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Journal of the European Ceramic Society 24 (2004) 2113–2124

www.elsevier.com/locate/jeurceramsoc

The role of sodium hexametaphosphate in the dissolution process of kaolinite and kaolin

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Received 31 January 2003; accepted 2 May 2003

Abstract

Suspensions of kaolinite and ceramic grade kaolin in sodium hexametaphosphate solutions at different concentrations were prepared and kept at constant temperature for 4 h: the solutions obtained after centrifugation and filtration were analysed using a ICP technique to determine the concentration of significant cations. The results allowed to stress the role of NaHMP in the dissolution process of kaolinite and ceramic grade kaolin. The role of accessory minerals in ceramic grade kaolin dissolution was discussed in the light of the obtained data.

Keywords: Chemical properties; Clays; Hexametaphosphate; Surfaces; Suspensions

1. Introduction

Sodium hexametaphosphate $(NaPO_3)_6$ is a deflocculant widely used in clay industry.[1] It exerts a deflocculant action increasing the negative charge on the clay micelles being adsorbed as an anion, giving complexes with the flocculant cations and substituting the cations in the double layer of the clay with Na^+ ions.[1,2] The change in ζ potential value gives the reason for all three mechanisms.

Several investigations[3,4] have been devoted to the analysis of the behaviour of sodium hexametaphosphate in water; they allow to identify the chemical species present in the solution and potentially able to interact with the surface of the clay. As in the case of all cyclic metaphosphates, the sodium hexametaphosphate ring undergoes cleavage by alkaline hydrolysis to form, in the first instance, the corresponding linear oligophosphate[3] through a first-order kinetic reaction respect to sodium hexametaphosphate.[4] Within metaphosphates, the stability of the ring to cleavage by NaOH increases rapidly increasing the ring size. As a matter of fact, sodium hexametaphosphate reveals a peculiar stability towards hydrolysis processes, in fact the half time for the ring cleavage by NaOH 0.1 N is about 1000 h.[4] The ring cleavage of metaphosphates, which is generally followed by the degradation of the resulting polyphosphates, is catalysed by several cations.[5] The linear hexaphosphate formed after the cleavage of the hexametaphosphate ring is largely degraded into lower phosphates before all the sodium hexametaphosphate has reacted.[4] In fact, like all polyphosphates, it undergoes degradation in aqueous solution at temperatures higher than 25 °C, at pH <7 and in the presence of cations. Two mechanisms, both of the first order with respect to the reagent, can occur.[4,6,7a,7b]

Kaolinite is an aluminium–silicate mineral whose chemical formula is $Al_2Si_2O_5(OH)_4$; the term "kaolin" refers to a rock whose percentage of kaolinite is higher than 50%;[8] in kaolin, kaolinite is often found in association with other minerals such as quartz, feldspar and micaceous (like muscovite and illite). Kaolin plays a remarkable industrial role because it is the most important clay raw material used in whiteware ceramic industry; in many steps of ceramic processing, industrial suspensions containing high amount of kaolin need the addition of some deflocculants, such as sodium hexametaphosphate, to be deflocculated.

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doi:10.1016/S0955-2219(03)00366-2

Huertas et al.[9] studied the dissolution phenomena that eventually occur in an aqueous suspension of kaolinite at different pH of the solution; the investigated kaolinite is of very pure grade (95% kaolinite with traces of quartz and anatase) and so the observed phenomena cannot be transferred directly to the kaolins used for industrial purposes. Most of all, when the sodium hexametaphosphate solution is used instead of simple water to prepare a suspension of kaolin, the deflocculant equilibria are modified by the presence of the clay, which in turn suffers the presence of the sodium hexametaphosphate.

Several papers[10–12] have been devoted to the interactions between sodium hexametaphosphate and clay: one of the mechanisms of action of this deflocculant involves a chemiadsorption step at the edges of the clay particles. The hexametaphosphate anions interact with the exposed atoms of aluminium, giving a complexed anion.[10] The chemiadsorption produces a surface excess of negative charge and therefore the increase of the repulsion forces between the particles; as a consequence, the ζ potential value of the clay particles increases. This mechanism is reaffirmed by Kronberg et al.[11] in a study on the competitive and cooperative adsorption of polymers and surfactants on the surface of kaolinite. Like Huertas, Kronberg used high-grade kaolinite and deflocculant adsorption was performed with the deflocculant solution eluting the kaolinite: the measurements were made in dynamic conditions, that is, without waiting for the system to reach equilibrium.

Choi et al.[12] also confirm that the condensed phosphates are adsorbed to form strong complexes with the positive sites on the edges of the kaolinite particles. This adsorption causes a change in the surface charge density, whereby the electrokinetic potential of the kaolinite becomes even more negative.

The complexing ability of sodium hexametaphosphate toward Ca^{2+} allows the additive to sequester the flocculant calcium cations.[13] Genichiro Kura and Shigeru Oashi[14] found that hexametaphosphate anion forms with calcium a strong 1:1 complex; they estimated the thermodynamic stability constant of this complex ($K = 10^{6.9}$) extrapolating to infinite dilution the conditional stability constants determined at various ionic strengths.

The aim of the present study is to assess the effects caused by the addition of sodium hexametaphosphate to a standard kaolinite suspension and compare the results with those obtained employing a kaolin used in ceramic industry and containing a certain amount of accessory minerals (impurities). The analysis of the results gets light on the interaction mechanism of hexametaphosphate anion with the clay surface and on the effect of the deflocculant in kaolinite and kaolin dissolution. Moreover, this comparison enables us to assess the role played by the accessory minerals of kaolin in ion release and reprecipitation phenomena of clay suspension. In fact, even low amount of accessory minerals can remarkably modify the chemical and rheological behaviour of the kaolin with respect to that of kaolinite. The introduction of the deflocculant causes surface modifications of the clay minerals and dissolution of ions able to interact with the deflocculant itself. For this reason the purpose of the whole research is to determine how the processes of dissolution of the clay in the presence of sodium hexametaphosphate may influence the deflocculating capability and, overall, the rheology of the clay suspension.

2. Experimental

2.1. Materials

(a) Well-ordered kaolinite (KGa-1b) from The Clay Minerals Society (The Clay Minerals Society, Source Clays Repository, University of Missouri, Columbia, MO) was used as reference mineral for pure kaolinite (hereafter, KGa-1b).
Some general properties of KGa-1b were measured: density was determined by the liquid pyknometry method ($d = 2.647 \pm 0.054$ g/ml); Brunauer–Emmitt–Teller (BET) specific surface area was measured (Micromeritics Gemini 2630) using nitrogen gas as an adsorbate at liquid nitrogen temperature; the sample previously had been outgassed at 110 °C for 4 h ($S_{BET} = 11.62$ m^2/g). The particle-size distribution, as ascertained by laser particle-sizer analyser (Fritsch Analyzette 22), had an average particle size $d_{50} = 1.66$ µm. The chemical composition by element oxide weight percentage was measured by the inducted coupled plasma technique (ICP Spectrophotometer, Varian mod. Liberty 200) (Table 1). The mineralogical composition as determined by the X-ray powder diffraction technique (Philips PW3710) was proved to be

Table 1
Chemical analysis of KGa-1b and of C.G.K

Component (wt.%)	KGa-1b	C.G.K.
SiO_2	44.7	47.1
Al_2O_3	38.7	36.1
CaO	0.03	0.40
MgO	0.01	0.27
Na_2O	0.04	0.59
K_2O	0.03	1.06
Fe_2O_3[a]	0.20	0.75
TiO_2	1.58	0.24
LOI[b]	13.87	12.49

[a] Fe total (Fe_2O_3 + FeO) is expressed as Fe_2O_3.
[b] LOI = Loss on ignition (1050 °C).

kaolinite with anatase as impurity (CuK_α radiation, 0.02°/s, 5–70° 2θ). The cation exchange capacity was found to be 2.1 meq/100 g.

(b) A ceramic-grade kaolin was used in this study (hereafter C.G.K.). Some general properties such as density ($d = 2.683 \pm 0.054$ g/ml), Brunauer–Emmitt–Teller (BET) specific surface area ($S_{\mathrm{BET}} = 15.01$ m^2/g), chemical composition by element oxide weight percentage (Table 1) and mineralogical composition were measured with the same instruments and methods used for KGa-1b; the mineralogical composition was found to be mainly kaolinite (91%) with micaceous clays (illite), quartz and feldspar as impurities. The particle-size distribution (Fritsch Analyzette 22) covered a broad range (bigger than that of kaolinite) with an average particle size of $d_{50} = 4.08$ μm. The cation exchange capacity was found to be 3.7 meq/100 g. As kaolin employed is not a "pure" material but a mixture of kaolinite, illite, quartz and feldspar, it is clear that the value of its properties (density, specific surface area, chemical composition and particle size distribution) is forced to be a sort of "weighed medium value".

(c) The deflocculant used in this study was sodium hexametaphosphate (hereafter NaHMP) in the powder form (Carlo Erba). Chemical analysis: $NaPO_3 \geqslant 96\%$, Cl $\leqslant 0.07\%$, Pb $\leqslant 0.0025\%$, sulphate $\leqslant 0.24\%$, As $\leqslant 0.0005\%$, Fe $\leqslant 0.006\%$.

2.2. Methods

Following the results of some rheological preliminary tests performed on C.G.K. (i.e. the raw material employed in industrial applications), a clay volumetric fraction of 35% v/v was chosen for both KGa-1b and C.G.K.; in fact, it allows the kaolin suspensions to have viscosity values low enough to be measured, yet high enough to fall within the range of sensitivity of the viscosimeter.

In the paper the deflocculant concentration is given as molarity; in any case, due to the remarkable role played by the surface area in the adsorption process and in order to refer concentration to surface area, the following equation converting deflocculant molarity in weight of deflocculant/clay surface area is given:

$$W_{\mathrm{s}} = ([\mathrm{NaHMP}] \cdot V \cdot M_{\mathrm{w}})/(w \cdot S_{\mathrm{BET}})$$

where: W_{S} is the weight of deflocculant referred to the clay surface area, [NaHMP] is the NaHMP molar concentration, V is the volume of the deflocculant solution in contact with a mass w of clay, M_{w} is the molecular weight of the deflocculant and S_{BET} is the specific surface area of the clay.

Suspensions of KGa-1b/C.G.K. and deflocculant solution at different concentrations were kept at a constant temperature of 30 °C in a thermostat; after 4 h (characteristic storage time of an industrial process) a complete solid–liquid separation was carried out in order to determine the concentration of some ions (P, Si, Al, Ca, Mg, K, Na) in the liquid phase. Time-dependent measurements performed on the concentrations of the ions (not reported here)[15] have clearly indicated that at least in the range 4–24 h no time dependence of the ion concentration, in particular HMP, occurs. For this reason all the measurements reported in the text have been performed after 4 h of contact between clay and deflocculant solution.

The suspensions were prepared in the following conditions:

1. Zero NaHMP concentration (plain distilled water), which served as a dummy sample for the following suspensions.
2. NaHMP concentrations in the range 0.005–0.03 M.

The comparison between the two batches of parallel measurements (performed on KGa-1b and on C.G.K.) allows to evaluate the role of clay impurities.

A standardized procedure was adopted in order to ensure the reproducibility of the results:

- KGa-1b was used as-received.
- C.G.K. underwent a standard treatment to render it homogeneous: it was delicately crumbled by hand in a porcelain mortar using a porcelain pestle. Each batch of kaolin thus disaggregated was mixed with the others in order to ensure the homogeneous texture of the samples.
- The required amount of KGa-1b/C.G.K. (93.912 g) was weighed in a beaker; both the suspensions were prepared at 35% v/v.
- The required amount of the NaHMP powder was weighed in a beaker, then the distilled water needed to prepare the deflocculant solution was added (the water volume added was 65.9 ml and 65.0 ml for KGa-1b and C.G.K., respectively).
- The KGa-1b/C.G.K. and the deflocculant solution were blended and dispersed in a laboratory fast ball mill (300 ml) with 10 alumina grinding balls ($\phi = 1$ cm) for 10 min.
- Immediately after dispersion, the suspension was transferred to a sealed plastic (PET) vessel and kept at a temperature of 30 °C in an immersion thermostat (Memmert WB/WB).
- After 4 h the suspension was removed from the thermostat, including the water that condenses on the lid, and rapidly transferred to a multi-speed centrifuge (ALC multi-speed centrifuge PK 121) in a centrifuge batch of 10 ml polycarbonate

tube. Centrifugation proceeded for 10 min at the rate of 14,000 rpm, then the separated liquid phase was centrifuged again under the same conditions.

- The liquid was filtered by Whatman cellulose nitrate membrane, 0.45 μm.
- The liquid was subjected to ICP analysis (ICP Plasma Varian mod. Liberty 200).
- The ICP measurements were performed twice under the same conditions; the findings refer to the average of the two series of measurements, which in any event differ by less than 5%.

Calculations have been performed in order to check if the release of cations (Ca, Mg, K) observed in the solutions are to be attributed only to cation exchange phenomena or also to contemporaneous clay degradation processes.

In fact, if only cation exchange phenomena are present, the number of the equivalents of Na^+ from NaHMP and disappeared from solution after contact with the clay must be equal to the sum of the equivalents of Ca^{2+}, Mg^{2+} and K^+ ions (i.e. the exchangeable cations) plus the equivalents of cation charge neutralizing the adsorbed anions (HMP in our case).

The number of equivalents of exchanged Na^+ was calculated subtracting those observed in solution after 4 h from the initial ones (i.e. the Na^+ equivalents introduced with the deflocculant). The number of equivalents of Ca^{2+}, Mg^{2+} and K^+ were calculated by the respective concentration measured after 4 h, being known the volume of the employed deflocculant solution. The equivalents of positive charge electro-statically co-adsorbed with the HMP anion onto clay (neutralizing charge) can also be calculated: in fact, as the HMP bare anion, which possesses six negative charges, is adsorbed onto the clay, it carries a number of equivalents of positive charge (given by cations in solution) corresponding to the negative charge of the bare anion, i.e. 6× the adsorbed moles of HMP; the equivalent number of positive charge co-adsorbed with the HMP anion after 4 h numerically corresponds to the equivalent number of HMP disappeared from solution.

A batch of rheological measurements were performed on suspensions of both KGa-1b and C.G.K. at different NaHMP concentrations prepared as described above and just after the dispersion. These rheological measurements were performed using a Control Rate Haake viscosimeter (VT 550) at 30 °C.

3. Results

3.1. Rheological measurements

3.1.1. KGa-1b

Rheological measurements performed on KGa-1b suspensions prepared with different NaHMP concentrations in the range 5.4×10^{-4}–1.62×10^{-2} M show that the minimum apparent viscosity is obtained for the NaHMP concentration about 2.7×10^{-3} M (Fig. 1a), corresponding to 0.1 mg/m^2.

3.1.2. C.G.K.

Rheological measurements performed on C.G.K. suspensions prepared with different NaHMP concentrations in the range 7.1×10^{-3}–3.19×10^{-2} M present a very different behaviour from KGa-1b suspensions: in fact, the minimum apparent viscosity is obtained for the NaHMP concentration about 2.12×10^{-2} M (Fig. 1b), corresponding to 0.6 mg/m^2. It is rather surprising that, while the difference between the specific surface area of KGa-1b and C.G.K. is not so remarkable, C.G.K. suspensions need very higher dispersant levels (8× in molarity) than KGa-1b to reach the minimum apparent viscosity. It is worth to note that the mineralogical composition of the clays dramatically influences the

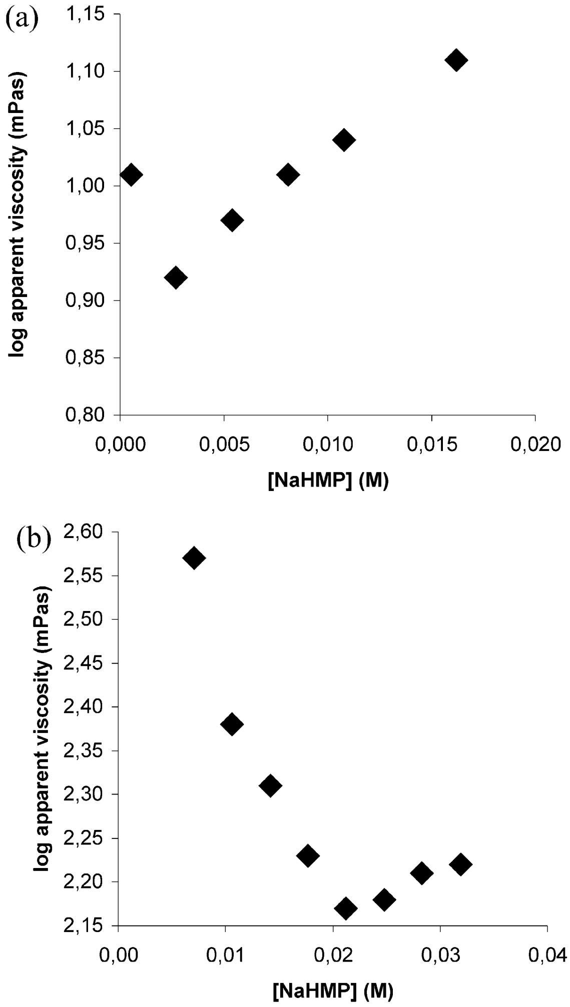

Fig. 1. Apparent viscosity log values (mPa s) measured at $\dot{\gamma} = 300\ s^{-1}$ for KGa-1b (a) and C.G.K. (b) 35% v/v suspensions as a function of the initial NaHMP concentration.

Table 2
Molar concentration of a collection of cations after 4 h of contact of KGa-1b and NaHMP solutions as a function of starting concentration of the deflocculant (expressed both in mg/m^2 and molarity and indicated as Ci and $[\mathrm{NaHMP}]_i$, respectively) at 30 °C and corresponding pH

Ci NaHMP (mg/m^2)	$[\mathrm{NaHMP}]_i$ (M)	[P] (M)	[Si] (M)	[Al] (M)	[Ca] (M)	[Mg] (M)	[K] (M)	[Na] (M)	pH
0	0	/	4×10^{-6}	$<0.2\times10^{-6}$	2×10^{-6}	1×10^{-6}	0.3×10^{-6}	1×10^{-6}	7.26
0.2	0.0054	0.0202	0.0016	0.0016	0.0013	0.0006	0.00002	0.0159	6.03
0.6	0.0162	0.0919	0.0019	0.0062	0.0057	0.0033	0.00005	0.0730	6.06
0.8	0.0223	0.1291	0.0017	0.0061	0.0058	0.0031	0.00005	0.1103	6.08

The mass of the KGa-1b was 93.91 g and the volume of the deflocculant solution 65.9 ml.

dependence of apparent viscosity by deflocculant concentration.[1,16, 17]

3.2. Adsorption measurements

3.2.1. KGa-1b

3.2.1.1. Suspension of KGa-1b in distilled water. The KGa-1b suspension prepared in distilled water has an initial pH of 7.26; the aluminium concentration is over one order of magnitude less than silicon and, generally speaking, the concentration of all the cations in solution is very low (Table 2). The cation concentration levels (especially aluminium ones) are of the same order of instrumental sensibility, but the sound result is not their absolute value, but the fact that they are extremely low.

3.2.1.2. Suspensions of KGa-1b in NaHMP solutions at different concentrations. Comparing the concentration of cations observed in KGa-1b suspensions prepared with different solutions of NaHMP with that observed in distilled water, one can see immediately that the presence of NaHMP produces a relevant increase in the concentration of Si, Al, Ca, Mg and K (Table 2). Moreover, the presence of NaHMP produces an inversion in the ratio of the concentration of Si and Al respect to distilled water: in fact, the Al concentration is higher (or, at least, equal in the case of the NaHMP concentration 0.0054 M) than Si one.Table 3 reports the loss in phosphorus concentration after 4 h respect to the amount introduced with the deflocculant for each initial NaHMP concentration. This 4 h loss in phosphorus concentration can be confidently attributed to adsorption processes. The trend of Δ[P] as a function of the introduced NaHMP concentration shows that increasing the NaHMP concentration the adsorption of NaHMP apparently decreases.

Table 3
Phosphorus concentration in KGa-1b suspensions (a) introduced with starting NaHMP solutions; (b) measured in solution after 4 h; (c) difference between (a) and (b) as a function of starting concentration of the deflocculant at 30 °C

$[\mathrm{NaHMP}]_i$ (M)	(a) $[\mathrm{P}]_i=[\mathrm{Na}]_i$ (M)	(b) [P] (M)	(c) Δ[P] (M)
0.0054	0.0324	0.0202	0.0122
0.0162	0.0973	0.0919	0.0054
0.0223	0.1340	0.1291	0.0049

The mass of the KGa-1b was 93.91 g and the volume of the deflocculant solution 65.9 ml.

3.2.2. C.G.K.

3.2.2.1. Suspension of C.G.K. in distilled water. Comparing the concentrations of the ions present in solution (Table 4) with those obtained in the same conditions but employing KGa-1b (Table 2), we can say that these concentrations are at least one order of magnitude higher than those observed in KGa-1b sample. Like KGa-1b sample in distilled water, the concentration of Si is higher than that of Al.

3.2.2.2. Suspensions of C.G.K. in NaHMP solutions at different concentrations. Like KGa-1b, also for C.G.K. the addition of NaHMP produces an increase in the concentration of all the cations in solution respect to C.G.K. in distilled water (Table 4).

The concentrations of ions in solution are much higher than those observed for KGa-1b sample at the different NaHMP concentrations (see Tables 2 and 4) and much more dependent on the initial NaHMP concentration.

The main difference between the last set of data (Table 4) and the others is the remarkably higher concentrations of Ca, Mg and K ions which confidently don't come from the amount of kaolinite present in C.G.K., but from accessory minerals. The role of the accessory minerals in the dissolution process of C.G.K. in the presence of NaHMP is confirmed by the ratio of the concentration of Si and Al, opposite to that of KGa-1b (see Tables 2 and 4). Analogously to that observed for KGa-1b suspensions (Table 3), the trend of Δ[P] as a function of NaHMP concentration (Table 5) shows that at the lowest NaHMP concentration the adsorption process is the most relevant.

Table 4
Molar concentration of a collection of cations after 4 h of contact of C.G.K. and NaHMP solutions as a function of starting concentration of the deflocculant (expressed both in mg/m^2 and molarity and indicated as Ci and $[NaHMP]_i$, respectively) at 30 °C and corresponding pH

Ci NaHMP (mg/m^2)	$[NaHMP]_i$ (M)	[P] (M)	[Si] (M)	[Al] (M)	[Ca] (M)	[Mg] (M)	[K] (M)	[Na] (M)	pH
0	0	/	0.0001	0.00004	0.00002	0.00002	0.00003	0.00002	8.38
0.2	0.0071	0.0202	0.0315	0.0156	0.0072	0.0043	0.0015	0.0198	7.53
0.4	0.0142	0.0737	0.0573	0.0336	0.0202	0.0114	0.0028	0.0502	7.76
0.6	0.0213	0.1109	0.0634	0.0393	0.0235	0.0130	0.0026	0.0768	7.49
0.8	0.0284	0.1501	0.0394	0.0192	0.0288	0.0141	0.0011	0.0984	7.91

The mass of the C.G.K. was 93.91 g and the volume of the deflocculant solution 65.0 ml.

Table 5
Phosphorus and sodium concentration in C.G.K. suspensions: (a) introduced with starting NaHMP solutions; (b), (d) measured in solution after 4 h, respectively; (c) difference between (a) and (b) columns; (e) difference between (a) and (d) columns as a function of starting concentration of the deflocculant at 30 °C

$[NaHMP]_i$ (M)	(a) $[P]_i = [Na]_i$ (M)	(b) [P] (M)	(c) Δ[P] (M)	(d) [Na] (M)	(e) Δ[Na] (M)
0.0071	0.0425	0.0202	0.0223	0.0198	0.0227
0.0142	0.0851	0.0737	0.0114	0.0502	0.0349
0.0213	0.1277	0.1109	0.0168	0.0768	0.0509
0.0284	0.1702	0.1501	0.0201	0.0984	0.0718

The mass of the C.G.K. was 93.91 g and the volume of the deflocculant solution 65.0 ml.

4. Discussion

4.1. KGa-1b

4.1.1. Suspension of KGa-1b in distilled water

KGa-1b in distilled water, after 4 h of clay-water contact, doesn't show a relevant dissolution process, according to what reported by Huertas et al.[9] after 1 day (the data obtained after 4 h are not reported) and at a similar pH value (Table 2). According to what suggested by Huertas et al.,[9] the non stoicheiometric molar ratio between Si and Al concentration (Table 2) can be ascribed to the precipitation of gibbsite $Al(OH)_3$: in fact, KGa1 kaolinite, structurally very similar to KGa1-b kaolinite investigated in this paper, gives this precipitation over the all pH range 5–11.

4.1.2. Suspensions of KGa-1b in NaHMP solutions at different concentrations

In the presence of NaHMP the concentrations of Si, Al, Ca and Mg in solution are much higher than those observed in distilled water. This fact shows the active effect of NaHMP towards kaolinite and may be explained taking into account both cation exchange phenomena and chemical aggression processes exerted by the deflocculant towards the clay mineral.

With regard to the cation exchange process, it is worth to note that the sodium equivalents disappeared from the solution of NaHMP after 4 h of contact with KGa-1b correspond to the sum of the calcium and magnesium equivalents released in solution after 4 h plus the equivalents of the positive charge coadsorbed with the hexametaphosphate anion on kaolinite surface (six positive charge equivalents for each mole of adsorbed HMP). Table 6 reports the charge equivalents associated with each species involved in the cation exchange processes. Calcium and magnesium ions are present on kaolinite edges since they neutralize the excesses of negative charge due to reticular insaturation and, in small amount, also on the faces to balance the negative charges caused by isomorphic substitution and reticular defectivity.[18]

Cation exchange processes are equilibrium phenomena and thus subjected to the mass effect: as the concentration of Na^+ introduced with the deflocculant increases, also the amount of Na^+ exchanged with the kaolinite increases, until the whole exchange (in our case only calcium and magnesium cations have been considered). Therefore, the exchanged Na^+ amount increases until a limiting value after which it remains constant. The fact that the equivalents of exchanged sodium are about the same for both the NaHMP concentration 0.016 and 0.022 M strongly suggests that these conditions are those to obtain a whole exchange of Na^+ with calcium and magnesium cations.

The fact that the aluminium concentration in solution is always higher than silicon suggests that the aggressiveness of NaHMP towards aluminium octahedral planes of kaolinite could be more pronounced than towards silicon tetrahedral ones.[10,19] As a matter of fact, polyphosphates are able to complex easily aluminium cations, preventing their precipitation even in slightly basic conditions. In any case, the non stoicheiometric molar ratio between the concentration of

Table 6
Number of milliequivalents of the species involved in the cation exchange process in KGa-1b suspensions referred to a mass of 100 g of the clay as a function of starting concentration of the deflocculant at 30 °C. Volume of the deflocculant solution 70.2 ml[a]

$[NaHMP]_i$ (M)	(a) No. meq. Na^+ exchanged	(b) No. meq. Ca^{2+} released	(c) No. meq. Mg^{2+} released	(d) No. meq. positive charge co-adsorbed with HMP anion	(e) Sum of meq. (b)+(c)+(d)
0.0054	1.16	0.18	0.08	0.86	1.12
0.0162	1.70	0.80	0.46	0.38	1.64
0.0223	1.66	0.82	0.44	0.34	1.60

[a] The contribution of potassium ions has been neglected due to the very low concentration which does not affect the computation of the equivalents.

silicon and aluminium in solution is difficult to explain with a simple precipitation of a new phase richer in silicon; in fact, in the investigated systems, the conditions requested for the precipitation of quartz and amorphous silica ($pH < 2$) are never reached.[20] Moreover, the precipitation of aluminium–silicates compounds should give a contemporary decrease in calcium and/or magnesium and/or sodium concentrations which, as previously demonstrated, depend only on the cation exchange phenomena.

X-ray diffraction spectra of KGa-1b do not show appreciable differences after treatment with NaHMP solutions, even at the higher concentrations.

The obtained data (Table 2) show that the silicon concentration doesn't change appreciably at increasing NaHMP concentration, while that one of aluminium increases until a constant value. This behaviour agrees with a progressive solubilization of the aluminium accessible to the deflocculant solution (i.e. potentially removable). These results can justify the anomalous adsorption of the deflocculant observed in correspondence of low NaHMP concentrations (Table 3): in fact, as HMP adsorbs only (or anyway preferentially) on aluminium sites,[10–12] the selective dissolution of octahedral planes observed at the higher deflocculant concentrations leads to a decrease of the surface disposable for adsorption. In this way, in the presence of low NaHMP concentration, the surface disposable for adsorption is more extended since the aggressive action of the deflocculant towards aluminium sites is weaker; at higher NaHMP concentrations, instead, the removal of the octahedral planes due to Al complexation diminishes the surface able to adsorb the deflocculant.

The rheological measurements show that the apparent viscosity increases when the NaHMP molar concentration increases from 2.7×10^{-3} to 1.62×10^{-2} M (Fig. 1a). This fact apparently contradicts one of the deflocculating mechanisms of NaHMP which consists in the inactivation of flocculant alkaline-earth cations by complexation: in fact, as the NaHMP concentration increases, also its complexation power towards calcium, magnesium and aluminium cations should become stronger and then lead to a decrease of the apparent viscosity. Indeed, due to the high affinity of these cations towards HMP,[13] they are always fully complexed at all the investigated deflocculant concentrations.

The observed rheological measurements could be explained taking into account the other mechanism of action of NaHMP: the adsorption on kaolinite.[10–12] In fact, the minimum apparent viscosity is found to be just in correspondence of the highest amount of the adsorbed NaHMP (in this condition the extent of the octahedral planes of aluminium on which NaHMP can adsorbs is the highest). For high NaHMP concentrations, instead, its adsorption and resulting deflocculant action is more limited, probably due to the progressive removal of Al octahedral planes on which NaHMP is adsorbed.

4.2. C.G.K.

4.2.1. Suspension of C.G.K. in distilled water

C.G.K. in distilled water—considering the system after 4 h of clay-water contact—doesn't show a remarkable dissolution process (Table 4), even though the concentrations of the cations in the centrifuged and filtered solutions are at least one order of magnitude higher than the KGa-1b corresponding ones, probably due to the presence of the accessory minerals.

In fact the high concentration of the cations Ca, Mg, K and Na shows that the dissolution of the accessory minerals[21] present in the C.G.K. is a remarkable phenomenon with respect to that of KGa-1b. Table 4 also shows a non stoicheiometric molar ratio between Si and Al concentration, already observed for KGa-1b in distilled water (Table 2): as above proposed, this result can be explained as a reprecipitation phenomena of Al ion in the form of gibbsite.[9]

4.2.2. Suspensions of C.G.K. in NaHMP solutions at different concentrations

Also in C.G.K. suspensions NaHMP shows a remarkable ability to solubilize cations (Table 4) as the consequence of cation exchange phenomena and chemical aggression processes towards the minerals of the clay. The disappearance of sodium ions and the concomitant appearance of calcium, magnesium and potassium ions in solution after 4 h can be only partially attributed to cation exchange processes; in fact, a simple cation exchange process should give a total equivalent concentration of Ca, Mg and K released into the solution and a number of equivalents of disappeared sodium cations lower or at least equal to that of CEC (3.7 meq/100 g). Looking at the data obtained (Table 7), one can see that starting from the NaHMP concentration of 0.014 M the sum of the equivalent of calcium, magnesium and potassium ions in solution is higher than CEC, and at the NaHMP concentration of 0.028 M also the equivalents of sodium disappeared after 4 h is higher than CEC. In all the cases, however, the reported data (Table 7) show that the equivalents of disappeared sodium (exchanged and possibly coadsorbed with HMP) are much lower than those of calcium magnesium and potassium released in solution. These results indicate that CEC doesn't account for all the complex phenomena that take place in solution; the particularly high concentration of calcium, magnesium, potassium, aluminium and silicon in solution reveals the presence of remarkable chemical aggression process toward the accessory minerals due to the NaHMP.

The strong complexing ability exerted by NaHMP towards cations present in the accessory minerals of C.G.K. accounts for the remarkable chemical aggression process which leads to the above mentioned high concentration of the cations. For example, it is possible to demonstrate that in the presence of NaHMP even high concentrations of Ca ions in solution do not provoke precipitation of $CaCO_3$ or $CaSO_4$ (the concentrations of CO_3^{2-} and SO_4^{2-} anions have not been determined here, but they are commonly observed in clay suspensions), due to the high stability constant ($K_{st}^{298\ K} = 10^{6.9}$) of the 1:1 strong outer-sphere complex formed between Ca and HMP;[14] in fact, the presence of the related complexation equilibrium causes the solubility equilibrium of the salt to be shifted towards the solution form (see Appendix).

The absence of phosphate precipitation is also related to the fact that the time of investigation (4 h) is not enough to obtain monophosphate units from NaHMP hydrolysis: it is known from literature[4] that NaHMP is particularly stable in aqueous solution, in fact the ring cleavage is characterised by a half living time of 1000 h in NaOH 1 N. So it is clear that, even though the solubility of calcium phosphate, magnesium ammonium phosphate, magnesium hydrogen phosphate, aluminium phosphate and hydroxyapatite at room temperatures is very low ($K_{PS} = 2.07 \times 10^{-33}$, $K_{PS} = 2 \times 10^{-13}$, $K_{PS} = 1.7 \times 10^{-6}$, $K_{PS} = 6 \times 10^{-19}$ and $K_{PS} = 3.2\ \ 10^{-58}$, respectively), the precipitation of any phosphate compound can be excluded in our experimental conditions.

It is worth to note that in the case of C.G.K. the solubilization processes are considerably wider than in KGa-1b (see Tables 2 and 4). The concentrations of the cations are much higher and more dependent on the NaHMP concentration than in the cases of kaolinite. This means that in C.G.K. suspensions chemical degradation processes are evident and involve especially the accessory minerals[21] which represent a not-negligible weight percentage (9%) of the clay.

Also the concentrations of silicon and aluminium are much higher than those observed for KGa-1b in the same conditions; moreover, it is worth to note that the silicon-aluminium molar ratio is opposite to KGa-1b case. This observation further supports the hypothesis that most of the cations comes from degradation processes acting on the accessory minerals (illite, feldspar, quartz and amorphous) and not on the kaolinite present in C.G.K.

X-ray diffraction spectra of C.G.K. reveal some remarkable differences after treatment with NaHMP solutions (Fig. 2). Most of all the peaks of illite result broader and doubled as a consequence of the interaction with NaHMP: this fact suggests the presence of adsorption processes involving also the interlayer frame of this mineral. Even though a random pattern cannot provide quantitative information for the analysis of the impurity minerals, the X-ray spectra suggest also a decrease in illite amount in the clays. No evidence of a new phase appearance is observed.

The dependence of the concentrations of the various cations on that of NaHMP is closely linked to their nature:

Si: the release of Si exhibits a peculiar behaviour, in fact the concentration of Si in solution shows a maximum at the NaHMP concentration of 2.12×10^{-2} M (Fig. 3, Table 4).

Table 7

Number of milliequivalents (1) of Na^+ disappeared (see text) from solution after 4 h; (2) of Ca^{2+}; (3) of Mg^{2+}; (4) of K^+ released in solution after 4 h; (5) sum of columns (2), (3) and (4) in C.G.K. suspensions referred to a mass of 100 g of the clay as a function of starting concentration of the deflocculant at 30 °C. Volume of the deflocculant solution 69.2 ml

$[NaHMP]_i$ (M)	(1) No. meq Na^+ disappeared	(2) No. meq Ca^{++}	(3) No. meq Mg^{++}	(4) No. meq K^+	(5) Sum of meq (2)+(3)+(4)
0.0071	1.57	0.997	0.595	0.104	1.69
0.0142	2.42	2.80	1.58	0.194	4.57
0.0213	3.52	3.25	1.80	0.180	5.23
0.0284	4.97	3.99	1.95	0.0761	6.02

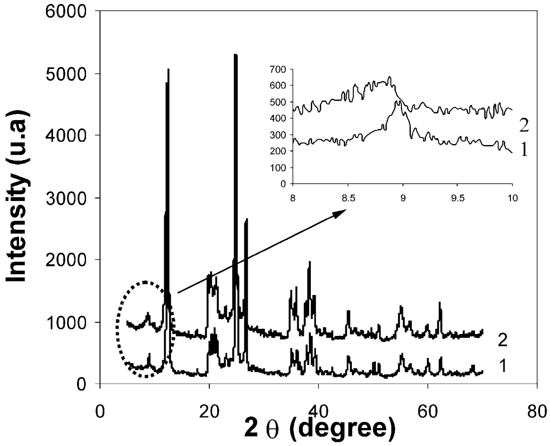

Fig. 2. X-ray diffraction spectra of C.G.K. before (1) and after (2) treatment with NaHMP solutions.

Al: the release of aluminium is qualitatively similar to that of silicon; in fact, also the concentration of Al in solution shows a maximum at the NaHMP concentration of 2.12×10^{-2} M (Fig. 3, Table 4).

Ca and Mg: the concentration of Ca and Mg in solution increases in line with that of NaHMP (Table 4).

K: the concentration of K released in solution shows a maximum at NaHMP concentration ranging from 1.42×10^{-2} to 2.12×10^{-2} M (Table 4). This behaviour is similar to that of Al and Si.

Na: the concentration of Na increases in line with that of NaHMP (Table 4). Since this cation is introduced with the deflocculant, its concentration in solution should be given most of all by the contribution of the deflocculant. Indeed, a remarkable amount of Na seems to disappear: Table 5 reports the amount of sodium lost from the solution dependent on the quantity of NaHMP introduced. The characteristic behaviour found for Si and Al examined together with the disappearance of Na from the solution (not justified only by simple cation exchange phenomena) could be indicative of reprecipitation phenomena occurring when the concentrations of the involved ions exceed the solubility product. Huertas et al.[9] put forward the hypothesis that a phase of Na-smectite might precipitate at pH 8, having compared the solubility product with the theoretical prediction of the solubility of this phase advanced by Drever[22] and calculated for a theoretical composition of $Na_{0.33}(Si_{3.67}Al_{0.33})Al_2O_{10}(OH)_2$. In our cases, no X-ray evidence of smectite precipitation has been observed (Fig. 2), nevertheless this process cannot be completely excluded due to the low amount of smectite which should precipitate. Whatever nature has the precipitate phase, its presence could affect the adsorption process of NaHMP and its deflocculating properties.

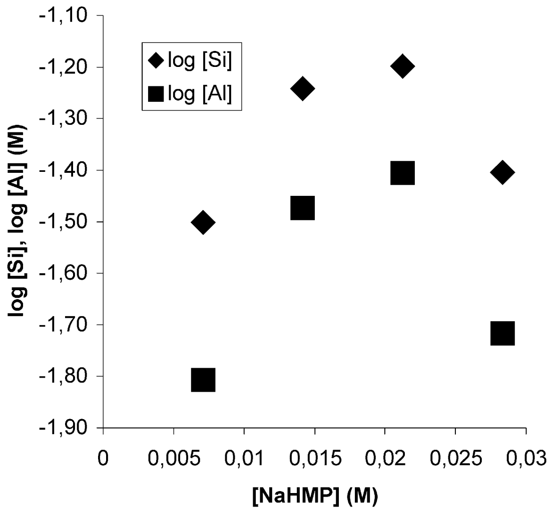

Fig. 3. Concentration log values of Si and Al cations in 4 h suspensions of C.G.K. as a function of initial NaHMP concentrations.

Table 5 shows the amount of adsorbed phosphorus in C.G.K. suspensions after 4 h as a function of the initial NaHMP concentration; the data must be considered taking into account complex adsorption processes due to the involvement of the different solid adsorbent species present in the C.G.K. In fact, also the illite present in C.G.K. can strongly adsorb anions and polyanions.[23–25] As already proposed for KGa-1b, the anomalous adsorption of the deflocculant at the lowest NaHMP concentration could be related with the less pronounced removal of octahedral planes of the Al at lower NaHMP concentration which allows more pronounced adsorption processes of NaHMP to occurr.

The data reported in Table 8 clearly indicate C.G.K. very more effective in NaHMP adsorption than KGa-1b. This fact can be related to the presence of considerable amount of accessory minerals, illite in particular; this last is characterized by a remarkable high specific surface area[26] available for adsorption.

Unlike KGa-1b, the minimum apparent viscosity is obtained in correspondence of a NaHMP concentration (2.12×10^{-2} M, see Fig. 1b) which doesn't correspond to the maximum amount of deflocculant adsorbed. As two of the three deflocculation mechanisms of NaHMP (complexation of the flocculant cations and substitution of the cations in the clay double layer with Na^+ ions) improve their action at high NaHMP concentrations, while the third (increase of the negative charge on the clay micelles by adsorption of the anion) at low ones, the minimum apparent viscosity is probably obtained at an intermediate concentration which corresponds to the best synergy of the three mechanisms; in fact, in the case of KGa-1b, the concentration of NaHMP in solution is sufficiently high to allow a complete complexation of the flocculant cations Ca^{2+} and Mg^{2+} (i.e. [HMP] > [Ca] + [Mg], Table 2), while in the case of

Table 8
Number of mols of phosphorus lost from solution after 4 h: (a) absolute values referred to a mass of 100 g of both KGa-1b (1) and C.G.K. (2); (b) referred to the specific surface area as a function of starting concentration of the deflocculant, expressed in mass of deflocculant/clay surface area (see Section 2) at 30 °C

Ci NaHMP (mg/m^2)	No. mols P (a1)	No. mols P (b1)	No. mols P (a2)	No. mols P (b2)
0.2	8.56×10^{-4}	7.37×10^{-7}	15.44×10^{-4}	10.26×10^{-7}
0.4	nd	nd	7.89×10^{-4}	5.26×10^{-7}
0.6	3.79×10^{-4}	3.26×10^{-7}	11.62×10^{-4}	7.74×10^{-7}
0.8	3.39×10^{-4}	2.92×10^{-7}	13.91×10^{-4}	9.27×10^{-7}

Volume of the deflocculant solution 70.2 and 69.2 ml for KGa-1b and C.G.K., respectively.

C.G.K. this condition is not reached even at the NaHMP concentration 2.83×10^{-2} M (Table 4). The fact that the minimum apparent viscosity for C.G.K. suspensions is obtained with an amount of deflocculant which is remarkably higher than the amount required for KGa-1b is probably due to the particularly high calcium and magnesium concentration of C.G.K. solutions: in fact, high levels of Ca and Mg ions, easily complexed by HMP anion, can reduce its deflocculant capability and cause an increase in the NaHMP demand to give deflocculation. Moreover, it is worth to note that also the structure of the clays can play a remarkable role in dispersant activity.[27]

5. Conclusions

The findings of this study allow to draw some significant conclusions:

- NaHMP exerts a direct and important effect on the dissolution of both kaolin and kaolinite.
- The accessory minerals in kaolin directly participate in the processes of dissolution of the raw material.
- The concentration of the released ions in solution depends on the clay material and on the NaHMP concentration, even though the effect is quantitatively different for the different cations.
- Re-precipitation phenomena seem to play a role in determining the characteristics of the solution in contact with the raw materials.

As a matter of fact, kaolin (C.G.K.) behaves as a sort of heterogeneous material (even if formed prevalently by kaolinite) and its dissolution must be seen as that of a heterogeneous material, every part of which (kaolinite, quartz, feldspar, micaceous minerals and, possibly, amorphous material) contribute—in different amount—to the dissolution process. Nevertheless, also kaolinite (KGa-1b, a pure mineral) undergoes dissolution process when treated with NaHMP, even though this process is different and remarkably less pronounced than that in kaolin sample.

Since the difference in composition between kaolin and kaolinite is the presence of accessory minerals and the dissolution process is more pronounced in kaolin rather than in kaolinite, the higher level of released ions (among which Si and Al) in kaolin suspension respect to that one of kaolinite can be confidently attributed to the presence of accessory minerals and, possibly, amorphous materials.

Research is now in progress to define the relationship that exists between the rheological response of the system and the above-reported phenomena.

Acknowledgements

Financial support by the MURST is gratefully acknowledged.

Appendix. Effect of simultaneous precipitation and complexation equilibria on calcium speciation in solution: the case of $CaCO_3$ and $Na_2Ca(PO_3)_6^{2-}$

Calcium ions in solution are involved in two type of equilibria which take place together: the equilibrium of complexation by NaHMP and the equilibrium of precipitation by specific anions; in this case we consider CO_3^{2-} anion because the solubility product of $CaCO_3$ is very smaller than that of $CaSO_4$.

Some of the Ca concentration reported in Table 4 would exceed the solubility of $CaCO_3$ if the precipitation of $CaCO_3$ was the only equilibrium involving calcium ions in solution; but, as the equilibrium of the complexation of calcium ions by NaHMP takes place together and its stability constant is very high, it is clear that this process influences the first precipitation equilibrium.

It is possible to demonstrate that the reported levels of calcium in solutions are not in contrast with the possibility of the precipitation of $CaCO_3$ by solving the corresponding stoicheiometric problem of two equilibria which take place together in solution: the precipitation of $CaCO_3$ and the complexation of calcium ions by NaHMP.

Data are: the K_{PS} of $CaCO_3$ at $298K = 1.96\times10^{-8}$, the K_{st} of calcium–hexemetaphosphate complex at $298K = 10^{6.9}$; the initial concentration of hexametaphosphate $[NaHMP]_i = [Na_2(PO_3)_6^{4-}]_i$ can assume four values (7.083×10^{-3}, 1.418 10^{-2}, 2.127 10^{-2}, 2.837 10^{-2} M).

Data:

$$CaCO_{3\,(s)} \leftrightarrows Ca^{2+}_{(aq)} + CO_3^{2-}(aq) \tag{A1}$$

$$Ca^{2+} + \left[Na_2(PO_3)_6^{4-}\right] \leftrightarrows \left[Na_2Ca(PO_3)_6^{2-}\right] \tag{A2}$$

$$K_{PS} = \left[Ca^{2+}\right]\left[CO_3^{2-}\right] = 1.96\times10^{-8} \tag{A3}$$

$$K_{st} = \left[Na_2Ca(PO_3)_6^{2-}\right]/\left\{\left[Na_2(PO_3)_6^{4-}\right]\left[Ca^{2+}\right]\right\} = 10^{6.9} \tag{A4}$$

$$\left[Na_2(PO_3)_6^{4-}\right]_i = 2.127\times10^{-2}$$

Resolution:

$$\left[CO_3^{2-}\right] = \left[Ca^{2+}\right] + \left[Na_2Ca(PO_3)_6^{2-}\right] \tag{A5}$$

as K_{st} of the complex $Na_2Ca(PO_3)_6^{2-}$ is very high we can consider $[Ca^{2+}]$ negligible and write:

$$\left[CO_3^{2-}\right] = \left[Na_2Ca(PO_3)_6^{2-}\right] \tag{A6}$$

moreover:

$$\left[Na_2(PO_3)_6^{4-}\right]_i = \left[Na_2(PO_3)_6^{4-}\right] + \left[Na_2Ca(PO_3)_6^{2-}\right] \tag{A7}$$

we can get $[Ca^{2+}]$ from Eq. (A4)

$$\left[Ca^{2+}\right] = \left[Na_2Ca(PO_3)_6^{2-}\right]/\left\{\left[Na_2(PO_3)_6^{4-}\right]10^{6.9}\right\} \tag{A8}$$

so Eq. (A3) can be written:

$$K_{PS} = \left[Na_2Ca(PO_3)_6^{2-}\right]/\left\{\left[Na_2(PO_3)_6^{4-}\right]10^{6.9}\right\}\left[CO_3^{2-}\right] = 1.96\times10^{-8}$$

and for the Eq. (A6)

$$K_{PS} = \left[Na_2Ca(PO_3)_6^{2-}\right]^2/\left\{\left[Na_2(PO_3)_6^{4-}\right]10^{6.9}\right\} = 1.96\times10^{-8}$$

We state:

$$x = \left[Na_2Ca(PO_3)_6^{2-}\right]$$

and therefore:

$$\left[Na_2(PO_3)_6^{4-}\right] = \left\{\left[Na_2(PO_3)_6^{4-}\right]_i - \left[Na_2Ca(PO_3)_6^{2-}\right]\right\} = \left\{\left[Na_2(PO_3)_6^{4-}\right]_i - x\right\}$$

$$K_{PS} = x^2/\left\{10^{6.9}\left(\left[Na_2(PO_3)_6^{4-}\right]_i - x\right)\right\} = 1.96\times10^{-8}$$

If we solve this equation for the four initial NaHMP concentrations, we find the results reported in Table 9.

Table 9
Concentration of the species in solution in the presence of $CaCO_3$ precipitation and $Na(PO_3)_6^{4-}$—calcium complexation equilibrium as a function of initial ligand cancentration

$[Na_2(PO_3)_6^{4-}]_i$ (M)	$[Na_2Ca(PO_3)_6^{2-}]$ (M)	$[Na_2(PO_3)_6^{4-}]$ (M)	$[Ca^{2+}]$ (M)
7.083×10^{-3}	0.00679	2.98×10^{-4}	2.87×10^{-6}
1.418×10^{-2}	0.0131	1.08×10^{-3}	1.53×10^{-6}
2.127×10^{-2}	0.0189	2.37×10^{-3}	1.00×10^{-6}
2.837×10^{-2}	0.025	3.37×10^{-3}	9.34×10^{-7}

The concentration of calcium ions present in solution and found by ICP analysis is the sum of calcium free ions and calcium complexed ions, but as the concentration of free calcium ions is extremely low (~1 μM), this sum may be considered equal to the concentration of calcium complexed ions.

Obviously, the values of calcium concentration reported in Table 4 are not "exactly" those of Table 9 because of the two equilibria discussed in this example are not the only equilibria present in the real solution (moreover, the results of the problem are referred to the temperature of 25 °C, while experimental data are referred to 30 °C), but the order of magnitude of the result obtained in the problem justifies the experimental data. This is true once again when we consider the precipitation of $CaSO_4$ instead of $CaCO_3$, because $CaSO_4$ has a higher K_{PS}.

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