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Accepted 00th January 20xx DOI: 10.1039/x0xx00000x Critical Elements: Opportunities for Microfluidic Processing and Potential for ESG-Powered Mining Investments

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Critical minerals are those containing elements, typically metals, and element allotropes, which have an irreplaceable role in the ongoing revolution in technology and manufacturing needed to progress society to a high-tech, clean energy future. The global market for critical minerals is highly vulnerable due to supply chain monopoly risks. Moreover, the mining, processing and refining of these elements involves substantial environmental and health risks, including, but not limited to, ecosystem degradation, chemical pollution, and hazards related to chemical and particulate exposure. Countries such as Australia, therefore, have developed national critical minerals strategies, which include investment in research to develop improved recovery methods and processing technologies. Australia has escalated continuous flow chemistry and critical minerals as critical priorities of national interest. In lieu of this, this review paper assesses the role of solvent extraction and other processing innovations using microchannel systems for recovery of critical minerals. Microfluidic devices have captured worldwide attention for miniaturising the reactor dimension and, hence, providing huge potential to advance application of chemical processes that require precise control, enhanced mixing and rapid reactions. For minerals processing, continuous-flow operation can lead to advantages for extraction efficiency, processing time (productivity), and selectivity. Thus, this review summarises the up-to-date extraction performance of microfluidic devices along classes of critical minerals, as defined by their grouping in the periodic table. Attention is given to the fluidic concept used, e.g. the flow patterns, and how the microfluidic system is configured. From there, the achieved performance is reviewed, both for model and real world extractant solutions; the latter including multiple minerals and issues of selectivity. Finally, a proposed recommendation is that microfluidics use should aim to impact the whole processing and supply chain, and to support and contribute to ESG (Environmental, Social, Governance) profiling, a crucial demand faced by the mining industry. The enabling technologies not only have potential to change the environmental profile, but will also require highly skilled and trained workforce, and hence can create new employment opportunities.

Introduction

What are the critical elements?

Based on their different uses and the needs of individual countries or territories, critical elements (often referred to as critical minerals) can be defined in various ways ¹. They have an irreplaceable role in the world's major and emerging economies. Currently, factors such as geological scarcity, geopolitical issues, and trade policies pose a severe risk to world supply ². However, the most important and common factor defining elements as "critical" are the risks to global supply

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chains needed for metallurgical processing and refining to commercial products ³. According to Geoscience Australia, the following elements are ranked as most critical by the US, Japan, Korea, European Union, and UK: rare earth elements (REE), cobalt (Co), niobium (Nb), magnesium (Mg), molybdenum (Mo), gallium (Ga), indium (In), tungsten (W), vanadium (V), platinum-group elements (PGE), antimony (Sb), tantalum (Ta), tellurium (Te), chromium (Cr), lithium (Li), nickel (Ni), and manganese (Mn) (Fig. 1) ^{4, 5}.

Critical elements, mostly metals and semi-metals, are used in the manufacture of high-tech applications such as smart devices (e.g. mobile phones, computers, monitors), wind turbines, solar panels, electric cars, light bulbs, photovoltaic cells, generators, and automobile exhaust catalytic converters ^{1, 6-8}. Other fields, such as electronics, specialist materials (alloys, glass, ceramics), catalysts, medical applications and the defence sector, also depend on critical elements ¹.

Seventy elements from across the periodic table can be found in a single mobile device (Fig. 2). Whereas a mobile phone is a good example of the vast range of metals that go into a single piece of consumer electronics, the greatest demand for critical minerals is likely to be in the transition to renewable energy,

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where critical minerals are essential components of batteries, photovoltaics, magnets for electric motors and wind turbines. Long-term strategic planning is currently being developed for the sustainable supply of these metals to meet future demand ⁹.



Fig. 1 Critical elements and their remaining reserves. Reproduced from ref.⁵ with permission from Wiley-VCH, copyright 2019.



Fig. 2 Critical elements in a modern smart phone. Reproduced from ref.¹⁰ with permission from Elsevier, copyright 2020.

Market share and supply risk of critical minerals

The global reserves of critical elements are unevenly distributed between nations and territories. As shown in Table 1, a significant proportion of critical elements and major production lines are concentrated in countries such as China (Sb, Ba, F, Ge, In, Ti, Si, Mg, W, V, REE), USA (Be, He, Hf, B), South Africa (Mn, W, V, Zr, Cr, PGE), Brazil (Nb, Si, Ta), Russia (Hf, Sc), Australia (Li, Zr, U) and the D.R. Congo (Co). For example, 23 out of 35 commodities recognised as critical minerals by the USGS pose "the greatest supply risk for the US manufacturing sector" ¹¹. The US is heavily reliant on imports for 14 commodities and many of these are produced, refined and supplied by China ^{1, 11}. The EU is also heavily dependent on the imports of critical minerals, such as rare earth magnets (98% from China), borate (98% from Turkey), and PGE (71% from South Africa) ¹².

In 2015, Graedel et al. proposed a definition of metal criticality based primarily on the possibility of supply disruption, the

impact of a supply disruption, and the environmental implications of critical mineral supply ¹³. Supply vulnerability due to concentrated production is the most important factor which makes an element critical. Many critical minerals markets are also subject to risks and uncertainties due to price volatility and locking customers into high-price, long-term contracts ¹. Other factors include:

- the role of the mineral in crucial technologies and applications
- the scarcity of the mineral resources
- the ease of substitution of one mineral with another in its major applications
- the dependence of a country or corporation on imports for supply
- the monopoly of supplier countries or companies in terms of control of markets for processed/refined products
- the imbalance between supply and demand in the market

To reduce reliance on critical minerals imports, developed nations, especially those that cannot mine or produce critical elements directly, are examining recycling of waste as a valuable resource ¹. There are also significant opportunities for countries with abundant reserves of critical minerals to expand their market share in this area by improving mining and processing technologies to produce higher value products for market.

Critical minerals mining and processing

The sources for critical elements can be divided into two major groups: primary sources and secondary sources. Primary sources refer to the mining and processing activities of minerals or mineral by-products originating from deposits mined underground or from surface. The typical procedure for producing minerals consists of six consecutive stages (Fig. 3): deposit exploration, mining, beneficiation, chemical treatment, separation and purification/refining. The schematic ignores the often lengthy pre-production feasibility and development stage that includes resource delineation, permissions, license to operate, ESG and much more.



Fig. 3 Processing procedure for minerals from primary sources. Reproduced from ref.¹⁴ with permission from Frontiers, copyright 2014.

For example, minerals containing REEs (e.g. bastnäsite, monazite, xenotime) are mined from open cut operations, including heavy mineral sands. The minerals containing REE are concentrated by physical separation (e.g. flotation, magnetic or gravity separation methods) followed by chemical treatment (or leaching). Individual REEs can be collected using separation methods and may then be further refined and purified.

Table 1List of recognised critical elements in 2020 and their major suppliers; includingAustralia's reserve potential ^{5, 15}.

		Criti	cal elem	ent List 2020		
Element	Symbol	EU	USA	Australia's Geological Potential	Major ore producing nations in 2017	Major refining nations
Antimony	Sb	✓	~	Moderate	China (87%), Vietnam (11%)	China, Kyrgyzstan, USA
Damita	D-		/		China (44 %), India (18 %),	
Baryte	Ва	v	v		Morocco (10 %)	China
Beryllium	Ве	✓	✓	Moderate	USA (90 %), China (8 %)	USA, Kazakhstan, China
Borate	В	~			Turkey (38 %), USA (23 %), Argentina (12 %)	Turkey, USA
Caladh	6-		/	11°-1-	D.R. Congo (64 %), China (5 %),	
Cobalt	Co	•	\checkmark	High	Canada (5 %)	China
Fluorspar	F	✓	✓		China (64 %), Mexico (16 %), Mongolia (5 %)	China
Calling	6.			11°-1-	China (85 %), Germany (7 %)	
Gallium	Ga		v	півн	Kazakhstan (5 %)	France, Japan, USA
Companium	<u>Ca</u>			u:-h	China (67 %), Finland (11 %)	China
Germanium	Ge	v	v	mgn	Canada (9 %), United States (9 %)	China
Hafnium	цf		1	Lligh	France (43 %), USA (41 %)	Australia South Africa
паннин	пі	v	v	півц	Ukraine (8 %), Russia (8 %)	Australia, south Africa
Liolium				Madarata	The USA (73 %), Qatar (12 %)	
пенит	пе			Moderate	Algeria (10 %)	-
Indium	In			Lliab	China (57 %), South Korea (15 %),	China
maium	III	·	·	півц	Japan (10 %)	China
Lithium	Li	✓	\checkmark	High	Australia (43 %), Chile (32 %), Argentina (12 %)	China
	N 4			Madavata	China (87 %)	China
Magnesium	IVIg	v	V	Moderate	USA (5 %)	China
Manganese	Mn		✓	High	South Africa (33 %), China (16 %), USA (14 %)	South Africa
Niobium	Nb	✓	\checkmark	High	Brazil (90 %), Canada (10 %)	Brazil

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					China (58 %), Vietnam (19 %)	
Phosphorus	Р	~	✓		Kazakhstan (13 %), USA (11 %)	China
Rhenium	Re		✓	Moderate	Chile (52 %), Poland (17 %), USA (16 %)	Chile
Scandium	S.c.	1	<u> </u>	High	China (66 %), Russia (26 %),	China
Scanuluin	30	•	·		Ukraine (7%)	China
	<u> </u>		1		China (28 %), Japan (23 %),	
Selenium	Se		•		Germany (22 %)	China
					China (61 %), Brazil (9 %),	
Silicon	Si	✓	✓		Norway (7 %), USA (6 %), France (5 %)	China
Strontium	Sr	✓			China (47%), Spain (28%), Mexico (22%); Argentina (3%)	China
		,	,		Rwanda (31 %), D.R. Congo (19 %),	
Tantalum	Ia	~	v	Hign	Brazil (14 %)	China
					China (67 %), Sweden (10 %),	
Tellurium	le		V		Japan (9 %)	China
					China (34 %), Myanmar (17 %),	
Tin	Sn		\checkmark		Indonesia (17 %)	China
Titanium	Ti	✓	✓	High	China (40 %), USA (19 %)	China
Tungsten	W	✓	✓	Moderate	China (53 %), South Africa (25 %), Russia (20 %)	China
Vanadium	V	√	✓	Moderate	China (53 %), South Africa (25 %), Russia (20 %)	-
Zirconium	Zr		✓	High	Australia (38 %), South Africa (25 %)	-
Platinum Group Elements (PGE)	Pd, Pt, Rh, Ir, Ru, Os	✓	~	High	South Africa (83 %)	South Africa
Heavy REE	Y, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	✓	~	High	China (95%)	China

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Light REE	La, Ce, Pr, Nd, Pm, Sm	✓	~	High	China (95%)	China
Uranium	U		✓	High	Kazakhstan (42%), Canada (13%), Australia (12%)	Australia, Canada, Kazakhstan

Secondary sources refer to the recycling and collecting minerals from alternative sources such as ore tailings or e-waste. The four steps concerning the latter are collecting, dismantling/preprocessing, processing, and recycling. For ore tailings and mineral by-products the final separation and purification steps apply as given in Fig. 3.

To place the potential of primary and secondary sources into perspective, one should look at their absolute values. Taking the example of REE as per 2019, approximately 120 million tonnes of the global reserves are distributed around the globe, mainly in China, Brazil, Vietnam, Russia, India, Australia, Greenland, USA ^{2, 16}. In 2019, over 200,000 tonnes of REE were produced from these primary sources, thus less than 0.2% of the reserve ¹⁶. On the other hand, 1.96 million tonnes of REE are contained within 4.6 billion tonnes of mine tailings; thus almost 4% of the global reserve ¹⁶. In the same year, 53.6 million tonnes of ewaste, with variable REE contents, were generated around the world ¹⁶⁻¹⁸. Typical e-wastes containing high concentration of REEs include permanent magnets (20-30% by weight), lamp phosphors (over 20%) and batteries, especially nickel-metalhydride batteries (over 10%). The cumulative REE contained in e-waste is, however, far lower in volume and weight than in mine tailings ^{19, 20}. Although the quantity of secondary sources is significant, it is not deemed sufficient to replace primary sources for reasons of limited extractability and economics.

Environmental impacts of metal ore mining and processing

Environmental concerns causing by mining activities are primarily related to mine waste (overburden, and barren rock), damage to the natural landscape and acid mine drainage ²¹. Mining activity generate involves remove of large quantities of rock from the ground to obtain metal ore.

Mineral processing activities generate hazardous waste, which, if poorly managed, can lead to soil, water and air pollution. Tailings and dump heap leach waste are produced from beneficiation plants, increasing in volume as ore grade decreases. Gaseous emissions, wastewater and solid wastes are produced from smelting and refining plants ²². For example, high SO₂ outputs from nickel and copper smelting at Sudbury, Ontario, have led to acidification of soil and lake water near the smelters (pH values of 3-4 and 4-5, respectively) ²³. The current technologies for refining minerals are effective for production of high purity metals but still require toxic and flammable chemicals and/or are difficult and expensive to automate. There is thus both an opportunity and a challenge to develop a greener and more sustainable route for refining, even if recycling activities may create pollution. A recent study showed that recycling of lithium-ion batteries used 38-45% more energy and released 16-20% higher greenhouse gas emissions than primary production ²⁴. Thus, despite the promising economic and environmental value of recycling of critical elements from end-of-life products, there remains significant economic and technological factors to overcome to reach this potential ^{14, 25, 26}.

Strategy towards future critical elements

The exploitation of critical minerals is a relatively recent endeavour for humankind, and therefore not as well developed as other commodities such as gold, silver, iron, copper or lead that have been mined for millennia. While critical mineral end-products carry a highvalue, they are commonly spread over many sites, occur in (often complex) mineral mixtures, and are accessible in only small ore volumes. Processing and refining facilities producing high purity end products tend to be concentrated in only a small number of countries, often allowing control or even manipulation of the global market.

A significant shift in the geopolitical distribution of metallurgical facilities is required to correct the current untenable situation. Countries with critical mineral resource potential now aim to capitalise on the opportunity to develop a sustainable supply chain for critical minerals ^{2.} In Australia's case, only limited information is available on the concentration and deportment of critical minerals in most of the country's currently exploited and future ores ² In the absence of a commercial incentive, national strategies and priorities on mining have to set the tone for technology development, as relevant to this paper ²⁷. Geoscience Australia have recommended research goals for the short-, medium- and long-term capitalisation on existing critical mineral opportunities (Table 2)². In the mediumterm, technological advances and the development of model supply scenarios are seen as the way forward, while in the long term, material flow analyses are intended to improve the robustness of critical assessments and understanding of the policy options for demand, supply, use and recycling. Increasing funding in geosciences, geochemistry and chemical engineering is a fundamental strategy to develop expertise and knowledge base to enable more efficient extracting critical minerals for meeting these goals ²⁸. Further investments in technological advances for treating waste materials, developing urban mining techniques and alternatives for low abundance critical minerals should also be prioritised ²⁹⁻³¹. The improvement in technologies also requires a skilled workforce for generating and maintaining a sustainable critical mineral supply chain ³². The final strategy that could impact the critical mineral economics of countries involves promoting the engagement of governments toward private companies in terms of reducing risks associated with mining and processing via stockpiling,

tax credits and loan guarantees based on the current status of the country $^{\rm 33}\!.$

Table 2 Research agenda concerning critical minerals; based on the example of Australia (redrawn after ²).

	Undertake critical minerals systems studies				
	Model supply scenarios				
Medium-	Increase awareness of critical minerals opportunities for smelters/refineries				
term (4-8 years)	Improve understanding of the metallurgical behaviour of critical minerals during ore processing				
	Develop methods to recover critical minerals from mine waste				
	Improve processing technology				
Long-term (8+ years)	Conduct material flow analyses (MFAs)				

This review focuses on the medium-term solution of "Improving process technology", which can catalyse the exploitation of both primary and secondary resources. As defined above and with relevance to this review, new extraction methods will need to be developed to recover critical minerals from mine wastes, such as tailings, smelter and refinery slags or residues ². Those extraction methods require, first of all, innovative processing technologies to be generated by the research community, embraced by the Mining Equipment, Technology and Services (METS) sector, and implemented by end-users.

This review aims to highlight research efforts that emphasize the major, hitherto unrecognised potential that microfluidic (continuous-flow) operations might play in the critical minerals space. These frontier technologies can overcome the limitations of conventional methodologies, including fast operation in confined spaces (e.g., underground), compatibility with varying concentrations of target elements, energy and water efficiency, reduction of expensive or toxic solvents, maintaining safe operational environments, better ESG profiles, and effective treatment of wastes to benign levels (e.g. radionuclides and other non-target components of the ore). Continuous flow chemistry is listed by Australia among its critical technologies and continuousflow processing is now used on an industrial scale in pharmaceutical processing. Given that continuous-flow has already proven to be efficient in solvent-based extraction for fairly concentrated high value materials, this paper reviews new applications of continuousflow processing in microchannel devices to critical minerals processing.

Microfluidics for critical minerals

Solvent extraction of critical minerals in microchannel systems

Microfluidic devices are designed to surpass limitations of macroscopic chemical process systems by their intrinsic properties, e.g., high surface-area-to-volume ratio, and improved and controlled level of heat and mass transfer, etc. ³⁴⁻³⁹. It is more than 30 years since the first microfluidics

experiments were conducted, and today many types of socalled microreaction technology devices have been developed and commercialised, differing in processing purpose, and microchannel shape and size ⁴⁰.

There has been extensive research effort in applications of microfluidic systems to liquid-liquid extraction of critical minerals. Table 3 outlines studies on the solvent extraction of different groups of critical elements via microchannel systems.

Fig. 4 documents this broad diversity in the design and fabrication of microfluidic devices. They range from compact lab-on-the-chip devices to microfabricated channel plates and flow chemistry-microcapillaries (such as the coiled flow inverter, CFI) to large-scale industrial equipment such as the reentrance flow reactor from Corning[®] reactor ⁴⁰⁻⁴². One example of the lab-scale Low-Flow reactor for the extraction of cobalt has been conducted by Wouters et al. ⁴¹. The Corning reactor module consists of 6 modules each with a long series of heartshaped channels (Fig. 4c) with an internal volume of 0.45 mL and can be operated under a flow rate between 120 and 1200 mL/min. The laboratory module shown is milli-flow, thus the manufacturer calls their reactors "Advanced Flow" (and not microfluidic). The Corning production reactor module is scaledout in internal dimensions and can be assigned as a meso-flow reactor. 3D printing of microfluidic devices has greatly advanced microfabrication and design capabilities, and, with increasing innovation in printed materials, now allows on-the-spot creation of microdevices for fast screening of new microdevice designs 43-45.

Alkali metals

The majority of the world battery-grade lithium is produced from acid leaching of ores or precipitation from brines ⁴⁶. These processes involve toxic chemicals, including acids for leaching/washing of lithium, and soda ash to produce lithium carbonate and they pose significant environmental risks ⁴⁶. Trace impurities co-extracted with lithium in tailings, processed water, waste storage ponds may also adversely affect human health ⁴⁷. Brine evaporitic technology may be an energy efficient method but it also impacts water usage and land subsidence 48, 49. Alternative technologies for water recycling, minimisation of waste, greater processing efficiency, and extraction of several materials from the same brine have been suggested to optimise current mining practices, protect the environment, and maintain the economic value. Microfluidics and flow technology may provide answers to these problems associated with lithium mining. <u>Potential for microreaction technology</u> As the number of discarded Li-containing devices increases and the price of the metal continues to climb, lithium recovery and recycling will soon become essential. Small-scale recovery processes need to be operable with various scenarios of achieving Li recovery from discarded electronic devices. The extraction-recovery of waste of Li-ion batteries, for example, contains multiple solutes, thus necessitating a knowledge of their impacts on extraction behaviour.



(c) t-maki

Flow direction





Fig. 4 Microfluidics devices (from chip to industrial reactor): (a) 3D printed microfluidic chip (Reproduced from ref.⁵⁰ with permission from Wiley-VCH, copyright 2016), (b) Coiled Flow Inverter as example for a flow chemistry capillary system (Reproduced from ref.⁵¹ with permission from Elsevier, copyright 2017) (c,d) Commercial re-entrance flow meso-flow reactor as example for a high-productivity industrial flow equipment (Corning Company) (Reproduced from ref.⁴¹ with permission from Elsevier, copyright 2021).

Group	Metal	Microfluidic principle	Extractant	Comment	Ref.
i s	Li	Y-junction microchannel	D2EHPA; EHPNA	Slug flow	52
vlkal leta	Li, Co	Y-junction microchannel	D2EHPA; D2EHPA-Na	Slug flow	53
۹ ک	Cs	Y-junction chip	D2EHPA	Slug flow	54
	Cr, Cu	Y-junction microchannel	LIX84-IC	bypassing the formation of a particle- stabilized crud	55
ı Metals	Cr	Y-junction microchannel	Alamine 336	 a) two homogeneous phases, water is receptor phase. b) a heterogeneous system, where Shellsol D-70 and Alamine 336 as the selective extractant 	56
Transition	Со	Y-junction microreactor	2-nitroso-1- naphthol; N,N-dimethyl-m- aminophenol	 a) Mass transfer under a mixed reaction-diffusion resistance regime b) Co-2-nitroso-5- dimethylaminophenol complex c) Co-2-nitroso-1-naphthol complex 	57-59
	Co, Cu	five inlets and two outlets microchip	2-nitroso-1-naphthol	multiphase flow network, continuous- flow chemical processing on microchip	60

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	Co, Ni	a) Coiled flow inverter (CFI)b) Re-entrance flow microreactorc) Interdigital micromixer	Cyanex 272; D2EHPA; PC88A;	a) High extraction efficiency, high selectivityb) Real asteroid samples	41, 51, 61, 62
	Co, Ni, Zn	helical capillary microreactor	D2EHPA	Slug flow	63
	Cu	 a) Y-junction microchannel b) Y-junction chip c) T-junction microchannel d) Microchip 	DZ988N; LIX84-IC; AD-100; 8-hydroxyquinoline	 a) Laminar flow pattern b) Study mass transfer coefficient c) pH study d) Metal ions extraction from particle-laden aqueous solutions e) Experimental mass transfer coefficient study f) Solvent extraction coupled with IDMS/ICP-MS 	64-69
	Cu, Zn	T-junction microchannel	Dithiozone	Slug flow, extraction-stripping microfluidic platform	70
	Cu, Fe, Zn	Interdigital micromixer	D2EHPA	99% extraction efficiency in a single stage	64
PGEs	Pt	a) Multi-stream microchipb) Y-junction microchip	Cyanex 572	 a) High throughput (up to 1 L/h for current platform) b) New type of contactor, two stage counter-current operation c) Modular scale up approach d) Extraction, striping and scrubbing on microchip 	71-74
	Pt, Pd	Y-junction microchip	Alamine 336	Extraction efficiency 99% for Pt and Pd and 90% Rh	75
very etal	Re	Y-junction microchip	Aliquat 336	Extraction & Stripping coupled with ICP-MS	76
Si S	In	T-junction microchannel	D2EHPA		77
		Microchannel	HDEHP	Slug flow, using laser micromachining to config inlet/outlet, TALSPEAK process	78
	Y, Eu, La	Microchannel	PC-88A	Laminar flow	79
Pr/Nd, Pr/Sm	Pr/Nd, Pr/Sm	Microchannel	PC-88A	Laminar flow, lighter element being transferred to organic phase a) The specific interfacial area of the Y-junction serpentine	80
REES	Y	e) Y-junction microchipf) T-junction microchip	ЕНЕНРА; РС-88А	of the T-junction microreactor. b) Slug flow	81-83
				c) Intermittent partition walls improve extraction efficiency	
	La	Y-junction microchip	P507	c) Intermittent partition walls improve extraction efficiency Laminar flow	84
	La Ce, Pr	 Y-junction microchip a) 3 stages chaotic advection micro extractor b) Y-junction microchip 	P507 P507	 c) Intermittent partition wails improve extraction efficiency Laminar flow a) Chaotic flow b) Slug flow, serpentine microreactor 	84 85, 86
	La Ce, Pr Pr, Nd	 Y-junction microchip a) 3 stages chaotic advection micro extractor b) Y-junction microchip Y-junction microchip 	Р507 Р507 ЕНЕНРА	 a) Chaotic flow b) Slug flow, serpentine microreactor 	84 85, 86 87

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	Nd	a) Microchannel b) Y-junction microchip	P507	 a) Slug flow, T-shape, G/O/W system b) Laminar flow 	89, 90
	Gd	Y-junction microchip	MDEHPA	Laminar flow, coupled with ICP-AES	91
	Sm	Y-junction microchip	P507	Slug flow	92
	HREEs and LREEs	Y-Y microchip	Cyanex 572	a) Industrial leach solutionb) High HREEs selectivity at pH = 0.7	93
Heavy element	U	 g) Y-junction microchip h) Y-junction microchannel i) T-junction microchannel j) Flow-focus junction 	Tributylphosphate (TBP); Aliquat 336;	 a) Slug flow b) Laminar flow c) Continuous microfluidic extraction and direct precipitation d) Droplet-flow, lab-on-a-chip e) Extraction & Stripping coupled with ICP-MS f) Microbores tubes connected to T- junction 	94-102

<u>Fundamentals: mass transfer</u> Muto et al. successfully extracted Li ions from the aqueous to organic phase through segmented flow in millimetre-diameter tubes ⁵². The high mass transfer coefficients of 1.62 - 2.48 L/s were achieved by adjusting the pH of the feed solution for the extraction of Li⁺ with D2EHPA.The study showed that the flow conditions are dependent on the pH of the aqueous phase. The combined adjustment of the pH and the high mass transfer of the segmented flow led to greatly improved performance.

<u>Real-world readiness: multi-solute mixtures</u> The majority of studies addressing liquid-liquid extractions in microreactors involve using an aqueous solution of a single metal ion. They are thus concerned with an ideal model situation, providing fundamental insights, yet being far from fit-for-purpose for industrial application. Fortunately, a few studies have considered multi-solute mixtures. Hirayama et al. used segmented-flow in microchannels to extract alkali metals in an aqueous phase and studied the selectivity of using the scavenger D2EHPA for separating Li⁺ and Co²⁺ in the feed solution ⁵³. The volumetric mass coefficients of Co²⁺ and Li⁺ were on the same order of magnitude as given by other segmented-flow extraction systems, and D2EHPA had a higher ion affinity toward Co than Li. In the mixed system, the Co extraction yield increased with the increase of the D2EHPA concentration, whereas the selectivity decreased.

<u>Real-world readiness: intricate solutes</u> A real-world problem of Libased recovery is that the separation of certain alkali metal ions operates with a poor separation factor. Optimisation of this deficiency can help the sustainability of Li recovery. Abdollahi et al. proposed a method for the efficient separation of species with low separation factors such as Ca²⁺ with the help of solvent extraction and microfluidic technology ¹⁰³. The optimal point for extracting Ca²⁺ was identified to be an aqueous phase with a pH of 5.85, a DC18C6 concentration of 0.014 M, and a flow rate of 20 µl/min. In this way, an extraction efficiency of 62% resulted. Furthermore, the overall volumetric mass transfer coefficients of 0.19 – 0.51 s⁻¹ were two orders of magnitude higher than those of conventional liquid-liquid

extraction. Using a different microfluidic set-up, but also aiming for microfluidic recovery of Li, Jahromi et al. found the extraction efficiency of Ca ions was close to 99% within an impressively short contact time of 1.5 s $^{104}.$

<u>Process development: productivity</u> The most efficient operation mode of microfluidics is segmented flow with its high mass transfer capability that is known to enhance the extraction rate significantly in many cases. This can reduce both the size of process equipment and the volume of reagents needed for liquid-liquid extraction. On this basis, the rapid extraction of Cs⁺ from an aqueous phase was performed by plug flow via a microreactor with a wide range of flow rates (0-100 mL/h) ⁵⁴. Compared to batch extraction dominated by turbulence mixing, the segmented-flow microreactor had an increased extraction rate and achieved extraction equilibrium within a short timeframe of 40 s.

Transition metals

Transition metals are also critical to the growth of technological innovation but many of these metals are mined as by-products. For example, 98% of cobalt production is derived as a by-product of large scale copper and nickel mining operations ¹⁰⁵. Solvent extraction, if properly controlled, is often a preferred process for efficiently removing impurity and separating cobalt from leachate at both large and small plants. However, a serious problem with this technology, especially in larger plants, is the need to control pH at the extraction stage, and usually requires use of sodium-based neutralising agents such as NaOH and Na₂CO₃ ¹⁰⁶. As a result, processing plants need to invest in either costly dam linings or a (very expensive) process to recover sodium sulphate ¹⁰⁷. There are similar issues when using ammonia as an alternative approach ¹⁰⁸. Larger plants also experience problems of oxidation, degradation and crud formation ¹⁰⁶. For the use of solvent, cobalt-nickel extraction reagents such as Cyanex 272 are relatively expensive and need to be handled delicately while Cyanex 301 requires strict process control to prevent

the presence of ferric or copper ions in the feed which will poison the reagent ¹⁰⁹. The fire risk and high cost of prevention measures are obvious drawbacks of the use of organic solvent in any extraction process, including the need to physically separate any units using this technology from the rest of the processing facilities Thus, it is essential to minimise the amount of solvent for extraction but still maintain efficiency and economic value.

<u>Modelling: predictability</u> Microfluidics have given us the promise of predictability in the sense of coupling experiments with advanced modelling. In lieu of this, Barasauri et al. (2019) developed a predictive mathematical model as guidance for the design of microfluidic extraction of Cr (IV) from an aqueous phase using Alamine 336 as the extractant ⁵⁶. Using a Y-Y shape micro-device, the experimental data fit to within 10% of the model data.

Fundamentals: mass transfer and selectivity Microfluidics also have enormous potential for improving process intensification; meaning to be "greener, smaller, better, faster and cheaper¹¹⁰⁻¹¹⁴" (in simple terms), all of which are highly relevant for critical mineral extraction problems. In this sense, the separation of Co from Ni is a particularly challenging task, as these metals possess similar physicochemical properties and commonly coexist in nature (in sulphide ores). New technologies that can overcome the shortcomings of conventional methods is required for their extraction and separation. Zhang et al. (2014) obtained a higher extraction efficiency in a counter-current flow interdigital micromixer at pH equilibrium of 3.8 to 5.4 and a lower number of stages of extraction (McCabe Thiele) 62. A microscale coiled flow inverter (CFI) was utilised by Zhang et al. (2017) to generate segmented plug flow to achieve high extraction ability ⁵¹. This set-up exhibited much higher k_L of Co (0.26–0.017 s⁻¹) and smaller of Ni (0.053–0.013 s⁻¹) compared with batch methods. The set-up also achieved better selectivity between the two metals at industrially relevant concentrations, as shown in Fig. 5.



Fig. 5 Effect of pH on the extraction efficiency of Co and Ni, (a) extraction ratio, and (b) separation factor (the ratio of Co extracted relative to Ni) in microflow and batch extraction. Reproduced from ref.⁵¹ with permission from Elsevier, copyright 2017.

<u>Process</u> <u>development: intensification</u> Microfluidics need to demonstrate scalability to the high capacities needed for the large process flows in mining and minerals processing. An industrial pilot scale microreactor consisting of 3D conical sections (Amar Company) that are symmetrically connected in 6 series, was evaluated for the extraction of Co from Ni sulphate with Cyanex 272 as extractant at a flow rate of 9 L/h (roughly corresponding to an annual metal separation capacity of 5 t/a). The cones constantly cause perturbation of the flow, renewing interfaces, which has been termed re-entrance flow in the literature. This kind of processing

produced an extraction efficiency of above 99.9% with good selectivity and a high volumetric mass transfer coefficient ⁶¹. A comparison between a coiled-flow inverter (CFI) and an industrial reentrance flow reactor (Corning SAS Company) has been studied by Wouters et al. in the extraction of Co from Ni solution ⁴¹. These authors observed that the CFI was superior with lower pressure drop and low energy input, whereas the industrial reactor performed at a higher flow rate that can negatively impact on productivity. Additionally, a leached solution originating from a real asteroid sample was fed into the CFI for investigation on the extraction ability ⁴¹. Due to the presence of iron in the solution, which was co-extracted, the maximum Co extraction efficiency was 87% at a flow rate of 120 mL/h and 60 s residence time.

Process development: scavenger The scavenger has the essential function in extraction to turn a mass-transfer to a reaction-masstransfer dominated process, typically making it faster. Dithiocarbamate derivatives have been widely known for their scavenging role in heavy metal extraction as chelating agents, but study of the effects of their different forms on the process is largely lacking. In the study of Morita et al. ⁶⁵ on the extraction of Cu ions using a two-phase microflow system, dithiocarbamates in acid forms were synthesised and their extraction properties investigated. The extraction ability of dioctyldithiocarbamate (dodtc) was higher than that of diethyldithiocarbamate (dedtc) under low pH conditions, as shown in Fig. 6. The authors noted that under basic conditions, the extraction of Cu ion with dodtc decreased due to the amphiphilic properties of dodtc. The kinetic study also revealed that the extraction rate was dependent on formation of the dodtc complex at the liquid-liquid interface.



Fig. 6 Copper (II) concentration in organic phase in microfluidic extraction at pH 1.1: (black circle) dodtc and (black square) dedtc. Reproduce from ref.⁶⁵ with permission from the Japan Association of Solvent Extraction, copyright 2010.

<u>Real-world readiness: slow phase separation</u> The interplay of microfluidics and particle flows can cause issues with extraction efficiency (the ratio of the element to be extracted relative to unwanted extraction of other elements or impurities). For example, a complex composition of solid particles and surfactants complicates phase separation in both bulk and microfluidic solvent extraction. To address the complexities of particle interaction in microfluidics, Priest et al. ⁵⁵ examined the extraction efficiency of Cu and Cr in a Y-junction microfluidic system. Their study took the particular motivation of bypassing the formation of a particle-stabilised crud by microfluidic solvent extraction of metal ions from particle-laden aqueous solutions (Fig. 7)–⁵⁵. The presence of hydrophilic silica

particles restricted phase disengagement in both the model solution (grey square points) and the real leach solutions, causing the organic phase to be trapped in the emulsion (black square points) in conventional bulk extraction (Fig. 7a). In the microfluidic extraction approach, despite having high loading of silica particles, the extraction remained comparable with bulk extraction of particle-free copper solution, as shown in Fig. 7b. Due to the short residence time of nanoparticles in the aqueous phase, the microfluidic system was able to operate continuously for more than 7 h without failure, with high particle concentrations (61 g/L, 80 nm hydrophilic silica and 5 g/L, 13 nm hydrophobic silica), whereas the bulk system suffered from prolonged phase separation or the formation of particle-stabilized emulsions 55 .

<u>Real-world readiness: impurities.</u> Since alloys are widely used, especially in electronic devices, the precise determination of impurities is crucial. For example, the low concentration of Cu in Al alloys is difficult to detect without any pre-treatment. Using microfluidic solvent extraction/back-extraction, Kagawa et al. (2009) were able to separate Cu from an Al alloy matrix for a fast and accurate online analysis of trace Cu. Regardless of the microfluidic extraction efficiency of 40%, the IDMS/ICP-MS combined with the system provided a total measurement time of about 40 s/sample with the sample volume of 10 μ L.



Fig. 7 (a) Conventional bulk extraction with and without silica particles in the copper solution. (b) Cu extraction as a function of time: (line) particle-free bulk extraction, (points) microfluidic extraction. Reproduced from ref.⁵⁵ with permission from Wiley-VCH, copyright 2012.

Platinum group elements (PGE)

The most well-known method for extracting and refining PGEs is precipitation with the advantages of low effluent volumes and low capital cost ¹¹⁵. This separation procedure, however, is not fully efficient as valuable material could be hold up in the refinery for an extended amount of time due to the repeat of dissolution and precipitation steps to achieve the required purity specification, which can increase the operating cost a refinery ¹⁰⁹. The solvent extraction process proposes better selectivity, higher first-pass yields, and reduced exposure to chemicals by workers. However, the concentration of the solution used in the solvent extraction methods is lower in comparison with precipitation, thus requiring greater process volumes. Improvement of the kinetics of solvent extraction for two key separations (Pd and Au) is needed because they are, though better than precipitation, still low which resulted in hold-up in refinery ¹¹⁶. Precise handling of the organic solvents is also important as they are highly flammable. Their entrainment in an aqueous phase is highly undesirable as the next step involves oxidation. Secondary amines are commonly chosen for primary extraction of Pd but can also co-extract small amount of Pt, Ru and Ir, complicating secondary purification of Pt ¹¹⁷. Thus, solventextraction in microfluidic system has been extensively studied to identify whether reducing the flow to microscale could counter the aforementioned problems.

<u>Process development: productivity</u>. With the aim of maximising productivity in mineral processing, researchers are developing high-throughput microfluidic systems for PGE extraction, since the majority of PGE extraction studies operated at low volumetric throughputs. To address this requirement, a microfluidic extraction chip was investigated, which comprises 49 inlets (24 aqueous and 25 organic streams) and a large contact area for separating Pt (IV) from an aqueous leaching solution, as shown in Fig. 8⁷². The device exhibited higher volumetric throughput, enhanced extraction efficiency, and allowed multi-stage counter-current microfluidic extraction. Recently, the multistream microchip has been up-scaled to successfully extract high value metals from industrial leach solution with a throughput up to 1 L/h without compromising extraction performance⁷¹.



Fig. 8 (a) Schematic illustration and (b) photo of the new chip design showing organic and aqueous inlets, streams merging, and the contact zone. Reproduced from ref.⁷² with permission from Wiley-VCH, copyright 2017.

Process development: integration Industrial operations are commonly process integrated in the sense of integrating operations for their mutual benefit (BASF's famous "Verbund concept"). With this background, a solution needs to cover the three stages involved in refining a solution containing high concentrations of target metals from primary sources: extraction; scrubbing; and stripping. Each of these stages require complex types of equipment that take up space and are energy-intensive in conventional plants due to the lengthy operating times involved. They can, however, be downsized and intensified using a microfluidic approach. Kriel et al. developed a microfluidic system capable of handling extraction, scrubbing and stripping for the extraction of Pt(IV) from an aqueous phase with high loading (Fig. 9) ⁷⁴. The extraction reached equilibrium within several seconds (2-6 s) while stripping equilibrium required a longer contact time (~12 s). In this research, a quantitative study of phase disengagement efficiency also revealed that both phases suffered cross contamination, with the aqueous phase containing up to 2-3% of the organic phase.



Fig. 9 Platinum extraction via a microfluidic system with three main unit operations: extraction, scrubbing and stripping. Reproduced from ref. ⁷⁴ with permission from Elsevier, copyright 2015.

<u>Sustainability: circularity</u> Microfluidics can play a key role in the circularity asset of processing critical minerals. Secondary (recycled) sources of PGEs, including those rich in high intrinsic value metals Pt and Pd, are only worth recovering if the manufacturer can employ a rapid and effective extraction system. The diffusion limited ion exchange mechanism and the microscopic dimensions of the system are expected to produce a rapid extraction rate, and indeed this was observed in the aforementioned work of Kriel et al., in which extraction equilibrium was achieved in just 2-6 s⁷⁴.

Boron group metals and transition metal group metals

Extraction efficiency Indium (In) plays an essential strategic role in the military, nuclear and computer technology sectors. The quality of In products can be severely compromised by impurity elements. The development of an effective extraction method for separating In from impurities is thus important. The extraction and separation of In from aqueous solution using microfluidics were optimised at pH of 0.7, a concentration of 30% and contact time of 60 s⁷⁷. The

microfluidic system employed showed capability to reduce the contact time by half and to significantly improve the separation factor between In and Fe/Zn/Al/Mg⁷⁷. Furthermore, the microfluidic chip also allows process integration via the connection of units (extraction and stripping) with process analytics through ICP-MS. In this way, a higher selectivity and effective handling of radioactive materials was achieved.

Rhenium was extracted and stripped using a Y-Y shaped microfluidic chip under a stable two-phase flow and analysed with ICP-MS 118 . The total process time for a 1 mL sample was less than 1.

Rare earth elements (REE)

The separation efficiency of REE can reach up to 99% using hydrometallurgical operations ¹¹⁹. Here again, solvent extraction is used by contact of an aqueous phase and an organic phase followed by the movement of metallic ions from one phase to another. This process is effective in removing metal ions from water and results in solutions of single rare earths and compounds with high purity ¹²⁰. Though being used commercially, this method is only applied to nondilute metal solutions, is time-consuming, labour-intensive, and requires high volumes of chemical reagents ¹²¹. Microfluidic devices have been shown to separate heavy REEs from mixed REE oxide after only 10 s¹²⁰. Nonetheless, microfluidic extraction of REE is only suitable for dilute solutions and require high energy input ⁹³ and can show inadequate phase separation times in complex solutions ¹²⁰. Hence, further studies have been designed to improve the performance of microfluidics for separation of REEs, including the use of ionic liquids ⁸⁸, modifying microfluidic chip design ⁸³, and testing multi-solute mixtures ^{86, 87}.

Fundamentals: designer solvents Ionic liquids are attracting attention as an alternative solvent for liquid-liquid extraction of metal ions from an aqueous phase. Additionally, ionic liquids as a diluent for appropriate extractants can yield a higher partition coefficient for the separation of lanthanides than conventional solvents. Despite this. their high production cost hinders their wider application at an industrial scale. Microreactors that require minimum amounts of solvent can be a solution for the aforementioned shortcoming of ionic liquids in liquid-liquid extraction. With that objective, Li et al. performed the extraction of Eu (III) from aqueous solution using an ionic liquid solution (n-octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO)–1.2 M tributylphosphate) in a smallscale separation unit ⁸⁸. The mass transfer coefficients in the small separation unit were higher than those of larger channels with the same flow conditions (i.e. velocity, composition, liquid-liquid ratio).

<u>Reactor development: stabilising walls</u> Although it is clear that microfluidics possess capability for highly efficient solvent extraction, phase separation is a vital challenge yet to be solved to ensure selectivity of the operation. A potential solution may lie in the integration of phase-separation flow structures in a microfluidic device. In 2002, a new design of a microchip integrated with guide structures (or walls) was proposed by Tokeshi et al. with the ability to separate coexisting metal chelates in less than 1s⁶⁰. Maruyama et al. showed that the addition of partition walls can stabilise the two-phase flow in the microfluidic device. The net result is an improvement in the extraction of yttrium ions from a feed aqueous

solution by 2-3 times at a very low contact time of 0.12 – 0.24 s, as shown in Fig. 10 $^{\rm 83}.$

<u>Reactor development: mixing</u> Xie et al. recognised the potential of chaotic advection microfluidics for enhancing mass transfer between two immiscible phases for application in the production of REEs⁸⁵. In their study, a three-stage micromixer based on the principle of passive chaotic advection micromixing was designed for the extraction and separation of Pr and Ce. Pr(III) and Ce(III) could be extracted from a nitric acid media with a high throughput of 100 mL/min and a short residence time of 0.029 s⁸⁵.

<u>Process development: intensification</u> Conventional extraction of La(III) usually comes with limitations such as long mass transfer distance and mixing time, large area requirements, high energy consumption, and in particular, the need for a large amount of organic solvent for dissolving extractant and extracted species. To address these issues, Yin et al. performed the extraction of La(III) in an aqueous phase using a stable two-phase flow in a microreactor, producing a high extraction efficiency (almost 100% at their optimal conditions) in a short contact time (0.37s) ⁸⁴.





Fig. 10 (a) Schematic illustration of the partition walls in microchannel. (b) Yttrium extraction in microchannel with partition walls (black circles) and without partition wall (white circles). Reproduced from ref.⁸³ with permission from Royal Society of Chemistry, copyright 2004.

<u>Process development: simplification</u> Gadolinium (Gd) can be extracted using the conventional method, but the efficiency of this process is significantly impacted by the operation cost and time. This requires multiple separation stages and issues such as emulsion formation, loss of analyte and extractant. To achieve a more efficient method for extracting Gd, the Y-Y microchannel used by Abbasi et al. was capable of separating Gd with the yield up to 95.5% in optimal conditions ⁹¹. As shown in Fig. 11, under a low concentration of Gd (2.9 vol%), their system managed to perform the extraction in 13.5 s. This highlights the potential of microfluidics for extracting strategic metals at low concentrations in a simple, fast and effective process.



Fig. 11 Effect of residence time on Gd extraction efficiency at pH = 3, feed concentration = 30 ppm and MDEPA concentration = 2 vol%. Reproduced from ref.⁹¹ with permission from Elsevier, copyright 2018.

Real-world readiness: multi-solute mixtures Real-world adaptability is relevant when using microfluidic systems. To turn an academic curiosity into a commercial product, there is a need to address the fact that most studies on microfluidic extraction of REEs focus on extracting only a single element from a simple aqueous phase. Realworld industrial leaching solutions will always contain multiple REE, as well as other metals including U and Th, and other components such as chloride solution, which will likely impact on extraction behaviour. The presence of radioactive Th and U in many REE deposits is a challenge for separation as it is vital to produce REE products with minimum associated radioactivity in downstream processing, and to mitigate environmental and safety issues. Kolar et al. studied the microfluidic extraction and separation of light and heavy REEs from a leach solution derived from industrial-grade mixed REE ore ⁹³. Their system exhibited good selectivity for heavy REEs at an aqueous feed pH of 0.7. Yin et al. and He et al. studied the extraction and separation of Pr/Ce or Pr/Nd. They used a Y-junction serpentine microreactor in chloride solution using lactic acid as complexing agents to buffer the high acidity ^{86, 87}. In the case of Pr/Ce (Fig. 12), the separation factor was greater than 3 at the optimised time of 12 s, while batch extraction achieved a separation factor of 2-3 and time of 300 s ⁸⁶. The separation factors of Pr/Nd for both microfluidic and batch experiments were relatively similar but the residence time for microfluidic was significantly shorter at about 12 s compared to 560 s⁸⁷.



Fig. 12 Rare earth elements as a function of contact time for (a) microfluidic and (b) batch extraction. Reproduced from ref.⁸⁶ with permission from Elsevier, copyright 2017.

Real-world readiness: low concentration. One common thread in the literature on solvent extraction of REE is the phase ratio. Most studies have investigated ratios of 1:1, even though in secondary sources such as wastewater, the REEs are present at markedly lower concentrations (<100 ppm), which translates to a high phase ratio in excess of 50:1. In this case, conventional methods require high external energy input, large volumes of solvent, long mixing times, and loss of extractant. Microfluidics have attracted interest as an alternative because they are able to handle the harsh chemical conditions involved in separating REEs. For example, Nd(III) can be extracted from an aqueous phase with a common set-up of microchannels. Zhang et al. separated Nd(III) from aqueous solution using P507 as extractant and obtained a duration of 1.5s for equilibrium extraction in a two-phase flow in a microchannel system (100 μ m in width and 120 μ m in depth) ⁹⁰. Addition of another phase, such as a gas phase, in the separation unit may pose positive effects on the overall extraction efficiency. Chen et al. investigated the extraction behaviour of Nd(III) using a gas-liquid-liquid system in a Tjunction microchannel ⁸⁹. The presence of a gas phase increased the mass transfer coefficient from 5 to 50 times and the extraction efficiency was higher than 90%, even at a high phase ratio of 200.

Actinides

Fundamentals: designer solvents Following the trend of green chemistry, researchers are searching for a greener solvent for extraction of metal ions, and ionic liquid has the potential to become an alternative solution. Tsaoulidis et al. extracted U from aqueous nitric acid solutions using TBP (30%) in ionic liquid ⁹⁵ with the overall volumetric mass transfer coefficients in agreement with results obtained in other studies using plug flow solvent extraction in microchannels.

<u>Process development: integration</u> Microbore tubes represent a cheap, simple solution for solvent extraction. However, these can only be used up to a certain flow rate, above which pressure drop and generation of fines would occur. To increase throughput, parallelisation can be implemented to expand the number of microbore tubes. Darekar et al. performed a study in multistage extraction and stripping of U using 20 parallel microbore tubes, as shown in Fig. 13a ¹⁰¹. In this study, coiling of microbore tubes was found to enhance the overall volumetric mass transfer coefficient (Fig. 13b) and the smaller the coil diameter was, the more pronounced the effect it had on mass transfer.



Fig. 13 (*a*) Schematic of monoblock distributor with integrated microfluidic junctions with 20 microbore tubes. (*b*) Effect of flow rate on overall volumetric mass transfer coefficient. Reproduced from ref.¹⁰¹ with permission from Elsevier, copyright 2018.

<u>ESG: radionuclide removal:</u> The literature focussing on the process of U recovery in microchannels is sparse. Nevertheless, implementation of this process by microchannel processing is beneficial in terms of mobility and efficiency. Sen et al. studied the effect of the organic-aqueous phase ratio on the extraction efficiency for a U recovery system from extraction to precipitation of U ⁹⁶. Their system could

<u>ESG: radionuclide removal</u> Development of an innovative and safe separation technology is essential for the reduction of radioactivity when separating critical minerals. Such technology must be able to handle removal of actinides as well as their short- to medium-half life daughter radionuclides from radioactive wastes. Related to that, microfluidics are attracting attention in reactions involving hazardous and explosive substances because of their small volumes and rapid processing times. Garciadiego-Ortega et al. investigated the extraction of U in small channels of different sizes under segmented flow ⁹⁴. The 4 mm channels proposed a segmented flow with good mass transfer performance and a high flow rate (11 L per day). Hotokezaka et al. studied the extraction of U(IV) from aqueous phase to organic phase (30% or 100 % TBP) to clarify extraction behaviour ¹⁰⁰.

Scalability

Up-scaling of microfluidic reactors has been practised for chemical reactions and flow chemistry, both for fundamental motivations (e.g. concerning flow distribution ³⁸) and for industrial uses at pilot- or production scale ¹²². In most cases, this has been done for liquid-phase reactions, and only a few times for gas-liquid and liquid-liquid reactions (since multi-phase processing at the micron scale suffers from flow distribution) ¹²³. Commercial offers of such high-capacity reactors have promoted industrial application ¹²⁴. As outlined below, this may involve a transition to milli- or meso-scale, and therefore the term continuous-flow may be more adequate for the scaled-out flow reactors.

In the ideal case, up-scaling of microfluidics means that the microchannel is repeated multiple times and operated in parallel fashion; this is also termed equalling-up or internal numbering-up ^{125, 126}. Nature uses the same concept by numbering-up cells in an organism. Schenk et al. have introduced the terms internal and external numbering-up, respectively ¹²⁵, for operation of parallel microchannels within one device and many parallel devices with a microchannel each. Solvent-extraction performance, for example, is maintained in numbered-up systems despite crossing several orders of magnitude throughput and minimises the inventory of potentially hazardous streams ⁷¹. Some internally numbered-up microstructured reactors for gas-phase reactions have been manufactured with several hundred or even thousand microchannels, demonstrating technical manufacturing capability ^{127, 128}.

For liquid-phase applications, as reported here, the equalling-up approach can face limits in terms of flow distribution quality, fouling, sensitivity, capital costs, and more. Nonetheless, especially for applications with microstructured mixers, highly-parallel microstructured devices have been reported and are commercially available ^{129, 130}. Those devices typically contain microchannels of very short length or just nozzles, which reduces pressure drops and allows high capacity ^{131, 132}.

In most cases for liquid-phase applications a different scale-up strategy pioneered by the Lonza Group is chosen; this has been termed scale-out ^{133, 134}. First, the reaction is intensified, meaning to utilise highest concentrations and temperature (and pressure) in the

microchannel, a strategy which Hessel et al. termed novel process windows ¹³⁵. Subsequently, the channel size is increased until the microreactor performance drops ¹³⁶. Often, this means scaling the characteristic channel dimensions to a few mm or, in a few cases, even larger so that meso-flow might be used ¹³⁷⁻¹⁴². This strategy has been largely adopted by pharmaceutical companies for medicinal flow chemistry ^{143, 144}. One common commercial flow reactor example is the Corning Advanced-Flow Reactor ^{41, 145}, with internal dimensions above the micron range.

Industrial flow reactors have flow rates of up to several 100 L/h 133 , 146 . Assuming a product load of up to 10% (at a density of 1 kg/L and an annual production of 300 days), this equates to an annual capacity of several hundred tons of product. These flow reactors have not been tested for minerals processing applications and would likely need a further increase in capacity to be industrially viable.

Real world minerals processing is often plagued by issues of fouling and corrosion phenomena, which are not currently known or reported in the flow chemistry and microfluidic literature. Such obstacles would therefore need to be overcome by substantial developmental research before continuous-flow reactors could reach applicability for the processing of real ores and extraction at an industrial scale. For the arguments given, microreactors will likely be best suited to high-end applications with relatively purified solutions at medium capacity.

Microfluidics for ESG in the mining industry

Environmental, social, and governance (ESG)

There is a growing awareness across industry that environmental, social, and governance (ESG) policy issues are central to major investment decisions, and to public perceptions of the minerals industry. Based on the framework designed by The Danish Veterinary and Food Administration (DVFA) and accepted by The European Federation of Financial Analysts Societies (EFFAS), the following criteria of ESGs is applied to all industry-groups ^{147, 148}:

- Environmental (E)
 - ESG1: Energy efficiency
 - o ESG2: Greenhouse gas emissions

- Social (S)

- ESG3: Staff turnover
- ESG4: Training and qualification
- ESG5: Maturity of workforce
- ESG6: Absenteeism rate
- Governance (G)
 - ESG7: Litigation risks
 - o ESG8: Corruption

A recent report by Meyers et al. ¹⁴⁹, stated that the impact of ESG on mining appears to be of highest priority, and far greater than the economic problems caused during the COVID-19 pandemic. Similar findings were highlighted by several mineral executives interviewed by EY between June and September 2021 ¹⁵⁰.

Mining is an emission-intensive sector responsible for around 4–7% of total worldwide greenhouse gas (GHG) emissions ¹⁵¹. Identifying alternative energy sources is a rapidly emerging issue, as is the sector's heavy consumption of (finite) water resources. There is

currently pressure from government, shareholders, and employees and the broader community to transform this heavy industry into a carbon-neutral one and to achieve this considering a wide range of ESG factors.

Although many miners have restructured and announced new policies to improve their ESG performance (by the International Council on Mining and Metals or from the World Bank or other financiers and investors), they are still struggling with development of affordable yet sophisticated tools to balance environmental impacts and economic opportunities. At the same time, national and international regulations and compliance are becoming increasingly complex and restrictive. ESG issues currently represent a critical threshold for the realisation of opportunities in mining and metal production, while balancing risks.

Thus, ESG should be an integral element of today's and tomorrow's business approaches and needs to be adopted as an integral component of company culture and values, with ESG performance reflected in terms of financial, operational, intellectual, reputational, human, and/or natural capital. For exploration of new critical mineral resources, it is important to evaluate the effects of mining activities on local communities, ecosystems, and the carbon-reduction targets of each country.

Better ESG assessment tools and measurements, however, can only advocate for the best practice using currently available technologies. On the contrary, emerging technologies can lead to step changes in business models. Microfluidic continuous-flow technology has arguably achieved that status in the pharmaceutical industry, with flow chemistry being officially listed as one of Australia's so-called frontier technologies ¹⁵². The pharmaceutical legislative authority in the USA, the Federal Administration of Food and Drug Administration (FDA), have termed flow chemistry as an emerging technology, and have invested in an implementation strategy including offering frontend discussion and advice to industry to foster product submissions to FDA approval ¹⁵³.

Thus, having already accomplished an industrial transformation and with the technological verifications presented in this review, the question is what advantages microfluidics can offer for ESG in the mining context? The Australasian Institute of Mining and Metallurgy (AusIMM), a peak body representing the mining industry and its employees, have highlighted the most important ESG challenges and risks for the mining sector ¹⁵⁴:

- 1. Urgent and visible pressure on the mining sector to climate change and environment
- Missed process optimisation opportunities ("green processing")
- 3. Poor ESG credentials can affect capital and investment
- 4. Poor ESG performance linked to problems attracting and retaining staff
- 5. **Regulations, compliance, and reporting frameworks** are becoming increasingly complex
- 6. Many mining companies lack sophisticated digital reporting tools

7. Shift in demand for critical minerals

Based on the pharmaceutical business case and the technological demonstration given in this review, microfluidics can offer several advantages for ESG in the mining context. While (3), (4), and (5) might be achieved through the adoption of new policies, (1), (2), and

(6) rely heavily on the application of new and emerging technologies. The latter three refer to the social-legislative impact of emerging technologies, which are difficult to access, yet are considered to be the primary drivers for implementation of microfluidics by the pharmaceutical industry. Fig. 14 shows potential solutions and benefits of using microfluidic continuous-flow technology for minerals processing, towards the ESG mining issues (1) - (6).



Fig. 14 Benefits of microfluidic flow technology, proven in the pharmaceutical industry, and their potential benefit to improve ESG factors in the mining sector.

Concerning issue (1) and with evidence from the examples mentioned in this review, a prime solution to minimise environmental impacts, including reduced consumption of water and energy, can come from microfluidics and flow chemistry. High leaching yields and extraction efficiencies lower the amount of waste created. Although they are demonstrably efficient at a small scale, work is currently underway to match the output of microfluidic systems to the industrial scale. Concerning issue (2) and with other examples covered in this review, microfluidics and flow chemistry have facilitated exploration of modular technologies by industry and the efficient use of green chemistry. The first allows, by, inter alia, flexible campaign manufacturing and distributed process installations at remote sites. The latter are supported by applying concepts of process simplicity, which are crucial for small-scale opportunities as opposed to dedicated large-scale plants with heavy investment. Concerning issue (3), microfluidics and flow chemistry have shown a capability to not only significantly reduce CAPEX costs but have potential to also reduce OPEX compared to conventional technologies 44, 155, 156. Microfluidic plants have small spatial footprints and allow rapid generation of cash-flow (break-even point) due to their modularisation for ease of construction, prelegislation, and fast start-up 146, 157. Concerning issue (4), microfluidics and flow chemistry can attract a career-oriented workforce by offering secure employment in a frontier technology sector seeing an expanding market. This may facilitate a switch from a mining engagement to a job in another industry sector and vice versa, increasing employee mobility and enhancing attractiveness of a career in the minerals industry. While any compliance impacts of microfluidics and flow chemistry, see issue (5), cannot be foreseen at this point of time, it is noteworthy that a global legislative authority (FDA) have established their Emerging Technology Program (ETP) to

examine compliance issues ¹⁵⁸. Concerning issue (6), and as partly shown in this review, microfluidics and flow chemistry have can offer fast process screening ¹⁵⁹⁻¹⁶¹ to explore all opportunities before making decisions on investment, which is fundamental to process automation ^{162, 163} and may play a role in the Industry 4.0 revolution. Most importantly microfluidics provides a direct pathway to scalability from the laboratory- to large-industrial scales that is desired for optimal productivity. Equalling up processing from the miniature laboratory scale to large industrial productivity has been achieved? ^{71, 72, 126, 164}, as shown for the extraction of Co and Ni using microfluidic technologies ^{41, 51, 61, 62}.

While this review has focussed on mineral refining applications of microfluidics, there are potential applications that extend across the entire processing and supply chain defined within the ESG context. For example, microfluidics may have capabilities for high-throughput screening discovery tools for geological site exploration and related process modelling, as well as benefits in terms of enhanced sustainability. Attempts have been made to develop pilot-scale systems for the extraction of high-value metals, as outlined in the recent work of Yang et al. in separating Pt from industrial leach solutions via a multistream microchip with a high throughput ⁷¹. Recycling light REE from end-of-life products via microfluidics and flow chemistry reduces environmental dispersal of pollutants (e.g. radioactive elements), has a lower carbon footprint, and is more sustainable than extraction from primary sources (i.e. mineral ores) ¹⁶⁵. From a social perspective, recycling light REEs can lead to the increase in the number recycling centres and create more jobs which is beneficial to human well-being ¹²⁰. From the governance point of view, the government can provide subsidies or financial incentives to encourage recycling of end-of-life light REE-bearing products, which can lead to a reduced dependence rely on importation of light REEs 120

Conclusions

Microfluidics, microreactors, flow chemistry and continuous-flow processing have demonstrated considerable process intensification at the laboratory scale with much promise for the processing of critical minerals. Their anticipated benefits include a reduction of processing time (and thus an increase in relative capacity), decrease in equipment footprint, and increased extraction efficiency. The latter is underlined by fundamental studies on mass transfer, such as determining the mass transfer coefficient. This follows expectations from known benefits of microfluidic technology for solvent-based extraction with other extractants. As a central issue to critical minerals and their multi-component mixtures, microreactors have demonstrated an increase in extraction selectivity, meaning extraction of a (much) higher proportion of the desired critical mineral species than the unwanted metals and impurities in the same mixture. This has been demonstrated especially well for the purification of a processing stream from a deposit in which critical minerals and radionuclides co-exist, and where the radionuclides represent not only a major and toxic impurity but may limit the saleability of product. A wide range of different critical minerals have been investigated, providing optimism for a broad technology application. The studies are often industrially motivated, with some already addressing the up-scaling of fluidic systems needed to

achieve larger capacity. Nevertheless, cost and environmental benefit analysis of this technology is in its infancy, unlike the chemical and pharmaceutical sectors where microreaction technology and microfluidics implementation is far more advanced. Thus, the next stage of research in this field is translation from laboratory demonstration to industrial applicability and will include studies aimed at separation of mixtures comprising complex separation problems, such as real ore/concentrate samples. This review has highlighted several attempts with model solutions, yet implementation can only be achieved once real-world separation problems have been successfully addressed. As a second threshold to industrial maturity, a scaling-up towards global-scale productivity is needed for the mining industry and its sub-challenge in minerals processing.

Outlook

This review demonstrates a proof of concept for the application of microfluidics technology in mineral processing. The next major step will be industrial-scale implementation of this processing capability for different critical minerals. This translation of laboratory curiosity to industrial practice will likely require the intimate involvement of the METS sector. In Australia, this sector has seen 200% in gross value added (GVA) growth since 2016, creating more than 1.1 million jobs. Continuous flow chemistry has been elevated to a critical technology by the Australian Government, making Australia, to the best of our knowledge, the only jurisdiction in the world giving microfluidics such prominence.

The introduction of a frontier downstream process technology such as microfluidics to critical mineral processing cannot be done without a robust plan for its symbiotic implementation into the whole processing and supply chain. Indeed, microfluidic technologies will be more powerful when addressing the comprehensive, pivotal needs of today's mining industry rather than being just an intensified solution to minerals processing alone.

The appropriate individual opportunities need to be identified. For example, microfluidics used in high-throughput sample screening tools represent an opportunity to support and complement faster geological site exploration in which process modelling uses machine learning of the complete mining value chain, inclusive of the ore type and mine-site location. As a further example, microfluidics can support concepts for holistic sustainability, starting with potential applications to reduce the impact of traditional mining techniques, e.g. in-situ mining using lixiviants, and then moving into enhanced refinery performance for hydrometallurgical processes. Holistic opportunities might include solutions that can contribute to reducing global warming, energy demand, minimal-invasive environmental damage, valorisation of radioactive waste, and proactive tailings management. Microfluidics can also contribute to a broader societal acceptance of the minerals industry as a crucial part of the solution to global sustainability.

The best bet for the first commercial application of the microfluidic technology may be within more traditional operations seeking to recover by-product metals from larger mining volumes, e.g. extraction of Co from Ni-(Cu) ores. Then, the operability and versatility might possibly be increased by a switch from dedicated processing plants to small mobile, modular processing plants that

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can be readily moved between distant mine sites. That may open 6. opportunities for mining smaller volumes of critical minerals, or those with more challenging separation problems (e.g. ores containing radionuclides).

Gazing further into the future, one might ask whether microfluidics would be feasible for mineral extraction in space. Space offers large reserves of critical minerals, e.g. on near-Earth asteroids. Such operations would, however, pose significant additional challenges, including microgravity, pressure and temperature conditions, and cosmic radiation, and would require a remote (automated) operation capability, modularisation to facilitate campaign processing (startup, shutdown), and an efficient, circular usage of resources. There is confidence that microfluidic technology can, overcome these issues to be a crucial tool for space chemistry (see Fig. 15). ¹⁶⁶⁻¹⁶⁸.



Fig.15 Microfluidic critical minerals processing in Space.

Conflicts of interest

There are no conflicts to declare

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