doi:10.3969/j.issn.2095-1744.2021.12.009

溶剂协同萃取分离锆和铪技术研究进展

徐志高[1]，徐　斐[1]，董攀飞[1]，吴　明[1]，何正艳[1]，瞿　军[1]，池汝安[2]
（1. 中南民族大学 资源与环境学院，催化转化与能源材料化学教育部重点实验室，
资源转化与污染物控制国家民委重点实验室，催化材料科学湖北省重点实验室，武汉 430074；
2. 武汉工程大学 兴发矿业学院，绿色化工过程教育部重点实验室，武汉 430074）

摘　要：核级锆铪是构建核反应堆不可替代的核心材料。锆元素和铪元素天然共生，但核性能差异巨大。因此，锆铪分离是制备核级锆和铪的技术关键。溶剂萃取分离技术是工业分离锆铪的主要途径。综述了溶剂协同萃取分离锆和铪的研究进展，重点介绍了中性-酸性、中性-碱性、碱性-酸性、中性-中性和酸性-酸性等五类溶剂协同萃取体系对锆铪分离的作用规律，发现大多数中性-酸性和中性-中性协同萃取体系对锆铪分离具有积极作用，尤其是中性有机膦类萃取剂的加入可显著提高协同萃取体系对锆或铪的萃取选择性，中性-碱性协同萃取体系在 HSCN 或 HCl 介质中具有协同增强效应，而酸性-碱性协同萃取体系则对锆铪萃取分离有反协同作用，酸性-酸性协同萃取体系的效果则与其酸性强弱有关。当前相关研究工作主要侧重于锆铪萃取分离工艺，而对协同萃取机理的探究较少。锆和铪的离子半径极为相近，溶液化学性质复杂，对协同萃取反应过程和机理影响巨大。因此需加强锆铪萃取分离机理的基础理论研究，为开发出新型绿色高效的萃取剂和协同萃取体系提供理论依据。

关键词：溶剂萃取体系；协同萃取；分离；锆；铪
中图分类号：TF841.4　　**文献标志码：**A　　**文章编号：**2095-1744(2021)12-0057-11

Research Progress on Separation of Zirconium and Hafnium by Synergistic Solvent Extraction System

XU Zhigao[1], XU Fei[1], DONG Panfei[1], WU Ming[1], HE Zhengyan[1], QU Jun[1], CHI Ru′an[2]
(1. Key Laboratory of Catalysis and Energy Materials Chemistry of Ministry of Education,
Key Laboratory of Resources Conversion and Pollution Control of the State Ethnic Affairs Commission &
Hubei, Key Laboratory of Catalysis and Materials Science, College of Resources and Environmental Science,
South-Central University for Nationalities, Wuhan 430074, China;
2. Key Laboratory of Green Chemical Process of Ministry of Education, College of Xingfa Mining Engineering,
Wuhan Institute of Technology, Wuhan 430074, China)

Abstract: Nuclear-grade zirconium and hafnium are irreplaceable core materials for building nuclear reactors. Zirconium and hafnium are naturally symbiotic, but their nuclear properties differ greatly, so the separation of zirconium and hafnium is the key to the preparation of nuclear-grade zirconium and hafnium. At present, solvent extraction separation technology is the main process of industrial separation of zirconium and hafnium. This paper reviews the research progress on synergistic solvent extraction and separation of zirconium and hafnium, focusing on the law of the separation of zirconium and hafnium by five types of cooperative solvent extraction systems namely:

收稿日期：2021-02-24
基金项目：国家自然科学基金资助项目(51774344，52104289)；湖北省自然科学基金资助项目(2020CFB165)；武汉市应用基础前沿项目(2019020701011449)
Fund: Supported by the National Natural Science Foundation of China(51774344, 52104289); Natural Science Foundation of Hubei Province of China(2020CFB165), Application Base Frontier Project of Wuhan Science and Technology Bureau(2019020701011449)

作者简介：徐志高(1975—)，男，博士，教授，研究方向为稀有金属湿法冶金。

引用格式：徐志高，徐 斐，董攀飞，等. 溶剂协同萃取分离锆和铪技术研究进展[J]. 有色金属工程，2021，11(12)：57-67.
XU Zhigao, XU Fei, DONG Panfei, et al. Research Progress on Separation of Zirconium and Hafnium by Synergistic Solvent Extraction System[J]. Nonferrous Metals Engineering, 2021, 11(12): 57-67.

neutral-acid, neutral-basic, basic-acid, neutral-neutral, and acid-acid. It is found that most neutral-acid and neutral-neutral synergistic extraction systems have a more positive effect on the separation of zirconium and hafnium, especially the addition of neutral organic phosphine extractants can significantly improve the effect of synergistic extraction systems on the extraction selectivity of zirconium and hafnium. The neutral-alkaline synergistic extraction system has a synergistic enhancement effect in HSCN or HCl media, while the acid-alkaline synergistic extraction system has a negative synergistic effect on the extraction and separation of zirconium and hafnium. The effect of acid-acid synergistic extraction system is related to its acidity. The current research work mainly focuses on the extraction and separation process of zirconium and hafnium, and there is little research on the synergistic extraction mechanism. The ionic radius of zirconium and hafnium are very similar, and the chemical properties of the solution are complex, which have a huge impact on the process and mechanism of the synergistic extraction reaction. Therefore, it is necessary to strengthen the basic theoretical research on the extraction and separation mechanism of zirconium and hafnium to provide a theoretical basis for the development of new green and efficient extractants and synergistic extraction systems.

Key words: solvent extraction system; synergistic extraction; separation; zirconium; hafnium

锆（Zr）和铪（Hf）是重要的稀有金属，广泛应用于原子能、冶金、石化、航空航天和新材料领域[1-2]，已成为国防建设和国民经济发展中不可替代的战略物质[3]。在自然界中，Zr 和 Hf 以类质同象的方式共存，没有单独存在的锆矿或铪矿。一般 Zr 化学品中 Hf 的质量含量约为 Zr 的 1%～3%[4]。受镧系收缩的影响，Zr 和 Hf 的电子结构与物理化学性质均极为相近，二者分离难度很高。然而，Zr 和 Hf 是构建核反应堆的核心材料，且作用差异巨大。其中 Zr 具有极低的热中子俘获截面，只有（0.18±0.02）b（1 b = 10^{-28} m^2/原子），主要被用作核反应堆结构材料、高性能燃料元件包壳材料和二氧化铀基燃料棒的包覆材料[5-7]，而 Hf 的热中子俘获截面较大（105 b），主要用作核反应堆的控制材料[8]。在核工业中，Zr 和 Hf 必须预先分离达到核级（亦称为原子能级），即要求 Zr 中 Hf 的质量含量小于 0.01%，Hf 中 Zr 的质量含量小于 2%[9]。因此，Zr 和 Hf 的分离是制备核级 Zr 和 Hf 材料的技术关键。

工业上分离 Zr 和 Hf 的方法有分步结晶法[9-11]、熔盐精馏法[12]、离子交换法[13-14]和溶剂萃取法[15-16]等，其中溶剂萃取法具有处理量大、成本低和易实现连续化生产等优点，已成为分离 Zr 和 Hf 最重要的方法[17]。目前，全世界 2/3 以上的核级锆采用甲基异丁酮（MIBK）萃取分离。该萃取剂可以优先萃取原料中含量较少的 Hf，因而分离效率较高。但是 MIBK 水相溶解度高达 1.7 g/L，萃取剂易损失；同时，该体系中 HSCN 助萃剂易分解，产生有毒物质[18]。工业上，也曾尝试采用磷酸正三丁酯（TBP）和三烷基胺（N 235）替代 MIBK 萃取分离锆铪。但 TBP 体系使用强硝酸作助萃剂，易使 TBP 分解，导致乳化和分相困难，同时 HNO_3 对设备腐蚀严重[19]。N235 体系对环境友好，但锆铪分离系数不高[20]。因此，目前工业上迫切需要开发出新型绿色高效的溶剂萃取体系，以克服传统萃取体系的不足。

相较于单一萃取剂，由两种或两种以上萃取剂组成的多元协同萃取体系，不仅可以提升对 Zr 或 Hf 的萃取率、提高萃取选择性、增强萃合物的稳定性，还可以有效消除萃取剂的乳化、抑制第三相的产生，从而提高锆铪萃取分离效率[21]。因此，开发协同萃取体系，现已成为锆铪溶剂萃取分离研究的重要发展方向，工业应用前景广阔。

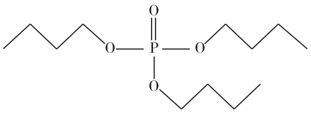
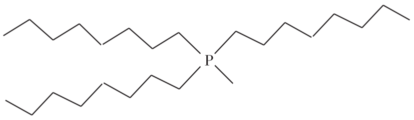
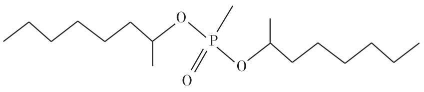
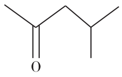
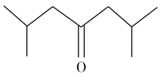
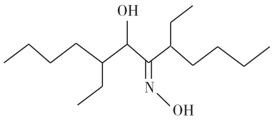
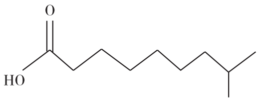
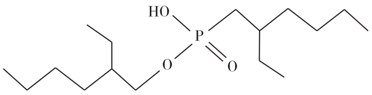
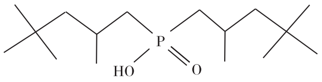
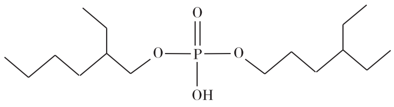
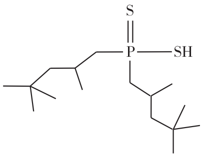
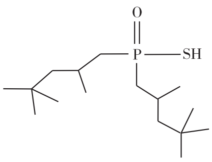
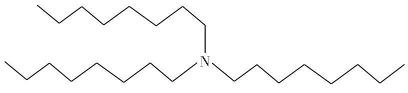
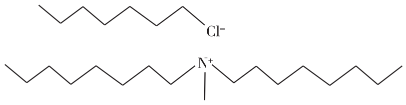
1 协同萃取体系分类与研究进展

协同萃取是指在相同条件下，由两种或两种以上萃取剂组成的多元萃取体系中，金属离子的萃取分配比大于每一种萃取剂单独使用时分配比之和，即认为这一多元混合萃取体系具有协同萃取效应。可见，萃取剂是开发协同萃取体系，实现 Zr 和 Hf 高效分离的关键[22]。

常见萃取剂可分为三类：中性萃取剂、酸性萃取剂、碱性萃取剂，其基本分子结构如表 1 所示。中性萃取剂一般又包括中性含氧萃取剂、中性含磷萃取剂、中性含硫萃取剂和酰碱性萃取剂。其中最常用于锆和铪萃取分离的中性含磷萃取剂有磷酸三丁酯（TBP）[23]、三辛基氧化膦（TOPO）[24]、P 350[25]等，中性含氧萃取剂有甲基异丁基酮（MIBK）[26]、二异丁基酮（DIBK）[27]等。常用的酸性萃取剂有 Lix 63[28]、Versatic Acid 10[29]、PC 88A[30]、Cyanex 272[31]、Cyanex 301[32]、Cyanex 302[33]和 D2EHPA[34]。碱胺类萃取剂主要有 Alamine 336[35]和 Aliquat 336[36]等。

表 1　Zr 和 Hf 分离常用萃取剂的分类及其基本结构

Table 1　Classification and basic structure of the commonly used solvent extractants for separation of Zr and Hf

Classification	Name	Structure	Ref.
Neutral extractants	TBP		[23]
	TOPO/Cyanex921		[24]
	P 350		[25]
	MIBK		[26]
	DIBK		[27]
Acidic extractants	Lix 63		[28]
	Versatic Acid 10		[29]
	PC 88A/P 507		[30]
	Cyanex 272		[31]
	D2EAHP/P 204		[32]
	Cyanex 301		[33]
	Cyanex 302		[34]
Alkaline extractants	Alamine 336/TOA		[35]
	Aliquat 336		[36]

协同萃取体系可以分为二元协同萃取体系和多元协同萃取体系，Zr和Hf的协同萃取研究主要集中在二元协同萃取体系。二元协同萃取体系分类较多，按照不同的萃取剂组合方式，可将协同萃取体系分五类：中性-酸性协萃体系、中性-碱性协萃体系、碱性-酸性协萃体系、中性-中性协萃体系、酸性-酸性协萃体系（见表2）。

表2 几类常用协同萃取体系的组成及效果

Table 2 Composition and effect for several commonly used synergistic solvent extraction systems

Classification		Synergistic extractants composition	Medium	Effect	Ref.
Binary synergistic extraction systems with different types of extractants	Neutral-acidic synergistic extraction systems	TBP＋Cyanex 272	HNO_3	Preferentially extract Zr； Separation factor up to 99.7	[37]
		TBP＋D2EHPA	HNO_3	Separation factor up to 44.8	[38]
		TBP＋Cyanex 301/D2EHPA	H_2SO_4	Preferentially extract Hf	[39]
		TBP/Cyanex 923＋Cyanex 301	HCl	Synergistic enhancement	[40，41]
		TOPO＋PC 88A	HNO_3	Synergistic enhancement	[42]
		TOPO＋D2EHPA/PC 88A/Cyanex 272	HCl	Synergistic enhancement	[43]
		TOPO＋Cyanex 272	HCl＋HNO_3	Preferentially extract Zr	[44]
		DIBK＋P 204	HSCN	Preferentially extract Hf	[45-48]
	Neutral-alkaline synergistic extraction systems	TOPO＋Aliquat 336	HSCN＋HCl	Synergistic enhancement	[49]
		Cyanex 921＋TOA	HCl	Increase in the extraction rate of zirconium	[51]
		Cyanex 923＋TOA	HCl	＞7 mol/L HCl，synergistic enhancement	[52]
	Alkaline-acidic synergistic extraction systems	TOA＋PC 88A	HNO_3	Slightly synergistic enhancement	[42]
Binary synergistic extraction systems with the same types of extractant	Neutral-neutral synergistic extraction systems	H2SbBP＋TOPO/TRPO/TBP	HCl	Synergistic enhancement	[59]
		HPBI＋TOPO/TRPO/TBP	HCl	Synergistic enhancement	[60]
		HPBI＋18C6/DC18C6/B15C5	HCl	Synergistic enhancement	[61]
		TBP＋Cyanex 923	HCl	Higher separation factor than single extractant system	[62]
		TBP＋Cyanex 923	HNO_3	Synergistic enhancement	[63]
		DIBK＋P 350/TBP/TOPO	HSCN	Preferentially extract Hf	[25，64-65]
	Acidic-acidic synergistic extraction systems	PC 88A＋Versatic Acid/Lix 63	HNO_3	Preferentially extract Zr	[28，42]
		Lix 63＋Cyanex 272/D2EHPA	H_2SO_4	Preferentially extract Hf	[66]

1.1 中性-酸性协萃体系

中性-酸性协萃体系是指中性萃取剂与酸性萃取剂组成的二元混合协同萃取体系。近年来，对锆和铪分离采取中性-酸性协萃体系的研究已有大量的报道。

TBP是一种优良的中性萃取剂，在锆铪分离研究中使用较为广泛。YADOLLAHI等[37]研究了TBP-Cyanex 272体系在HNO_3介质中对Zr和Hf的萃取分离效果，发现TBP-Cyanex 272体系对Zr的萃取存在协同效应，对Hf的萃取表现为反协同作用，分离系数达99.7。认为可能是由于在HNO_3溶液中，Zr和Hf的阳离子配合物应与NO_3^-结合形成中性的可萃取配合物，通过溶剂化机理萃取，而且Zr与NO_3^-结合的能力比Hf的更强（由于其电荷密度较小），导致Zr在HNO_3介质中的选择性萃取优于Hf。TBP-Cyanex 272体系协同萃取的配合物为$ZrO(NO_3)_2 \cdot 2\text{Cyanex 272} \cdot 2\text{TBP}$，对Zr的萃取反应如式(1)所示：

$$ZrO(NO_3)_2 + 2\text{Cyanex 272} + 2\text{TBP} \rightleftharpoons ZrO(NO_3)_2 \cdot 2\text{Cyanex 272} \cdot 2\text{TBP} \qquad (1)$$

JIRANDEHI等[38]研究了TBP-D2EHPA体系对Zr和Hf的萃取行为，建立了TBP-D2EHPA体

系萃取 Zr 和 Hf 的统计模型,预测 HNO_3 介质中协萃剂 TBP/D2EHPA 体积比为 5 时优先萃取 Zr,分离系数最大达 44.8。

WANG 等[39]研究了中性磷类萃取剂 TBP 分别与 Cyanex 301 和 D2EHPA 在 H_2SO_4 介质中选择性萃取 Hf 时发现,与单一的 Cyanex 301/D2EHPA 相比,TBP-Cyanex 301/D2EHPA 体系具有反协同作用。TBP-Cyanex 301 体系和 TBP-D2EHPA 体系对 Zr 和 Hf 萃取的抑制可能与有机相中的相互作用有关。

REDDY 等[40]发现由中性磷类萃取剂(TBP 和 Cyanex 923)和酸性有机膦萃取剂(Cyanex 301 和 Cyanex 302)组成的二元协萃体系,TBP-Cyanex 301 体系和 Cyanex 923-Cyanex 301 体系在 0.01 mol/L HCl 中有协同增强作用,而 TBP-Cyanex 302 体系和 Cyanex 923-Cyanex 302 体系却有反协同作用。当 HCl 浓度为 1.00 mol/L 时,TBP-Cyanex 301 体系比单一的 Cyanex 301 体系更有利于其分离,分离系数略微提升[41]。

WANG 等[42]发现 HNO_3 介质中 TBP-PC 88A 体系对 Zr 和 Hf 的萃取分离效果比单一的 PC 88A 影响较小,而 TOPO-PC 88A 体系对 Zr 和 Hf 的萃取分离效果改善显著。WANG 等[43]还发现 HCl 介质中 TOPO-PC 88A 体系对 Zr 和 Hf 的萃取具有协同增强作用,萃取机理可能是溶剂化反应。还发现其他酸性萃取剂 D2EHPA 和 Cyanex 272 分别与 TOPO 组成的混合体系也有协同增强作用。不同 HCl 浓度下协萃体系的协同增强系数见表 3。由表 3可知,协同增强系数随 HCl 浓度的增加而增大。有机膦萃取剂与 TOPO 组成协萃体系在低浓度 HCl 介质中可获得较高的分离系数,而高浓度 HCl 则有利于单一有机膦萃取剂对其分离。

表 3　协同萃取剂对 Zr 或 Hf 萃取的协同增强系数[43]

Table 3　Synergistic enhancement factor(*R*) of the mixed extractants for extraction of Zr or Hf[43]

R for Zr or Hf	Extractants	Concentration of HCl/(mol · L^{-1})			
		1	2	3	4
R_{Zr}	TOPO+D2EHPA	2.63	1.91	2.53	9.78
	TOPO+PC 88A	4.14	2.19	2.09	9.09
	TOPO+Cyanex 272	5.15	5.68	7.89	30.35
R_{Hf}	TOPO+D2EHPA	2.38	1.78	2.88	8.13
	TOPO+PC 88A	0.86	1.01	1.85	9.15
	TOPO+Cyanex 272	2.29	4.15	7.75	18.25

Note:$R=D_{mix}/(D_A+D_B)$;D_{mix}=Distribution coefficient of metal ions with the mixed extractant of A and B;D_A=Distribution coefficient of metal ions with single extractant A;D_B= Distribution coefficient of metal ions with single extractant B.

易师等[44]研究发现有机相的配比为 20% TOPO+10% Cyanex272+70%磺化煤油,料液中盐酸和硝酸混合酸酸度为 5.0 mol/L,萃取相比为 2∶1时,锆的萃取率最高为 98.68%,铪的萃取较少为 4.35%,且油水两相分层较快,界面清晰,没有乳化现象。用 3.0 mol/L HNO_3洗涤,0.5 mol/L HCl 做反萃剂,有机相中 Hf 的反洗率达 97.33%,最终获得的 ZrO_2 产品纯度达到 99.90%,Hf 含量仅为 0.0030%,满足核级 Zr 的标准。

DIBK 与 MIBK 具有相似的分子结构,萃取机理也几乎相似。单一 DIBK-HSCN 体系优先萃取 Hf,但 Hf 的萃取率仅 21.56%。徐志高等[45-48]在此基础上研究了 DIBK-P204 协同萃取体系萃取分离 Zr 和 Hf 的性能,发现 DIBK-P204 体系在 HSCN 介质中优先萃取 Hf,分离系数随着 P204 浓度的增加而增加。此外,在水相溶液中加入 $(NH_4)_2SO_4$,可以使更多的 Hf 萃取进入有机相,改善 Zr 和 Hf 之间的萃取分离,还推导出协萃配合物的组成分别为 $Zr(SCN)_3 \cdot HA_2 \cdot DIBK$ 和 $Hf(SCN)_3 \cdot HA_2 \cdot DIBK$,协萃反应方程式可写作方程(2):

$$M^{4+}+3SCN^{-}+DIBK(o)+H_2A_2(o)\rightleftharpoons M(SCN)_3 \cdot DIBK \cdot H_2A_2(o) \qquad (2)$$

中性-酸性协萃体系在 HCl 和 HNO_3 体系中优先萃取 Zr,对 Zr 和 Hf 的萃取率均高于单萃取剂体系。中性-酸性-H_2SO_4 体系优先萃取 Hf,但是其对 Zr 和 Hf 的萃取具有反协同作用。中性含氧萃取剂与酸性萃取剂在 HSCN 体系中优先协同萃取 Hf,且盐析剂的加入有利于改善 Zr 和 Hf 的分离。

1.2　中性-碱性协萃体系

碱性萃取剂一般是指伯胺、仲胺、叔胺和季胺,在金属分离中得到广泛应用,萃取机理主要按阴离子交换或加成反应机理与金属离子形成离子缔合

物。胺类分子中的N原子是电子供体，伯胺与仲胺与N连接的H原子具有一定的受体特征，因此胺类应该也可以通过溶剂化萃取中性分子。

MISHRA等[49]报道了TOPO-Aliquat 336体系在HCl存在下和硫氰酸盐介质中萃取Zr和Hf，发现对Hf有协同增强作用。BANDA等[50]发现，随着碱性萃取剂浓度的增加，TOPO-Aliquat 336体系、TOPO-Alamine 308体系和TOPO-Alamine 336体系对Zr和Hf的萃取率均有所降低，即TOPO与碱性萃取剂具有反协同效应。BHATTA等[51]以煤油为稀释剂，用Cyanex 921-TOA二元协萃体系从HCl溶液中萃取Zr，发现具有较强碱性的中性供体Cyanex 921的加入，可以取代金属配体中的水分子，从而形成更加疏水的萃合物，提高了TOA对Zr的萃取率。BHIKARI等[52]发现当盐酸酸度低于6 mol/L时，对Zr的萃取能力大小为TOA体系＜Cyanex 923-TOA体系＜Cyanex 923体系，而在较高的HCl浓度下（7 mol/L），对锆的萃取有协同作用。

中性-碱性-HSCN体系对Hf的萃取有协同增强的作用。中性-碱性协萃体系在高浓度HCl溶液中对Zr的萃取率有所提高；在低浓度HCl溶液中，由于HCl的竞争萃取对锆和铪的萃取有反协同作用。

1.3 酸性-碱性协萃体系

酸性萃取剂是指含有－COOH、P（O）OH和$-SO_3H$等活性基团的萃取剂，一般采用阳离子交换机理萃取金属离子，通过金属离子交换下萃取剂活性基的氢离子来萃取[53]。按酸的种类不同可将酸性萃取剂分为羧酸类萃取剂、酸性磷类萃取剂和磺酸类萃取剂，其中多采用酸性磷类萃取剂和羟肟酸类萃取剂（Lix 63）用于锆和铪的萃取。

WANG等[54]研究了在HCl介质中碱性萃取剂（Alamine 336和Aliquat 336）分别与酸性磷（膦）类萃取剂（D2EHPA、PC 88A和Cyanex 272）组成的协萃体系对Zr和Hf的萃取行为，发现与单一酸性磷（膦）类萃取剂相比，Alamine 336和Aliquat 336分别与酸性磷（膦）膦类萃取剂组成的混合体系降低了Zr和Hf的萃取率，说明该体系在HCl介质中具有反协同作用[55-56]。有机相中，有机膦酸（HA）与胺（R_3N）的酸碱相互作用会导致有机膦萃取剂游离浓度降低，从而不利于Zr和Hf的萃取，萃取方程如式(3)[57]：

$$R_3N(o)+HA(o) \leftrightarrow R_3NH\cdot A(o) \tag{3}$$

然而，WANG等[42]发现在2 mol/L HNO_3介质中，PC 88A-TOA体系对Zr和Hf的萃取略有增强，分离系数达到了17，可能是由于TOA对含硝酸盐离子的Zr和Hf阴离子配合物的萃取。

在HCl介质中，由于酸性萃取剂和碱性萃取剂的酸碱相互作用降低了有机膦萃取剂的游离浓度，酸性-碱性协萃体系有反协同作用。在HNO_3介质中酸性-碱性协萃体系对Zr和Hf的萃取影响不大。

1.4 中性-中性协萃体系

中性-中性协萃体系一般是中性螯合萃取剂与中性磷（膦）类萃取剂混合，对Zr和Hf的萃取具有协同增强作用，增强效果与中性磷（膦）类萃取剂磷酰氧原子的供体能力有关。中性磷（膦）类萃取剂P＝O（磷酰基）基团与Zr或Hf离子形成配位，萃取能力强弱与磷酰氧原子的电子云密度有关。萃取剂分子中C—P键越多，诱导效应越强，磷酰氧原子（P＝O）电子云密度越大，萃取能力越强[58]。

REDDY等[59]研究了4-癸二酰基双（1-苯基-3-甲基5-吡唑啉酮）（H2SbBP）与中性磷（膦）类萃取剂（TOPO、TRPO和TBP）组成的协萃体系在HCl介质中协同萃取Zr和Hf的行为，发现协同增强因子随中性磷（膦）类萃取剂浓度的增加而增大，Zr和Hf与各种中性磷（膦）类萃取剂的络合强度按以下顺序递减：TOPO＞TRPO＞TBP。中性磷（膦）类萃取剂磷基氧的供体能力强弱控制着协同混合物的亲和力。中性磷（膦）类-H2SbBP萃取体系对Zr和Hf的萃取方程如式(4)所示：

$$MO^{2+}+2H_2X(o)+S(o)\leftrightarrow MO(HX)_2\cdot S(o)+2H^+ \tag{4}$$

REDDY等[60]还研究了3-苯基-4-苯甲酰-5-异恶唑酮（HPBI）与中性磷（膦）类萃取剂（TOPO、TRPO和TBP）组成的二元协萃体系在HCl介质中萃取分离Zr和Hf的行为，发现络合强度也按以下顺序排列TOPO＞TRPO＞TBP。HPBI与存在位阻支链萃取剂TRPO协同萃取时，协同增强效果尤为显著。中性磷（膦）类-HPBI萃取体系在HCl溶液中对Zr和Hf的萃取方程如式(5)所示：

$$MO^{2+}+2HPBI(o)+2S(o)\rightleftharpoons MO(PBI)_2\cdot S(o)+2H^+ \tag{5}$$

REDDY等[61]又将HPBI与不同的冠醚CEs（18C6、DC18C6和B15C5）混合在HCl介质中

萃取分离 Zr 和 Hf，发现 HPBI-CEs 体系有较大的协同增强作用，其协萃配合物为 $ZrO(PBI)_2 \cdot CE$ 和 $HfO(PBI)_2 \cdot CE$，HPBI-B15C5 体系的分离系数达 5.28，高于 HPBI 体系的 2.09。

AMARAL 等[62]研究了 TBP-Cyanex 923 体系在 HCl 介质中对 Zr 和 Hf 的萃取行为，发现该协萃体系的分配系数比单独 TBP 或 Cyanex 923 的高。TAGHIZADEH 等[63]发现 TBP-Cyanex 923 体系在酸性硝酸盐溶液中有显著协同增强作用，不会形成第三相。与传统 TBP-HNO_3体系相比，具有萃取率较高、分离系数高、酸浓度低等优点。

徐志高等[24,64]研究了 DIBK 和中性磷(膦)类萃取剂(TBP、P350 和 TOPO)组成的协萃体系在硫氰酸盐介质中选择性萃取 Hf 的行为，发现其优先萃取 Hf，协萃体系的分离系数也高于单一 DIBK、TBP、P350 和 TOPO 等萃取体系，大小按 TOPO＞P350＞TBP 顺序排列。

中性-中性协萃体系对 Zr 和 Hf 的萃取具有协同增强作用，不仅提高了 Zr 和 Hf 的萃取率，还提高了它们的选择性。协萃体系里中性磷(膦)类萃取剂磷酰氧原子的供体能力越强，协同效应越强，其中中性含氧萃取剂 DIBK 与中性磷(膦)类萃取剂协同优先萃取 Hf，且分离系数较高。

1.5　酸性-酸性协萃体系

酸性-酸性协萃体系一般指酸性磷(膦)类萃取剂和螯合或非螯合肟萃取剂混合所组成的萃取体系，具有协同增强作用。

WANG 等[28,42]研究了 Lix63-PC88A 体系和 Versatic Acid-PC88A 体系在 HNO_3介质中优先萃取 Zr，随着 PC88A 的浓度逐渐增加，Zr 的萃取显著增强，而对 Hf 的萃取略微降低。Lix63-PC88A 协萃体系的分离系数最高达 46。

WANG 等[54]研究了酸性磷(膦)类萃取剂(D2EHPA、PC88A 和 Cyanex 272)与酸性萃取剂(Versatic Acid 10 和 Lix 63)组成的协同萃取体系，发现有机磷(膦)类-Versatic Acid 10 萃取体系对 Zr 和 Hf 的萃取低于单一酸性磷(膦)类萃取剂，Cyanex 272-Lix 63 体系分离效果最好，分离系数为 9.5 左右；而酸性磷(膦)类-Lix 63 萃取体系存在反协同作用。

BANDA 等[65]研究了 Lix 63 与酸性磷(膦)类萃取剂(Cyanex 272 和 D2EHPA)在 H_2SO_4介质中分离 Zr 和 Hf 的性能，发现 D2EHPA 或 Cyanex 272 的加入显著提高了 Lix 63 对 Zr 和 Hf 的萃取，相应地降低了它们的选择性。在不同浓度的H_2SO_4介质中，Cyanex 272-Lix 63 体系和 D2EHPA-Lix 63 体系存在显著差异，可能是因为磷酸衍生物的酸性强于次磷酸衍生物[49]。

酸性-酸性萃取剂协同效应的强弱与其酸性强弱有关。酸性-酸性-H_2SO_4体系优先萃取 Hf，且对 Zr 和 Hf 的萃取率均有所提高。

2　结论

1)溶剂萃取法分离 Zr 和 Hf 是最常规、最重要的方法。协同萃取体系可以有效提高 Zr 和 Hf 的分离效果，作为溶剂萃取法中的一个重要分支受到了越来越多的关注。影响协同效应的因素较多，如萃取剂酸碱性、不同萃取剂组合、萃取剂浓度、萃取剂的比例、酸性介质、水相 pH 值和盐析剂等，不同协同萃取体系产生协同效应的机制也不相同。

2)大多数中性-酸性萃取体系和中性-中性协同萃取体系对 Zr 和 Hf 的萃取分离都有着积极的作用。中性-碱性协同萃取体系在 HSCN 介质对 Hf 的萃取有协同增强的作用；而在高浓度 HCl 溶液中对 Zr 的萃取率有所提高。因酸性萃取剂和碱性萃取剂的酸碱相互作用可能会降低有机膦萃取剂的游离浓度，不利于 Zr 和 Hf 的萃取。酸性-酸性萃取剂协同效应的强弱与其酸性强弱有关。

3)由于 Zr 和 Hf 的化学性质复杂，在不同水相介质、不同酸度溶液中的赋存状态不同，协萃反应机理研究难度较大。目前的研究工作主要集中于新的萃取体系的探索，侧重于 Zr 和 Hf 的萃取分离工艺研究，而对协同萃取机理的探究较少，不够深入。另外，需加强萃取机理的基础理论研究，为开发新型的绿色高效萃取剂或协同萃取体系提供理论依据。

参考文献：

[1]　郑仕鸿，赵卓，柴延全. 火法分离锆铪技术的研究进展[J]. 稀有金属与硬质合金，2017，45(2)：6-12，19.
ZHENG Shihong, ZHAO Zhuo, CHAI Yanquan. Research progress on pyrometallurgical separation technology of zirconium and hafnium[J]. Rare Metals and Cemented Carbides，2017，45(2)：6-12，19.

[2]　DING F, WANG C Y, ZHANG T, et al. High

performance cutting of Zr-based bulk metallic glass: A review of chip formation[J]. Procedia CIRP, 2018, 77: 421-424.

[3] 陈华祝.海南锆矿资源开发利用现状分析建议[J].中国金属通报,2018(4):97-98.
CHEN Huazhu. Analysis and suggestions on the development and utilization of zirconium mineral resources in Hainan province[J]. China Metal Bulletin, 2018(4):97-98.

[4] 汪泉发.锆铪分离技术述评[J].广东化工,1989(3):8-12.
WANG Quanfa. A review of zirconium and hafnium separation technology [J]. Guangdong Chemical Industry, 1989(3):8-12.

[5] WANG L Y, LEE M S. Solvent extraction of Zr(IV) and Hf(IV) from sulfuric acid solutions by acidic extractants and their mixtures with TBP[J]. Journal of the Korean Institute of Resources Recycling, 2016, 25(2):3-9.

[6] 田胜军,刘艳,陈刚,等.锆铪的分离技术及应用[J].铀矿冶,2006,25(2):103-109.
TIAN Shengjun, LIU Yan, CHEN Gang, et al. Separation techniques and application of Zr and Hf[J]. Uranium Mining and Metallurgy, 2006, 25(2): 103-109.

[7] 张力.锆铪分离工艺的发展及现状[J].稀有金属快报,2004,23(5):26-29.
ZHANG Li. The development and the status of zirconium and hafnium separation process[J]. Rare Metals Letters, 2004, 23(5):26-29.

[8] 车德华,徐刚,徐盛明.溶剂萃取法分离锆铪技术进展[J].有色金属工程,2014,4(1):75-80.
CHE Dehua, XU Gang, XU Shengming. Progress in separation of zirconium and hafnium by solvent extraction[J]. Nonferrous Metals Engineering, 2014, 4(1):75-80.

[9] WANG L Y, LEE M S. A review on the aqueous chemistry of Zr(IV) and Hf(IV) and their separation by solvent extraction[J]. Journal of Industrial and Engineering Chemistry, 2016, 39:1-9.

[10] POSTMA C J, NIEMAND H F, CROUSE P L. A theoretical approach to the sublimation separation of zirconium and hafnium in the tetrafluoride form[J]. Journal of the Southern African Institute of Mining and Metallurgy, 2015, 115(10):961-965.

[11] BRANKEN D J, LACHMANN G, KRIEG H M, et al. Influence of KF and HF on the selectivity of Zr and Hf separation by fractional crystallization of $K_2Zr(Hf)F_6$[J]. Industrial & Engineering Chemistry Research, 2010, 49(2):797-808.

[12] 刘敏娉,丁燕,张泽光,等.锆与铪分离技术的研究现状及应用前景[J].广东有色金属学报,2001,11(2):115-119.
LIU Minping, DING Yan, ZHANG Zeguang, et al. Present research status of separation technologies and application prospects of Zr and Hf[J]. Journal of Guangdong Non-ferrous Metals, 2001, 11(2):115-119.

[13] FELIPE E C B, LADEIRE A A C Q. Separation of zirconium from hafnium by ion exchange[J]. Separation Science and Technology, 2018, 53(2):330-336.

[14] AGATA J K, MAREK S, JAROSZEK H. The influence of the treatment of Zr(IV) and Hf(IV) sulfate solution on the ion-exchange purifying of zirconium from hafnium on Diphonix resin[J]. Hydrometallurgy, 2013, 140:77-81.

[15] 柴延全,郑仕鸿,赵卓.锆铪分离技术的研究现状及发展趋势[J].有色金属工程,2017,7(2):29-34,40.
CHAI Yanquan, ZHENG Shihong, ZHAO Zhuo. Research status and trend of zirconium and hafnium separation[J]. Nonferrous Metals Engineering, 2017, 7(2):29-34,40.

[16] WANG L Y, LEE M S. Development of a separation process for the selective extraction of hafnium(IV) over zirconium(IV) from sulfuric acid solutions by using D2EHPA[J]. Hydrometallurgy, 2016, 160: 12-17.

[17] XU L, XIAO Y, SANDWIJK A V, et al. Production of nuclear grade zirconium: A review[J]. Journal of Nuclear Materials, 2015, 466:21-28.

[18] BAND R, LEE M S. Solvent extraction for the separation of Zr and Hf from aqueous solutions[J]. Separation and Purification Reviews, 2015, 44(3): 199-215.

[19] IVANOV P, MU J, LEAY L, et al. Organic and third phase in HNO_3/TBP/n-dodecane system: No reverse micelles[J]. Solvent Extraction and Ion Exchange, 2017, 35(4):251-265.

[20] 侯崇寿,尤曙彤,冯松,等.改进的 N235-H_2SO_4 流程萃取分离锆和铪制取原子能级氧化锆[J].稀有金属,1991,15(6):405-410.
HOU Chongshou, YOU Shutong, FENG Song, et al. Extraction and separation of Zr and Hf by the

improved N 235-H_2SO_4 process for preparing atomic energy grade zirconia[J]. Chinese Journal of Rare Metals,1991,15(6):405-410.

[21] TIAN M, MU F, JIA Q, et al. Solvent extraction studies of zinc(Ⅱ) and cadmium(Ⅱ) from a chloride medium with mixtures of neutral organophosphorus extractants and amine extractants[J]. Journal of Chemical & Engineering Data,2011,56(5):2225-2229.

[22] 王俊莲,付家帅,许文,等. 基于锆铪溶剂萃取分离的萃取剂性能[J]. 稀有金属,2020,44(6):658-667.
WANG Junlian, FU Jiashuai, XU Wen, et al. Performance of various extractants for zirconium and hafnium separation by solvent extraction[J]. Chinese Journal of Rare Metals,2020,44(6):658-667.

[23] AMARAL J C, MORAIS C A. Equilibrium of zirconium and hafnium in the process of extraction with TBP in nitric medium-Influence in the Zr/Hf seperation[J/OL]. Minerals Engineering, 2020, 146: 106138. https://doi.org/10.1016/j.mineng.2019.106138.

[24] NAYL A A, El-NADI Y A, DAOUD J A. Extraction and separation of Zr(IV) and Hf(IV) from nitrate medium by mome CYANEX extractants[J]. Separation Science and Technology,2009,44(12):2956-2970.

[25] 张文杰,吴明,徐志高,等. DIBK-P350 和 DIBK-TOPO 负载有机相中铪和锆的反萃[J]. 有色金属(冶炼部分),2018(5):41-45,49.
ZHANG Wenjie, WU Ming, XU Zhigao, et al. Stripping of Hf and Zr from loaded organic phase of DIBK-P350 and DIBK-TOPO[J]. Nonferrous Metals(Extractive Metallurgy),2018(5):41-45,49.

[26] 吕标起,徐志高,张力,等. MIBK-HSCN 体系萃取分离锆铪影响因素的研究[J]. 稀有金属,2008,32(6):754-757.
LYU Biaoqi, XU Zhigao, ZHANG Li, et al. Influence parameters of separation of zirconium and hafnium in MIBK-HSCN systems[J]. Chinese Journal of Rare Metals,2008,32(6):754-757.

[27] 徐志高,王力军,池汝安,等. DIBK 溶剂萃取法分离锆铪[J]. 有色金属(冶炼部分),2012(3):35-38,42.
XU Zhigao, WANG Lijun, CHI Ru′an, et al. Solvent extraction and separation of hafnium from zirconium with DIBK[J]. Nonferrous Metals(Extractive Metallurgy),2012(3):35-38,42.

[28] WANG L Y, LEE M S. Separation of zirconium and hafnium from nitric acid solutions with LIX 63, PC 88A and their mixture by solvent extraction[J]. Hydrometallurgy,2014,150:153-160.

[29] LEE H Y, KIM S G, OH J K. Stoichiometric relation for extraction of zirconium and hafnium from acidic chloride solutions with Versatic Acid 10[J]. Hydrometallurgy,2004,73(1/2):91-97.

[30] REDDY B R, KUMAR J R, REDDY A V. Solvent extraction of tetravalent hafnium from acidic chloride solutions using 2-ethyl hexyl phosphonic acid mono-2-ethyl hexyl ester(PC-88A)[J]. Minerals Engineering,2004,17(4):553-556.

[31] TAGHIZADEH M, GHASEMZADEH R, ASHRAFIZADEH S N, et al. Stoichiometric relation for extraction of zirconium and hafnium from acidic nitrate solutions with Cyanex 272[J]. Hydrometallurgy,2009,96(1/2):77-80.

[32] VERMAAK V, KRIEG H M, DE BEER L, et al. Mechanistic study of hafnium and zirconium extraction with organophosphorus extractants[J]. Solvent Extraction and Ion Exchange,2018,36(2):150-161.

[33] SABERYAN K, MEYSAMI A H, RASHCHI F, et al. Proposal of a new Hf(Ⅳ)/Zr(Ⅳ) separation system by the solvent extraction method[J]. Chinese Journal of Chemistry,2008,26(11):2067-2072.

[34] REDDY B R, KUMAR J R, RAJA K P, et al. Solvent extraction of Hf(Ⅳ) from acidic chloride solutions using Cyanex 302[J]. Minerals Engineering,2004,17(7):939-942.

[35] BANDA R, LEE H Y, LEE M S. Separation of Zr from Hf in hydrochloric acid solution using amine-based extractants[J]. Industrial & Engineering Chemistry Research,2012,51(28):9652-9660.

[36] PORIEL L, FAVRE-REGUILLON A, PELLET-ROSTAIING S, et al. Zirconium and hafnium separation, Part Ⅰ. Liquid/liquid extraction in hydrochloric acid aqueous solution with Aliquat 336[J]. Separation Science and Technology,2006,41(9):1927-1940.

[37] YADOLLAHI A, SABERYAN K, TORAB-MOSTAEDI M, et al. Solvent extraction separation of zirconium and hafnium from nitric acid solutions using mixture of Cyanex-272 and TBP[J]. Radiochimica Acta,2018,106(8):675-684.

[38] JIRANDEHI V R, FATMEHSARI D H, FIROOZI S, et al. Statistical Modeling of Zr/Hf Extraction using TBP-D2EHPA Mixtures[J]. Metallurgical and Materials Transactions B,2012,43(6):1262-1268.

[39] WANG L Y, LEE M S. Solvent Extraction of Zr(Ⅳ)

and Hf(IV) from sulfuric acid solutions by scidic extractants and their mixtures with TBP[J]. Journal of the Korean Institute of Resources Recycling, 2016, 25(2):3-9.

[40] REDDY B R, KUMAR J R, REDDY A V. Solvent extraction of zirconium(Ⅳ) from acidic chloride solutions using the thiosubstituted organophosphorus acids Cyanex 301 and 302[J]. Journal of Chemical Technology & Biotechnology, 2004, 79(11):1301-1307.

[41] MIN S H, LEE M S. Solvent extraction of zirconium and hafnium from hydrochloric acid solution by Lix 63 and Cyanex 301[J]. Journal of the Korean Institute of Resources Recycling, 2013, 22(6):19-25.

[42] WANG L Y, LEE H Y, LEE M S. Solvent extraction separation of Zr and Hf from nitric acid solutions by PC 88A and its mixture with other extractants[J]. Metals and Materials International, 2015, 21(1):166-172.

[43] WANG L Y, LEE H Y, LEE M S. Solvent extraction of zirconium and hafnium from hydrochloric acid solutions using acidic organophosphorus extractants and their mixtures with TOPO[J]. Materials Transactions, 2013, 54(8):1460-1466.

[44] 易师，费志勇，刘荣丽，等. 从氧氯化锆母液中分离制备氧化锆的研究[J]. 矿冶工程，2016，36(4):80-82，87.
YI Shi, FEI Zhiyong, LIU Rongli, et al. Separation and preparation of zirconium oxide from mother liquor containing zirconium oxychloride[J]. Mining and Metallurgical Engineering, 2016, 36(4):80-82, 87.

[45] XU Z G, WANG L J, WU M, et al. Separation of zirconium and hafnium by solvent extraction using mixture of DIBK and P204[J]. Hydrometallurgy, 2016, 165:275-281.

[46] 徐志高，王力军，吴延科，等. DIBK-P 204体系萃取分离锆和铪的机理[J]. 中国有色金属学报，2013，23(7):2061-2068.
XU Zhigao, WANG Lijun, WU Yanke, et al. Mechanisms of extraction and separation of zirconium and hafnium by DIBK-P 204 system[J]. Chinese Journal of Nonferrous Metals, 2013, 23(7):2061-2068.

[47] 徐志高，王力军，池汝安，等. DIBK-P204体系萃取锆和铪的动力学[J]. 有色金属(冶炼部分)，2013(3):28-31.
XU Zhigao, WANG Lijun, CHI Ru'an, et al. Extraction kinetics of zirconium and hafnium in DIBK-P204 system[J]. Nonferrous Metals(Extractive Metallurgy), 2013(3):28-31.

[48] 徐志高，王力军，吴延科，等. DIBK-P 204体系萃取锆铪的热力学研究[J]. 稀有金属，2013，37(2):266-271.
XU Zhigao, WANG Lijun, WU Yanke, et al. Thermodynamic of solvent extraction of zirconium and hafnium with DIBK-P 204 system[J]. Chinese Journal of Rare Metals, 2013, 37(2):266-271.

[49] MISHRA P K, CHAKRA VORTTY V, DASH K C, et al. Extraction and separation of Zr, Nb and Hf by Aliquat 336 and its mixtures with TOPO from acidic thiocyanate media[J]. Journal of Radioanalytical and Nuclear Chemistry, 1992, 162(2):289-298.

[50] BANDA R, LEE H Y, LEE M S. Separation of Zr from Hf in acidic chloride solutions by using TOPO and its mixture with other extractants[J]. Journal of Radioanalytical and Nuclear Chemistry, 2013, 298(1):259-264.

[51] BHATTA B C, PANDA N, MISHRA S. Extraction of Zr(Ⅳ) from hydrochloric acid with tri-octyl amine and Cyanex 921 in kerosene[J]. International Journal of Minerals Metallurgy and Materials, 2013, 20(9):823-828.

[52] BHIKARI C B, SUJATA M. Binary mixture of tri-octyl amine and Cyanex 923 as extractant for the extraction of Zr(Ⅳ) from acidic chloride medium[J]. International Journal of Nonferrous Metallurgy, 2014, 3(2):9-17.

[53] JADAV G L, ASWAL V K, SINGH P S. In-situ preparation of polydimethylsiloxane membrane with long hydrophobic alkyl chain for application in separation of dissolved volatile organics from wastewater[J]. Journal of Membrane Science, 2015, 492:95-106.

[54] WANG L Y, LEE H Y, LEE M S. Solvent extractive separation of zirconium and hafnium from hydrochloric acid solutions by organophosphorous extractants and their mixtures with other types of extractants[J]. Chemical Engineering Communications, 2015, 202(10):1289-1295.

[55] BANDA R, NGUYEN T H, LEE M S. Recovery of HCl from chloride leach solution of spent HDS catalyst by solvent extraction[J]. Chemical and Process Engineering, 2013, 34(1):153-163.

[56] AGRAWAL A, KUMARI S, SAHU K K. Liquid-liquid extraction of sulphuric acid from zinc bleed stream[J]. Hydrometallurgy, 2008, 92(1/2):42-47.

[57] QUINN J E, WILKINS D, SOLDENHOFF K H. Solvent extraction of uranium from saline leach liquors using DEHPA/Alamine 336 mixed reagent[J]. Hydrometallurgy,2013,134-135(3):74-79.

[58] 马荣骏. 萃取冶金[M]. 北京:冶金工业出版社,2009:74-79.
MA Rongjun. Extractive metallurgy [M]. Beijing: Metallurgical Industry Press,2009:74-79.

[59] REDDY K J, KUMAR J R, REDDY A V, et al. Synergistic extraction of zirconium(Ⅳ) and hafnium(Ⅳ) with 4-acylbis(1-phenyl-3-methyl-5-pyrazolones) in the presence of neutral organophosphorus extractants[J]. Solvent Extraction & Ion Exchange, 2006,24(3):419-432.

[60] REDDY K J, REDDY A V, SHAIBU B S, et al. Enhanced extraction and separation of zirconium(Ⅳ) and hafnium(Ⅳ) with 3-phenyl-4-benzoyl-5-isoxazolone in presence of various neutral organophosphorus extractants[J]. Radiochimica Acta, 2007, 95(5): 289-295.

[61] REDDY K J, KUMAR J R, REDDY M L P, et al. Synergistic enhancement and separation of zirconium(Ⅳ) and hafnium(Ⅳ) with 3-phenyl-4-benzoyl-5-isoxazolone in the presence of crown ethers[J]. Separation Science and Technology,2009,44(9):2022-2040.

[62] AMARAL J C B S, DE MORAIS C A. Study of zirconium and hafnium separation by solvent extraction technique from nitric and hydrochloric solutions with acid, basic and neutral extractants[J]. World Journal of Engineering and Technology, 2016, 4(3):138-150.

[63] TAGHIZADEH M,GHANADI M,ZOLFONOUN E. Separation of zirconium and hafnium by solvent extraction using mixture of TBP and Cyanex 923[J]. Journal of Nuclear Materials,2011,412(3):334-337.

[64] XU Z G,WANG L J,WU Y K,et al. Solvent extraction of hafnium from thiocyanic acid medium in DIBK-TBP mixed system[J]. Transactions of Nonferrous Metals Society of China,2012,22(7):1760-1765.

[65] BANDA R,MIN S H,LEE M S. Selective extraction of Hf(Ⅳ) over Zr(Ⅳ) from aqueous H_2SO_4 solutions by solvent extraction with acidic organophosphorous based extractants[J]. Journal of Chemical Technology & Biotechnology,2014,89(11):1712-1719.