INFLUENCE OF PHOSPHATE IONS ON THE EXTRACTION OF ALUMINUM BY 8-HYDROXYQUINOLINE FROM OH-AL SUSPENSIONS

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Aluminum was extracted from OH-Al-suspensions ($[Al^{3+}] = 6.4 \times 10^{-4} \text{ mol L}^{-1}$; OH/Al molar ratio = 1.0, 1.5, 2.2) aged 5 and 18 mo by 8-hydroxyquinoline into four different species: readily extractable (Al_{re}), moderately extractable (Al_{me}), slowly extractable (Al_{se}) and nonextractable (Al_{ne}) aluminum. In all the systems, the percentages of Al_{re} were the highest of the ultrafiltered hydrolytic products of Al, ranging from 68.1 to 21.1%, whereas the percentages of Al_{me} and Al_{se} were $\leq 12.3\%$. The higher the OH/Al molar ratio and the longer the aging period of OH-Al-suspensions, the lower the percentages of Al_{re} , Al_{me} and Al_{se} , and the higher the percentages of Al_{ne} (ranging from 13.3 to 71.1%). With addition of phosphate ions, increasing the P/Al molar ratio from 0.05 to 0.5 decreased Al_{re} and increased Al_{ne} . Finally, it was ascertained that the ultrafiltered aluminum was not completely extracted by 8-hydroxyquinoline after 3 h. More aluminum was extracted from 3 to 48 h from the suspensions containing phosphate ions than from those without phosphate.

Key words: Aluminum hydrolytic products, phosphate, aluminum extraction, 8-hydroxyquinoline

[Effets des ions phosphate sur l'extraction de l'aluminium de suspensions OH-Al à l'aide d'hydroxy-8 quinoline.]

Titre abrégé: Effets des ions phosphate sur l'extraction de l'aluminium.

Nous avons procédé à l'extraction de l'aluminium de suspensions OH-Al ($[Al^{3+}] = 6,4 \times 10^{-4} \text{ mol l}^{-1}$; rapport molaire OH/Al = 1,0, 1,5, 2,2) âgées de 5 ou de 18 mois à l'aide d'hydroxy-8 quinoline et obtenu 4 espèces différentes : facilement extractible (Al_{re}), modérément extractible (Al_{me}), difficilement extractible (Al_{se}) et non extractible (Al_{ne}). Dans tous les systèmes, les pourcentages de Al_{re} étaient les plus élevés des produits de l'hydrolyse de l'aluminium après ultra-filtration, variant de 68,1 à 21,1%. Les pourcentages de Al_{me} et de Al_{se} étaient égaux ou inférieurs à 12,3%. Un rapport molaire OH/Al plus élevé et une période de vieillissement des suspensions OH/Al plus longue entraînent une baisse des pourcentages de Al_{re} , de Al_{me} et de Al_{se} et une augmentation des pourcentages de Al_{ne} (variant de 13,3 à 71,1%). L'ajout d'ions phosphate provoque une augmentation du rapport molaire P/Al de 0,05 à 0,5, diminuant le taux de Al_{re} et augmentant le taux de Al_{ne} . On a finalement constaté que l'aluminium ultra-filtré n'était pas complètement extrait par l'hydroxy-8 quinoline après trois heures. Nous avons extrait plus d'aluminium, de 3 à 48 h, à partir des suspensions contenant des ions phosphate qu'à partir des suspensions sans phosphate.

Mots clés: Produits de l'hydrolyse de l'aluminium, phosphate, extraction de l'aluminium, hydroxy-8 quinoline

It is known that aluminum ions hydrolyze forming various monomeric, polymeric and solid species. Many researchers (Matijevic and Tezak 1953; Brosset et al. 1954; Hsu and Bates 1964; Aveston 1965; Turner 1968), using different analytical methods, have tried to demonstrate the existence of different soluble hydrolytic products of aluminum, from simple monomers or polynuclear ions (e.g., Al^{3+} , AlOH^{2+} , $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_3$, $\text{Al}_2(\text{OH})_5^+$, $\text{Al}_3(\text{OH})_6^+$) to large polymers (e.g., $\text{Al}_6(\text{OH})_{13}^{3+}$, $\text{Al}_8(\text{OH})_{20}^{4+}$, $\text{Al}_{24}(\text{OH})_{66}^{12+}$, $\text{Al}_{54}(\text{OH})_{144}^{18+}$).

The first attempts to determine the various forms of aluminum in solution were carried out by Okura et al. (1962), Turner (1968, 1969), and Turner and Ross (1970). According to Turner (1969), in aluminum salt solutions partially neutralized with a base, the aluminum extractable after 10 s by 8-hydroxyquinoline is considered to be made up only of monomers, whereas the aluminum extracted after 30 min or 3 h is made up of polynuclear ions $\text{Al}_6(\text{OH})_{13}^{3+}$ or amorphous solid species, respectively. Turner (1968, 1969) and Turner and Ross (1970) demonstrated that the initial OH/Al molar ratio, the temperature, the speed of addition of a base, the presence of different anions (Cl^- , ClO_4^- , NO_3^-) and the aging period of solutions have considerable influence on promoting the formation of one form of the hydrolytic products of Al instead of another.

Luciuk and Huang (1974) and Kwong and Huang (1977) showed that in the presence of anions with strong affinity for aluminum (silicate or citrate), the different forms of Al (monomers, polymers and solid species) cannot be determined accurately. Thus, it is more expedient to divide the Al species on the basis of their reactivity with 8-hydroxyquinoline. Also, it is well known that hydrolytic products of aluminum and iron strongly hold phosphate ions and made them difficultly available for plants (Bolan et al. 1985).

The aim of this work was to study the influence of phosphate ions on the extrac-

tion of aluminum by 8-hydroxyquinoline from suspensions formed at different OH/Al molar ratios aged for various periods of time.

MATERIALS AND METHODS

Stock solutions (500 mL) of 2.56×10^{-3} mol L^{-1} AlCl_3 were neutralized by slowly adding (1 mL min^{-1}) 0.01 mol L^{-1} NaOH until suspensions with OH/Al molar ratios of 1.0, 1.5, 2.2 were obtained. During the titration, the solutions were thoroughly stirred and their final volumes brought to 2 L with deionized water to obtain a total aluminum concentration of 6.4×10^{-4} mol L^{-1} . All the suspensions were kept in polyethylene bottles and aged up to 18 mo.

During the aging process, aliquots of each suspension (50–100 mL) were filtered through Millipore MF filters of 0.025- μm pore size to remove amorphous and/or crystalline solid phases ($>0.025 \mu\text{m}$). The various forms of aluminum were determined in the filtrate as described below.

Determination of Various Forms of Aluminum by 8-hydroxyquinoline

Aluminum was determined by extraction with 8-hydroxyquinoline by the method proposed by Okura et al. (1962) and modified by Turner (1969). Aliquots of the filtrates were transferred to 50-mL separatory funnels which contained 5 mL of H_2O and 14 mL of 8-hydroxyquinoline solution (2 g of 8-hydroxyquinoline previously dissolved in 5 mL of glacial acetic acid and 200 mL of H_2O). The readily-extractable aluminum (Al_{re}) was determined by adding 10 mL of chloroform, shaking for 10 s and rapidly removing the chloroform phase. The moderately (Al_{me}) or slowly (Al_{se}) extractable aluminum species were determined by shaking the OH-Al-suspensions for 30 min or 3 h, respectively, with the solution of 8-hydroxyquinoline. After a suitable time of contact, 10 mL of chloroform were added. After shaking for 15 s, the chloroform phase was removed. The concentration of aluminum in the chloroform extract was determined spectrophotometrically at 395 μm . The moderately-extractable aluminum (Al_{me}) was determined by subtracting the concentration of the aluminum determined after 10 s from the concentration of aluminum determined after 30 min. The slowly-extractable aluminum (Al_{se}) was determined by subtracting the concentration of aluminum ex-

tracted after 30 min from the concentration of aluminum extracted after 3 h. The slowly-extractable aluminum was also determined after 6, 18 and 48 h of contact with 8-hydroxyquinoline solutions. The nonextractable aluminum (Al_{ne}) was determined from the difference between the initial total aluminum concentration (6×10^{-4} mol L^{-1}) and that determined after 3, 6, 18 or 48 h.

Determination of Aluminum after Addition of Phosphate Ions

Different quantities of 0.025 mol L^{-1} KH_2PO_4 solution were added to aliquots of the OH-Al-suspensions, aged 5 or 18 mo and thoroughly stirred to obtain systems with P/Al molar ratios of 0.05, 0.08, 0.17 or 0.5. Before adding the KH_2PO_4 solution, its pH was adjusted to the same pH as that of the suspension to which it was added. After 24 h, the suspensions were filtered on Millipore filters (0.025- μm pore size) and the various forms of aluminum were determined as previously reported.

RESULTS AND DISCUSSION

Table 1 shows the percentages of readily- (Al_{re}), moderately (Al_{me}) or slowly extractable (Al_{se}) aluminum, and of aluminum nonextractable after 3 h (Al_{ne}) in the OH-Al-

suspensions (OH/Al molar ratio = 1.0, 1.5 or 2.2), aged 5 or 18 mo before and after addition of phosphate ions (P/Al molar ratio = 0, 0.05, 0.08, 0.17 or 0.5). Al_{re} was the most abundant form of Al in the filtrates ranging from 72.0 to 91.3% of the aluminum extracted after 3 h ($Al_{re} + Al_{me} + Al_{se}$) in all suspensions.

In the absence of phosphate, the amounts of Al_{re} ranged from a maximum of 68.1% in the suspension at OH/Al = 1.0 aged 5 mo to a minimum of 21.1% in the suspension at OH/Al = 2.2 aged 18 mo (Table 1). The percentages of Al_{me} or Al_{se} reached a maximum of 12.3 or 6.3%, respectively, in the system at OH/Al = 1.0 aged 5 mo. It was found that the higher the initial OH/Al molar ratio or the longer the aging period, the lower the amounts of Al_{re} , Al_{me} or Al_{se} , and the higher the amounts of Al_{ne} . After aging the systems from 5 to 18 mo, Al_{ne} increased from 13.3 to 39.3% in the suspension at OH/Al = 1.0, from 22.8 to 52.6% in the suspension at OH/Al = 1.5, and from 39.2 to 71.1% in the suspension at OH/Al = 2.2.

The addition of phosphate to the aged

Table 1. Percentage of hydrolytic products of aluminum (initial OH/Al molar ratio = 1.0, 1.5, or 2.2) aged 5 and 18 mo in the absence or presence of phosphate ions (P/Al molar ratio = 0, 0.05, 0.08, 0.17 or 0.5)

Aluminum species	Aged 5 mo P/Al molar ratio				Aged 18 mo P/Al molar ratio				
	0	0.08	0.17	0.5	0	0.05	0.08	0.17	0.5
<i>OH/Al = 1.0 ($pH_i = 4.49$; $pH_f = 3.98$)</i>									
$Al_{re}^\dagger$	68.1	66.6	64.9	49.2	51.9	46.7	46.2	41.6	35.4
Al_{me}	12.3	11.9	9.0	6.3	7.3	9.2	1.4	2.3	2.0
Al_{se}	6.3	4.8	8.0	4.9	1.5	3.7	3.0	3.3	4.1
Al_{ne}	13.3	16.7	18.1	39.6	39.3	41.4	48.4	52.8	58.5
<i>OH/Al = 1.5 ($pH_i = 4.60$; $pH_f = 4.09$)</i>									
Al_{re}	59.7	51.9	49.8	37.8	42.0	37.7	36.7	31.2	26.4
Al_{me}	12.3	11.7	8.0	6.6	5.0	3.3	1.2	0.9	0.8
Al_{se}	5.2	4.4	6.9	3.7	0.4	1.7	3.6	5.6	6.1
Al_{ne}	22.8	32.0	35.3	51.9	52.6	57.3	58.5	62.3	66.7
<i>OH/Al = 2.2 ($pH_i = 5.00$; $pH_f = 4.28$)</i>									
Al_{re}	45.3	34.8	27.3	25.2	21.1	18.0	16.6	14.2	14.1
Al_{me}	11.6	9.8	8.0	5.3	3.9	3.3	0.9	0.7	0.7
Al_{se}	3.9	3.3	5.2	2.7	3.9	3.7	2.8	2.7	1.5
Al_{ne}	39.2	52.1	59.5	66.8	71.1	75.0	79.7	82.4	83.7

$^\dagger Al_{re}$ = readily-extractable aluminum; Al_{me} = moderately-extractable aluminum; Al_{se} = slowly-extractable aluminum; Al_{ne} = nonextractable aluminum; pH_i = initial pH; pH_f = final pH (after 18 mo of aging).

OH/Al-suspensions decreased Al_{re} and Al_{me} and increased Al_{se} (Table 1). Al_{se} slightly increased at certain P/Al molar ratios. However, the sum of the percentages of Al_{me} and Al_{se} was usually less than that determined in the phosphate-free systems.

Clearly, phosphate ions, because of their strong affinity for Al ions (Hsu 1975, 1977, 1978; Bowden et al. 1980; Bolan et al. 1985; Violante and Huang 1985) promoted the formation of new solid and/or soluble species (as will be discussed later) and influenced the extractability of the Al ions by 8-hydroxyquinoline. Our data extend the work of Kwong and Huang (1977) showing that the presence of foreign ligands strongly influences the rate of removal of Al from suspensions. Kwong and Huang (1977) found that the effect of citric acid, co-precipitated with Al, on the formation of the readily-extractable Al and moderately-extractable Al by 8-hydroxyquinoline varied with the initial concentrations of Al and citric acid, and OH/Al molar ratios of the OH-Al-suspensions. From our study it is evident that the addition of phosphate ions increased the proportion of nonextractable

aluminum at the expense of the readily, and moderately-extractable aluminum.

Table 2 shows the percentage decrease of Al_{re} with respect to Al_{re} at P/Al molar ratio = 0, after addition of different amounts of phosphate ions. Generally, at a given P/Al molar ratio, the higher the initial OH/Al molar ratio or the longer the aging period of the OH-Al-suspensions, the greater was the percentage decrease of Al_{re} . For example after addition of 0.17 mol of phosphate per mol of aluminum, the percentage decreases of Al_{re} were 4.7, 16.6 and 39.7%, respectively, in the systems at OH/Al = 1.0, 1.5 and 2.2 aged 5 mo. In the same suspensions aged 18 mo, the percentage decreases of Al_{re} , after addition of 0.17 mol of phosphate were 19.8, 25.7 and 32.7%, respectively.

These findings cannot be interpreted without ambiguity, because the nature of hydrolytic products of aluminum and the reaction products between phosphate and Al ions are not known precisely. However, a possible explanation is that in the OH-Al-suspensions with higher OH/Al molar ratios (i.e., OH/Al = 2.2) or aged for a longer

Table 2. Percentage decrease of Al_{re} in OH-Al-suspensions aged 5 and 18 mo after addition of different amounts of phosphate ions (from the data reported in Table 1)

P/Al molar ratios	Aged 5 mo		Aged 18 mo	
	% decrease Al_{re}	R†	% decrease Al_{re}	R†
<i>OH/Al = 1.0</i>				
0.05	—	—	10.0	2.0
0.08	2.2	0.3	11.0	1.4
0.17	4.7	0.3	19.8	1.2
0.5	27.7	0.5	31.8	0.6
<i>OH/Al = 1.5</i>				
0.05	—	—	10.2	2.0
0.08	13.1	1.6	12.6	1.6
0.17	16.6	1.0	25.7	1.5
0.5	36.7	0.7	37.1	0.7
<i>OH/Al = 2.2</i>				
0.05	—	—	14.7	2.9
0.08	22.5	2.8	21.3	2.7
0.17	39.7	2.3	32.7	1.9
0.5	44.4	0.9	33.2	0.7

† R indicates the ratio between the percentage decrease of Al_{re} and the P/Al molar ratio expressed as percentage (5, 8, 17 or 50% P).

period of time (i.e., 18 mo), the hydrolytic soluble products of Al are much more neutralized and have a lower positive charge per Al atom (Hsu and Bates 1964; Smith and Hem 1972; Bersillon et al. 1980). The reaction of such species with phosphate ions would further decrease their positive charge, with a consequent lower electrostatic repulsion of the species formed, which could then more easily coalesce and precipitate (Hsu and Bates 1964; Hsu 1977, 1978).

Table 2 also shows the ratios (R) between the percentage decrease of Al_{re} and the P/Al molar ratio expressed as a percentage (5, 8, 17 or 50%). These ratios may be used as an indicator of the capacity of phosphate ions to decrease the aluminum readily extractable by 8-hydroxyquinoline. These results show that increasing the P/Al molar ratios increased the percentage decrease of Al_{re} in all the suspensions aged 5 or 18 mo, but usually decreased the R values (Table 2). For example, in the suspension at OH/Al = 1.0 aged 18 mo, by increasing the P/Al ratio from 0.05 to 0.5, the percentage decrease of Al_{re} increased from 10 to 31.8 whereas the R values decreased from 2.0 to 0.6. These data suggest that at the lower P/Al molar ratios (Al present in larger excess than phosphate), the more Al was removed for each phosphate ion added. Our results seem to confirm the findings of Hsu (1975) that phosphate reacts completely with Al only in the presence of a large excess of Al ions and that the higher the P/Al molar ratio, the higher the amount of phosphate re-

maining in solution. Indeed the fixation of phosphate ions makes the surface of the hydrolytic products of aluminum more negative at all pH values (Bowden et al. 1980), probably preventing the further adsorption of other phosphate ions, mainly at higher P/Al molar ratios.

Kinetics of Aluminum Extraction

Table 3 shows the percentages of aluminum extracted by 8-hydroxyquinoline after 3, 6, 18 and 48 h from the OH-Al-suspension at OH/Al = 1.5 aged 18 mo after addition of increasing amounts of phosphate (P/Al from 0 to 0.5). According to Turner (1968, 1969) and Turner and Ross (1970), 3 h of contact should be sufficient to extract all the soluble species of aluminum as well as an initial solid phase present in partially neutralized Al salt solutions.

Our results show that in the absence or presence of phosphate, aluminum was not completely extracted after 3 h. In the absence of phosphate, aluminum continued to be extracted even after 48 h, although the amount extracted between 3 and 48 h did not exceed 15% of the total amount extracted after 48 h (Table 3). Evidently, in the absence of phosphate, filterable solid species (< 0.025 μ m) of different crystallinity or large and/or well-structured polymers (Hsu and Bates 1964; Turner 1976; Bersillon et al. 1980) could be the species from which Al was extracted after more than 3 h. The Al extracted between 3 and 48 h with respect to the total Al extracted after 48 h was higher from the suspensions

Table 3. Effect of extraction time on the percentage of aluminum extractable by 8-hydroxyquinoline from ultrafiltered OH-Al-suspensions (OH/Al = 1.5) aged 18 mo with differing P/Al molar ratios

Time of extraction (h)	P/Al molar ratio				
	0	0.05	0.08	0.17	0.5
3	47.5	42.7	41.6	37.8	33.3
6	51.1	46.8	43.9	45.5	37.8
18	53.6	49.0	49.4	47.2	39.6
48	55.3	54.1	51.9	52.6	50.3
Percent of Al extracted between 3 and 48 h to Al extracted after 48 h	14.1	21.1	20.0	28.1	33.8

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containing phosphate ions than from those without phosphate. Furthermore, increasing the P/Al molar ratio increased the amount of Al extracted after 3 h.

It is interesting to note that after 3 h of extraction by 8-hydroxyquinoline, 47.5% of aluminum was removed from the suspension at P/Al = 0, whereas only 33.3% was extracted from the suspension at P/Al = 0.5. In contrast, after 48 h of extraction, the amounts of aluminum removed in the presence of different P/Al ratios were similar ranging from 55.3% (P/Al = 0) to 50.3% (P/Al = 0.5; Table 3).

Evidently, the addition of phosphate ions caused the formation of amorphous solid species (Hsu 1978; Violante and Huang 1985) of extremely small size ($< 0.025 \mu\text{m}$) as well as soluble species with a lower charge, as shown, for example, in Fig. 1.

The Al ions from the solid or soluble species are slowly extractable by 8-hydroxyquinoline because of the strong binding of Al with phosphate ions. Such species would prevail in the systems with higher P/Al molar ratios and require longer than 3 h to be extracted.

Kwong and Huang (1977) found that citrate ions decreased the amount of Al precipitated ($> 0.025 \mu\text{m}$) whereas we found that phosphate ions strongly increased the amount of Al_{ne} (Tables 1 and 3) which included precipitated hydrolytic products retained by filtration. Although the exact amount of Al precipitated ($> 0.025 \mu\text{m}$) was not determined in this study, it seems logical to conclude that the large increases of Al_{ne} (Table 1) after addition of phosphate ions were due to the formation of soluble species and/or very fine colloidal particles ($< 0.025 \mu\text{m}$), both very slowly extractable by 8-hydroxyquinoline (Table 3), rather than to the formation of precipitates ($>$

$0.025 \mu\text{m}$) which were retained by ultrafiltration.

In conclusion, the interaction between phosphate ions and the hydrolytic products of aluminum leads to the formation of new solid and/or soluble species and retards the rate of removal of aluminum ions from solution by 8-hydroxyquinoline. The decrease of readily, moderately or slowly extractable aluminum seems to be influenced not only by the amount of phosphate ions added (P/Al molar ratio), but also by the initial OH/Al molar ratio and aging period of the OH-Al-suspensions. Generally at a given P/Al molar ratio, the higher the initial OH/Al molar ratio or the longer the aging period of the OH-Al-suspensions, the lower the amount of Al extracted after 3 h. Lastly, more aluminum was extracted by 8-hydroxyquinoline from 3 to 48 h from the suspensions containing phosphate ions than from those without phosphate.

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Fig. 1. A possible formation of an Al soluble species by the addition of phosphate.

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