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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Extraction of Rhenium(VII) with Aliphatic Alcohols from Acid Solutions

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Abstract—Extraction of rhenium(VII) with C_7–C_{10} aliphatic alcohols from HCl and H_2SO_4 solutions was examined. The rhenium(VII) distribution coefficients were examined in relation to the acidity and temperature. The composition of the extracted complexes and the thermodynamic parameters of extraction were determined. The extraction method of recovery and preconcentration of rhenium(VII) from H_2SO_4 solutions with secondary octyl alcohol was tested in the counterflow mode.

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Selective recovery of rhenium from solutions with complex salt composition extensively utilizes liquid-liquid extraction [1]. Hydrometallurgical processing of rhenium-containing raw materials in most cases produces acid multicomponent solutions in which rhenium occurs as ReO_4^- anion [1]. Anions can be extracted with the use of anion exchangers or neutral extractants. There are published data on rhenium(VII) extraction with various amines and quaterenary ammonium bases [1–4]. Rhenium(VII) is efficiently extracted from acid media with neutral organophosphorus compounds (TBP (tributyl phosphate), alkylphosphine oxides [1–4]) and their derivatives (HBTA (hexabutyltriamide of phosphoric acid), alkylphosphine sulfides [3]) and analogs (trioctylarsine oxide, trioctlyamine oxide [4]), various synergistic mixtures (TBP + TOPO (trioctylphosphine oxide), TBP + D2EHPA (di(2-ethylhexyl)phosphoric acid), TBP + CMPO (carbamoylmethylphosphine oxide) [3, 4]), as well as with neutral extractants such as ketones and aliphatic alcohols [2, 4–9]. The latter received inadequate attention, though they exhibit fairly high distribution coefficients in rhenium(VII) recovery from acid solutions [2, 5–9].

Aliphatic alcohols C_5 were first suggested as extractants for rhenium(VII) recovery in the 1950s for analytical purposes. More recently [5–8], extraction properties of alcohols with higher molecular weights, promising as commercial extractants for rhenium recovery, were examined.

As regards their physicochemical properties, aliphatic alcohols containing 7–10 carbon atoms in the hydrocarbon chain satisfy the major requirements posed on commercial extractants (poor solubility in aqueous phase, high flash point, low density, and low viscosity, which provides for fast phase segregation, and chemical stability). In extraction power with respect to rhenium(VII) alcohols rank below amines and organophosphorus compounds, but exhibit a higher selectivity and are less expensive than such extractants [7].

Here, we examined the extraction properties of isomeric C_7–C_{10} aliphatic alcohols in rhenium(VII) recovery from sulfuric and hydrochloric acid solutions.

EXPERIMENTAL

As extractants we used higher aliphatic alcohols produced in Russia: 1-heptanol and 4-heptanol; 1-octanol and DL-2octanol; 1-nonanol, 2-nonanol, 4-nonanol; and 1-decanol and 4-decanol (all pure grade), as well as "97.8%, for synthesis" 2-heptanol, 3-heptanol, and 3-octanol, available from foreign firms, without further dilution, if not specified otherwise. Table 1 lists the major physicochemical properties of the extractants used.

Since aliphatic alcohols are able of extracting mineral acids [9], the extractants were preliminarily saturated with H_2SO4 or HCl to prevent additional isolation of a mineral acid in the course of rhenium(VII) extraction from acid

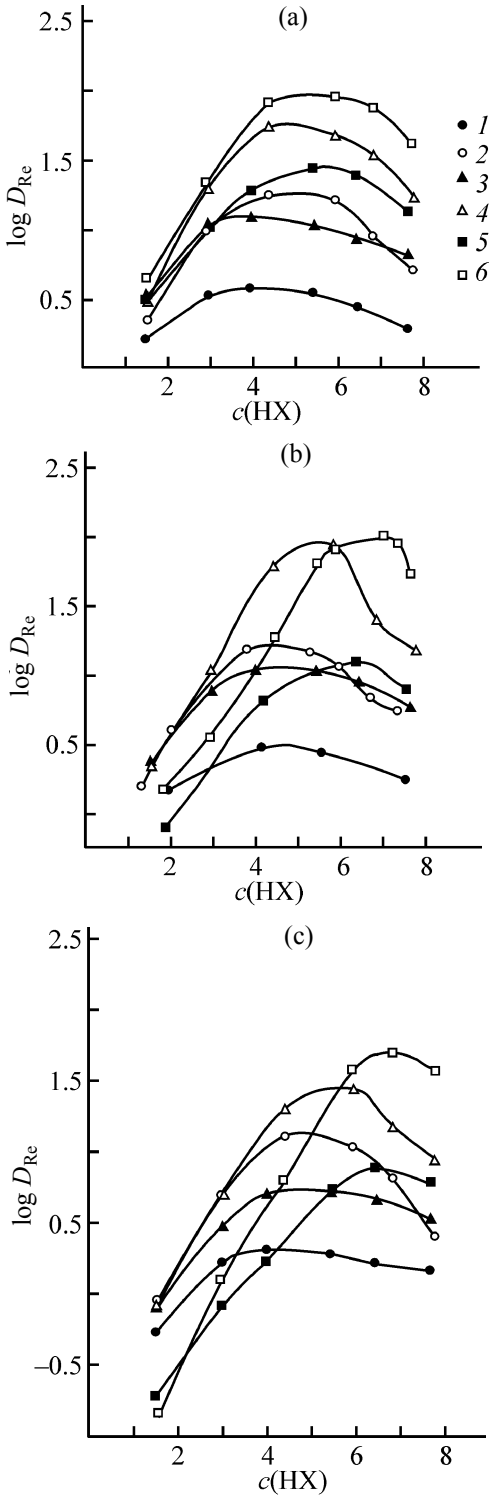


Fig. 1. Rhenium(VII) distribution coefficient DRe vs. mineral acid concentration in the aqueous phase c(HX), M, in extraction with aliphatic alcohols C_7–C_9 from HCl and H_2SO_4 solutions. Extraction: from (*1, 3, 5*) HCl and (*2, 4, 6*) H_2SO_4 (a): (*1, 2*) 1-heptanol, (*3, 4*) 2-heptanol, and (*5, 6*) 4-heptanol; (b): (*1, 2*) 1-octanol, (*3, 4*) 2-octanol, and (*5, 6*) 3-octanol; and (c): (*1, 2*) 1-nonanol, (*3, 4*) 2-nonanol, (*5, 6*) 4-nonanol.

Table 1. Selected physicochemical properties of C_7–C_{10} aliphatic alcohols [10, 12]

Extractant	Flash point, °C	Water solubility, g cm^{-3}, 20°C	Density, g cm^{-3}, 20°C
1-Heptanol	70	1.0	0.822–0.823
2-Heptanol	59	1.0	0.817–0.818
3-Heptanol	54	–	0.818–0.822
4-Heptanol	–	Insoluble	0.818
1-Octanol	90	0.5	0.826
2-Octanol	60	1.1	0.819
3-Octanol	68	Insoluble	0.823
1-Nonanol	98	1.0	0.827–0.828
2-Nonanol	96	Insoluble	0.819–0.823
4-Nonanol	–	Insoluble	0.821–0.828
1-Decanol	82	0.4	0.829–0.830
4-Decanol	82	Insoluble	0.826

Table 2. Rhenium(VII) distribution coefficient in extraction with isomers of C_7–C_{10} aliphatic alcohols at the optimal HCl and H_2SO_4 concentrations

Extractant	c_{init}(HCl), M	D_{Re}	c_{init} (H_2SO_4), M'	D_{Re}
1-Heptanol	4.0	3.8	4.4	17.7
2-Heptanol	4.0	12.4	4.4	54.2
3-Heptanol	5.4	23.6	–	–
4-Heptanol	5.4	27.4	5.9	90.3
1-Octanol	4.1	2.9	5.3	14.3
2-Octanol	6.1	8.2	5.9	54.4
3-Octanol	6.3	12.1	6.9	98.4
1-Nonanol	4.0	2.1	4.4	13.2
2-Nonanol	5.4	5.3	5.9	28.9
4-Nonanol	6.4	7.8	6.8	50.6
1-Decanol	–	–	6.1	9.6
4-Decanol	–	–	6.8	56.5

solutions. To this end, the organic phase was brought into contact with the appropriate mineral acid of the required concentration at 1:1 aqueous to organic phase volume ratio for 5 min, which is sufficient for establishment of equilibrium in the aliphatic alcohol–mineral acid system.

Rhenium(VII) was extracted from model solutions containing nearly 10^{-3} M pure-grade NH_4ReO_4 and the calculated amounts of chemically pure grade H_2SO_4 or HCl. The process was run in 0.05-l calibrated test tubes with manual shaking and room temperature (20 ± 2°C). The influence of temperature on the extraction was

Table 3. Temperature dependences of the distribution coefficient D_{Re} and thermodynamic parameters of rhenium(VII) extraction with 2-octanol from HCl and H_2SO_4. c(HX) = 6.0 M

Medium	D_{Re} at T, °C					$\Delta H°$, kJ mol^{-1}	$\Delta S°$, J mol^{-1} K^{-1}
	20	30	40	50	60		
HCl	8.5	8.7	8.1	6.6	6.1	−10.77	−17.4
H_2SO_4	54.4	45.3	33.2	27.6	24.6	−15.45	−19.8

examined in a thermostated 0.25-l round-bottomed flask with a mechanical stirrer.

Our preliminary experiments showed that 3–5 min is sufficient for establishment of equilibrium in rhenium(VII) extraction with aliphatic alcohols. Hence, the phase contact time in our experiments was 5 min, and the volume ratio of organic to aqueous phase was 1:1.

The rhenium(VII) content in the aqueous phase was determined spectrophotometrically from the color intensity of the thiocarbamide complex of rhenium(IV) formed in the presence of a reducing agent, Sn(II), by measuring the light absorption on a KFK-3 spectrophotometer at λ= 390 nm [13]. The rhenium(VII) concentration in the organic phase was calculated as the difference in its content in the aqueous phase before and after extraction. The concentration of the mineral acids in solutions was determined titrimetrically in the presence of phenolphthalein.

An important factor affecting the extraction equilibrium is the acidity of the aqueous medium [14]. Figure 1 shows the distribution coefficient of rhenium(VII) D_{Re} in relation to the nature and concentration of the mineral acid in the initial solution during extraction with isomers of aliphatic alcohols C_7–C_9.

Figure 1 shows that the distribution coefficient for rhenium(VII) in extraction with aliphatic alcohols from hydrochloric acid solutions is nearly an order of magnitude lower than that for sulfuric acid solutions. From nitric acid solutions rhenium(VII) is extracted with alcohols with even lower D_{Re} values [7], for which reason we did not consider here the rhenium(VII) extraction with aliphatic alcohols from HNO_3.

The log D_{Re}–c(HX) plots for all the examined alcohols pass through a maximum at acid concentrations within 4–7 M, depending on the structure of the alcohol. The initial growth of the extraction power of the alcohols with increasing mineral acid concentration is associated with participation of H^+ in extraction by the hydration-solvation mechanism [8, 13]:

$$ReO_4^- + H_3O^+ + nH_2O + q\text{ROH} \rightleftarrows [H_3O(H_2O)_n(\text{ROH})_q]^+\text{ReO}$$

Clearly, an increase in the H^+ concentration shifts the equilibrium to the right.

Subsequent decrease in the distribution coefficients of rhenium(VI) is associated with intensification of the competing extraction of the mineral acid with alcohols, suppressing the extraction of microamounts of perrhenate ion at high acid concentrations in the system [8, 9]. Moreover, a decrease in D_{Re} in this case can be associated with complexing by rhenium(VII) at a high acidity of the aqueous medium [8, 15].

Table 2 presents the D_{Re} values in extraction with aliphatic alcohols C_7–C_{10} from solutions with the optimal concentration of HCl and H_2SO_4 for ReO_4^- anion extraction.

Table 2 shows that, with lengthening of the hydrocarbon radical, D_{Re} mainly decreases to a certain extent, which is usually attributed to the hydrocarbon dilution effect [14]. The rhenium(VII) extraction is more strongly affected by the position of the OH functional group of the alcohol. In changing from primary to secondary alcohols, the distribution coefficients tend to increase several times. This is evidently due to a higher basicity of the secondary alcohols compared to primary alcohols, which is associated with intensification of the +I inductive effect exerted by the alkyl substituents in changing from primary to secondary alcohols having an OH groups in positions 2, 3, and 4 [16, 17].

In view of the fact that rhenium(VII) extraction with aliphatic alcohols is accompanied by coextraction of the mineral acid, which also depends on a number of factors, these relationships are not always valid (Figs 1b, 1c).

In Russia, the most readily available reagents among high-molecular-weight aliphatic alcohols are octyl alcohol isomers, for which reason specifically octanols were

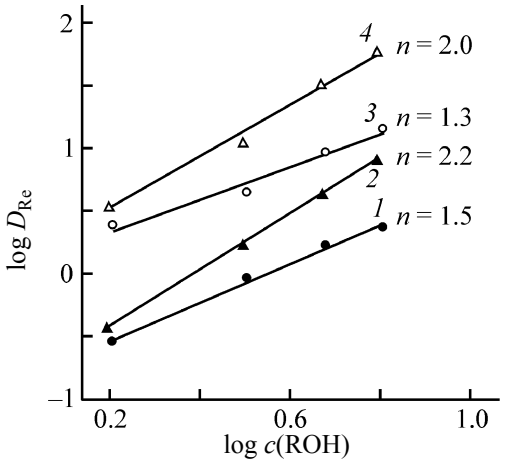


Fig. 2. Rhenium(VII) distribution coefficient DRe vs. extractant concentration in the organic phase. c(HX) = 6.0 M; the same for Fig. 3. c(ROH)) Alcohol concentration in *n*-dodecane, M. Extraction: from (*1, 2*) HCl and (*3, 4*) H_2SO_4. (*1, 3*) 1-octanol and (*2, 4*) 2-octanol.

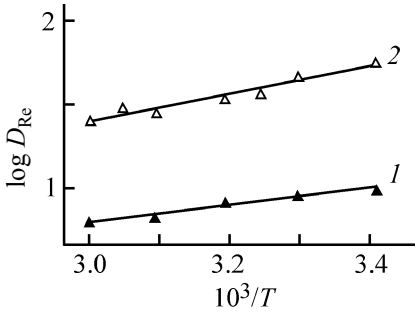


Fig. 3. Temperature dependence of the distribution coefficient of rhenium(VII) in extraction from (*1*) HCl and (*2*) H_2SO_4.

chosen by us for further examination of the rhenium(VII) extraction with aliphatic alcohols.

Using the graphic method described in [18], we determined the composition of the complexes extracted in recovery of rhenium(VII) with 1- and 2-octanols (Fig. 2). The solvation numbers for the secondary alcohol (2.0 and 2.2 in extraction from H_2SO_4 and HCl, respectively) proved to be higher than those for the primary alcohol (1.3 and 1.5, respectively). These data suggest that rhenium(VII) is extracted with 2-octanol as disolvate complexes, and with 1-octanol, as a mixture of di- and monosolvates.

Table 3 shows how the rhenium(VII) extraction with 2-octanol is affected by the temperature. With increasing temperature D_{Re} tends to decrease, which suggests that rhenium(VII) extraction with aliphatic alcohols is an exothermic process (Fig. 3). From the D_{Re} vs. 1/T plot we estimated the thermodynamic characteristics of the extraction [19]. Least-squares processing of the results yielded the following equations: $\log D_{Re}^{HCl} = 562.6/T - 0.9082$, correlation coefficient 0.96; $\log D_{Re}^{H_2SO_4} = 807.2/T - 1.0329$, correlation coefficient 0.94.

Table 3 also lists the apparent thermodynamic characteristics of the rhenium(VII) extraction with 2-octanol from HCl and H_2SO_4, estimated from these relationships.

The apparent standard Gibbs energy and extraction constant for rhenium(VII) can be calculated by the equation presented in [4]

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = RT \ln K_{eq}.$$

Hence, for hydrochloric acid solutions $\Delta G^\circ = 17.4T - 10770$, and for sulfuric acid solutions, $\Delta G^\circ = 19.8T - 15450$. At 298 K, these values were estimated at –5.59 and –9.56 kJ mol^{-1}, respectively. The apparent constant of rhenium(VII) extraction with 2-octanol at 298 K were estimated at 0.998 and 0.996, respectively.

Like in the case of TBP [4], extraction of rhenium(VII) with aliphatic alcohols is accompanied by a decrease in entropy ($\Delta S^\circ < 0$). Evidently, passing of hydration-solvation complexes of rhenium into the organic phase causes ordering of the orientation of the extractant molecules [20].

Examination of rhenium(VII) reextraction from the 2-octanol phase showed that the most efficient reextractants are alkaline solutions, in particular, NH_4OH. Water reextraction does not allow recovery of rhenium(VII) from the extract. The use of reagents having oxidant properties in rhenium(VII) reextraction did not affect the degree of reextraction. Hence, insignificant reextraction of ReO_4^- cannot be associated with reduction in the organic phase.

Rhenium(VII) recovery in reextraction with various reagents from extract based on 2-octanol. $c_{Re}^{org} = 10^{-3}$ M; $V_o:V_a$=1:1, τ = 5 min

Reextractant	H_2O	1 M HNO_3	1.5 M H_2O_2	3 M NH_4OH
E, %	24.0	21.4	30.4	99.6

Inexhaustive reextraction is evidently due to stability of the hydration-solvation complexes of rhenium(VII), formed in the extractant phase in the acid media, which degrade only upon contacting alkaline solutions.

Such behavior of rhenium(VII) in water reextraction is not a drawback, since this allows water rinsing of a rhenium-containing alcohol reextract without losing significant amounts of the valuable component, with removal of the major part of the mineral acid contained in the extract, which is easily reextracted with water from aliphatic alcohols [21].

Based on the result obtained, a new extraction method was proposed for recovery and preconcentration of rhenium(VII) [22] with a secondary aliphatic alcohol as extractant, which passed large-scale laboratory tests.

Considering the facts that the appropriate technologies most often involve sulfuric acid rhenium-containing solutions [1] and that rhenium (VII) is more efficiently recovered with aliphatic alcohols form H_2SO_4 solutions, the laboratory tests used specifically sulfuric acid solutions and 2-octanol as extractant.

Figure 4 presents the isotherm of rhenium(VII) extraction with 2-ocatanol from 6 M H_2SO_4.The isotherm is virtually linear, which suggests that, under the actual conditions (up to c_{Re}^{org} = 40 g l^{-1}), no saturation of the organic phase is achieved. The extractant exhibits a high capacity with respect to rhenium(VII), which allows preconcentration of this element in the organic phase.

To optimize the rinsing stage, additional experiments were carried out in order to elucidate how rhenium(VII) and H_2SO_4 were distributed between the organic and aqueous phases in water reextraction with different volume ratios of the organic to aqueous phase (Table 4).

Table 4 shows that water rinsing at V_o:V_a =5:1 allows isolation from the extract of the major part of the acid, with a minimal amount of rhenium(VII) passed to the rinsing water. Moreover, under these conditions, insignificant volumes of the rinsing solution containing H_2SO_4 in a high concentration (~ 5 M) are formed, which allows this solution to be recycled to the extraction stage without significant decrease in the acidity of the initial solution.

Those data were used for optimizing the process as part of large-scale laboratory tests of the method proposed (see scheme) in a cascade of blending-settling extractors, available from Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials, Kola Scientific Center, Russian Academy of Sciences. As the initial solution served a model sulfuric acid solution containing 230 mg l^{-1} rhenium and 6.5 M H_2SO_4. The cascade comprised four extraction steps, one rinsing step, and two reextraction steps. As extractant served 2-octanol additionally containing H_2SO_4 ($c_{H_2SO_4}^{org}$ =1.2 M). Extraction and reextraction were run in the counterflow mode at V_o:V_a = 1 : 5 and 5 : 1, respectively. Rinsing with distilled water was carried out at V_o : V_a=5 : 1, and the rinsing waters were recycled into the extraction stage. We used 3 M NH_4OH solution for reextraction. The extraction data for the cascade after the experiment are summarized in Table 5.

Table 4. Rhenium and H_2SO_4 recovery in water reextraction from the extract based on 2-octanol in relation to the volume ratio of the organic to aqueous phase. c_{Re}^{org} = 10^{-3} M, $c_{H_2SO_4}^{org}$ = 1.2 M

V_o : V_a	E_{Re}	$E_{H_2SO_4}$
	%	
1:1	46.2	100.0
2:1	12.3	99.6
5:1	1.5	83.8
10:1	0.5	59.5

Table 5 shows that extraction-reextraction of rhenium(VII) with secondary octyl alcohol in the counterflow mode with several cascade steps allowed > 99% recovery of the metal from the sulfuric acid solution and preconcentration in the ammonia reextract.

It should be noted that water rinsing of the extract under the actual conditions allowed recycling of rinsing waters ($c_{H_2SO_4}$ = 4.1 M) to the onset of the process, and this was not accompanied by a significant decrease in the H_2SO_4 concentration in the solution supplied to extraction.

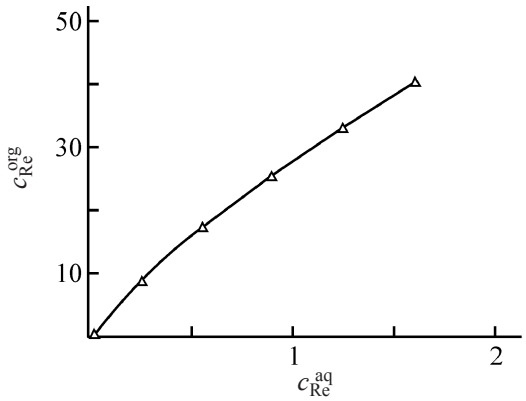


Fig. 4. Isotherm of rhenium(VII) extraction with 2-octanol from solution containing 6.0 M H_2SO_4 (c_{Re}^{org}) Equilibrium concentration of rhenium(VII) in the organic phase, g l^{-1}, and (c_{Re}^{aq}) equilibrium concentration of rhenium(VII) in the aqueous phase, g l^{-1}.

Table 5. Distribution of rhenium(VII) over the extraction cascade steps

Operation step no.	c_{Re}^{org}	c_{Re}^{aq}
	mg l^{-1}	
Extraction, $V_o:V_a$ = 1:5		
1	15.2	0.8
2	71.1	2.0
3	382.1	8.7
4	1368.0	51.6
Water rinsing, $V_o:V_a$ = 5:1		
5	1353.4	52.3
Ammonia extraction, $V_o:V_a$ = 5:1		
6	196.9	4261.0
7	12.3	911.7

Thus, secondary aliphatic alcohols are suitable for recovery and preconcentration of rhenium(VII) from concentrated sulfuric acid solutions.

CONCLUSIONS

(1) The extraction power of aliphatic alcohols with respect to rhenium(VII) in acid solutions varies with the alcohol structure, as well as with the nature and concentration of the mineral acid utilized. The rhenium(VII) distribution coefficients tend to increase in changing from HCl to H_2SO_4, from primary to secondary alcohols, and also tend to slightly decrease with lengthening of the hydrocarbon radical in the alcohol.

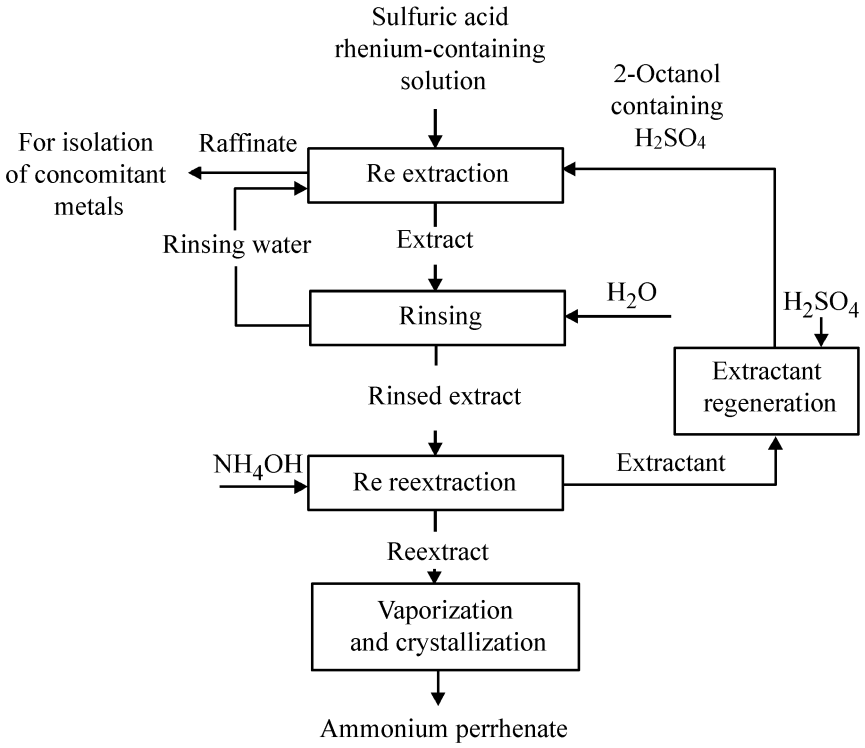
(2) The log D_{Re} vs. c(HX) plots for all the examined alcohols pass through a maximum at acid concentrations within 4–7 M, depending on the structure of the alcohol. A decrease in D_{Re} for

strongly acidic solutions is associated with suppression of the ReO_4^- extraction by competing isolation of the mineral acid, as well as with a possible change in the state of rhenium(VII) in concentrated solutions of mineral acids.

(3) The composition of the complexes extracted in rhenium(VII) recovery from acid solutions is primarily affected by the structure of the aliphatic alcohol. With primary alcohol rhenium(VII) is extracted as a mixture of di- and monosolvate complexes, and with secondary alcohol, as disolvates.

(4) Extraction of rhenium(VII) with aliphatic alcohols is an exothermic process and is accompanied by a negative entropy change.

Flow-sheet of extraction recovery of rhenium(VII) from sulfuric acid solutions with secondary octyl alcohol



(5) Large-scale laboratory tests on rhenium(VII) recovery from sulfuric acid solutions with 2-octanol yielded ammonium perrhenate in the final stage.

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