vast deposits in the Saldanha Bay environs.

By treating a fluorine containing water with a small quantity of this phosphate ground to an impalpable powder, a colloidal suspension is formed which defies filtering. It has been found possible to break this suspensoid and obtain a treated water containing less than 1 p.p.m. fluorine. Studies in this connection are being continued.

METHODS OF ANALYSIS.

The treated waters were analysed for their phosphate, sulphate, and fluorine contents. The residual Ca in solution was not taken into consideration as this factor can readily be controlled.

Phosphate was determined colorimetrically by the Fiske and Subbarow method. In all cases except one the treated water contained less than 1 p.p.m. phosphate as P.

Sulphate was determined gravimetrically and residual concentrations of less than 10 p.p.m. are designated by "trace".

In this investigation it was found necessary to have a rapid and accurate method for the determination of the fluorine content of the treated waters.

Various colorimetric methods, based on the specific bleaching reaction of the fluoride ion towards the Zirconium lake of certain anthraquinone dyes, are encountered in the literature. The methods of Sanchis (1934) and Elvove (1933) seemed the most promising. According to Scott (1937), 0.1 mgr. fluorine in 100 c.c. is about the limiting amount for a good colour distinction when using the Sanchis modification of the Zirconium alizarin bleach. Apparently this 1 p.p.m. F in water is the limiting concentration to effect a good colour distinction adopting the method of Sanchis.

Treated waters contain less than 1 p.p.m. F. Thus the problem of determining residual fluorine is confined to the determination 0.50 micrograms of fluorine, adopting 50 c.c. volumes of treated water. By modifying the methods of Elvove and Sanchis the author was able to obtain a decided bleach for 2 micrograms per 50 c.c. being equivalent to 0.04 p.p.m. By interpolation adopting a series of standards differing from each other by 5 micrograms of fluorine, the fluorine value of the treated water can be ascertained to the nearest 0.05 p.p.m.

The question as to whether or not fluorine can be completely removed from water, calls for a micro analytical procedure. The micro titrimetric procedure propounded by Armstrong (1936), together with its numerous modifications did not prove itself entirely satisfactory in the determination of fluorine traces, chiefly due to the difficulty encountered in recognizing the indefinite endpoint.

A micro procedure developed in this laboratory for the determination of fluorine in quantities less than 20 micrograms, was applied in the present investigation in the case of treated waters low in residual fluorine. The findings in all cases were well in line with the results obtained by the modification of the Sanchis and Elvove bleaching methods.*

SUMMARY.

1. Methods are described whereby the concentration of solute fluorides in water can be reduced to a safe level for human consumption, at a very low cost.

2. The active defluorinizing agent is derived from commercial superphosphate. The sulphate and fluorine compounds present in superphosphates are precluded from passing into solution.

3. By adopting the concentrate method of fluorine removal, it is estimated that 1 Kilogram of double superphosphate can remove from 9 to 10 grams of fluorine from solution. The figure obtained by Klein, Adler and Lindsay (1938), for tri-calcium phosphate in filter beds, amounts to 1.8 grams of fluorine per Kilogram tricalcium phosphate, for ten consecutive cycles.

* These methods are modifications of the original method of de Boer and Basart (1926).

4. The reaction between the defluorinizing agent and the fluorine in solution is apparently accelerated by heat. Suspensions boiled for 5 to 10 minutes leave a lower residual fluorine content than cold agitations over a 24 hour period. That the process of defluorinization is however a time reaction, culminating in a quantitative adsorption or precipitation of solute fluorides is proved by the fact that prolonged cold agitations result in an almost complete removal of the fluorine in solution.

5. The process of fluorine removal is concomitant with an improvement in the general nature of the water subjected to treatment. A reduction in total solids including a reduction in the concentration of metals forming insoluble secondary and tertiary phosphates, is encountered.

6. The chemical combination in which the fluorine compound is present in the water is of no importance as far as its removal is concerned, NaF, CaF₂ and silicofluorides being reduced with equal ease.

7. Insignificant traces of selenium, boron and arsenic were found in the concentrates, adopted in this investigation.

8. The possibility of utilizing the naturally occurring wavelite as defluorinizing agent, is indicated.

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