Lussi A (ed): Dental Erosion.
Monogr Oral Sci. Basel, Karger, 2006, vol 20, pp 77–87

Chemical Factors

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Abstract

pH value, calcium, and phosphate and to a lesser extent fluoride content of a drink or foodstuff are important factors explaining erosive attack. They determine the degree of saturation with respect to tooth minerals, which is the driving force for dissolution. Solutions oversaturated with respect to dental hard tissue will not dissolve it. Addition of calcium (and phosphate) salts to erosive drinks showed protection of surface softening. Today, several Ca-enriched soft drinks are on the market or products with naturally high content in Ca and P are available (such as yoghurt), which do not soften the dental hard tissue. The greater the buffering capacity of the drink or food, the longer it will take for the saliva to neutralize the acid. The buffer capacity of a solution has a distinct effect on the erosive attack when the solution remains adjacent to the tooth surface and is not replaced by saliva. A higher buffer capacity of a drink or foodstuff will enhance the processes of dissolution because more ions from the tooth mineral are needed to render the acid inactive for further demineralization. Further, the amount of drink in the mouth in relation to the amount of saliva present will modify the process of dissolution. There is no clear-cut critical pH for erosion as there is for caries. Even at a low pH, it is possible that other factors are strong enough to prevent erosion.

Chemical Factors

This chapter is aimed at revealing the interplay between the erosive potential of food and beverages and their chemical properties. The term 'chemical factors' is used to describe parameters inherent to erosive beverages, food or other products (table 1). Several in vitro and in situ studies on humans as well as on animals have evaluated the erosive potential of different food and beverages [1–14]. They all show that the erosive potential of an acidic drink is not exclusively dependent on its pH value, but is also strongly influenced by its mineral content, its titratable acidity ('the buffering capacity') and by the calcium-chelation properties of the

Table 1. Chemical factors influencing the erosive potential with respect to food and beverages

- pH and buffering capacity of the product
- Type of acid (pK_a values)
- Adhesion of the product to the dental surface
- Chelating properties of the product
- Calcium concentration
- Phosphate concentration
- Fluoride concentration

food and beverages (see chapter 6 by Featherstone et al., this vol, pp 66–76). The pH value, calcium, phosphate and fluoride content of a drink or foodstuff determine the degree of saturation with respect to the tooth mineral, which is the driving force for dissolution. Solutions oversaturated with respect to dental hard tissue will not dissolve it. A low degree of undersaturation with respect to enamel or dentine leads to a very initial surface demineralization which is followed by a local rise in pH and increased mineral content in the liquid surface layer adjacent to the tooth surface. This layer will then become saturated with respect to enamel (or dentine) and will not demineralize further. Consequently, no softening can be measured with most of the methods used nowadays. An increase in agitation (e.g. when a patient is swishing his/her drink in the mouth) will enhance the dissolution process because the solution on the surface layer adjacent to tooth mineral will be readily renewed. When an excess of an erosive agent is present the pH is probably the most decisive factor whereas the buffering capacity is more important at the liquid surface layer adjacent to the tooth surface and/or when there is only a small amount of acid present around the tooth surface. Further, the amount of drink in the mouth in relation to the amount of saliva present will modify the dissolution process.

The chelating properties of citric acid (for example) can enhance the erosive process in vivo by interacting with saliva as well as directly soften and dissolving tooth mineral. Up to 32% of the calcium in saliva can be complexed by citrate at concentrations common in fruit juices, thus reducing the super saturation of saliva and increasing the driving force for dissolution with respect to tooth minerals [15]. In addition, calcium-chelating agents may directly dissolve tooth mineral. The greater the buffering capacity of the drink, the longer it will take for saliva to neutralize the acid. Some beverages appear to be less erosive than others within the same pH class. It may also be possible to reduce the erosive potential of beverages by modifying the amount and type of acid used in formulations, e.g., using maleic acid instead of citric acid [16]. In experiments conducted in vitro, citric acid caused more erosion than phosphoric acid at comparable acidity [17]. The erosive character of different pure acids at pH 2, 2.3 and 3 during incubation of bovine enamel between 1 and 5 min was high for lactic acid and lower for maleic and hydrochloric acid compared to other tested acids (acetic, citric, oxalic, phosphoric and tartaric acid) [18]. Diluting drinks containing organic acids with high buffering capacity with water will hardly reduce the pH but will reduce the relative titratable acidity. But dilution will also reduce the concentrations of Ca and P (if present), which have a protective effect [9, 19, 20].

The calcium and phosphate contents of a foodstuff or beverage are important factors for the erosive potential as they influence the concentration gradient within the local environment of the tooth surface. Indeed, addition of calcium (and phosphate) salts to erosive drinks showed promising results. Larsen [21] suggested that erosion potential could be calculated based on the degree of saturation with respect to both hydroxyapatite and fluorapatite by determining the pH, calcium, phosphate and fluoride content of a beverage. Orange juice (pH 4) supplemented with calcium (42.9 mmol/l) and phosphate (31.2 mmol/l) did not erode enamel after immersion for 7 days [22]. Only a small change in the degree of saturation by adding Ca (and a small amount of phosphate), without changing the pH may reduce the erosive potential in vitro [23]. One percent citric acid solution (pH 2.2) supplemented with different concentrations of calcium, phosphate and/or fluoride reduced the erosive potential of the solution [24]. The same was true when soft drinks were modified with calcium, phosphate and/or fluoride. The most effective reduction of enamel dissolution was achieved by adding either 1.0 mmol/l calcium or a combination of 0.5 mmol/l calcium plus 0.5 mmol/l phosphate plus 0.031 mmol/l fluoride to the citric acid [25].

It has to be kept in mind that with the added mineral enamel dissolution could not always be completely prevented. But the progression can be retarded which has some implications for the patient and the clinician.

Today, several Ca-enriched orange juices are on the market which hardly soften the enamel surface (fig. 1). Addition of calcium to a low pH blackcurrant juice drink has been shown to reduce the erosive effect of the drink [26]. In a follow-up study, a blackcurrant drink with added calcium was compared to a conventional orange drink in situ. Servings of 250 ml of each drink were consumed four times per day during 20 working days. Measurements of enamel loss were made by profilometry on enamel samples for up to 20 days. The experimental carbonated blackcurrant drink supplemented with calcium caused significantly less enamel loss than the conventional carbonated orange drink at all time points measured [27].

Sports drinks are often erosive [13, 28–30] and when consumed during strenuous activity when the person is in a state of some dehydration, the possible destructive effects may be enhanced further. A calcium-enriched experimental

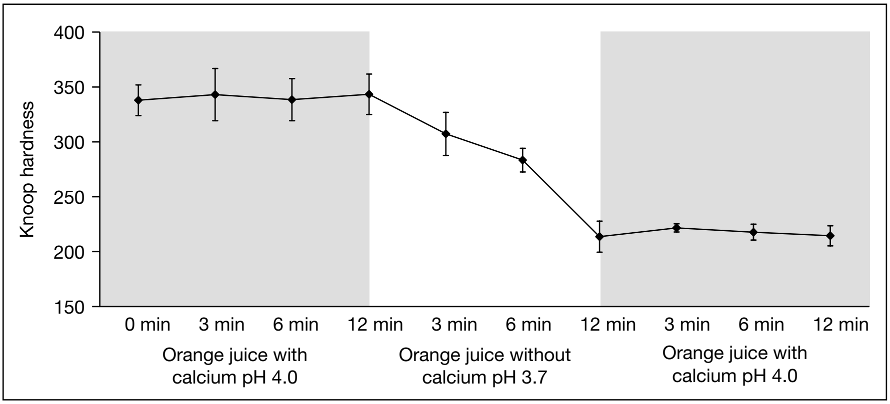

Fig. 1. Impact of a conventional and a Ca-enriched orange juice on softening of enamel.

Table 2. Content of some minimally erosive beverages (ready to drink) [in part from 30, 46]

Available beverage	pH	Added level of calcium (mg/l)
Ribena really light blackcurrant[a]	3.7–4.0	630
Ribena really light apple[a]	3.7–4.0	440
Ribena really light berry burst[a]	3.7–4.0	400
Ribena really light strawberry[a]	3.7–4.0	400
Ribena really light orange tropical[a]	3.7–4.0	200
Lucozade sport hydroactive citrus fruits (and summer) flavor[a]	3.7–4.0	370
Orange-flavored sports drinks[b]	3.8	320
Orange juice Michel[c]	3.8	160

[a]GlaxoSmithKline, Coleford, GB.
[b]Novartis Consumer Health, Basel, Switzerland.
[c]Rivella, Rothrist, Switzerland.

sports drink consumed during controlled sporting activities showed only minimal erosion compared with a commercially available sports drink [29]. A recently published study [31] showed a significant reduction of the erosive potential of a sports drink when phosphopeptide-stabilized amorphous calcium phosphate was added. As mentioned above, the pH increased and the titratable acid decreased with increasing phosphopeptide stabilized amorphous calcium phosphate concentrations. The same was true when Ca was added to another brand of sports drink (table 2) [30]. Yoghurt is another example of a food with a low pH (~4.0), yet it has hardly any erosive effect due to its high calcium and phosphate content, which makes it supersaturated with respect to apatite. A yoghurt or another milk-based food may have an erosive potential, when it has a low content of Ca and/or P and a low pH. It seems that the reduction in enamel dissolution caused by a minor increase in pH is likely to be small [32].

Larsen and Nyvad [22] and Larsen and Richards [33] reported that fluoride is unable to reduce dental erosion. Theoretically, fluoride has some protective effect in a drink with a pH higher than that indicated by the saturation curve of fluorapatite at given Ca and PO_4 concentrations. Lussi et al. [9, 20] and Mahoney et al. [34] found an inverse correlation of the erosive potential with fluoride content of different beverages. It is unlikely that fluoride at the concentration present in beverages alone has any great beneficial effect on erosion, because the challenge is high. However, it is possible that under conditions in which the other erosive factors are not excessive, fluoride in solution may exert some protective effect [34]. Due to health concerns, adding fluoride to drinks is not practical. After an initial demineralization, an intensive fluoridation is capable of inhibiting the erosive mineral loss in dentine completely. This is probably due to the buffering capacity of the proteins in the dentine matrix [35].

Table 3 gives an overview of the chemical properties of different beverages and foodstuffs. The pH, the titratable acid to pH 7.0, phosphorus and calcium concentration, fluoride content, and the degree of saturation with respect to hydroxyapatite as well as to fluorapatite are given. The methods used were as follows [9]: Caries-free human premolars with no cracks on the buccal sites were ground flat under water-cooling on a rotating polishing machine (Knuth-Rotor, Struers, Copenhagen, Denmark). The procedure was such that 200 μm of tooth substance in the center of the window was polished away. To quantify the softening of the enamel, measurement of surface microhardness (SMH), using a Knoop diamond under a load of 50 g, was performed before and after immersion for 3 or 20 min in the foodstuffs and beverages [9, 20]. A positive value denotes a hardening of the surface while a negative value represents softening. All substances were analyzed for phosphorus, calcium and fluoride using standard procedures. The pH and the amount of base added to raise the pH to 7.0 were measured using a pH electrode. To do so, 50 ml of each substance was titrated with NaOH and the amount of base added (mmol/l) was calculated.

The degrees of saturation (pK–pl) with respect to hydroxyapatite and fluorapatite were calculated using a computer program developed and later modified by Larsen [36]. This program assumes a solubility product for hydroxyapatite of $10^{-58.5}$ [37], for fluorapatite of 10–$^{59.6}$, for calcium fluoride of $10^{-10.5}$ [38]. Orange juice, for example is undersaturated with respect to both hydroxyapatite and fluorapatite as expressed by pK–pl, and caused surface softening in the

Table 3. pH, titratable acid, inorganic phosphorus, calcium and fluoride content, degree of saturation with respect to hydroxy- and fluorapatite as well as change of surface microhardness (Knoop SMH) after 3 and 20 min incubation in different beverages and foodstuffs [in part from 47]

	pH	mmol OH^-/l to pH 7.0	P_i (mmol/l)	Ca (mmol/l)	Fluoride (ppm)	pK–pl HAP	pK–pl FAP	Change in SMH after 3 min	Change in SMH after 20 min
Beverages (nonalcoholic)									
Citro light	3.0	75.0	<0.01	3.2	0.08	−25.7	−19.4		−103
Coca Cola	2.6	34.0	5.4	0.8	0.13	−19.2	−12.6	−136	−77
Fanta orange	2.9	83.6	0.1	0.8	0.05	−22.2	−16.1		−78
Ice tea	3.0	26.4	0.1	0.6	0.83	−22.3	−15.0	−107	−224
Isostar	3.8	34.0	1.6	1.8	0.14	−10.2	−4.2		−86
Isostar orange	3.6	31.4	3.4	5.8	0.18	−8.9	−2.6		−29
Aproz mineral water (sparklet)	5.3	24.0	<0.01	10.8	0.11	−5.8	−1.3		+6
Valser mineral water (sparklet)	5.4	34.6	0.01	10	0.58	−3.0	2.1	+8	+5
Valser lemon mineral water (sparklet)	3.3	68.0	<0.01	10.9	0.63	−17.2	−10.2	−54	−201
Orangina	3.2	70.0	0.4	0.4	0.07	−19.7	−13.6		−134
Pepsi light	3.1	34.6	3.9	0.9	0.04	−15.9	−9.8		−65
Perform	3.9	34.0	5.9	1.1	0.16	−9.2	−3.2		−6
Red Bull	3.4	91.6	<0.01	1.7	0.36	−19.8	−13.1	−123	−232
Sinalco	2.9	56.6	0.1	0.3	0.03	−23.7	−17.8		−110
Schweppes	2.5	88.6	<0.01	0.2	0.03	−32.8	−26.8		−136
Sprite	2.64	36.2	<0.01	0.2	0.04	−33.4	−27.3	−140	
Sprite light	2.9	62.0	<0.01	0.3	0.06	−30.5	−24.3		−162
Vitamin C effervescent tablet	3.98	105.4	<0.1	<0.1	0.03	−16.5	−11.3	−106	
Beverages (alcoholic)									
Carlsberg beer	4.4	40.0	7.3	2.2	0.28	−3.8	2.0		+8
Corona beer	4.2	8.2	3.3	2.1	0.11	−6.4	−0.8		+2
Hooch lemon	2.8	67.2	0.4	1.2	0.18	−19.8	−13.1		−257
Red wine	3.4	76.6	3.2	1.9	0.16	−12.3	−5.9		−71
White wine	3.7	70.0	3.2	0.9	0.35	−11.5	−5.0		−30

	pH	mmol OH^-/l to pH 7.0	P_i (mmol/l)	Ca (mmol/l)	Fluoride (ppm)	pK–pl HAP	pK–pl FAP	Change in SMH after 3 min	Change in SMH after 20 min
Fruit juices									
Apple juice	3.4	82.0	1.7	4.0	0.11	−11.4	−5.2	−134	−154
Pineapple juice	3.43	60	1.9	1.7	0.04	−12.9	−7.2	−71	
Apple sauce	3.4	88.8	3.1	1.5	0.03	−13.2	−7.5		−186
Beetroot juice	4.2	49.2	10.0	2.1	0.08	−5.4	0.1	−40	−81
Carrot juice	4.2	42.0	8.4	5.0	0.09	−3.5	1.9	−5	−58
Grapefruit juice	3.2	218.0	2.6	3.1	0.16	−13.3	−6.8		−120
Grapefruit juice fresh squeezed	3.1	70.6	0.2	3.5	0.08	−16.4	−10.1		−109
Kiwi juice fresh squeezed	3.6	147.2	5.3	4.2	0.06	−9.2	−3.3	−102	−164
Multivitamin juice	3.6	131.4	6.5	4.8	0.12	−8.7	−2.5	−84	−137
Orange juice fresh	3.64	135.6	5.7	2.1	0.03	−9.7	−4.2	−115	
Orange juice	3.7	109.4	5.5	2.2	0.03	−9.4	−3.9	−26	−81
Milk products									
Milk	7.0	4.0	18.9	29.5	0.01	16.3	18.1		+11
Drinking whey	4.7	32.0	9.7	6.0	0.05	0.1	4.9		+1
Sour milk	4.2	56.0	39.2	69.0	0.03	2.4	7.4		+9
Yoghurt, natural	4.2	105.6	49.8	32.8	0.03	1.4	6.3	+1	
Yoghurt, kiwi	4.1	99.6	34.0	42.5	0.06	0.7	6.0	+4	+15
Yoghurt, lemon	4.1	110.4	39.9	32.0	0.04	0.4	5.6		+18
Yoghurt, orange	4.2	91.0	43.0	31.6	0.05	0.3	5.6	+1	+8
Yoghurt drink, orange	4.25	68.6	43.0	21.2	0.05	0.8	6.0	−1	
Probioplus yoghurt	4.26	81.6	47.2	27.6	0.03	1.4	6.4	+5	
Miscellaneous									
Rhubarb puree	2.77	344.8	7.75	12.974	0.4	−12.4	−5.3	−47	−62
Salad dressing	3.6	210.0	1.6	0.3	0.14	−15.6	−9.3		−109
Vinegar	3.2	740.8	2.2	3.4	1.20	−13.4	−6.0		−303

experiment (table 3). Many of the herbal teas were found to be even more erosive than orange juice [39]. In contrast to that, the milk products were all supersaturated with respect to both minerals and did not cause any softening of the surface after immersion of enamel in the respective products. Some flavored mineral water has in contrast to plain mineral water an erosive potential (table 3). This has some implication concerning the tooth health because the public is not aware of the erosive potential of these acidic drinks labeled as mineral water.

Fluoride present in the mouth during the daily de- and remineralization cycles gives rise to the formation of fluorapatite or fluorhydroxyapatite, which have a lower solubility than hydroxyapatite. Many of the acidic beverages or foodstuffs have a composition and a pH such that they are undersaturated with respect to these minerals and consequently even the outermost layer consisting of fluor(hydroxy)apatite will dissolve. Therefore, the protective effect of this outermost fluoride-rich mineral in preventing erosion is less important than it is in preventing caries. However, treatment with fluoride varnish (2.26%) for 24 h and high concentration F rinses (1.2%) for 48 h applied prior to acidic challenge have been shown to offer in vitro protection against erosion [11]. It is assumed that this protection is due to precipitation of calcium fluoride-like particles adhering to tooth surfaces which subsequently released fluoride over time. Hence, gentle fluoride application (without destruction of the protective acquired pellicle) before the erosive challenge would be most beneficial. The formation of the CaF_2-like layer on the tooth surface would act as a 'barrier' against acid attacks. This layer provides some additional mineral to be dissolved during an acid attack before the underlying enamel is attacked [40]. It is still controversial if these particles can be formed on sound tooth surface in vivo and in reasonable time. It has, however, been shown in vitro that KOH-soluble fluoride globules precipitate within a short time and in a higher amount when a low pH fluoride solution is used [41, 42]. The study by Larsen and Richards [41] further showed a beneficial effect of saliva on the formation of calcium fluoride-like material. Both a low pH of a fluoride solution with some subsequent loss of mineral and the calcium-rich saliva seem to be important factors in providing the system with calcium. It follows that deduction of a ranking for the in vivo erosivity of different acidic food and drinks based on pH, titratable acidity, Ca, P and F is rather complicated if not impossible. Besides these chemical factors, behavioral factors (such as eating and drinking habits, diets high in acidic fruits and vegetables, excessive consumption of acidic foods and drinks, oral hygiene practices) and biological factors (such as saliva flow rate, buffering capacity, acquired pellicle, dental anatomy and anatomy of oral soft tissues, physiological soft tissue movements) also have to be taken into account.

The adhesiveness and displacement of the liquid are other factors to be considered in the erosive process. There appear to be differences in the ability of beverages to adhere to enamel based on their thermodynamic properties, e.g. the thermodynamic work of adhesion [43]. The greater the adherence of an acidic substance is, the longer the contact time with the tooth surface and the higher the likelihood of erosion will be. It has been shown that displacement of saliva by Cola required 14 mJ/m^2, by Diet Cola 5 mJ/m^2. However, displacement of Cola film by saliva required 45 mJ/m^2, of Diet Cola by saliva 52 mJ/m^2. It seems to be more difficult to displace a soft drink film by saliva than it is to displace a salivary film by a soft drink [44]. Further research is needed to quantify the impact of all these factors in more detail. This has to be done by using reproducible and standardized methods. Guidelines on the testing of the erosive potential of foods derived from an international workshop were edited by Curzon and Hefferren [45].

In summary, it has been shown that the two very-often-cited parameters, pH and the titratable acidity, do not readily explain the erosive potential of food and drink. The mineral content is also an important parameter, as is the ability of any of the components to complex or chelate calcium and remove it from the mineral surface. Besides, these chemical factors several others such as the components of saliva and the flow rate of saliva have an impact on dental erosion in vivo. The degree of saturation with respect to the tooth mineral, hydroxyapatite and fluorapatite also strongly influence the erosion outcome. All of the above have to be taken into account to explain or even predict to some extent the influence of foods and beverages on dental hard tissue. Further, there is no clear-cut critical pH for erosion below which erosion will occur. Even at a low pH it is possible that other factors are strong enough to prevent erosion. At higher pH, it is possible that chemicals that complex calcium can cause erosion. The influence of all the factors described above in the fluid layer immediately in contact with the tooth surface determines whether erosion can proceed or not.

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