Original Paper

Chemical solubility of phosphate glasses in the system $Na_2O-CaO-MgO-P_2O_5-Al_2O_3-TiO_2$ in aqueous solutions of different pH values

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Phosphate glasses of different composition ranges show very different solubility behaviour in aqueous solutions of pH 4 and 5.8. With increasing P_2O_5 concentrations between 38 and 52 mol%, in the system $Na_2O-CaO-MgO-P_2O_5$, the dissolution rate generally increases, however, the most notable increase is observed at P_2O_5 concentrations larger than 48 mol%. Additives of TiO_2 and Al_2O_3 increase the stability to corrosion. Glasses with compositions in the metaphosphate range show larger dissolution rates in slightly acidic medium than glasses near the invert glass range. Glasses in the invert glass range show a stronger increase in the dissolution rates with decreasing pH value and also deceleration of the dissolution with time.

1. Introduction

Phosphate glasses exhibit structures very different from those of silicate glasses and, hence, also possess other properties, e. g. with respect to their chemical solubility. While conventional silicate glasses are, for example, easily dissolved in fluoric acid, phosphate glasses are resistant to this agent [1]. With respect to biomaterials, the solubility behaviour is of special importance. Here, numerous phosphate glasses and glass-ceramics are worthy of mention [2 to 4]. Depending on their composition, and in the case of glass-ceramics also on their microstructure, alloplastic implants in the human (or animal) body show a large variation of biological properties. In the classical case of bone replacement implantology, a strong adherence of the implant to the bone is required. This is usually initiated by a partial dissolution in an early stage after implantation. To achieve a long-term stability, the dissolution process should decelerate with time [5]. As previously described [6], such glass-ceramic implants have been developed in the system $Na_2O-CaO-MgO-P_2O_5$ by adding nucleating agents such as iron oxides, TiO_2 or ZrO_2. Alternatively, a complete and homogeneous dissolution of the whole implant may be required, if the replacement of the implant by vital bone is intended. In principle, the latter is decisive for resorbable, mostly porous implants [7]. Usually, the pH value of the body fluid lies between 7.1 to 7.5. However, in the course of an immuno reaction against a foreign body, inside encapsulating macrophages, the pH value may temporarily decrease to val-

ues as low as 4 to 4.5 [8]. Hence, a notably larger dissolution rate at smaller pH values may facilitate the dissolution of foreign bodies also in the case of inorganic inhaled dust. While generally inorganic materials should possess high chemical stability in a neutral environment, a comparatively large dissolution rate in an acidic medium usually does not restrict their application. The chemical instability of silicate glasses in alkaline media is well known [9]. In slightly acidic medium, the dissolution rate is not notably larger than that in neutral solution. This is predominantly due to the formation of an SiO_2 rich protective layer formed by ion exchange (e. g. Na^+ against H_3O^+). By contrast, phosphate glasses are usually less stable in acidic than in neutral media. However, the dissolution rate is strongly affected by the glass composition, especially the P_2O_5 concentration. Previous studies have shown that especially at compositions between the invert and the metaphosphate range, glass properties may drastically change also with respect to the dissolution rate in various media [10].

2. Experimental procedure

Glasses in the system $Na_2O-CaO-MgO-Al_2O_3-TiO_2-P_2O_5$ were prepared. Here, the metaphosphate range (series A), the invert glass range (series C) and an intermediate range (series B) were considered. The composition ranges are summarized in table 1.

The glasses were melted from the raw materials $Ca(PO_3)_2$, $Mg(PO_3)_2$, $Al(PO_3)_3$, Na_2CO_3, $Al(OH)_3$ and TiO_2 (anatase). The glass compositions were analytically controlled by inductively coupled plasma emission optical spectroscopy (ICP-EOS). The analytical compositions devi-

Table 1. Composition ranges of the glasses studied (in mol%)

	Series A	Series B	Series C
P_2O_5	47 to 55	41 to 45	39 to 41
CaO/MgO	26 to 30	28 to 32	24 to 30
Na_2O/K_2O	16 to 25	15 to 16	20 to 25
Al_2O_3	5 to 6	5 to 6	5 to 10
TiO_2	2 to 5	2 to 5	2 to 5

ated from the batch compositions especially with respect to the P_2O_5 concentration. Around 10 % of the batch P_2O_5 concentration was vapourized during melting. In order to obtain the intended compositions, the P_2O_5 concentration in the batch was increased by 10 % (relative). The glass compositions studied are summarized in table 2.

Solubility measurements were carried out with the grain fraction from 0.315 to 0.63 mm. In analogy to DIN/ISO 719 [11], 2 g of glass were soaked in 50 ml solution at 98 °C. As aqueous solutions, deionized water (initial pH value: 5.8) and diluted chloric acid (pH: 4.0) were used. In order to determine the dissolution rate as a function of time, the glasses were soaked for 1, 2, 4 and 8 h. The solutions were analysed with respect to their phosphate, alkali, alkaline earth, alumina and titania concentration using ICP-EOS. The analyses were illustrated by the element concentrations.

3. Results and discussion

Figure 1 shows the leaching behaviour of a relatively stable phosphate glass-ceramic (sample A) which contains considerable concentrations of Al_2O_3 (8.3 mol%) and FeO
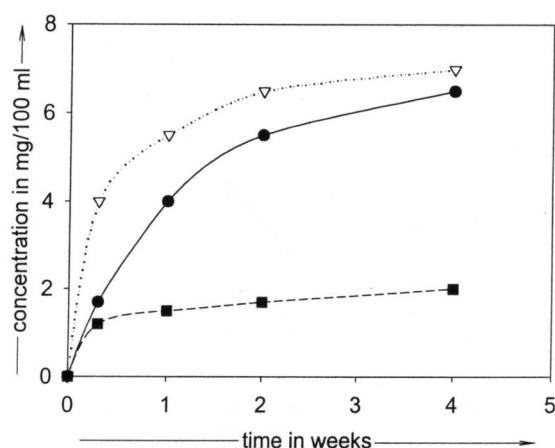

Figure 1. Leaching of a relatively stable phosphate glass-ceramic in Tris-buffer solution (sample A); ■: Ca, ●: P, and ▽: Na.

(5 mol%) as well as of fluorine (4.7 mol%). The corrosion rate is large at the beginning, but decelerates with time. It should be noted that the concentrations of P_2O_5, Na_2O and CaO in the leaching solution do not run exactly parallel. In figure 2, the leaching behaviour of resorbable phosphate glasses which are used as implant materials are shown (samples B, C and D). The solution used was Tris-buffer with a pH $\approx$ 7.3, which is equivalent to the pH in biological environment. Sample B exhibits the largest Na_2O concentration (25 mol%) and shows the largest corrosion rate, which by contrast to sample A does not decelerate, but even increases with time. Sample C has a much lower solubility, a smaller Na_2O concentration and additionally contains 5.2 mol% TiO_2. Sample D possesses the same TiO_2 concen-

Table 2. Chemical composition of the glasses studied (in mol%)

sample	P_2O_5	CaO	MgO	Na_2O	K_2O	TiO_2	Al_2O_3	B_2O_3	SiO_2	FeO	F^-
A	33.7	26.5	—	21.8	—	—	8.3	—	—	5.0	4.7
B	38.9	30.6	5.5	25	—	—	—	—	—	—	—
C	36.9	29	5.2	23.7	—	5.2	—	—	—	—	—
D	33.6	26.4	13.2	21.6	—	5.2	—	—	—	—	—
E	—	8	7.1	16.4	—	—	0.6	8.9	58.8	—	—
F	40.9	30.6	—	14	6.6	2.4	5.5	—	—	—	—
G	47	26	4	16	—	2	5	—	—	—	—
H	45	22	5	8	8	5	6	—	—	—	—
I	47	18	8	12	4	5	6	—	—	—	—
K	39	30.4	5.6	25	—	—	—	—	—	—	—
L	43	28.4	5.2	23.4	—	—	—	—	—	—	—
M	47.5	26.2	4.8	21.5	—	—	—	—	—	—	—
N	52.5	23.7	4.3	19.5	—	—	—	—	—	—	—
O	39	29.4	5.4	23.9	—	2.3	—	—	—	—	—
P	43	27.5	5	22.3	—	2.2	—	—	—	—	—
Q	48	25	4.6	20.4	—	2	—	—	—	—	—
R	52.5	22.9	4.2	18.6	—	1.8	—	—	—	—	—
S	39	28.6	5.3	23.5	—	3.6	—	—	—	—	—
T	43	26.8	4.9	21.9	—	3.4	—	—	—	—	—
U	48	24.4	4.5	20.0	—	3.1	—	—	—	—	—
V	52.5	22.3	4.1	18.3	—	2.8	—	—	—	—	—
W	39	30.7	—	25.0	—	—	5.3	—	—	—	—
X	43	28.7	—	23.4	—	—	4.9	—	—	—	—
Y	47.5	26.4	—	21.5	—	—	4.6	—	—	—	—
Z	52	24.1	—	19.7	—	—	4.2	—	—	—	—

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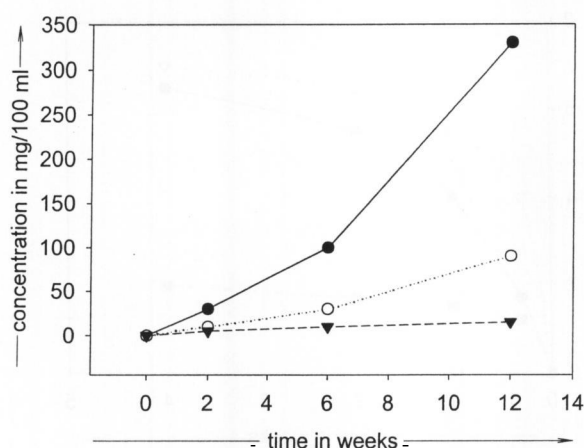Figure 2. Leaching of phosphorus from resorbable phosphate glasses in Tris-buffer solution (pH 7.3, $T = 37\ °C$); ●: sample B, ○: sample C, and ▼: sample D.
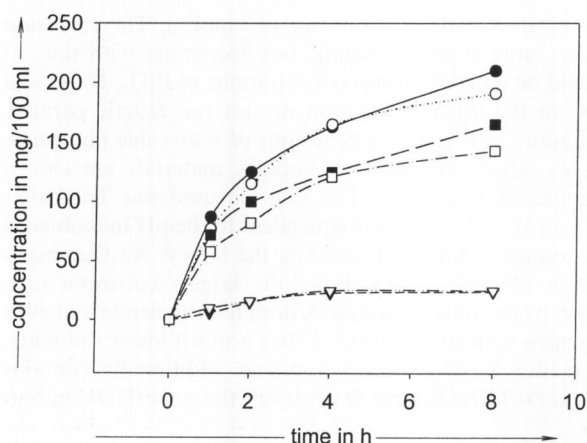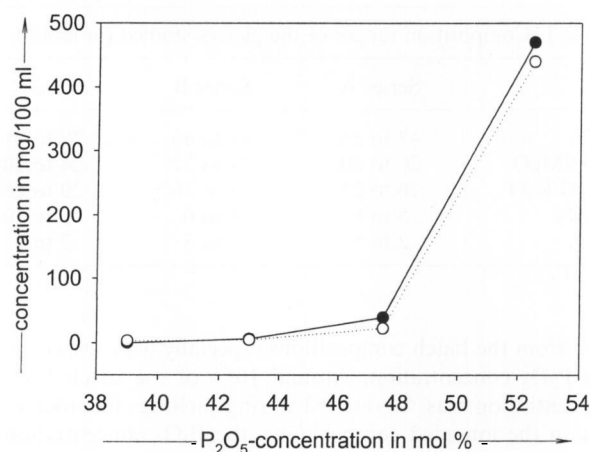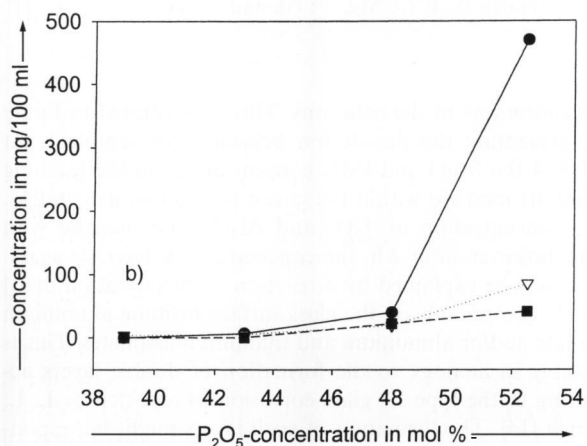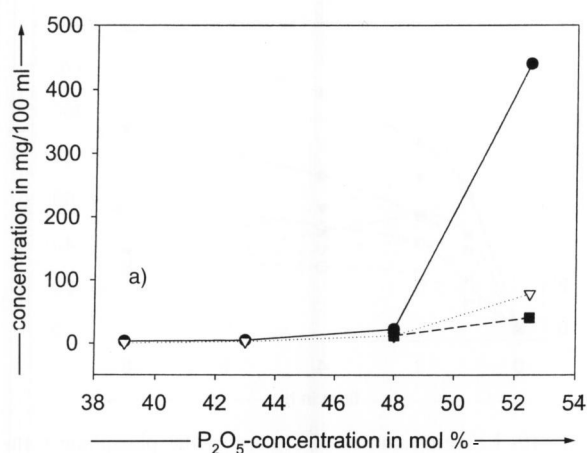

Figure 4. Solubility of phosphate (expressed as P) of glasses in the $Na_2O-CaO-MgO-P_2O_5$ system (samples K, L, M and N) as a function of the P_2O_5 concentration at pH 4 (full symbols) and pH 5.8 (hollow symbols).

Figure 3. Leaching of a silicate glass (sample E) in solvents of pH 4 (full symbols) and pH 5.8 (hollow symbols); ○: Si, □: Ca, ▽: Na.

tration as sample C, however, the MgO concentration is much larger (13.2 mol%). The corrosion rate is the smallest of the three samples. Obviously, both MgO and TiO_2 decelerate the dissolution of the phosphate glass. By comparison, the leaching behaviour of a silicate glass used for thermally insulating glass fibre composites is shown in figure 3. Here, by analogy to figure 1, a strong deceleration of the dissolution rate with time at both pH values of 4 and 5.8 is seen. Figures 1 to 3 clearly show that phosphate glasses may possess a solution behaviour similar to SiO_2 glasses or, however, may exhibit a dissolution rate which is independent of time or may even increase with time. In the following, the corrosion behaviour of phosphate glasses with systematically varied composition is reported and discussed.

3.1 Phosphate dissolution as an effect of the P_2O_5 concentration and additives in the system $Na_2O-CaO-MgO-P_2O_5$

In figure 4, the leaching behaviour of phosphate glasses in the system $Na_2O-CaO-MgO-P_2O_5$ is shown as a func-

tion of the P_2O_5 concentration (sample K, L, M and N). Here, the phosphate concentration is varied, while the molar ratios of the other components are kept constant. It is shown that increasing P_2O_5 concentrations lead to increasing P_2O_5 dissolution. At a pH value of 4, the quantity of P_2O_5 dissolved is slightly smaller than at an initial pH value of 5.8 for all compositions studied. Increasing the P_2O_5 concentration of the glass from 48 to 52 mol% P_2O_5 results in a drastic increase of the solubility. In summary, the dissolution rate can be increased by more than two orders of magnitude if the P_2O_5 concentration is raised from 39 to 52.5 mol%. In figures 5a and b, the leaching behaviour of the samples K to V is shown at pH values of 4 and 5.8, respectively. By analogy to figure 4, the P_2O_5 concentration is varied while the molar ratios of the other components in the respective sample series are kept constant. Samples K to N do not contain TiO_2, while the samples O to R contain around 2 % TiO_2. The largest TiO_2 concentration (2.8 to 3.6 mol% TiO_2) is present in samples S to V. In all three sample series studied, the solubility decreases with increasing TiO_2 concentration. The solubility at pH 4 is larger than at pH 5.8. Adding 3 to 4 mol% TiO_2 leads to a notable decrease in the solubility without changing the ratio of P_2O_5 dissolved in acidic and neutral solution. In figure 6, the effect of the P_2O_5 concentration on the dissolution behaviour of Al_2O_3 containing glasses (samples W to Z) is shown. In analogy to figures 4 and 5, the molar ratios of the other glass components are kept constant. Also here, the solubility increases with increasing P_2O_5 concentration and is larger at pH 4 than at pH 5.8. In analogy to TiO_2, the addition of Al_2O_3 notably decreases the dissolution rate. The effect of Al_2O_3 (concentrations of up to 5 mol% Al_2O_3) is even stronger than that of TiO_2. Increasing Al_2O_3 concentration results in drastically decreased solubilities. Furthermore, the P_2O_5 dissolution is notably larger in the acidic solution. At P_2O_5 concentrations < 46 mol%, the ratio of the P_2O_5 concentrations dissolved in acidic and neutral solution is approximately 5:1, while it is around 2:1 for P_2O_5 concentrations > 48 mol%.

As known from ^{31}P MAS NMR, in the invert glass range the concentration of diphosphate groups decreases while Al_2O_3 is introduced into the melt. Simultaneously, the

a)

b)

Figures 5a and b. Solubility of phosphate of glasses in the $Na_2O-CaO-MgO-P_2O_5$ (TiO_2) system as a function of the P_2O_5 concentration at a) pH 4 and b) pH 5.8; ●: samples K, L, M and N, ∇: samples O, P, Q and R, and ■: samples S, T, U and V.
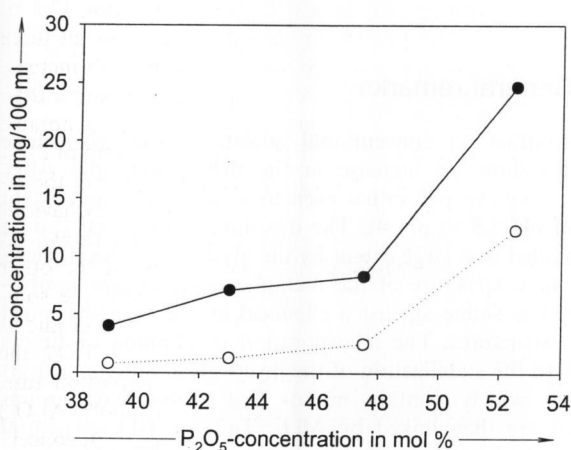

Figure 6. Solubility of phosphate of the glasses in the $Na_2O-CaO-MgO-P_2O_5$ (Al_2O_3) system (sample W, X, Y and Z) as a function of the P_2O_5 concentration at pH 4 (full symbols) and pH 5.8 (hollow symbols).

concentration of orthophosphate groups increases [12 and 13]. In these glasses, alumina is predominantly incorporated as AlO_4^- tetrahedra, i.e. as network former. It should hence
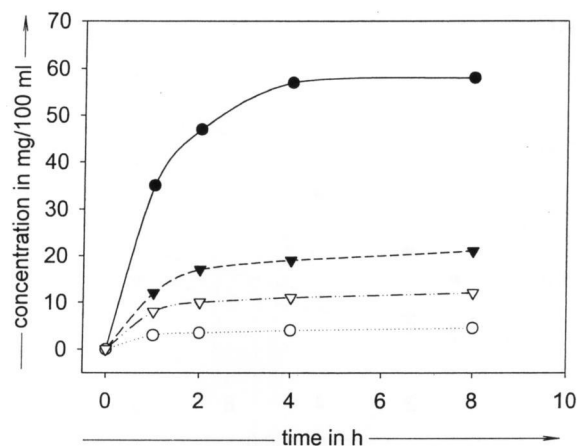

Figure 7. Leaching curves of a phosphate glass (sample F) at pH 4 (full symbols) and pH 5.8 (hollow symbols); ○: P, and ∇: Na.

be concluded that AlO_4^- tetrahedra interconnect the orthophosphate groups with each other. Simultaneously, the formally negative charge of the AlO_4^- tetrahedra needs to be compensated by alkali or alkaline earth ions, which then no longer give rise to the formation of nonbridging oxygen. This should notably contribute to the increase in viscosity with increasing alumina concentration.

In summary, the quantity of P_2O_5 dissolved as well as the effect of the pH value can be adjusted by the P_2O_5 concentration of the glass and by the additives TiO_2 and Al_2O_3. Especially in glasses with compositions near the invert glass structure, these effects are well pronounced. For further experiments, glasses in the system $Na_2O-CaO-MgO-P_2O_5-Al_2O_3-TiO_2$ were used. Here, both the metaphosphate as well as the invert glass range were studied. The analyses were extended to all glass components not only to P_2O_5.

3.2 Glasses near the invert glass range

Figure 7 shows the dissolution behaviour of a glass near the invert glass range (sample F) at both pH 4 and pH 5.8. The curves seem to run parallel for P_2O_5 and Na_2O and both pH values. Glasses in the composition range C (see table 1) show a relatively small dissolution rate in neutral solution, while it is notably larger in acidic solution. At both pH values, the dissolution decreases with time and seems to approach a constant value (see figure 7). In many cases, already after soaking for 2 h, the maximum concentrations in the leaching solutions is nearly reached. Surprisingly, this is the case for all glass components. The ratio of the quantities dissolved in acidic and neutral solutions may rise to a value of 5:1.

3.3 Glasses in the metaphosphate range

Glasses in the composition range A (see table 1) show a behaviour different from that in range C. Figure 8 shows the dissolution behaviour of sample G at pH 4 and pH 5.8. In comparison to figure 7, the dissolution rates are much larger and do not decelerate with time. The ratio of the
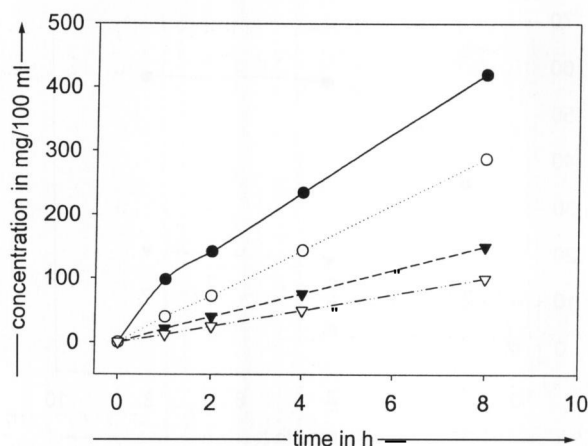
Figure 8. Leaching curves of a glass in the metaphosphate composition range (sample G) at pH 4 (full symbols) and pH 5.8 (hollow symbols); O: P, and ▽: Na.

Figure 10. Leaching curves of a glass in the phosphate transition range (sample I) at pH 4 (full symbols) and pH 5.8 (hollow symbols); △: P, O: Mg, ▽: Al, and □: Ti.
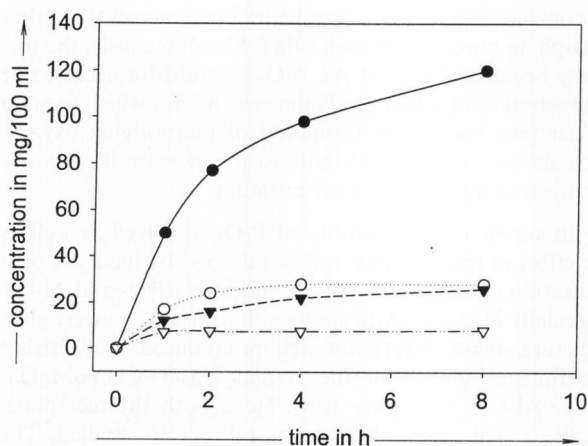

Figure 9. Leaching curves of a glass in the phosphate transition range (sample H) at pH 4 (full symbols) and pH 5.8 (hollow symbols); O: P, and ▽: Na.

concentrations in the solutions. This is illustrated in figure 10, presenting the dissolution behaviour of sample I. At pH = 4 the MgO and P_2O_5 concentrations in the leaching solutions increase within the entire period of time studied. The concentration of TiO_2 and Al_2O_3 first increase with time, however, after 2 h, the concentrations decrease again. This may be explained by a reaction or precipitation of Al and Ti compounds on the glass surface forming aluminium titanate and/or aluminium and titanium phosphates. This is possibly in analogy to the formation of double layers according to the type III glass corrosion as reported by L. L. Hench [14]. The formation of such layers might be responsible for the dissolution behaviour observed, however, the layers do not completely inhibit the further dissolution of other glass components. At pH 5.8 the effect is not as pronounced. Here, the Al_2O_3 concentration decreases with time, however, in contrast to the behaviour at pH = 4, the TiO_2 concentrations increase steadily. Surprisingly, the MgO concentration is notably smaller.

quantities dissolved in acidic and neutral solutions is smaller, near 1.5:1. As shown in figure 8, the dependency of the dissolution rate on time is much smaller than in the invert glass range. A plateau is not observed; in some cases the dissolution rate slightly decreases with time.

3.4 Glasses in the intermediate range invert glass/metaphosphate glass

Glasses in the composition range B (see table 1) lie in between the invert glass and the metaphosphate range. They possess P_2O_5 concentrations in the ranges of 41 to 45 mol%. Also with respect to their dissolution behaviour, these glasses lie in between the composition range A and C. The dissolution rates are larger than those in range C, however, notably smaller than in range A. In figure 9 the dissolution behaviour of sample H is shown. The ratio of the quantities dissolved in acidic and neutral solutions are up to 4:1 and hence notably larger than in range A. In neutral solutions, the dissolution decelerates after 2 h, while this is not as pronounced in the acidic medium (see figure 9). An unexpected behaviour was observed with respect to the Al_2O_3 and TiO_2
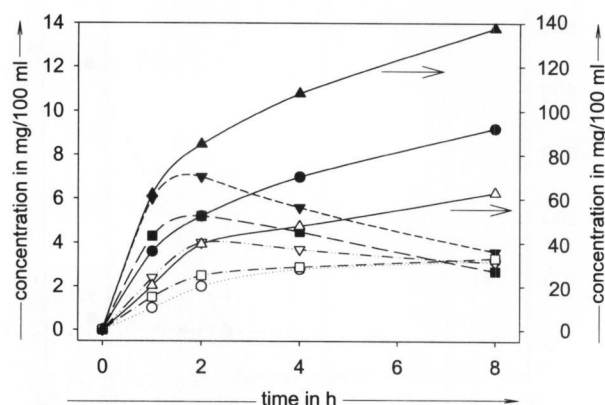
4. General remarks

In contrast to conventional silicate glasses, phosphate glasses show an increase in the dissolution rates while decreasing the pH values even to a relatively small extent (from pH 5.8 to pH 4). The dissolution behaviour can be controlled to a large extent by the glass composition. Here, the chain structure of the metaphosphate glasses is obviously less stable against a chemical attack than the invert glass structures. The incorporation of alumina or titania leads to the stabilization of the invert glass structure. Invert glasses widely contain mono- and diphosphate groups which are then linked by AlO_4, TiO_4 or TiO_6 structural units which strengthen the glass network. The structures formed affect the dissolution rates to a larger extent in acidic media than in the case of metaphosphate glasses. The chemical attack is decelerated after a comparatively short time and a relatively stable state is reached. Here, the formation of protective layers may play an important part. A similar behaviour is also observed in bioactive glass-ceramics with long-term stability. The decrease in the dissolution rate with time is much less pronounced in the case of metaphosphate glass compositions.

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