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Research and development trends of hydrometallurgy: An overview based on *Hydrometallurgy* literature from 1975 to 2019

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Abstract: Modern hydrometallurgy has been developing for more than 100 years and the related articles keep piling up. Based on a bibliometric analysis of the articles in *Hydrometallurgy*, the most authoritative journal in the field of hydrometallurgy, we try to catch the research and development trends from a global perspective. Firstly, keywords burstness shows that rare earth, recycling, lithium, ionic liquid, and thorium are the hotspots in recent years, and the economic and technological reasons behind them were discussed in depth. Secondly, the proportion of biohydrometallurgy grows fast from 5% to 13% and the related articles are almost all about bioleaching. There are some new directions such as direct preparation of materials in hydrometallurgical processes and ion-imprinted techniques. Thirdly, the advanced instrument analysis methods such as XAFS (X-ray absorption fine structure), gene sequencing, and micro-CT promote the deep understanding of hydrometallurgy mechanism. Finally, the cooperation network and contribution of the main institutes were mapped.

Key words: development trends; leaching; solvent extraction; biohydrometallurgy; electro-hydrometallurgy; CiteSpace

1 Introduction

The history of hydrometallurgy may be traced back to the period of alchemists. In China, it can be traced back to the Western Han Dynasty in 200 AD, when there were records about cementation of copper by iron from copper sulfate solution [1]. Modern hydrometallurgy began with two important processes at the end of the 19th century: the Bayer process for alumina and the MacArthur–Forrest process for gold [2]. Later, owing to the development of the nuclear industry during the Second World War, solvent extraction and ion exchange were developed sharply. In the 1950s, the pressure leaching method was developed to treat sulfide ores. Furthermore, electrochemistry and microbiological technology continued to inject vitality into hydrometallurgy. Now, with the decline of ore grade and increasingly strict environmental protection wants, the wet process plays a more and more important role in producing nonferrous metals, and the challenges it faces are increasing too. In this work, we hope to make statistical analysis of the most authoritative journal *Hydrometallurgy*, to find out the changes of research contents and methods, the current hotspots, and the world pattern of hydrometallurgy.

Why did we choose the *Hydrometallurgy* journal to analyze the research and development trends of hydrometallurgy? In 1975, Gordon Ritcey from CANMET (the Canada Centre for Mineral and Energy Technology) and Neville Rice from the University of Leeds founded *Hydrometallurgy*,

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which belongs to the Elsevier group. Their original aim was to launch a multidisciplinary journal that drew upon chemistry, engineering, mineralogy, economic and environmental principles and brought together papers that focused on the fundamentals and application of hydrometallurgical processes that would otherwise be scattered among various journals or conference proceedings with limited circulation [3]. At that time, *Hydrometallurgy* was a relatively young discipline with focus on the pressure leaching of sulfides, the extraction of uranium, solvent extraction of base metals, rare earth metals and so on, bacterial leaching and chloride process, and the treatment of the three wastes (waste gas, wastewater, and industrial residue) [3,4]. Meanwhile, the *Hydrometallurgy* journal ranks 8/76 in the area of metallurgy and metallurgical engineering. Considering that the first 7 journals are prone to material researches, it is the most influential journal in the field of hydrometallurgy.

It has been 45 years since the first issue of Hydrometallurgy. By the end of 2019, the ScienceDirect gathered more than 4500 articles. There are so many papers, how can we analyze them? With the rapid development of science and technology, the articles in many areas, such as biology, medicine, and computer, are increasing rapidly. It is difficult for researchers to keep collecting, arranging, and analyzing the information through reading. Scientists hope to rely on computer aids to solve this problem [5,6]. The scientific knowledge map originated from a seminar organized by the National Academy of Sciences of the United States in 2003, is a good way. It aims at analyzing, structuring, and visualizing the big data of the literature for easy understanding, with the help of computer technology. There are many science mapping analysis tools, such as Sci2, SciMAT, VOSviewer, and CiteSpace. Using one of the knowledge tools, CiteSpace, we hope to catch the development trends of hydrometallurgy from the articles.

2 Methods and data

2.1 Methods

CiteSpace, developed by CHEN [7] in 2006, is a Java program and it is powerful for literature analyzing and visualizing in bibliometrics. The software integrates many programs to achieve works including text mining, network pruning, clustering and naming, and burstness detection. The processing results can be visualized in the form of knowledge maps [8]. The basic items of a map include nodes, connections, and colors. A node represents a keyword, an author, an institute, or a reference. The connections of the nodes show the co-citations of references, co-occurrences of keywords, or cooperation of authors or institutes. The radius of a node represents the times and the gradual colors represent the period, blue earlier and orange later. The purple outer rings represent the centrality.

2.2 Data

The bibliographic data of *Hydrometallurgy* was collected from Scopus and Web of Science (WOS) with a period of 45 years (1975–2019). There are 4694 records in Scopus (excluding the reviews), and 4445 in WOS. Through the analysis and comparison of the data, we find that the information before 1997 is incomplete, losing a large number of author keywords and references. The earlier data of Scopus are relatively complete. The data of the two databases after 1998 are almost the same. Scopus can provide independent retrievals for the abstracts and author keywords, so the retrieval based on Scopus is more flexible and accurate.

3 Results

The number of articles and the total cited times of *Hydrometallurgy* each year are shown in Fig. 1. The number of articles has two leaps from 1975 to 2019, 50 articles average each year before 1992 to 100 articles from 1992 to 2010, and 175 articles after 2010. It can be seen from the total cited times that the influence of the journal has been significantly promoted. Time lag leads to a decline after 2010. The statistical data from WOS shows that the impact factor of *Hydrometallurgy* rises from 0.575 in 1997 to 3.465 in 2018. Locating in Q1 (the first quartile) in the area of metallurgy and metallurgical engineering and ranking 8/76, *Hydrometallurgy* is the most influential journal in the field of hydrometallurgy.



Fig. 1 Yearly distribution of articles and total cited times (1975–2019)

3.1 Thematic trends

First of all, thematic trends are identified in the way of burst keywords (measured by the frequency change of the keywords) as shown in Table 1. "Strength" based on a statistical formula, is used to measure the burstness of keywords.

Uranium has two main uses, that is, nuclear

weapons, and nuclear power. Correspondingly, there are two epochs: immediately after the end of the Second World War, through the early 1970s, uranium was largely used for defense purposes; from the middle 1970s forward, uranium was largely used as an input into electricity production, with nuclear power reactors. With the large-scale application of nuclear power, the price of U₃O₈ soared rapidly (from less than 44 US\$/kg to nearly 132 US\$/kg) until the reactor at Three Mile Island suffered a partial meltdown in March of 1979. Almost overnight, the interest in nuclear energy in the U.S. waned; the demand for uranium collapsed, along with the price of the resource, and plans to build new plants were put on hold [9]. The revival of nuclear power in recent years has been mainly due to the growing demands for energy in developing countries represented by China (There are presently 19 nuclear reactors under construction in China [10]) and concerns about climate change. Certainly, the two booms led to two upsurges in uranium extraction research.

From 1987 to 1992, adsorption and carbon become hot keywords. This reflects the activated

Table 1 Thematic trends based on keywords burstness (The red line indicates that the keywords appeared more frequently in that year)

Keywords	Strength	Timespan		
Uranium	6.6067	1975	1997*	
Adsorption	5.6754	1975	1997*	
Carbon	5.2988	1975	1997*	
Biosorption	6.3259	1998	2019	
Heavy metal	5.2761	1998	2019	
Indium	4.6150	1998	2019	
Recycling	5.2679	1998	2019	
Rare earth	13.845	1998	2019	
Thorium	4.9042	1998	2019	
Uranium	4.1215	1998	2019	
Lithium	4.1873	1998	2019	
Ionic liquid	4.0219	1998	2019	

^{*}Due to the missing of keywords before 1998, the burstness detection was based on the phrases extracted from the titles

carbon adsorption process in the 1980s which is a milestone for gold extraction. The gold extraction at that time reached a climax and there are economic reasons behind it. Gold can be traded freely in 1967 and the price was 1.23 US\$/g. Later, because of inflation and economic recession, people lose confidence in the financial system, therefore, gold was favored. The price of gold underwent the first big leap in history, from less than 1.76 US\$/g in the early 1970s to 14.11 US\$/g in the 1980s, with a peak of over 21.16 US\$/g [11].

From 2002 to 2005, "biosorption" and "heavy metal" become hot keywords. This reflects a research upsurge about biological adsorption of heavy metals from wastewater. The biomass used for adsorption includes bacteria, algae, plant residue, and so on. The heavy metals are mainly copper, lead, cadmium, and chromium. The search results from WOS show that the articles on biosorption and heavy metals have been continuously increasing since then. Therefore, our results do not reflect the research trends. This is because there are more excellent journals to choose for this type of article, such as *Bioresource* Technology, Chemical Engineering Journal, and Water Research.

Recycling related papers are all about metal resource recycling. With the industrialization of developing countries, the demand for base metals is steadily increasing, and the intelligent manufacturing and green manufacturing need more and more special rare metals like lithium and rare earth. The imbalance between supply and demand leads to price growth, which inevitably makes the unprofitable recycling industry more and more profitable. As the European Commission report on critical raw materials and the circular economy said, a few materials have a good rate of recycling at end-of-life (e.g. recycling rate for PGMs reaches up to 95% for industrial catalysts and 50%-60% for automotive catalysts) [12]. As a matter of course, recycling research will become hotter and hotter.

From 2003 to 2006, the price of indium increased from 100 U\$/kg to a peak of 1000 U\$\$/kg, which drove the research hotspot later. However, when the price began their climb to over 1000 U\$\$/kg the improvement and scale-up of ITO (indium tin oxide) recycling techniques became a priority to ITO target manufacturers serving the LCD (liquid crystal display) industry [13]. The ITO recycling capacity in Japan and Korea together with the economic crisis of 2008 dropped the price of indium to 400 US\$/kg which cooled the research on indium. What's more, the articles often lag behind research for 2–5 years. So we can see that there are more articles on "indium" in 2010 and 2011.

The most obvious hotspot in recent years has been rare earth. Because of the excessive exploitation of rare earth and environmental deterioration, the government of China controlled the exploitation and export of rare earth, which had caused the rare earth crisis in the years 2010–2012. Then, the rising price of rare earth attracted a huge amount of capital. Statistic data showed that the capital inflows of 28 rare-earth-related Junior Mining Companies had risen to 1.09×10¹⁰ US\$ (2010, 2011) and 2.06×10¹⁰ US\$ (2012) from about 1×10⁹ US\$ before 2010 [14,15]. Undoubtedly, some of these capitals flowed to and promoted the research of rare earth extraction. For thorium, on one hand, it is commonly associated with the rare earth elements in different minerals. The separation of thorium from rare earth is one of the most important tasks for the REE process. Meanwhile, there are a large amount of leaching residues of the ion-absorbed-rare-earth ores in the south of China, which enrich radioactive elements like thorium and uranium. And the radioactive pollution promotes the extraction and separation of thorium and uranium [16]. So, the growing of articles on thorium is largely due to the increase of rare earth researches. On the other hand, thorium has been a potential nuclear fuel that can make up the shortage of uranium resources. All these lead to the booming of thorium extraction and separation.

For lithium, as we all know, it is the rapidly increasing demand for batteries to power electric cars, laptops, and other high-tech devices that promote the research of lithium. More than half of the researches are about lithium extraction from salt lake brine, and the rest from seawater and lepidolite. Moreover, the recycling of spent lithium batteries is getting hot.

The first article about keywords ionic liquids in *Hydrometallurgy* appeared in 2006 for palladium extraction from nitric acid [17], and the number increased to 14 documents in 2017. Recent researches have focused on the separation of rare earth, precious metals, copper, and lithium [18–27]. Ionic liquids as "green solvents" in green chemistry show great potential in the separation processes. It has the potential to solve the problems caused by traditional solvent extraction such as Na^+ or NH_4^+ -containing wastewater, lower separation factor, and complicated process.

To sum up, the research hotspots can be roughly divided into two categories. One is ionic liquids and biosorption, which is brought about by environmental protection requirements. The other is uranium, lithium, rare earth, indium, and so on, which is due to the imbalance between supply and demand. Through the above analysis, we can conclude that the drastic price changes in the metal market could affect the direction of academic research. And the output of academic achievements usually takes two years or more, so it is very important to find out the metals which are sensitive to the international market and to make technology reserves in advance to ensure the healthy operation of the economy. The EU, the US, and Australia all have a list of key materials calculated based on supply risk and economic importance. Figure 2 shows the critical raw materials (CRMs) of Europe in 2017, which did not change much compared with previous years [28,29]. To some extent, it applies to most countries and represents global trends. As shown in Fig. 2, the closer the metal is to the upper right like rare earth, magnesium, and antimony, the more indispensable it is, the greater the risk of supply, the more volatile its price is, and it is easier to become a future research hotspot, which should be paid more attention. With the increase of the exploitation cost of traditional mineral resources and the gradual increase of the scale of urban mines, the study of resource recycling will gradually become the mainstream.

3.2 Content analysis

In the last section, the hot spots of hydrometallurgy in different periods since 1975 are excavated and the causes are discussed. In this section, the main contents of hydrometallurgy are analyzed, and the main plates (leaching, solvent extraction, biohydrometallurgy, electrohydrometallurgy) are analyzed in detail by the methods of reference co-citation, clustering and keywords co-occurrence.

Based on the text mining of topics and term frequency, it can be concluded that the contents of *Hydrometallurgy* mainly include leaching, solvent

extraction, biohydrometallurgy, electrohydrometallurgy, ion exchange, precipitation, adsorption, and cementation. The relative proportion of each period is shown in Fig. 3. There are two obvious changes. First, the proportion of solvent extraction research has decreased from 31% in the early stage to 19% in recent ten years. Taking the increase of the total articles as shown in Fig. 1 into account, the number of articles related to solvent extraction is increased steadily. Second, the proportion of biohydrometallurgy has increased from 5% in the early stage to 13% recently. The proportion decrease of solvent extraction is due to the early upsurge of solvent extraction research and the



Fig. 2 Critical raw materials (gray area) according to report of European Commission in 2017 [29]



Fig. 3 Relative proportion change of content (1975–2019) of *Hydrometallurgy*

diversification of researches nowadays. While the proportion increase of biohydrometallurgy is attributed to the more and more attention paid to biohydrometallurgy from the academic community for its cleaner and lower-cost process (especially for low-grade sulfide ore), regularly holding of International Biohydrometallurgy Symposium and the occasional publication of special issues.

Next, we try to catch the main contents of the major plates (leaching, solvent extraction, biohydrometallurgy, electro-hydrometallurgy) by reference and keywords analysis. Reference analysis is the most important approach for bibliometrics, which can reflect the framework and evolution of knowledge. References co-citation network and the cluster of leaching and electro-hydrometallurgy are given as shown in Figs. 4 and 5, respectively. The figures contain three elements: points, lines, and frames. Points represent references, links indicate that they are cited by the same article, and if the articles have similar topics they are clustered into a black frame. The clusters are sorted by the number of nodes in each cluster.

For leaching, the references cited most



Fig. 4 Co-citation network and cluster of leaching related references (Timespan: 1998–2019, slice length=2, *g*-index=6, *LRF*=-1, *LBY*=-1, *e*=2, *N*=171, *E*=355)



Fig. 5 Co-citation network and cluster of electrochemistry related references (Timespan: 1998–2019, slice length=2, *c/cc/ccv*:2/2/20, *LRF*=–1, *LBY*=–1, *e*=2, *N*=286, *E*=1637)

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frequently are about laterite nickel ore, gold and silver, copper ore (mainly chalcopyrite), and zinc ore. Words frequency statistics shows that the most frequent elements are iron (124 articles), copper (120 articles), gold (82 articles), zinc (80 articles), silver (56 articles), and nickel (56 articles), and the most frequent mineral is chalcopyrite. To sum up, precious metals and base metals including copper, nickel, and zinc are the main research objects for leaching. Manganese ore, ilmenite, lithium, mechanical activation, and microwave-assisted leaching also appear in the cluster. We notice that X-ray tomography is an emerging method to study the mechanism of heap leaching (Detailed discussion in instrument analysis below). Keywords Kinetics occurs up to 176 times in leaching. Compared with the pyrometallurgy, the biggest difficulty of hydrometallurgy is that the leaching reaction rate is lower due to the relatively low operating temperature. Therefore, the key direction is kinetics research and leaching strengthening. And the most frequent reference about kinetics is the famous book Chemical Reaction Engineering [30].

For electro-hydrometallurgy related articles, the cited reference groups are mainly about the electrochemical research of zinc electrowinning, electrochemical oxidation of chalcopyrite, and electrochemical properties of chalcopyrite, pyrite, gold-bearing minerals, and their leaching solution. In addition, there are many studies on lead-based electrodes for electro-winning. In recent years, recovering valuable metals such as copper, gold, and zinc from waste printed circuit boards and waste batteries by electro-assisted leaching and/or electrodeposition in a single-cell process has been a research hotspot as shown in Fig. 5 (#5) [31–33].

The reference clustering results of solvent extraction and biohydrometallurgy are bad, from which we cannot draw any useful conclusions. So, the co-occurrence analysis of keywords was made as shown in Figs. 6 and 7. The high-frequency keywords for solvent extraction include D2EHPA, nickel, zinc, cobalt, copper, stripping, cyanex272, cyanex923, TBP, and rare earth. As it is, although there are hundreds of extractants, the most studied extractants are D2EHPA, cyanex series, and TBP. Other separation technologies related to solvent extraction include ionic liquids (ILs), emulsion liquid membrane (ELM), and supported liquid membrane (SLM). Ionic liquids and rare earth coexist frequently as shown in Fig. 6. About one-third of the articles on ionic liquids are about



Fig. 6 Co-occurrence network of solvent extraction related keywords (Timespan: 1998–2019, slice length=2, *g*-index=8, *LRF*=-1, *LBY*=-1, *e*=2, *N*=130, *E*=183)



Fig. 7 Co-occurrence network of biohydrometallurgy related keywords (Timespan: 1998–2019, slice length=2, *g*-index=8, *LRF*=-1, *LBY*=-1, *e*=2, *N*=137, *E*=175)

rare earth extraction. Compared with traditional volatile organic solvents, ionic liquids have many obvious advantages. First of all, it is known that the number of ILs is far more than that of conventional organic solvents, which can be as high as 10^{18} . So, it is obvious that ILs provide us more choices. What's more, the distinctive properties such as viscosity, conductivity, hydrophilicity, hydrophobicity, polarity, and hydrogen bond ability are extraordinarily tunable, relying on the selection of appropriate anion and cation [34]. So, there is a promising future for ILs in hydrometallurgy [35-37]. The liquid membrane separation, including support liquid membrane and non-support liquid membrane (mainly ELM), is an improved technology in the use of the solvent extractant by making the extraction and stripping run simultaneously which removes the balance limit of the reaction. Figure 8 shows schematic diagrams of the two types of liquid membrane. In Fig. 8(a), if the SLM is replaced by ionic liquids, it can be called a supported ionic liquid membrane (SILM).

Biohydrometallurgy mainly includes bioleaching, bioremediation, and bio-beneficiation. It can be seen from the keywords co-occurrence network (Fig. 7) that bioleaching accounts for the overwhelming majority. It can be seen from the co-occurrence relationship that bioleaching mainly deals with chalcopyrite, and the bacteria mainly



Fig. 8 Schematic diagrams of supported liquid membrane (a) and emulsion liquid membrane (b)

used are Thiobacillus ferrooxidans. Biosorption and heavy metals have high co-occurrence. It is mainly about biomass adsorbed and removed heavy metals from solution, classified as bioremediation. Bacteria commonly used in biometallurgy include Thiobacillus ferrooxidans, Sulfolobus metallicus, Leptospirillum ferriphilum, Thiobacillus thiooxidans, and Thiobacillus thermophilus. Among them, Thiobacillus ferrooxidans is one of the most important and widely used bacteria in the bioleaching process. And the modern era of bioleaching began with the discovery of the bacterium, Thiobacillus ferrooxidans (now Acidithiobacillus ferrooxidans) in the mid-1940s and in 1958 Kennecott Mining Company patented the use of Thiobacillus ferrooxidans for copper extraction [38]. Through cooperation of CSU (China) with TIGR (USA), the sequence information of 3217 genes of the bacteria Acidithiobacillus ferrooxidance was revealed in 2004 [39]. In 2007, functional gene arrays (FGAs) method was first used in biohydrometallurgy, which can detect and analyze the population structure, community dynamics and functional activity of microorganism in biomining in a rapid, accurate and high-throughput manner [40]. This technology realized the fundamental transformation from phenotype to genotype in the screening of highefficiency bacterial strains.

In addition to the above contents, there are many new research directions in hydrometallurgy such as direct preparation of materials in hydrometallurgical processes, and ion-imprinted polymer technology.

As far as we know, direct preparation of materials during the hydrometallurgy process is a promising direction, and there are some articles published in the Hydrometallurgy. The basic idea is that in the hydrometallurgy process, we can selectively purify the leaching solution and prepare materials directly. For example, MENG et al [41] purified the leaching solution of nickel-copper sulfide ore, regulated the ratio of the elements in the solution, and added some cobalt and manganese precursor salts, and then precipitated the Ni_{0.8}Co_{0.1}Mn_{0.1}OH₈, and finally calcined together with lithium hydroxide to prepare cathode material LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂. WU et al [42] directly prepared TiO₂ nanowires using rutile. As it is, direct preparation of materials in the hydrometallurgy process can avoid unnecessary steps, such as preparing pure metal, which can shorten the total process and save the cost. With the focus of metallurgical research gradually shifting from traditional minerals to urban mines, it is more reasonable to decompose and re-prepare materials directly for many cases, such as prepare cathode materials in the process of recycling lithium-ion batteries [43-47].

From 2007 to 2019, there are nine articles ion-imprinted polymer about technology in Hydrometallurgy. Ion-imprinted polymers are mainly used for ion sensors and selective adsorption and separation of metal ions. For ion sensors, rare earth ions can be quantitatively identified by cyclic voltammetry based on an ion-imprinted polymermodified electrode. This ion-imprinted material is prepared by a covalent combination of polyamine ligands and bentonite [48]. For adsorption and separation, many studies have shown high separation coefficients [49,50]. The synthesis approach of ion-imprinted polymers is shown in Fig. 9. The screening of functional monomers is the core of obtaining excellent separation materials. Chitosan and silica gel are usually used as polymer matrixes. Ion-imprinted material always has high selectivity. For example, the separation of La^{3+} , Ce^{3+} , and Pr^{3+} ions can be realized at the picometre scale by using the ion surface-imprinted polymer material [51]. However, the adsorption capacity is always lower, which may be overcome by the ion-imprinted membrane [49]. This technique may be of great application in the adsorption, enrichment, and deep separation of elements.



Fig. 9 Schematic diagram of synthesis mechanism of metal ion-imprinted polymer

3.3 Elements

The content analysis of the previous section mainly reflects the general contents of each plate of hydrometallurgy. In this section, we have retrieved and analyzed the main elements involved in hydrometallurgy. The elements with more than 10 articles are shown in Table 2. The most studied elements are copper, iron, zinc, nickel, and gold. As we all know, there are so many researches on base metals, for their demands and consumptions are large, and gold also occupies a large proportion in hydrometallurgy for its scarcity and high preservation ability. For iron, the related researches are mainly focused on iron removal by precipitation, solvent extraction and separation of iron, and iron-sulfur oxidizing bacteria leaching.

Of base metals, articles on aluminum are relatively few, for the Bayer process for aluminum is relatively mature and stable. For copper, the research is mainly on bioleaching of chalcopyrite, oxygen pressure leaching, and chlorination leaching, followed by electrochemistry of copper sulfide leaching, electrochemical oxidation leaching, and the catalytic action of silver ions in the leaching process. The researches of zinc mainly include alkali leaching of oxide ore, bioleaching of sulfide ore, iron removal of the lixivium, recovery of associated indium from zinc ferrate and sphalerite, zinc leaching from zinc silicate, zinc electrodeposition, zinc cementation, and zinc recovery from spent dry cells containing zinc. The main researches of nickel include oxygen pressure acid leaching, oxidation leaching, bioleaching leaching solution purification of laterite nickel ore, solvent 3156

Base metal	Number of articles	Precious metal	Number of articles	Rare metal	Number of articles	Others	Number of articles
Al	234	Ag	207	REES	253	As	116
Cu	921	Au	366	Nb,Ta	30	Cd	83
Pb	183	Pt	64	V,Ti	240	Cr	52
Zn	529	Pd	66	W,Mo,Rh	178	Mg	86
Со	222			Zr,Hf	40	Sb	57
Ni	393			Li	104	Fe	634
				U,Th	195	Mn	210
				In,Ga	71		

Table 2 Number of articles on the most studied elements

extraction and separation of copper, cobalt, and nickel, recovery of valuable metals from spent Ni-Cd Ni-MH battery, and bioleaching of nickel sulfide ore.

The most frequent co-occurrence keywords of gold are cyanidation, passivation, silver, thiosulfate, copper, and thiourea. The main contents include thiosulfate leaching of gold-bearing minerals and secondary resources and ion exchange extraction of gold from the leaching solution, electrochemical dissolution of gold-bearing minerals, cyanidation process and passivation, thiourea leaching, and bacterial oxidation leaching.

The high-frequency co-occurrence words of rare earth include solvent extraction, lanthanum, neodymium, and yttrium. The main researches include solvent extraction, recovering rare earth from secondary resources such as waste fluorescent powder and spent catalyst, and extracting rare earth by ionic liquids.

The researches of some other rare metals center on a few institutes, and show a resource location relevance to some extent, for the resources are always concentrated and scarce, the scale of production is small, and there is no need to invest too much research force. For example, the researches on vanadium are mainly attributed to Yi ZHANG, from Chinese Academy of Sciences, about the extraction of vanadium from coal gangue and vanadium titanomagnetite. Titanium extraction is attributed to Chun LI, from Sichuan University, China, mainly about the extraction of titanium from Panzhihua ilmenite. The researches on tungsten and molybdenum mainly concentrate in Central South University, China, the contributors include Zhong-wei ZHAO, Xing-yu CHEN, Gui-qing ZHANG, et al. The researches on indium are mainly attributed to Xing-bin LI and Wei CHANG from Kunming University of Science and Technology. In addition, zirconium and hafnium, R. K. BISWAS from Rajshahi University, and Man Seung LEE from Mokpo National University; tantalum and niobium, Shi-li ZHENG from Chinese Academy of Sciences.

3.4 Instrument analysis

Advanced instrumental analysis can provide powerful support for the study of hydrometallurgy mechanism. Besides the most commonly used XRD, SEM, EDS/EDX, IR, XPS, CV (cyclic voltammetry) and NMR, other methods including Raman, TEM, Mossbauer, XAFS (X-ray absorption fine structure), gene sequencing, and CT (computed tomography, the most frequently used is X-ray computed tomography) are also used in hydrometallurgy. Among them, XAFS, gene sequencing, and CT appeared late (in 2005, 2001, and 2013, respectively). Based on XAFS (including XANES and EXAFS), we can analyze the element species and coordination of complexes, and furthermore, to reveal the reaction mechanism. Gene sequencing, usually based on the PCR denaturing amplification and gradient gel electrophoresis (DGGE) and sequencing of 16S rRNA gene fragments, is used to analyze the microbial community inhabiting which is a key issue to improve commercial applications of the microbes. The institutes using this instrument include Imperial College (micro-CT, micro means that the pixel sizes of the cross-sections are in the micrometer range), the Melbourne University, the French National Scientific Research Centre, the

University of Stellenbosch, University of South Australia, and so on. CT is a non-destructive 3D imaging technique that permits visualization of the internal structure within the sample. As we all know, the traditional kinetics usually takes a single particle as the research object. With the help of CT, the reaction mechanism of the packing particles can be clearly understood. The large-scale reaction kinetics of heap or column leaching can be studied, and the kinetic model obtained is closer to the truth. For heap leaching, micro-CT has been used to track the extent of leaching within ore particles, and morphological parameters such as the size and shape of particles and the distribution of the mineral grains within them [52]. For fast imaging, dynamic process imaging, or high-resolution imaging, X-ray based on synchrotron is needed [53]. On a larger scale, the leaching mechanism of the in-situ leaching process can be analyzed by electrical resistance tomography [54]. However, instruments like CT and XAFS are very scarce and expensive. Strengthening cooperation across institutes is necessary for related researches.

3.5 The most influential institutes and authors

Before 1997, the Internet was not popularized, which may be a reason for the lacking of cooperation across institutes worldwide. Furthermore, the format of the articles at that time was not standardized, resulting in a large number of data missing. So, the map only from 1998 to 2019 is drawn, as shown in Fig. 10. The purple outer ring indicates that the organization is more inclined to cooperate with other institutes. The lines show the cooperation and the color of a line shows the time of the first cooperation. The top 10 productive institutes are Central South University, Chinese Murdoch University, Academy of Sciences, University of British Columbia, Commonwealth Scientific and Industrial Research Organization (CSIRO), Korean Institute of Geosciences and Mineral Resources (KIGAM), India Centre of Scientific and Industrial Research (CSIR), Kunming University of Science and Technology, India Bhabha Atomic Research Center, and the University of Cape Town, respectively.

Figure 11 shows the influence of the 17 most productive authors sorted by the number of articles. This paper only makes a brief analysis of the first five productive or influential authors. The most



Fig. 10 Cooperation network and article ring diagram of main institutes (Timespan: 1998–2019, slice length=2, *g*-index=5, *LRF*=–1, *LBY*=–1, *e*=2, *N*=144, *E*=88, pruning: pathfinder)



Fig. 11 Paper influence of top 17 most productive authors (1975–2019, the radius of a circle represents the H-index)

productive author is F. J. ALGUACIL from Spanish National Research Council. His H-index is far ahead and the total cited times is second to F. VEGLIO. The main research directions are solvent extraction and membrane separation. The second is Yi ZHANG from Chinese Academy of Sciences, and the main research area includes leaching, and impurity removal of vanadium, titanium and aluminum, and so on. The main directions of Zhong-wei ZHAO from Central South University are tungsten and molybdenum extraction and lithium extraction from a saline lake. R. P. DAS from CSIR is mainly engaged in the research of value metals extraction from manganese nodules and the extraction of cobalt, nickel, and zinc. Many of his articles are about the leaching mechanism

of copper, gold, nickel, manganese, and so on. Specifically, F. VEGLIO from the University of Aquila in Italy has the highest total cited times with 22 articles, which have been up to 1624 times. The main research direction is bio-adsorption.

4 Conclusions

(1) The current hot topics in hydrometallurgy are rare earth, recycling, lithium, ionic liquids, and thorium. The emergence of these topics can be attributed to the market changes, technological progress, and environmental protection. We can draw a conclusion based on the hotspots analysis of gold, indium, lithium, and rare earth that the future research hotspots in the field of hydrometallurgy will concentrate on the critical raw materials which are more important to economic development while the supply cannot be guaranteed. Meanwhile, with the increase of the exploitation cost of traditional mineral resources and the gradual increase of the scale of urban mines, the study of resource recycling will gradually become the mainstream.

(2) Since the founding of *Hydrometallurgy*, the article proportion about biohydrometallurgy has increased significantly, whereas the proportion of solvent extraction has an obvious decrease. However, the number of articles on solvent extraction increases steadily. New directions such as direct preparation of materials in hydrometallurgical processes and ion-imprinted techniques are noticeable.

(3) There are a large number of researches on basic metals and precious metals. Except for rare earth, the researches of rare metals center on a few institutes, and show a resource location relevance to some extent.

(4) Some advanced instrument analyses such as XAFS, gene sequencing and micro-CT have been used, which provide the possibility for further understanding of hydrometallurgy mechanism.

(5) Institutes including Central South University, Chinese Academy of Sciences, Murdoch University, University of British Columbia, Commonwealth Scientific and Industrial Research Organization (CSIRO), etc. are the main contributors to *Hydrometallurgy*. The most productive authors include F. J. ALGUACIL, Yi ZHANG, Zhong-wei ZHAO, R. P. DAS, Jae-chun LEE, K. INOUE, F. VEGLIO, et al.

As it is, the development of hydrometallurgy will gradually enter a new stage. There will be more and more researches on secondary resources. The new instrument analysis methods will gradually apply to the deep exploration of the hydrometallurgical mechanism. With the fast-growing resources demands for the lasting economic development and the increasingly serious environmental challenges, developing countries like China and India will conduct more and more researches on hydrometallurgy, and make more contributions to hydrometallurgy.

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湿法冶金研究趋势:基于 1975—2019 年 《Hydrometallurgy》文献的综述

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摘 要:当代湿法冶金已发展一百多年,相关领域的论文越来越多。《Hydrometallurgy》是湿法冶金领域最有代表性的期刊,基于对该期刊的文献计量分析,从全局角度获得湿法冶金的研究发展趋势。首先,关键词突发性筛查结果显示,稀土、回收循环、锂、离子液体和钍是近些年的研发热点,对这些热点的经济和技术背景进行探讨。 其次,生物冶金文献的比例从早期的 5%快速增长到近些年的 13%,且相关论文主要是生物浸出。在湿法冶金过程中直接制备材料和离子印迹技术是近些年出现的新技术。第三,新出现的仪器分析方法如 X 射线吸收精细结构 谱、基因测序和高分辨断层扫描能促进人们对湿法冶金机理的深入理解。最后,绘制并分析世界主要研究机构的 合作图谱。

关键词:发展趋势;浸出;溶剂萃取;生物冶金;电化学湿法冶金;CiteSpace

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