*Journal of the European Ceramic Society* **6** (1990) 73–83

# Characterization of the Crystallinity of Silicates by Dissolution Conductimetry*

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(Received 15 November 1989; revised version received 29 January 1990; accepted 30 January 1990)

## Abstract

*The liberation of protons during the dissolution of silica and alumina in dilute hydrofluoric acid leads to an increase in electrical conductivity that can be used to characterize the disorganization state of solids of the silica–alumina system. Experimental data chosen for the characterization are the variation of conductivity ($\Delta\sigma$) associated with the rapid dissolution of the disorganized phase and the specific initial dissolution rate ($r_{si}$). The former allows the determination of a 'disorganization factor' (Fd) from a binary conductimetric diagram experimentally drawn from investigations on pure amorphous silica and alumina. The latter allows interesting comparisons to be made between the chemical reactivity of solids of a given composition and, like the disorganization factor Fd, is well correlated to other parameters related to crystallinity.*

*The proposed method was applied to the characterization of different solids, e.g. silica (quartz, silica gel, microsilica or silica fumes), clay minerals (kaolinite and metakaolinite, montmorillonites thermally activated or not) and synthetic mullites. Both limitations and possible other applications of the method are presented.*

*Die Freisetzung von Protonen während des Auflösens von $SiO_2$ und $Al_2O_3$ in verdünnter Flußsäure führt zu einem Anstieg der elektrischen Leitfähigkeit, die genutzt werden kann, um die Fehlordnung im Festkörper des $SiO_2$–$Al_2O_3$-Systems zu untersuchen. Zur Charakterisierung werden die experimentellen Daten der Änderung der Leitfähigkeit ($\Delta\sigma$), die mit der schnellen Auflösung der fehlgeordneten Phase verknüpft ist, und der spezifischen Auflösungsrate ($r_{si}$) herangezogen. Die zuerst genannten Daten erlauben die Bestimmung eines Fehlordnungsfaktors (Fd) aus einem binären Leitfähigkeitsdiagramm, das aus der Auftragung experimenteller Daten aus Untersuchungen von amorphem $SiO_2$ und $Al_2O_3$ ermittelt wurde. Die zweiten Daten erlauben interessante Vergleiche zwischen der chemischen Reaktivität eines Festkörpers einer gegebenen Zusammensetzung, die, wie der Fehlordnungsfaktor Fd, in guter Übereinstimmung mit anderen Parametern stehen, die sich auf die Kristallinität beziehen.*

*Die vorgeschlagene Methode wurde zur Charakterisierung verschiedener Feststoffe, z.B. $SiO_2$ (Quarz, Silicagel, Mikrosilica oder kolloidales $SiO_2$), Tonmineralien (Kaolin, Metakaolin, thermisch aktivierte und nicht aktivierte Montmorillonite) und synthetischer Mullite, verwendet. Es werden sowohl die Grenzen als auch mögliche andere Anwendungen der Methode dargestellt.*

*La libération de protons lors de la dissolution de silice et d'alumine dans l'acide fluorhydrique dilué conduit à un accroissement de la conductivité électrique qui peut être utilisée pour caractériser l'état de désordre des solides du système silice–alumine. Les données expérimentales choisies pour cette caractérisation sont la variation de la conductivité ($\Delta\sigma$) associée à la dissolution rapide de la phase désordonnée, et la vitesse initiale de dissolution spécifique ($r_{si}$). La première permet la détermination d'un 'facteur de désordre' (Fd) à partir d'un diagramme conductimétrique binaire tracé expérimentalement à partir de résultats obtenus sur la silice et l'alumine pures et amorphes. La seconde permet des comparaisons intéressantes entre la réactivité chimique d'un solide de composition donnée et est, comme le facteur de désordre Fd, bien corrélé aux autres paramètres liés à la cristallinité.*

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* Paper summarized as poster at the International Forum on Ceramics 89 at Limoges, France, 26 September 1989.

*Journal of the European Ceramic Society* 0955-2219/90/$3.50

*La méthode proposée a été appliquée à différents solides comme la silice (quartz, gel de silice, microsilice ou poussières de silice), les argiles (kaolinite et métakaolinite, montmorillonites activées ou non) et les mullites synthétiques. Les limites et les extensions possibles de la méthode sont présentées.*

## 1 Introduction

Chemical equilibria involved during the dissolution of silica and alumina in aqueous hydrofluoric acid solutions can be written

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O \qquad (1)$$

$$H_2SiF_6 \leftrightarrow SiF_6^{2-} + 2H^+ \qquad (1a)$$

and

$$Al_2O_3 + 12HF \rightarrow 2H_3AlF_6 + 3H_2O \qquad (2)$$

$$2H_3AlF_6 \leftrightarrow 2AlF_6^{3-} + 6H^+ \qquad (2a)$$

respectively. As a matter of fact, the reaction rate of chemical attack of the silica surface (and probably of the alumina surface) essentially depends on the concentration of $HF_2^-$ ions[1-3] formed in solution from dissociation of hydrofluoric acid:

$$HF \leftrightarrow H^+ + F^- \qquad (3)$$

$$HF + F^- \leftrightarrow HF_2^- \qquad (3a)$$

The formation of complex fluorosilicic and fluoroaluminic acids, but above all the appearance of protons in solution (reactions (1a) and (2a)), permits the employment of a conductimetric method, either to follow the dissolution kinetics or to determine the lattice crystalline disorganization state of a given solid, owing to the very noticeable differences between the dissolution rates according to whether the solid is in an entirely amorphous state, a partially amorphous state or a crystalline state.

Different types of dissolution curve can be obtained (Fig. 1):

(a) for a crystalline solid, a generally linear variation of conductivity versus time, with a more or less low slope (curve no. 1);

(b) for an entirely amorphous solid, a very high dissolution rate and then a plateau corresponding to the end of dissolution (curve no. 2);

(c) for a partially amorphous solid (called a binary 'amorphous crystal' system in the text), a rapid initial dissolution, part followed by a linear variation of conductivity versus time (curve no. 3); and

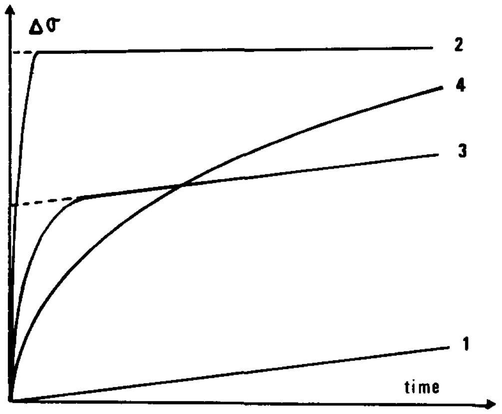

**Fig. 1.** Conductimetric dissolution curves of a crystal (curve no. 1), an entirely amorphous solid (curve no. 2), a partially amorphous solid or binary 'amorphous crystal' (curve no. 3) and a not-well-defined disorganized solid (curve no. 4).

(d) for solids that present a disorganization state that is not well defined (and particularly those whose grains may present a radial gradient of disorganization), a continuous dissolution curve with decreasing slope when the dissolution time increases (curve no. 4).

All these considerations must be applied to a solid with a given grain size distribution.

The kinetic dissolution curve of a solid corresponding to a binary 'amorphous crystal' system (dissolution of type (c)), when investigated by measurement of the weight loss of the solid after dissolution at a given time (gravimetric method), presents two successive parts: a rapidly increasing one (part AB in Fig. 2) up to a given time, corresponding to the superimposition of the dissolution of both the amorphous and the crystalline phases, and a second linear one (BC) with a low slope, corresponding to the slower dissolution of the residual crystalline solid. As previously pointed out by one of us from a theoretical kinetic approach to the phenomenon,[4,5] extrapolation of the linear part

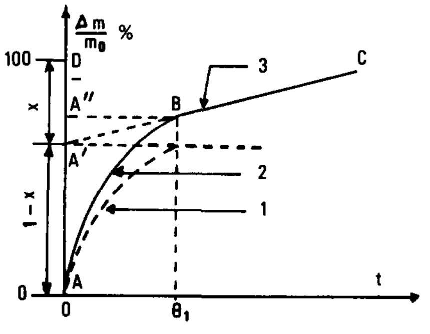

**Fig. 2.** Dissolution curve of a binary 'amorphous crystal' (gravimetric method: $\Delta m/m_0$ = weight variation of the sample): (1) theoretical dissolution curve of the amorphous phase; (2) experimental dissolution of a binary 'amorphous crystal'; (3) experimental dissolution curve of the residual crystal.

BC to $t=0$ gives the weight content $(1-x)$ as a percentage (part OA′ in Fig. 2) of the amorphous phase contained in the sample.

This method is more accurate than that previously proposed by Duvigneaud[6] and reported by De Keyser,[7] who measured the content of the 'amorphous phase' in industrial mullite refractories from the quantity of dissolved solid (part OA″ in Fig. 2) at the dissolution time corresponding to point B.

The dissolution of type (d) is quite different from that of type (c), and no extrapolation method can be used. But the measurement of the initial rate $r_i$ (the limit of slope of the curve when $t=0$) can lead to interesting comparisons.

The same type of curves as those presented in Fig. 1 may be obtained more quickly by using the conductimetric method, as shown by one of us,[8] but the establishment of a correlation between conductivity variation and crystallinity of the sample requires the determination of the expression giving the conductivity variation ($\Delta\sigma$) in relation to the quantity of dissolved solid. What is *a priori* not evident is the relation between electrical conductivity ($\sigma$) and the nature of the dissolved chemical species:

$$\sigma = \sum \mu_i C_i \tag{4}$$

where $\mu_i$ and $C_i$ are the mobility and concentration of the $i$ component in solution, respectively. At a given time of dissolution, these components are non-dissociated HF and a series of ions such as $F^-$, $HF_2^-$, $H^+$, $SiF_6^{2-}$ and $AlF_6^{3-}$. But, to a first approximation and for the entire dissolution of silica or alumina corresponding to the entire consumption of HF, only $H^+$, $SiF_6^{2-}$ and $AlF_6^{3-}$ are the dissolved ions, and proton mobility can be largely considered higher than the mobility of the complex metallic fluoro-anions. Effectively, the most mobile ions are the hydrogen ion and, slightly less so, the hydroxyl ion ($\mu = 316$ and $176\ \Omega^{-1}\ cm^2$ at 291 K, respectively), precisely the ions that may be formed from and may combine to regenerate solvent molecules. The mobility of complex ions is always lower ($\mu \ll 100\ \Omega^{-1}\ cm^2$) than that of hydrogen ion and shows a regular decrease with the increase in ionic weight.[9]

## 2 Experimental

The conductimetric experimental device (Fig. 3), developed in the laboratory to follow dissolution kinetics, is composed of a 1 litre polyethylene reactor, placed in a thermostatized device (25°C) and containing the electrical cell (two platinum discs as electrodes inserted into a PTFE support) and a magnetic stirrer.

The electrical cell is connected to a Tacussel CD6 NG conductimeter, itself connected to a Graphirac BGD electronic recorder.

Dissolution was realized in 0·5 litre of 0·5M HF (the equivalent conductivity of a solution of pure HF does not greatly vary[8] for a concentration higher than 0·2M; Fig. 4). The solid sample for investigation is introduced at the top of the reactor at a time $t=0$. The $\Delta\sigma = f(t)$ curve is directly recorded, and the values of both $\Delta\sigma_0$ and the initial dissolution rate are measured ($r_i$ is given by a computer). When the BET specific surface ($S$) of the sample is known, the specific initial dissolution rate $r_{si}$ (the significance of which is greater than the significance of $r_i$ in

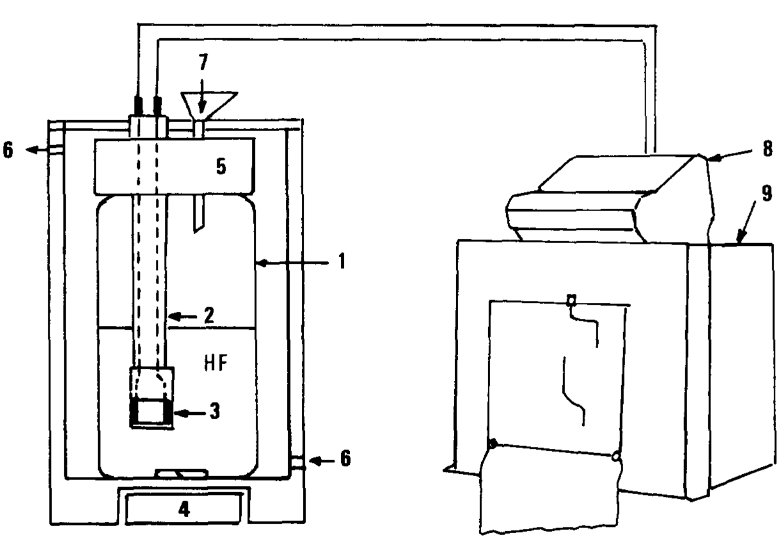

**Fig. 3.** Conductimetric experimental device: 1, polyethylene reactor; 2, electrode support; 3, electrodes (platinum discs); 4, magnetic stirrer; 5, reactor cover; 6, circulation of thermostated fluid (25°C); 7, solid sample introduction; 8, conductimeter; 9, electronic recorder.

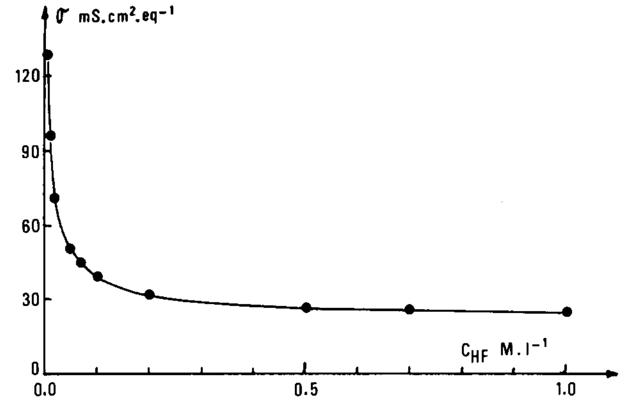

**Fig. 4.** Variation of the equivalent electrical conductivity of hydrofluoric acid aqueous solution versus HF concentration.

chemical kinetics) can be calculated from the expression

$$r_{si} = r_i/S \qquad (5)$$

Sample mass differs according to the nature of the solid investigated. In the conditions of total stoichiometric dissolution in 0·5 litre of 0·5M HF, the masses of pure silica and pure alumina are 2·5 and 2·125 g, respectively. Investigations on a given solid of the silica–alumina system need knowledge of the chemical composition; a simple calculation[8] shows that the mass ($m_0$) to be employed is given by the following expression:

$$m_0 = 2{\cdot}125/(1 - 0{\cdot}0015Ps) \qquad (6)$$

where $Ps$ is the percentage (in mass) of $SiO_2$ in the sample.

To determine if the dissolution process is stoichiometric or not, 2 ml of solution were extracted from the reactor through a filter at a given dissolution time and then analysed to obtain the quantity of Si and Al passed through the solution. All chemical analyses were carried out at the Service Central d'Analyses du CNRS, Vernaison.

## 3 Results and Discussion

### 3.1 Investigation of dissolution of types (a)–(c)

### *3.1.1 Dissolution of pure amorphous silica and alumina*

Generally, the conductimetric curve $\Delta\sigma = f(t)$, obtained with a sample of a given crystallinity (binary 'amorphous crystal'), is identical to curve no. 3 of Fig. 1: the extrapolation, at $t = 0$, of the linear BC part does not give directly the content $(1 - x)$ of the amorphous phase, but gives a quantity $(\Delta\sigma_0)$ that can be related to $(1 - x)$ when the relation between the conductivity variation $(\Delta\sigma)$ and the mass of dissolved solid is known.

This relation was obtained by investigations on two solids used as reference: a pure amorphous silica gel (Rhône–Poulenc Industry sample), at 68·5% $SiO_2$ and 31·5% $H_2O$, and an entirely amorphous alumina, at 91% $Al_2O_3$ and 9% $H_2O$, obtained by Delmastro at Politecnico of Turin (Italy) by thermolysis of a concentrated aluminium nitrate solution in the presence of an organic reductor. Dissolution being realized in 0·5 litre of 0·5M HF and taking into account the maximum quantities of silica and alumina that can be dissolved under these conditions, dissolution experiments must be made with maximum sample masses of 3·65 and 2·335 g for the silica gel and amorphous alumina samples, respectively. (Dilution of HF solution by the quantity of water initially contained in the two solids is <0·2% and is negligible.)

Dissolution is very rapid and complete after two or three minutes, and the conductimetric curve is like curve no. 1 of Fig. 1. Experiments made with increasing sample masses up to the maximum values previously given allow us to obtain the $\Delta\sigma = f(m)$ curves (Fig. 5, an example of the dissolution of silica), where $m$ is the mass of silica or alumina; these two curves are of the same form and can be represented by the following empirical expression (obtained by computing the experimental results):

$$\Delta\sigma = Am/(1 - Bm + Cm^2) \qquad (7)$$

with $A = 7{\cdot}1$ and $B = C = 0{\cdot}118$ for silica, and $A = 1{\cdot}476$, $B = 0{\cdot}071$ and $C = 0{\cdot}091$ for alumina. A theoretical approach justifying eqn (7), and based on the values of the equivalent conductivity of fluorosilicic or fluoroaluminic acid given by Onsager's

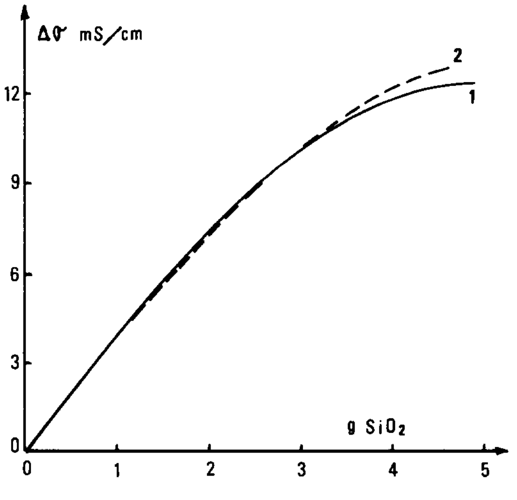

**Fig. 5.** Variation of the conductivity of 0·5M HF solution versus weight of silica gel dissolved: (1) experimental curve (full line); (2) curve given by theoretical modelling (dotted line).

expression, has been given elsewhere;[8] this approach leads to a curve not greatly different from the experimental one (Fig. 5).

This result has led us to draw a binary conductimetric diagram for the dissolution of the phases of the silica–alumina system in 0·5 M HF.[8,10,11]

### *3.1.2 Establishment of the binary conductimetric diagram*

Two extreme points of the diagram are known (results obtained by dissolution of both pure amorphous silica and alumina: $\Delta\sigma_0 = 12{\cdot}32$ and 2·56 mS/cm for pure amorphous silica and pure amorphous alumina, respectively). The fact that the conductivity variation associated with the total dissolution of one mole of alumina is lower than that associated with dissolution of one mole of silica indicates that fluoroaluminic acid is less dissociated than fluorosilicic acid.

The drawing of the complete diagram was possible from both experimental points and points obtained from calculation from the curve $\Delta\sigma = f(m)$.

Experimental points were obtained by mixing, in different proportions, two solutions prepared by dissolution of 2·5 g of silica (3·65 g of silica gel) or 2·125 g of alumina (2·335 g of amorphous alumina sample) in 0·5 litre of 0·5 M HF, on the hypothesis that mixing the two solutions does not lead to a significant volume variation ('dilute solution' approximation). By dilution of the prepared mixed solutions with different quantities of 0·5 M HF, it was possible to prepare $HF–H_2SiF_6–H_3AlF_6$ solutions at different concentrations, the conductivity of which allows one, with the aid of an HP 86 microcomputer, to draw the binary conductimetric diagram containing a lattice of abacus (Fig. 6). Experimental results have confirmed those obtained by calculation from eqn (7).

This system of abacus allows one to characterize the disorganization state of a solid (or the content of the amorphous phase in a binary 'amorphous crystal' system) by graphical determination of the 'disorganization factor' (*Fd*) given by

$$Fd = m/m_0 \quad (\text{with } 0 \leq Fd \leq 1) \qquad (8)$$

where $m$ is the dissolved mass (calculated from the measurement of $\Delta\sigma_0$) and $m_0$ the mass of the sample submitted to dissolution and given by eqn (7).

For a solid at *Ps*% $SiO_2$ and containing a given content of the amorphous phase, and on the hypothesis of a stoichiometric dissolution in HF, the $\Delta\sigma = f(t)$ curve gives, by extrapolation at $t = 0$, the value of $\Delta\sigma_0$. On the conductimetric–composition diagram (the binary conductimetric diagram), the intersection of the vertical line $yy'$ passing through the composition of the solid and the horizontal line $\Delta\sigma_0$ occurs on or between two given values of the *Fd* abacus; *Fd* is given by this intersection (for example, point A in Fig. 6, with $Fd = 0{\cdot}62$).

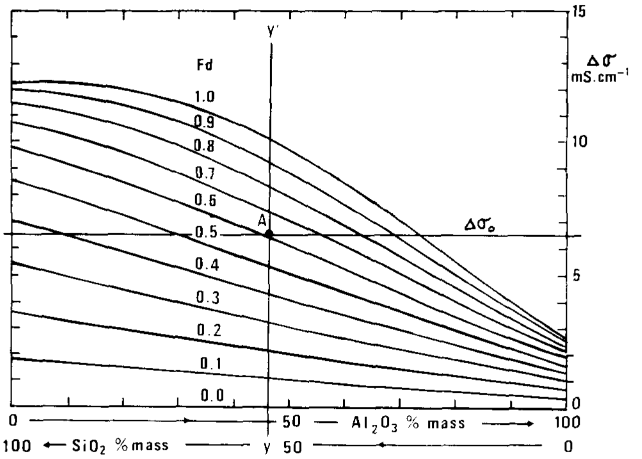

**Fig. 6.** Binary 'conductivity–composition' diagram. To keep the figure clear, representations of intermediate values of *Fd* (by increments of 0·02) have not been drawn.

For a solid that is entirely amorphous, the dissolution curve presents a rapid increase of conductivity followed by a horizontal plateau; this leads to a $\Delta\sigma_0$ value placed on $Fd = 1$ (the upper abacus in the diagram).

A well-crystallized solid leads to a value of $\Delta\sigma_0$ equal to zero, which corresponds to $Fd = 0$ (a point on the abscissa of the diagram).

### *3.1.3 Non-stoichiometric dissolution*

All considerations previously described require that dissolution is stoichiometric.

In the case of a non-stoichiometric dissolution, it is necessary to determine, by chemical analysis, the quantity of species passed into the solution at two points on the linear part of the $\Delta\sigma = f(t)$ curve. This allows one to fix the composition point (% $SiO_2$) on the abscissa of the diagram.

### *3.1.4 Examples of exploitation of the diagram*

The binary conductimetric diagram previously proposed has been exploited to determine the amorphous phase content in a solid which presents a stoichiometric or non-stoichiometric dissolution.

### *3.1.4.1 Stoichiometric dissolution*

### *3.1.4.1(a) Dissolution of metakaolinite*

The example chosen concerns the dissolution of metakaolinite, the transitory phase with a disorganized structure resulting from dehydroxylation of kaolinite.

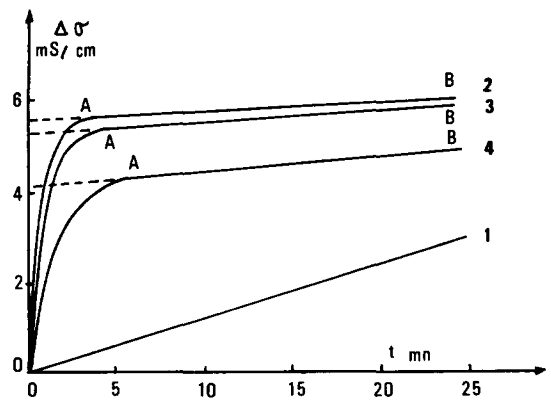

**Fig. 7.** Conductimetric curve for kaolinite (curve no. 1) and for metakaolinite prepared at 638, 732 and 837°C (curves nos 3, 2 and 4, respectively).

The conductimetric dissolution curve of metakaolinite in 0·5M HF differs greatly from that of the raw kaolinite: for raw kaolinite, $\Delta\sigma$ varies linearly with time and $\Delta\sigma_0 = 0$ (curve no. 1, Fig. 7); for metakaolinite, the curve is typical of a binary 'amorphous crystal' solid (curve nos 2–4, Fig. 7). The determination of chemical species passed into solution after 5 and 10 min points out the stoichiometric character of the dissolution (molar ratio $SiO_2/Al_2O_3 \simeq 2{\cdot}0$, Table 1), which corresponds to 54% $SiO_2$ (by weight) in the dissolving solid (point A on the abscissa of the binary diagram, Fig. 8). Point B, which defines the *Fd* value, is obtained from the value of $\Delta\sigma_0$ measured on Fig. 7.

The application of this method to a series of metakaolinite samples,[12,13] prepared between 500 and 987°C, has shown that *Fd* was never higher than 0·52 (point B on Fig. 8) and that this maximum value, very different from unity, was obtained for the sample prepared[13] at 732°C.

Thus, with well-defined experimental conditions and for a given raw kaolinite, the disorganization state of metakaolinite depends on the preparation temperature, a phenomenon previously observed by one of us using other experimental methods giving information on the chemical reactivity,[12] short-range disorder index (*Cd*) measured by infrared spectroscopy[14,15] and dissolution enthalpy ($\Delta Hd$).[16,17] But the present data obtained by dissolution conductivity show that metakaolinite is not entirely amorphous (a simple mix of amorphous silica and amorphous alumina corresponding to the chemical $2SiO_2 . Al_2O_3$ formula of metakaolinite, which would give dissolution curve no. 3 in Fig. 9) as the X-ray diagram indicates, but rather a semi-crystalline solid, as supposed by other authors;[18,19] hence, during dehydroxylation of kaolinite, the lattice does not collapse entirely.

**Table 1.** Content of silica and alumina passed into solution at different times during dissolution of metakaolinite prepared at 732°C

| *Time (min)* | *$SiO_2$ (g/litre)* | *$Al_2O_3$ (g/litre)* | *Molar ratio $SiO_2/Al_2O_3$* | *Total dissolved (g/500 ml)* |
|---|---|---|---|---|
| 2 | 0·883 | 0·800 | 1·870 | 0·841 |
| 5 | 1·020 | 0·875 | 1·980 | 0·947 |
| 10 | 1·123 | 0·951 | 2·007 | 1·037 |
| 15 | 1·176 | 1·030 | 1·940 | 1·206 |

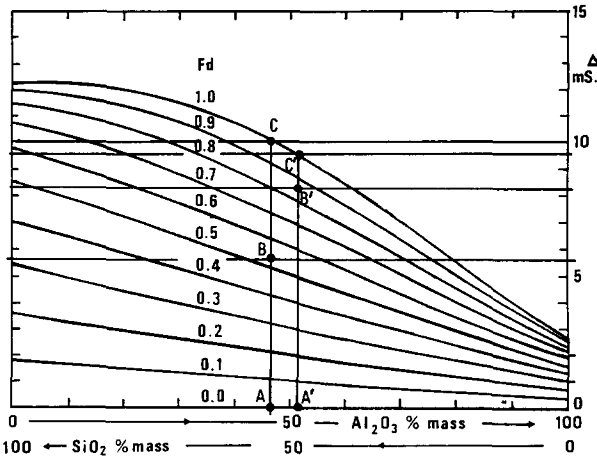

**Fig. 8.** Exploitation of the binary conductimetric diagram in the case of metakaolinite. Points B′ and B give values of *Fd* for metakaolinite prepared at 720°C and ground for 10 h or unground, respectively. Points C and C′ represent theoretical *Fd* values (*Fd* = 1) when samples would be entirely amorphous.

On the other hand, the specific initial dissolution rate also presents its maximum value for a preparation temperature of 732°C, which points out an evident correlation between $r_{si}$ and the other parameters measured (*Fd*, *Cd* and $\Delta Hd$).[13]

### *3.1.4.1(b) Dissolution of microsilica (or silica fumes)*

The silica content (approximately 90% $SiO_2$) of silica fumes (by-products from silicon and ferrosilicon manufacture) is variable according to the producer.[20,21] The material is of very low grain size ($\ll 1\ \mu m$) and silica is generally supposed to be entirely amorphous (with only a large diffuse halo at $d \simeq 4{\cdot}05$ Å on the X-ray diagrams).

Application of the conductimetric method (investigation on 2·5 g of silica fumes) allows the characterization of such materials (Fig. 10); by comparison with the dissolution curve of silica gel used as reference (curve no. 1), it appears that silica contained in silica fumes is less amorphous and that the $\Delta\sigma_0$ value differs according to the origin of the sample (8 and 6·8 mS/cm, which correspond to $Fd =$ 0·46 and 0·38, respectively). These values may be

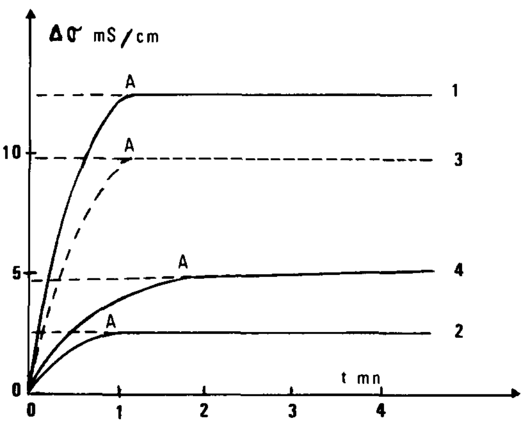

**Fig. 9.** Conductimetric dissolution curves of amorphous silica gel (curve no. 1), amorphous alumina (curve no. 2), metakaolinite ($2SiO_2 . AlO$) supposed to be entirely amorphous (curve no. 3) and metakaolinite (experimental) (curve no. 4).

considered only as approximate because silica fumes are not made entirely of silica and contain some impurities (not burnt carbon), but the difference between the measured *Fd* and unity is too high to consider that silica is entirely amorphous in the samples investigated. On the other hand, after a thermal treatment at 850°C (curve no. 4, Fig. 10), if the slight increase of $\Delta\sigma_0$ is without significance, owing to the burning of residual carbon during heating at 850°C (which increases the silica content in the 2·5-g sample used for investigations), on the contrary, the decrease in the initial dissolution rate is significant and certainly corresponds either to a decrease in the BET specific surface and to a decrease in $r_{si}$ or to a possible modification of the disorganization state of silica after thermal treatment. The latter modification is certainly predominant and is due to a partial recrystallization of silica into cristobalite and tridymite during burning at 850°C, as was observed by Holm and Thronaes.[22]

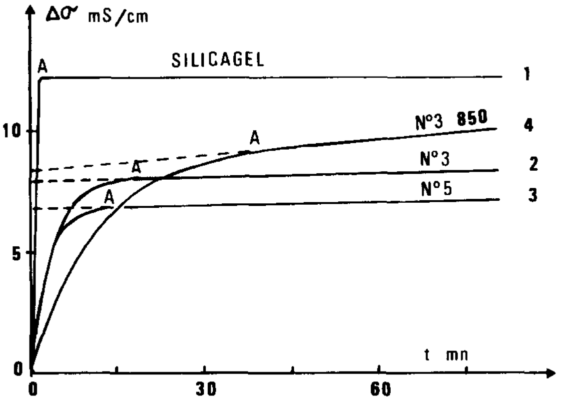

**Fig. 10.** Comparison of conductimetric dissolution curves for silica gel (curve no. 1), silica fumes (two different samples, curves nos 2 and 3) and silica fume No. 5 after heating for 3 h at 850°C (curve no. 4).

This result lets us suppose that the dissolution conductimetry may be used to analyse with great accuracy the process involved during thermal recrystallization of amorphous solids.

*3.1.4.2 Non-stoichiometric dissolution*

Examples of non-stoichiometric dissolution have concerned mechanically activated metakaolinite and synthetic mullites.

*3.1.4.2(a) Mechanically activated metakaolinite*

A sample of metakaolinite, prepared at 720°C, was mechanically activated by grinding for times ranging from one to ten hours. Conductimetric curves have the same appearance as the curve obtained with the unground sample, but grinding leads to a more rapid initial dissolution (curve no. 2, Fig. 11) and a higher value of $\Delta\sigma_0$ as compared with the unground sample. Chemical analysis of the species passed into the solution at different times shows that, after a grinding for only one hour, the dissolution is non-stoichiometric. For example, the $SiO_2/Al_2O_3$ value is equal to 1·61 for a sample ground for ten hours, which corresponds to 48·6% $SiO_2$ in the dissolving solid (point A′ on Fig. 8). The value of *Fd*, given by point B′, is 0·85 against 0·515 for the unground sample. This confirms the semi-crystalline character of metakaolinite and led us to suppose that grinding for a sufficiently long time would lead to the entire disorganization of the lattice.

*3.1.4.2(b) Synthetic mullites (Baïkowski samples)*

Many synthetic mullite samples are not entirely crystalline and contain a certain amorphous part which cannot be accurately determined by X-ray diffraction.[5]

Two samples were investigated by dissolution conductimetry. The $\Delta\sigma = f(t)$ curve presents the same

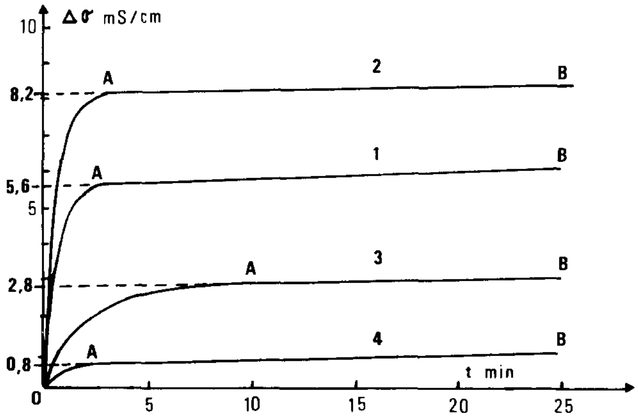

**Fig. 11.** Conductimetric dissolution curve for unground metakaolinite (curve no. 1), ground metakaolinite (curve no. 2) and two different synthetic mullite samples (curves nos 3 and 4).

aspect as preceding examples (curve nos 3 and 4, Fig. 11). The determination of *Fd*, in the hypothesis of a stoichiometric dissolution, leads to a content of the amorphous phase quite different from that previously determined by a gravimetric method.[4,5] The analysis of species passed into solution demonstrates that dissolution is strongly non-stoichiometric, the short-time dissolution of silica being more rapid than the dissolution of alumina (67% $SiO_2$ passes into solution at point A against 39% corresponding to the chemical formula of mullite). Taking this result into account for the two samples, with the $\Delta\sigma_0$ values measured on the $\Delta\sigma = f(t)$ curve, leads to *Fd* values of 0·22 and 0·07, respectively, which agree well with the preceding determination (22% and 7·5% of amorphous phase in the samples) obtained by a gravimetric method.[4,5]

This investigation on synthetic mullites also justifies the validity of the proposed binary conductimetric diagram.

### 3.2 Investigation of dissolution of type (d)

The dissolution curve for type (d) leads to a continuous $\Delta\sigma = f(t)$ curve with a slope continuously decreasing. This occurs, for example, for dissolution of thermally activated montmorillonites[23] (Fig. 12) and for mechanically activated quartz (grinding for a long time up to 360 h) (Fig. 13).[24]

Except for short-time grinding of quartz (up to 5 h), which gives a dissolution curve of type (c) (which confirms the formation of a disorganized but limited superficial layer corresponding to $Fd = 0{\cdot}05$), it is not possible to refer to the binary conductimetric diagram to obtain a value of the disorganization factor *Fd*. Effectively, after lengthy grinding, the behaviour of quartz is quite different from that of a binary 'amorphous crystal' system, as can be seen in Fig. 14, which gives dissolution curves of different mixes of crystalline quartz and amorphous silica gel.

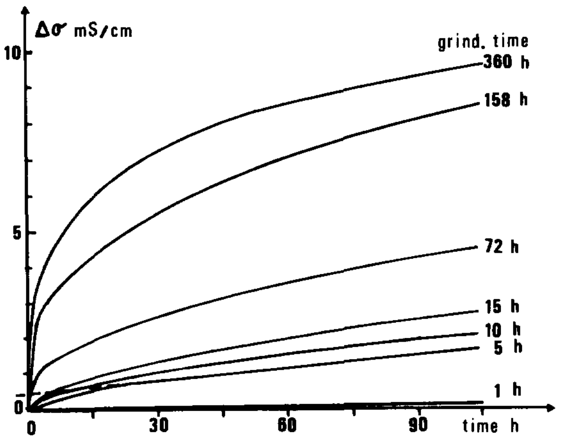

**Fig. 13.** Conductimetric dissolution curves of quartz ground for different times ranging from 1 to 360 h.

Thus the only parameter to be taken into account in the case of curves of type (d) is the specific initial dissolution rate ($r_{si}$).

A clear explanation of the form of the conductimetric curve is difficult.

For dissolution of quartz ground for a long time, the continuous form of the curve is not due to variation of the grain size (all grains <1 μm). Grinding may lead to the formation of a radial gradient of crystalline disorganization inside the grains. Hence the $\Delta\sigma = f(t)$ curve should be the envelope of successive curves of type (c), each successive elementary spherical layer in the grain obeying the binary 'amorphous crystal' process with a decrease in the disorganization state from the edge to the centre of the grain. But a mathematical modelling of such a hypothesis has not yet been possible.

For thermally activated montmorillonites, such an explanation does not hold. The role of grain size must be also discarded because it does not greatly change during calcination of montmorillonites.[25]

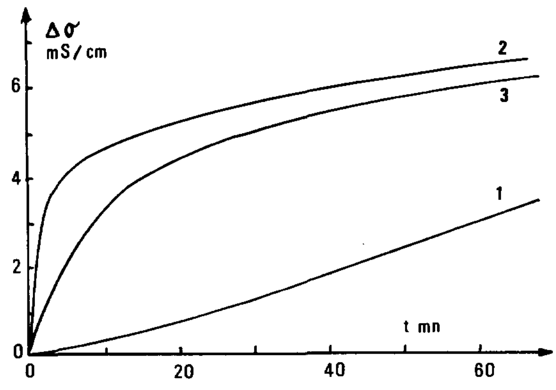

**Fig. 12.** Conductimetric dissolution curves of Na montmorillonite before (curve no. 1) and after thermal activation at 800°C (curve no. 2) or 850°C (curve no. 3).

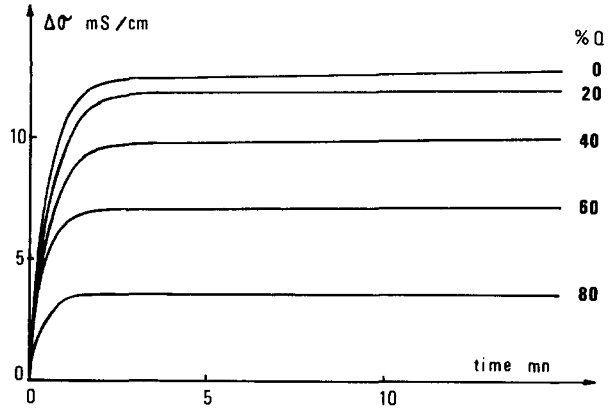

**Fig. 14.** Conductimetric dissolution curve of synthetic quartz–silica gel mixes (wt% of quartz is indicated on the figure).

Independently of these considerations, we must consider the variation of the parameter $r_{si}$:

- —in the case of the dissolution of thermally activated montmorillonite, $r_{si}$ passes through a maximum for samples prepared at about 800°C: that corresponds to a maximum value of the short-range disorder index (*Cd*) of the silica sheet in the lattice, as shown by infra-red spectroscopy,[26] and to the higher reactivity of samples (chemical reaction with saturated calcium hydroxide solution);[23,25]
- —for ground quartz, $r_{si}$ continuously increases and can be correlated either with the increase in the lattice distortion index ($\tau$), measured by X-ray diffraction, or with the short-range disorder index (*Cd*), measured by infra-red spectroscopy.[24]

Thus, in the case of a curve of type (d), the measurement of the specific dissolution rate gives information of the same degree of interest as the non-measurable parameter *Fd* provides, which can be controlled with data obtained by other techniques.

## 4 Limitations of the Method

Two situations can limit the proposed conductimetric method: the non-congruent nature of the dissolution process and the degree of purity of the solid investigated.

### 4.1 Non-congruent dissolution process

The method is not well adapted to test a solid able to dissolve in a non-congruent way; that is to say, to dissolve with reprecipitation of a new solid phase. Effectively, when the reprecipitation is a high-rate process after the increase of conductivity associated with the dissolution of the disorganized phase, it leads, as a result of the supersaturation, to a disappearance of some species in solution (the reprecipitation process) and consequently to a more or less rapid decrease in conductivity with time. This occurs especially with chemical systems containing alkaline-earth oxides, such as calcium, strontium or barium oxide.

A typical example of this phenomenon is given in Fig. 15 and concerns the dissolution of a glass of the $SiO_2.CaO.CaF_2$ system; the increase in conductivity associated with the dissolution of the glass is followed by a decrease in conductivity due to precipitation of a solid phase (probably a hydrated calcium silicofluoride).

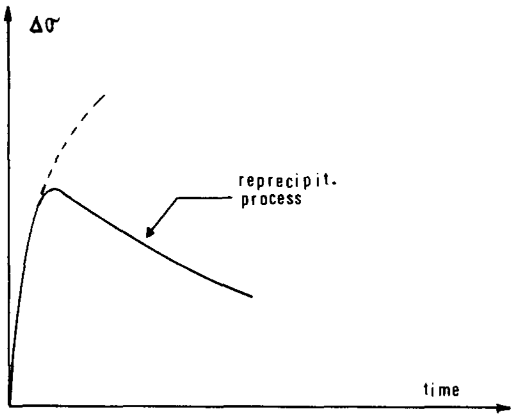

Fig. 15. Conductimetric dissolution curve of a synthetic glass of the $SiO_2$–CaO–$CaF_2$ system.

But, when the reprecipitation is a low-rate process, some valuable information could be obtained, particularly concerning the initial dissolution rate.

### 4.2 Degree of purity of the solid investigated

The electrical conductivity of an aqueous solution is very sensitive to the nature of impurities, and especially those that present a high degree of mobility (see eqn (4)).

An example of the influence of impurities is that of dissolution of fly ash (partially amorphous silicoaluminate powder recovered from purification of waste gas from coal-driven power stations). Gravimetric investigation applied to the determination of the content of amorphous phases in such materials, by using the graphical extrapolation described in the introduction of the paper,[4,5] leads to valuable data. By contrast, investigation by a conductimetric method does not give any accurate information, even when the iron oxide fraction has been extracted by a magnetic process. Dissolution conductimetric curves are of type (c), but there is no direct correlation between the parameter $\Delta\sigma_0$, obtained by graphical extrapolation, and the quantity of amorphous silica and alumina passed into the solution.

The present result confirms the preceding observation of Majumdar and Larner,[27] who have concluded that the conductimetric method is not at all suited to characterizing fly ash, owing to the high level of impurity content in such a material.

## 5 Conclusion

The dissolution conductimetric method is a very simple one and not at all sophisticated. According to the form of the dissolution $\Delta\sigma = f(t)$ curve, it is possible to measure either a conductimetric parameter ($\Delta\sigma_0$) associated with the dissolution of a disorganized phase in an 'amorphous crystal' mix, and/or to measure the initial dissolution rate (or the specific initial dissolution rate when the BET specific surface of the sample is known). These parameters are directly connected to the crystalline structure of the sample investigated.

The recording of the $\Delta\sigma = f(t)$ dissolution curve of a phase of the silica–alumina system allows the determination of the disorganization state of this phase from a binary 'conductimetry–composition' diagram drawn from both experimental and calculated data. However, this requires a knowledge of both the chemical composition of the sample and the nature (stoichiometric or not) of the dissolution process. The former is necessary to determine the weight of the sample to dissolve in a given volume of dilute HF (0·5M HF in the present case), the latter to place the composition parameter on the abscissa of the binary conductimetric diagram, which requires determination of the value of the $SiO_2/Al_2O_3$ ratio in solution at a given time.

The proposed method, which is more sensitive than X-ray diffraction analysis to the detection of a low content of an amorphous or disorganized phase in a solid but nevertheless presents a 'destructive' character owing to the dissolution process involved, can be extended to other binary systems, e.g. silica (or alumina)–iron oxide, silica (or alumina)–zirconia, etc., when the metallic fluoro-acid is sufficiently dissociated in solution. But the dissolution must be congruent to avoid the reprecipitation of a new solid phase (which can sensitively modify the dissolution kinetics) and the solids investigated must be pure and not contain too high a level of foreign components (impurities).

It could be employed to follow the behaviour (ageing) of particular solids, such as gels prepared by sol–gel process.

Another aspect of the determination of the disorganization state of a given solid may concern the approach of processes involved during the devitrification of glass: the conductimetric method would certainly be well suited to follow specific structural evolutions, such as those that occur, for example, in ceramic fibres after a comparatively long time in industrial furnaces and in glass–ceramics during manufacture.

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