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Solvent Extraction of Zr(IV) from Nitric Acid Solutions using CYANEX 272, CYANEX301 and CYANEX 302

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ABSTRACT

The extraction of Zr(IV) from nitric acid solutions using CYANEX 272 (bis(2,4,4-trimethylpentyl) phosphinic acid), bis (2,4,4-trimethylpentyl) dithiophosphinic acid (CYANEX 301) or (bis(2,4,4-trimethylpentyl) monophosphinic acid (CYANEX 302) in kerosene has been investigated. The various factors affecting the extraction process of Zr(IV) by each of the investigated extractants such as contact time, loading capacity, extractant, metal ion and nitric acid concentration as well as temperature, are separately investigated. The stripping of the extracted zirconium from loaded organic solutions is also carried out using different stripping reagents. The results are compared and the potential advantages of each extractant over the others are exploited in terms of higher loading capacity and selectivity, less nitric acid extraction, equilibration period and reagent concentration.

Key Words: Zr(IV) Extraction/ CYANEX 272/ CYANEX 301/ CYANEX 302

INTRODUCTION

Zirconium is one of the main fission products which is present in high level active waste or in spent nuclear fuel and can represent significant contribution to released dose impact on repository performance. Commercial organophosphorus extractants of the CYANEX series , have been successfully used, not only for the selective separation of many metal ions in hydrometallurgy, but also in removal of some fission products which are present in spent nuclear fuel or high radioactive waste solution. In this respect, bis (2,4,4,trimethylpentyl) dilthiophosphinic acid (CYANEX 301) has proved to be a highly effective extractant for Am/rare earths separation from aqueous nitrate solution of high active waste (HAW) [(1-3)]. Studies on the extraction of zirconium from acidic chloride solutions into CYANEX 923 (a mixture of 4 trialkylphosphine oxides) showed that zirconium is extracted as the tetrachloride complex forming a disolvate [(4)]. CYANEX 302, which effective constituent is bis (2,4,4,-trimethylpentyl) monothio- phosphinic acid, was found to be advantageous over other organophospohorus extractants for the extraction and separation of some main group elements such as Sb(III), Bi(III), Sn(IV) and Ti(III) [(5)]. Jensen and Bond [(6)] studied the influence of aggregation on the extraction of trivalent lanthanides and actinides from nitrate medium by purified CYANEX 272, CYANEX 301 and CYANEX 302 and reported that the average aggregation of the extractant depends greatly on the studied extracatent concentration range. Mansingh et al [(7)] studied the extraction behaviour of Th(IV) by CYANEX 272, CYANEX 301 and CYANEX 302 in benzene and reported that the order of Th(IV) extraction efficiencies from nitric acid is CYANEX 272> CYANEX 302 >CYANEX 301, and is just reversed in sulphuric acid medium. Daoud et al. [(8)] studied the extraction of U(VI), U(IV) and Th(IV) from nitric acid medium using CYANEX 272, CYANEX 301 and CYANEX 302 in kerosene and reported that CYANEX 272 is preferred for U(VI) and U(IV) extraction while CYANEX 301 and CYANEX 302 give high Th(IV) extraction. Wang and Li [9] studied the liquid-liquid extraction of Sc(III), Zr(IV), Th(IV), Fe(II) and Lu(III) with CYANEX 301 and CYANEX 302 and reported that CYANEX 301 exhibited a poor selectivity for these metals. Extraction of U(IV) by CYANEX 302 in kerosene from nitric acid solution showed that the extraction decreases with the increase in the hydrogen ion and nitrate ion concentrations in the medium [10]. Thorium extraction by CYANEX 272 from aqueous nitrate solution showed that the extracted species is $Th(OH)_3A.(HA)_3$, where $(HA)_2$ denotes the dimer of CYANEX 272 in kerosene [11] . Studies on the extraction and separation of Th(IV) and Pr(III) from nitrate medium using CYANEX 301 and CYANEX 302 showed that CYANEX 302 is more effective than CYANEX 301 for separating thorium from praseodymium [12]. El-Hefny et al.[13] studied Zr(IV) extraction from nitrate medium by thenoyltrfluoroacetone in six different diluents and reported that both aliphatic and aromatic diluents with smaller dielectric constants provide better extraction of zirconium;

In the present work the possible use CYANEX 272 (bis(2,4,4 trimethylpentyl) phosphinic acid), bis (2,4,4-trimethylpentyl) dithiophosphinic acid (CYANEX 301) or (bis(2,4,4-trimethylpentyl) monophosphinic acid (CYANEX 302) in kerosene for the extraction of Zr(IV) from nitric acid solutions has been investigated. The various factors affecting the extraction and stripping processes of Zr(IV) by each of the investigated extractants are investigated.

EXPERIMENTAL

Chemicals and Reagents

Most of the used chemicals were of analytical grade (AR) reagents and used without purification. Nitric acid and zirconium nitrate are products of Prolabo. CYANEX 272 (bis(2,4,4-trimethylpentyl) phosphinic acid), bis (2,4,4-trimethylpentyl) dithiophosphinic acid (CYANEX 301) or (bis(2,4,4-trimethylpentyl) monophosphinic acid (CYANEX 302) were kindly supplied by Cytec Inc. and used as received. Kerosene is a product of Misr Petrol Ltd., Egypt.

General Procedure

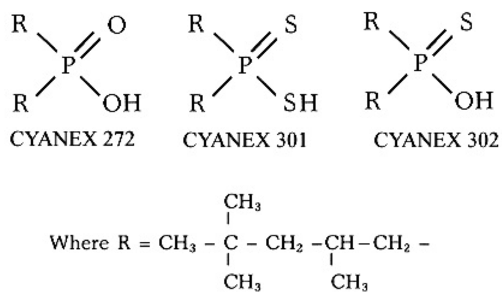
Unless otherwise stated, the aqueous phase contained 0.0109M Zr(IV) in 3M nitric acid solution while the organic phase was 0.5% CYANEX 272, CYANEX 301 or CYANEX 302 in kerosene, represented by $(HA)_2$ as these extractants are known to be present as dimers in the aliphatic diluents [14]. The extraction equilibrium procedure was carried out by vigorously shaking equal volumes of the aqueous and organic phases in stoppered glass tubes using a thermostated water bath adjusted at $25\pm0.1\ ^{o}C$. Preliminary experiments on the effect of time on the extraction of the investigated metals showed that the extraction equilibrium was reached after less than 30 minutes; therefore a shaking time of 30 minutes was used for the extraction investigations carried out in the present work. After centrifugation and phase separation, the concentration of Zr(IV) in the aqueous nitrate medium was spectrophotometrically determined through their respective maximum absorbance at 575 nm by Arsenazo(III) method [15] using a Shimadzu double-beam spectrophotometer model 160A. The concentration of Zr(IV) in the organic phase was determined by difference between its concentration in the aqueous phase before and after extraction. The percentage of extracted metal, E %, was calculated from the relation,

$$E\% = \frac{100\ D}{D + V_a / V_o}$$

Where D is the distribution ratio, V_a and V_o are the volumes of the aqueous and organic phases, respectively.

RESULTS AND DISCUSSION

Comparable investigations on the extraction of Zr(IV) by CYANEX 272, CYANEX 301 or CYANEX 302 in kerosene are presented as the effect of the different parameters on the extraction process to exploit the advantages of each of these extractants over the others. These extractants have the following structures:



Experiments on the extraction of nitric acid by CYANEX 272, CYANEX 301 or CYANEX 302 in kerosene showed that it is nearly not extracted by either of the three extractants under the used experimental conditions. Therefore, extraction investigations were carried out without pre-equilibration of the organic and aqueous phases.

1-Effect of nitric acid concentration

The variation of nitric acid concentration within a range of 0.1-5M showed that when using CYANEX 272 the increase in the acidity of the aqueous medium from 0.1 to 1M increases markedly the extraction percent of Zr(IV) and remains nearly constant in the range 1-5M, Fig.1. However a different extraction behavior of Zr was observed for CYANEX 302.

The effect of nitric acid molarity within the same range show a slight increase in the extraction of Zr(IV) by CYANEX 301 with the increase in the acid concentration from 0.1 to 2M then decreases with further increase in the acidity of the medium, Fig.1.This goes parallel with the reported decomposition of CYANEX 301 in nitric acid more than 2M [16]. These results show that the extraction of Zr(IV) with CYANEX 272 or CYANEX 302 in the investigated concentration range is higher than that with CYANEX

301; in addition, the maximum extraction with CYANEX 272 is nearly constant in the range 1-5 M.

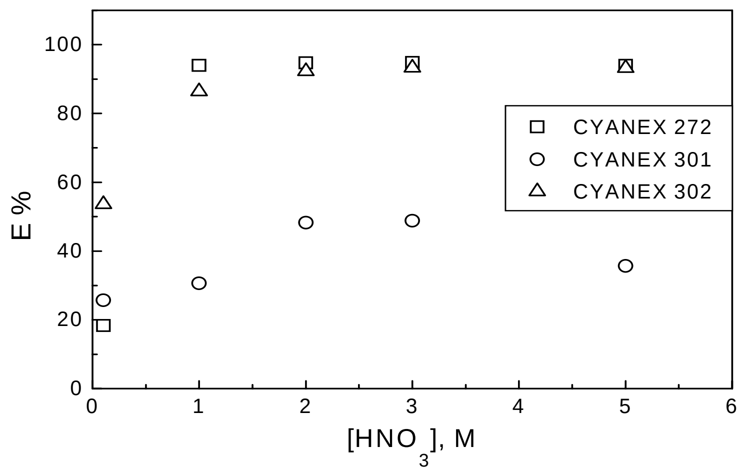


Fig.1 Effect of nitric acid concentration on the extraction of Zr(IV) by 0.5% extractants/kerosene solutions

2- Effect of extractants concentration

The effect of extractant concentration on the extraction of 0.0109M Zr(IV) was carried out by varying the concentration of the investigated extractants / kerosene solutions in the range 0.1-30%. The results represented in Fig.2 show that the extraction with CYANEX 272 increases with the increase in its concentration and reaches its maximum (>99.99 %) at extractant concentration 1% or higher. In case of CYANEX 301 system, no extraction was detected at extractant concentration less than 0.5 %, while complete extraction was observed at 5% or higher concentrations. On the other hand, the complete extraction of Zr(IV) by CYANEX 302 was reached when the extractant concentration is 3% or more. The extraction of Zr(IV) by 0.5% extractant/kerosene solution increases in the order CYANEX 301 << CYANEX 302 < CYANEX 272 .

3-Effect of Zr(IV) concentration

The increase in Zr(IV) concentration in the range $2.74x10^{-3}$-0.0109M decreased the extraction process with either of the investigated extractants. The results represented in Fig.3 show a slight decrease in case of CYANEX 272 and CYANEX 302 with the increase in metal concentration. On the other hand, a sharp decrease in the extraction process was observed with the increase in Zr(IV) concentration in case of CYANEX 301. This may be due to the formation of other zirconium species which are not extracted by the used system or the insufficient capacity of the used extractant concentration to extract Zr(IV) of high concentrations.

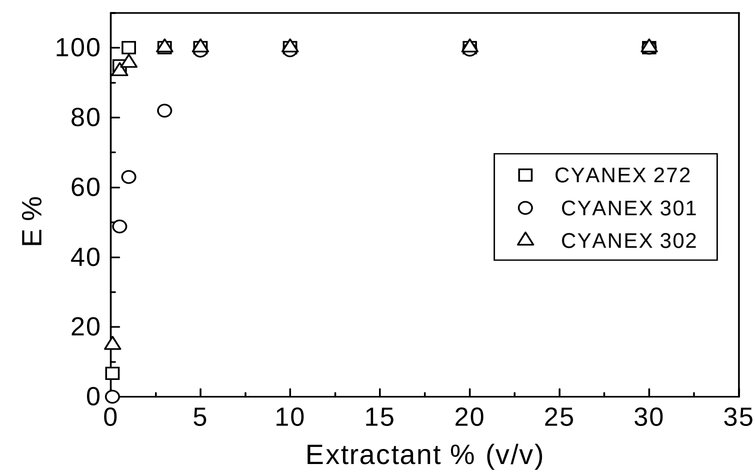


Fig.2 Effect of extractants concentration on the extraction of Zr(IV) from 3M nitric acid solution

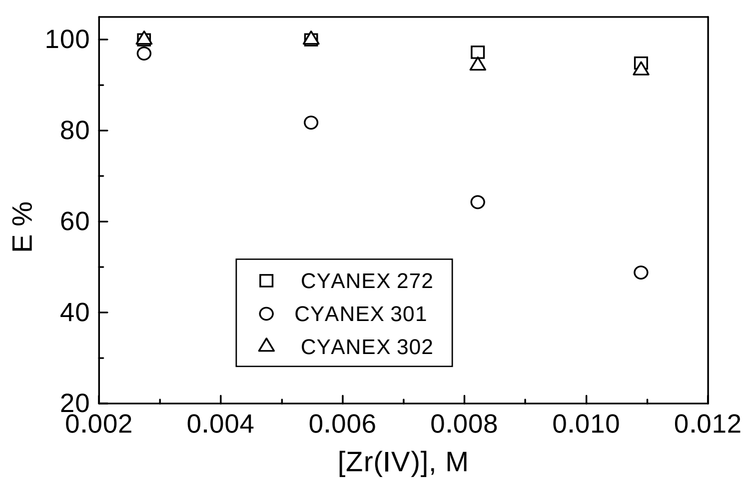


Fig.3 Effect of Zr(IV) concentration on its extraction from 3M nitric acid by 0.5% CYANEX 272, CYANEX 301 or CYANEX 302

4-Effect of temperature

The effect of temperature on the extraction of 0.0109M Zr(IV) by 0.5% CYANEX 272, CYANEX 301 or CYANEX 302 in kerosene from 3M nitric acid was investigated in the range 15-55 ^oC. The results represented in Fig.4 show the increase in the extraction process with the increase in temperature in case of CYANEX 272 from 15 to 35 ^oC, where almost complete extraction is reached (>99.9%) then remains constant with further increase in temperature. In case of CYANEX 302 this maximum extraction is reached at 55 ^oC. The variation in temperature has a relatively small effect on the extraction of Zr(IV) with CYANEX 301, where a maximum extraction of 64% is reached at 55 ^oC.

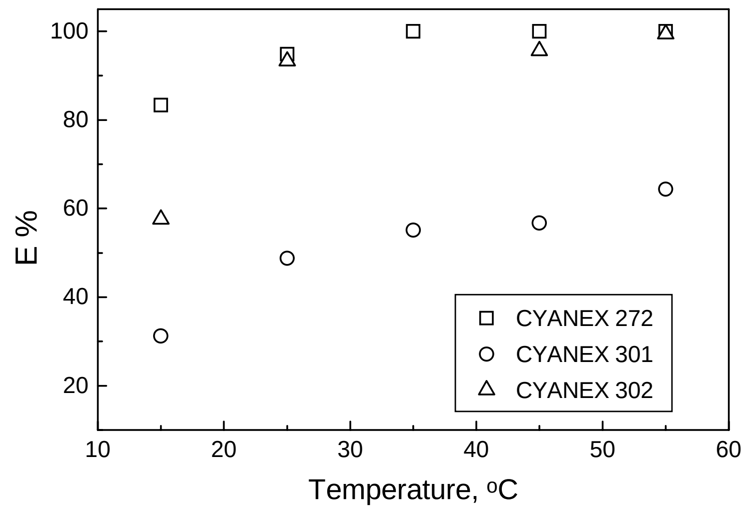


Fig.4 Effect of temperature on the extraction of Zr(IV) with 0.5% CYANEX 272, CYANEX 301 or CYANEX 302 from 3M nitric acid solution

5- Stripping investigations

Stripping investigations of Zr(IV) from the loaded organic solutions indicated that Zr(IV) could be stripped using a mixture of equal concentrations of oxalic acid, sodium carbonate and ammonium carbonate. In this respect, three concentrations were tested, namely 0.01, 0.03 and 0.05M and Zr(IV) was stripped when the concentration of each of these reagents is 0.01M, while at higher concentrations the stripping was negligible, Table 1.

Table2. Effect of molar concentration of oxalic acid, sodium carbonate and ammonium carbonate on the stripping percent of Zr(IV) from loaded CYANEX 272, CYANEX 301 and CYANEX 302 solutions at phase ratio 1:1 and T=25^{o}C.

[oxalic acid], M + [sodium carbonate], M + [ammonium carbonate], M	**Stripping %**		
	CYANEX 272	**CYANEX 301**	**CYANEX 302**
0.01 + 0.01 + 0.01	4.76	8.76	13.42
0.03 + 0.03 + 0.03	-	-	-
0.05 + 0.05 + 0.05	-	-	-

This mixture has the advantage of not stripping Th(IV) or U(IV) when extracted by either of the studied extractants which could contributes in the Zr(IV)/Th(IV) and Zr(IV)/U(IV) separations by stripping. However, the back extraction of Zr(IV) from the different loaded organic solutions using this mixture was found to decrease in the sequence

CYANEX 302>CYANEX 301>CYANEX 272

This may be explained by the increase in the strength of the formed complexes which make the stripping progressively more difficult in the same order.

On the other hand, complete stripping of Zr(IV) from the loaded CYANEX 272 and CYANEX 301 solutions was reached when using 2.5 and 2M sulphuric acid, respectively; quantitative stripping of the metal from loaded CYANEX302 concentration (76%) was obtained with 2.5M H_2SO_4, Table 2.

Table2. Effect of H_2SO_4 molarity on the stripping percent of Zr(IV) from loaded CYANEX 272, CYANEX 301 and CYANEX 302 solutions at phase ratio 1:1 and T=25°C.

	Stripping %		
[H_2SO_4],M	**CYANEX 272**	**CYANEX 301**	**CYANEX 302**
0.01	-	-	5.36
0.05	8.44	7.8	8.85
1	26.12	23.12	27.97
1.5	91.82	58.24	84.04
2	>99.9	73.07	86.77
2.5	>99.9	75.82	>99.9

6-Loading capacity

The loading capacity of the used extractants was studied by contacting 0.0109M Zr(IV) with 0.5% CYANEX 272, CYANEX 301 or CYANEX 302 in kerosene at fixed organic :aqueous ratio of 1:1; after separation of the two phases, the same organic was used again with fresh Zr(IV) solution. This procedure was repeated until the extractant had no ability to extract the metal. The results represented in Fig.5. indicate that maximum Zr(IV) concentrations of $3.41x10^{-3}$ M, $1.61x10^{-4}$ and $3.04x10^{-4}$ M were respectively reached with CYANEX 272, CYANEX 301 and CYANEX 302 after 5 extraction stages. The high loading of Zr(IV) by CYANEX 272 can be related to the high tendency of zirconium to coordinate to oxygen donor than to sulphur donors extractants like CYANEX 301 and CYANEX 302.

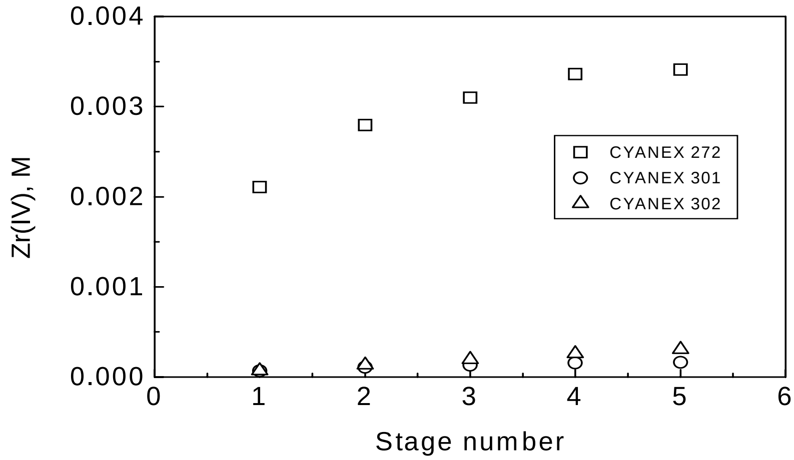


Fig.5 Loading capacity of CYANEX 272, CYANEX 301 and CYANEX 302 for the extraction of Zr(IV) from 3M nitric acid solution

CONCLUSIONS

-CYANEX 272, CYANEX 301 and CYANEX 302 can extract Zr(IV) from nitric acid medium .

-The investigated commercial extractants have the advantage of not extracting nitric acid and the efficiency of extraction at low concentrations, which make them promising for the removal of zirconium from radioactive waste solutions.

-Maximum extraction of Zr(IV) from 3M nitric acid increases in the sequence CYANEX 301<CYANEX 302 < CYANEX 272 .

-The increase in temperature from 15 to 35^{o}C leads to maximum extraction of Zr(IV) from 3M nitric acid with 0.5% CYANEX 272 in kerosene (>99.99%).

-Zirconium could be stripped selectively from the loaded organic solutions using a mixture of oxalic acid, sodium carbonate and ammonium carbonate (0.1M each) in the sequence
CYANEX 302>CYANEX 301>CYANEX 272

-Stripping of Zr(IV) from the loaded CYANEX 272 and CYANEX 301 solutions reached >99.9% when using 2.5 and 2M sulphuric acid, respectively, while 76% stripping of the metal from the loaded CYANEX 302 was obtained with 2.5 M H_2SO_4 .

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