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Self inhibition of aluminum leaching from coal fly ash by sulfuric acid

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Abstract

The coal fly ash (CFA) that is produced by coal fired power plants in Israel is alkaline and contains aluminum that can be leached by different acids. In this work, the mechanism of aluminum leaching from CFA by sulfuric acid is considered. It is shown that higher CFA content, which indicates higher solid to liquid ratio in the leaching suspension, decreases the fraction of leached aluminum by means of sulfuric acid. This behavior constitutes a new unexplained phenomenon, which could not be explained by analysis of the mass action law of the dissolution reactions, but rather by mass transfer considerations. It is shown that the leaching process involves a self inhibition mechanism due to the precipitation of calcium sulfate on the surface and within the CFA particles. The effects of CFA content, acid concentration, temperature, and pre-leaching conditioning, upon leaching rates and yields, were tested.

Increasing the acid concentration produces two opposing effects simultaneously. An increase in concentration of the hydronium ion enhances the dissolution of aluminum, whereas the increase in concentration of the sulfate and the dissolved calcium ions intensifies the formation of calcium sulfate precipitates. These precipitates hinder mass transfer across the surface of the CFA particles, and in this sense they generate a self inhibition effect. Conditioning of the CFA with hydrochloric acid at pH 4 removes 65% of the calcium. Consequently, the conditioned CFA can be leached more efficiently with sulfuric acid. This higher leachability is linked to the reduction in calcium sulfate precipitation on the CFA.

Keywords: Coal fly ash; Aluminum leaching; Self inhibition

1. Introduction

Coal fly ash (CFA) is a residue of coal combustion in power plants. The composition of CFA depends on properties of the raw coal and the conditions under which it is combusted. Typical CFA consists of oxides of silicon, aluminum, iron, calcium and magnesium, and it usually contains trace elements such as (Co, Cr, V, Cu, Pb, Cd, Ni, Mo and Zn). The potential leaching of the major elements from CFA, under different conditions and ambient conditions in particular, was investigated extensively in the last two decades and reviewed by Mattigod et al. [1]. De Groot et al. [2] considered the effect on leaching of liquid/solid ratio and pH in the $4<pH<13$ range, and concluded that pH differences are far more important than ash composition. Harris and Silberman [3] measured the leaching rate by pH 7.4 solutions of chelating agents. Roy and Griffin [4] developed a model for CFA leaching in de-ionized water in a long term leaching session of up to 140 days. Kress [5] monitored CFA leaching at a deep sea dumping site in the Mediterranean sea.

The chemical and mineralogical composition of the CFA are important factors that affect the leaching process as regards efficiency and leachability of metals [4,6–12]. However, none of these works deal with the leaching mechanism of CFA in the presence of concentrated sulfuric acid, where the leaching response is expected to demonstrate different characteristics.

The mechanisms of aluminum leaching from CFA by sulfuric acid involve complicated reactions and mass transfer sequences [13,14]. For example, they involve heterogeneous reactions of aluminum dissolution by H^+ ions, from the CFA particles, and cross diffusion of the reactants and products. The reactants diffuse from the solution bulk toward a CFA particle and the reaction products diffuse away from the particle surface, into the bulk solution.

The production of large quantities of CFA by coal fired power plants presents a worldwide problem. This concerns the Israeli power plants in particular, because they are located along the shore line and close to densely populated

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areas. Consequently, there is a need to utilize the CFA or find suitable ways for its disposal.

The CFA is currently used for the manufacture of cement and as an additive in concrete mixtures. Recent studies showed that the CFA can be used as a primary component in solidified mixtures containing cement and fixed heavy metals [15]. Disposal options at sea or land are limited because of environmental considerations, scarcity of land, as well as handling costs. This calls for the application of additional utilization and disposal methods.

The relatively high aluminum content in the CFA and the presence of other metals in various proportions suggest the possibility of utilization of CFA as a source for recovery of metals. The direct acid leach (DAL) process of Electric Power Research Institute (EPRI) has been thoroughly studied [16–18] but, as yet, it has not reached commercial applications. The chemical processes for recovery of aluminum from fly ash, which were investigated, involve elevated temperatures and pressures. Not withstanding their technological feasibility, these processes were found to be economically inferior to aluminum extraction from bauxite deposits that have higher metal (approximately 60%) content.

Although sulfuric acid is known to be less efficient, as a dissolving agent, than hydrochloric acid, at the same leaching conditions [19], it has an advantage of being a product of the *Thiobacillus* bacteria metabolism, so that it can be used as the main chemical agent in bioleaching processes [20–22]. However, prior to the application of biochemical leaching of CFA with *Thiobacillus* bacteria as suggested by Fass et al. [23] and Shelef et al. [24], the leaching mechanism should be studied.

The purpose of this work is to study and establish the mechanism controlling the leaching process of aluminum from alkaline CFA with sulfuric acid, to provide proof for the self inhibition effect and to determine the conditions in which aluminum leaching can be enhanced. A mathematical model of the leaching kinetics is presented elsewhere [13,14]. The conditions for enhanced leaching are defined here as those, which eliminate retarding factors to mass transfer, of reactants and products, and concurrently improve the kinetics of the process.

2. Materials and methods

2.1. Materials

CFA was supplied by the Israel Electric Corporation from two sources, the 1400 MW Orot Rabin (formerly named Maor David) and the 1100 MW Rutenberg power plants. These power plants are located on the coast along the shore line near the cities of Hadera and Ashkelon, respectively.

Ten samples, each of 10 kg, were obtained from the electric precipitator collection bins of the two coal fired power plants. Five samples were taken from each plant. The samples were collected during 5 days in summer 1993. Each sample was thoroughly mixed in order to increase its bulk uniformity, and then it was stored in a sealed container.

Analytical grade acids were used for leaching. Sulfuric acid (98% w/w) was purchased from Frutarom, Israel. Hydrochloric acid (37% w/w) was purchased from Ridel-deHaen, Germany.

2.2. Chemical analyses

2.2.1. Elemental analyses

Elemental analyses of aqueous solutions were done by flame atomic absorption spectrometry (FAAS) using Perkin-Elmer 460. CFA elemental analysis was conducted according to the ASTM procedure (ASTM, Designated D 3683-78, 1989). According to this procedure the ash is dissolved first by mineral acids, and then the relevant elements in solution are determined by atomic absorption spectrometry. The National Bureau of Standards, standard reference material (SRM) 1633a, was used primarily as a calibration standard for the trace elements.

2.2.2. Control and measurement of pH

The pH was monitored using a Consort r301 pH controller and the El Hama digital pH meter. When the H^+ concentration was above the value corresponding to pH 1, a 1 ml sample of the suspension was taken and diluted so as to give a measurable pH between 2 and 3, and then the actual H^+ concentration in the suspension was determined by calculation.

2.2.3. Sulfates concentration

Sulfates concentration was determined according to the 4500-SO_4^{2-} C gravimetric Standard Method [25].

2.2.4. Characterization of the solid phase

Characterization of the CFA particles and surface composition was carried out by scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS).

EDS provides data on atomic compositions at the surface. This data can be used to formulate stoichiometric relations in order to test and corroborate hypotheses of compositions.

Raw CFA, and samples from leached suspensions, were taken for SEM and EDS analyses. The different CFA samples were prepared under the following conditions: (1) raw or untreated CFA; (2) leaching of 10% raw CFA in suspension by sulfuric acid at pH 1.5; (3) grinding with mortar and pestle of a mixture of sample 2 and 1.2–1.4 mm zirconia beads, and then, after separating the zirconia, washing with water and drying; (4) second stage leaching of CFA from sample 3 with sulfuric acid at pH 1.5; (5) leaching of raw CFA by hydrochloric acid at pH 4.

The samples taken from the suspensions, during the leaching process, were prepared by filtration on 0.2 μm Poretics Polycarbonate membranes, and then they were air dried. The resulting dry CFA powders were mounted on aluminum sample holders with a double stick tape, and then they were coated with gold or carbon (when EDS tests were executed) and examined in a Jeol 5400 SEM, and Voyager EDS of Noran.

The results obtained from the EDS analyses show the surface composition with respect to specific elements. The carbon peaks, resulting from the coating or residual carbon, were eliminated and all calculations were carried out without them.

2.3. Leaching tests

2.3.1. Experimental program

The leaching tests were designed to meet the two objectives of the work, namely, to study the leaching mechanism and its self inhibition effect, and to improve the rate and extent of aluminum leaching. To this end, an extensive experimental program was carried out. The primary leaching test, that is described below, addressed determination of the effects of leaching time, sulfuric acid concentration and CFA content in the leaching suspension. The entire set of experiments follows this approach with some modification as specified below. The effect of stirring method and temperature on the leaching process was also investigated.

A second set of experiments was carried out with a view to confirm the role of sulfuric acid concentration and accumulation of leaching products. The effect of sulfuric acid concentration was determined in a two-step leaching experiment, wherein a given batch of CFA was submitted to two consecutive leaching steps, each with fresh leachant. The effect of accumulation of leaching products was studied by means of seven leaching cycles. In each cycle, a fresh batch of CFA was leached by the same solution that was used to leach the previous batches. This produced accumulation of leached products in the original leachant.

The final set of experiments was designed to find conditions that enhance leaching rates and extraction levels. Here, the effects of leaching in the presence of glass beads and the application of a pre-leaching conditioning step with hydrochloric acid, were investigated.

2.3.2. Primary leaching tests

Batch leaching tests were performed in shakers. The required concentration level of sulfuric acid was set by its dilution with de-mineralized water. A pre-determined amount of CFA was added to 500 ml Erlenmeyer flasks containing 300 ml of acid each, so that the solids content in the suspension was set between 0.1% and 30% (weight/volume). Each suspension was prepared in duplicates. The tests were performed at ambient temperature (25–28°C), using AK 15, INFORS AG, HT shakers at 200 rpm, in order to ensure efficient mixing of the leaching suspension.

Experiments were performed at either variable or fixed pH. In the latter case, controlled dosage of concentrated sulfuric acid, were administered.

Samples of 1.5 ml suspension were taken periodically from the flasks, centrifuged at 12 000 g for 5 min, and then the supernatant was submitted to elemental analysis by FAAS, and the solid was analyzed microscopically as described above.

The following steps were performed prior to further processing of the leachate and/or the solid matter. The leaching suspension was allowed to settle, the supernatant was decanted, centrifuged at 12 000 rpm and filtered through GF/A Whitman filter. All the filtered CFA was collected and dried at 105°C.

2.3.3. Effect of stirring method and temperature level

The effect of method and intensity of stirring and temperature, on leaching kinetics and yield, were tested using shakers at 50, 100, 150 and 200 rpm. The control was defined as a leaching test without shaking. Prior to leaching, the suspension was stirred vigorously until the CFA became uniformly dispersed in the leaching medium.

In order to investigate the effect of temperature, the suspensions were shaken in thermostatic water bath shakers that were set at 5 different temperatures, in the range 20–80°C.

2.3.4. Effect of acid concentration: two-step leaching experiment

Leaching tests in two consecutive steps were carried out in the following manner. In the first step, the primary leaching test was carried out, and then the CFA was filtered and dried. In the second step, the dry solids were subjected to leaching by fresh acid under the same conditions as prescribed in the first step. In this series, the initial acid concentration was set at four different levels, 1, 2, 4 and 6 N.

2.3.5. Effect of accumulation of leaching product: a leaching test of seven cycles

Each test consisted of 7, 48 h leaching cycles. Upon completion of a cycle, the solids were removed from the leaching medium, and fresh CFA was added to the filtered leachate. The tests were performed with suspensions containing an initial content of 2% CFA at three different pH levels: 1.5, 1 and 0.5.

2.3.6. Effect of mild attrition of the CFA with glass beads

Leaching tests with 1 mm glass beads were carried out for 48 h in a 1 N acid suspension. Composition of the leaching suspensions, with respect to their CFA and glass beads contents, are specified in Table 1.

2.3.7. Pre-leaching conditioning process

The purpose of conditioning the CFA was to reduce its acid neutralization, or buffer, capacity, and to decrease the calcium content, prior to the metal leaching stage. A pre-leaching conditioning process with HCl, was performed using 2 l of de-ionized water and 300 g CFA in a 3 l flask.

Table 1
CFA and beads composition of the leaching medium in leaching tests with glass beads

CFA content (%)	Glass beads content (%)
1	0
1	4
1	9
5	0
5	5
5	10
10	0
10	5

The mixture was adjusted to pH 4, by adding 92 ml of 10 N hydrochloric acid, and stirred for 24 h. After 24 h the mixture was centrifuged and the supernatant was removed. The CFA was then washed with de-ionized water which was removed thereafter. This process was repeated four times. Finally the conditioned particles were collected and dried at 110°C, yielding approximately 240 g of dry conditioned CFA.

3. Results and discussion

The coal used for combustion in Israel is imported from several sources: about two thirds from South Africa and the rest from Colombia, Australia and USA. The resulting mixtures have variable compositions and leachability. Nevertheless, due to the relatively high calcium content all the mixtures are alkaline, and hence they raise the pH of water which comes in contact with them to 10–11. A typical chemical composition of CFA from the Rutenberg Power plant is summarized in Table 2.

The major process parameters dominating aluminum leaching are time, CFA content and sulfuric acid concentration. The CFA content and acid concentration play an important role in the simultaneous enhancement, and self inhibition of the leaching kinetics. This is discussed in the sequel.

Table 2
Major elements in CFA samples from Rutenberg Power Plant

Content range[a] (%)	Content[b] (%)	Element
20–26	23.84	Si
5–17.5	15.54	Al
0.5–17.5	2.34	Ca
2.5–13	3.70	Fe
0.4–3.3	0.62	K
0.5–4.5	1.24	Mg
0.1–4.5	0.95	Na[c]
	10–11	pH[c]

[a] Israel Electric Co.: Unpublished internal report.
[b] Analysis by FAAS.
[c] Equilibrium pH of fly ash in water suspensions.

3.1. Effect of CFA content on aluminum leaching

The leaching of aluminum can be characterized as follows: the leaching rate decreases with time (see Fig. 1). In absolute terms more aluminum is leached, in a given time, as the CFA content increases. However, the leached fraction of aluminum decreases as the CFA content increases (Fig. 2). The final acid concentration decreases linearly with the initial CFA content (Fig. 2).

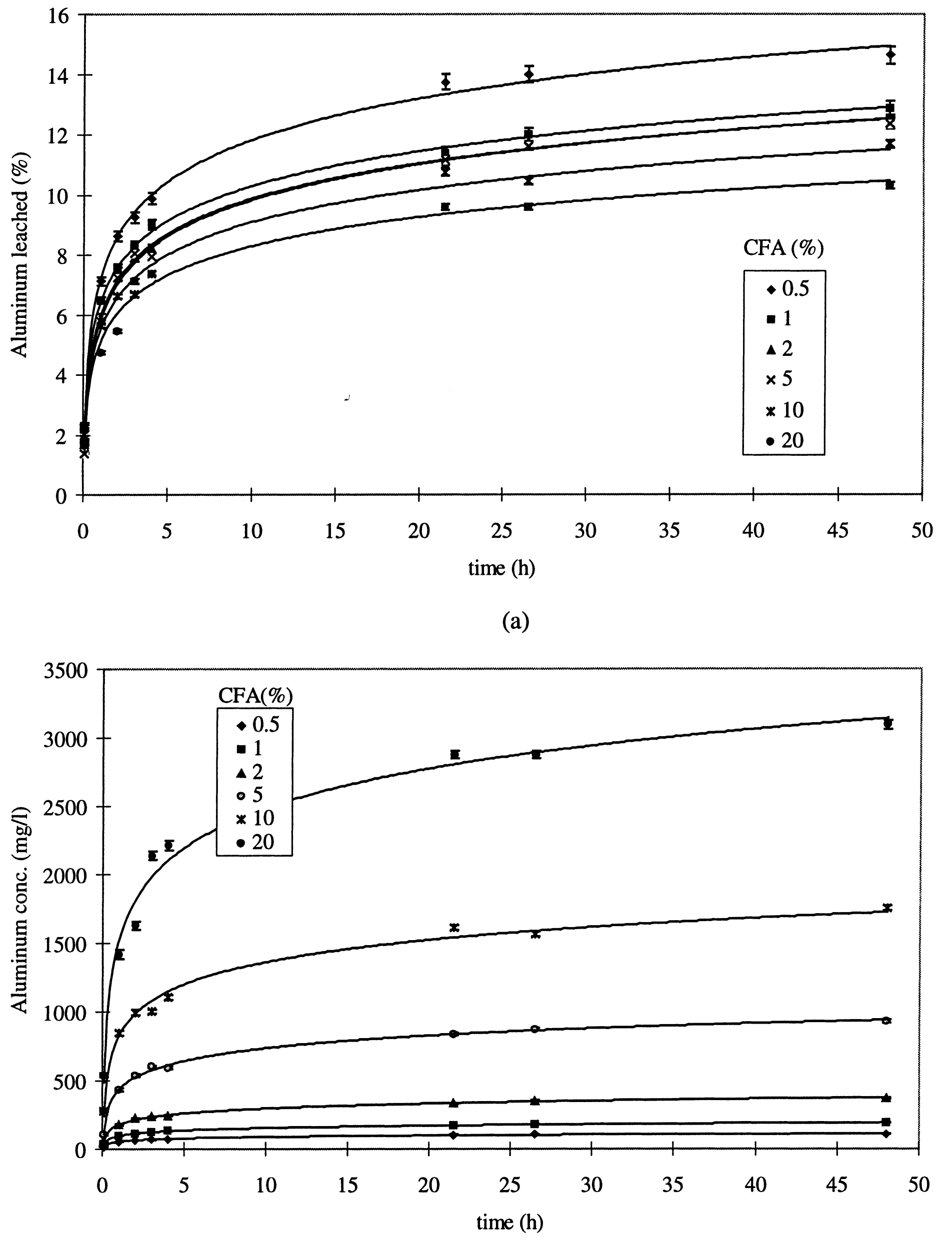
Preliminary leaching tests of 1% CFA suspension, at fixed pH 0.8, for a period of 100 days, showed that 30%±2% of the original aluminum content in the CFA was leached. This seems to be the maximum extractable fraction of aluminum by leaching with sulfuric acid, at $\mathrm{pH}\geq 0.8$, $t\leq 100$ days, under ambient temperature and pressure conditions. Similar leaching levels were also reported by Berry et al. [12]. Kelmers et al. [19,26] reported data of aluminum dissolution at test conditions of 8 N acid, 110°C (reflux), 10% CFA content and time of 18–20 h with agitation. The fraction of soluble aluminum ranged between 18% and 85% of the initial aluminum content. According to the authors, this wide range of leaching levels reflects the effect of the coal origin and power plants at which it was combusted. The calcium content of the tested samples ranged between 0.4% and 17.5%. However, no direct correlation was found between the calcium content and the level of leaching.

Berry et al. [12] concluded that aluminum, and other elements present in the ash, are dissolved from its glassy phases and not from insoluble crystalline components such as mullite. Furthermore, it was noted that some glassy components are more susceptible to acid leaching than others. According to these findings, it is reasonable to expect that the leaching process will be limited, for example, by the content of glassy components in the CFA. However, the inverse relation between the metal leachability and solids concentration (see Fig. 2) requires further considerations.

Other factors that are likely to cause this unexpected behavior may be linked to precipitation of aluminum sulfate, exhaustion of H^+, and precipitation of other leaching products that cover the CFA particles and inhibit aluminum leaching. We will consider each one of these factors and show that the most likely limiting factor is an inhibiting product of the leaching process. In this sense the leaching becomes a self inhibiting process.

3.2. Effect of calcium sulfate precipitation

The reason for the relatively low recoverability of aluminum, under the studied conditions, and the decrease of the leaching yield with increased solids content, can be the result of deposition of leaching products on the CFA particles. In this context, a primary product is expected to be calcium sulfate that has a solubility product of 2.45×10^{-5} [27]. As an estimate, 1 N sulfuric acid produces 0.5 M of sulfate ions. Hence, precipitation of calcium sulfate from



(a)

(b)

Fig. 1. Effect of CFA content in suspension on aluminum leaching. Aluminum leached by 1 N sulfuric acid versus time (a) fraction of leached aluminum and (b) concentration in solution, at six levels of CFA content, from 0.5% to 20%.

1 N sulfuric acid solution is expected to commence once the calcium concentration exceeds 2 mg/l. Since, in this work, the CFA contains 2–8% soluble calcium, most of it is expected to precipitate as calcium sulfate under leaching conditions with a 1 N sulfuric acid, and CFA contents that exceed a threshhold level of 0.1%, appreciably. For example, a content of 7.8% calcium in the CFA is equivalent to 1.95 mM calcium in 0.1% CFA (Fig. 3), and the sulfate concentration at pH 1.5 is 16.2 mM. Hence, the value of the concentration product, e.g., $16.2\times10^{-3}\times1.95\times10^{-3}=3.16\times10^{-5}$, slightly exceeds the K_{sp}. This means that if any precipitation occurs, it is expected to be marginal. The results shown in Fig. 3, for the 0.1% CFA, corroborate this calculation, in the sense that the maximum expected leaching level of approximately 30% was realized. However, at higher CFA contents, this concentration product is expected to exceed the K_{sp}, and hence, an inhibition effect of the precipitate can be expected. This implies that mass transfer limitations are not expected to be significant when leaching is performed on dilute CFA dispersions (e.g., 0.1% or less). However, as the CFA content is increased, the availability of both calcium and sulfate for the formation of calcium sulfate precipitates, and inhibition of mass transfer in the leaching process, also increases.

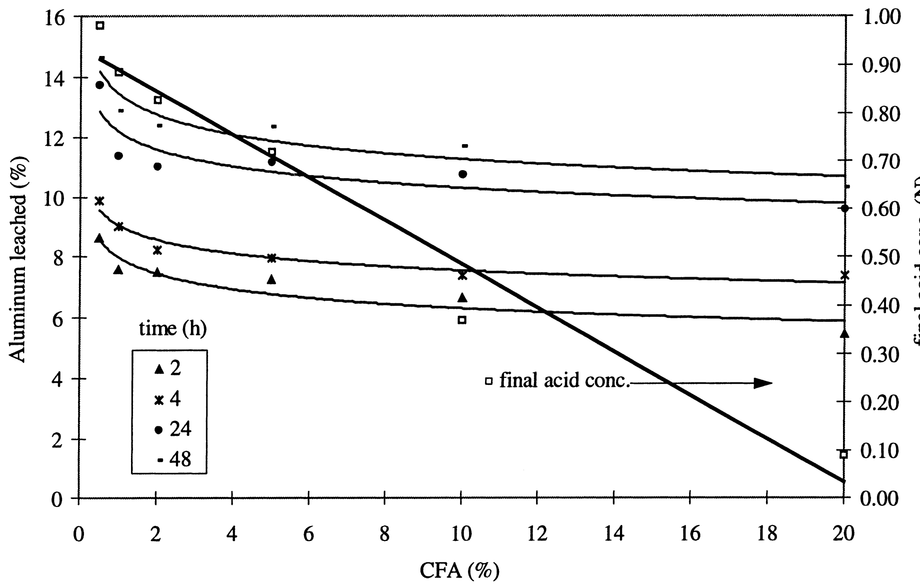


Fig. 2. Fraction of leached aluminum, and final acid concentration, versus initial CFA content in suspension, at four leaching times. The sulfuric acid concentration was set at 1 N prior to start of leaching.

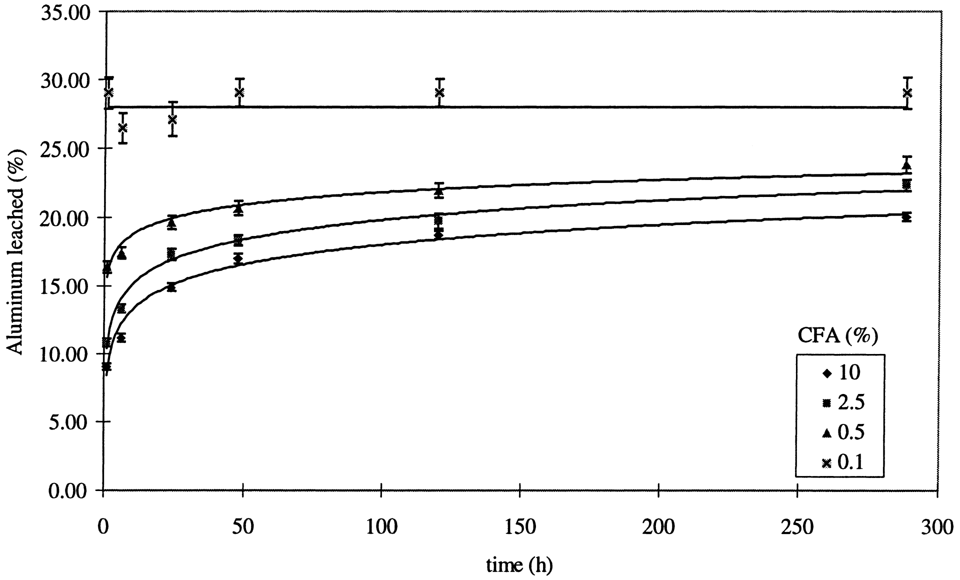


Fig. 3. Effect of CFA content in suspension on aluminum leaching at constant pH 1.5: fraction of aluminum leached vs. leaching time.

Fig. 4 shows a typical SEM micrograph of CFA, that was leached with sulfuric acid at pH 1 for 25 days. The spherical CFA particles, 5–20 μm in size, are covered with flaky precipitates of calcium sulfate. The nature of this precipitate was confirmed by EDS analysis. Untreated CFA (not shown here) appear as rather smooth spherical particles. Note that the calcium sulfate precipitate is seen on the particles, as well as in the form of other particulate matter that are detached from the CFA.

Effect of leaching on CFA surface composition is shown in Fig. 5. Fig. 5(a) shows that the different samples consist of 50–60% oxygen, 15–20% aluminum, 15–20% silicon, 2–10% calcium, and 1–10% sulfur. Mass balance is satisfied by all components. The surface composition of raw CFA (Fig. 5(b), sample 1) is consistent with that obtained for bulk CFA using FAAS elemental analysis, the only exception being the iron. In this context, most of the iron appears as magnetite in nearly free particles.

In sample 2 (Fig. 5(b)) the fraction of calcium and sulfur at the surface increases to approximately 10% each. This stoichiometric 1:1 relation and the simultaneous increase in surface concentration of calcium and sulfur, support the claim that calcium sulfate precipitates on the surface of leached CFA particles. Further support to this claim is provided by the results of the third and fourth samples (Fig. 5(b)). After grinding with zyrconia, the contents of

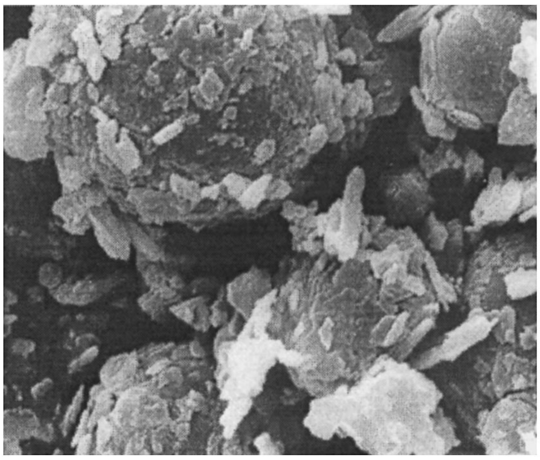


Fig. 4. SEM micrograph of CFA particles after 25 days of leaching by sulfuric acid at pH 1, magnification×3500. The CFA particles are covered with micron size flaky calcium sulfate.

calcium and sulfur on the surface decrease, but the 1:1 stoichiometric relation remains unaffected. This is expected in view of the applied attrition and the subsequent removal of calcium and sulfur, as calcium sulfate, from the surface. The second stage leaching increase the calcium and sulfur contents at the surface once again. In the fifth sample, of conditioned CFA, the fraction of calcium at the surface has been decreased from approximately 6% (in the raw material) to 2%. This result is consistent with that obtained from bulk elemental analysis which showed a removal of 65% of the calcium by the conditioning with hydrochloric acid. Furthermore, the low sulfur content observed on the surface of the fifth sample shows that no precipitation of aluminum sulfate compounds on this surface occurs. Consequently, the self inhibition effect is likely to be primarily due to precipitation of calcium sulfate, as expected.

These results demonstrate that both sulfur and calcium are present on the particles surface as compounds that are formed during leaching with sulfuric acid, in 1:1 stoichiometric relation. Fig. 6 shows the concentrations of calcium and sulfate in the leachates of the fixed pH 1.5 experiment. The equilibrium anhydrite ($CaSO_4$ pK=4.59) and gypsum ($CaSO_4{\cdot}2H_2O$ pK=4.85) curves are also plotted. In all cases tested, equilibrium is virtually reached with anhydrite. Roy and Griffin [4] found that the ash samples they used for fly ash–water leaching experiments, were in equilibrium with anhydrite within 7 days of extraction. Moreover, they found no equilibrium with calcium carbonate, and concluded that the calcium activities were controlled by the solubility of anhydrite.

Mattigod et al. [1] also indicate that dissolution of different compounds consisting of the major elements, and the precipitation of secondary phases, might be expected to control the geo-chemical behavior of these elements in fossil fuel wastes. They explained that adsorption/desorption mechanisms do not significantly influence the concentrations of the major elements.

Aluminum hydroxide precipitates [4] such as amorphous $Al(OH)_3$ (pK=31.77), gibbsite ($Al(OH)_3$ pK=32.77), bohemite ($AlO(OH)$ pK=33.57) and diaspore ($AlO(OH)$ pK=35.31), are not likely to be formed under the acidic experimental conditions as applied in this work.

3.3. Comparative solubility calculations

Solubility calculations were performed by MINTEQA2 which is a geochemical equilibrium speciation model for dilute aqueous systems. The program was run assuming 10% CFA in suspension at 28°C and molal concentration of the following ions: Al^{+3}, 0.110; C_a^{+2}, 0.040; M_g^{+2}, 0.0018; Fe, 0.006 (1/6 II, 5/6 III); K^+, 0.002; Na^+, 0.002; SO_4^{-2}, 0.370. The program output indicates precipitation of 0.0346, 0.00244 and 0.0185 molal solid gypsum, hematite and $AlOHSO_4$ (for Al^{+3} exceeding 2565 ppm), respectively. The dominance of precipitation of gypsum is clear. However, no precipitation of anhydrite is specified, contrary to the data given in Fig. 6, that suggests its dominant role in $CaSO_4$ precipitation. Furthermore, our experimental results show no evidence for precipitation of sulfates on the surface of conditioned CFA particles (Fig. 5(b) sample 5) and a clear capacity of the leachate to accumulate Al (Fig. 8 below), in contrast with the predicted precipitation of $AlOHSO_4$. The discrepancy may be resolved if part of the precipitate exists in the colloidal form in solution, so that its contribution to the self inhibition mechanism is marginal, e.g., as compared to that of $CaSO_4$. Note that the low concentration limitation that applies to the MINTEQA2 program may be responsible for some discrepancies when it is applied to the system studied in this work.

Furthermore, the program does not provide kinetics of dissolution processes as it uses fixed initial compositions. The dissolution of calcium is much faster than that of aluminum. In fact, most of the calcium must be dissolved prior to the onset of any significant aluminum leaching, e.g., at sufficiently low pH. The dissolution of the calcium is expected to advance far ahead prior to accumulation of Al^{+3} to the level of 2565 ppm that initiates precipitation of $AlOHSO_4$. Removal of calcium by HCl prior to the leaching with sulfuric acid (see details in the sequel) produces significantly enhanced kinetics of the latter. This provides further evidence for the dominance of $CaSO_4$ precipitation, over that of other possible compounds, in determining the leaching kinetics.

3.4. Effect of concentration of sulfuric acid on aluminum leaching

Fig. 2 shows that in suspensions containing up to 20% CFA, the final acid concentration, e.g. after 48 h of leaching, is a decreasing linear function of the CFA content. The fact that the $[H^+]$ is maintained higher than 0.1 N, suggests that exhaustion of the H^+ is not the main limiting factor of the

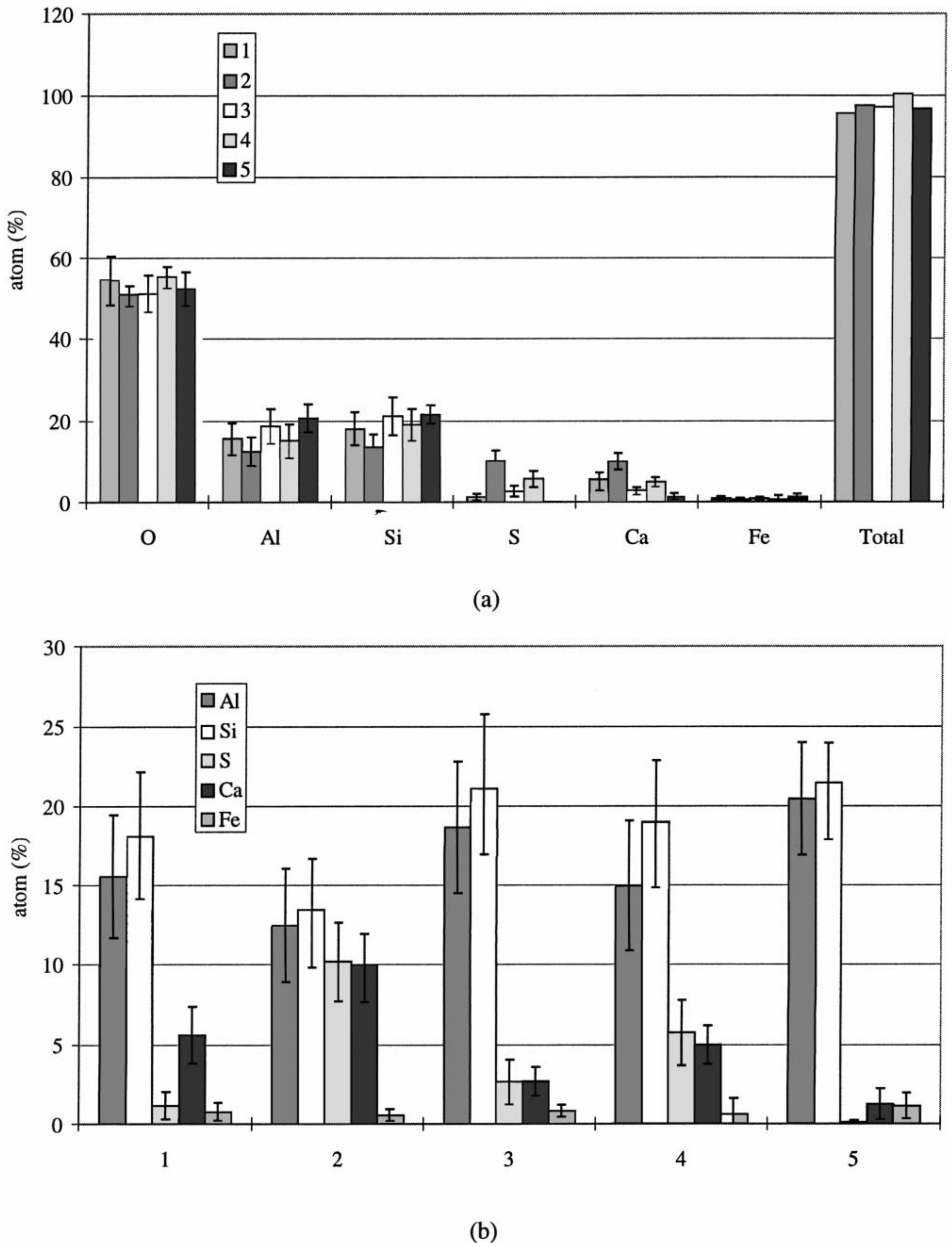


Fig. 5. Effect of leaching on CFA surface composition. Results of EDS analysis of five CFA samples: (1) raw material; (2) material leached by H_2SO_4 at pH 1.5; (3) material leached by H_2SO_4 at pH 1.5 and then ground with zirconia; (4) second stage leaching of sample no. 3; (5) material conditioned with HCl at pH 4. (a) Presentation by elements for five samples. (b) Presentation by samples for five elements.

leaching process, or else the pH would have been driven much higher. In order to investigate further the significance of exhaustion of H^+, a leaching test at constant pH was performed. A fixed level of pH 1.5 was selected, thus setting $[H^+]$ lower than 0.1 N.

The leaching yield, at fixed pH 1.5 (Fig. 3), exceeded, by approximately 5%, the one previously obtained using the initial 1 N acid concentration (Fig. 1). Thus, acid exhaustion during the leaching process at variable pH can be a cause for changes in yields.

Higher acid concentration increases the initial reaction rate, and the highest leaching rate is observed in the first 10 min (Fig. 7(a)). Furthermore, above 1 N an increase in acid concentration has a marginal effect on the leaching (Fig. 7(b)). This suggests that higher acid concentration enhances the initial reaction rate, but concurrently it produces the self inhibition effect. Comparing the experimental points at 1 and 2 N in Fig. 7(b), shows that the actual measured yield at 2 N is lower than that at 1 N. This suggests the beginning of self inhibition dominance above 1 N. Further support to this observation was obtained in a two-step leaching test.

When CFA is subjected to a two-step leaching process, in which leached CFA from the first step is exposed to fresh

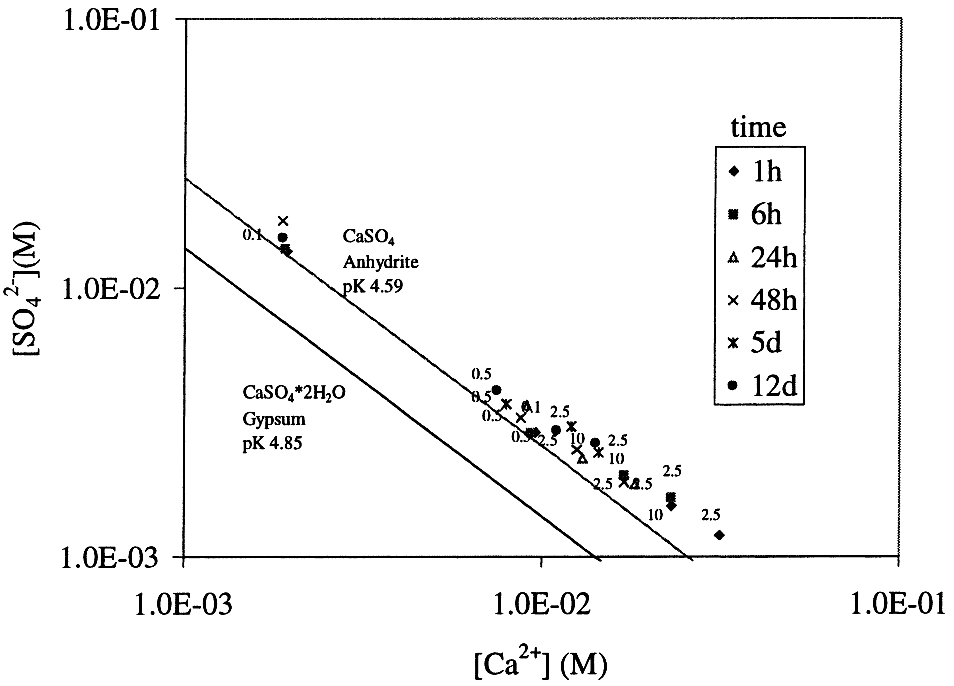


Fig. 6. Calcium vs. sulfate concentrations of CFA leachates at fixed pH 1.5, and different leaching times, for 0.1–10% CFA suspensions. The numbers that appear next to the concentration marks indicate the CFA contents in the suspensions.

acid of the same initial concentration, the increase in acid concentration, from 1 to 6 N, in the first step, causes a decrease in aluminum leaching, from 12% to 8%, respectively. Since only 8–12% of the aluminum was leached in the first step, we could expect significant leaching also in the second step. However, the second step produced additional yield of less than 1.5%. These results support the hypothesis that calcium sulfate precipitation slows down the leaching process. A second leaching step may have been efficient if the inhibiting factor could be removed with the leachate of the first step. As this did not occur, we are justified in concluding that calcium sulfate, which stays with the solids, is indeed the major inhibiting factor. Moreover, the addition of more concentrated fresh acid does not allow re-dissolution of the precipitate, and hence the effect of the major inhibiting factor is virtually unchanged in the second leaching step.

It is also clear that imposing a fixed pH constitutes a controlling factor of the leaching process, and acid concentration is indeed the governing parameter driving the leaching process. This has been confirmed by a 7-cycle leaching test (Fig. 8). The figure shows that no significant change of leaching level takes place in any of the first six cycles, and no accumulation of calcium in solution is observed. The additional soluble calcium of every new batch of CFA is precipitated as calcium sulfate, and subsequently removed with the solid phase.

The seventh cycle shows a significant decrease in the amount leached. As yet, this decrease has no satisfactory explanation. For example, it might indicate a saturation limit imposed by the high ionic strength of the solution, and effects related to high aluminum concentration. However, there is a need for further study to this end.

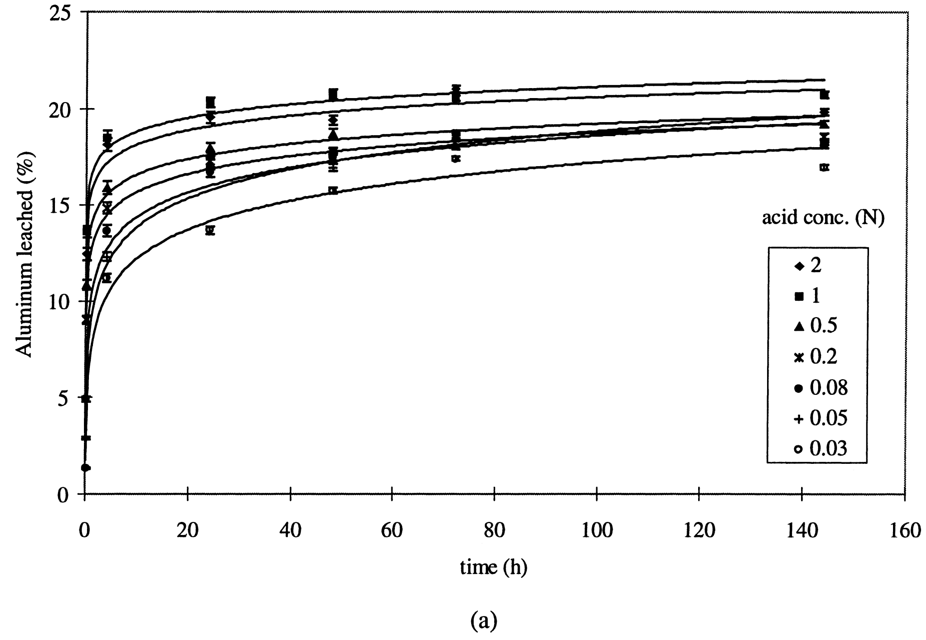
3.5. *Effect of accumulation of dissolved products on aluminum leaching*

Fig. 1(b) shows that 48 h of leaching produced dissolved aluminum that did not exceed 3200 mg/l. The initial acid concentration dictates a maximum sulfate concentration of 48 g/l (0.5 M). As the solubility of aluminum sulfate [27,28], at 25°C, is 48 g/100 ml, and the maximum amount of aluminum sulfate that could be formed in the leachate was 20.3 g/l, e.g., 2 g/100 ml, no precipitation of aluminum sulfate on the CFA particles is expected. This precludes aluminum sulfate from being an inhibiting factor. This is also corroborated by results of the seven-cycle leaching test (Fig. 7), where accumulation of leaching products in the leachate, especially aluminum, did not hinder the leaching process from 6 batches of fresh CFA.

3.6. *Effect of stirring and temperature*

The stirring method and intensity were found to have no significant effect on the leaching characteristics of the samples studied in this work.

The effect of temperature on kinetics of leaching is shown in Fig. 9. Enhanced leaching rates were found at elevated temperatures. The effect is strongest in the first 5 h and then it levels off and diminishes. For example, there is approxi-



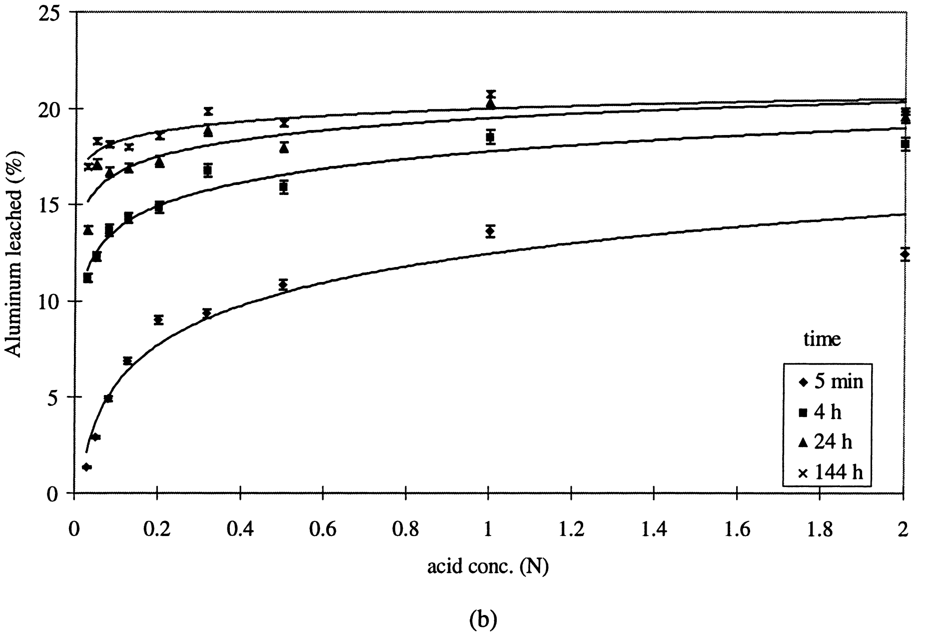


Fig. 7. Leaching as a function of acid concentration. Fraction of leached aluminum: (a) versus leaching time, for different levels of initial acid concentration; (b) versus initial acid concentration, for different leaching times at 2% CFA content in suspension.

mately an order of magnitude difference between the time required to leach the same amount of aluminum (in the 12–15% range) at 20°C and at 80°C. In this context, Kelmers et al. [26] found that the behavior of different CFA samples at different temperatures varies considerably, as regards aluminum leachability. The decrease of the leaching rate with time observed at all temperatures that were tested is in agreement with literature data [19,26]. The maximum aluminum yield, after 24 h of leaching, was less than 20% even at 80°C.

The effect of temperature on leaching of aluminum, in the range 20–80°C, involves a number of factors. This has been verified by the analysis of outputs of the MINTEQA2 program. In the range 20–35°C, calcium sulfate precipitates as gypsum, whereas above 35°C it turns anhydrite. The temperature dependence of the solubility of $CaSO_4$ [27] changes at 50°C. Below 50°C, the solubility is a decreasing function of temperature, whereas above 50°C the reverse applies. Furthermore, precipitation of $AlOHSO_4$ is predicted in the range 20–35°C. This precipitation, which practically vanishes above 35°C, is not expected to hinder significantly the kinetics of aluminum leaching. However, it changes the balance between leached and unleached or precipitated aluminum.The combined effect of these factors

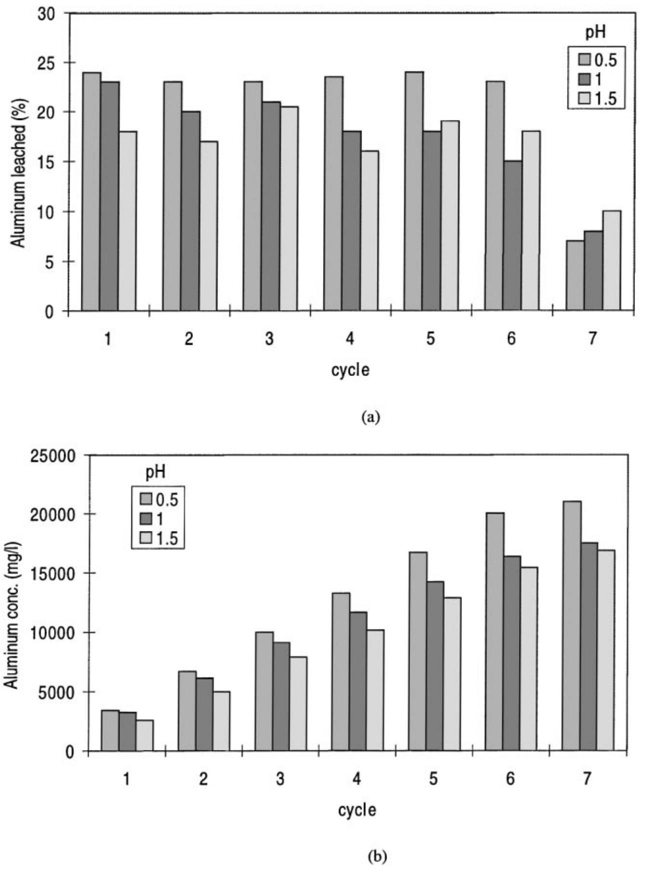


Fig. 8. Effect of aluminum accumulation in the leaching medium: Multiple cycle leaching of CFA at three different fixed pH levels: 1.5, 1 and 0.5, and 2% solids: (a) fraction of leached aluminum versus cycle number; (b) cumulative aluminum concentration in the leachate after completion of each cycle.

produces enhanced leaching kinetics at elevated temperatures.

3.7. *Means to reduce the self inhibition effects*

The leaching mechanism suggested two possible ways to reduce the self inhibition due to calcium sulfate precipitation. In the first, an attempt was made to remove the precipitates by mechanical attrition with glass beads. The second approach involves removal of calcium from the CFA, with no significant leaching of aluminum, in a pre-leaching conditioning stage with hydrochloric acid.

3.8. *Effect of presence of glass beads*

Glass beads were introduced to the leaching suspension with the notion to generate mild attrition, e.g., without comminution, and subsequent removal of precipitates from the surface of the progressively leached CFA particles. Addition of glass beads increased aluminum leaching in suspension of 1% CFA, but no such effect was observed on 5% and 10% CFA suspensions. This indicates that the rather small (1 mm) and light beads that were used, are not effective as an attrition agent at higher CFA contents, and in order to achieve effective attrition, larger and heavier beads are called for.

3.9. *Effect of pre-treatment by hydrochloric acid on subsequent aluminum leaching with sulfuric acid*

The use of hydrochloric acid for leaching of aluminum from CFA (DAL process) was considered by several investigators [18,19,26]. This leaching process involves relatively high temperature and pressure levels, whereas we

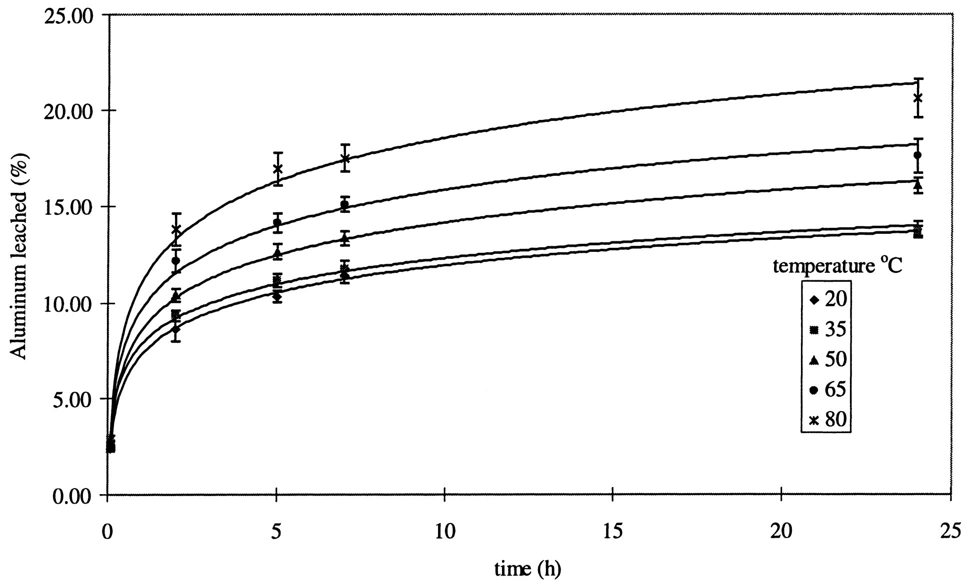


Fig. 9. Effect of temperature on kinetics of aluminum leaching from CFA, as a fraction of leached aluminum vs. time.

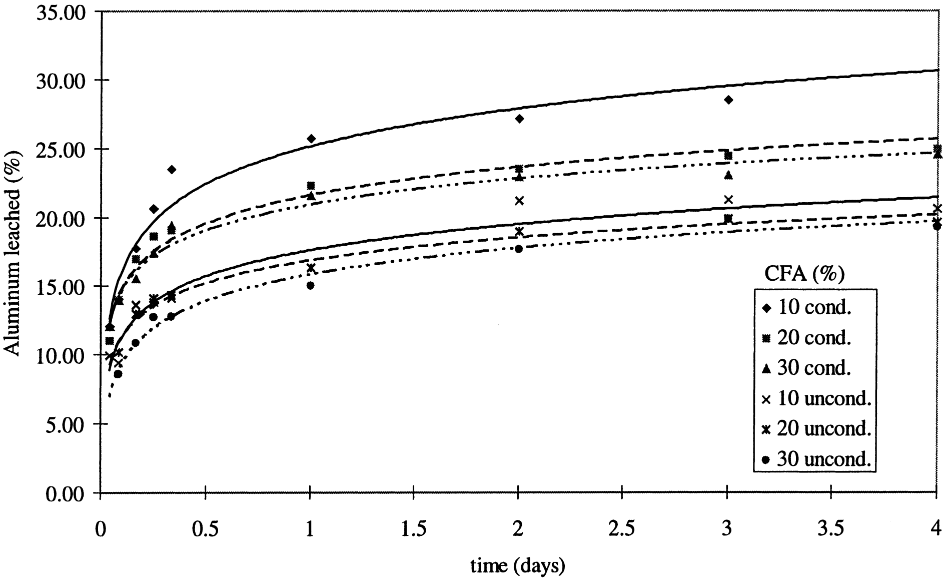


Fig. 10. Effect of HCl conditioning (24 h at pH 4) on subsequent aluminum leaching from CFA by sulfuric acid. Aluminum leached from 10–30% conditioned (cond.) and unconditioned (uncond.) CFA, at fixed pH 1.5. The results are presented as pairs of conditioned and unconditioned leaching values for a given CFA content.

are interested (for future work) in leaching under relatively mild conditions that prevail in bioleaching. In order to facilitate more amenable conditions for leaching by sulfuric acid, a preliminary conditioning stage for the removal of calcium from the CFA, with no significant loss of aluminum, was considered. To this end, the CFA was conditioned in hydrochloric acid at constant pH 4 for 24 h. The results show that, there was no significant dissolution of aluminum due to the pre-leaching, 24 h, conditioning process. In contrast, during this conditioning process, 65% of the calcium were dissolved, and the calcium bearing leachate was removed thereafter.

Following this conditioning stage, the CFA, was subjected to a leaching process with sulfuric acid. Approximately 28% of the aluminum was leached from a 10% suspension of conditioned CFA after three days, while during this period of time it was possible to leach only 20% from the unconditioned control sample (Fig. 10). The trend of decreasing rates and recoverability (as percent leached), with CFA content, persists also in the case of conditioned CFA. It was established that whereas the rates and recoverability obtained with 20% and 30% suspensions of conditioned CFA are significantly lower, as compared to 10% conditioned CFA, they are still higher than those of the corresponding 10% unconditioned CFA. In this sense, the effectiveness of the conditioning step, in enhancing leaching rates and recoverability, is established.

4. Summary and conclusions

1. Two governing parameters of the leaching process from CFA, of a given composition, are the concentration of acid, which determines the availability of H^+, and the CFA content.
2. The leaching rate of aluminum from the CFA, by sulfuric acid, decreases with an increase in the CFA content of the leaching medium. This phenomenon cannot be reconciled by using exclusively considerations of the dissolution reactions that govern the process.
3. The leaching of aluminum from CFA by sulfuric acid is a self inhibiting process by its nature. The self inhibition mechanism involves precipitation of calcium sulfate on the surface and within pores of the CFA particles.
4. The contribution of aluminum bearing compounds, such as $AlOHSO_4$ and aluminum sulfate, to the self inhibition effect is expected to be marginal as compared to that of calcium. This is due to lag in solubility and slower kinetics of dissolution of the aluminum as compared to that of calcium.
5. Increasing the concentration of sulfuric acid produces two opposing effects. The increase in concentration of H^+ enhances the aluminum dissolution, whereas the simultaneous increase of the available sulfate ions intensifies the self inhibition due to formation of calcium sulfate.
6. The fraction of calcium and sulfur at the surface of leached CFA particles is higher than that originally present in the raw, unleached material. A stoichiometric 1:1 relation of these elements on the surface of leached CFA, was established. This stoichiometric relation, and the simultaneous increase in surface concentration of calcium and sulfur, support the claim that calcium sulfate precipitates on the surface and within pores of CFA particles.

7. Elevation of temperature, in the range 20–80°C, enhances the kinetics of the leaching process. This concerns leaching rate of the aluminum as well as the total amount leached.
8. Conditioning the CFA by a pre-leaching process with hydrochloric acid at pH 4, improves the subsequent leachability of the aluminum. This applies to enhancement of leaching rates and time dependent recoverability of the aluminum, but the maximum extraction level remains unchanged.

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