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湿法磷酸萃取技术发展现状与研究进展

黄欣雨[1], 甘　晨[1], 张名扬[1], 邱丽娜[1,2]✉, 弓爱君[1,2], 董　艺[1]

1) 北京科技大学化学与生物工程学院, 北京 100083　2) 北京科技大学功能分子与晶态材料科学与应用北京市重点实验室, 北京 100083

✉通信作者, E-mail: qiulina@ustb.edu.cn

摘　要　磷酸作为一种重要的化工原料, 在化工业中占有极其重要的地位. 磷酸的应用主要由磷酸的纯度决定, 低纯度磷酸可用于工业和农业领域, 而高纯度磷酸则可用于医药、食品和电子等行业. 我国磷矿以低品位磷矿为主, 生产磷酸主要采用湿法工艺. 相比热法生产, 湿法工艺更加清洁环保, 但产品杂质含量多、种类复杂, 故发展磷酸净化技术尤为重要. 本文从湿法磷酸纯化技术中的萃取法出发, 综述了萃取法的主要研究进展. 重点介绍了溶剂萃取法、双水相萃取法、反胶团萃取法、超声协助萃取法和超临界流体萃取法的基本原理和发展趋势. 分析了不同萃取方法的优缺点、分离效果和适用条件. 突出介绍了溶剂萃取法, 梳理了磷酸除杂的主要萃取剂, 特别强调了复合萃取剂和新型萃取剂在磷酸纯化方面的显著优势, 最后, 对磷酸的萃取技术做出了前景展望.

关键词　磷酸; 湿法磷酸; 萃取; 萃取剂; 双水相萃取; 反胶团萃取; 超声协助萃取; 超临界流体萃取

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Development status and research progress of wet phosphoric acid extraction technology

HUANG Xinyu[1], GAN Chen[1], ZHANG Mingyang[1], QIU Lina[1,2]✉, GONG Aijun[1,2], DONG Yi[1]

1) School of Chemistry and Biological Engineering, University of Science and Technology Beijing, Beijing 100083, China

2) Beijing Key Laboratory for Science and Application of Functional Molecular and Crystalline Materials, University of Science and Technology Beijing, Beijing 100083, China

✉Corresponding author, E-mail: qiulina@ustb.edu.cn

ABSTRACT　Phosphoric acid, as a vital chemical raw material, holds an important position in the chemical industry. Its applications span across various sectors, determined largely by its purity. Low-purity phosphoric acid can be used in industrial and agricultural sectors, while high-purity phosphoric acid is essential for pharmaceuticals, food, electronics and other industries. The rising demand for batteries and semiconductors in recent years has led to increased requirements for phosphoric acid purity. There are two main methods for manufacturing phosphoric acid. The thermal method, while effective, is energy-intensive and environmentally unfriendly, conflicting with China's green chemistry development goals. On the other hand, the phosphoric acid process, characterized by lower energy consumption, is more adept at handling China's low-grade phosphate rock despite resulting in bulk and complex product impurities. Among various purification technologies, such as chemical precipitation, crystallization, electrodialysis, and ion exchange resin, the extraction method stands out. It offers environmental benefits, simple operation, and the capacity for large-scale production, marking it as a promising technique for phosphoric acid purification. This article summarizes in detail the research status of various extraction methods in recent years. It focuses on solvent extraction, aqueous two-phase extraction, reverse micelle extraction, ultrasonic-assisted extraction, and supercritical fluid extraction. It sorts out the solvent extraction method along with various extractants. The research on single extractants such as tri-n-butyl phosphate (TBP), methyl isobutyl ketone (MIBK), and n-octanol (NOA) has been primarily focused

on identifying the optimal extraction conditions, including the O/A phase ratio, temperature, and air pressure. However, these single extractants typically target a single impurity, which limits their effectiveness in purifying phosphoric acid when multiple impurities are present. This limitation underscores the significant advantages of composite extractants in the purification process. Current research on composite extractants emphasizes determining the ideal proportion of extractants, often based on volume ratio, and establishing the optimal conditions for effective extraction. In addition to composite extractants, the development of new extractants offers promising solutions to the challenges posed by the low extraction efficiency of single extractants. Looking forward, the future of phosphoric acid extraction technology is poised for exciting developments: (1) The development of green composite extractants, alongside new extractants and materials combined with extractants, aims to achieve more efficient separation of impurities from phosphoric acid; (2) There is a growing interest in expanding research into the application of aqueous two-phase extraction and reverse micelle extraction for ion extraction, including the exploration of new aqueous phase systems; (3) The use of ultrasonic technology to accelerate the extraction process, coupled with studies on how supercritical fluids can improve the solubility and extraction efficiency of ions, represents another avenue for innovation. These advancements seek to reduce costs and explore specific application areas.

KEY WORDS phosphoric acid; wet phosphoric acid; extraction; extractant; aqueous two-phase extraction; reverse micelle extraction; ultrasonic-assisted extraction; supercritical fluid extraction

磷矿是国家的重要战略资源, 在医药、军工、农业生产等诸多国家重点领域上都有着广泛的应用. 以磷矿为原料制得的磷酸在国民经济中也有着重要地位. 磷酸不仅是生产磷肥和磷酸盐的中间原料, 还被广泛应用于烘焙、饮料、洗涤剂和食品添加剂等工业和家用领域. 随着中国新能源和电子产业的发展, 磷酸作为生产新型磷材料的基础资源, 需求不断增加, 具有广阔的应用前景. 因此, 开发现有磷矿来生产磷酸已成为我国的当务之急.

工业上生产磷酸的方法主要有湿法和热法两种, 所得产品分别称为湿法磷酸和热法磷酸. 热法以黄磷为原料, 在过量空气中燃烧水合后, 得到纯度较高、杂质较少的磷酸, 提纯后可得到食品级磷酸. 但因能耗大, 生产成本高昂, 工业上很少采用此法. 湿法生产磷酸的主要原理是利用无机酸溶解矿石, 浸出溶液得到磷酸. 此法具有简单高效、环境友好等特点[1], 适用于低品位磷矿, 能耗小、污染少、成本低, 但得到酸纯度低, 需要进一步纯化才能投入使用. 据国家资源局统计, 中国磷矿以中低品位磷矿为主, 矿石 P_2O_5 平均品位仅为16.85%, 适合使用湿法处理磷矿. 湿法磷酸目前占全球磷酸总产量的85%~90%[2], 但这种方法制得的产品存在各种悬浮的、溶解的杂质和重金属离子. 因此, 湿法磷酸或来自湿法工艺的磷酸盐通常仅用于生产对磷酸纯度要求低的磷肥, 不能用于新能源和电子等对磷酸纯度要求极高的行业. 想要获取高纯度的磷酸, 就必须扩大磷酸纯化的研究工作.

目前湿法磷酸净化的方法有: 物理吸附法、化学沉淀法、溶剂萃取法、离子交换法和结晶法等.

其中, 萃取法中的溶剂萃取是目前湿法磷酸净化所使用的最广泛的方法[3], 而溶剂萃取中萃取剂的选择是该方法的关键所在[4]. 因此, 本文综述了醇类、酯类、酮类等不同种类的萃取剂和复合萃取剂对湿法磷酸的净化效果. 同时还将溶剂萃取法与双水相萃取法、反胶团萃取法、超声协助萃取法和超临界流体萃取法进行对比研究.

1 湿法磷酸中的杂质种类

湿法磷酸中的杂质大多数来自原料磷矿(PR)[5]和硫酸药剂, 少量来自生产过程中添加的药剂, 以及设备与管道的磨蚀和腐蚀[6]. 不同来源的磷矿中主要元素的含量如表1所示. 湿法磷酸中的主要杂质如表2所示.

2 萃取法

2.1 溶剂萃取

溶剂萃取法效率高、效果好[7], 是去除湿法磷酸中杂质最有效的方法[8], 也被称为溶质的两相分布, 其定义为溶质在两个相互接触的不混相液相中的分散[9], 如图1所示. 工艺流程主要由萃取、洗涤、反萃取三个基本步骤构成, 在磷酸中加入非互溶性或低互溶性的有机萃取剂进行萃取, 之后再进行洗涤操作, 此时已经脱除磷酸中的大部分阳离子和阴离子杂质, 最后用纯净水反萃得到净化后的磷酸.

2.1.1 常见萃取剂

醇类萃取剂是目前各大研究机构使用最多的溶剂[9,11], 主要有正丁醇[12]、正己醇[12]和正辛醇(NOA)[12-14]等. Amin 等[12]采用丁醇、己醇、辛醇

表 1　不同来源磷矿中主要元素的含量[5]

Table 1　Mass fraction of major elements in the phosphate rocks from various origins[5]

PR	Mass fraction of major elements/%								
	P_2O_5	CaO	Al_2O_3	F	Fe_2O_3	MgO	Na_2O	SO_3	SiO_2
PR1	29.0	53.2	0.51	3.12	0.64	1.31	1.54	3.36	2.93
PR2	28.7	53.4	0.33	3.53	0.21	0.341	0.61	1.46	8.67
PR3	30.4	57.1	0.13	3.32	0.27	0.348	0.52	2.68	1.67
PR4	29.4	48.4	0.44	3.47	0.55	1.01	1.09	2.71	2.66
PR5	31.2	55.8	0.51	4.07	2.31	0.413	0.6	2.36	5.77

表 2　湿法磷酸中的主要杂质[6]

Table 2　Main impurities in wet-process phosphoric acid[6]

Main dissolved impurities in wet phosphoric acid		Main insoluble impurities in wet phosphoric acid	
Cationic type	Anionic type	Crystalline	Colloidal type
Ca^{2+}, Mg^{2+}, Pb^{2+}, Fe^{3+}, Al^{3+}, As^{3+}, K^+, Na^+, Fe^{2+}, etc.	Cl^-, SO_4^{2-}, F^-, etc.	Undecomposed phosphate and gangue ores, sulfates, fluorides, fluorosilicates, etc.	$SiO_2 \cdot n H_2O$, acidic phosphate of iron, aluminum and potassium, acidic phosphate of iron and sodium, etc.
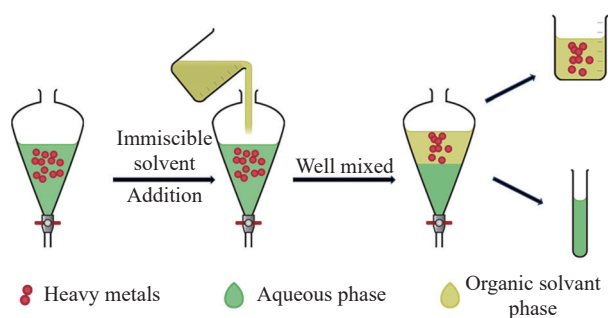
图 1　溶剂萃取原理[10]

Fig.1　Solvent extraction principle[10]

纯化商业磷酸. 在温度为 25 ℃，商业磷酸浓度为 9.2 mol·L^{-1}，丁醇、己醇、辛醇的 A/O（水相/有机相体积比）为 1∶1、1∶3、1∶5 的条件下，丁醇、己醇和辛醇的萃取率分别为 86%、94% 和 87%. 酯类萃取剂有磷酸三丁酯（TBP）、丁基-N, N-二（2-乙基己基）氨基甲酰基壬基膦酸酯（DEHCNPB）[15] 等. 为改善传统提取工艺在萃取效率、磷收率和余液利用率等方面不理想的问题，Wang 等[16] 报道了一种以 P507（乙基己基磷酸单-2-乙基己酯）为萃取剂，高效、深度去除粉煤灰硫酸浸出液中 Fe^{3+} 的可持续方法. 在最佳条件下，Fe^{3+} 的有效去除率可达 97.6% 以上. 酮类萃取剂以甲基异丁基酮（MIBK）为主. Torabi 等[17] 在不同温度（298.2、308.2、318.2 K）和相同气压（101.3 kPa）下探究 1-戊醇和 MIBK 的溶解度曲线，研究结果表明，随着温度的升高，1-戊醇和 MIBK 的萃取效果逐渐降低；MIBK 的萃取效果优于 1-戊醇，可能是因为官能团的差异，酮中的

羰基官能团比醇中的羟基官能团具有更好的分离因子，因此萃取效果更好.

其他萃取剂如二丁基亚砜（BDSO）[18] 在萃取过程中可形成萃取物 $H_3PO_4 \cdot 0.3DBSO$，对 Mg^{2+} 和 Al^{3+} 的选择性较强，对 Fe^{3+}、F$^-$和 SO_4^{2-} 的选择性适中，可用于低品位磷矿湿法磷酸的萃取. Cao 等[19−20] 研究了四元体系硝酸+硝酸钙+水+三辛胺（TOA）和五元体系硝酸+磷酸+硝酸钙+水+TOA 的萃取效率. 研究发现，相比于硝酸钙，TOA 对 HNO_3 具有更高的选择性，特别是在 HNO_3 较低浓度范围内. TOA 可以作为一种有效的溶剂从硝酸和硝酸钙的混合物中提取硝酸，也是硝酸法生产湿磷酸中提取硝酸的优良萃取剂.

2.1.2　新型萃取剂

除了一些传统萃取剂，各大研究机构也在着重研发一些新型萃取剂. 传统的酸性磷酸酯萃取剂 P204（二（2-乙基己基）磷酸酯）和 P507 的萃取性能随着水相酸度的增大而急剧下降，同时也会产生大量的盐污染废水. 为解决这一问题，Han 等[21] 基于苯环的共轭效应合成了一种耐酸磷酸苯酯萃取剂（DAP/MAP）. DAP/MAP 对 Ni^{2+}、Co^{2+} 和 Mn^{2+} 的萃取率分别为 57.58%、69.42% 和 75.70%，远大于在相同条件下，P204 和 P507 对 Ni^{2+}、Co^{2+} 和 Mn^{2+} 的萃取率. Han 等[22] 提出了一种新型萃取剂 2-（双（（2-乙基己基）氧）磷基）-2-羟基乙酸（HPOAc），可从氟吸附型稀土矿硫酸盐浸出液中选择性提取和高效富集稀土元素，结果表明它对金属离子杂质

的分离性能优于 P204、P507, 特别是对于典型杂质 Al(Ⅲ). Wang 等[23] 则研制了一种 P-15 萃取剂, 能有效去除湿法磷酸中的镁离子.

结合萃取金属的新材料, 但 da Silva 等[24] 用二-(2-乙基己基) 磷酸修饰尼龙-6 纳米纤维, 选择性提取锌和镍离子, 结果证实这种纳米纤维与传统液–液萃取的效率相等, 但大大减少了有害物质的使用. Yamada 等[25] 合成了基于硫代磷酸盐和基于磷酸盐的萃取剂 1, 3-二 (二氧基硫代磷酰氧基) 苯 (Ext 1) 和 1, 3-二 (二氧基硫代磷酰氧基) 苯 (Ext 2), 并研究了它们从 HCl 和 HNO$_3$ 体系中萃取 Pd^{2+} 的能力. Ext 1 择性地提取了 HCl 溶液中 90% ~ 99.9% 的 Pd^{2+} 和 HNO$_3$ 单金属溶液中 99.8% 的 Pd^{2+}, 而 Ext 2 在两种溶液中都无法对 Pd^{2+} 进行提取.

对于以上几种常见的萃取剂的优缺点进行总结, 如表 3 所示.

2.1.3 复合萃取剂

由于粗磷酸中杂质含量高, 组成复杂, 往往无法通过一种萃取剂完成粗磷酸的纯化, 使用复合萃取剂可以克服单一萃取剂的不足, 提高萃取效率和产品质量, 因此工业上常采用复合净化法达成净化标准. Hu 等[32] 报道了混合 Cyanex272 和 Cyanex923 萃取剂在硫酸溶液中协同萃取 Sc(Ⅲ) 的过程. 探究了 Sc(Ⅲ) 在 HCl、H$_2$SO$_4$ 和 H$_2$C$_2$O$_4$ 协同体系中的溶出性能. 得出结论, 三者的溶出性能表现为: H$_2$C$_2$O$_4$>H$_2$SO$_4$>HCl. 在低 H$_2$SO$_4$ 浓度下, Cyanex272 和 Cyanex923 对 Sc(Ⅲ) 有明显的协同萃取作用.

Jian 等[33] 分别用磺化煤油稀释 N, N-二 (1-甲基庚基) 乙酰胺 (N503)、甲基膦酸二甲庚酯 (P350) 和 TBP, 从盐酸溶液中萃取铟, 发现铟的萃取效率依次为 N503>P350>TBP. 铟与 N503 和 P350 萃取剂的配合物为 [InCl$_4$]$^-$[2S·H]$^+$; 与 TBP 形成的配合物为 [InCl$_4$]$^-$[3S·H]$^+$, 其中 S 为中性萃取剂种类. 从含有高浓度盐酸的溶液中提取铟, N503 是三者中最好的萃取剂. Zeng 等[34] 提出用 TBP 和 P507 的混合物作为萃取剂, 分离低品位白钨矿盐酸预浸液中的 Mo、W 和 Fe, 研究了不同萃取剂对 TBP 的萃取作用, 发现 P507 对 Mo 和 W 的萃取有协同作用, 对 Fe 的萃取有较强的拮抗作用. Reuna 与 Väisänen[35] 采用在煤油中稀释过的二-2-乙基己基磷酸 (DEHPA) 作为萃取剂, 从稀磷酸中提取铝, 在 pH 为 2.5、DEHPA 浓度为 0.6 mol·L^{-1}、A/O 1∶2 的条件下, 铝的萃取率可达 99%.

我国磷矿品位低, 所制得的湿法磷酸杂质含量高, 磷酸含量低. 为了提高从低浓度混合物中萃取磷酸的效率, Chen 等[36] 提出了一种由三辛癸烷基叔胺 (N235)、异戊醇和磺化煤油组成的混合溶剂, 该溶剂具有萃取量大、溶剂损失小的优点. 在低磷酸浓度下, 该混合溶剂的萃取量明显高于大多数常用溶剂, 在分离氯离子和磷酸盐离子方面具有明显的优势, 有利于后续磷肥的生产.

Banerjee 与 Sivamani[37] 建立了乳状液膜萃取废水中六价铬的动力学模型. 该团队采用含 O$_2$ 基部分的单油酸山梨醇、磷酸二辛酯 (D2EHPA) 和煤油分别作为非离子表面活性剂、载体和稀释剂制备该膜. 通过考察进料中 HCl 浓度、膜中载体浓度、溶出相 pH 值, 计算出萃取相和溶出相的速率常数. 结果表明, 由于萃取速率和溶出速率的差异, 络合扩散速率影响了膜相中 Cr(Ⅵ) 的转移和积累. Ncib 等[38] 开发了一种新型聚合物包合膜 (PIM), 用于分离铜 (Ⅱ) 和镍 (Ⅱ) 离子. PIM 由质量分数为 45% 的三乙酸纤维素、质量分数为 40% 的 D2EHPA 和质量分数为 15% 的乙酰化硫酸盐木质素组成. PIM 萃取法可萃取废液中 88% 的 Cu, 而仅萃取 25% 的 Ni, 优化后的 PIM 从合成废液中提取金属离子的顺序为 Cu^{2+}>Cr^{3+}>Ni^{2+}.

表 4 中展示了溶剂萃取法去除磷酸中杂质离

表3 各种萃取剂的优缺点

Table 3 Advantages and disadvantages of various extractants

Extractant	Advantage	Disadvantage	Reference
TBP	Insoluble in water, little impurity content	High price, high density viscosity and difficult to layer	[26]
NOA	Efficient, cheap, easy to use, separate quickly	Poor purification effect of anions, large solubility, high recovery costs, and the purification of high-concentration phosphoric acid is not thorough enough	[12]
P204, P507	Low price, high extraction rate	Poor selectivity, difficult to reflux, easy to emulsify	[27−28]
MIBK	Good selectivity, stable operation	Water-soluble, volatile and costly	[29]
N235 (trioctyl tertiary amine)	High extraction rate, mature technology, good selectivity	Volatile, flammable and explosive, susceptible to impurity ions	[30−31]

表 4　溶剂萃取法去除磷酸中杂质离子的效果对比

Table 4　Comparison of solvent extraction methods for removing impurity ions from phosphoric acid

Extracted elements	Extractant(volume fraction)	O/A ratio	Extraction efficiency/%	Reference
Fe	12.5%TBP + 87.5%Kerosene	1∶1	100	[39]
	50%P204 + 50%Monoalkyl phosphate	2∶1	91	[40]
	15%TBP + 5%D2EHPA + 80%Kerosene	1∶1	99	[41]
	10%P507 + 20%N235 + 70%Sulfonated kerosene	1∶1	89.4	[42]
H_3PO_4	70%TBP + 30%Isopropyl ether	4∶1	76.9	[43]
	80%TBP + 20%Kerosene	2∶1	83	[44]
	80%TBP + 20%Sulfonated kerosene	6∶1	70	[45]
I	Kerosene	1∶2	99.25	[46]
	Simethicone	3∶1	99	[47]
U	N-propylpropan-1-amine + Kerosene	1∶1	95.3	[48]
	30%TBP + 70%Kerosene	1.5∶1	96.67	[49]
Zn	30%TOA + 20%Iso-octanol + 50%Sulfonated kerosene	2∶1	83.75	[50]
	15%TBP + 5%D2EHPA + 80%Kerosene	1∶1	80	[41]
In	33.33%Ionic liquids + 16.67%P204 + 50%TBP	1∶3	98.11	[51]
	30%D2EHPA + 70%Kerosene	1∶5	98.5	[52]
Sc	P204	1∶3	95	[53]
	10%P204 + 5%TBP + 85%Sulfonated kerosene	1∶10	99	[54]
F	70%TBP + 30%Silicon oil	1∶5	98.4	[55]
Cl	30%N235 + 20%Isooctanol + 50%Sulfonated kerosene	2∶1	78.9	[56]
P_2O_5	90% N-butanol + 10%Isopropyl ether	5∶1	90	[57]
Li	40%TBP + 20%Ethyl butyrate + 40%Kerosene	2∶1	87.12	[58]
Co	30%N235 + 70%Kerosene	2∶1	99.997	[59]
Mg	20%TBP + 80%NOA	1∶1	72.11	[60]
Cu	30%MIBK + 70%TBP	1∶1	99	[61]

子的效果对比情况.

2.2　双水相萃取

　　双水相萃取（ATPE）是一种液–液分离技术，双水相体系（ATPS）指高聚物之间、高聚物与无机盐、正负离子表面活性剂等在水中溶解后形成的互不相溶的两相体系[62]. 聚乙二醇是 ATPE 中使用最广泛的聚合物组分之一，因为它们价格低廉，储量丰富，无毒，可生物降解且对环境安全[63]. Falcon-Millan 等[64]利用聚乙二醇/Na_2SO_4 水两相体系，从水溶液中提取磷酸到富聚合物相. 磷酸 ATPS 萃取示意图如图 2 所示. 实验结果表明大约 75% 的负载 H_3PO_4 有可能转移到富聚合物相，首次证明了 ATPS 在绿色磷酸净化过程中的可能应用.

　　为了阐明物种转移到水两相体系的富聚合物相的分子机制，Falcon-Millan 等[65]采用 ATPS 系统对 H_3PO_4 进行萃取，利用拉曼光谱法和分子动力

○　Polyethylene glycol 1000 g·mol^{-1}

Phosphorie acid

■　Impurities

Sodium sulfate (Na_2SO_4)
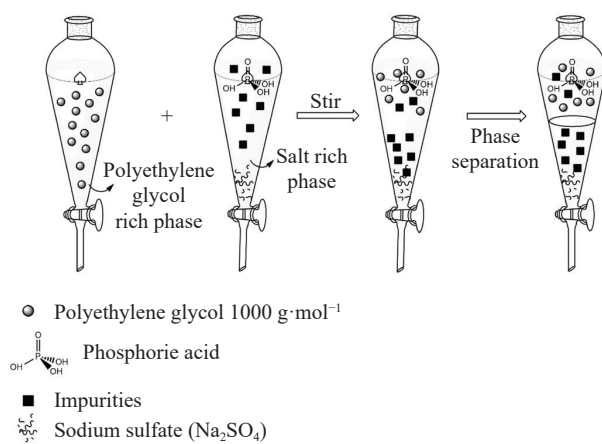
图 2　磷酸 ATPS 萃取示意图[64]

Fig.2　Phosphoric acid extraction diagram using ATPS[64]

学模拟阐明聚乙二醇和磷酸在水两相体系中萃取磷酸的关键相互作用，提出了一种由氢键相互作用控制的溶剂化机制：在富含聚合物的水溶液中，

当 H_3PO_4 浓度较低时，磷酸分子与聚乙二醇的相互作用较弱；当磷酸浓度增加到一定临界值以上时，聚乙二醇分子通过氢键与 H_3PO_4 分子发生强烈的相互作用. Sun 等[66]则证明了 ATPS 中 Cr(Ⅵ)离子进入富含聚乙二醇相的驱动力为疏水作用，拓宽了 ATPS 中离子分配性质的解释.

2.3　反胶团萃取

反胶团萃取（Reverse micelles extraction），又称为反胶束萃取，最早用于生物产品的萃取，近些年来，也被活跃用于溶液中金属的萃取[67]. 在水溶液的胶束中，表面活性剂的排列方向是极性基团在外侧与水接触，非极性基团向内形成一个非极性核，此时胶束被称为正胶束；而在有机溶剂中，表面活性剂的极性基团朝胶束内形成一个极性核，此时胶束被称为反胶束. 亲水物质进入吸水极性核，达到分离目的. Bley 等[68]引入了一种预测模型，该模型用于描述溶剂萃取中反胶束增溶水的现象，能够更准确地了解和控制溶剂萃取中液相之间的反胶束效应，为提高核废料管理和湿法冶金回收效率提供了有力的工具.

二壬基萘磺酸（DNNSA 或 HD）常被用于反胶团萃取湿法磷酸中的金属离子，如铁离子[69]、镁离子等. 其中，在 DNNSA 萃取湿法磷酸溶液中 Mg^{2+} 的过程中，Mg^{2+} 可与反胶团发生化学反应，形成萃合物 $MD_2·6HD$，加快萃取进程[70]. Luo 等[71]探究了负载有机相中的反胶束的形态和物理化学特性对相分离行为的影响，结果表明：影响相分离行为的最有效的参数是负载有机相的黏度和过量吸水率. Dong 等[72]报道了季磷型离子液体萃取剂 $[P_{6,6,6,14}]$[EHEHP] 和 $[P_{6,6,6,14}]$[BTMPP] 在甲苯中协同萃取稀土的首次研究，揭示了反胶束在稀土元素分离和回收中的优势. $[P_{6,6,6,14}]$[EHEHP] 和 $[P_{6,6,6,14}]$[BTMPP] 形成的反向胶束示意图如图 3 所示.

2.4　超声协助萃取

超声协助萃取（UAE）是利用超声波特有的辐射效应作为辅助效果，从而加速被萃取物质进入萃取溶剂里的一种成熟的新型萃取方法. 在工业生产磷酸过程中，往往常规的净化萃取手段存在速率慢、时间长、萃取用量大、仪器设备复杂等问题. 但 UAE 技术凭借其独特的超声空化效应、热效应以及机械效应，展现出了效率高、速度快、萃取化学结构稳定等优点[73]. 图 4 展示了超声空化过程.

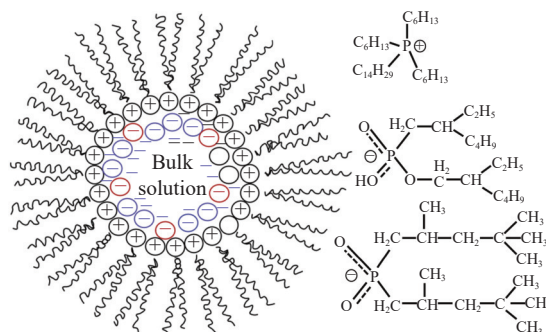Preethi 等[75]对比了常规分散液–液微萃取，温控分散液–液微萃取和超声辅助分散液–液微萃取方法在萃取过程中萃取条件对萃取回收率的影响.

图 3　$[P_{6,6,6,14}]$[EHEHP] 和 $[P_{6,6,6,14}]$[BTMPP] 形成的反向胶束示意图[72]

Fig.3　Schematic of the reverse micelle formed by $[P_{6,6,6,14}]$[EHEHP] and $[P_{6,6,6,14}]$[BTMPP][72]
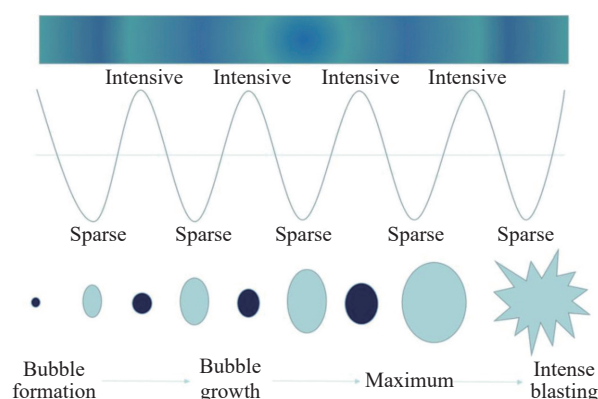
图 4　超声空化过程示意图[74]

Fig.4　Schematic diagram of the ultrasonic cavitation process[74]

在这三种方法中，超声波辅助分散液–液微萃取方法获得了最大的萃取回收率. Zhang 等[76]在萃取酸洗废液中的锌时，预处理阶段使用超声强化还原 Fe^{3+}，大大缩短了处理时间. Xia 等[77]合成了新型萃取剂 PN-1 萃取湿法磷酸中的 Mg，建立了超声辅助微通道萃取系统，发现超声功率为 74 W、O/A 比为 4、水相流速为 0.2 mL·min^{-1} 时，Mg^{2+} 的提取率可达 89.09%.

2.5　超临界流体萃取

研究发现，当温度和压力超过临界点时，物质不再具有明确的液态或气态，而是处于一种介于液、气态之间的超临界状态. 而超临界流体萃取（SFE）正是利用了物质在超临界条件下的特殊性质的一种分离和提取化合物的新型萃取技术. 在这个过程中，通常使用二氧化碳作为超临界流体实现萃取分离. 超临界流体萃取流程图如图 5 所示.

如今，SFE 已被创新性地运用于湿法磷酸的净化技术中，其高选择性、条件温和、绿色环保、效率高等优点引起了广泛关注. 采用含有 TBP、D2EHPA 及其加合物的二氧化碳与 HNO_3 进行超临界流体
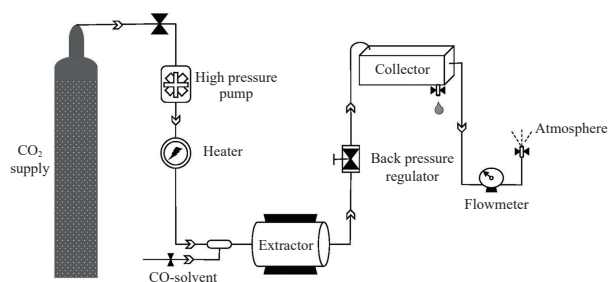
图 5　超临界流体萃取之流程图[78]

Fig.5　Flow diagram of the supercritical fluid extraction[78]

萃取, 从单氮石精矿和磷石膏中萃取稀土金属、钍和铀, SFE 方法可显著提高萃取的效率, 增大被萃取物的成分含量[79]. 影响 SFE 效率的关键因素是螯合剂及相应金属螯合剂的溶解度, Ding 等[80] 通过典型实例说明了主要使用的螯合剂的萃取机理, 详细介绍了原位螯合和在线螯合两种主要的络合方法. 尽管 SFE 作为一种新型的绿色萃取技术, 已被广泛应用于多种金属的萃取, 但 SFE 特殊的高压条件带来的成本高、操作要求高、环境要求高的缺点也十分明显, 这也是今后需要研究解决的关键问题之一[81].

表 5 对以上五种磷酸的萃取方法进行了对比.

3　国内外应用情况

湿法磷酸净化技术长久以来就是磷酸制备工艺的一大技术难点, 国外早在 1914 年就开始探索净化湿法磷酸, 并在 20 世纪七八十年代迅速发展出成套食品级磷酸净化技术, 基本可以应付各类磷矿的复杂工况[88], 但这些技术一直对外保密. 目前, 国际上投入工业性生产的湿法磷酸净化流程主要有: 巴登化学法、奥布拉威尔森法 (A&W)、以色列矿业公司法 (IMI)、Rhone-Poulenc 法和比利

时 Prayon 法等[89]. 其中规模最大、产品质量最稳定的有: 巴登化学法、A&W 法和 Rhone-Poulenc 法. 国内溶剂萃取湿法磷酸技术研究起步较晚, 但经过四十年的发展, 我国溶剂萃取净化湿法磷酸技术已成功研制并打破了国外技术垄断[90]. 溶剂萃取法的国内外应用情况如表 6 所示. 目前国内有多家企业和机构在开展湿法磷酸纯化研究, 在实际生产中取得应用的主要有瓮福集团技术、四川大学技术和华中师范大学技术. 其中, 瓮福集团在2006 年引进以色列 IMI 技术, 在此基础上进行自主研发, 2010 年开始湿法磷酸净化的工业化, 并与多家化工企业达成合作. 四川大学技术和华中师范大学技术则为国产化技术, 工艺不完备, 仍有需要完善的地方. 截至 2018 年, 国内净化湿法磷酸产能已接近 10^6 t·a^{-1}.

4　磷酸的溶剂萃取法的前景展望

磷酸一直都是我国重要的化工原料. 生产磷酸的方法大致分为湿法和热法, 但鉴于热法磷酸所需能耗大, 对环境污染大, 且我国磷矿多为中低品位磷矿, 湿法磷酸将成为生产磷酸的大趋势. 因湿法磷酸产品杂质含量大, 所以开发磷酸纯化技术迫在眉睫. 在众多纯化技术中萃取法以其操作简单、绿色环保、成本低廉等优点脱颖而出. 但我国湿法磷酸净化技术研究相较于国外起步较晚, 近四十年来, 我国一直在探索净化湿法磷酸的工艺, 国内高校和磷化工公司经过多年相关研究, 已经初步掌握了湿法磷酸的净化方法.

本文介绍了湿法磷酸萃取纯化技术, 综述了溶剂萃取法、双水相萃取法、反胶团萃取法、超声波萃取法、超临界萃取法的优缺点及其应用, 并对

表 5　磷酸主要萃取方法对比

Table 5　Comparison of the main extraction methods of phosphoric acid

Method	Advantage	Disadvantage	Reference
Solvent extraction	Simple process flow, good selectivity, continuous operation, large production capacity, and high separation efficiency	Large amounts of organic solvents	[82]
ATPE	Environmentally friendly, excellent separation efficiency, high product yield, short phase splitting time	The reverse extraction is difficult, the separation of the target compounds is difficult, and the extraction process is unstable	[62−63, 83]
Reverse micelle extraction	Selective separation and extraction, stable extraction system, mild conditions, flexibility and controllability, energy saving, efficient extraction, and the molecular structure of the compound can be retained during the extraction process	Poor phase separation	[71, 84−85]
UAE	High efficiency, fast speed, stable extraction of chemical structure	High energy consumption, large-scale equipment, high cost, and the thermal effect is relatively weak	[80, 86]
SFE	Can replace organic solvents and reduce the risk of reaction, moderate critical point, inert, non-toxic, non-flammable, low price, easy to recycle, combined with the high diffusion of gas and good solubility of liquid, almost no secondary waste, and the product is easy to recover	High equipment cost, complex operation, and poor sample versatility	[73−74, 87]

表6 溶剂萃取法国内外应用情况[89, 91−94]

Table 6 Application of solvent extraction methods at home and abroad[89, 91−94]

Technology	Extractant	Final product (mass fraction of phosphoric acid)	Grade	Remark
Weng fu	MIBK	85% Industrial phosphoric acid	Food grade	The domestic scale is about 450000 t·a^{-1}
Sichuan University	Mixed solvents (TBP, N-butanol, Isoamyl alcohol, etc.)	75% Phosphoric acid	Industrial grade	The domestic scale is about 210000 t·a^{-1}
Central China Normal University	Central China Normal University's patented synergistic extractant	85% Industrial phosphoric acid	Industrial grade	The domestic scale is about 60000 t·a^{-1}
A&W	MIBK	75%–85% Phosphoric acid	Food grade	The sulfate content of the product is high
Rhone-Poulenc	TBP	60% Food grade phosphoric acid	Food grade	—
IMI	85%(volume fraction) Isopropyl ether + 15% N-butanol (or Isopropyl ether)	—	Feed grade	The sulfate content of the product is high
Prayon	Isopropyl ether + TBP	—	Industrial grade or Food grade	The fluorine content of the product is high
Iprochim/Icechim	N-butanol	—	Industrial grade	The sulfate content of the product is high
Budenheim	Isopropyl ether	75% Industrial phosphoric acid	Industrial grade	Followed by H-type cation exchange resin after extraction

不同萃取剂进行了比较. 未来磷酸的净化呈现出多种净化技术并存的态势, 为此, 本文对湿法磷酸净化技术未来的发展方向提出了如下的前景展望：

（1）溶剂萃取法的研究主要集中在萃取剂上, 当前单一萃取剂主要有 TBP 和 MIBK 等, 主要探究萃取过程中温度、相比、搅拌时间、离子分配比等的最佳条件. 但单一萃取剂往往无法满足多种离子的萃取纯化, 未来溶剂萃取将主要集中在复合萃取剂的研发上. 复合萃取剂结合多种萃取剂, 可通过实验探究最佳分配比, 大大提高萃取效率. 同时, 多种技术耦合高效集成实现磷酸的净化是大势所趋. 开发新型萃取剂, 研究新型萃取方法, 使萃取剂和各种材料结合, 实现湿法磷酸萃取的绿色化和高效化需求.

（2）双水相萃取和反胶团萃取最大的特点就是绿色环保, 操作简单. 二者最初都应用于生物提取上, 但近些年关于离子萃取上的研究也逐渐增多, 这些主要集中于处理重金属离子等有害物质. 双水相萃取的研究主要集中在探索新的双水相体系. 二者在离子提纯方面仍然处于探索阶段, 其应用范围和效果还有待进一步验证和完善.

（3）超声协助萃取重点在"协助", 利用超声波技术辅助, 可加快萃取进程, 具有极大的应用前景. 超临界流体萃取技术的萃取效率高, 对环境污染小, 但一方面, 超临界流体对大部分离子的溶解度较低, 需要进一步研究如何提高离子的溶解度和萃取效率. 另一方面, 超临界流体萃取技术的成本

较高, 需要进一步降低成本才能在实际中得到更广泛的应用. 预测超临界流体萃取技术将来会和其他技术结合, 应用于特定领域.

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