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Vanadium Extraction from Fly Ash—Preliminary Study of Leaching, Solvent Extraction, and Sorption on Chitosan

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ABSTRACT

Fly ashes resulting from the combustion of fuel containing high concentrations of vanadium that can be slightly removed by water and more efficiently by alkaline or acid solutions. This uncontrolled release can contaminate water sources and requires appropriate storage of fly ashes. This study investigated the possibility of cleaning the ashes by leaching the material and recovering vanadium by solvent extraction (for metal concentration solutions higher than $200\,\mathrm{mg\,V\,L^{-1}}$) using several amine extractants (Primene JM-T, Amberlite LA-2, Alamine 336, and Alamine 304), a quaternary ammonium salt (Aliquat 336), and by a sorption

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process (for low-metal concentration solutions) using chitosan. Extraction and stripping were investigated with liquid extractants and showed that Aliquat 336 was the best of these extractants. However, since Aliquat 336 exhibits a greater difficulty at stripping, secondary or tertiary amine extractants appear more suited for the extraction process. Vanadium sorption occurs on chitosan through anion exchange with a maximum sorption capacity of 400 to 450 mg V g^{-1} at pH 3. The treatment of acid leachates with chitosan does not appear possible, since it requires a pH control to pH 3, which precipitates ferric ions and coprecipitates vanadium. Alternative routes could be the alkaline leaching of fly ashes and a further pH control.

Key Words: Vanadium; Fly ash; Leaching; Amine extractants; Solvent extraction; Chitosan sorption.

INTRODUCTION

The composition and properties of fly ash depend on the type and origin of the fuel used, as well as the combustion conditions.[1] For many fuels, the presence of vanadyl porphyrins in the crude oil[2] may explain the high concentration of vanadium that can be detected in fly ash. Vanadium can also be identified in fly ash resulting from the combustion of coal, peat, and wood.[3–5] These fly ashes can be made inert by inclusion as a binder in the fabrication of concrete.[6] However, due to the ready mobility of some of the metals included in the mineral fraction, it is usually necessary to closely and carefully store these ashes before use. Another way to reduce the potential impact of these ashes on the environment consists in the cleaning of the material by leaching.[7] Several studies were dedicated to the leaching of fly ash to decontaminate the product and to recover valuables,[6–8] or, alternatively, to evaluate the environmental risk at discharging the waste material under noncontrolled conditions.[9,10]

In this study, experiments were performed on ashes resulting from the combustion of crude oil in thermal power plant. Vanadium was considered as the tracer since it is present in many ashes and is typically representative of its chemical series (including molybdenum and tungsten). The first part of the work focused on V(V) leaching from the material using water, alkaline, and acidic solutions. The solvent extraction of vanadium was studied for the treatment of relatively high-metal concentrations (concentration higher than 200 mg V L^{-1}).[11–14] Several amine extractants were tested, including Primene JMT (primary amine), Amberlite LA-2 (secondary amine), Alamine 304 (tertiary amine: trilaurylamine), Alamine 336 (tertiary amine: tri-n-octyl/decyl amine), and Aliquat 336 (quaternary ammonium salt: tri(caprylyl)methylammonium chloride).[13] Stripping was performed using ammonium hydroxide, sodium hydroxide, or ammonium chloride (alone or mixed with ammonium nitrate). For low-metal solution concentration (lower than 200 mg V L^{-1}), vanadium was extracted from low-concentration sulfuric acid solutions through a sorption process using chitosan. Indeed, chitosan has proved very efficient for removing molybdate and vanadate from acidic solutions.[15–17] This biopolymer is obtained by deacetylation of chitin, the most abundant biopolymer after cellulose, which is extracted from shellfish. This biopolymer is characterized by its high content of amine function, which is responsible for metal sorption through different mechanisms[18]; metal cations can be sorbed through chelation in near-neutral solutions, while metal anions can be sorbed through anion exchange on protonated amine functions in acidic solutions.[17] After saturation of the sorbent, vanadate can be recovered by elution using sodium hydroxide or ammonium hydroxide, and the sorbent can be recycled, similar to molybdate sorption and desorption.[19]

MATERIAL AND METHODS

Materials

Fly ashes were collected from a dump of waste materials from a thermal power plant. The material was dried to constant weight at 100°C. The stock was divided into several identical fractions. The powder was sieved, and the fraction below 500 μm was used for further studies. Several representative aliquots (100, 200, and 300 mg) were mineralized (in duplicate) using aqua regia (20 mL). The volume was adjusted to 250 mL, filtered, and the filtrate analyzed for vanadium (and other metals when relevant) content using an inductively coupled plasma atomic emission spectrometer, ICP-AES, ICP JY 2000 (Jobin Yvon, France). The vanadium content was 0.93% (in weight).

Amberlite LA-2 and Primene JMT were kindly donated by Rohm and Haas (Germany). Aliquat 336 and Alamine 336 were kindly donated by Henkel (Germany). Chitosan was provided by France Chitine (France). The material has been previously characterized: the deacetylation degree was 87% and the molecular weight was 125,000 g mol^{-1}.[15]

The material was ground and sieved; the 125- to 250-μm fraction was selected for sorption experiments. Other reagents were purchased from Fluka (France); vanadium monovanadate, isodecanol, ammonium hydroxide, sodium hydroxide, sulfuric acid, and kerosene were analytical grade reagents.

Methods

Leaching was performed by mixing, for varying contact times (1 to 96 h), known amounts of dry ashes (2 to 20 g) with 200 mL of the leaching agent. Demineralized water, sulfuric acid, and sodium hydroxide solutions were used at different concentrations. After the appropriate contact time, the mixtures were filtered, and the filtrate was analyzed after appropriate dilution using ICP-AES.

Solvent extraction was performed by mixing 20 mL of aqueous solution with 20 mL of the organic phase for selected contact times. The organic phases were prepared by dilution of the extractant in kerosene (Fluka). Isodecanol (Fluka) was added to the solution to give a 5% (v/v) concentration to prevent the formation of a third phase during the extraction process. The extractant concentration was adjusted at selected values. Preliminary experiments were performed with synthetic vanadium solutions (1000-mg $\mathrm{V\,L^{-1}}$) to define the optimum experimental conditions. The residual concentration of vanadium in the aqueous phase was determined by ICP-AES. The results were then applied to leachates when relevant (for concentrations higher than 200 $\mathrm{mg\,L^{-1}}$). Stripping was performed by contact of equal volumes of organic and stripping phases (sodium hydroxide or ammonium hydroxide, at known concentration) for 30 minutes, unless specified otherwise, except for the kinetic studies where 5-, 10-, 15-, 30-, 45-, 60-, and 90-minute contact times were used. The concentration of vanadium in the aqueous phase was used for the determination of the stripping efficiency.

The sorption of vanadium on chitosan was performed in batch by contact of 100-mL volumes of leachates with known amounts (10 to 50 mg) of chitosan. After 4 days contact, the solution was filtered, and the filtrate was analyzed for metal content. The mass-balance equation was used for the calculation of sorption capacity (q, $\mathrm{mg\,V\,g^{-1}}$) and sorption efficiency. The desorption was performed using sodium hydroxide molar solutions, and alternatively ammonium hydroxide, or ammonium chloride and ammonium nitrate.

RESULTS AND DISCUSSION

Fly Ash Leaching

Influence of Contact Time

The leaching kinetics for vanadium using sodium hydroxide solutions (2 M) at different liquid/solid ratios (L/S) are shown in Fig. 1. When the fly ash was contacted with demineralized water, 24 to 48 hours of contact were sufficient to reach the equilibrium concentration in solution (not shown). However, the concentrations were very low and did not exceed a few dozen mg V L^{-1}. The leaching efficiency did not exceed a few percent (less than 10%). More interesting are the results for sodium hydroxide solutions. The contact time required to reach the equilibrium was longer (about 96 hours), especially for low L/S ratios, but the extraction efficiency exceeded 90% at high L/S ratios with 2-M NaOH solutions. For further experiments, the contact time was fixed at 4 days of contact. Under the most favorable leaching conditions (i.e., 96 hours of contact time with a 2-M sodium hydroxide solution and a L/S ratio of 10), concentrations as high as 700 mg V L^{-1} were reached.

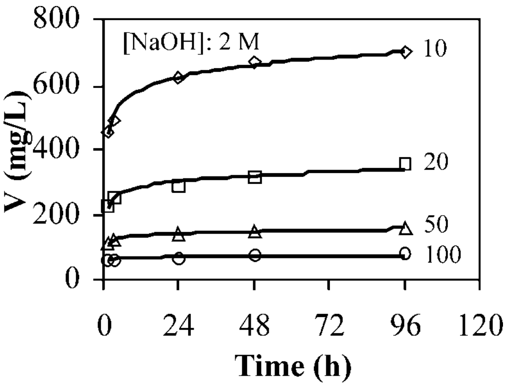

Figure 1. Influence of contact time on vanadium leaching from fly ash using sodium-hydroxide solutions at different liquid/solid ratios (numbers on the curves).

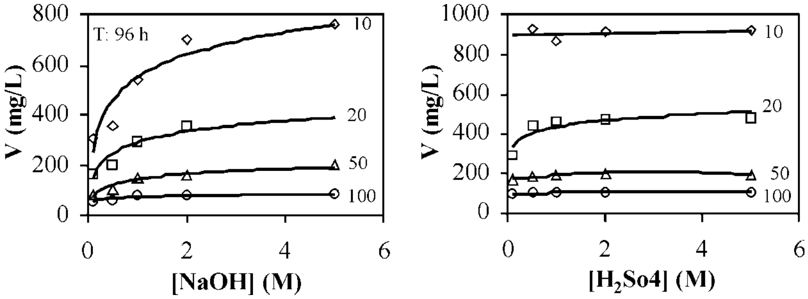

Figure 2. Influence of the concentration of leaching agent (left, sodium hydroxide; right, sulfuric acid) on vanadium leaching at different liquid/solid ratios (numbers on the curves).

Influence of the Concentration of the Leaching Agent

The influence of the concentration of sodium hydroxide and sulfuric acid on the concentration of vanadium in the leachate for different L/S ratios is presented in Fig. 2. As expected, the vanadium concentration increased with increasing concentration of the leaching agent, especially in the case of low L/S ratios. For both sulfuric acid and sodium hydroxide solutions, at $L/S = 100$, the concentration did not vary significantly with increasing concentrations of leaching agent. On the other hand, when the L/S ratio decreased, the leachate concentration diminished, and the concentration of the leaching agent might be increased to maintain the complete leaching of vanadium. With sodium hydroxide solutions, the maximum vanadium concentration was $760\,\mathrm{mg\,V\,L^{-1}}$, and the leaching efficiency exceeded 80% at NaOH concentration of 5 M for $L/S = 10$, while a 1-M concentration of sodium hydroxide was sufficient to reach the same leaching efficiency for $L/S = 100$. In the case of sulfuric acid at all L/S ratios, vanadium concentration in the leachate exceeded $900\,\mathrm{mg\,V\,L^{-1}}$, and the leaching efficiency tended to be 100% for concentrations of sulfuric acid higher than 0.1 M.

Sodium hydroxide and sulfuric acid solutions exhibited comparable leaching efficiency, though sulfuric acid solutions perform slightly better. Chitosan is not soluble in sulfuric acid; vanadium sorption only occurs in acidic solutions; and vanadium extraction with amine extractants is usually enhanced in acidic solutions. Thus, the use of sulfuric acid appears to be more appropriate for the leaching of vanadium from these ashes for both solvent extraction and sorption on chitosan. For the preparation of leachates, the concentration of the acid was fixed to 0.5 M and the L/S ratio to 10, while the contact time was set at 24 hours. Under these selected conditions, both high-leaching efficiency and high-vanadium concentration are reached.

Vanadium Solvent Extraction

Extraction Kinetics

The extraction process is very fast (kinetics not shown). Indeed, more than 96% of the total vanadium was extracted within the first 5 minutes of contact. However, for several extractants, excluding Aliquat 336 and Alamine 336, the aqueous phases remained cloudy, and a fine precipitate was observed on aging the solution for the samples that were contacted with the organic solution for short contact times (less than 30 minutes). For contact times higher than 30 minutes, these precipitates dissolved again. Whatever the extractant, the extraction efficiency did not change after 30 minutes of agitation. For these reasons, the contact time selected for the study of other experimental parameters was fixed to 30 minutes.

Effect of pH

Figure 3 presents the influence of pH on the logarithm of the distribution coefficient (ratio of vanadium concentration in the organic phase to that in

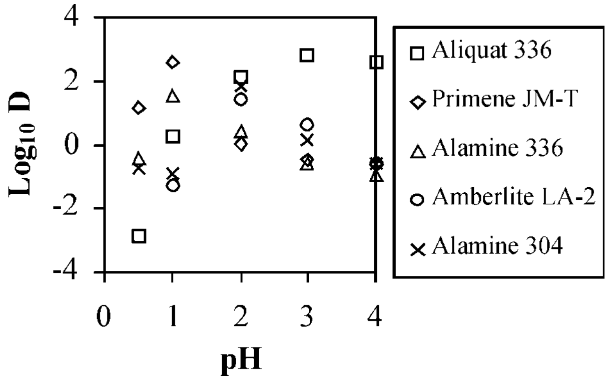

Figure 3. Influence of the pH on vanadium-distribution coefficient using different extractants dissolved in kerosene (vanadium concentration: 950 mg V L^{-1}; $V_{org} = V_{aq} = 20$ mL; extractant concentration: 60 mM).

the aqueous phases) of vanadium using different extractants. The maximum extraction was observed in a narrow optimum pH range (ca. pH 1 to 2) with most extractants, excluding Aliquat 336. For the latter, the distribution coefficient continuously increased with increasing pH value from 0.5 to 3 and reached a plateau above pH 3. Under the optimum extraction conditions, the distribution coefficient ranged between 10^2 and 10^3, for all extractants. All these extractants have amine functional groups, but they differ by the hydrophobic moieties and, more specifically, by the type of amine involved in the extraction. These differences affect the acid–base properties of the extractants, more specifically, their protonation and their ability to ion exchange these metal ions. The plotting of log D vs pH is frequently used to determine the stoichiometry of the proton exchange; the slope of the curve represents the number of protons exchanged during metal extraction. In the present case, it was impossible to find a linear relationship. It is consistent with previous results on vanadium and molybdenum extraction by Primene JM-T[13]; the coexistence of several polynuclear hydrolyzed species, which proportion changes with total metal concentration and pH, makes the interpretation of extraction mechanism very complex. Therefore, several different species may be extracted at different pH.

Influence of Extractant Concentration

The influence of extractant concentration on the extraction efficiency is given in Fig. 4. For Aliquat 336, the high affinity of the extractant for vanadium allows vanadium to be almost completely extracted. The distribution

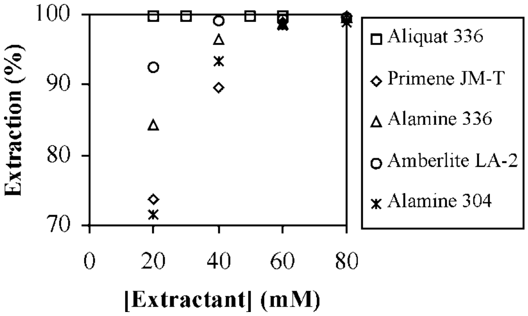

Figure 4. Influence of extractant concentration on vanadium-extraction efficiency using different extractants diluted in kerosene (vanadium concentration: 950 mg V L^{-1}; pH 2 or 3, depending on the extractant; $V_{org} = V_{aq} = 20$ mL).

coefficient was not significantly changed by an increase of extractant concentration, and the mean value exceeds 400 (not shown). For the other extractants, the extraction efficiency increases with the concentration of the extractant. However, when the concentration exceeds 50 mM, vanadium is quantitatively extracted. The distribution coefficient strongly increased with increasing extractant concentration from 3 to 300.

Influence of Volume Ratio V_{aq}/V_{org}

Figure 5 shows the influence of increasing the V_{aq}/V_{org} on the extraction efficiency. Aliquat 336 was again the most efficient among the extractants for vanadium separation at every selected ratio. Even with a ratio of 5, vanadium was completely extracted from the aqueous solution. Above the ratio of 5, the extraction efficiency started to decrease. The other extractants showed continuously decreasing extraction efficiency. Greater volume reductions can be expected by using Aliquat 336 than for the other extractants.

Stripping of Loaded Extractant Phase

The preliminary tests showed that Aliquat 336 exhibited a greater efficiency and enhanced ability to extract vanadium from acid solutions

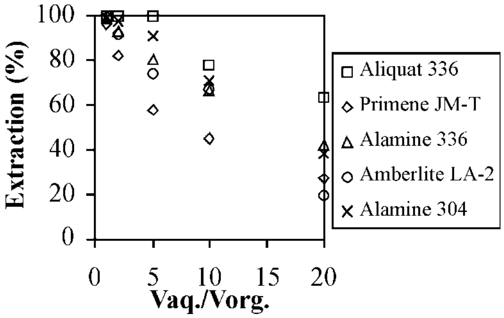

Figure 5. Influence of the volume ratio of organic and aqueous phases (V_{org}/V_{aq}) on the extraction efficiency of vanadium using different extractants diluted in kerosene (vanadium concentration: 950 mg V L^{-1}; pH 2 or 3 depending on the extractant; extractant concentration: 60 mM).

than the other primary, secondary, and tertiary amines. However, it is well known that quaternary ammonium salts are less efficiently stripped than other primary-to-tertiary amine extractants. It was then necessary to check the stripping ability of the used systems before selecting the appropriate extractant. For these experiments Aliquat 336, Alamine 304, and Amberlite LA-2 were selected after being loaded with vanadium at pH 2 (controlled with sulfuric acid) from 0.9 to $1\,\mathrm{g\,V\,L^{-1}}$ solutions.

Influence of Stripping Agent and Concentration on Stripping Efficiency

Several different stripping agents were tested depending on the extractant agent: 1-M sodium hydroxide, 1-M ammonia, 1-M sulfuric acid, and, alternatively, 1.5-M ammonium chloride or 1.5-M ammonium nitrate (alone or in the presence of 1.5-M ammonia). In the case of Aliquat 336, the stripping was efficient only with ammonium chloride and ammonium nitrate in the presence of ammonia with stripping efficiency greater than 98%, while with sodium hydroxide stripping did not exceed 30%. The still less efficient stripping agents were ammonia and sulfuric acid, for which the stripping efficiency was lower than 5%. The stripping is efficient when the pH is moderately alkaline (imposed by the ammonium equilibrium), and the stripping solution contains anions able to be exchanged with vanadate species. The concentration of ammonium chloride (in 1.5-M ammonia solution) was varied between 1 and 2 M, and it appeared that the stripping efficiency was close to 100% when the concentration was greater or equal to 1.5 M (only 50%, with a 1-M concentration).

In the case of Amberlite LA-2, preliminary experiments showed that comparable stripping efficiencies were obtained with 1.5-M ammonium chloride/ammonia solutions, 1.5-M ammonium nitrate/ammonia solutions, 1-M ammonia, and 1-M sodium hydroxide solutions; they were 94%, 100%, 99%, and 98%, respectively. In this case, the key parameter seems to be the control of the pH: an alkaline medium is required while the presence of chloride or nitrate anions is not needed. This is in contrast with the case of Aliquat 336, but these differences were expected since Aliquat 336 is a quaternary ammonium salt that is less sensitive to pH for extraction, and, more specifically, for stripping. For ammonia, the concentration (0.5 to 2 M) did not significantly change the stripping efficiency, which was greater than 98%, whatever the concentration.

Influence of Contact Time and Volume Ratio V_{aq}/V_{org} on Stripping Efficiency

In both cases (Aliquat 336 and Amberlite LA-2), the stripping efficiency was tested for three different contact times: 15, 30, and 60 minutes; and it appeared that 30 minutes were sufficient to achieve complete stripping of vanadium from the loaded organic phases. However, it appeared that stripping was faster with Amberlite LA-2 than with Aliquat 336, since, after 15 minutes of contact, almost 90% of vanadium was recovered in the aqueous phase with the secondary amine. For the same contact time with the quaternary ammonium salt, the stripping did not exceed 60%. The volume ratio between the aqueous and the organic phases is also an important criterion since it determines the possibility to concentrate the metal to be recovered. In the case of Amberlite LA-2, the stripping of vanadium from loaded organic phase was almost complete (96%) even with a volume ratio of 0.5. However, at the same volume ratio, Aliquat 336 exhibited a stripping efficiency as low as 50% and reached the same stripping efficiency (96%) with volume ratios equal to 1 or greater.

These results confirm that despite its high efficiency at extracting vanadium from acidic solutions, Aliquat 336 is not the best extractant for vanadium recovery since the stripping step is more complex than that of Amberlite LA-2. Moreover, the stripping of vanadium from loaded Aliquat 336 requires both the control of pH to alkaline media and the presence of exchangeable anions (nitrate or chloride) in the stripping phase, while vanadium can be stripped from loaded Amberlite LA-2 using only pH control (alkaline conditions).

Vanadium Sorption on Chitosan

Influence of pH on Vanadium(V) Sorption

The influence of the pH on vanadium sorption capacity (q, $\mathrm{mg\,V\,g^{-1}}$, vanadium concentration in the sorbent) using chitosan is shown in Fig. 6. The maximum sorption efficiency was observed in the medium acidity range. Figure 6 also presents the protonation fraction of amine groups of chitosan as a function of pH. The pK_a of chitosan, which depends on the deacetylation degree of the biopolymer and its neutralization yield, is about 6.5. In acidic solutions, amine groups of the polymer are protonated, and the sorbent acts like a weakly basic anion exchanger and NH_3^+ adsorb anionic vanadate species. Since anionic vanadium species only predominate in acidic solutions,

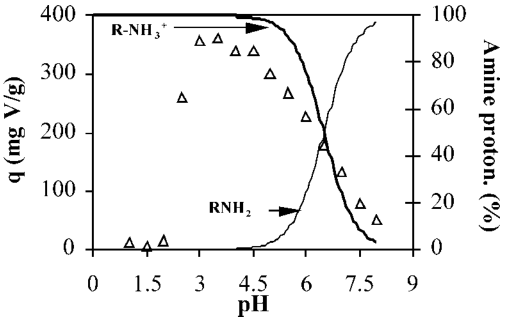

Figure 6. Influence of pH on vanadium(V) sorption capacity (q: mg V g^{-1}; symbols) using chitosan and amine protonation (%; curves).

vanadium sorption is expected to occur in acid solutions. However, vanadium chemistry is very complex since many different anionic species may coexist at low pH, including mono or polynuclear vanadate species. Previous investigations have correlated sorption efficiency to the presence of highly adsorbable species such as decavanadate species.[20] The existence of these decavanadate species and their concentrations are controlled by both the pH and the total vanadium concentration. The optimum pH was observed at intermediary acidic pH since a pH value below pH 2.5 involves strong competition of counter ions for sorption on protonated amine groups and a decrease in the concentration of decavanadate species, the most adsorbable species.

The influence of pH on sorption isotherms is shown in Fig. 7 and the influence of metal concentration on sorption kinetics at pH 3. By increasing

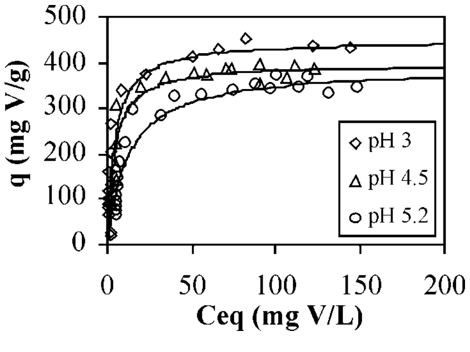

Figure 7. Influence of pH on vanadium-sorption isotherms using chitosan.

the pH of the solution from pH 3 to pH 5.2, a slight decrease in the maximum sorption capacity was observed that can be explained by two reasons: (1) the overall charge of the polymer decreases at higher pH and (2) the speciation of vanadium is shifted to the formation of less adsorbable species. The sorption isotherms are very favorable and almost irreversible since the sorption capacity sharply increased at low-residual concentration (especially at pH 3 and pH 4.5). It was followed by a plateau for residual concentration greater than 40 mg L^{-1}. The affinity coefficient (initial slope of the curves) progressively decreased at higher pH. This confirms the greater affinity of chitosan for vanadate ions at low pH. The sorption capacity did not increase above a residual concentration of 50 mg V L^{-1}. This intermediary result confirms that the sorption process is more likely to be appropriate for the treatment of low-concentration solutions.

Uptake Kinetics

Figure 8 (left) presents the uptake kinetics for low- (50 mg V L^{-1}) and high- (200 mg V L^{-1}) vanadium concentrations at pH 3. Obviously, the time required to reach the equilibrium was greater for high-metal concentration, 3 days compared to 10 hours in the case of low-vanadium concentration. A high-initial concentration is usually expected to increase sorption rate since the concentration gradient between the surface of the sorbent and the solution is favorable for fast mass transfer from the solution to the sorbent surface. The initial slopes of the curves were similar, but the second stage of the process was strongly influenced by the concentration. The second stage is frequently

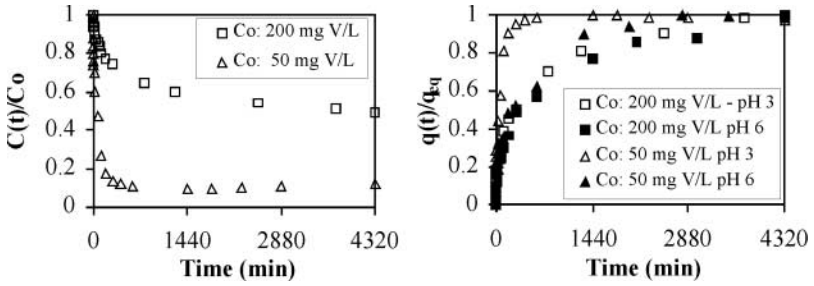

Figure 8. Influence of initial concentration on vanadium-sorption kinetics (pH 3) (left) fractional approach to equilibrium as function of time for vanadium sorption on chitosan: influence of pH, and metal concentration (right) (Co: 200 mg V L^{-1}: ■/□; Co: 50 mg V L^{-1}: △/▲; open symbols: pH 3; closed symbols: pH 6).

controlled by intraparticle diffusion, which again may be controlled by the size of the solute and its affinity for the sorbent. The change in the speciation of metal ions may influence these two steps. Indeed, the greater the concentration, the greater the fraction of vanadium under the form of adsorbable decavanadate species.

An additional experiment was performed with the same initial concentrations at pH 6. The fractional approach to equilibrium $[q(t)/q_{eq}]$ allows the influence of relative saturation of the sorbent to be taken into account at the selected pH. Figure 8 (right) shows the comparison of sorption kinetics (fractional approach to equilibrium) for these experimental conditions. It appears that at high concentration and high pH, the fractional approach to equilibrium was significantly depressed compared to the experiment performed at low pH with low-metal concentration. The great affinity of the sorbent for polynuclear vanadate species involves a fast initial sorption that causes a 30 to 40% decrease in the residual concentration within the first hours of contact. Consequently, in the experiments performed at low-initial concentration, the residual concentration in the solution was very low, and the metal existed in a less adsorbable form at low pH, while at high pH, polynuclear hydrolyzed species remained in the solutions. The large size of polynuclear hydrolyzed species may restrict their access to internal sites, and the sorption kinetics is slowed down. The same limitations may be expected at high-metal ion concentrations.

Vanadium Desorption

The application of chitosan for vanadium recovery from dilute solution depends on the possibility of recovering the metal and reusing the sorbent for several cycles. Based on the results of the sorption processes and the interpretation of the sorption mechanism, it appears that the sorption can be reversed by changing the pH of the solution. Indeed, vanadate species interact with chitosan between pH 2.5 and 6.5. Outside this pH range, the affinity of the sorbent for vanadate species decreases, partly due to the decrease in the positive charge of the sorbent and to the appearance of less adsorbable species in the solution (above pH 7), or to the excessive acidity and presence of other anions (below pH 2), which can compete for sorption on protonated amine groups (brought by the dissociation of the acid used for pH control, for example). Figure 9 shows the influence of the pH on the desorption of vanadium from the loaded sorbent. The pH was controlled with either sulfuric acid or sodium hydroxide. As expected, below pH 2 and above pH 9, vanadium desorption increased strongly.

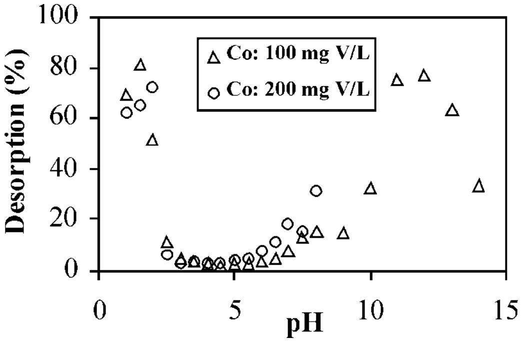

Figure 9. Influence of pH on vanadium desorption from loaded-chitosan. Experiments performed on chitosan samples saturated with vanadium solutions at concentrations of 100 mg V L^{-1} and 200 mg V L^{-1}.

Treatment of Leachates

The leaching of fly ash was performed at a pH that was significantly lower than the optimum pH for sorption on chitosan to achieve the complete removal of vanadium. The pH was raised to pH 2 with sodium hydroxide; however, the sorption efficiency was drastically reduced compared to theoretical values. Further experiments were performed by increasing the pH of the leachate to pH 3. Under these conditions, precipitation of ferric hydroxide occurred. During the precipitation of ferric ions, vanadium was coprecipitated or adsorbed on the precipitate, and the vanadium residual concentration approached zero. Therefore, the sorption process cannot be used for the treatment of acidic leachates. It would be preferable to leach vanadium from fly ash using alkaline media and then to acidify the solutions for further treatments involving the liquid/liquid extraction and the sorption on chitosan. Figure 10 shows the influence of the pH on the precipitation of vanadium, aluminum, and iron from acid leachates. Fly ash was extracted with a 0.5-M sulfuric acid solution (the L/S ratio being 4). Vanadium, aluminum, and iron concentrations were 1919 mg V L^{-1}, 405 mg Al L^{-1}, and 844 mg Fe L^{-1}, respectively. It appears that both iron and vanadium started simultaneously to precipitate at pH 2, while aluminum precipitated at a slightly higher pH. At pH 4, the complete precipitation of the three metals was achieved.

Preliminary experiments were performed with alkaline leachates. Vanadium leaching was performed with NaOH (2 M) at two different L/S ratio, 4 and 10. The vanadium concentrations were 1273 and 532 mg V L^{-1}, respectively. Similarly, the aluminum concentrations were 94 and

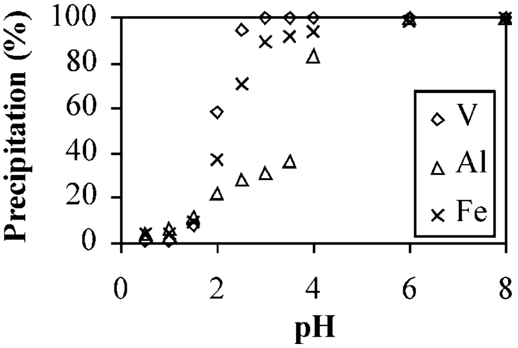

Figure 10. Influence of pH on the precipitation of vanadium, aluminum, and iron from acid leachate (leaching: L/S: = 4; sulfuric acid 0.5 M, contact time 24 hours; [V]: 1919 mg V L^{-1}; [Al]: 405 mg Al L^{-1}; [Fe]: 844 mg Fe L^{-1}).

40 mg Al L^{-1}, respectively. Iron content in the leachate was negligible (below 10 mg L^{-1}). The pH of the solutions was adjusted to pH 3 with sulfuric acid. Extraction was performed with Aliquat 336 (60-mM isodecanol: 5% in kerosene) at different ratios of aqueous to organic phases (V_{aq}/V_{org}). Vanadium was almost completely extracted from the leachate when the ratio V_{aq}/V_{org} was below 5. At $V_{aq}/V_{org} = 5$, the residual vanadium concentration was 15 mg V L^{-1}. The extraction efficiency fell to 69% with a ratio of 10 (residual concentration: 366 mg V L^{-1}) and to 31% with a ratio of 20 (vanadium concentration: 840 mg V L^{-1}). In the case of aluminum, extraction efficiency was around 30% up to a ratio V_{aq}/V_{org} of 5 and below 5% with ratios of 10 and 20. The stripping was performed using ammonium chloride/ammonia (1.5-M) solution, using a V_{aq}/V_{org} ratio of 1. The stripping efficiency reached 76% for vanadium, while aluminum was not stripped under the selected experimental conditions.

A complete treatment may be proposed, including the alkaline leaching of fly ash, followed by a pH control to pH 2 to 3 with sulfuric acid for solvent extraction using Aliquat 336 or Amberlite LA-2. The aqueous phase may then be treated by adsorption on chitosan at pH 3. The loaded organic phase may be stripped using a 1.5-M ammonium chloride/ammonia mixture (leading to concentrated solutions, which can be treated to recycle the metal). The loaded sorbent may be regenerated by desorption using molar ammonia or sodium hydroxide solutions. The eluate can be treated by solvent extraction (after pH control). The process minimizes metal loss and water discharge to the environment.

CONCLUSION

Vanadium-containing fly ashes from thermal power plants can be effectively treated by a leaching procedure to recover vanadium; both alkaline and acid treatments are effective. However, due to the better efficiency of both liquid/liquid extraction and sorption on chitosan at removing vanadium from acidic solutions, the leachates were prepared by contacting sulfuric acid (0.5 M) with fly ash (L/S ratio: 10) for 24 hours. Vanadium extraction was complete and resulted in solutions containing concentrations as high as $0.9\,\mathrm{g\,V\,L^{-1}}$. Preliminary experiments were performed on synthetic solutions for the liquid/liquid extraction of vanadium using several amine-based extractants using comparable pH and vanadium concentrations. Aliquat 336 exhibited very good extraction efficiency, better than those of Primene JM-T, Amberlite LA-2, Alamine 336, and Alamine 304. However, the stripping of vanadium from loaded Aliquat 336 was more difficult than with Amberlite LA-2, for example. The $\mathrm{pK_a}$ characteristics of the extractants may explain these differences in the stripping efficiency and mechanisms. While vanadium can be easily stripped from the secondary amine extractant by changing the pH to alkaline value, the presence of chloride (or nitrate) anions was required in the case of the quaternary ammonium salt.

The sorption of vanadium on chitosan proceeds through anion-exchange mechanism, and the sorption capacity has a maximum at pH 3. Sorption isotherms are very favorable and can reach sorption capacities as high as 400 to $450\,\mathrm{mg\,V\,g^{-1}}$ (i.e., 8 to $9\,\mathrm{mmol\,V\,g^{-1}}$); but above a residual concentration of $50\,\mathrm{mg\,V\,L^{-1}}$, the sorption capacity does not increase. The sorption process, therefore, seems to be best suited for the treatment of low-vanadium concentration solutions. This conclusion is confirmed by the sorption kinetics, which are significantly faster for low-concentration solutions ($50\,\mathrm{mg\,V\,L^{-1}}$) than for high-residual concentrations ($200\,\mathrm{mg\,V\,L^{-1}}$). The distribution of vanadium species controls the affinity of the sorbent for vanadium and its maximum sorption capacity, but kinetic factors are important, also.

The acid leaching of fly ash also dissolves other metal ions (e.g., ferric ions). The adjustment of the pH of the leachates at a pH compatible to vanadium sorption on chitosan (pH 3) leads to the precipitation of ferric hydroxide, which coprecipitates vanadium. This nonselective precipitation precludes the recovery of vanadium and its further sorption on chitosan. An alternative process could be the alkaline leaching of fly ash, which could allow the selective leaching of vanadium and vanadium-like metals followed by a control of the pH to the standard pH for liquid/liquid extraction (i.e., pH 2) and for sorption on chitosan (i.e., pH 3).

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