Aluminium Contamination from Fluoride Assisted Dissolution of Metallic Aluminium

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(Received 17 March 1987; revised version received 6 July 1987; accepted 8 July 1987)

ABSTRACT

Trace amounts ($\mu g g^{-1}$ quantities) of fluoride ion are found to catalyse the dissolution of metallic aluminium in very slightly acidic or alkaline aqueous media. Possibly hazardous levels of aluminium could get leached from cooking utensils if fluoridated water or fluoride rich foodstuffs are used. The fluoride assisted corrosion of aluminium is most dramatic in oxalic, tartaric acids or sodium bicarbonate. Carbon dioxide also corrodes aluminium in the presence of the fluoride ion, generating collodial hydrated aluminium oxide which is readily soluble in dilute organic and mineral acids.

INTRODUCTION

No other metal is more exposed to materials meant for human consumption than aluminium. Cooking utensils, domestic containers and wrappers for food stuffs, drugs and cosmetics are made from aluminium. In less developed parts of the world, aluminium pots are used for storage of drinking water and milk. Numerous other instances where this metal is directly exposed to the things that go into the human system can be mentioned. The effects of aluminium intake are documented in several reports (Shore & Wyatt, 1982; Wisniewski *et al.*, 1982; Brusewitt, 1984; Wurtman, 1986), and the indications are that it is neurotoxic. Kidney dialysis with aluminium rich

Environ. Pollut. 0269-7491/88/\$03.50 (C) Elsevier Applied Science Publishers Ltd, England, 1988. Printed in Great Britain

solutions is known to cause dementia (Alfrey *et al.*, 1976). Rabbits and cats injected with solutions containing aluminium salts develop symptoms of neurotoxicity and the metal is found to accumulate in the neural tissue (Wisniewski *et al.*, 1982). It is believed that a brain disease prevalent in Guam is caused by high levels of aluminium in drinking water (Wurtman, 1986). An unusual case, where accidental implantation of metallic aluminium in the brain resulted in complications, leading to epilepsy, has also been investigated (Foncin & El Hachimi, 1986). Recently, it was found that senile plaque cores of patients with Alzheimer's type of dementia contain abnormally high levels of aluminium (Candy *et al.*, 1986). Although the connection between Alzheimer's disease and aluminium is not established (Foncin & El Hachimi, 1986; Wurtman, 1986), there is an urgent necessity for studying the cumulative effects of aluminium poisoning, how this metal enters the body and the ways in which aluminium salts can leach from the metal into the substances consumed by man.

Aluminium is a highly electropositive element. In fact, it is the metal highest in the electrochemical series that has come into everyday use. Its apparent inertness results from the protective film of α -Al₂O₃ which is resistant to most ionic species in weakly acidic or alkaline aqueous media (Durrant & Durrant, 1977). Any agent that disrupts the oxide film allows rapid corrosion, e.g. amalgamation with mercury breaks the oxide film oxidising the metal in air or water. Chloride ions also have some influence in assisting the corrosion of aluminium (Durrant & Durrant, 1977); however, in commercial uses of the metal this process is largely suppressed by alloying it with small quantities of Fe, Cu and/or Si.

In a brief note (Tennakone & Wickramanayake, 1987), we have reported that the leaching of aluminium from cooking utensils is enhanced in the presence of $(\mu g g^{-1})$ quantities of the fluoride ion. Savory *et al.* (1987) have reported that leaching of aluminium from utensils at $1 \mu g g^{-1}$ of fluoride is minimal and not as dramatic as reported by us (Tennakone & Wickramanayake, 1987). Repetition of the experiments confirms their result at $1 \mu g g^{-1}$. However, when the fluoride concentration is higher, significant leaching is certainly observed. The present work discusses the influence of fluoride ions on the corrosion of aluminium in aqueous media and also gives details about the degree of fluoride-catalysed leaching of aluminium from cooking utensils under different conditions.

EXPERIMENTAL

The corrosion of aluminium in aqueous media is accompanied by hydrogen evolution and the formation of aluminium ions, aluminate ions and/or aluminium hydroxide, depending on the pH and the quantity of acid or

alkali present. We have noted that aluminium levels in solution can be continuously recorded by monitoring the dissolved hydrogen concentration with a polarographic detector (The molarity of reacted aluminium is 2/3times that of H₂.) For this purpose the hydrogen detector supplied by Applied Photophysics was used. This instrument consists of a thermostatted quartz reaction vessel (40 ml) fitted with a Clark's electrode, coupled to an electrochemical processor, to measure the electrode potential. An arrangement is also provided to stir the contents magnetically. A strip of commercial aluminium $(2.5 \times 0.5 \text{ cm}, \text{thickness} = 2 \text{ mm})$ was kept suspended in the middle of the reaction cell (Fig. 1). Pure aluminium (Aldrich Gold label 99.999%) of the same size was also tested for comparison. The cell was filled with deionised distilled water containing known amounts of sodium fluoride ($\mu g g^{-1}$ quantities), pH in the acidic direction was adjusted using different mineral and organic acids, and alkaline pHs were achieved with sodium bicarbonate or dibasic sodium phosphate. A polarographic H₂ detector gives reliable indications only in the absence of large quantities of



Fig. 1. Apparatus used for measuring the corrosion rates of aluminium. 1—Reaction cell;
2—outer water jacket; 3—aluminium sample; 4, 5—gas inlet and outlet; 6—polarographic membrane; 7—leads to the electrochemical processor; 8—magnet for stirring.

 O_2 ; consequently, all solutions were degased with nitrogen. The other methods (e.g. atomic absorptin spectroscopy) of aluminium detection showed that the corrosion rates are uninfluenced by dissolved O_2 . With the above arrangement very small rates of aluminium dissolution can be detected. (The limit of H_2 detection is *ca*. 0.05 μ mol litre⁻¹, corresponding to an aluminium concentration of *ca*. 0.01 μ g g⁻¹.) When the saturation level of H_2 in water is exceeded, the experiment was repeated by degasing the solution with N_2 . The Clark's electrode is known to have a linear response. It was calibrated by noting the electrode potentials when the water in the cell is degased with N_2 and saturated with H_2 .

Aluminium concentrations [A1] in the solutions were also estimated by atomic absorption spectroscopy (Hitachi 130-70 Instrument) using a freshly prepared solution of aluminium chloride as the standard. The limit of detection by this method is *ca*. $1 \mu g g^{-1}$. Once this limit was exceeded both methods gave almost identical results.

Experiments were also conducted to simulate the actual cooking conditions. To obtain reproducible results, the following procedure was used. Aluminium plates (12×6 cm) cleaned with sodium hydroxide were boiled for 10 min in 500 ml of citric acid (pH 3·0). The contents were transferred to a glass vessel, acidified with conc. HCl and concentrated by evaporation. Aluminium in the solution was determined by atomic absorption spectroscopy. For confirmation, the Alumion reagent was also used; this method can detect [A1] exceeding $3 \mu g g^{-1}$. As a check, the leached aluminium was also determined by noting the loss in weight of the plates.

RESULTS AND DISCUSSION

Figure 2 shows the dissolution of aluminium in very dilute mineral and organic acids (HCl, H₂SO₄, HNO₃, H₃PO₄, citric, tartaric, oxalic, acetic and maleic acids) at pH \simeq 2 and a fluoride concentration ([F]) of 15 µg g⁻¹. The organic acids selected are the ones that are found in vegetables, or used as food additives. The variation of the reaction rates (in HCl and oxalic acid) with pH at constant [F⁻] and at varying [F], when pH is kept fixed, are presented in Fig. 3. These rates are seen to increase rapidly with the decrease of pH and increase of [F⁻]. In the absence of F⁻, significant rates of corrosion are not observed with organic acids. (Oxalic acid releases very small quantities of Al at elevated temperatures.) With mineral acids in the absence of F⁻, dissolution is noticeable only if the pH is less than *ca*. 3.5. It is also important to note the difference between commercial and pure aluminium (Fig. 2); pure metal corrodes faster in the presence of F⁻. Again,



Fig. 2. Dissolution of aluminium in dilute acids, $pH \simeq 2$, $[F] = 15 \mu g g^{-1}$, $T = 26^{\circ}C$. 1— Oxalic acids, 2—Citric acid, 3—tararic acid, 4—HCl, 5—H₂SO₄, 6—maleic acid, 7—acetic acid, 8—HNO₃, 9—H₃PO₄. Dotted curve-pure aluminium in HCl.



Fig. 3. Variation of the dissolution rate ($\mu g g^{-1}$ of Al released cm⁻² min⁻¹) with (a) pH when $[F^-] = 15 \mu g g^{-1}$, (b) $[F^-]$ when pH = 2 (1-oxalic acid, 2-HCl, $T = 26^{\circ}$ C).

different acids behave differently. Out of the mineral acids we have examined, the rates are fastest with oxalic, tartaric acids, HCl and slowest with H_3PO_4 . The passivity of aluminium in HNO₃ is removed by F⁻, but the rate of dissolution remains small compared to HCl or H_2SO_4 (Fig. 2). We do not understand why the corrosion is least with H_3PO_4 , presumably a protective film of aluminium phosphate inhibits the reaction. Another



Fig. 4. Dissolution of aluminium in sodium bicarbonate. (a) Time development of [AI] when $[F^-] = 15 \mu g g^{-1}$, pH = 9. Variation of the reaction rate with (b) pH when $[F^-] = 15 \mu g g^{-1}$ (c) $[F^-]$ when pH = 9.

feature common to all mineral acids, citric acid and acetic acid, is the quick approach of a saturation level (SL). Clearly, this is caused by the removal of active F^- ions in complexing with Al^{3+} to form AlF_6^{3-} . Oxalic and tartaric acids show a different behaviour. Here rapid dissolution takes place for a longer interval of time, until most acid is consumed, and thereafter continues almost indefinitely at a slower rate, producing aluminium hydroxide as the reaction product. Evidently, the above effect is caused by complex formation of oxalic and tartaric acids with the Al^{3+} ions. When Al^{3+} ions are consumed in this manner, the F^- removal by complexing is suppressed.

Aluminium readily dissolves, even in weak solutions of the alkalis, NaOH, KOH, etc., yielding the aluminate ion (AlO_2^-) . However, any dissolution is undetectable even in a strong solution of sodium bicarbonate. The influence of F⁻ on aluminium corrosion in sodium bicarbonate is dramatic (Fig. 4); here the fluoride acts as a true catalyst and dissolution continues indefinitely, producing $Al(OH)_3$ and a small percentage of aluminate ions. It is interesting to note that, to begin with, the dissolution rate in sodium bicarbonate is slower and that, as the oxide film gets disrupted, the rate increases and then remains more or less constant (Fig. 4(a)). Basic sodium phosphate also dissolves aluminium when the F⁻ is present, but the rate is very much smaller compared to sodium bicarbonate at the same pH.

An increase of temperature by a few degrees increases the reaction rates and the SLs. The SLs are independent of the surface area exposed to the liquid. However, when the surface to volume ratio is large, the SL is attained more quickly. Because of the removal of F^- by the aluminium ions liberated during leaching, the SLs in the presence and absence of fluoride do not differ significantly, if the [F] is in the $1 \mu g g^{-1}$ region. In the experiment with utensils (Tennakone & Wickramanayake, 1987) we had made an error in the estimation of aluminium by atomic absorption spectroscopy. Experiments

TABLE 1Results of the Experiment with Aluminium Plates(Plates boiled for 10 min in 500 ml citric acid at pH 3;numbers given within brackets are obtained fromweight loss measurements, the other numbers are
atomic absorption values.)

[F] (ppm)	[<i>AI</i>] (<i>ppm</i>)
0	$4.5 \pm 0.90 (4.0 \pm 1.4)$
1	4.9 ± 1.0 (4.3 ± 1.0)
2	5.7 ± 0.9 (6.2 ± 1.4)
10	15.1 ± 2.5 (14.2 ± 1.5)
100	98.7 ± 1.2 (92.0 ± 5.0)

with aluminium plates indicated that leaching under cooking conditions at $1 \mu g g^{-1}$ fluoride is minimal as reported by Savory *et al.* (1987). Higher, and certainly significant, levels of leaching are observed when [F] exceeds $1 \mu g g^{-1}$. Table 1 gives the results of the experiment with aluminium plates that simulated the cooking environment. We have also observed a synergic effect of chloride and fluoride. In the presence of chloride there is a considerable increase in the fluoride assisted leaching, which is noticeable even at the $1 \mu g g^{-1}$ level (Table 2). The mechanism involved in synergism is unclear.

TABLE 2

Results of the Experiment with Aluminium Plates in the Presence of Sodium Chloride (Plates boiled for 10 min in 500 ml citric acid at pH 3, containing 10 g NaCl; numbers given within brackets are obtained from weight loss measurements, the other numbers are atomic absorption values.)

[F] (<i>ppm</i>)	[<i>Al</i>] (<i>ppm</i>)
0	$4.5 \pm 1.9 (4.7 \pm 1.7)$
1	6.8 ± 1.7 (7.6 ± 2.0)
2	8.7 ± 2.2 (7.7 ± 1.9)
10	$21 \cdot 2 \pm 5 \cdot 8 (18 \cdot 7 \pm 5 \cdot 1)$

The fluoride assisted corrosion of aluminium undoubtedly results from the permeability of the protective oxide film to the F^- ions (ionic radius = 1.36 Å) which disrupt the film. However, further work is necessary to elucidate the exact mechanism by which the corrosion is initiated. At low [F] and strongly acidic pH, fluoride would exist as HF not F^- ; this could also have some influence on the fluoride assisted corrosion of aluminium.

CONCLUSION

The above investigation shows that a fluoride concentration of $1 \mu g g^{-1}$ is sufficient to initiate corrosion of aluminium, if the pH is slightly acidic or alkaline and possibly hazardous leaching occurs when [F] is the range $10 \mu g$ g^{-1} . In a neutral medium, corrosion is detectable if [F⁻] exceeds *ca*. 100 μg g^{-1} . Under acidic conditions the product of corrosion is an aluminium salt (i.e. Al³⁺ ions or a complex ion containing aluminium). Once the acid is consumed, collodial hydrated aluminium oxide is produced. When the pH is weakly alkaline (e.g. sodium bicarbonate) a small quantity of aluminate ions and a large amount of hydrated oxide are generated. The hydrated aluminium oxide produced under these conditions is readily soluble in weak mineral and organic acids. A $[F^-]$ of $1 \mu g g^{-1}$ is the permitted level of fluoridation (Pike & Brown 1984). Water consumed in several localities contains $10 \mu g g^{-1}$ or more of fluoride. Again, some food materials have excessively large amounts of fluoride (Aswathanarayana *et al.*, 1985) (500 μg g^{-1} in tea, 100–700 $\mu g g^{-1}$ in fish). Cooking in aluminium utensils with fluorinated water or foodstuffs containing high levels of fluoride could be hazardous, if the pH deviates even slightly from neutral. (Strictly neutral conditions are never realised in practice.) Alkaline pHs resulting from the use of sodium bicarbonate or acidic pHs with vegetables containing organic acids could be the most hazardous. Furthermore, in some cases, factors that complex readily with aluminium may occur; in such a situation the removal of F^- by Al³⁺ gets suppressed and almost continuous fluoride assisted corrosion is possible. Again, synergic effects need further investigation.

Another noteworthy observation we have made is corrosion of aluminium in F^- containing carbonic acid. A significant rate of dissolution is observed when $[F^-] \simeq 10 \,\mu g \, g^{-1}$ or more (Fig. 5). The product of corrosion is hydrated aluminium oxide and the reaction continues



Fig. 5. Fluoride catalysed dissolution of aluminium in carbon dioxide saturated water, i.e. plot of [AI] per unit surface area vs. time. (Numbers indicated near each curve are the $[F^-]$ values in $\mu g g^{-1}$.)

indefinitely, because F^- ions are not removed. Prolonged storage of fluoride-containing water in aluminium pots could also contaminate water.

It is possible that, in absorption from the intestines or crossing the blood-brain barrier, F^- and Al^{3+} mitigate each other's effect by forming complexes (Waring, 1987). Large stable complex ions are generally less permeable to biomembranes. However, the important fact to note is that Al^{3+} ions, far in excess of the amount that can be removed by complexing with F^- , are produced in fluoride catalysed corrosion of aluminium.

ACKNOWLEDGEMENT

One of the authors (C.A.N.F.) is supported by a grant RG/86/P1 from the Natural Resources, Energy and Science Authority of Sri Lanka.

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