# Development of a Bleaching Process for a Kaolin of Industrial Interest by Oxalic, Ascorbic, and Sulfuric Acids: Preliminary Study Using Statistical Methods of Experimental Design

**4 AUTHORS**, INCLUDING:

Francesco Veglio
Università degli Studi dell'Aquila
**213** PUBLICATIONS **4,628** CITATIONS

SEE PROFILE

Luigi Toro
Sapienza University of Rome
**134** PUBLICATIONS **2,076** CITATIONS

SEE PROFILE

+ +

**1680** *Ind. Eng. Chem. Res.* **1996,** *35,* 1680−1687

# Development of a Bleaching Process for a Kaolin of Industrial Interest by Oxalic, Ascorbic, and Sulfuric Acids: Preliminary Study Using Statistical Methods of Experimental Design

**F. Vegliò,\* B. Passariello,[†] L. Toro, and A. M. Marabini[†]**

*Dipartimento di Chimica, Ingegneria Chimica e Materiali, Università degli Studi de L'Aquila,
67040 Monteluco di Roio, L'Aquila, Italy, and Istituto per il Trattamento dei Minerali CNR,
via Bolognola, 7, 00138 Rome, Italy*

In the present work a preliminary study of iron removal from a yellow kaolin supplied by ECC International (Europe) Ltd. was performed using mainly oxalic and ascorbic acids in sulfuric acid solutions. The aim of the initial phase of research was to determine the effects of the main factors which can potentially influence the iron-removal process. Two-level fractional factorial experimentation was thus utilized to establish the main factors having an influence on the iron removal and to define a subsequent experimental test design. The factors involved in this study were: temperature, concentration of oxalic and ascorbic acids, mineral concentration, mixing conditions, and concentration of the sulfuric acid. The experimental results shown that the effect of oxalic and ascorbic acids and of the temperature are the most important. In the investigated conditions, the maximum iron extraction yield was 43−45% after 3−4 h of treatment indicating a limit of iron removal for the mineral. Further study is in progress to define the best operative conditions considering the economic point of view.

## Introduction

The problem of the dissolution of ferric oxides is of particular interest for the producers of industrial minerals like kaolin, since many major deposits of such materials are contaminated by small amounts (0.5−3%) of iron minerals (Groudev et al., 1978).

The presence of submarginal quantities of ferric and/or ferrous iron in kaolin, quartz sand, and clay can prevent their use for ceramics. In particular iron(III) gives an orange tint to kaolin thus greatly lowering its market value (Yan et al., 1978). Ferrous iron is also undesirable in ceramics because it is oxidized into ferric iron when the products are kilned.

Considerable efforts have been made to remove iron contaminants by physical and chemical means. However, physical separation techniques such as flotation are generally less effective for iron removal than chemical bleaching. HGMS (high-gravity magnetic separation) or blending processes are also employed in the beneficiation of industrial minerals (Guimares et al., 1987).

Conventional chemical bleaching is performed by means of reagents such as sodium hypochlorite, sulfur dioxide, and sodium dithionite (Conley and Lloyd, 1970). The maximum degree of whiteness (a measure of the reflectance of the mineral using ASTM E313 considering $BaSO_4$ or PTFE as standard) that can be attained with a kaolin is around 85−88%, because sodium acid sulfite cannot reduce and eliminate all the iron present in different chemical forms. Thus there is considerable interest in the development of alternative technological methods such as organic acid leaching which may be more effective and environmentally acceptable.

The use of different inorganic and organic acids or complexing agents in the dissolution of iron compounds has been the subject of a number of theoretical and experimental studies. Most of these are focused on the mechanism of dissolution on hematite and magnetite dissolution, using different chemicals and experimental conditions.

In particular, as regards the dissolution of iron oxides, protonation of surface sites weakens metal-oxygen lattice bonds, accelerating the rate of detachment (Stone and Morgan 1987), and leaching with different acids was proposed (Patermarakis and Paspaliaris, 1989).

The reduction of ferric to ferrous iron brings about a large increase in the rate of dissolution, because of the greater lability of the Fe(II)−O bond compared to the Fe(III)−O bond (Baumgartener,1983). This is attributable to the fact that the charge-to-radius ratio is smaller when the surface metal species are in the lower valence form, which results in a weakening of the metal−oxygen bonds to the lattice (Waite and Morel, 1984). For example Stone and Morgan (1987) showed that Fe(II)-phase amakinite is more soluble than Fe(III)-phase hematite over a wide pH range.

Reductive dissolution of iron oxide minerals by organic reagents has been investigated by several researchers, and many experimental studies on the basic mechanisms involved have been published (Blesa and Maroto, 1986; Borghi et al., 1989; Dos Santos Afonso et al., 1990; Segal and Sellers, 1984; Torres et al., 1990). The mechanism of reductive dissolution was described by Stone and Morgan (1987). Their model for reductive dissolution involves the following surface chemical reactions: diffusion of reductant molecules to the oxide surface; surface chemical reaction with formation of inner sphere complex (where the metal coordination center binds directly to the ligand which substitutes surface $H_2O$ and OH) or outer sphere complex (where the inner coordination sphere of the metal centre remains intact); release of oxidized organic product; release of reduced metal ion.

Examples have been reported of iron dissolution using various reagents, for instance, EDTA (Litter and Blesa, 1988; Blesa et al., 1984), citric acid (Waite and Morel, 1984), thioglycolic acid (Blesa and Maroto, 1986), ascorbic acid (Dos Santos Afonso, 1990), and oxalic acid

† Instituto per il Trattamento dei Minerali CNR.

(Blesa et al., 1987; Baumgartener et al., 1983; Torres et al., 1990).

It would seem that of all the possible complexing carboxylic ligands, oxalic acid is the most effective for iron removal (Baumgartener et al., 1983; Torres et al., 1990). It is known that this reacts with surface ferric ions to form complexes according to a mechanism of the type reported by Blesa et al. (1987).

Once the surface complex has been formed the dissolution mechanism differs depending on the type of iron mineral concerned. In the case of magnetite, where both ferric and ferrous ions are present on the surface (Cornell and Scindler, 1987; Baumgartener et al., 1983; Sellers and Williams, 1984), the mechanism involves the reductive dissolution of surface Fe(III) ions, and an autocatalytic process attributable to the formation of ferrous oxalate has been observed. Thus, the mechanism is similar to those of reductive dissolution proposed earlier (Stone and Morgan, 1987).

Other scientists (Cornell and Scindler, 1987) have indicated that the dissolution of goethite by oxalate occurs via the release of the ferric oxalate surface complex (Martell and Smith, 1974). According to the sources cited the process results in the very fast dissolution of iron by oxalic acid.

As regards ascorbic acid (Dos Santos Afonso,1990), the mechanism postulated for the release of Fe is the classic one of reductive dissolution (Stone and Morgan, 1987) and it has been shown that the process proceeds at a slower rate than in the case of oxalic acid.

Besides these studies using synthetic iron compounds some process works have been performed to study the iron dissolution from minerals of industrial interest using carbohydrates as reducing agents (Vegliò et al., 1993, 1994) or using microorganisms (Toro et al., 1990; Groudev et al., 1978).

From the analysis of this literature it is possible to note that considerable attention has been paid to the mechanism studies using synthetic minerals such as hematite, goethite, and magnetite and ignoring the complex interactions that can be established in the iron dissolution from industrial minerals such as bauxite, kaolins, silica, and feldspathic sands.

For these reasons, the work reported here deals with leaching by means of organic reagents under different experimental conditions, for dissolving contaminating iron oxides on a kaolin sample. Reducing and complexing agents such as ascorbic acid and oxalic acid were employed.

The use of the oxalic and ascorbic acids was investigated because the literature is very poor of papers regarding their application on the leaching of kaolins. Moreover, their use could be more environmentaly acceptable with respect to the use of other kind of reagents such as sodium hypochlorite, sulfur dioxide, and sodium dithionite (Vegliò et al., 1994).

The objective of the research is to develop a commercially-viable process for the removal of iron from kaolin (noted as YK no. 2) by acid leaching in the presence of reducing and/or complexing agents. The leaching solutions that were adopted were $H_2SO_4$ in the presence of oxalic acid (OA) or ascorbic acid (AA). The main goal of the initial phase of this research (economically supported by a European Union contract) was the estimation of the effects of the main factors which can potentially influence the iron-removal process using ascorbic acid and oxalic acid as reagents in the bleaching treatment. Besides these compounds, sulfuric acid

**Table 1. Chemical Analysis of the Kaolin Sample (YK No. 2)**

| compound | % |
|---|---|
| $SiO_2$ | 48.210 |
| $Al_2O_3$ | 38.030 |
| $Fe_2O_3$ | 0.840 |
| $TiO_2$ | 0.034 |
| CaO | 0.031 |
| MgO | 0.210 |
| $K_2O$ | 0.910 |
| $Na_2O$ | 0.050 |
| L.O.I. | 13.900 |

effect on the iron-removal process was also investigated to compare the action of the organic acids with the inorganic acid. Two-level fractional factorial experimentation was thus utilized to establish the main factors having an influence on Fe removal and to define the subsequent experimental test design. More precisely, experimental work was performed to assess the influence of the factor tested on the iron extraction yield (IEY) and the extraction of other elements such as Si, Al, Mg, and Ca.

## Materials and Methods

A sample of yellow kaolin (noted in this work as YK no. 2), supplied by EEC International (Europe) Ltd., was used for the leaching tests. A complete chemical analysis is reported in Table 1. The results of the mineralogical study, carried out by scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray fluorescence (XRF), reveal that the main mineralogical forms are kaolinite (85%), illite (12%), vermicullite, and mixed-layer minerals (3%).

SEM analysis was performed using a 30 keV Zeiss DSM-960 with thin-windows PGT-SUN microanalysis. XRD analysis was performed with a Siemens D-500 diffractometer with a curved graphite crystal monochromator, Cu tube, proportional scintillation detector, and digital count chain connected to an A/D converter with serial computer interface. XRF analysis was performed on a Philips PW 1400 spectrometer.

The particle-size analysis was performed with a Sympatec laser instrument and centrifugal pipette. For the particle-size analyses on sample YK no. 2 performed using a centrifugal pipet the procedure was as follows: 2.5 g of sample was dispersed by means of 160 mg of hexametaphosphate and diluted in aqueous solution, followed by separation in a centrifugal pipet at 750 rpm, with fractions being taken at 1, 2, 4, 8, 16, 32, and 64 min. The cumulative particle-size analysis curves indicate a $d_{80}$ less than 2.5 $\mu$m (80% of the kaolins is below 2.5 $\mu$m in size distribution) and a $d_{50}$ of less than 1 $\mu$m (50% of the kaolins is below 1.0 $\mu$m in size distribution). Distribution of the particles is not uniform, however. It is bilobed, there being two maxima, one centered at about 0.3 $\mu$m and the other at 0.9 $\mu$m. This distribution may represent the presence of at least two important groups of minerals in the sample (kaolinite and illite).

The leaching tests were carried out in a 2 L glass thermostated vessel which was mechanically stirred (six flate-blade stirrer; diameter 4 cm): a quantity of mineral was suspended in 500 mL of solution containing oxalic acid and/or ascorbic acid regulating the pH with $H_2SO_4$. Ascorbic acid, oxalic acid, and other chemicals were of reagent grade.

Several samples were collected at different times of leaching treatment for the analysis of the liquor leach

**Table 2. Factors and Levels Investigated in the Leaching Tests[a]**

| | factor | level | |
|---|---|---|---|
| | | low | high |
| A | temperature (°C) | 60.0 | 90.0 |
| B | oxalic acid (OA) (g/L) | 0.0 | 8.0 |
| C | ascorbic acid (AA) (g/L) | 0.0 | 4.0 |
| D | mineral concn (g/L) | 100.0 | 300.0 |
| E | stirring (1/s) | 5.0 | 8.3 |
| F | $H_2SO_4$ (mM) | 1.5 | 250 |

[a] The first five factors are used in the ANOVAs shown in Figures 4 and 5.

**Table 3. Factors and Levels Used in the ANOVA Shown in Figure 6 (Time of Treatment = 6 h)**

| | factor | level | |
|---|---|---|---|
| | | low | high |
| A | temperature (°C) | 60.0 | 90.0 |
| B | oxalic acid (OA) (g/L) | 0.0 | 8.0 |
| C | ascorbic acid (AA) (g/L) | 0.0 | 4.0 |
| D | mineral concn (g/L) | 100.0 | 300.0 |
| E | $H_2SO_4$ (mM) | 1.5 | 250.0 |

after centrifugation. The chemical analyses were performed using inductively coupled plasma (ICP) and inductively coupled plasma−mass spectrophotometry (ICP−MS). The instruments used were an ICP-400 and an ICP-MS Elan 5000, both from Perkin Elmer Co. Fe(II) was determined using a UV/visible Cary 1 spectrophotometer from Varian with the *o*-phenanthroline method (Koltoff, 1974). All the experimental tests were planned using techniques of design of experiments (DOE) such as full and fractional factorial designs (Montgomery, 1990; Davies, 1978).

## Experimental Results

**Fractional Factorial Experiments.** The leaching tests were mainly performed to investigate the effect of the selected factors on the iron removal process. The factors and the levels investigated are shown in Table 2. The execution of a full-factorial design would involve the performance of 64 experimental tests, but as it was not considered important at this stage to assess high interactions and as it was wished to ensure an effective reduction in the number of experimental tests, it was decided to implement two fractional factorial designs with 16 tests and 5 factors. The five factors involved in the two-level factorial design were temperature (*A*), oxalic acid concentration (*B*), ascorbic acid concentration (*C*), mineral concentration (*D*), and stirring conditions (*E*). Sixteen leaching tests were carried out instead of 32, taking into consideration a fractional factorial design. The 16 treatments involved in the fractional design were obtained by confounding (Montgomery, 1990; Davies, 1978) the interaction *ABCD* with the effect of factor *E* (defining contrast I, −*ABCDE*).

The treatments of the fractional factorial experiment are shown in Table 4. Test 16 was repeated five times in order to have an estimate of the variance of the experimental error. All these tests were performed at two different concentrations of $H_2SO_4$. In fact, in order to consider the effect of the $H_2SO_4$ as well, the 16 treatments were performed at two different levels of acidity (0.0015 and 0.25 M $H_2SO_4$).

The factors investigated and their levels were selected considering the following reasons:

1. If the effect of some factors, such as $H_2SO_4$, is obvious in the iron dissolution process (Chiarizia et al.,

**Table 4. Treatments of the Fractional Factorial Design (FFD): I, −ABCD as Defining Contrast**

| | | | | | | run no. | |
|---|---|---|---|---|---|---|---|
| treatment | A (°C) | B (g/L) | C (g/L) | D (g/L) | E (1/s) | 1.5 mM $H_2SO_4$ | 250.0 mM $H_2SO_4$ |
| (1) | 60.0 | 0.0 | 0.0 | 100.0 | 5.0 | 1 | 17 |
| ae | 90.0 | 0.0 | 0.0 | 100.0 | 8.3 | 2 | 18 |
| be | 60.0 | 8.0 | 0.0 | 100.0 | 8.3 | 3 | 19 |
| ab | 90.0 | 8.0 | 0.0 | 100.0 | 5.0 | 4 | 20 |
| ce | 60.0 | 0.0 | 4.0 | 100.0 | 8.3 | 5 | 21 |
| ace | 90.0 | 0.0 | 4.0 | 100.0 | 5.0 | 6 | 22 |
| bc | 60.0 | 8.0 | 4.0 | 100.0 | 5.0 | 7 | 23 |
| abce | 90.0 | 8.0 | 4.0 | 100.0 | 8.3 | 8 | 24 |
| cde | 60.0 | 0.0 | 0.0 | 300.0 | 8.3 | 9 | 25 |
| ad | 90.0 | 0.0 | 0.0 | 300.0 | 5.0 | 10 | 26 |
| bde | 60.0 | 8.0 | 0.0 | 300.0 | 5.0 | 11 | 27 |
| abe | 90.0 | 8.0 | 0.0 | 300.0 | 8.3 | 12 | 28 |
| cde | 60.0 | 0.0 | 4.0 | 300.0 | 5.0 | 13 | 29 |
| acde | 90.0 | 0.0 | 4.0 | 300.0 | 8.3 | 14 | 30 |
| bcde | 60.0 | 8.0 | 4.0 | 300.0 | 8.3 | 15 | 31 |
| abcd | 90.0 | 8.0 | 4.0 | 300.0 | 5.0 | 16 | 32 |

1991), the behavior of the acid must be different for different kinds of minerals, with the iron dissolution depending on from the mineralogical nature and accessibility of the mineral to the reagents.

2. The levels of the factors investigated were selected so widely taking into consideration that the main goal of this work is a preliminary study of leaching tests to plan further experimental works. Regarding $H_2SO_4$ concentration, the levels were chosen much larger with respect to the other factors such as OA and AA concentrations considering its effect on the iron-removal process. Previous studies (Vegliò et al., 1993, 1994) have shown that to obtain large iron extraction yields relatively large $H_2SO_4$ concentrations had to be used.

Considering the fractional factorial design, 32 treatments were effected instead of 64. It should be noted that the 6 factors considered could be studied together in a single factorial design of 32 tests. One of the reasons for selecting the solution indicated was to have comparable iron extraction curves. In a fractional factorial design, of course, no treatment can be compared with another belonging to the same experimental design (owing to the principle of orthogonality of the experimental design). In this manner the fractional factorial tests at the two acidity levels can be compared under the same experimental conditions.

**Results of the Leaching Tests: Iron Extraction Yield as Response.** The results of the experimental tests corresponding to the 32 treatments are illustrated in Figures 1 and 2, while Figure 3 indicates the iron extraction yield (IEY) of the repeated tests corresponding to treatment 16. All the leaching tests were randomized.

Two different treatment times (2 and 5 h) were also considered when deriving the analysis of the variance (ANOVA) of the results obtained with the two experimental designs.

In fact, for each experimental condition (i.e., setting the temperature, the OA and AA concentrations, mineral concentration, stirring, and $H_2SO_4$ concentration) different samples were collected to follow the kinetic behavior of the iron dissolution process. In this manner the ANOVA has been carried out for each time independently, so it is possible to observe how the effects of the factors investigated change during the process.

The experimental conditions analyzed via ANOVA may be summarized as follows: case I, 0.0015 M $H_2SO_4$, treatment time 2 h; case II, 0.0015 M $H_2SO_4$,
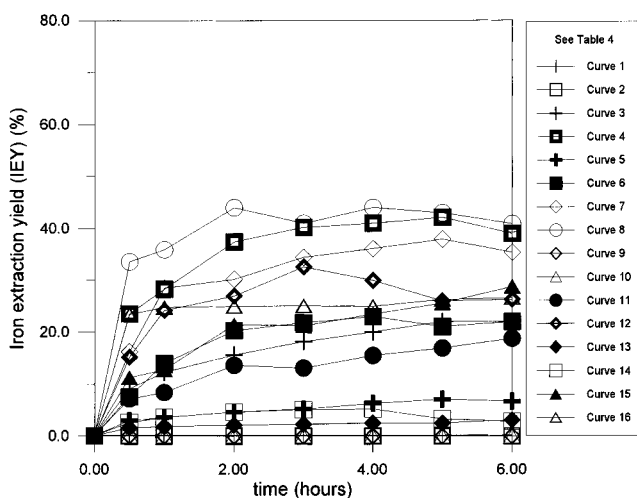
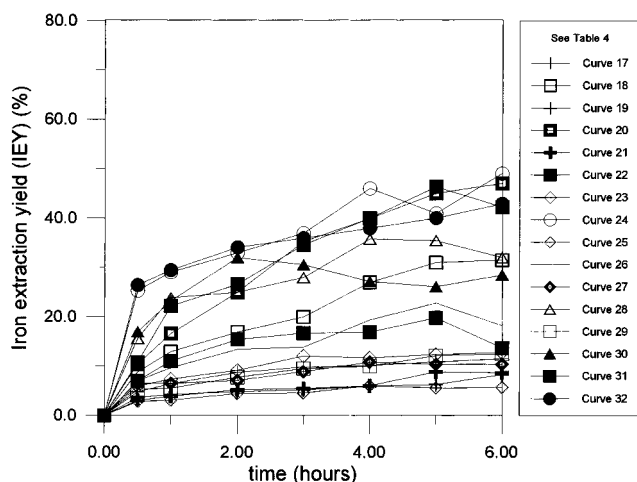**Figure 1.** Leaching of YK no. 2: experimental results in 0.0015 M $H_2SO_4$.



**Figure 2.** Leaching of YK no. 2: experimental results in 0.25 M $H_2SO_4$.
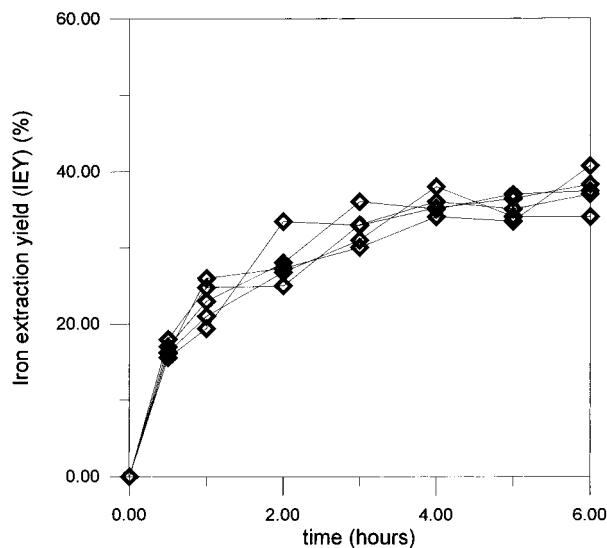


**Figure 3.** Leaching tests of YK no. 2: test no. 16 replicated five times.

treatment time 5 h; case III, 0.2500 M $H_2SO_4$, treatment time 2 h; case IV, 0.2500 M $H_2SO_4$, treatment time 5 h.

The ANOVAs obtained in the four cases were performed to estimate the statistical significance of the estimated effects (Montgomery, 1990). Table 5 shows the ANOVA in case II as an example (the variance of

**Table 5. ANOVA in Case II: 1.5 mM $H_2SO_4$; Time of Treatment 5 h**

|  | effect (%) | MS | significance (%) |
|---|---|---|---|
| A | 7.25 | 210.30 | 99.96 |
| B | 26.30 | 2756.30 | 100.00 |
| AB | 4.00 | 64.00 | 97.50 |
| C | 9.50 | 361.00 | 100.00 |
| AC | −0.25 | 0.25 | 12.20 |
| BC | 0.75 | 2.25 | 35.30 |
| DE | 3.50 | 49.00 | 95.50 |
| D | −6.80 | 182.30 | 99.90 |
| AD | −2.00 | 16.00 | 76.80 |
| BD | −1.50 | 9.00 | 63.50 |
| CE | −0.75 | 2.30 | 35.31 |
| CD | −2.30 | 20.30 | 81.90 |
| BE | −0.50 | 1.00 | 24.04 |
| AE | −3.00 | 36.00 | 91.90 |
| E | −3.25 | 42.30 | 93.90 |

the experimental error was estimated to be 10.5 with 28 degrees of freedom). Figures 4 and 5 illustrate the effects with significance of $p > 95\%$ for the two levels of acidity tested (0.0015 and 0.25 M). The following points emerge from examination of the experimental results:

1. Positively significant factors (those which increase the iron extraction yield) are the main effects of OA ($B$), temperature ($A$), and AA ($C$). The positive interaction $AB$ (temperature−OA) is also important (see Figure 4).

2. A negatively significant factor is the effect of pulp density ($D$) considering, however, only the tests run with 0.0015 M $H_2SO_4$ (see Figure 4): this effect is not significant in the case of the tests with 0.25 M $H_2SO_4$ although there are two kinds of interaction with this factor (see Figure 5).

3. The stirring is not statistically significant except for the positive interaction $DE$ found when considering the ANOVA in case IV (Figure 5).

4. The effect of the OA decreases at lower pH values, for both 2 and 5 h of treatment (Figures 4 and 5). This decrease indicates that the presence of the organic acid is less important at higher $H_2SO_4$ concentrations. The same result also appears to occur with AA. The decrease in the effect of OA at the higher acidity level can be observed in Figures 1 and 2 as well. It can be seen that while the presence of OA is the only factor that increases the iron extraction yield compared with the tests conducted using 0.0015 M $H_2SO_4$ without OA (tests 2 and 4), at the higher $H_2SO_4$ concentration (0.25 M) the presence of OA increases the extraction yield together with the positive effect of the $H_2SO_4$ (tests 18 and 20). In this case the effect of the mineral acid is preponderant, however, compared with the effect of the OA concentration.

5. At lower pH values the effect of temperature is greater than the same effect evaluated at lower acid concentrations.

6. The maximum extraction yields obtained are 43−45% under the most drastic experimental conditions and the most effective reducing−complexing agent is OA (under the experimental conditions adopted).

7. At higher $H_2SO_4$ concentrations the extraction rates are seen to be lower during the first few hours of the process, even though at the end of the treatment (after 5 or 6 h) extraction yields similar to those at the lower acidity level are attained: in this latter case, when OA and AA are present the maximum extraction yields are achieved after 3 or 4 h treatment.

**Further Data Processing.** Considering that the mixing factor does not appear significant for each acidity
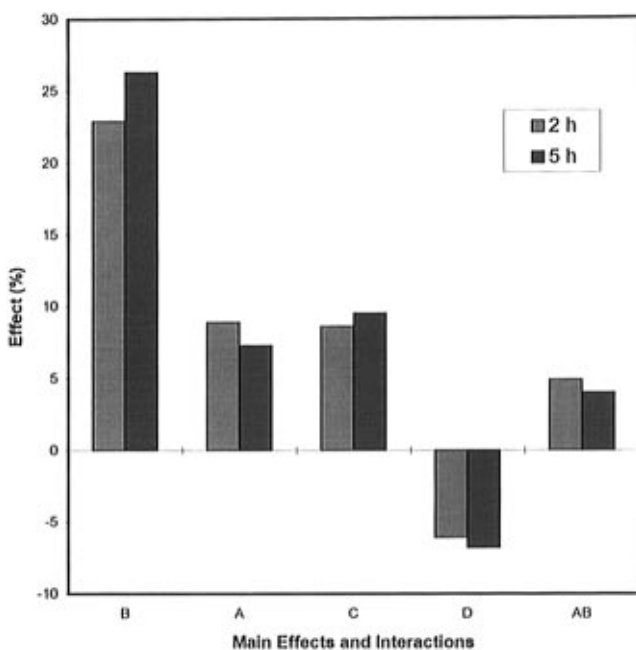
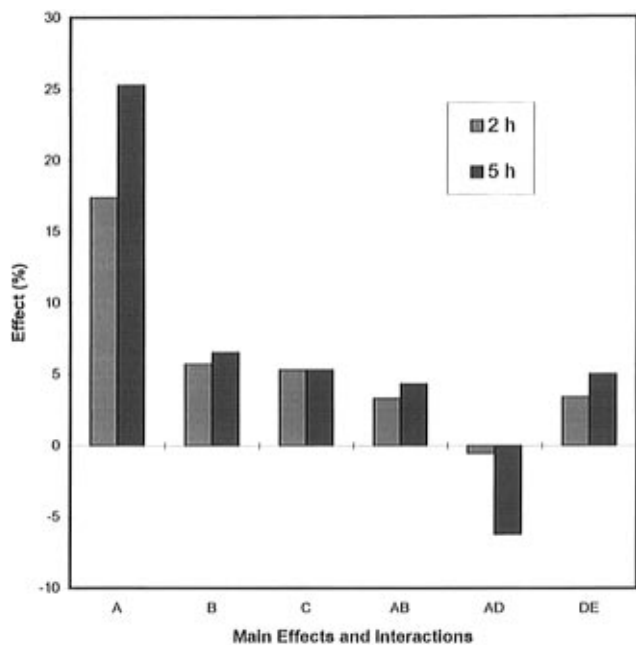**Figure 4.** Results of the ANOVA (case I and II): 0.0015 M $H_2SO_4$.



**Figure 5.** Results of the ANOVA (case III and IV): 0.25 M $H_2SO_4$.



**Figure 6.** Results of the ANOVA of the full factorial design.
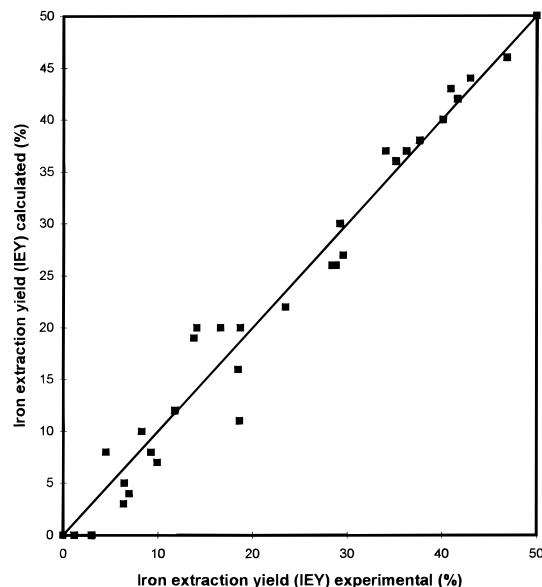


**Figure 7.** Residual analysis of the full factorial design.

level, the 16 treatments effected become the results of a full-factorial design with four factors. The experimental results have thus been reprocessed substituting the factor $H_2SO_4$ concentration with the factor $E$ (stirring condition). The factors and the levels investigated are thus those reported in Table 3 but considering in factor $E$ the effect of the $H_2SO_4$ concentration.

The data were processed by ANOVA (not reported here). The results of the processing are indicated in Figure 6 which illustrates the effects with significance >95%. The mathematical model (Davies, 1978) of the factorial design is

$$Y = 20.53 + 7.91X_2 + 7.85X_1 - 5.22X_2X_5 + 3.4X_3 + 4.22X_1X_5 + 3.03X_5 - 2.47X_4 + 2.35X_1X_2 \quad (1)$$

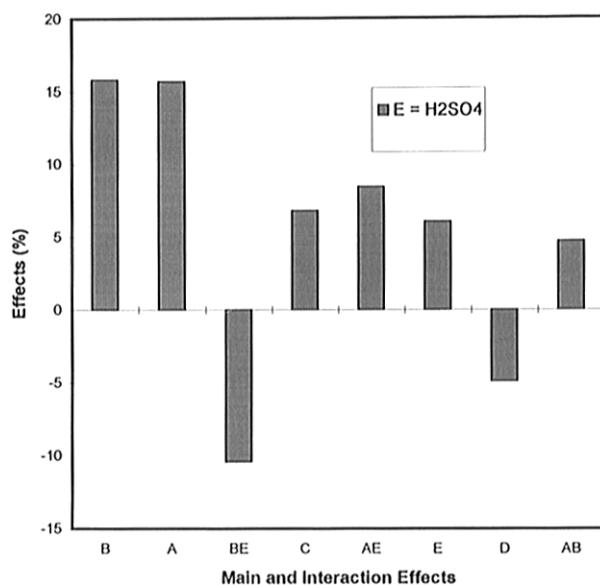where $X_i$ are the factor's levels in coded form ($-1$ or $+1$)

(Davies, 1978). For example the levels of factor A (temperature) has been coded in the following manner:

$$X_1 = \frac{T - 75}{15}$$

where $T$ is the temperature value (°C) for a given trial. Figure 7 shows the residual analysis of the model utilized in the factorial design to check the assumption about the experimental error (Montgomery, 1990). The results of this analysis show good adaptation of the model to the experimental results (Montgomery, 1990).

It ensues from examination of these results that OA exerts a positive effect on the extraction yield and that, together with the temperature effect, it represents the most important factor. A negative interaction is observed with the acid concentration factor (BE): in other words, the effect of OA decreases as the $H_2SO_4$ concentration increases.

At the higher acid concentrations it can be seen that temperature has a greater effect, indicated by the presence of the interaction AE in Figure 6. It is also

evident that at high acid concentrations the effect of treatment time is greater, a lower extraction rate being indicated (Figures 1 and 2).

In other words it would seem that, in the case of the two levels of acidity tested, the dissolution mechanism as a whole differs.

In fact, at lower acid concentrations (0.0015 M) this factor has no effect; OA has a considerable effect, together with AB; the rate is high (in fact there is no great difference between the yield at 2 h and that at 5 h).

At higher acid concentrations (0.25 M) instead, $H_2SO_4$ has a positive effect which reduces the effect of OA, though this still remains positive (negative interaction BE in Figure 6); temperature has a greater effect, something which generally happens in iron dissolution processes where there are no reducing substances (Chiarizia et al., 1991); the dissolution rate is lower in the first minutes of the process with respect to the leaching tests carried out with the lower $H_2SO_4$ level.

So, at low $H_2SO_4$ concentrations, the effect of the acid is much more reduced compared with that of the OA alone, while at high $H_2SO_4$ concentrations the action of the OA is drastically reduced, not least because of the presence of a negative interaction between $H_2SO_4$ and the organic acid. In other words the effect of OA decreases as the concentration of the mineral acid increases. This could be due to the reduced complexing action of the OA toward the iron, owing to a shift to the right of the dissociation equilibrium:

$$-OOC-COO^- + 2H^+ \rightarrow C_2H_2O_4$$
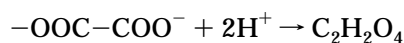
Further confirmation of this hypothesis is provided by consideration of the results obtained for the reduction of the iron in solution. In fact, at the lower $H_2SO_4$ concentrations there are no high concentrations of Fe(II) in solution, while at higher concentrations the ferrous ion predominates.

It would appear evident from these considerations that the dissolution mechanism may be substantially different: at high pH the complexing action of the OA prevails, increasing the dissolution rate, while at low pH values dissolution of the Fe is prevalently by the mineral acid, is more markedly influenced by temperature, and occurs at a slower rate.

It may also be remarked that at the lower acid concentrations the effect of the pulp density is negative, while at the higher $H_2SO_4$ concentrations this effect is not significant. At the moment no hypotheses have been given to explain this result because the main goal of this study was to investigate the effects of the factors investigated in a preliminary way.

To conclude, although AA is seen to exert a positive effect, this is lower than that of OA, perhaps because of the concentrations used. Anyway these concentrations were considered in excess with respect to the stoichiometric conditions calculated considering the iron content in the mineral.

In addition to these effects and interactions, the positive interaction between OA and temperature is particularly important, the action of OA being enhanced at the higher temperatures adopted.

In addition to assessing the effects of the tested factors on the dissolution of iron, experimental tests were also run to evaluate their effect on reduction of dissolved Fe by measuring the Fe(II) present in the leach solutions.
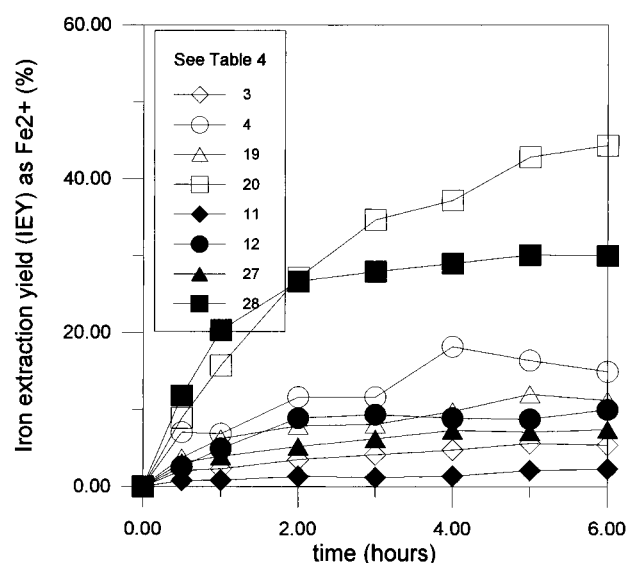


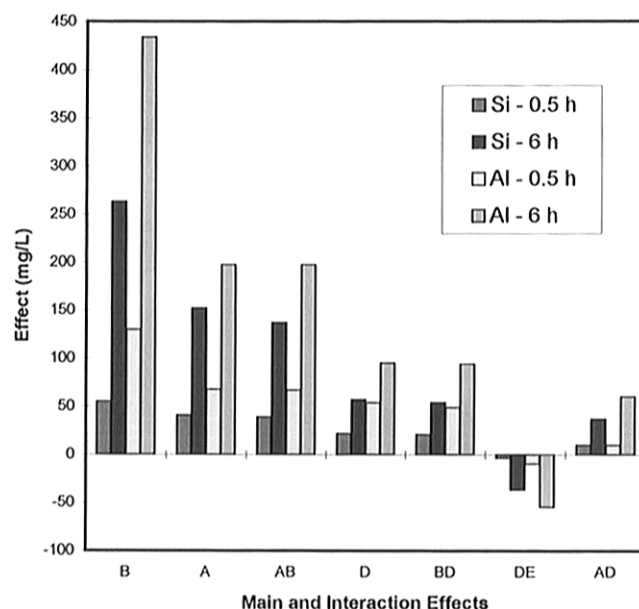**Figure 8.** Effect of some factors on the IEY as Fe(II) in solution.



**Figure 9.** Results of the ANOVA in the Si and Al dissolutions.

Figure 8 illustrates the trends of Fe(II) in solution during the bleaching process at two different pulp densities (10% and 30%), at diverse $H_2SO_4$ concentrations and temperatures. Analysis of the results indicates that (1) reduction of the iron dissolved in the leach solutions is greater in the tests conducted at higher $H_2SO_4$ concentrations (tests 19, 20, 27, and 28) and (2) reduction of the Fe(III) is better at higher temperatures (tests 20 and 28). There is also a positive synergism between acid concentration and temperature. In other words the positive effect of temperature on reduction is further improved at higher $H_2SO_4$ concentrations.

**Process Response: Si and Al Extraction Yields.** Considering the same tests performed for determining the effect of the tested factors on the iron dissolution process, an analysis was made of their influence on the dissolution process of other elements present, such as Si and Al. In this case measurements were made after treatment for 0.5 and 6 h. The experimental results (here not shown) were obtained for the two acidity levels tested, namely 0.0015 and 0.25 M. The data were processed by ANOVA respectively for each element and for each treatment time and acidity level considered.
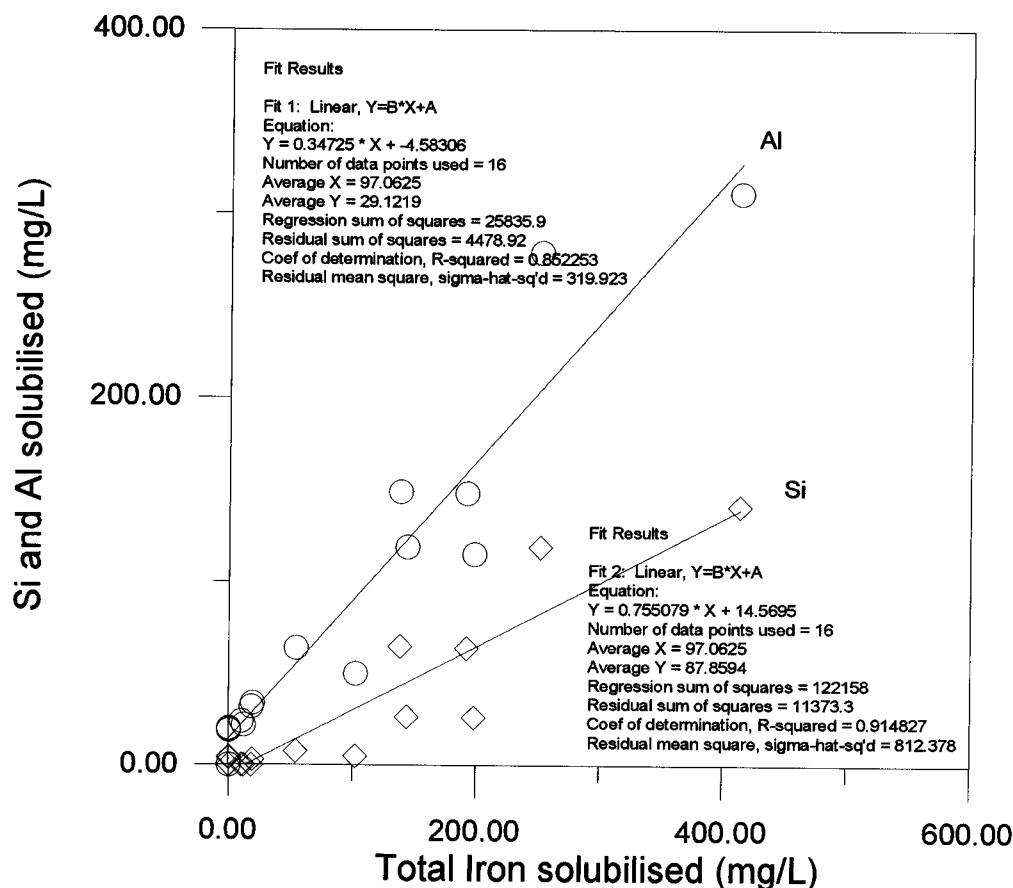
**Figure 10.** Relation among the dissolutions of Fe, Al, and Si.

Figure 9 illustrates the results of the data processing. In particular, the effects having a significant influence on the dissolution of these elements are shown. The results obtained for each element are outlined below. For silicon and aluminum dissolution it is possible to observe the following:

1. In the tests performed with 0.0015 M $H_2SO_4$, OA and temperature improve Si and Al dissolution; there is also a positive interaction between these two factors.

2. Other effects exist but compared with those exerted by OA and temperature these are of minor importance: they include the effect of the pulp and its interaction with OA (BD).

3. At this level of $H_2SO_4$ concentration, the stirring effect is not important even though minor interactions with other factors appear (DE, AE, etc.).

4. Treatment time exerts a considerable effect on Si and Al dissolution.

5. In the tests performed with 0.25 M $H_2SO_4$ the order and importance of the effects change radically. In fact, in this case pulp density and temperature are the most important, while OA has little influence on Si and Al dissolution and indeed it has a negative effect after 6 h of treatment.

6. Stirring (E) and AA (C) are not important factors.

From the analysis of Figure 10 it is possible to observe that the solubilization of the iron from the mineral is strictly related to the Al and Si dissolution. On the other hand, a similar conclusion can be obtained from the ANOVA when considering IEY, Si, and Al dissolution: In fact it is possible to observe that the same effects influencing the IEY act on the Al and Si dissolutions. In particular the OA effect positively increases

the three responses indicating that during the solubilization of the iron compounds, Si and Al are strictly involved.

**Conclusions**

The following points emerge from the analysis of the experimental results:

1. In the tests run at $H_2SO_4$ concentrations of 0.0015 M, OA and temperature markedly improve iron dissolution. The same factors also have a positive effect on the Si and Al dissolutions.

2. In tests run at higher $H_2SO_4$ concentrations (0.25 M), the behavior of the tested factors is different for the dissolution of both iron and other elements such as Si and Al. In this case temperature is the predominant factor, while OA (and some of the reactions thereof) either exerts no effect or even has an adverse effect in some cases. Only regarding iron dissolution does OA have a positive effect (though this is less than that of temperature where the tests with 0.0015 M $H_2SO_4$ are concerned) accompanied, however, by a negative interaction with acid concentration.

3. Further tests are needed to establish more clearly the mechanism of iron dissolution from the kaolin considered. However, the virtual lack of influence of stirring and the strong effect of temperature would appear to point to a heterogeneous process of iron dissolution from the kaolin matrix under chemical control (Levenspiel, 1972). In other words, the fact that stirring has no effect excludes the presence of a kinetic control due to the resistance of the transfer of reagent and/or product matter around the kaolin particle, while the effect of temperature indicates the importance of the

superficial chemical reaction of the reagents with the iron minerals present. The tests do not completely exclude the possibility of resistance to the transfer of reagent and/or product matter to within the particle although the size distribution of the ore could exclude this possibility.

4. While the positive effect of temperature emerges in both tests conducted at the two acid concentration levels, the mechanisms governing the dissolution of iron and the other elements seem different in the two cases. This could indicate that under lower $H_2SO_4$ concentrations the complexing action of OA prevails over the reducing action which occurs at higher $H_2SO_4$ concentrations.

Further studies are in progress starting from these preliminary results to try to understand the mechanism of iron dissolution.

### Acknowledgment

### Nomenclature

$X_1$ = level of temperature in coded form (dimensionless)
$X_2$ = level of oxalic acid concentration in coded form (dimensionless)
$X_3$ = level of ascorbic acid concentration in coded form (dimensionless)
$X_4$ = level of mineral concentration in coded form (dimensionless)
$X_5$ = level of sulfuric acid concentration in coded form (dimensionless)
$Y$ = iron extraction yield (IEY) (%)

### Literature Cited

Baumgartener, E.; Blesa, M. A.; Marinovich, H. A.; Maroto, A. J. G. Heterogeneous Electron transfer as a pathway in the dissolution of magnetite in oxalic acid solutions. *Inorg. Chem.* **1983**, *22*, 2224−2226.

Blesa, M. A.; Maroto, A. J. G. Dissolution of metal oxides. *J. Chem. Phys.* **1986**, *83*, 757.

Blesa, M. A.; Borghi, E. B.; Maroto, A. J. G.; Regazzoni, A. E. Adsorption of EDTA and iron-EDTA complexes on magnetite and the mechanism of dissolution of magnetite by EDTA. *J. Colloid Interface Sci.* **1984**, *98* (2),

Borghi, E. B.; Regazzoni, A. E.; Maroto, A. J. G.; Blesa, M. A. Reductive dissolution of magnetite by solutions containing EDTA and FeII. *J. Colloid Interface Sci.* **1989**, *130*, 2.

Chiarizia, R.; Hortwiz, E. P. New formulations for iron oxides dissolution. *Hydrometallurgy* **1991**, *27*, 339−360.

Conley, R. F.; Llyod, M. K. Improvement of iron leaching in clays: optimizing processing parameters in sodium dithionite reduction. *Ind. Eng. Chem. Process Des. Dev.* **1970**, *9* (4), 595−601.

Davies, O. L.; et al. *The design and analysis of industrial experiments*; Davies, O. L., Ed.; Longman: New York, 1979.

Dos Santos Afonso, M.; Morando, P.; Blesa, M.; Banwart, S.; Stumm, W. The reductive dissolution of oxides by ascorbate.The role of carboxylate anions in accelerating reductive dissolution. *J. Colloid Interface Sci.* **1990**, *138*, 1.

Groudev, S. N.; Genchev, F. N.; Gaidarjiev, S. S. Method of biocatalytic removal of iron from mineral raw materials. Bulgarian patent 29063, 1978.

Guimares, S. J. F.; De Olivera, N.; De Salles, F. L. Purification of registro kaolin by magnetic separation. *Min. Metall.* **1987**, *51* (485), 13−17.

Koltoff, I. M. *Analisi Chimica Quantitativa*; Koltoff, I. M., Ed.; Piccin: Padova Italy, 1974.

Levenspiel, O. *Chemical Reaction Engineering*; Levenspiel, O., Ed.; Wiley: New York, 1972.

Litter, M. I.; Blesa, M. A. Photodissolution of iron oxides. *J. Colloid Interface Sci.* **1988**, *125*, 2.

Martell, A.; Smith, R. M. *Critical stability constants*; Martell, A.; Smith, R. M., Ed.; Plenum Press: New York and London, 1974; Vol. 3.

Montgomerey, D. C. *Design and Analysis of Experiments*; Montgomerey, D. C., Ed.; J.Wiley & Sons: New York, 1991.

Passariello, B. Processo per la deferrizzazione di caolino, sabbie quarzifere, carica per carta, pigmento pomice e materiali per l'elettronica. Italian patent C 04 B33/04, 1989.

Patermarakis, G.; Paspaliaris, Y. The leaching of iron oxides in boehmitic bauxite by hydrochloric acid. *Hydrometallurgy* **1989**, *23*, 77−90.

Segal, M. G.; Sellers, R. M. In *Advances Inorganic Bioinorganic Mechanisms;* Sykes, A. G., Ed.; Academic Press: London, 1984; Vol. 3, p 97.

Stone, A. T.; Morgan, J. J. Reductive dissolution of metal oxides. In *Aquatic Surface Chemistry;* Stumm, W., Ed.; Wiley: New York, 1987.

Torres, R.; Blesa, M.; Matijevic, E. Interaction of metal hydrous oxides with chelating agents. *J. Colloid Interface Sci.* **1990**, *134*, 2.

Toro, L.; Paponetti, B.; Marabini, A.; Passariello, B. Processo per la rimozione del ferro da concentrati di caolino. quarzo ed altri minerali di interesse industriale. Italian Patent 21707A/90, 1990.

Toro, L.; Paponetti, B.; Vegliò, F.; Marabini, A. Removal of iron kaolin ores using different microorganisms: the role of the iron reductase and the organic acid. *Part. Sci. Technol.* **1992**, *10*, 201−208.

Vegliò, F.; Toro, L. Factorial experiments for the development of a kaolin bleaching process. *Int. J. Miner. Process.* **1993**, *39*, 87−99.

Vegliò, F.; Toro, L. Process development of kaolin bleaching using carbohydtrates in acid media. *Int. J. Miner Process.* **1994**, *41*, 239−255.

Yan, L. G.; Yu, Y. J.; Song, S. S.; Nan, H. L.; Cheng, Y. L.; Li, X. M.; Kong, Q. W.; Dai, Y. M. Development of Superconducting High Gradient Magnetic Separator for Beneficiation of Kaolin Clay. *Proceedings of the Second World Congress on Non-Metallic Minerals*, Beijing, China; 1978; p 17-2.

Waite, D.; Morel, F. M. M. Photoreductive Dissolution of Colloidal Iron Oxide: Effect of Citrate. *J. Colloid Interface Sci.* **1984**, *102* (1), 1211−137.