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Nathalie Dumont[a]; Alain Favre-Réguillon[a]; Branko Dunjic[a]; Marc Lemaire[a]
[a] INSTITUT DE RECHERCHES SUR LA CATALYSE LABORATOIRE DE CATALYSE ET SYNTHÈSE ORGANIQUE UCBL/CPE/IRC, VILLEURBANNE CEDEX, FRANCE

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Elimination of Vanadium and Arsenic from VKCs Catalysts

NATHALIE DUMONT, ALAIN FAVRE-RÉGUILLON, BRANKO DUNJIC, and MARC LEMAIRE*
INSTITUT DE RECHERCHES SUR LA CATALYSE
LABORATOIRE DE CATALYSE ET SYNTHÈSE ORGANIQUE
UCBL/CPE/IRC
43 BD DU 11 NOVEMBRE 1918, 69622 VILLEURBANNE CEDEX, FRANCE

ABSTRACT

Vanadium and arsenic eliminations from an alkaline leaching solution of spent VKCs catalysts were studied. To this end, several commercial resins or polymers synthesized in the laboratory were evaluated in a solid–liquid batch extraction. Conditions for an effective extraction of vanadium and arsenic were determined. An extraction process, using a glass column, is described for the recovery of the vanadium. The elimination of arsenic by precipitation is proposed.

INTRODUCTION

It has become obvious to chemical manufacturers that the amount of spent catalysts disposed of in landfills should be reduced. At the present time, few processes for metal recovery exist. A great deal of effort, in research and development, is necessary to solve this problem. A research program, REMESPECAT (1), was developed to obtain general processes for metal recovery from spent catalysts. We studied the treatment of catalysts used in the synthesis of sulfuric acid. These catalysts contain V_2O_5 and various promoters like sodium and potassium sulfates. Recently, some catalysts, such as VKCs, also contain cesium, which is added in order to increase the deactivation temperatures of the catalysts. Van Lierde and Foguenne (2) studied an alkaline leaching treatment of spent

* To whom correspondence should be addressed.

catalysts. In that study a residue and an alkaline leaching solution, which contained cations (Na, K, and Cs) and anions (vanadates, arsenites/arsenates, and sulfates), were obtained. So it was considered economically interesting to recover cesium and vanadium so they could be reused. Furthermore, it was also considered necessary to eliminate arsenic to reduce the toxic bulk.

In a previous paper we described the recovery of cesium (3) by using an ion-exchange column. We found that a column loaded with 1 g of resorcinol-formaldhyde resin could fix the cesium contained in 18 mL of NaOH leaching solution with a high alkaline pH. The loading capacity of this column was 96 g Cs/kg resin, 78 g Na/kg resin, and 54 gK/kg resin. A diluted acid, 0.1 N HCl, was used to eliminate Na and K, and only 8 mL of 1 N HCl was necessary to recover all the cesium fixed on 1 g of resin. This process gave a cesium-free basic solution and, after elution, an acid solution which contained cesium in high purity (99.5% w/w).

The aim of the study described in this paper is to eliminate vanadium and arsenic from the basic solution obtained after cesium extraction.

Liquid–liquid extraction of vanadium is commonly used to obtain specific complexes for spectrophotometric detection. The active sites of principal extractants are amines (4–6) or 8-hydroxyquinoline (6). These extractants are only used in acidic medium. Vanadium is strongly chelated (7–9) by the Chelex resin in an acidic medium. Nevertheless, Greenberg and Kingston (9, 10) noticed a difficult elution of this element. This resin is effective for preconcentration/separation procedures and for a direct determination of vanadium in the resin. The species of vanadium in the leaching solutions are vanadates, so an anion exchanger is necessary to recover them. The different species of arsenic (arsenate, arsenite, methylated species) were separated by ion-exchange chromatography (11–15) or gas-phase chromatography (16–18). The principal extractants have pyridine functions. Liquid–liquid extraction (19, 20) was also employed. In these extractions the extractants were halides (21) or dithiocarbamate (21, 22). In these cases the species extracted were cations.

Because of the toxicity of the solvents used in liquid–liquid systems, we chose to use solid–liquid extraction. To extract the anions of vanadium and arsenic, some commercial resins with pyridinium or ammonium functions and a polymer synthesized in our laboratory were evaluated. A column extraction is proposed.

EXPERIMENTAL

Materials

Dowex 1X8 (Fluka) in chloride form (spherical beads 20–50 mesh) was used without purification. Its capacity is about 3.5 meq/g dry.

Reillex 402 and HPQ (Reilly) were treated with excess 2 N H_2SO_4, washed with a large volume of distilled water, and dried in a vacuum oven. Reillex 402 was in the form of granular powder (60–200 mesh), and Reillex HPQ was in the form of spherical beads (30–90 mesh). Their capacities are about 8.8 meq/g dry and 4.6 meq/g dry respectively.

Sulfuric acid (Prolabo), hydrogen peroxide (Janssen Chimica, 35%), and acetic acid (Laurylab) were used as received. Sodium hydrogencarbonate (RP Normapur) was used as a 70% (w/w) solution in water.

Poly(4-vinylpyridine-*N*-oxide) was synthesized by oxidation of poly(4-vinylpyridine) (Reillex 402) with hydrogen peroxide according to a method already described (23).

Solid–Liquid Batch Extraction

In order to determine extraction capacities and selectivities of resins toward vanadium and arsenic, we performed a solid–liquid extraction. The leaching solution (the solution test) was shaken for 5 hours with a known amount of resin at room temperature (20–22°C). After filtration the concentrations of the elements present in the filtrate were determined by atomic emission spectrometry (Perkin-Elmer type 1100 M: air-acetylene flame) and by inductively coupled plasma emission spectrometry (Spectro D).

Backextraction

First, the resin is used for a batch extraction with a solution test. Then the resin is washed with distilled water and dried for 24 hours in a vacuum oven. Known amounts of Reillex 402 are shaken for 5 hours with different solutions: H_2SO_4, HCl, NaOH at (0.1 N, 1 N, 2 N), and distilled water. The quantities of the elements recovered are determined by inductively coupled plasma.

Extraction Using a Column

The internal diameter and the length of the glass column used for each extraction are 1.5 and 25 cm respectively. Fractions of eluate (5–10 ml) are collected with a fraction collector and analyzed.

To extract vanadium, the glass column is loaded with 1.5 g of resin and the column volume is 10.6 cm^3. To eliminate arsenic, the glass column is loaded with 4 g of resin and the column volume is 27 cm^3. Solutions are passed through the column at a flow rate of 0.6 column volumes per hour (cv/h). Fractions of 5–10 mL are collected until vanadium or arsenic appear in the eluent at the end of the column. Then vanadium and arsenic,

fixed on the resins, are respectively eluted with 1 N NaOH or with 1 N HCl at a flow rate of about 2 cv/h.

RESULTS AND DISCUSSION

Batch Extraction

In order to choose a selective resin for vanadium and arsenic extractions, we performed a solid–liquid extraction with NaOH leaching solution (without cesium) of spent VKCs catalysts. Its composition is given in Table 1 (Sample 1). Three commercial resins and a polymer, which had been synthesized previously (Fig. 1), were evaluated.

Dowex 1X8 is a strong base and can work as an anion-exchange resin whatever the medium of extraction. Reillex HPQ contains 70% strong base exchange sites and 30% weak base exchange sites (24). Reillex 402 is a weak base resin but is able to coordinate with transition metals. Their pyridinium sites, if protonated with an acid, function as anion-exchange resins.

Anion extraction was not effective in basic media. Kunin and Myers (25) showed that extraction by ammonium or pyridinium sites depends on the structure, size, and valence of the anions. Vanadates and arsenic both have a high valence in basic media. So we assumed that anion extraction was prevented at pH 12.5 due to the high valence of the anions. Extraction in acid media, where the anions are monovalent, was then proposed. The leaching solution, which contained no cesium, was acidified with concentrated sulfuric acid. A precipitate appeared at pH 12 and was dissolved at pH 2. We then proposed two ways in which anion extraction could be studied: extraction in acid media at pH < 2 or extraction after precipitation was complete.

TABLE 1
Composition of the Different Test Solutions[a]

Test solution	pH	K (g/L)	Na (g/L)	V (g/L)	Al (mg/L)	As (mg/L)	SO_4^{2-}
Leaching solution after cesium extraction, Sample 1	13.5	31.3	34.6	7.6	0.167	0.069	—
Leaching solution after cesium extraction, Sample 2	13.2	15	36	8.6	0.085	0.104	85
Stable solution after neutralization, Sample 3	6.8	15	36	0.7	2	48	—
Stable solution after neutralization, Sample 4	6.8	15	36	1.1	0.5	53	112
Vanadium free solution	6	15	36	0.15	40	0	110
Industrial solution	2	0.01	38	0	0.21	1.08	—

[a] Standard deviation: ±2%.

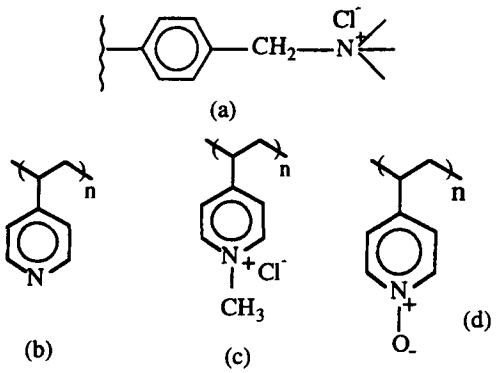

FIG. 1 Commercial or synthesized resins evaluated in batch extraction Dowex 1X8 (a), Reillex 402 (b), Reillex HPQ (c), and poly(4-vinylpyridine-*N*-oxide) (d).

Extraction in an Acid Media

The first method involved the acidification of a solution which contained no cesium (Table 1, Sample 2) until the precipitate disappeared. We obtained stable solutions at high acidities (>1 N). As shown in Table 2, the resins were evaluated using solutions at different acid concentrations. Dowex 1X8 and poly(4-vinylpyridine-*N*-oxide) could not be used with high acidity.

TABLE 2
Percentage Extraction Obtained at Different Acidities with Resins Reillex 402 and Reillex HPQ[a]

Acidity of solution (N)	Percentage extraction[b]				
	Na	K	V	As	Al
			Reillex 402		
1	0	0	40	41	39
1.5	0.6	0	28	31	40
2	0	0	0	0	0
			Reillex HPQ		
1	0	0	42.5	39	64
1.5	10.8	2.7	26	28	34
2	6.9	2.6	21.7	24.7	56.4

[a] Conditions of extraction: $V = 5$ mL, $m = 500$ mg.
[b] Standard error: ±5%.

The degree of anion extraction decreased when the acidity of the solution increased. Chanda and Rempel (24) assumed competition between sulfates and other anions took place in the solution. The exchange capacity of the resins was not satisfactory for column extraction.

Extraction after Precipitation Was Complete

The second method involved consideration of when the maximum precipitation of the elements contained in the solution was achieved. The cesium-free solution (Table 1, Sample 2) was acidified using 3.6 N H_2SO_4. Figure 2 represents the precipitation yields relative to the pH of the solution.

The maximum precipitation of the elements was observed at pH 5–6: 75% for aluminum, 30% for arsenic, and 60% for vanadium. Gupta and Krishnamuthy (26) showed that complete precipitation of vanadates occurs at pH 7. The precipitation was complete after 1 hour at pH 6.8: 98% for aluminum, 92% for vanadium, and 54% for arsenic. The composition of the solution obtained is described in Table 1, Sample 3.

Foguenne and Van Lierde (27) showed that arsenic was completely precipitated when aluminum was 10 times more concentrated. We then added aluminum [as $Al(OH)_3$] to the solution in an attempt to completely precipitate the arsenic. The results achieved did not show any increase in the level of arsenic precipitation. Yatsenko et al. (28) assumed the formation of aluminovanadates when concentrated H_2SO_4 was added, so we assume that competition between vanadates and arsenic in the solution prevented effective arsenic precipitation.

The stable solution at pH 6.8 was used for evaluation of extractants (Table 3). The solution was acidified until pH values of 5.2, 4, 2.2, and 1.2 were reached, and used for evaluation of extractants too (Table 3).

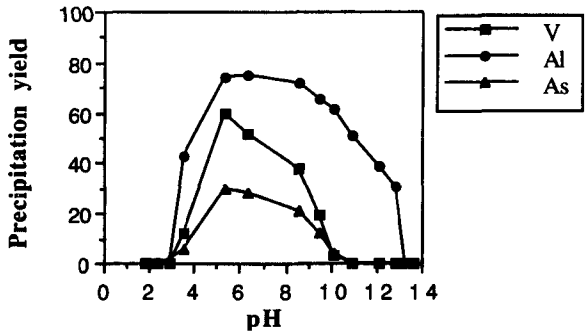

FIG. 2 Precipitation yield (%) for elements relative to the pH.

TABLE 3
Percentage Extraction Obtained at Varying pH Values with Different Extractants[a]

pH of solution	Percentage extraction[b] V	As	Al
Reillex 402			
6.8	100	44	100
5.2	100	44	100
4	100	36	100
2.2	100	41	91
1.2	92	56	30
Reillex HPQ			
6.8	99	24	81
5.2	99	34	91
4	99	19	89
2.2	100	31	92
1.2	89	47	32
Dowex 1X8			
6.8	99	22	82
5.2	99	21	94
4	98	20	95
2.2	99	32	51
1.2	87	41	25
Poly(4-vinylpyridine-N-oxide)			
6.8	53	5	79
5.2	81	20	90
4	98	11	88
2.2	100	22	91
1.2	97	59	30

[a] Conditions of extraction: $V = 5$ mL, $m = 500$ mg.
[b] Standard error: ±5%.

One hundred percent of the vanadates present in the solution were extracted by Reillex 402 at pH > 2.2. The vanadium extracted by poly(4-vinylpyridine-*N*-oxide) increased with the acidity of the solution. According to Zipperian and Raghavan (29) maximum extraction of vanadium by basic resins is obtained at pH 5–6. They explained that either the VO_2^+ species or the $V_{10}O_{28-z}(OH)_z^{(6-z)}$ species are present at pH < 1.5 and pH > 1.5, respectively. The size of the hydrolyzed species (<0.1 μm) was not a negligible parameter. Before analysis, the solutions were filtered on a Durapore Filter (Millipore SA) with pores of 0.1 μm diameter. No

significant variation of vanadium and arsenic concentrations was observed before and after this filtration.

The arsenic extraction was below 60% regardless of the pH value and resin used. At pH 1.2, maximum extraction was achieved with Reillex 402 and with poly(4-vinylpyridine-*N*-oxide). Frenzel et al. (30) explained that only arsenates (As^{5+}) were fixed on an anion exchanger.

The aluminum extraction was the same as that of vanadium extraction, so formation of aluminovanadates could be assumed.

Regardless of these results, we assume Reillex HPQ and Dowex 1X8 extract by an anion-exchange process, whatever the solution pH. Poly(4-vinylpyridine-*N*-oxide) resin coordinates vanadium and arsenic. This process increases with the acidity of the media. The process of extraction by Reillex 402 is more difficult to explain. We assume that this resin can extract both by coordination and by anion exchange in acid media.

In order to improve extraction, we studied the neutralizing effects of anions on the pyridinium functions. Reillex 402 and HPQ were used in the chloride, sulfate, and acetate forms. Resins were treated with excess 2 N H_2SO_4, 2 N HCl, or 2 N CH_3COOH, washed with distilled water and dried in a vacuum oven. Finally, the resins were submitted to batch extraction with an industrial solution at pH 2 (Table 1).

The results described in Table 4 indicated that extraction with resins in sulfate or acetate forms was more difficult to achieve than extraction with the chloride form. For extraction from sulfate media, we preferred to use the sulfate form.

TABLE 4
Percentage Extraction of the Elements Using Resins in Different Forms

Resins	Percentage extraction		
	V	Al	As
	Reillex 402		
$-SO_4^{2-}$	25.6	8.1	48
$-Cl^-$	48	21	48.7
$-CH_3COO^-$	15	0	40
	Reillex HPQ		
$-SO_4^{2-}$	20	0	25
$-Cl^-$	64	0	35.8
$-CH_3COO^-$	21	0	20

It was previously shown (25) that the exchange power depends more upon the nature of the anions than upon the nature of the acid. It has long been postulated (24, 25) that ion-exchanger sorption rates are controlled by diffusion, with the rate-determining step being represented by diffusion through either a resin bead (particle diffusion control) or an externally adherent liquid film (film diffusion control). Film diffusion control is the principal step with low solution concentration and small particle size. Chanda and Rempel (24) showed the rate of sorption is inversely proportional to the square of the bead radius. Our results were in accordance with their observation. Reillex 402 contains less water (5–7%) than Reillex HPQ (55–65%) and Dowex 1X8 (43%). Because Reillex 402 was more effective for extracting anions, one can assume that the water content is a parameter related to extraction (31).

Vanadium Extraction Using a Column

For column extraction we used a solution at pH 6.8 (Table 1, Sample 4) and the resin Reillex 402 treated with H_2SO_4. To extract vanadium, 240 mL of solution was passed through the column. By considering the concentration of the elements present in each fraction, C, and their initial concentrations, C_i, we determined the ratio C/C_i. We then plotted the ratio C/C_i against the volume of percolation (Fig. 3).

Sodium, potassium, and arsenic appeared in the first fraction collected after extraction was started. Vanadium and aluminum appeared after 240 mL of percolation. Under these conditions, the capacity of Reillex 402

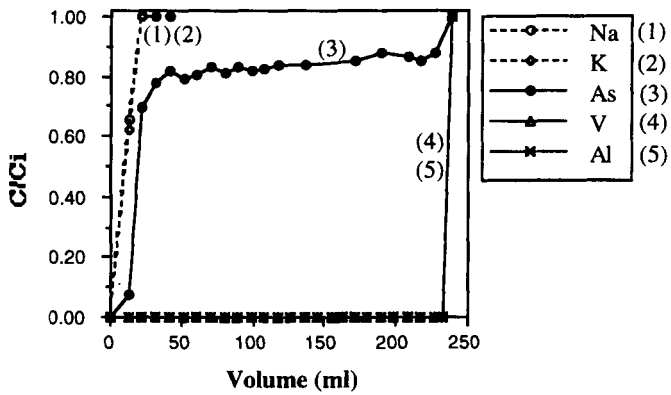

FIG. 3 Ratio C/C_i for various elements during the percolation of a solution at pH 6.8 on a column containing Reillex 402.

was 22 g V/dm^3 resin, 0.3 g As/dm^3 resin, and 7 mg Al/dm^3 resin. Its total capacity was about 3 meq/g dry. This value is low compared to the data supplied by the manufacturer (8.8 meq/g dry). We assumed that low concentrations of solution and the use of multisite coordination explain this result. Vanadium, aluminum, and arsenic were concentrated by factors of 22, 23, and 5.4, respectively. The initial volume of toxic material was 240 mL and we had collected only 10.6 cm^3 of loaded resin when the experiment was complete. Therefore, the volume of toxic material decreased by a factor of approximately 22.6 in doing this extraction.

The elements fixed on the resin were then eluted using 1 N NaOH (24). The elements were almost entirely eluted using 32 mL of 1 N NaOH. Therefore, in this case the volume of toxic material was decreased by a factor of approximately 7.5. This basic solution contained 4.7 g/L of vanadium, 6.6 mg/L of arsenic, and 3 mg/L of aluminum. It was necessary to use a minimum of 120 mL of NaOH to eliminate the traces of elements which remained fixed to the resin. This solution could be recycled and the resin used in another extraction. After percolation, we obtained a vanadium-free solution which contained arsenic (Table 1). It was therefore necessary to eliminate arsenic from this solution and also to decrease the toxic volume.

Arsenic Elimination

We then proposed two methods by which the arsenic could be eliminated: extraction from an acidic medium using a column, or elimination, by precipitation, while competitive vanadates were absent from the solution.

Arsenic Extraction, Using a Column, from an Acidic Medium

In order to eliminate the arsenic, the vanadium-free solution was acidified to pH 1. Then the solution was passed through a column loaded with Reillex 402. We used an industrial solution supplied by our partner (32) (Table 1) to study arsenic extraction using this column. The concentrations at the bottom of the column were determined and the ratio C/C_i was calculated (Fig. 4).

Aluminum appeared immediately in the first sample collected after the extraction was started. Arsenic appeared after 60 mL of percolation. Under the conditions used, the capacity of column was 0.6 mg As/dm^3 resin and 1.4 mg Al/dm^3 resin. Arsenic was concentrated by a factor of approximately 3 on the resin. We had an initial toxic volume of 60 mL

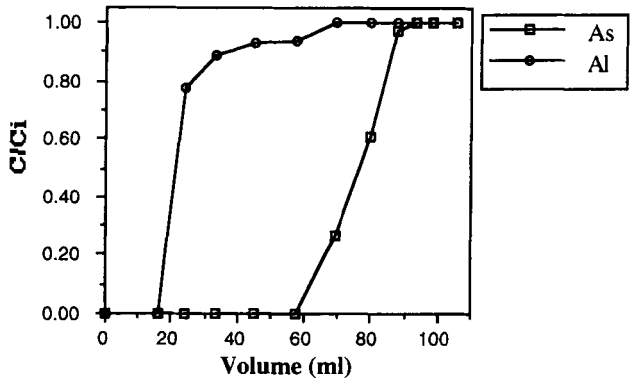

FIG. 4 Ratio C/C_i for elements during percolation of the industrial solution using a column packed with Reillex 402.

and obtained 27 cm^3 of loaded resin from the column. Therefore, the toxic volume decreased by a factor of approximately 2.2.

According to Chanda and Rempel (24), elements fixed on pyridinium can be eluted using NaOH. To determine an effective eluent, we performed a backextraction. The amount recovered of each element from the Reillex 402 resin is detailed in Table 5.

The amount of each element recovered by backextraction increased with the acidity of the eluent. Therefore, a concentrated acid, 1 N HCl, was a good eluent for use in the recovery of the arsenic fixed on Reillex 402. To recover all of the arsenic fixed on the resin, 42 mL of 1 N HCl was required. The decontamination factor was about 1.5. After this treatment, the resin could be reused for another arsenic elimination.

Arsenic Elimination by Precipitation

Another way to eliminate the arsenic was via arsenic precipitation after addition of aluminum to the solution. To the vanadate-free solution initially obtained using the column packed with Reillex 402 at pH 6–7 (Table 1) were added different amounts of $Al(NO_3)_3 \cdot 9H_2O$. These solutions were made basic by adding 1 N NaOH. The precipitation yields of arsenic and aluminum were determined at varying pH values when different amounts of aluminum were initially added (Figure 5).

For an initial aluminum concentration of 0.4 g/L or more, arsenic precipitation yields were about 90% at pH 5–9. After 1 hour of agitation of a

TABLE 5
Amounts of Elements Obtained by Backextraction[a]

Eluent	As (mg/L)	Al (mg/L)
H_2SO_4:		
0.1 N	0.105	0.519
1 N	0.159	0.774
2 N	0.171	0.93
HCl:		
0.1 N	0.128	0.622
1 N	0.182	1.05
2 N	0.181	0.894
Distilled water	0.127	0.385
NaOH:		
0.1 N	0.118	0.209
1 N	0.089	0.546
2 N	0.023	0.685

[a] Conditions of backextraction: $V = 5$ mL, $m = 500$ mg. Standard error: ±5%.

solution whose initial composition is presented in Table 6, we obtained a solution and a residue whose compositions are also detailed in Table 6.

The solution obtained after precipitation did not contain toxic levels of arsenic. This solution could therefore be simply thrown away, and the small amount of residue obtained (8 g for 1 L of initial solution) could be disposed of in landfills.

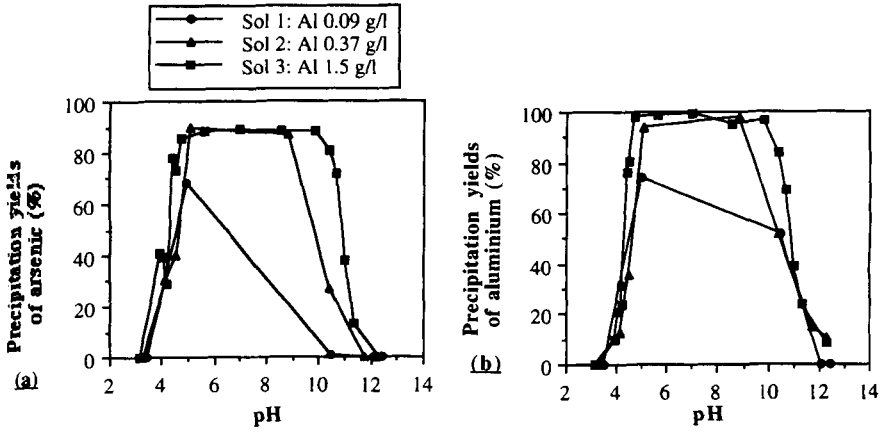

FIG. 5 Precipitation yields of arsenic (a) and aluminum (b).

TABLE 6
Composition of the Initial Solution, the Same Solution after 1 Hour at pH 7, and the Residue Involved

Elements	As	Al
Initial solution, pH 2	40 mg/L	1.3 g/L
Solution after precipitation (1 hour) at pH 7	0.9 mg/L	12 mg/L
Residue (mg/g residue)	5	106

CONCLUSION

To recover vanadium and to decrease the toxic volume of leaching solution, we could fix vanadium in an extraction column and eliminate arsenic by precipitation (Fig. 6).

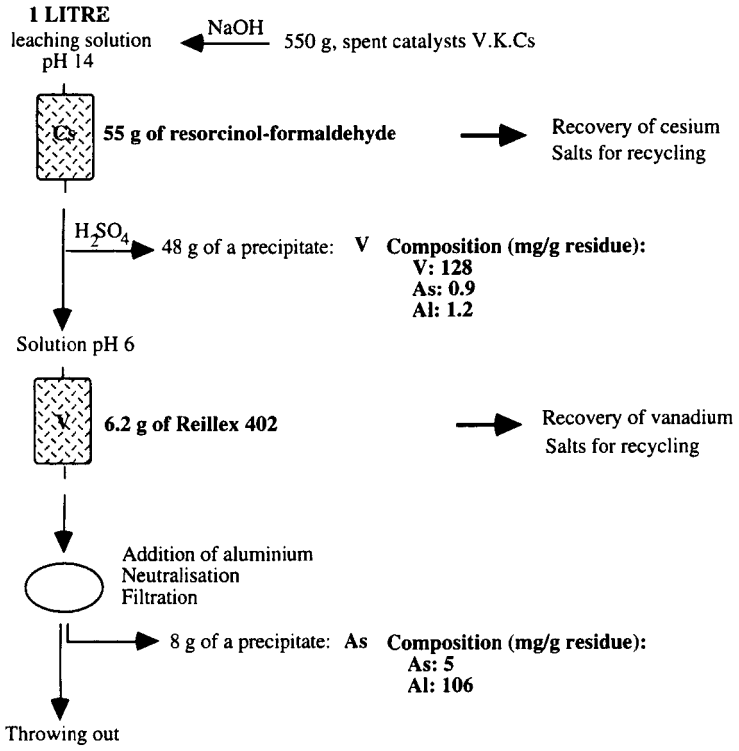

FIG. 6 Process for elimination of vanadium and arsenic from 1 L of alkaline leaching solution (550 g of spent catalysts treated).

The first step was acidification of the cesium-free leaching solution (3) to pH 6–7. On the one hand, we obtained a residue of 48 g for 1 L of treated solution. The composition of this precipitate was (in g/kg) 142 of sodium, 72 of potassium, 128 of vanadium, 1.2 of aluminum, and 0.9 of arsenic. On the other hand, we obtained a solution containing vanadium and arsenic. The second step consisted of fixing vanadium on a column loaded with Reillex 402. The vanadium concentration eluted with 1 N NaOH was 4.7 g/L. The third step was to add aluminum to the vanadate-free solution and then to neutralize it: 98% of the arsenic precipitated and the solution obtained was not toxic.

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