

Vanadium recovery from oil fly ash by leaching, precipitation and solvent extraction processes

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Abstract

In order to reduce the environmental impact due to land disposal of oil fly ash from power plants and to valorize this waste material, the removal of vanadium was investigated using leaching processes (acidic and alkaline treatments), followed by a second step of metal recovery from leachates involving either solvent extraction or selective precipitation. Despite a lower leaching efficiency (compared to sulfuric acid), sodium hydroxide was selected for vanadium leaching since it is more selective for vanadium (versus other transition metals). Precipitation was preferred to solvent extraction for the second step in the treatment since: (a) it is more selective; enabling complete recovery of vanadate from the leachate in the form of pure ammonium vanadate; and (b) stripping of the loaded organic phase (in the solvent extraction process) was not efficient. Precipitation was performed in a two-step procedure: (a) aluminum was first precipitated at pH 8; (b) then ammonium chloride was added at pH 5 to bring about vanadium precipitation.

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1. Introduction

There are many well established applications of vanadium: as an alloying element in steel and iron, as an additive to titanium alloys (for aerospace applications), and as catalysts (for the chemical and polymer industries) (Moskalyk and Alfantazi, 2003). The principal commercial use of vanadium is as an alloying element in steel and cast iron: using vanadium in the fabrication of steel alloys improves the hardness and wear resistance of the material (Gupta and Krishnamurthy, 1992).

Vanadium is currently recovered as a by-product or at best a co-product from mineral resources: the former sources of concentrated ore deposits are now depleted (Gupta and Krishnamurthy, 1992). The common grade

of vanadium in processed ores is usually less than 2%. As a consequence, many industrial sub-products have been investigated and used for vanadium recovery, including converter and smelter slag, or spent catalysts (Gupta and Krishnamurthy, 1992). Although the treatment of these sub-products is made difficult by the association of vanadium with some refractory elements, the high level of vanadium, which can reach up to 20–30%, has made them the focus of interest in many studies (Zhang et al., 1995; Lozano and Juan, 2001). Another interesting source of vanadium is the treatment of oil fly ash produced by the combustion of crude oil (Akita et al., 1995; Tsai and Tsai, 1998; Vitolo et al., 2000; Miura et al., 2001a; Vitolo et al., 2001; Guibal et al., 2003). Indeed, some crude oils, such as Venezuelan, can contain up to 500 ppm of vanadium. The combustion of these crude oils produces oil fly ashes that are characterized by a high content of vanadium, nickel, iron, aluminum, silicon, sulfur and non-burnt carbon. Gupta and Krishnamurthy (1992) reported the chemical composition of petroleum fly ash from various origins and observed a great diversity in their composition:

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2.5–40% for vanadium (V_2O_5), 0.8–6% for nickel (NiO), 0.7–8.6% for iron (Fe_2O_3), 0.5–14.6% for Al(Al_2O_3), 2.5–24.8% for Si(SiO_2), 2–30% for S and 1–54% for C. It is thus an interesting source for the recovery of vanadium. The production of these oil fly ashes is of economic concern (for the valorization of vanadium) but is also of environmental concern (Gangloff et al., 1997; Mohapatra and Rao, 2001; Choi et al., 2002). Indeed, uncontrolled disposal of the ashes may cause a dispersion of fine particles containing products hazardous to health (Fernandez et al., 2003). Exposure to vanadium may cause coughing, bronchial irritation, gastrointestinal diseases and conjunctivitis. The effects are similar for short-term exposure to high grade levels (occupational exposure) and for long-term exposure to low grade levels (chronic contamination). Although no definite evidence has yet been found to indicate that vanadium and its compounds are mutagenic or carcinogenic, several metabolic effects have been found to be associated with chronic low grade exposure to vanadium (Fernandez et al., 2003). These effects may have an impact on health through the inhibition of cholesterol synthesis, the reduction of coenzymes A and Q, and the activation of monoamine oxidase. The toxicity of vanadium and its effect on health is highly dependent on its speciation, vanadium pentoxide being one of the most toxic forms. The speciation of metals and especially vanadium in the ashes is not well documented. However, several studies have shown that the vanadium found in the ashes is mainly in the form $VOSO_4$ (Eatough et al., 1984; Lytle et al., 1986; Manivanan and Seehra, 2000). The dispersion of fine particles of oil fly ash and the high solubility of vanadium may cause a dispersion of vanadium in water and soil. Due to the low toxicity of vanadium compared to other heavy metals, the accepted levels for vanadium in water supplies and irrigation water are 200 ppb and 10 mg L^{-1} , respectively (Juste et al., 1995). However, regulations imposed in many countries require companies to process the waste materials in order to recover the valuable materials and avoid the dissemination of toxic products.

Many studies have focused on the recovery of vanadium from oil fly ash using several processes: leaching (after preliminary roasting) (Fytianos et al., 1998; Iretskaya et al., 1999; Querol et al., 2001; Choi et al., 2002; Janos et al., 2002; Seferinoglu et al., 2003) or bioleaching (Brombacher et al., 1998; Seidel et al., 2001) followed by precipitation (Chmielewski et al., 1997; Vitolo et al., 2001), ion exchange (Tokuyama et al., 2003), or solvent extraction (Lozano and Juan, 2001; Miura et al., 2001b; Guibal et al., 2003).

The present work focuses on the design of integrated processes for vanadium recovery from oil fly ash. The processes firstly consist in a leaching step, either alkaline or acidic, and a second step of metal recovery from the leachates, involving either precipitation or solvent extraction. The composition of the leachates depends considerably on the leaching technique and therefore affects the selection of the complementary treatment. The options investigated for the reprocessing of leachates were precipitation and sol-

vent extraction. Additional tests were performed using chitosan for the sorption of vanadium, as a polishing treatment.

2. Materials and methods

2.1. Materials

Oil fly ashes were collected from disposal sites of waste materials from a thermal power plant in Mexico. Amberlite LA-2 and Primene JMT were kindly donated by Rohm and Haas (Germany). Aliquat 336, Alamine 304 and Alamine 336 were kindly donated by Henkel (Germany). Chitosan, an aminopolysaccharide made of glucosamine and acetylglucosamine units, was provided by France Chitine (France). Other reagents were purchased from Fluka: vanadium monovanadate, isodecanol, ammonium chloride, ammonium hydroxide, sodium hydroxide, sulfuric acid and kerosene were analytical grade reagents.

2.2. Characterization of oil fly ash

The oil fly ash was dried to a constant weight at $110 \text{ }^\circ\text{C}$. The water content was close to 1%. The powder was sieved and the fraction below $500 \text{ }\mu\text{m}$ was used for further studies. The stock was divided into several identical fractions. Several representative aliquots (100, 200 and 300 mg) were mineralized (in duplicate) using aqua regia (20 mL) in a microwave furnace, model MAR5X (CEM, USA). The volume was adjusted to 250 mL and filtered, and the filtrate was analyzed for vanadium content using an inductively coupled plasma atomic emission spectrometer, ICP-AES, ICP JY 2000 (Jobin Yvon, France). The vanadium content was 1.6% (in weight). The metal content of the oil fly ash is given in Table 1. In addition, the C element content of the oil fly ash (inclusive carbonate, carbon and residual oily material) was evaluated by thermal decomposition at $1000 \text{ }^\circ\text{C}$. The weight loss from thermal decomposition at $1000 \text{ }^\circ\text{C}$ for 6 h was about 85%. The silicon content was not measured, but was evaluated at between 3% and 4% by X-ray fluorescence analysis, using a Siemens 1328 X-ray fluorescence spectrometer.

2.3. Leaching procedures

The leaching procedure was performed in agitated flasks at room temperature (unless specified) using a Cole Parmer 51502 reciprocal shaker (agitation speed 200 rpm). The contact time was 24 h (unless specified). The liquid/solid ratio was varied, but unless specified was 4 mL g^{-1} . The leaching agents were H_2SO_4 , NaOH and Na_2CO_3 . After

Table 1
Metal content in oil fly ash

	V	Cu	Al	Fe	Ni	Ca	Mg
Content (% w/w)	1.6	0.01	0.64	1.7	0.85	0.2	0.14

the required contact time, the flasks were left to settle overnight; the supernatant was then filtered and the filtrate was analyzed for its vanadium, aluminum, silicon, iron and nickel content, depending on the leaching procedure. Indeed, with alkaline leaching, metals such as iron and nickel were not extracted due to in situ precipitation. Exact experimental conditions are directly given in the figures. To remove water-phase metal impregnating the solid, after the leaching step the oil fly ashes were submitted to three successive rinsing steps using water (at the same liquid/solid ratio, i.e., 4 mL g⁻¹); each rinsing step lasted for 1 h followed by filtration.

Acidic leaching was performed using sulfuric acid solution (100 g of oil fly ash in 400 mL of sulfuric acid 2 M for the leaching step, and 400 mL of water for rinsing steps with a contact time of 24 h for leaching and 1 h for rinsing). The concentration of five metals (V, Al, Si, Ni and Fe) was determined in the leachates and also in the three rinsing fractions in order to evaluate the amount of the different metals that can be recovered in the leachate fraction and that can be washed out from the treated oil fly ash.

The amount of metal removed from the solid waste was determined at each step, considering the initial volume of solution (leaching agent, or water for the rinsing step). These data served to determine the *total percentage* of metal removed from oil fly ash and to evaluate the *mean concentration* of the metal in the whole volume of solution used for the treatment of the solid (including leaching and rinsing batches). The *cumulative metal recovery* (percentage) served to quantify the amount of metal removed at each step of the treatment, compared to the total amount of metal recovered at the end of the process.

2.4. Solvent extraction procedure

Solvent extraction was performed by mixing 20 mL of leachate with 20 mL of the organic phase for 30 min. The organic phase was prepared by dilution of the extractant in kerosene (Fluka). Isodecanol (Fluka) was added to the solution to give a 5% (v/v) concentration in order to prevent the formation of a third phase during the extraction process. The extractant concentration was adjusted to the selected values. Preliminary experiments were performed with synthetic vanadium solutions (close to 1000 mg V L⁻¹) in order 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 the leachates when relevant (for V concentrations higher than 200 mg L⁻¹). The leachates were submitted to a pre-treatment with hydrogen peroxide in order to oxidize any fraction of vanadium that could be in a reduced form (V(IV), less extractable): a 50% excess of hydrogen peroxide was added compared to the total amount of V. The pH of the leachate was then controlled at the suitable value (generally pH 3). Stripping was performed by contacting equal volumes of the organic and stripping phases (NaOH, NH₃, NH₄Cl/NH₃, NH₄NO₃)

at known concentration for 30 min. The concentration of vanadium in the aqueous phase was used in the mass balance equation for the determination of the stripping efficiency.

2.5. Precipitation procedure

Acidic leachates were precipitated using sodium hydroxide for pH control. In the case of alkaline leachates, the pH of the solutions was controlled to pH 5–6 using sulfuric acid. Ammonium chloride was therefore added to the solution to reach a final concentration of 1 M. The reaction time (under agitation) was set to 7 days. The precipitate was then filtered and the filtrate was analyzed for metal content.

2.6. Sorption on chitosan

The solutions were mixed with chitosan (particle size <125 µm) for 3 days. The pH of the solution was controlled to 3 using sulfuric acid. The standard sorbent dosage was 700 mg L⁻¹. The solution was finally filtered, and the concentration of metal ions in the filtrate was measured using ICP-AES.

3. Results and discussion

3.1. Leaching

Several leaching treatments were carried out: acidic solutions (sulfuric acid), and alkaline solutions (either NaOH or Na₂CO₃). Changing the type of leaching agent may change the efficiency of the process, the selectivity of metal leaching and also the speciation of the metals, which in turn may affect their behavior in terms of solvent extraction and precipitation. Based on the speciation of vanadium in solution (Guzman et al., 2002), vanadium is expected to be in the form of VO₂⁺ in acidic solutions and in the form of VO₃(OH)²⁻ and VO₄³⁻ in alkaline solutions. Eatough et al. (1984) carried out several analytical procedures (pH-calorimetric measurements, ionic chromatography and proton-induced X-ray emission analysis) to identify extractable V species. They concluded that vanadium was present as both VO₂⁺ and VO²⁺ in the water leachates of oil fly ash (the pentavalent form being the principal species).

3.1.1. Acidic leaching

The acidic leaching was performed using 0.5 M sulfuric acid solutions. Taking into account the composition of oil fly ash and the experimental procedure (mass of oil fly ash, volumes of leaching solution and rinsing solution) for the leaching process, it was possible to calculate the extraction percentage for the various metals in relation to the total amount in oil fly ash. Vanadium recovery reached 98% (mean concentration: 1067 mg V L⁻¹), Al leaching was 68% (mean concentration: 295 mg Al L⁻¹), Fe removal

reached 42% (mean concentration: 480 mg Fe L⁻¹), Ni leaching was close to 12% (mean concentration: 70 mg Ni L⁻¹) and Si removal was 4% (mean concentration 96 mg L⁻¹). These values are of the same order of magnitude as the values cited by Tsai and Tsai (1998) using 0.5 N sulfuric acid solutions, except for nickel recovery, which was significantly lower in the present study (8% versus 60%). Vitolo et al. (2000) extensively investigated the leaching of Orimulsion fly ashes using sulfuric acid (varying liquid/solid ratio, temperature, and acid concentration). They found that vanadium recovery varied in the range 60–90%. In a later paper, they showed that the roasting of the fly ash may have either a positive or negative impact on metal recovery depending on burning temperature (Vitolo et al., 2001): below 950 °C, the roasting step increased leaching efficiency, while above this temperature the formation of refractory V–Ni compounds limited metal availability. Some studies have shown that self-inhibition of aluminum leaching from oil fly ash can occur in the presence of sulfuric acid, which forms a calcium sulfate precipitate that hinders mass transfer across the surface of the oil fly ash (Seidel et al., 1999).

Metals were removed at each step of the process (leaching and rinsing steps). Fig. 1 shows the distribution of metal recovery throughout the procedure in function of the total recovery reached at the end of the process. The extraction behavior appeared to be independent of the metal involved. Acidic leaching extracted the metals to various extents, but non-negligible concentrations of each of them were also present in the rinsing baths. It is especially important to take into account the objective of the process, i.e., the selective recovery of vanadium. The presence of several metals in the leachates increases the difficulty of separating the metals for the subsequent processing steps (i.e., solvent extraction and/or precipitation). For this reason it is important to find another leaching agent that could avoid the simultaneous leaching of some of these metals, especially iron and nickel. These metals precipitate

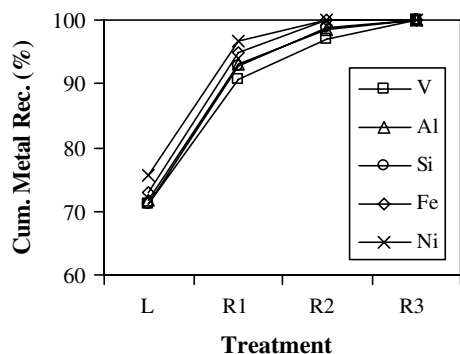


Fig. 1. Acidic leaching of oil fly ash using 0.5 M H₂SO₄ solutions – cumulative metal (V, Al, Si, Fe, Ni) extraction after leaching (L) and rinsing (R) steps (cumulative percentage of metal recovered at each step of the process in relation to the total amount of metal removed throughout the process) – extractable metal fraction with respect to total metal in the oil fly ash: V: 98%, Al: 68%, Si: 4%, Fe: 42%, Ni: 12%.

in the same pH range as vanadium. Alkaline leaching agents may be appropriate since they are able to leach vanadium while maintaining iron and nickel precipitation. Sequential leaching has been suggested as an alternative for the separation of metals according to their solubility/precipitation and redox properties: Zn and Pb were separated from Fe, for example, by using different leaching agents (i.e., water, followed by acidic treatment) (Van Herck and Vandecasteele, 2001). Two different alkaline reagents were used for alkaline leaching in this study: sodium hydroxide and sodium carbonate.

3.1.2. Alkaline leaching with sodium hydroxide

Figs. 2 and 3 show V, Al and Si leaching using 2 M NaOH according to different experimental procedures. Nickel and iron were not recovered during NaOH treatment. Fig. 2 shows cumulative metal recovery for a simple leaching step followed by three rinsing steps (100 g of oil fly ash in 400 mL of 2 M NaOH for the leaching step and 400 mL of water for rinsing steps with a contact time of 24 h for leaching and 1 h for rinsing), while Fig. 3 shows cumulative metal recovery for six successive leaching/

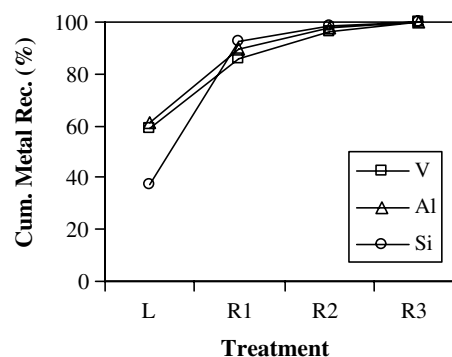


Fig. 2. Alkaline leaching of oil fly ash using 2 M NaOH solutions – cumulative metal (V, Al, Si) extraction after leaching (L) and rinsing (R) steps – extractable metal fraction with respect to total metal in the oil fly ash: V: 90%, Al: 54%, Si: 8.5%.

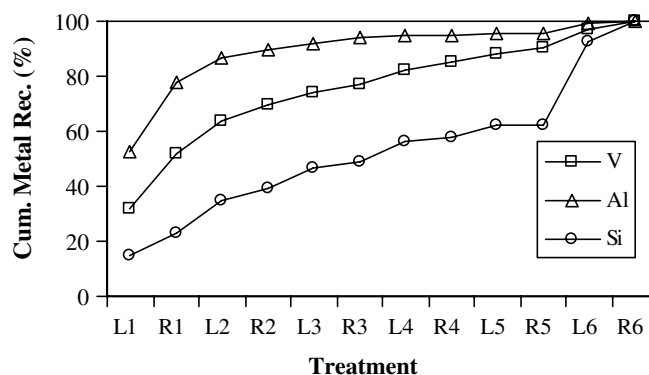


Fig. 3. Alkaline leaching of oil fly ash using 2 M NaOH solutions – cumulative metal (V, Al, Si) extraction after 6 successive leaching (L) and rinsing (R) steps – extractable metal fraction with respect to total metal in the oil fly ash: V: 98%, Al: 55%, Si: 5%.

rinsing steps (100 g of oil fly ash, 400 mL of 2 M NaOH and 400 mL of water for leaching and rinsing steps, respectively; contact time was 1 h for the leaching step, except for the sixth leaching: 6 h, and 10 min for the rinsing steps). These figures show the distribution of metal recovery throughout the procedure in function of the total recovery reached at the end of the process. When using a single-leaching step, more than 85% of total metal recovered from oil fly ash was obtained after the leaching and the first rinsing step (Fig. 2). Total metal leaching reached 90% for vanadium, 54% for aluminum and less than 9% for silicon. The mean concentrations of the metals in the leachate (mixing leaching and rinsing solutions) were 993 mg V L⁻¹, 239 mg Al L⁻¹ and 206 mg Si L⁻¹.

These results are basically consistent with those presented by Tsai and Tsai (1998), who found that vanadium extraction exceeded 80% with 2 M NaOH leaching solutions, while nickel was not significantly removed from oil fly ash. Conversely, Tsai and Tsai (1998) observed that a mixture of ammonium sulfate/ammonia selectively removed Ni from V in oil fly ash. Chmielewski et al. (1997) also found that the acidic treatment of oil fly ash was less efficient in vanadium recovery than an alkaline leaching agent; in the case of NaOH solution, leaching efficiency reached up to 94% for V.

On the other hand, when using several successive leaching/rinsing steps (with shorter contact time) the extraction efficiency significantly decreased and the metals were regularly and progressively leached. However, the recovery of the metals did not all follow the same trends: Al was strongly recovered during the first two steps; supplementary steps only recovered 5–10% of total Al recoverable under the selected experimental conditions. In the case of V leaching, the metal was strongly recovered during the first two steps but metal extraction continued to be progressively removed from the oil fly ash up to the sixth step. For Si recovery, metal leaching was low and almost constant over the first five steps while metal extraction sharply increased at the sixth step. It seems that a longer contact time was necessary for Si (the sixth leaching lasted for 24 h compared with 1 h for the other leaching steps). Total metal extraction with this second procedure reached 98%, 55% and 5% for V, Al and Si, respectively. In this case,

metal concentrations were significantly lower than those obtained in the first procedure: 434 mg V L⁻¹, 101 mg Al L⁻¹ and 48 mg Si L⁻¹. Increasing contact time led to increased leaching efficiency rather than multiplying the number of leaching batches (with short contact time).

The influence of temperature on V and Al leaching using NaOH solutions (20 g of oil fly ash for 80 mL of 2 M NaOH) was investigated in function of contact time. The alkaline leaching batch was regularly changed/analyzed at given times: 2 days, 5 days, 8 days, 12 days and 16 days (Fig. 4). While V was recovered with the same efficiency and the same kinetics, independently of reaction temperature, in the case of Al, increasing reaction temperature surprisingly decreased leaching kinetics above $T=40\text{ }^{\circ}\text{C}$. With such long contact times, total extraction efficiency was drastically increased and V was completely removed while Al leaching reached 68–80% (Table 2). Therefore, the kinetics of V and Al leaching were more precisely compared at $T=20$ and $80\text{ }^{\circ}\text{C}$ (Fig. 5). This figure confirms that the temperature had a very limited effect on V leaching efficiency and kinetics; the curves almost overlapped and a contact time of 12 h was sufficient to remove most extractable V. The leaching of Al did not follow the same behavior. At $20\text{ }^{\circ}\text{C}$, Al recovery increased with increasing contact time up to 12 h and stabilized above 12 h; this was completely different at $80\text{ }^{\circ}\text{C}$, since Al recovery maintained a constant level during the first 2 h of contact; and sharply decreased up to a contact time of 48 h, certainly due to metal precipitation. Under the selected conditions ($T=80\text{ }^{\circ}\text{C}$ and long contact time: 48 h), Al concentration in the leachate did not exceed 80 mg Al L^{-1} . It was almost possible selectively to remove V from Al, but at the expense of maintaining oil fly ash in contact with NaOH at high temperature for a long contact time.

Table 2

Influence of temperature and leaching steps on V and Al leaching from oil fly ash (NaOH leaching) – total metal recovery (%) compared to metal content in oil fly ash after 16 days

Metal	$T=20\text{ }^{\circ}\text{C}$	$T=40\text{ }^{\circ}\text{C}$	$T=60\text{ }^{\circ}\text{C}$	$T=80\text{ }^{\circ}\text{C}$
V	98	99	99	99
Al	70	80	72	68

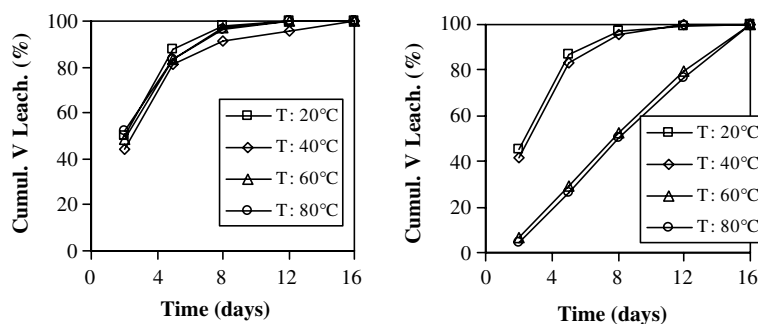


Fig. 4. Influence of temperature and leaching steps on vanadium and aluminum leaching from oil fly ash (2 M NaOH leaching) (leaching solutions were changed/recovered at time: 2, 5, 8, 12 and 16 days).

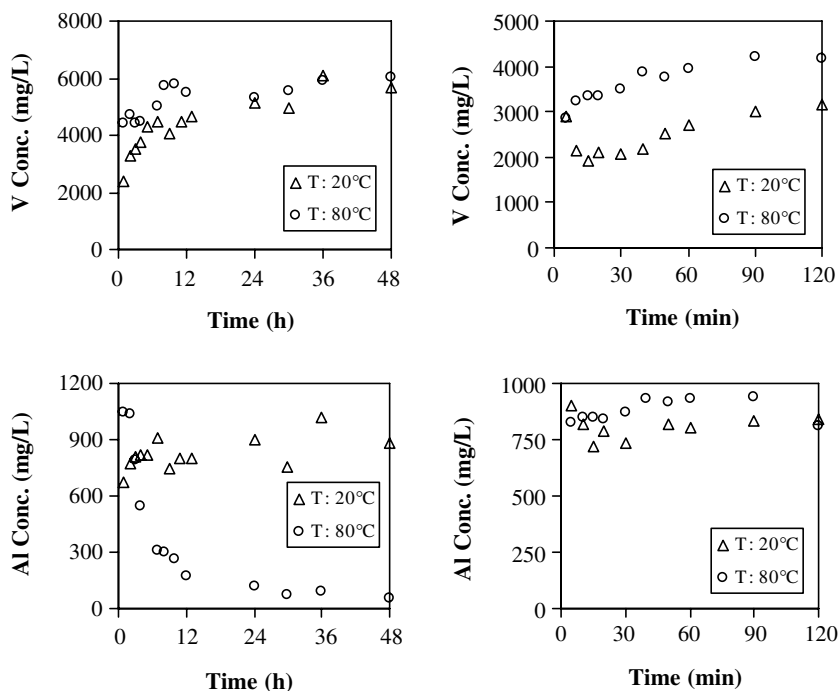


Fig. 5. Kinetics of vanadium and aluminum alkaline leaching (2 M NaOH leaching) – long contact time (left panels) and short contact time (right panels).

3.1.3. Alkaline leaching with Na_2CO_3

The presence of Si in the leachate may induce complications in the separation of the metals during the following extractions steps (solvent extraction, precipitation, etc.). Sodium carbonate was therefore tested in order to increase leaching selectivity (Fig. 6). Indeed, Si was not recovered when using 0.66 M sodium carbonate solutions (at room temperature): Si concentration did not exceed 10 mg L^{-1} (not shown). Vanadium leaching followed approximately the same trend as that obtained with NaOH: more than 80% of total extractable V was recovered after the leaching and first rinsing steps. Aluminum recovery was less effective than in the case of NaOH leaching during these first two steps; however, Al leaching significantly increased during the third rinsing step. Actually, it appeared that aluminum can be removed only when V was not present in significant

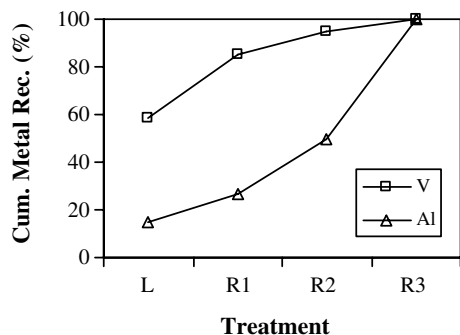


Fig. 6. Alkaline leaching of oil fly ash using 0.66 M Na_2CO_3 solutions – cumulative metal (V, Al) extraction after leaching (L) and rinsing (R) steps – extractable metal fraction with respect to total metal in the oil fly ash: V: 80%, Si: 2.8%.

quantities in the solid waste: this suggests that vanadium contributes to increasing the stability of aluminum in oil fly ash.

The total leaching of V did not exceed 80% (with a mean concentration in the leachate of 893 mg V L^{-1}). Aluminum recovery was below 3% of total Al in oil fly ash (Al concentration in the leachate was below 70 mg Al L^{-1}).

These alkaline leaching operations using either NaOH or Na_2CO_3 show different behaviors for metal recovery with different advantages and drawbacks (leaching efficiency and leaching selectivity). Solvent extraction was investigated on the leachates produced by both NaOH and Na_2CO_3 leaching.

3.2. Solvent extraction

3.2.1. Pre-selection of extractant and stripping agent using synthetic solutions

The first step in the study was aimed at selecting the optimum extractant using a primary amine (Primene JMT), a secondary amine (Amberlite LA-2), tertiary amines (Alamine 304, Alamine 336) and quaternary ammonium salt (Aliquat 336). The selection criteria were the effect of pH, extractant concentration and the $V_{\text{aq.}}/V_{\text{org.}}$ ratio (concentration effect). Fig. 7 shows the results obtained with this selection of extractants, which are known for their potential for extracting metal anions such as vanadate, molybdate (Olazabal et al., 1991, 1992; Schrötterova et al., 1994; Nekovar and Schrötterova, 1999, 2000; Miura et al., 2001a,b). Aliquat 336 showed increasing vanadate recovery efficiency with increasing pH while the other extractants showed a sharp optimum

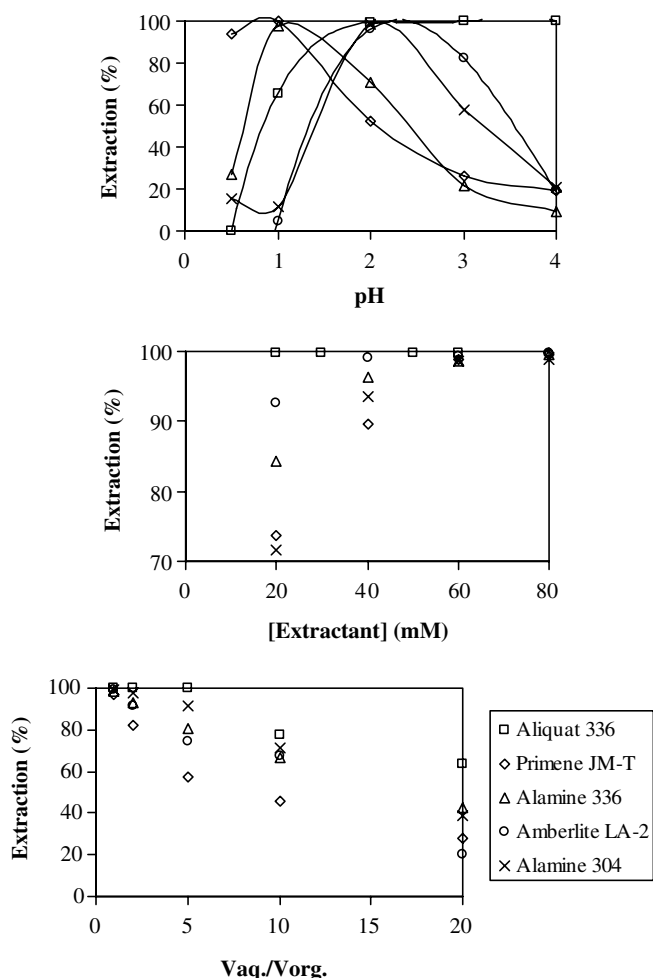


Fig. 7. Selection of extractant and operating conditions (pH: top panel; extractant concentration: middle panel and influence of V_{aq}/V_{org} on extraction efficiency: bottom panel) for vanadium recovery from synthetic solutions (loading with an aqueous solution containing 900 mg V L^{-1} ; contact time: 30 min; except when varied: extractant concentration: 60 mM and V_{aq}/V_{org} : 1, pH 1 for Primene JMT and Alamine 336, pH 2 for Amberlite LA-2 and Alamine 304, pH 3 for Aliquat 336).

pH (at pH 1 or pH 3). The extraction of vanadate species by Primene JMT in acidic solutions has been correlated to the region of predominance of decavanadate species (Nekovar and Schrötterova, 1998). Similar conclusions have been reached using other primary or tertiary amine extractants (Lozano and Juan, 2001; Lozano and Godinez, 2003) and quaternary ammonium salt (Miura et al., 2001b). Since the leaching agents that showed the best selectivity for V recovery were alkaline agents, Aliquat 336 appeared more appropriate for V extraction.

The concentration of the extractant was varied and extraction took place at the optimum pH (given in the previous section: i.e., pH 1 for Primene JMT and Alamine 336; pH 2 for Amberlite LA-2 and Alamine 304; and pH 3 for Aliquat 336). Fig. 7 clearly shows that the smallest amount of extractant required to achieve complete vanadium extraction was with Aliquat 336 (followed by Amberlite LA-2). This confirms the greater efficiency of Aliquat 336

for vanadium recovery compared to other extractants. The middle panel of Fig. 7 confirms this partial conclusion. The concentrating effect of Aliquat 336 was also significantly greater than that obtained with other extractants. Amberlite LA-2 was the extractant with the highest extraction performances after Aliquat 336. The last part of Fig. 7 shows the influence of the V_{aq}/V_{org} ratio on vanadium recovery from synthetic solutions for different extractants. Except for Aliquat 336, vanadium extraction continuously decreased with increasing V_{aq}/V_{org} ratio. The greatest impact of this parameter (which gives an indication on the concentrating effect of the solvent extraction process) was obtained with Primene JMT. In the case of Aliquat 336, a complete extraction of vanadium was maintained until V_{aq}/V_{org} reached 5; above this limit ratio metal extraction decreased, but even with a large excess of water (i.e., $V_{aq}/V_{org} = 20$) extraction remained greater than 65%. Due to their higher efficiency for vanadium extraction, Aliquat 336 and Amberlite LA-2 were used to investigate stripping efficiency. Table 3 compares the stripping efficiency of different chemical agents for vanadium recovery from the loaded organic phase. In the case of Amberlite LA-2, vanadium recovery was readily achieved using alkaline media (NaOH, ammonia) and mixed media (ammonia and ammonium salt) with quantitative recovery of the metal. In the case of Aliquat 336 the stripping was much more difficult and a severe selection of the stripping agent was required. The quantitative recovery of vanadium was only achieved using concentrated mixed solutions of ammonia and ammonium salt (1.5 M $\text{NH}_3 + 1.5 \text{ M NH}_4\text{NO}_3$ or NH_4Cl). Other stripping agents released vanadium only partially. These results are consistent with the literature: the low efficiency of NaOH for vanadium recovery from V-loaded quaternary ammonium salt extractant (Aliquat 336) had previously been established (Lozano and Juan, 2001; Bal et al., 2002). The $\text{NH}_4\text{Cl}/\text{NH}_3$ mixture was selected as the optimum stripping agent for further investigation. Table 4 compares stripping kinetics for Aliquat 336 and Amberlite LA-2, and shows that the fastest vanadium stripping was obtained with the latter extractant, though the difference was only significant at low contact

Table 3

Influence of stripping agent and concentration on vanadium stripping from loaded organic phase (Aliquat 336 and Amberlite LA-2)

Stripping agent	Stripping efficiency (%)	
	Aliquat 336	Amberlite LA-2
$\text{NH}_4\text{Cl}/\text{NH}_3$ (1.5 M each)	100	94
$\text{NH}_4\text{Cl}/\text{NH}_3$ (1 M each)	50	n.d.
$\text{NH}_4\text{NO}_3/\text{NH}_3$ (1.5 M each)	94	100
$\text{NH}_4\text{NO}_3/\text{NH}_3$ (1 M each)	48	n.d.
NaOH (1 M)	28	98
NH_3 (1 M)	3	100
NH_3 (0.5 M)	n.d.	98
NH_3 (2 M)	n.d.	100
H_2SO_4 (1 M)	2	5

n.d.: not determined.

Table 4
Influence of contact time on stripping efficiency (NH₄Cl/NH₃, 1.5 M each)

Contact time (min)	Stripping efficiency (%)	
	Aliquat 336	Amberlite LA-2
15	60	90
30	98	100
60	100	100

Table 5
Influence of V_{aq}/V_{org.} on stripping efficiency (NH₄Cl/NH₃, 1.5 M each)

V _{aq} /V _{org.}	Stripping efficiency (%)	
	Aliquat 336	Amberlite LA-2
0.5	51	48
1	92	100
2	100	100

time. Table 5 evaluates the influence of the V_{aq}/V_{org.} ratio on vanadium stripping efficiency for both Aliquat 336 and Amberlite LA-2. The differences were not very marked and the stripping step can be considered to have the same concentrating effect for these two extractants. Stripping was generally more efficient with Amberlite LA-2 than Aliquat

336. However, taking into account the significantly greater efficiency of Aliquat 336 during the extraction step, this extractant was selected for further experiments on vanadium recovery from leachates.

3.2.2. Testing of extraction and stripping steps on alkaline leachates (NaOH)

Fig. 8 reports the results obtained in the integrated treatment (alkaline leaching + solvent extraction) of oil fly ash using sodium hydroxide as the leaching agent. The concentration of NaOH was varied and three successive leaching steps were performed (using an L/S ratio of 4 mL g⁻¹; contact time: 24 h). Vanadium leaching reached a maximum at a NaOH concentration of 0.5–0.75 M and tended to stabilize at higher concentrations, while Al leaching continuously increased with NaOH concentration. The final pH of the solutions obtained at the different leaching steps was monitored and correlated to V and Al leaching efficiency (not shown). Due to the acidic behavior of oil fly ash the pH of the solution at the end of the first leaching step was close to neutrality with a low concentration of NaOH, which may explain the low leaching efficiency in these cases. Controlling the pH to 12 could be a possible

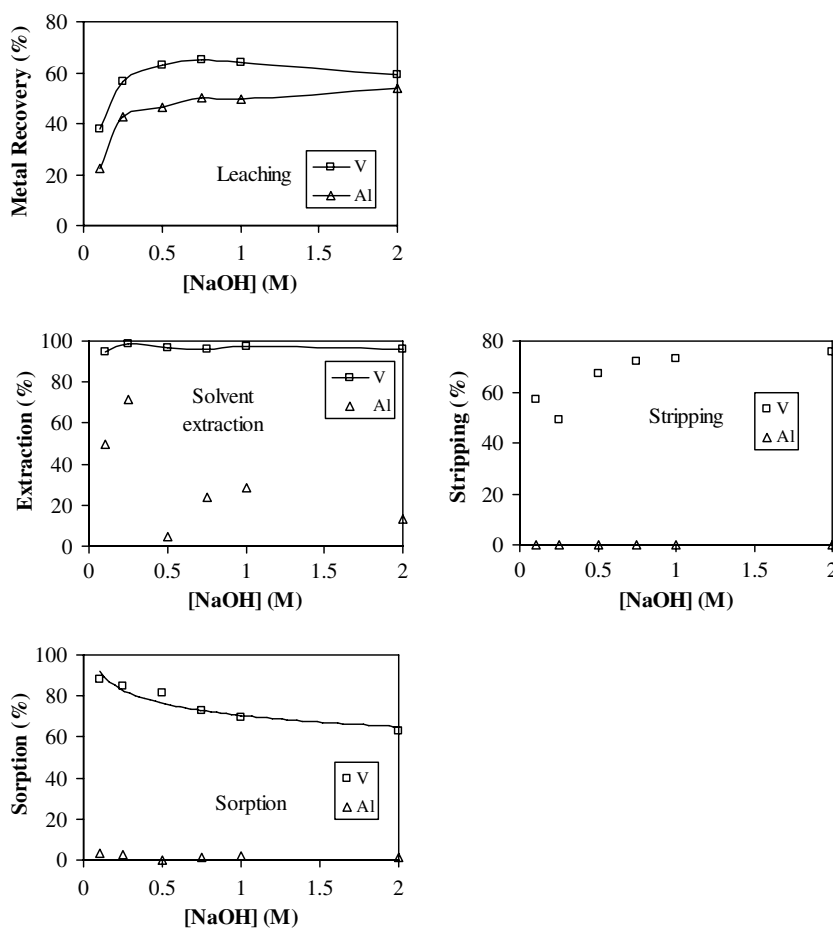


Fig. 8. Vanadium leaching using NaOH, solvent extraction and stripping and treatment of aqueous residues by sorption on chitosan – influence of NaOH concentration used in leaching step (experimental conditions: three leaching steps with NaOH, contact time: 24 h, L/S: 4 mL g⁻¹, room temperature; solvent extraction: pre-treatment of leachate with H₂O₂ and pH control to 3 with H₂SO₄, contact time 30 min; Aliquat 336: 60 mM, V_{aq}/V_{org.}: 1; stripping: NH₄Cl 1.5 M + NH₃ 1.5 M, contact time: 30 min, V_{aq}/V_{org.}: 1; sorption on chitosan: 700 mg L⁻¹, pH 3 controlled with H₂SO₄, contact time: 3 days).

solution for optimizing alkaline leaching with NaOH, using solutions of different concentrations during the successive leaching steps: 0.5 M at the first step and 0.05 M for the next two leaching steps. Leachates for the different leaching steps were mixed and treated with hydrogen peroxide in order to oxidize vanadium to its pentavalent form and finally the pH was controlled to pH 3 using sulfuric acid. Vanadium extraction by Aliquat 336 (60 mM, in kerosene with 5% of isodecanol to prevent the formation of a third phase) was performed with a contact time of 30 min and a $V_{aq}/V_{org.}$ ratio of 1. Vanadium was almost completely extracted (efficiency greater than 95%) independently of the concentration of NaOH leaching agent. Aluminum extraction was much more variable and rarely exceeded 50%. A correlation was observed between the final pH of the aqueous solution (at the end of the extraction process) and the efficiency of Al extraction: when the pH increased Al extraction increased, and below pH 3.4 Al extraction was less than 10% (not shown). Controlling the pH of the aqueous phase would be a solution for improving the selective separation of Al and V.

The stripping of the metals was performed using equimolar 1.5 NH_4Cl/NH_3 solutions (agitation for 30 min with a $V_{aq}/V_{org.}$ ratio of 1). Vanadium stripping varied between 60% and 80%, while Al was not stripped at all. This may significantly limit the applicability of the process since it would not be possible to re-use the extractant for a number of cycles, unless equilibrium is established for Al between aqueous and organic phases, which, in turn, limits the possibility for the organic phase to accumulate increasing concentrations of Al. Aluminum is suspected of behaving as a competitor for V extraction.

The last part of Fig. 8 shows the results obtained in the sorption of V and Al on chitosan from metals present in the aqueous solution after solvent extraction. In the case of V recovery, the sorption efficiency was significantly influenced by the concentration of NaOH that was used for leaching operations. Increasing the concentration of NaOH produced very alkaline leachates, and pH control prior to solvent extraction resulted in the addition of large amounts of sulfuric acid. The concentration of competitor anions (sulfate) increased, which in turn decreased the efficiency of V sorption on chitosan. This may explain the strong decrease in sorption efficiency compared to V uptake from pure synthetic solutions (Guzman et al., 2002). It is another piece of evidence for the necessity of using less concentrated NaOH solutions. Fig. 8 clearly shows that Al was negligibly sorbed on chitosan, unlike V. The process is obviously selective: V remained on the sorbent while Al was left in the solution.

3.2.3. Testing of extraction and stripping steps on alkaline leachates (Na_2CO_3)

Fig. 9 shows the results obtained in the solvent extraction of V and Al from sodium carbonate leachates. With varying $V_{aq}/V_{org.}$ ratios, vanadium extraction was in the range 50–90% while Al was simultaneously extracted (effi-

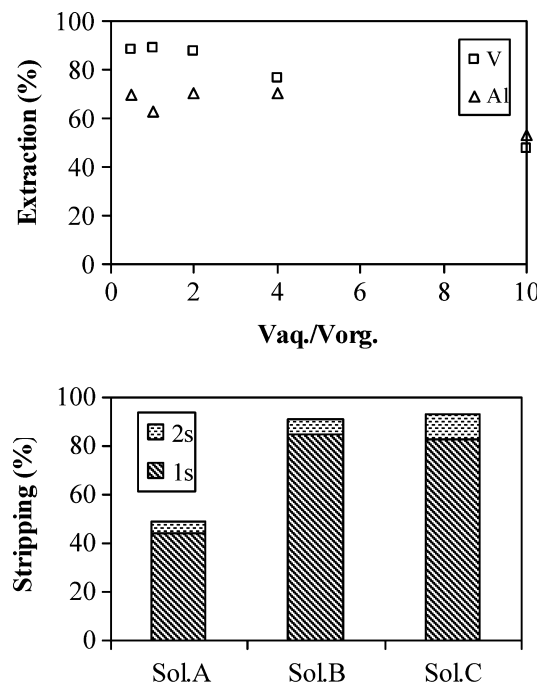


Fig. 9. Solvent extraction of vanadium and aluminum from Na_2CO_3 leaching of oil fly ash (top) using Aliquat 336 and vanadium stripping with $NH_4Cl + NH_3$ (1.5 M) (bottom) (Experimental conditions: leaching: Na_2CO_3 (0.66 M), contact time: 24 h, L/S: 4 mL g^{-1} , room temperature; solvent extraction: pre-treatment of leachate with H_2O_2 and pH control to 3 with H_2SO_4 , contact time 30 min; Aliquat 336: 60 mM; stripping: contact time: 30 min, $V_{aq}/V_{org.}$: 1; Sol. A, B, C correspond to $V_{aq}/V_{org.}$ of 2, 1 and 0.5, respectively, in the solvent extraction step).

ciency between 50% and 70%). Stripping of loaded organic phases was performed using an equimolar 1.5 M NH_4Cl/NH_3 solution. Experiments were only performed with solutions obtained from $V_{aq}/V_{org.}$ ratios of 2, 1 and 0.5 since for higher ratios a precipitate was observed at the interface between the aqueous and organic phases. Aluminum was not stripped from the organic phase while vanadium stripping reached 90% after two stripping steps. Again, the inability of Al to be removed from the organic phase and the accumulation of Al and V in the extracting phase may limit the possibility of using the extractant for successive extraction/stripping steps. Solvent extraction seems to be efficient for the recovery of V but the simultaneous extraction of Al and the difficulty of stripping Al (and to a lesser extent V) renders the applicability of the process debatable. For this reason, complementary experiments were performed to adapt a precipitation procedure for the selective recovery of V and Al from leachates.

3.3. Precipitation

The influence of pH and the presence of ammonium chloride was tested on the precipitation of the metals that were present in acidic leachates (V, Al, Ni, Fe, Si), resulting from 0.5 M H_2SO_4 leaching and alkaline leachates, produced from 2 M NaOH (V, Al, Si) and 0.66 M Na_2CO_3 (V, Al) treatments.

In the case of acidic leaching (Fig. 10), it was impossible to find suitable conditions (pH and presence or absence of ammonium chloride) for separating vanadium from other metals since each of the other metals precipitate to a variable extent in the optimum range of vanadium precipitation (i.e., pH 4–7), independently of the presence of ammonium chloride. The process does not appear to be appropriate for the selective recovery of vanadium from acidic leaching. Vitolo et al. (2000) obtained good results for the precipitation of vanadium from acidic leaching; they used a slightly different procedure consisting in the addition of an oxidant to the precipitation medium (oxidation of V(IV) to V(V)) at pH 2.3. They observed the presence of iron as a co-precipitate and high concentrations of sodium in vanadium precipitate, which preclude its use in the preparation of ferrovanadium alloys: a washing step of the precipitate with acidic solutions was necessary.

With sodium hydroxide leachates, Si and Al precipitated above pH 3.5 (Fig. 11). At pH 5, the precipitation of these metals was almost complete in the presence of

ammonium chloride. In the absence of ammonium chloride it is necessary to increase the pH above 7 to achieve complete Si precipitation. In the case of vanadium, in the absence of ammonium chloride, vanadium did not precipitate while the addition of this salt (at 2 M concentration) led to the precipitation of more than 90% of the metal. It is thus possible to propose a procedure for selective separation of V from Al and Si mixtures by precipitation. Controlling the pH to 8 (without ammonium chloride) enables Al and Si precipitation while maintaining V in solution. After the simultaneous recovery of Al and Si, the addition of ammonium chloride (at 1–2 M concentration) causes V precipitation at pH 5.

In the case of sodium carbonate leachates (Fig. 12), similar trends were observed as in the case of sodium hydroxide treatment. Aluminum precipitation can be performed quantitatively at pH 7 in absence of ammonium chloride (V remained in solution) and after Al recovery by precipitation and solid/liquid separation, V can be precipitated at pH 5 after addition of ammonium chloride (at 1 M concentration).

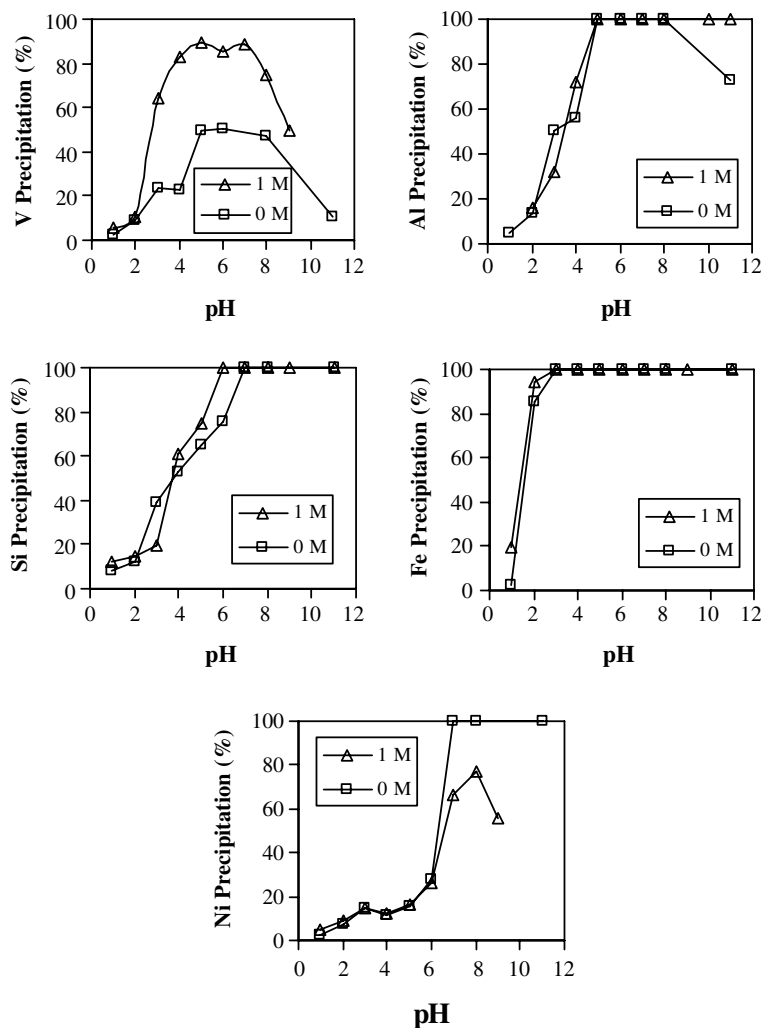


Fig. 10. Influence of pH and NH₄Cl addition (1 M) on metal precipitation from acid leachates (H₂SO₄ leaching) (initial metal concentrations: 1070 mg V L⁻¹, 416 mg Al L⁻¹, 138 mg Si L⁻¹, 692 mg Fe L⁻¹, 101 mg Ni L⁻¹).

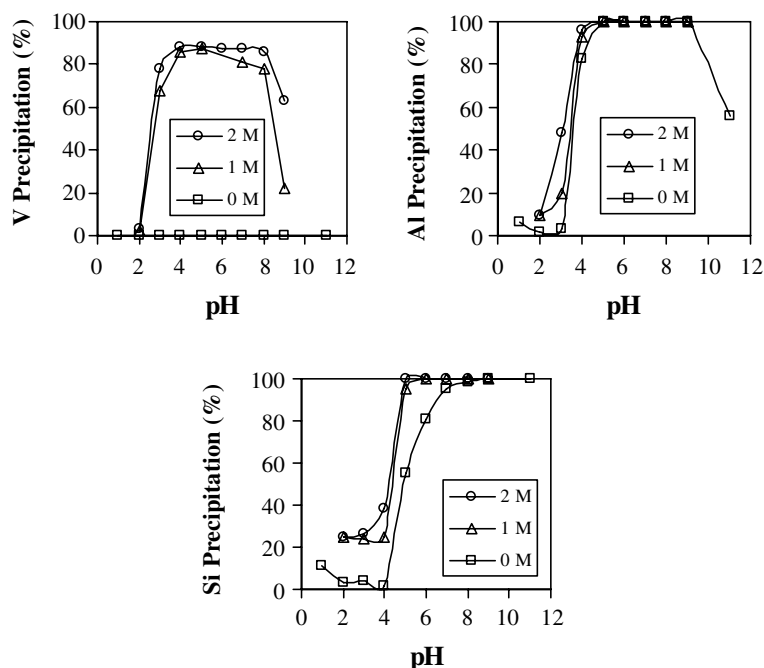


Fig. 11. Influence of pH and NH_4Cl concentration on metal precipitation from alkaline leachates (NaOH leaching) (initial metal concentrations: 1420 mg V L^{-1} , 360 mg Al L^{-1} , 200 mg Si L^{-1}).

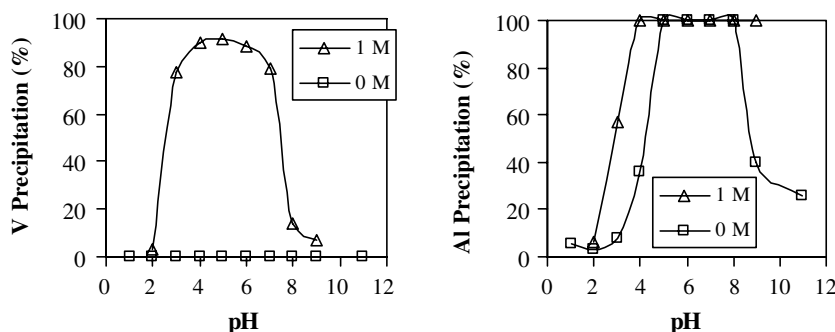


Fig. 12. Influence of pH and NH_4Cl addition (1 M) on metal precipitation from alkaline leachates (Na_2CO_3 leaching) (initial metal concentrations: 1270 mg V L^{-1} , 42 mg Al L^{-1}).

Precipitation seems to be an appropriate process for the selective separation of V from Al and Si mixtures produced during the alkaline leaching of oil fly ashes. Sodium hydroxide gives higher V leaching efficiencies than sodium carbonate solutions. The presence of Si in the case of NaOH leachates is not a problem since it can be simultaneously precipitated with Al.

3.4. Comparison of separation performances and proposal for an integrated treatment

These results enable an integrated process to be proposed, which is presented schematically in Fig. 13. Despite the high efficiency of acidic leaching for V recovery, the simultaneous leaching of other metals, which cannot be selectively removed from the liquor by solvent extraction and by precipitation processes, requires the selection of an alkaline leaching process. Since sodium hydroxide

enabled high leaching efficiencies to be reached (without co-leaching of other transition metals such as Ni and Fe), this leaching agent was selected for the integrated process.

Leaching was operated in three successive steps by contact (for 24 h) with sodium hydroxide maintaining the pH at 12 (the liquid/solid ratio was maintained at 4 mL g^{-1}). Vanadium leaching was about 61%, while Al leaching did not exceed 49%. The leachates were treated by both (a) solvent extraction; and (b) selective precipitation.

Solvent extraction was operated by contact of the extractant (Aliquat 336, 60 mM in kerosene completed by 5% isodecanol (v/v)) with the pre-treated leachates (oxidation of vanadium to V(V) by reaction with H_2O_2 for 30 min and pH controlled to 3). The contact time was 30 min and the $V_{\text{aq.}}/V_{\text{org.}}$ ratio was 1. Vanadium extraction reached 99% while aluminum extraction did not exceed 24%. The aqueous phase was treated with chitosan by contact of the residual solution (whose pH was controlled to 3 with

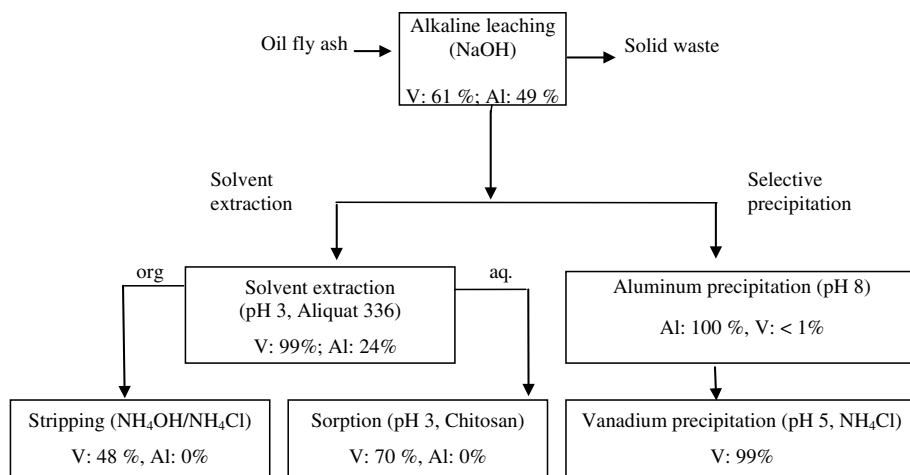


Fig. 13. Integrated process for oil fly ash treatment (the total recovery of selected metals at each step is reported as percentage of total metal content in the waste material).

sulfuric acid) for 3 days with a sorbent concentration of 700 mg L^{-1} . Vanadium sorption reached 70% while Al was not sorbed at all. Vanadium can be fully desorbed using 1 M NaOH solutions from V-loaded chitosan (not shown). The stripping of the organic phase was performed using a mixture of ammonium chloride and ammonia (at the same concentration, 1.5 M). The organic phase was mixed with the stripping agent for 30 min with a $V_{\text{aq.}}/V_{\text{org.}}$ ratio of 1. While Al was not stripped, only 48% of vanadium was recovered from organic phase, limiting the possibility of re-using the solution for a high number of extraction/stripping cycles.

Alternatively, the leachates were treated by precipitation in a two-step procedure. The leachates were partially neutralized by pH control to 8 using sulfuric acid. Aluminum completely precipitated while V precipitation did not exceed 1%. Therefore, ammonium chloride at a concentration of 1 M was added to the solution and the pH was controlled to 5 with sulfuric acid. Vanadium present at this stage of the process in the solution was precipitated to 99%, the residual concentration of vanadium in the solution after precipitation did not exceed 10 mg V L^{-1} . This sequence of operations is consistent with the treatment strategy cited by Chmielewski et al. (1997).

The combination of an alkaline leaching step using sodium hydroxide (at controlled pH, ca. pH 12) and a precipitation procedure (in two steps: pH 8 for Al precipitation, and pH 5 in the presence of 1 M NH_4Cl for vanadium precipitation) allows the selective recovery of pure vanadium in the form of an ammonium vanadate (red cake). Though vanadium recovery was not complete from oil fly ash (with a 70% recovery level), the proposed procedure allowed an efficient, simple and complete recovery of vanadium (greater than 98%) from the leachate in the form of a pure product, that could be valorized. Improving the process would consist in increasing vanadium leaching efficiency.

The proposed treatment for the recovery of vanadium from oil fly ash is complex, requiring a series of processing

steps that make vanadium valorization economically debatable. However, considering vanadium as a by-product of the washing of oil fly ash, its recovery may contribute, at least, to reduce the net cost of the treatment by the production of valorizable sub-products. However, complete recovery of vanadium is not necessary if the treated oil fly ash is not environmentally hazardous. It would be important to check where the process has removed all the labile vanadium. If it can be proved that the residual fraction of vanadium is stable on the final product the treated oil fly ash will be suitable for land disposal with a reduced impact on the environment. The possibility to landfill treated ashes remains subject to the control of residue handling. The treatment may be destructive of the structure of the ashes. However, the alkaline treatment contributes to the stabilization of some metals present in the oil fly ashes. Additionally, the “washed” fly ash containing lower amounts of toxic metals could be used in the manufacturing of cements. The introduction of oil fly ash in the cement processing has been documented (Hall and Livingston, 2002); “washing” the fly ash (containing lower amounts of toxic metals) could contribute to facilitate its admission in the production scheme.

4. Conclusions

The treatment of oil fly ash from power plants for the selective recovery of vanadium can be performed in a two-step procedure consisting of an alkaline leaching using sodium hydroxide and a precipitation procedure. The sequential precipitation of aluminum at pH 8 followed by the addition of ammonium chloride and precipitation obtained a quantitative recovery of vanadium in the form of an ammonium vanadate (red cake). Alkaline leaching was preferred to acidic leaching since it avoids the leaching of metals such as Fe and Ni that interfere in the precipitation process. The extraction efficiency with the alkaline procedure is lower than that obtained with an acidic treatment but the process is significantly better in terms of selective

recovery of vanadium. The solvent extraction using amine extractants (of which Aliquat 336 appeared the most suitable) was also studied. The extraction was quantitative for V but Al was simultaneously and partially extracted. The difficulty in stripping V and Al from loaded organic phase strongly limits the possibility of using the process for the treatment of alkaline and acidic leachates. For this reason the selective precipitation process was selected as the final treatment after alkaline leaching.

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