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Effects of additives on sintering and some properties of calcium phosphates with various Ca/P ratios

TAKAFUMI KANAZAWA, TAKAO UMEGAKI, KIMIHIRO YAMASHITA
Department of Industrial Chemistry, Faculty of Technology, Tokyo Metropolitan University, Fukasawa 2-1-1, Setagaya-ku, Tokyo 158, Japan
HIDEKI MONMA
National Institute for Research in Inorganic Materials, Tsukuba-shi, Ibaraki 305, Japan
TATSUSHI HIRAMATSU
Nihon Cement Co. Ltd, Ootemachi, Chiyoda-ku, Tokyo 100, Japan

The effects were studied of additives on the sintering and properties such as the compressive strength and chemical durability of ceramics of calcium pyrophosphate, tricalcium phosphate and hydroxyapatite. In improving the compressive strength of these calcium phosphates, the effect of additives was found to be in the order $Na_2O \gg CaF_2 > MgO \gg Al_2O_3$, SiO_2 for the case of single-doping, and was most marked in the combination of Na_2O–MgO–Al_2O_3 for the complex addition. It was also found that the chemical durability of the calcium phosphates was improved greatly by using a single or complex additives.

1. Introduction

Because of their excellent biocompatibility, ceramics of calcium phosphates, especially hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (denoted as HAp here) and tricalcium phosphate $Ca_3(PO_4)_2$ (TCP) [1–3], have attracted much attention as bio-implant materials. A large part of the recent studies have been devoted to improving the mechanical properties of sintered calcium phosphates. To date, using very dense ceramics with or without additives, strengths comparable with or superior to those of human bone and tooth have been realized. Contrasting with dense ceramics, the mechanical properties of porous ones are inferior [4, 5]. However, on considering biocompatibility, as reported in [6], porous sinters of calcium phosphates have the advantage of being completely converted to natural bone, although their application is restricted to places that are not subjected to high stress. It is therefore valuable to strengthen porous sinters of calcium phosphates. This study was undertaken to investigate the effects of additives on the fundamental properties of various calcium phosphates.

2. Material preparation

Reagent-grade calcium phosphate dihydrate ($CaHPO_4 \cdot 2H_2O$) and anhydrous calcium carbonate ($CaCO_3$) were employed as the sources for calcium and phosphorus. Both reagents were pretreated at 120 °C for 10 h for dehydration and decarbonation, respectively. Silica was prepared by drying quartz powder washed in 1 wt % HCl aqueous solution. Other additives such as Na_2O, MgO and Al_2O_3 were used after drying reagent-grade powders.

Starting powders with or without additives, in the ratios listed in Table I, were mixed by shaking in a polystyrene bottle. The Ca/P ratio was taken as 2, 3 and 4 as CaO/P_2O_5. For simplicity, the materials employed are hereafter referred to by the symbolized names given in Table I. Mixed powders were calcined at 800 to 1100 °C for 1 to 10 h, depending on the type and concentration of additives. With pellets of 200-mesh sieved calcines uniaxially pressed at 3.7 Pa, sintering was carried out at 885 to 1200 °C for 4 to 44 h. These temperatures were determined from differential thermal analysis (DTA) and were dependent on the composition of the specimen. The typical size of a sinter was 10 mm in diameter and 15 mm thickness.

3. Experimental procedure

For the identification of the phases present in the products after calcination or sintering, X-ray diffraction (XRD) and infrared (IR) absorption analyses were performed on powders or pellets. The mechanical and chemical properties of sinters were studied in order to evaluate the effects of additives. The compressive strengths were measured on cylindrical sinters with various phases and porosities. The chemical durability was estimated by the weight change of sintered bodies immersed in water, citric acid or sodium hydroxide aqueous solutions.

TABLE I Composition, notation and the conditions for the calcination and sintering of specimens

Specimen	CaO/P_2O_5[a]	Additive (molar ratio to P_2O_5)						Calcination/sintering temperature (° C)–time (h)
		Na_2O	MgO	Al_2O_3	SiO_2	CaF_2	$CaSO_4$	
$2CaO\cdot P_2O_5$	2							900–6/1150–11
2N005–05	2	0.05–0.5						800 980–4–5/885 1050–4–44
2M01, 05	2		0.1, 0.5					1150–4/1050–3–7
2A01, 05	2			0.1, 0.5				1150–1–4/1050–3–6
2S01, 05	2				0.1, 0.5			900–4–6/1150–5–19
2MA01	2		0.1	0.1				900–4/1150–7
2MS01	2		0.1		0.1			900–4/1150–7
2AS01	2			0.1	0.1			900–4/1150–7
2NMAS05	2	0.5	0.5	0.5	0.5			1100–10/1200–10
$3CaO\cdot P_2O_5$	3							900–4/1150–10
3N005–05	3		0.05, 0.5					900–4/1150–10
3M01, 05	3		0.1, 0.5					900–4/1150–7
3A01, 05	3			0.1, 0.5				900–4/1150–7
3S01, 05	3				0.1, 0.5			900–4/1150–7
3NM01	3	0.1	0.1					900–4/1150–7
3NA01	3	0.1		0.1				900–4/1150–7
3NS01	3	0.1			0.1			900–4/1150–7
3MA01	3		0.1	0.1				900–4/1150–7
3MS01	3		0.1		0.1			900–4/1150–7
3AS01	3			0.1	0.1			900–4/1150–7
3NMA01	3	0.1	0.1	0.1				1100–10/1300–10
3NMS01	3	0.1	0.1		0.1			1100–10/1300–10
3NAS01	3	0.1		0.1	0.1			1100–10/1300–10
3MAS01	3		0.1	0.1	0.1			1100–10/1300–10
3NMAS05	3	0.5	0.5	0.5	0.5			1100–10/1400–10
$10/3CaO\cdot P_2O_5$	10/3							1100–10/1400–10
10/3N01	10/3	0.1						1100–10/1400–10
$4CaO\cdot P_2O_5$	4							1100–10/1400–10
4NMA01	4	0.1	0.1	0.1				1100–12/1400–10
4NMS01	4	0.1	0.1		0.1			1100–12/1400–10
4NAS01	4	0.1		0.1	0.1			1100–12/1400–10
4MAS01	4		0.1	0.1	0.1			1100–12/1400–10
4NMAS05	4	0.5	0.5	0.5	0.5			1100–12/1400–10
$5CaO\cdot P_2O_5$	5							1100–10/1400–10
$6CaO\cdot P_2O_5$	6							1200–10/1400–10
2F01	2					0.1		1100–10/1200–10
3F01	3					0.1		1100–10/1400–10
4F01	4					0.1		1100–10/1400–10
FAC	10/3					1/3		1200–6/1300–7
FACN01	10/3	0.1				1/3		1200–6/1300–7
FACN05	10/3	0.5				1/3		1100–6/1300–7
FACNM01	10/3	0.1	0.1			1/3		1100–6/1300–7
2G1	3						1	900–14/1300–10
2G2	4						2	900–14/1300–10

[a] Molar ratio.

4. Results and discussion

4.1. Sintering behaviour

Some results of DTA are shown in Fig. 1, in which the endothermic peaks around 450 °C are attributed to the decomposition reaction of calcium hydrogen phosphate to calcium pyrophosphate (C_2P):

$$2CaHPO_4 \rightarrow Ca_2P_2O_7 + H_2O(g)$$

The mixture with Na_2CO_3 added shows endothermic peaks around 630 and 850 °C, which can, respectively, arise from the solid-state reaction between calcium phosphate and sodium oxide, and the decomposition (851 °C) or melting (852 °C) of unreacted Na_2CO_3. As can be seen from the figure, the possible solid-state reactions of all specimens are apparently completed up to 1400 °C; sintering temperatures were chosen for each specimen as those indicated in Table I.

In Table II, the apparent densities of the sintered bodies are listed together with the porosities, which were calculated from the true densities measured for crushed powders by picnometry. As a whole, Na_2O addition seems to promote sintering, since specimens with Na_2O added exhibited a larger shrinkage during sintering. Al_2O_3, SiO_2 and MgO appear to have no significant effect on the sintering of the present materials.

4.2. Crystal phases of calcium phosphates with various additives

Crystal phases present in the calcined and sintered specimens were dependent mainly on the Ca/P ratio. Those identified by XRD are shown in Table III. At a Ca/P ratio of 2, the main phase was C_2P in undoped

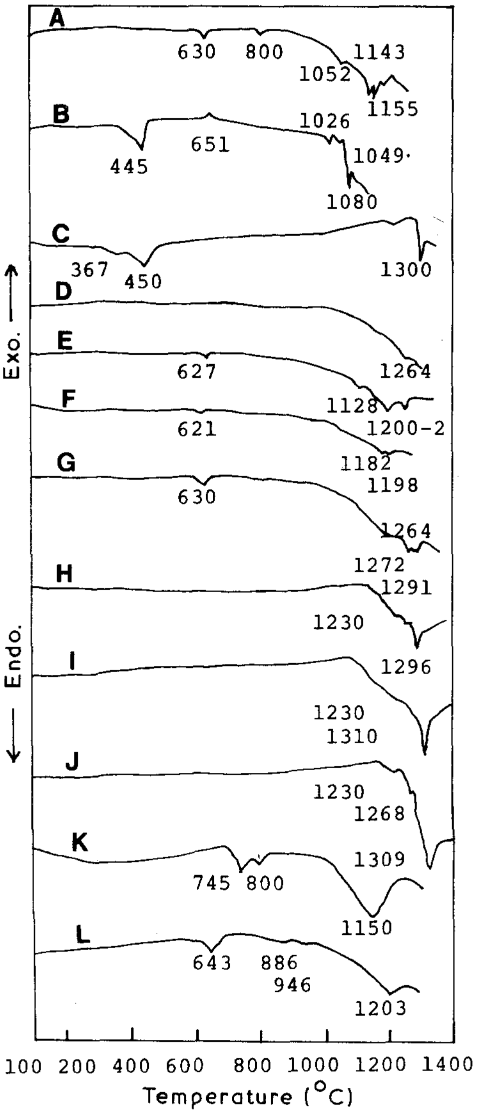

Figure 1 Differential thermal analysis of various calcium phosphates. Specimens: A, 2N05; B, 2M05; C, 2A05; D, 2S05; E, 2NM01; F, 2NA01; G, 2NS01; H, 2MA01; I, 2MS01; J, 2AS01; K, 2NMAS05 and L, 3NMAS05.

TABLE II Density and porosity

Specimen	Bulk density ($g\,cm^{-3}$)	True density ($g\,cm^{-3}$)	Porosity (%)
$10/3CaO\cdot P_2O_5$	1.93	3.18	39.1
$5CaO\cdot P_2O_5$	2.09	3.28	36.2
4NMA01	2.38	3.07	22.3
2NMAS05	2.48	3.04	18.1

specimens, whereas β-TCP was obtained as the main or a second phase in the specimens with more than 10 mol % oxide additives such as Na_2O, MgO, Al_2O_3 and SiO_2.

At Ca/P = 3 and 10/3 the dominant phase was β-TCP in all of the calcined and sintered specimens with additives.

At Ca/P = 4 the result was complex, since HAp, α- and β-TCP phases were found, depending on the combination of additives. In the sintered specimens 4NMA01 and 4NMS01, HAp was the main phase, whereas β-TCP was observed in 4NAS01 and 4MAS01 sinters. In 4NMAS05, $Ca_5Na_2P_4O_{16}$ and $MgAl_2O_4$ were produced during sintering.

In the specimens with CaF_2 added, fluorapatite (FAp: $Ca_{10}(PO_4)_6F_2$) was obtained in addition to β-TCP. In FACN05 β-$CaNaPO_4$ was obtained.

In specimens with $CaSO_4$ added 2G1 (Ca/P = 3) and 2G2 (Ca/P = 4), β-TCP and HAp were obtained as the single phase.

Phase analysis was also carried out by means of IR spectroscopy. The IR spectra of some additive-bearing specimens are shown with standards in Fig. 2. HAp can be distinguished by the absorption at around 3500 cm^{-1} from C_2P and TCP. C_2P and TCP were distinguished from each other in the absorption peak at around 725 cm^{-1}. Using those peaks, most of the phases identified by XRD were confirmed by IR analysis.

4.3. Effects of porosity, additive and Ca/P ratio on the compressive strength of sintered calcium phosphates

The effect of porosity on the compressive strengths (σ) of sinters of various calcium phosphates is shown in

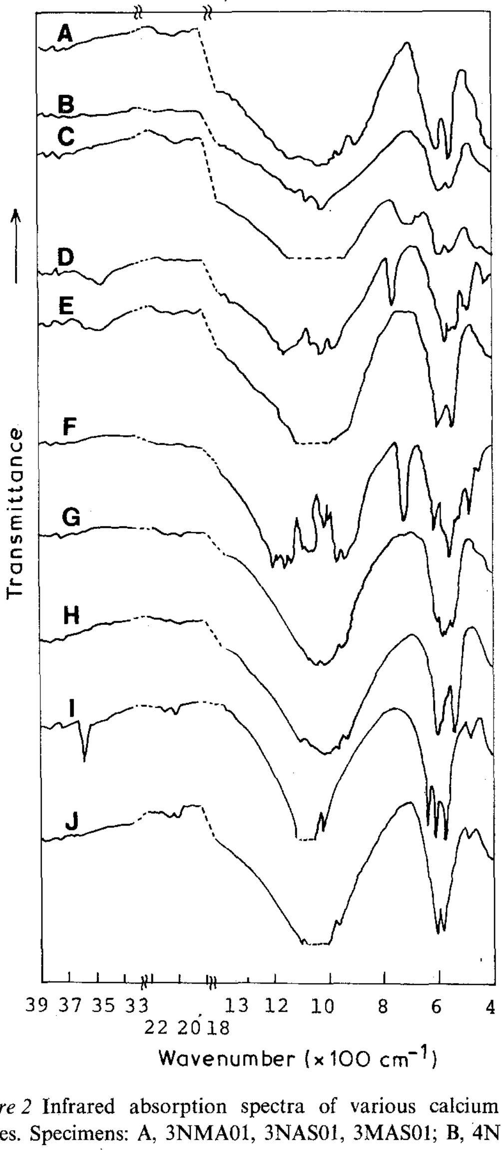

Figure 2 Infrared absorption spectra of various calcium phosphates. Specimens: A, 3NMA01, 3NAS01, 3MAS01; B, 4NMA01, 4NAS01; C, 2NMAS05; D, 2F01; E, 2G1; F, α-TCP; G, β-TCP; H, β-C_2P; I, HAp and J, FAp.

TABLE III Crystal phases present in specimens after calcination and sintering

Specimen	Phases	
	Calcined	Sintered
2CaO·P$_2$O$_5$, 2N005, 2A01	β-C$_2$P	β-C$_2$P
2N01	β-C$_2$P	β-TCP
2M01	β-C$_2$P	β-C$_2$P, β-TCP^a
2M05	β-TCP, β-C$_2$P^a	β-TCP
2A05	β-C$_2$P, β-TCP^a	β-TCP
2S01	β-C$_2$P	β-C$_2$P, β-TCP^a
2MA01, 2MS01		β-C$_2$P, β-TCP^a
2AS01		β-C$_2$P
2NMAS01	β-TCP	
2NMS01, 2NAS01 2MAS01	β-C$_2$P, β-TCP^a	
2NMAS05		
3CaO·P$_2$O$_5$, 3N005 05 3S01, 3S05 3NM01, 3NA01, 3NS01 3MA01, 3MS01, 3AS01 3NMA01, 3NMS01, 3NAS01 3MAS01, 3NMAS05 10/3CaO·P$_2$O$_5$,10/3N01	β-TCP	β-TCP
4CaO·P$_2$O$_5$	β-TCP	α-TCP, HAp^a
4NMA01, 4NMS01	β-TCP, HAp^a	HAp, β-TCP^a
4NAS01	β-TCP, HAp^a	α-TCP
4MAS01	β-TCP, HAp^a	β-TCP, α-TCP^a
4NMAS05	Ca$_5$Na$_2$P$_4$O$_{16}$, β-TCP^a	Ca$_5$Na$_2$P$_4$O$_{16}$, MgAl$_2$O$_4$^{a}
5CaO·P$_2$O$_5$	β-TCP, HAp^a, CaO^a	HAp
6CaO·P$_2$O$_5$		HAp, α-TCP^a, CaO^a
2F01	β-C$_2$P, FAp^{ab}	β-TCP
3F01	FAp, β-TCP^a	FAp
4F01	FAp, β-TCP^a	β-TCP, FAp^a
FAC	FAp	α-TCP, FAp^a
FACN01	FAp	β-TCP
FACN05	CaO, β-CaNaPO$_4$^{a}	β-CaNaPO$_4$
FACNM01	FAp	MgO, FAp
2G1	β-TCP, CaSO$_4$	β-TCP
2G2	CaSO$_4$, β-TCP	HAp

[a] Minor phases.
[b] Fluorapatite.
C$_2$P calcium pyrophosphate; TCP, tricalcium phosphate; HAp, hydroxyapatite.

Fig. 3, in which the horizontal axis expresses the shrinkage of green bodies during sintering. As is seen from the figure, the value of σ increases with decreasing porosity, and 3F01, FCA and 4NMA01 exhibited irregularly high strengths.

Those results can also be evaluated in relation to the phases present in the sinters. Fig. 4 summarizes the σ-phase relation, indicating the σ-order of HAp > TCP > C$_2$P for non-additive calcium phosphates, and FAp with TCP $\gg$ α- and β-TCP, C$_2$P with β-TCP > C$_2$P for calcium phosphates with additives. In the case of single-doping, the following order was found in the effect of improving the strength: Na$_2$O $\gg$ CaF$_2$ > Al$_2$O$_3$, SiO$_2$. For complex addition the effect was most marked in the combination of Na$_2$O–MgO–Al$_2$O$_3$.

The effect of the amount of an additive was estimated in calcium phosphates with Na$_2$O added. The result is shown in Fig. 5. It is seen that the addition of about 0.15 mol mol^{-1} P$_2$O$_5$ was the most efficient.

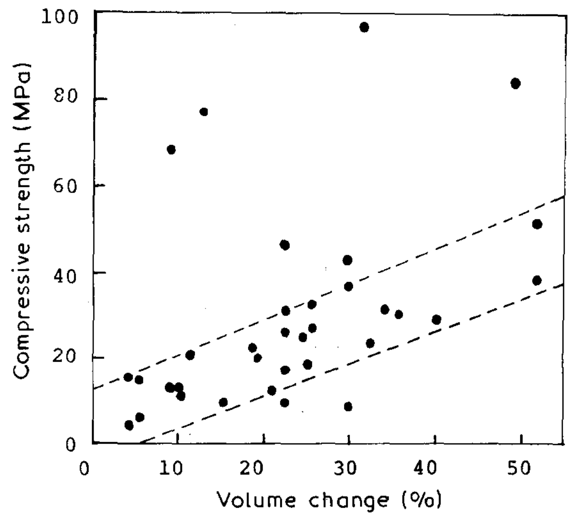

Figure 3 The effect of porosity on the compressive strength of various calcium phosphates ceramics. The volume change on the horizontal axis expresses the shrinkage of green bodies during sintering.

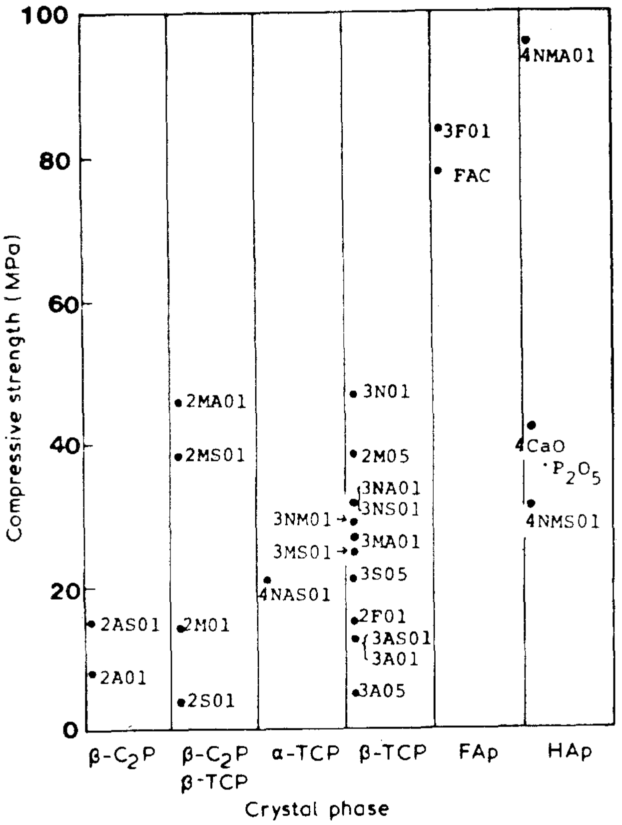

Figure 4 Compressive strength–phase relationship for various calcium phosphates ceramics.

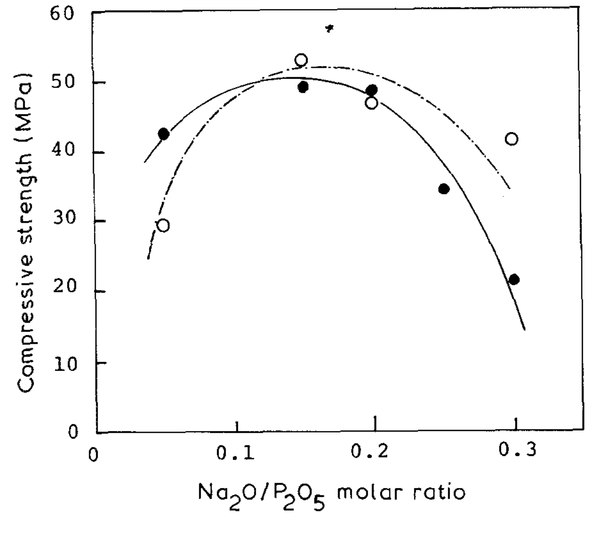

Figure 5 The effect of the amount of an additive on calcium phosphates with Na_2O added.

4.4. Effects of additive on chemical durability of sintered calcium phosphates

Water durability was excellent in all of the specimens. Table IV lists the decrease in weight of some sinters after immersion for 315 h in water at room temperature.

TABLE IV Water durability

Specimen	Decrease in weight after 315 h (%)
$2CaO \cdot P_2O_5$	0.2
3NS01	0.2

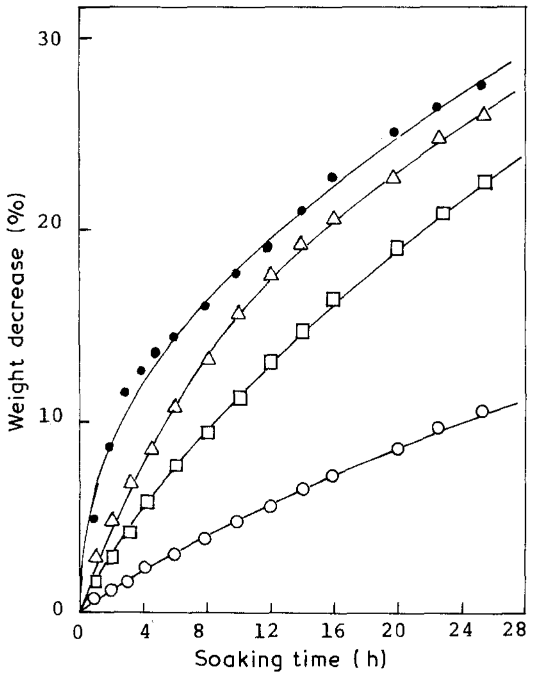

Figure 6 Change with time of the weight of some calcium phosphate ceramics immersed in 2% citric acid. Specimens: (○) 3MAS01, (□) 4NMA01, (△) 4MAS01 and (●) 4NAS01.

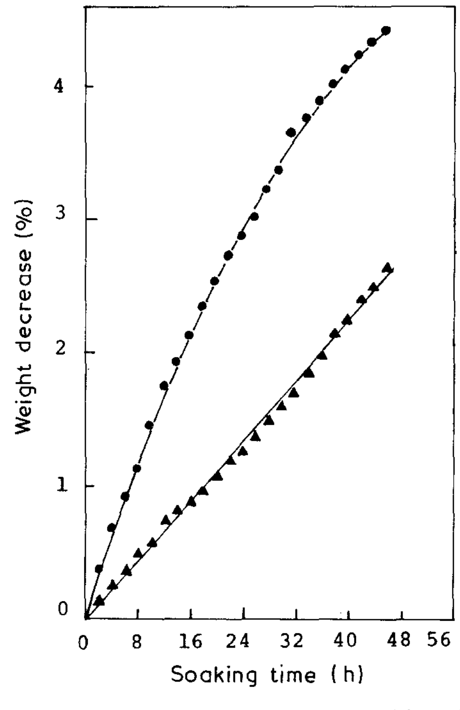

Figure 7 Change with time of the weight of some calcium phosphate ceramics immersed in 2% citric acid. Specimens: (●) FAC and (▲) FACN01.

The acidic (2% citric acid) durability of those calcium phosphates is shown in Fig. 6, indicating dissolution was almost linear with time. Table V summarizes the acidic durability of some specimens. The specimens of 3S05, 3NM01 and 3F01 exhibited superior durability. As shown in Fig. 7, however, the specimens of FAC and FACN01 gradually dissolved to a considerable degree in the solution.

The durability of the calcium phosphates in alkaline aqueous solution was also excellent. Fig. 8 shows the

TABLE V Acidic durability of various calcium phosphates

Solvent	Soaking time (h)	Specimen	Decrease in weight (%)
2% citric acid	192	2MS01	14.6
	192	3S05	6.8
	192	3NM01	7.7
5% citric acid	635	10/3CaO · P_2O_5	60.4
	635	4CaO · P_2O_5	59.8
	635	5CaO · P_2O_5	37.1
	635	3F01	36.8
	635	2NMAS04	49.8
	635	3NMAS05	56.7
	635	4NMAS05	42.5

change with time of the weight of some specimens immersed in 1 M NaOH, indicating that additives were effective in improving the alkaline durability of calcium phosphates.

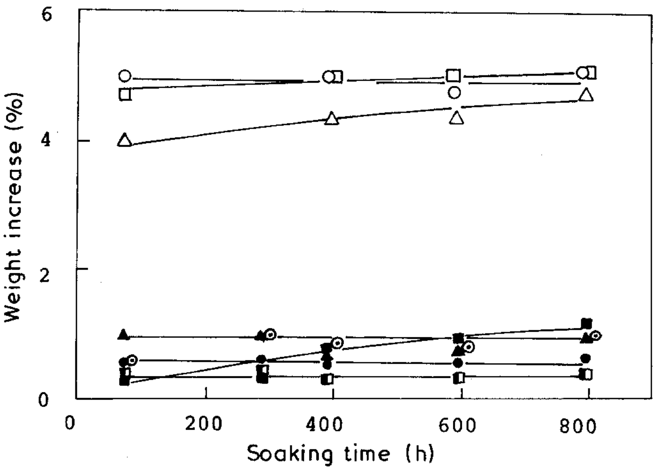

Figure 8 Durability of calcium phosphate ceramics in alkaline aqueous solution. Specimens: (○) 4CaO · P_2O_5, (□) 5CaO · P_2O_5, (△) 3F01, (▲) 2F01, (◉) 10/3N01, (●) 10/3CaO · P_2O_5, (◧) 2G1 and (■) 2G2.

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