

SELECTIVE EXTRACTION OF THE AMORPHOUS Al, Fe AND Si OXIDES USING AN ALKALINE TIRON SOLUTION

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ABSTRACT: A selective chemical dissolution method has been worked out in order to characterize quantitatively amorphous Al, Fe and Si oxides simultaneously in soils. Based on theoretical considerations an alkaline Tiron solution was tried out. Experiments on well-characterized synthetic and natural substrates were carried out in order to find the optimum set of conditions of pH, temperature and reaction time. These are: an alkaline medium consisting of 0.1 M Tiron and buffered at pH 10.5, an extraction temperature of 80°C and an extraction time of 1 h.

INTRODUCTION

The amorphous inorganic soil fraction mainly consists of an ill-defined, more or less hydrated complex mixture of silica and sesquioxides of iron and aluminium. As physical methods are not suitable to extract selectively and quantitatively analyse this amorphous complex, the use of a chemical method is recommended. This method should be able to separate the amorphous and crystalline soil fractions using their different stability and dissolution kinetics. As the oxides of Al, Si and Fe are frequently intimately mixed or even bound together, a simultaneous dissolution of the three elements is advisable. Such a procedure has not been described in literature until now. Therefore, a study was undertaken to find a suitable selective and quantitative extraction method, taking into account the above mentioned purposes.

THEORY

In order to define the problem, the solubility of the Al, Fe and Si species as a function of pH is given in Fig. 1. This figure has been drawn using the equilibrium relations summarized in Table 1, and neglecting non-ideal behaviour of the system. The frequently used values, $10^{-31.7}$ and $10^{-38.5}$ (Table 1) respectively were chosen as the solubility product of the hydroxides of Al and Fe, indicated as AlOx or FeOx. It is clear from Fig. 1 that no simple acid or alkaline solution simultaneously dissolves AlOx, FeOx and SiO₂ in equivalent proportions. In acid medium silica acts as the limiting factor, whereas in alkaline medium iron oxides are insoluble.

However, it is easier to increase the solubility of iron oxides, e.g. by complexation or chelation, than to increase the solubility of the silicate-ion. A complexing agent for iron in alkaline medium, catecholdisulphonic acid di-sodium salt (Tiron), can be used to do this.

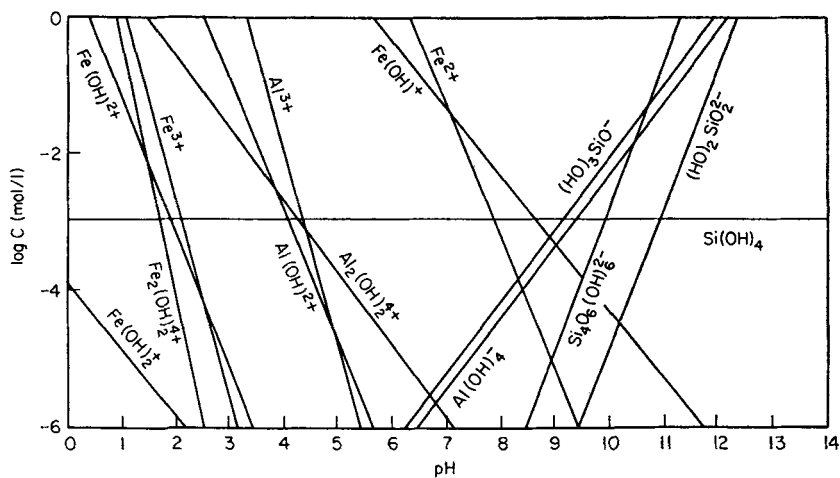
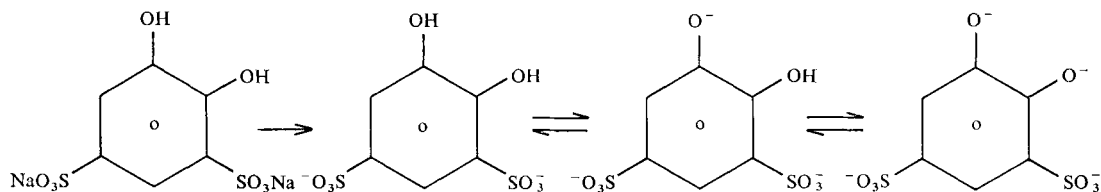


FIG. 1. Solubility diagram of Al(OH)_3 , Fe(OH)_3 , Fe(OH)_2 , SiO_2 and related complexes as a function of pH at 25°C .

TABLE 1. Equilibrium equations related to oxides or hydroxides of aluminium, iron and silicon in aqueous medium at 25°C (Sillen & Martell, 1964; Stumm & Morgan, 1970)

Equilibrium equations	Form	$\log K_s$	$\log K$
$\text{FeO(OH)}_{(s)} + \text{H}_2\text{O} \rightleftharpoons \text{Fe}^{3+} + 3\text{OH}^-$	Goethite	-44.0	
	am.FeOx	-36.5	
	frequently used	-38.5	
$\text{Fe}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{Fe(OH)}^{2+} + \text{H}^+$			-2.60
$\text{Fe(OH)}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Fe(OH)}_2^+ + \text{H}^+$			-4.70
$2\text{Fe}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Fe}_2(\text{OH})_2^{4+} + 2\text{H}^+$			-2.85
$\text{Fe(OH)}_{2(s)} \rightleftharpoons \text{Fe}^{2+} + 2\text{OH}^-$		-15.1	
$\text{Fe}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{FeOH}^+ + \text{H}^+$			-7.15
$\text{Al(OH)}_{3(s)} \rightleftharpoons \text{Al}^{3+} + 3\text{OH}^-$	Gibbsite	-33.51	
	am.AlOx	-29.92	
	frequently used	-31.7	
$\text{Al(OH)}_{3(s)} + \text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}_4^- + \text{H}^+$		-12.4	
$\text{Al}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}^{2+} + \text{H}^+$			-4.96
$2\text{Al}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Al}_2(\text{OH})_2^{4+} + 2\text{H}^+$			-8.06
$\text{Al}^{3+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}_4^- + 4\text{H}^+$			-20.30
$\text{SiO}_{2(s)} + 2\text{H}_2\text{O} \rightleftharpoons \text{Si(OH)}_2$	Quartz	-3.7	
	am.SiOx	-2.85	
$\text{Si(OH)}_4 \rightleftharpoons \text{H}^+ + \text{SiO(OH)}_3^-$			-9.46
$\text{SiO(OH)}_3^- \rightleftharpoons \text{H}^+ + \text{SiO}_2(\text{OH})_2^{2-}$			-12.56
$4\text{Si(OH)}_4 \rightleftharpoons \text{Si}_4\text{O}_6(\text{OH})_6^{2-} + 2\text{H}^+ + 4\text{H}_2\text{O}$			-12.57

The following equilibria of Tiron in aqueous medium can be given:



The acid dissociation constants and the complexing properties of Tiron for Fe^{3+} and Al^{3+} are given in Table 2. Using these data, it can be concluded that an alkaline medium can be created in which the silicate and aluminate anions exist together with the water-soluble iron and aluminium complexes.

TABLE 2. The equilibrium properties of Tiron at 25°C as related to H^+ , Fe^{3+} and Al^{3+} (Sillen & Martell, 1964)

Ion	Equilibrium equation	log <i>K</i>
H^+	$\text{H}^+ + \text{T}^{4-} \rightleftharpoons \text{HT}^{3-}$	12.6
	$\text{H}^+ + \text{HT}^{3-} \rightleftharpoons \text{H}_2\text{T}^{2-}$	7.66
Fe^{3+}	$\text{Fe}^{3+} + \text{HT}^{3-} \rightleftharpoons \text{FeHT}$	10.0
	$\text{Fe}^{3+} + \text{T}^{4-} \rightleftharpoons \text{FeT}^-$	20.7
	$\text{FeT}^- + \text{T}^{4-} \rightleftharpoons \text{FeT}_2^{5-}$	15.2
	$\text{FeT}_2^{5-} + \text{T}^{4-} \rightleftharpoons \text{FeT}_3^{9-}$	11.0
Al^{3+}	$\text{Al}^{3+} + \text{T}^{4-} \rightleftharpoons \text{AlT}^-$	19.02
	$\text{AlT}^- + \text{T}^{4-} \rightleftharpoons \text{AlT}_2^{5-}$	12.08
	$\text{AlT}_2^{5-} + \text{T}^{4-} \rightleftharpoons \text{AlT}_3^{9-}$	2.4

A clear insight into the dissolving mechanism can be obtained by calculating the molar concentrations and the species distribution of the different ions and complexes as a function of pH, and with an excess of AlOx and FeOx . Therefore a series of equations is determined, permitting the total concentration of Fe and Al in solution for a given concentration of Tiron to be calculated as a function of pH.

$$\text{T}_{\text{tot}} = [\text{H}_2\text{T}] + [\text{HT}] + [\text{T}] + [\text{FeHT}] + [\text{FeT}] + 2[\text{FeT}_2] + 3[\text{FeT}_3] + [\text{AlT}] + 2[\text{AlT}_2] + 3[\text{AlT}_3]$$

$$\text{Fe}_{\text{tot}} = [\text{Fe}^{3+}] + [\text{FeOH}^{2+}] + [\text{Fe}(\text{OH})_2^+] + 2[\text{Fe}_2(\text{OH})_2^{4+}] + [\text{FeHT}] + [\text{FeT}] + [\text{FeT}_2] + [\text{FeT}_3]$$

$$\text{Al}_{\text{tot}} = [\text{Al}^{3+}] + [\text{AlOH}^{2+}] + 2[\text{Al}_2(\text{OH})_2^{4+}] + [\text{Al}(\text{OH})_4^-] + [\text{AlT}] + [\text{AlT}_2] + [\text{AlT}_3]$$

T_{tot} , Fe_{tot} and Al_{tot} represent the total concentrations in solution [mol/l.] of respectively Tiron, Fe and Al in equilibrium with the solid phases. Using these equations, the total Fe and Al concentration and fractional abundance of the most important iron and aluminium species in solution were calculated for a combination of amorphous and

crystalline FeOx and AlOx. The results of these calculations, at pH 10.0 and 10.5 and $T_{\text{tot}} = 0.1 \text{ M}$, are given in Table 3.

This table shows that the Tiron distribution with respect to Fe and Al varies as a function of the oxide crystallinity. Increasing crystallinity of one phase induces a decrease of its solubility when the solubility product of the other phase keeps constant. The higher affinity of Tiron for iron becomes clear when both oxides are present in the amorphous

TABLE 3. Total Fe and Al concentration (mol/l) and fractional abundance (%) of the most important iron and aluminium species in solution

pK _s FeOx:		36.5		44.0	
pK _s AlOx:		29.92	33.51	29.92	33.51
pH 10.0	Fe _{tot}	0.032	0.033	10 ⁻⁶	0.015
	Al _{tot}	0.006	0.004	0.054	0.031
	[FeT ₃ /T _{tot}] %	96.37	99.93	0.00	44.29
	[AlT ₂ /T _{tot}] %	3.57	0.00	99.97	54.59
	[Al(OH) ₄ ⁻ /Al _{tot}] %	69.06	99.98	7.38	12.72
pH 10.5	Fe _{tot}	0.033	0.033	10 ⁻⁶	0.025
	Al _{tot}	0.013	0.013	0.063	0.025
	[FeT ₃ /T _{tot}] %	98.83	99.98	0.00	74.27
	[AlT ₂ /T _{tot}] %	1.15	0.00	99.94	24.37
	[Al(OH) ₄ ⁻ /Al _{tot}] %	95.64	100.00	20.12	50.75

TABLE 4. Standard clay minerals

Mineral	Origin	Fraction (μm)	% SiO ₂	% Al ₂ O ₃	% Fe ₂ O ₃
Kaolinite no. 7	Dixie Rubber Pit, Bath, S.C.	0.2-2	44.6	36.1	—
Halloysite no. 29	Wagon Wheel Gap, Colorado	0.2-2	44.8	37.5	—
Nontronite no. 33a	Garfield, Washington	<0.2	42.7	4.2	29.7
Illite no. 35	Fithian, Illinois	0.2-2	50.5	23.7	6.3
Montmorillonite no. 25	Upton, Wyoming	<0.2	54.3	17.4	3.8
Glauconite	Werl, Westfalen	0.2-2	50.2	7.5	13.1

form. A crystalline phase in the presence of an amorphous oxide will practically remain undissolved in the presence of Tiron. Increasing pH from 10 to 10.5 enhances the aluminate concentration, while the concentration of the Al-Tiron complex is decreased.

MATERIALS AND METHODS

The following crystalline and amorphous sesquioxides were used: gibbsite: alcoa product 710, spec. surface 6-8 m²/g (BET), 0-2 μm; goethite: mapico product yellow, spec. surface 22.4 m²/g (BET), 0.4-0.8 μm; amorphous iron hydroxide: prepared by the

addition of NH_4OH to an FeCl_3 solution, spec. surface $173 \text{ m}^2/\text{g}$ (BET); amorphous aluminium hydroxide: prepared after Vanderdeelen & Baert (1972), spec. surface $74 \text{ m}^2/\text{g}$ (BET).

The standard clay minerals used and their characteristics are listed in Table 4.

An extraction method with alkaline Tiron solutions was tested using the above-mentioned amorphous and crystalline substrates. It was the aim of the authors to find optimum experimental conditions of pH, temperature and reaction time. The criterion evaluated was a maximum dissolution of the amorphous products together with a minimum solubility of the crystalline fraction. The pH-values varied between 9.5 and 11.0, using 0.1 N Na_2CO_3 buffers, temperatures from 80 to 100°C were necessary because complexation reactions need a high activation energy. Reaction times from 0.25 to 1 h were used. The Tiron concentration was taken as high as possible, but within the practical limit of 0.1 M. All extractions were done in closed plastic containers.

Before any determination, Tiron and eventually soil organic matter were destroyed. For the Al and Fe determination, HClO_4 destruction was used during 0.5 h at 250°C . For the Si analysis, 50 ml teflon cylinders containing the samples were dipped in a paraffin bath for 2 h at 200°C .

After the destruction of organic matter Si in the samples was taken up in 1 N NaOH. Iron was analysed using the O-phenanthroline method of Toth *et al.* (1948); aluminium using eriochromcyanine R (Vanderdeelen *et al.*, 1973), and silicon using the ammonium molybdate method (Weaver *et al.*, 1968).

RESULTS AND DISCUSSION

In order to find the optimum condition of pH, temperature and reaction time, different combinations of these parameters were tested. In these preliminary runs with 25 mg sesquioxide per 100 ml 0.1 M Tiron solution, it was seen that amorphous AlOx was

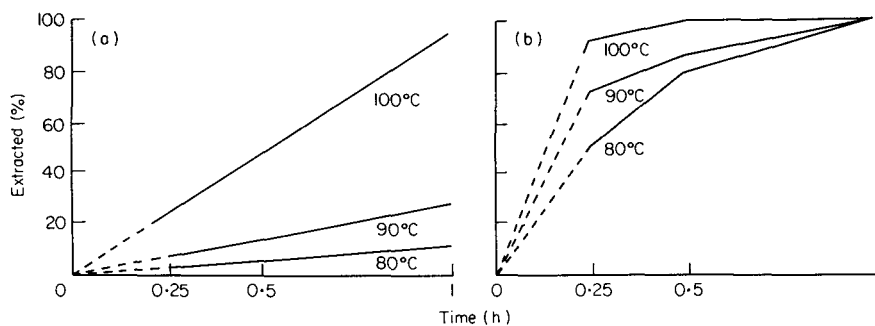


FIG. 2. Percentage gibbsite (a) and amorphous FeOx (b) extracted under different conditions.

completely dissolved under gentle conditions (pH 10.0, 0.25 h, 80°C) whereas goethite remained intact even under severe conditions (pH 11.0, 1 h, 100°C). The optimum set of experimental conditions, however, should be the one whereby the amorphous iron hydroxide completely dissolves and the crystalline aluminium hydroxide only dissolves at a minimum rate.

The experimental results, obtained at different pH values, temperatures and reaction times for gibbsite and amorphous FeOx, are presented graphically in Fig. 2. This figure clearly illustrates that the percentage of dissolved substrate increased with increasing pH and temperature as well as reaction time. At 100°C, crystalline AlOx was dissolved considerably, except for the conditions pH 10.0 and 0.25 h. Under the same conditions, however, only 51.3% amorphous FeOx was dissolved. Also at 90°C, too much of gibbsite was dissolved, while the dissolution of the amorphous FeOx was complete. The condition,

TABLE 5. Fraction per cent solubilized from 500 mg samples in 100 ml 0.1 M Tiron solution at pH 10.5 and 80°C by three successive extractions (A, B and C) of 1 h each

Mineral	Al ₂ O ₃			Fe ₂ O ₃			SiO ₂		
	A	B	C	A	B	C	A	B	C
Kaolinite	2.81	1.95	1.58	—	—	—	1.54	1.01	0.82
Halloysite	3.22	2.77	2.52	—	—	—	2.34	2.10	2.05
Illite	2.21	1.65	1.25	12.78	1.76	1.08	1.11	0.74	0.58
Nontronite	10.77	10.23	9.55	5.02	4.93	4.79	5.07	4.12	3.56
Montmorillonite*	1.01	—	—	3.32	—	—	1.02	—	—
Glauconite	4.58	3.48	2.70	3.80	1.53	1.26	1.80	1.66	1.64
Goethite	—	—	—	0.25	0.18	0.14	—	—	—
Gibbsite	13.51	12.29	8.66	—	—	—	—	—	—

* Only one extraction was done because of very difficult filtration on millipore.

TABLE 6. Percentage solubilized in different mineral mixtures under the conditions pH 10.5, 1 h, 80°C

	Gibbsite	Amorphous AlOx	Halloysite
% FeOx	100.0	99.0	100.0
% AlOx	13.0	100.0	1.2
% SiO ₂	—	—	1.0

best suiting the proposed criterion was pH 10.5 80°C and 1 h reaction time. At these conditions, the amorphous material was quantitatively dissolved, while the crystalline fraction was only slightly attacked.

Fig. 2 also shows the different kinetics of the dissolution reactions of gibbsite and amorphous iron hydroxide within the experimental conditions. Reaction rates are very high during the first minutes of the reaction for amorphous FeOx, whereas for gibbsite dissolution is linear with time. This is due to the different specific surface areas and different stabilities of the two materials.

The 0.1 M Tiron solution, pH 10.5, was tested in three successive extractions (A, B and C) of 1 h each at 80°C, on a series of standard clay minerals. The experimental results are given in Table 5, and show that gibbsite and nontronite are the most unstable minerals under these conditions. The montmorillonite sample, although of the same particle size

TABLE 7. % SiO₂, Al₂O₃ and Fe₂O₃ dissolved by different methods

Mineral	Proposed method			Follet <i>et al.</i> (1965)						Hashimoto & Jackson (1958)	
	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	Na ₂ CO ₃			Na ₂ S ₂ O ₄			Al ₂ O ₃	SiO ₂
				Cold 5%	Hot 5%	NaOH 0.5 N					
Halloysite	3.2	2.3	—	1.0	2.4	32.0	7.8	—	—	8.2	8.9
Illite	2.2	1.1	12.8	0.1	2.4	3.3	4.6	1.7	1.3	3.5	9.3
Montmorillonite	1.0	1.0	3.3	0.1	2.7	4.7	5.9	1.9	1.4	2.5	12.4
Gibbsite	13.5	—	—	11.2	—	73.7	—	—	—	100.0	—
Amorphous AlOx	100.0	—	—	93.0	—	7.0	—	—	—	100.0	—
Goethite	—	—	0.2	—	—	—	—	—	—	—	—
Amorphous FeOx	—	—	100.0	—	—	—	—	—	—	—	—

as the nontronite sample, was much less soluble. The larger amounts dissolved in the first extraction, particularly from illite and glauconite, suggest that amorphous coatings are removed first, whereas disturbed surface layers of the crystalline matrix are dissolved by further extractions.

Theory shows that in mixed mineral systems the components interact and therefore the dissolution of simple mineral mixtures was studied. The results are given in Table 6 for simple mixtures of amorphous FeOx with gibbsite, halloysite and amorphous AlOx respectively. The mixtures consisted of 25 mg amorphous FeOx and 500 mg gibbsite, 25 mg amorphous FeOx and 500 mg halloysite, 25 mg amorphous FeOx and 25 mg amorphous AlOx. From the results in Table 6 it is clear that the theoretical trends can be verified experimentally. Under the proposed conditions the Tiron solution shows an acceptable selectivity for the amorphous components in mineral mixtures. As shown in Table 6, halloysite is unattacked, only 13% gibbsite is dissolved, while the amorphous components of mixtures are however quantitatively dissolved.

In Table 7 the results obtained with the proposed method are compared with the results of the well-known methods of Hashimoto & Jackson (1958) and Follet *et al.* (1965). There is a good agreement between the results of the proposed method and the cold Na₂CO₃ and Na₂S₂O₄ solutions in the dissolution of Al, Fe and Si oxides from clay minerals. Dissolution is complete for amorphous AlOx by every method. The solubility of gibbsite, however, is much higher in hot Na₂CO₃ and 0.5 N NaOH than could be accepted for selective extraction purposes. Rather high values for SiO₂ are obtained with 0.5 N NaOH in comparison with the proposed method. The high solubility of halloysite Al₂O₃ in hot Na₂CO₃ is striking. Goethite as well as amorphous FeOx are completely dissolved by Na₂S₂O₄, while the proposed method shows a very high selectivity. The extracted Fe₂O₃ values of illite in the Tiron solution and in Na₂S₂O₄ confirm the proposed amorphous character of an FeOx coating.

CONCLUSION

From the experiments on well-defined substrates it can be concluded that the following conditions are optimum in order to separate the amorphous and crystalline soil fractions: an alkaline medium consisting of 0.1 M Tiron, buffered at pH 10.5, an extraction temperature of 80°C and an extraction time of 1 h.

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RÉSUMÉ: Une méthode de dissolution chimique sélective a été imaginée de façon à caractériser simultanément des oxydes quantitativement amorphes d'Al, de Fe et de Si dans les sols. Une solution alcaline de Tiron, basée sur des considérations théoriques, a été mise à l'essai. Des expériences effectuées sur des substrats synthétiques et naturels bien caractérisés ont été exécutées afin de découvrir l'ensemble optimum de conditions de pH, de température et de temps de réaction. Il s'agit d'un moyen alcalin consistant en 0.1 M de Tiron et tamponnées à pH 10.5, une température d'extraction de 80°C et un temps d'extraction de 1 h.

KURZREFERAT: Es wurde ein selektives chemisches Lösungsverfahren entwickelt, um gleichzeitig in Böden vorhandene amorphe Al-, Fe- und Si-Oxide quantitativ zu charakterisieren. Aufgrund theoretischer Überlegungen wurde ein Versuch mit einer basischen Tironlösung unternommen. Es wurden Versuche im Zusammenhang mit gut ausgeprägten synthetischen und natürlichen Substraten ausgeführt, um die günstigste Kombination von pH, Temperatur und Reaktionszeit zu bestimmen. Das günstigste Ergebnis wurde mit einer basischen Lösung von 0.1 M Tiron erzielt, die bei pH 10.5 gepuffert war; die Extraktionstemperatur betrug 80°C und die Extraktionszeit 1 h.

RESUMEN: Se ha concebido un método selectivo de disolución química con objeto de caracterizar cuantitativamente y de manera simultánea los óxidos amorfos de Al, Fe y Si en los suelos. Basándose en consideraciones teóricas se probó una solución alcalina de Tiron. Se efectuaron experimentos sobre sustratos sintéticos y naturales bien caracterizados para hallar el conjunto óptimo de condiciones de pH, temperatura y tiempo de reacción. Estas condiciones son: un medio alcalino consistente en 0.1 M Tiron tamponado a un pH de 10.5, una temperatura de extracción de 80°C y un tiempo de extracción de 1 hora.