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

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Extraction of Cesium from an Alkaline Leaching Solution of Spent Catalysts Using an Ion-Exchange Column

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

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ABSTRACT

The selective extraction of cesium from an alkaline leaching solution of spent catalysts using phenolic resins was studied. The resins were synthesized by alkaline polycondensation of formaldehyde by phenol, resorcinol, catechol, and phloroglucinol. Their ionoselectivities for five alkali metals were evaluated with a solid–liquid extraction, and their ion-exchange capacities were compared. The resin with the best selectivity for cesium was tested with a real solution at different pH values. An on-column extraction is proposed to obtain cesium with high purity.

INTRODUCTION

Sulfuric acid production represents the most important tonnage of the output of the United States and European chemical industries (1). The V.K.Cs catalysts used for the synthesis of this acid were consumed in great quantity, several thousand tons per year, and the spent catalysts are simply disposed in landfills because reprocessing knowledge does not exist. Within the scope of a European program (2), an alkaline solution specifically developed for the leaching of spent catalysts has been studied at the Université Catholique de Louvain (3) which produces a final alkaline

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* To whom correspondence should be addressed.

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effluent saturated in sodium- and potassium-containing cesium, vanadium, and traces of aluminum and arsenic. The aim of this study was to develop an efficient process to concentrate, purify, and recover cesium from an alkaline leaching solution of spent catalysts which could then be reused as raw material for catalyst preparation.

For the extraction of cesium from aqueous media, two systems were used: liquid–liquid and solid–liquid extractions (4). The latter, which employs an extraction column, is preferred because it does not require a costly and toxic organic solvent. The ion-exchange materials used for cesium extraction may be organic compounds (5) such as resorcinol–formaldehyde–iminodiacetic acid resins and Duolite ARC-359, or inorganic compounds such as a zeolitic ion-exchange material (6), or the hexacyanoferrate of transition metals (7).

The solution which was treated is an alkaline solution, so the choice of resin depends on its selectivity for cesium in this media. Miller and Kline (8) showed that phenolic resins have a great capacity for cesium extraction in alkaline media and, more recently, Samanta and Ramaswamy (9) used resorcinol–formaldehyde resin for cesium removal from nuclear waste. On the basis of these results, we tested four condensation resins for cesium extraction. To date, all the systems described in the literature simply serve to eliminate cesium; our aim was to recover it.

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EXPERIMENTAL

Materials

Phenol, resorcinol, catechol, and phloroglucinol (Sigma-Aldrich), formaldehyde (37% aqueous solution, Laurylab), alkali hydroxides (Aldrich) in the form of a monohydrate for cesium and lithium, and hydrochloric and sulfuric acids (Prolabo) were used without further purification.

Synthesis

For the synthesis of the resins we used a method already described (10) with some modifications (the components are mixed with thermal regulation: 0°C) to improve reproducibility. The resins were synthesized by alkaline polycondensation of formaldehyde with phenolic components.

Competitive Solid–Liquid Extraction in Batch

In order to compare the ionoselectivities of the resins for all alkali metals, competitive batch extractions were performed at room temperature (11). A known amount of the resin was shaken for 5 hours with a solution of salts. After filtration, the concentration in the solution was determined by atomic emission spectroscopy (Perkin-Elmer type 1100M: air-acetylene flame) and the distribution coefficient D was calculated as follows:

$$D = \frac{C_i - C_f}{C_f} \times \frac{V}{m}$$

where C_i, C_f: concentration of element before and after extraction
V: volume of solution (mL)
m: mass of resin (g)

The ion-exchange capacities ($H^+ \rightarrow Na^+$) were compared. To this end, 50 mL of 0.1 M NaOH solution containing 5% NaCl was shaken overnight with 250 mg resin in the H^+ form (9). The amount of Na^+ consumed in the $H^+ \rightarrow Na^+$ reaction was determined by titrating the remaining NaOH with 0.098 M HCl solution using a pH meter (2000A Suntex).

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Ion-Exchange Column

A glass column with an interior diameter of 1.1 cm was loaded with 2.5 g resin. A leaching solution containing Cs, V, As, Al, Na, and K was passed through the column at a flow rate of 3 column volumes per hour (cv/h). Fractions (2 mL) were collected until the ratio C_i/C_f reached approximately 1 for sodium and potassium. The column was subsequently washed with bidistilled water until C_i/C_f was about 0.01. The cesium retained by the column was then eluted with 0.1 M and 1 M HCl at a flow rate of 3 cv/h.

RESULTS AND DISCUSSION

Distribution Coefficients for Several Formo-Phenolic Resins

In order to choose the best resin for cesium extraction, we performed a competitive extraction of five alkali metals. Four resins were synthesized with phenol (a), resorcinol (b), catechol (c), phloroglucinol (d), and tested by batch extraction with alkali hydroxides (Fig. 1).

The distribution coefficient D (mL/$g_{(dry)}$) for each alkali and for each resin is reported in Table 1 as well as the selectivity ($S_{X/Y} = D_X/D_Y$) and the total amounts of ions extracted in mmol per gram resin (dry). The moisture regain for the resins was determined by heating a known quantity in an air oven at 100°C for 24 hours. The loss in weight gives the percentage of water in the resin: 10% (w/w) for the phenol–formaldehyde resin (PFR), 12.1% for the resorcinol–formaldehyde resin (RFR), 8.6% for the cate-

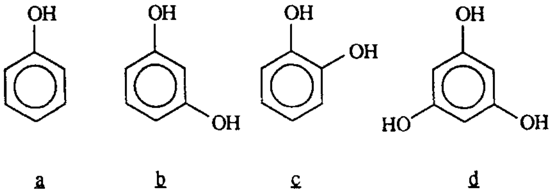

FIG. 1 Formo-phenolic resins were synthesized with phenol (PFR) (a), resorcinol (RFR) (b), catechol (CFR) (c), and phloroglucinol (PhFR) (d).

chol–formaldehyde resin (CFR), and 14.4% for the phloroglucinol–formaldehyde resin (PhFR).

According to the results presented in Table 1, PFR gave the lowest distribution coefficients (excepted for Cs) and total amount extracted, but the selectivities were the best. With PhFR, the distribution coefficients, the selectivities, and the total amount extracted were low. The total amounts extracted for resorcinol and catechol–formaldehyde resins were similar but the distribution coefficients and selectivities were significantly different. CFR was selective for lithium and RFR was the most selective for cesium. We thus conclude that the position of the phenolic-OH group is important for extraction selectivity. We assume that the resorcinol–formaldehyde resin presents the best structure for cesium extraction.

If we assume that the repeat unit for the polymers is given by the following formula (9)

$$(C_6H_{3-n})(OH)_n(CH_2)_{3/2}$$

TABLE 1

Distribution Coefficients D (mL/$g_{(dry)}$) and Selectivities for Alkali Metals Extracted by Formo-phenolic Resins and the Total Amounts Extracted (mmol/$g_{(dry)}$) for Each Resin[a]

	Distribution coefficient (mL/$g_{(dry)}$)[b]					Selectivity		Total amount extracted
Extractant	Li	Na	K	Rb	Cs	Cs/Na	Cs/K	(mmol/$g_{(dry)}$)
PFR	10.5	0.01	8.0	13.0	79.8	7980	10.0	1.58
RFR	93.9	59.4	71.9	85.2	229.5	3.9	3.2	6.26
CFR	128.2	66.7	68.5	77.5	112.8	1.7	1.6	5.58
PhFR	50.2	37.9	46.8	48.8	58.8	1.5	1.2	3.70

[a] Conditions of extraction: [LiOH] = [NaOH] = [KOH] = [RbOH] = [CsOH] = 0.02 mol/L. V = 5 ml, m = 25 mg, T (shaking) = 5 hours.

[b] Standard deviation: ±5%.

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where $n = 1$ for PFR, $n = 2$ for RFR and CFR, $n = 3$ for PhFR, the theoretical capacities for the resins are 8.8 meq/g for PFR, 15.6 meq/g for RFR and CFR, and 20.8 meq/g for PhFR. The experimentally determined ion-exchange capacities ($H^+ \rightarrow Na^+$) are listed in Table 2.

The ion-exchange capacities were lower than the theoretical capacities because many of the phenolic groups were not accessible in the resin but they were nevertheless better than those found in the literature (9). If we compare the experimental and theoretical values: 64% of the phenolic groups for PFR, 65% for RFR, 60% for CFR, and 56% for PhFR were occupied. PhFR presented the best ion-exchange capacity but the ratio between the ion-exchange capacity and the theoretical capacity is low. The resorcinol–formaldehyde resin gave the best ratio with a sizable ion-exchange capacity. This resin presents a well-adapted structure for the extraction of monovalent cations.

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Batch Extraction of Cesium from Real Solution

Our partner (3) has given us two types of solution: one after leaching the V.K.Cs catalyst with NaOH and another after KOH leaching. The compositions of the solutions are given in Table 3.

The leaching yields for each solution are similar, so the choice for alkaline leaching depends on the extraction results obtained with the resorcinol–formaldehyde resin. The distribution coefficients obtained and the total amounts extracted from two leaching solutions are summarized in Table 4.

During the extraction, the pH decreased and reached 6 at the end, giving rise to a yellow precipitate. Of the metals contained in the NaOH and KOH leaching solutions, the following weight percentages were precipitated: aluminum (90%), arsenic (50%), vanadium (50%), potassium (5%), sodium

TABLE 2
Ion-Exchange Capacities and Theoretical Capacities (mmol/$g_{(dry)}$) for Phenolic Resins

Extractant	Ion-exchange capacity (mmol/$g_{(dry)}$)	Theoretical capacity (mmol/$g_{(dry)}$)	$\frac{\text{Ion-exchange capacity}}{\text{Theoretical capacity}} \times 100$
PFR	5.6	8.8	64
RFR	10.1	15.6	65
CFR	9.3	15.6	60
PhFR	11.7	20.8	56

TABLE 3
Composition (g/L) of the NaOH and KOH Leaching Solutions

Solution	pH	Cs	V	Na	K	Al	As
NaOH	12.5	6	7.6	34.6	31.3	0.167	0.069
KOH	10.5	6.6	7.4	2.4	52	0.058	0.064

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(5%), and cesium (25%). Hence, the distribution coefficients given in Table 4 are overestimated.

In order to avoid the formation of a precipitate and to increase the distribution coefficients for cesium, we adjusted the pH by adding different quantities of NaOH to the real solutions: 4 g/L (pH 13), 20 g/L (pH 13.7), and 40 g/L (pH 14). The distribution coefficients obtained with alkaline leaching solutions at different pH values and the total amounts extracted are given in Table 5.

The distribution coefficients for vanadium, aluminum, and arsenic decreased when the pH increased. A possible explanation is that these anions were not extracted by ion exchange but were precipitated on the resin. This phenomenom decreased when the pH increased and disappeared with high alkaline pH.

Cesium extraction increased with the pH, while the extractions of sodium and potassium were independent of the basicity of the solution. The quantity extracted increased with the pH. The best results (3.7 mmol/g) were obtained with the KOH leaching solution at pH 14, compared to 2.7 mmol/g obtained with the NaOH leaching solution at pH 14. This differ-

TABLE 4
Distribution Coefficients (mL/$g_{(dry)}$) and the Total Amounts Extracted (mmol/$g_{(dry)}$) for Resorcinol–Formaldehyde Resin with NaOH and KOH Leaching Solutions[a]

	Distribution coefficient (mmol/$g_{(dry)}$)[b]						Total amount extracted
Solution	Cs	V	Na[c]	K[c]	Al	As	(mmol/$g_{(dry)}$)
NaOH	17.6	6.1	0.3	1.1	2036	9.9	1.91
KOH	24.5	284	1.6	1.1	722	12.5	2.50

[a] Conditions of extraction: $V = 1$ mL, $m = 200$ mg, T (shaking) = 5 hours.
[b] Standard deviation: ±5%.
[c] Standard deviation: ±10%.

TABLE 5
Distribution Coefficients (mL/$g_{(dry)}$) and the Total Amounts Extracted (mmol/$g_{(dry)}$) for Resorcinol–Formaldehyde Resin with Real Solutions at Different pH Values[a]

Solution pH	Distribution coefficient (mL/g)[b]						Total amount extracted (mmol/g)
	Cs	V[c]	Na[c]	K[c]	Al	As[c]	
			NaOH Leaching				
13	12.0	0.8	1.2	1.4	437	1.6	2.8
13.7	23.7	0.11	1.0	1.0	350	0.6	2.9
14	73.7	0.01	0.8	1.5	184	1.1	3.1
			KOH Leaching				
13	14.7	5.8	1.5	1.2	204	2.4	2.2
13.7	22.1	0.23	1.0	1.6	126	0.01	2.4
14	59.9	0.01	1.8	2.5	254	0.01	4.2

[a] Conditions of extraction: $V = 1$ mL, $m = 200$ mg, T (shaking) = 5 hours.
[b] Standard deviation: ±5%.
[c] Standard deviation: ±10%.

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ence is mainly due to greater potassium and sodium extractions. The best selective cesium extraction from a real solution was obtained from the NaOH leaching solution with the pH adjusted to 14. Although the largest quantity extracted was obtained with the KOH leaching solution, we chose the NaOH leaching solution because of its better selectivity for cesium.

Extraction of Cesium on a Column

For the study of the extraction with an ion-exchange column, we used a NaOH leaching solution with pH adjusted to 14 (Table 6) and the resorcinol–formaldehyde resin as extractant.

TABLE 6
Composition of NaOH Leaching Solution at pH 14

Elements	Cs	V	Na	K	Al	As
Concentration (g/L)	6.6	9	61.4	26.1	0.016	0.133
Weight percentage	6.4	8.7	59.5	25.3	0.01	0.1

Our aim was to obtain high purity cesium (≥99%). To this end, we fixed cesium onto the column by passing 40 mL (5 column volumes) of the NaOH leaching solution.

By comparing the concentrations in the NaOH leaching solution before and after the column, we determined the quantities of the elements fixed onto the column. The amount extracted by the resorcinol–formaldehyde resin under our conditions was 11.4 mmol/$g_{(dry)}$. This value was comparable to the ion-exchange capacity $H^+ \rightarrow Na^+$ determined experimentally in the batch extraction (10.1 mmol/$g_{(dry)}$). Vanadium and arsenic were not fixed on the resin.

After washing the resin with 40 mL bidistilled water, 80 mL of 0.1 M HCl, and 20 mL of 1 M HCl were used as eluent. The elution curves are presented in Fig. 2.

The recovery of ions bound by the resin was performed as follows: sodium and potassium were recovered by elution using 80 mL of 0.1 M HCl, the eluent was then changed, and high purity cesium was obtained by passing 20 mL of 1 M HCl. Using this method, we recovered all the cesium fixed onto the column. The composition of the solution obtained is given in Table 7.

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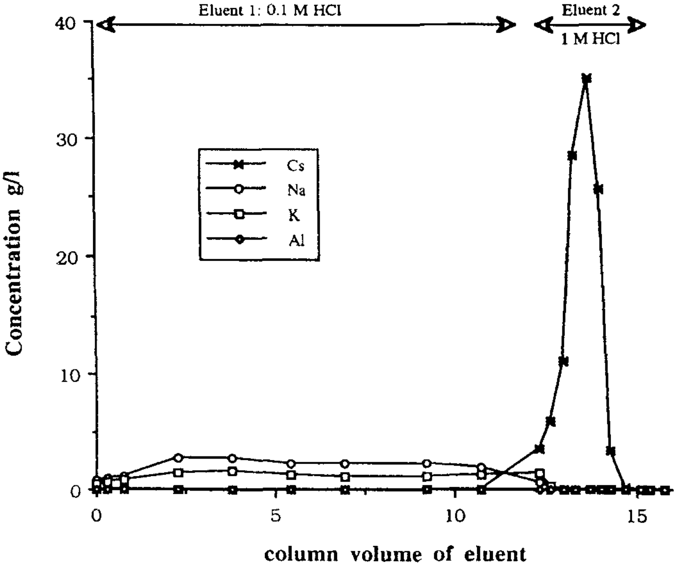

FIG. 2 Elution curves with 0.1 M HCl and 1 M HCl as eluent.

TABLE 7
Composition of the Solution Obtained with 1 M HCl

Elements	Cs	V	Na	K	Al	As
Concentration (g/L)	11.5	0	0.015	0.033	0.008	0
Weight percentage	99.5	0	0.13	0.29	0.07	0

The system of elution 0.1 M HCl/1 M HCl permitted the separation of cesium from sodium and potassium. The concentration factor of cesium was about 2 and its purity was greater than 99.5% compared to 6.4% in the initial solution.

The properties of the column were not affected appreciably even after three cycles.

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CONCLUSION

Four phenolic resins were tested in a competitive solid–liquid extraction of five alkali metals, and the resorcinol–formaldehyde resin was found to bind cesium with the greatest selectivity. This resin was used to concentrate the cesium contained in the solutions obtained by alkaline leaching of spent catalysts. The NaOH leaching solution with high alkaline pH permitted the most selective extraction of cesium without precipitate formation. The elements were deposited on the column, containing 2.5 g resorcinol–formaldehyde resin, and were recovered by elution with 0.1 M HCl/1 M HCl. Vanadium and arsenic were not fixed, sodium and potassium were eluted with 0.1 M HCl, and high purity cesium (99.5% w/w) was eluted with 1 M HCl solution.

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