

Session 1

Sources and Availability of Materials for Lithium Batteries

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ABSTRACT

Lithium, as a feedstock for the battery industry, originates from two primary sources: hard-rock (generally spodumene and petalite), and brines. Brine processing results in the direct production of lithium chemicals, whereas the output from hard-rock production is tradeable mineral concentrates that require downstream processing prior to delivery, as refined chemicals, into the battery market. The processors of the concentrates, the 'converters', are the major constraint in a supply chain blessed with abundant mineral feed. The battery industry must overcome the constraints imposed by the converters, and this can be achieved through the application of the Sileach™ process, which produces lithium chemicals from concentrates direct, without the need for roasting.

The cathode chemistries of the most efficient lithium batteries have a common thread – a high dependence on cobalt. Battery manufacturers consume around 40% of the current production of cobalt, a by-product of the nickel and copper industries. This means cobalt is at a tipping point – production will not keep up with demand. In the short term, the solution lies in developing alternative cathode compositions, while in the longer term recycling may be the answer. Lithium Australia NL is researching the application of its Sileach™ process to waste batteries to achieve a high-grade, low-cost source of battery materials and, in so doing, ease the supply constraints on cathode metals.

To ensure that the battery industry is sustainable, better utilisation of mineral resources, more efficient processing technology, an active battery reprocessing capacity and less reliance on cobalt as a cathode material are all necessary.

THE LITHIUM PRODUCTION LANDSCAPE

Until the early 1980s, global lithium production was dominated by hard-rock mining, primarily from pegmatites. The advent of lithium chemical production from brines, primarily in South America, created a paradigm shift in operating costs. By the 1990s the low-cost brine producers, operating at half the cost of more conventional sources, after potash credits, dominated the market (USGS, 2016). This forced the closure of most hard-rock operations. Only those producing high-purity spodumene concentrates for specialist applications maintained viability, since they did not compete in the same market as producers of the low-cost chemicals emanating from brines.

The market for high-purity spodumene concentrates for the ceramics industry remained an opening that, today, is dominated by supply from the Greenbushes mine in Western Australia. That mine currently produces about 40% of the world's lithium requirements, much of which goes into glass and ceramic applications.

TO ROAST OR NOT TO ROAST?

The lithium chemical value equation

The principal ore mineral of lithium is spodumene, a lithium aluminosilicate containing 6 to 7% lithium oxide (Li_2O). Production of lithium chemicals from silicate minerals is achieved by roasting and subsequent leaching, the main cost component being the energy input for the roasting stage. Producing lithium carbonate, the most commonly traded lithium chemical, from spodumene costs around US\$4,000/tonne (Figure 1). During processing of the spodumene, the low-temperature polymorph α -spodumene must undergo a temperature-induced phase change to β -spodumene before effective leaching can occur.

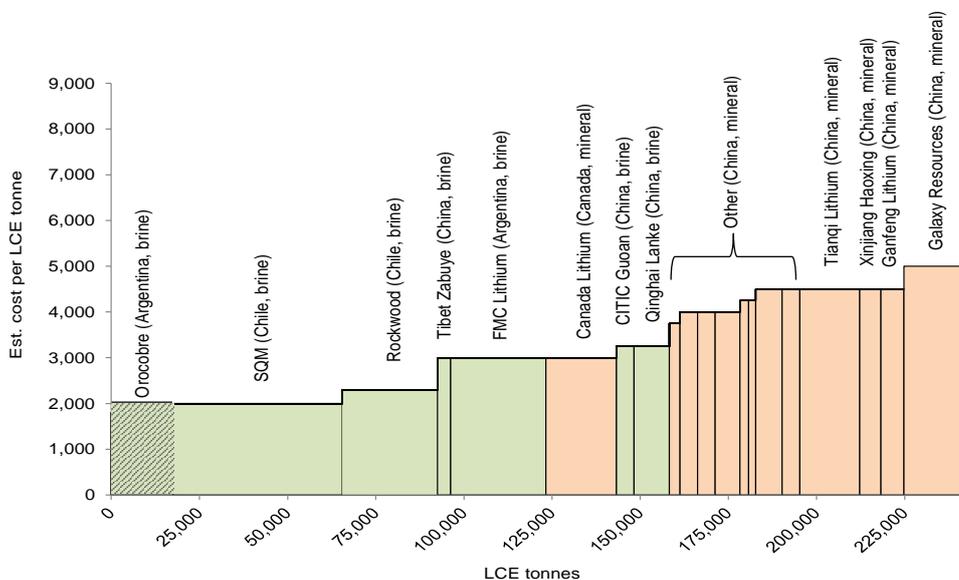


Figure 1. Estimated global lithium cost curve [source: Roskill (with modifications), 2014].

Adopting the same processing strategy for lithium micas with a grade of around 2% Li_2O , during which similar amounts of energy and reagents would be consumed, would make the cost of producing lithium carbonate from those micas about three times greater than the cost of producing it from spodumene.

Producing lithium carbonate from brines, where no roasting is required, costs around US\$2000/tonne.

Thus, it is the energy involved in roasting that renders the cost of lithium from silicates uncompetitive compared to the production of lithium chemicals from brines.

Removing energy from the equation

Hydrometallurgy has the potential to recover lithium from silicates without roasting. In its simplest form, an elevated-temperature sulphuric acid leach is capable of recovering lithium from silicates with a degree of success and potentially at an operating cost comparable with that of the brine producers. However, not all silicates are created equal, and reaction rates and recoveries vary considerably – to the extent that refractory phases such as α -spodumene do not react at all. Figure 2 shows leach rates for some of the common silicates, in sulphuric acid and at elevated temperature.

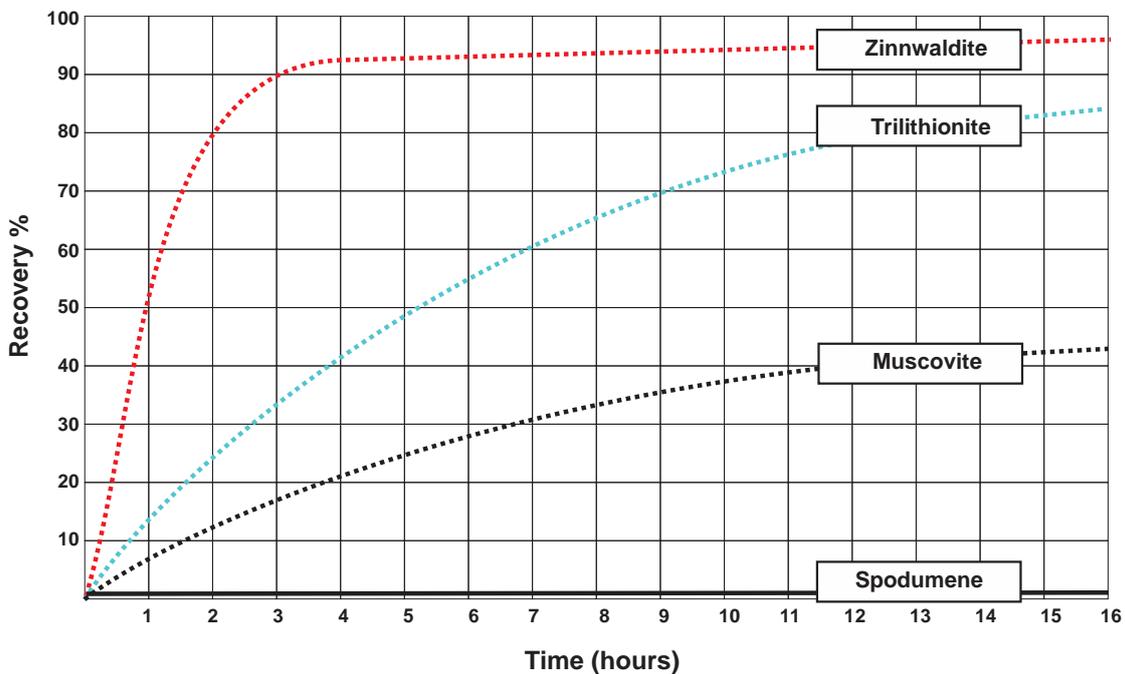


Figure 2. Extraction rates of lithium silicates in sulphuric acid at an elevated temperature.

HYDROMETALLURGY – MORE THAN CONTROL OF SULPHURIC ACID AND pH?

While there may be a case for a simple sulphuric acid leach, it does not achieve the best kinetics; nor does it optimise recovery. With simple sulphuric acid processes, the control of leach kinetics is limited to temperature and acid concentration, such control being far from optimal.

To assume that hydrometallurgy involves merely a sulphuric acid leach and refining of the pregnant liquor by subsequent pH adjustment is simplistic. Optimisation of the leach process involves identifying the crystal chemistry of the target species, determining the reaction mechanism and designing a bespoke lixiviant to achieve the desired outcome.

While sulphuric acid may be a great starting point for the recovery of lithium from silicates, it is not the ultimate driver of the digestion reaction. Lithium Australia NL ('Lithium Australia' or 'the Company') initially targeted a process for dissolving spodumene but has since developed a chemical formula for determining the optimal composition of a non-selective lixiviant for any silicate mineral. Creating an acidic lixiviant involves the addition of other reagents and catalysts to sulphuric acid. Initial development and testing of the lixiviants so devised by the Company is occurring under the terms of an intellectual property agreement between ANSTO Minerals (a division of the Australian Nuclear Science and Technology Organisation) and Lithium Australia. This work is funded in part by an Innovations Connections Grant under the auspices of the Australian federal government's Entrepreneurs Programme, run by the Department of Industry and Science.

THE SILEACH™ PROCESS

The Sileach™ process, with its zero energy footprint, is fueled by production of the very reagents that make it work. Figure 3 is a diagrammatic flowsheet of the process.

Oxidation of the sulphur that produces the sulphuric acid used in the Sileach™ process generates significant heat. Harvested as high-temperature steam, this heat feeds steam turbines to co-generate electrical power. Steam of a lower temperature is discharged for use in the heat exchangers that control the temperature of the metallurgical process circuit.

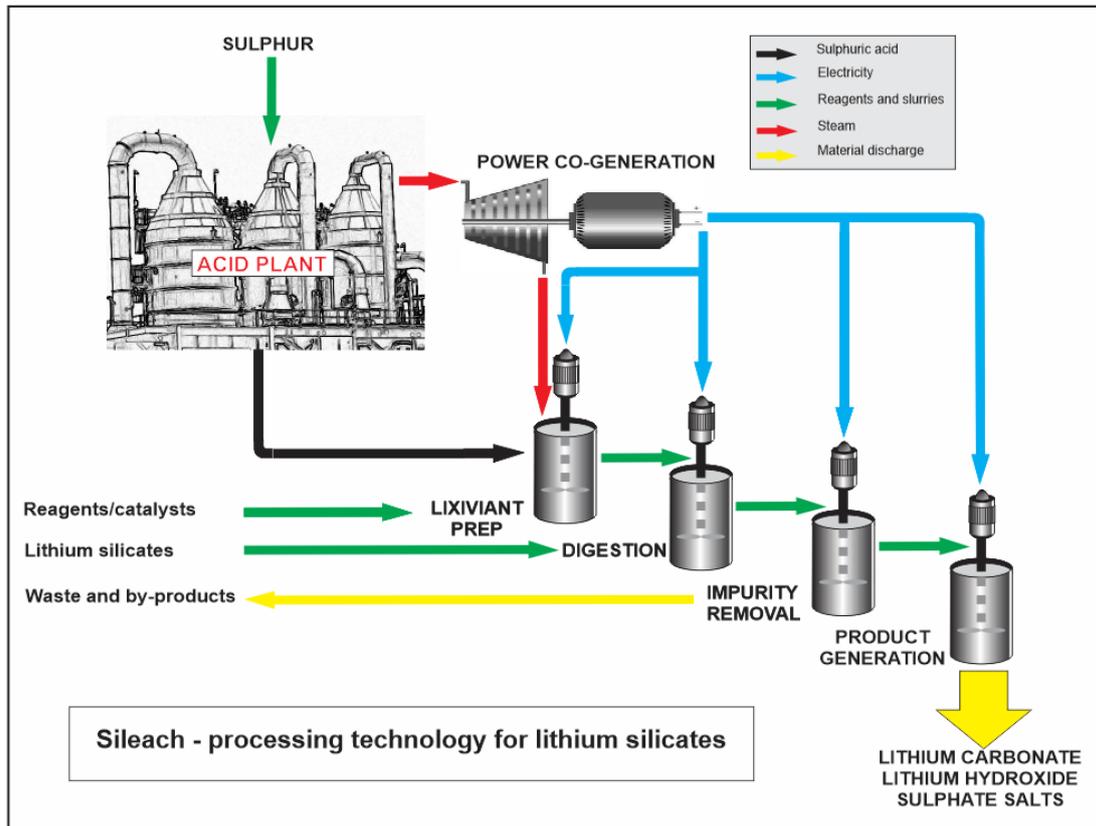


Figure 3. The Sileach™ process, which is capable of dissolving any lithium silicates, generates bespoke lixiviants via the reaction of sulphuric acid with other reagents and catalysts. Conventional power co-generation and heat recovery from the process producing the lixiviant enhance the energy efficiency of the process.

Using the Sileach™ process to recover lithium, particularly from spodumene, represents a paradigm shift in processing philosophies. For the first time, spodumene can be processed without roasting to produce lithium chemicals from that source at the bottom of the cost curve. Application of the technology will allow spodumene producers to supply direct to the battery industry.

BYPASSING THE LITHIUM CONVERTERS

Presently, spodumene processing involves the sale of concentrates to a third-party refiner or 'converter', which then generates the lithium chemicals. With limited new capacity in brine production, hard-rock production is a logical alternative, notwithstanding the fact that the operating costs of conventional processing technologies cannot currently compete with those for the production of lithium chemicals from brines.

With little spare capacity, lithium converters form a significant bottleneck in the supply chain. In addition, quality control is often less than ideal.

Application of the Sileach™ process is a convenient means of bypassing supply chain constrictions and delivering lithium chemicals direct from the mine gate to the end user. Output can be matched to the requirements of the end user by providing the option of supplying either lithium carbonate or lithium hydroxide. Lithium Australia is also investigating the production of other lithium chemicals that may better suit the battery market or niche applications.

With the Sileach™ process, producing lithium chemicals from commercial-grade spodumene concentrates (in the range 6 to 7% Li₂O) can be cost-competitive compared to their production from brines. This is a significant breakthrough for the hard-rock lithium industry. The lower cost profile of the Sileach™ process could also facilitate the processing of lower-grade spodumene concentrates, enabling lower cut-off grades to be assigned to existing resources. Inventories could thus be expanded without the need for further drilling.

Demand for battery-grade lithium chemicals is escalating. This places enormous pressure on maintaining the cost-competitiveness of hard-rock lithium operations. Adoption of the Sileach™ process for the production of lithium chemicals has the potential to save the industry hundreds of millions of dollars annually.

THE FORGOTTEN RESOURCE

Despite being developed initially for use with spodumene, the Sileach™ process can be applied to other silicate minerals as well. The process was developed specifically to deconstruct silicate mineral lattices, releasing all metals into solution. As such, the reaction mechanism can be more accurately described as 'dissolution' or 'digestion' rather than a leach (the latter selectively removes particular metal components while much of the silicate framework remains intact).

Lithium micas are the world's most abundant lithium minerals; however, they do have a grade penalty when compared with spodumene. The micas are typically in the range of 1.5 to 3% Li₂O, compared to spodumene at 6 to 7% Li₂O.

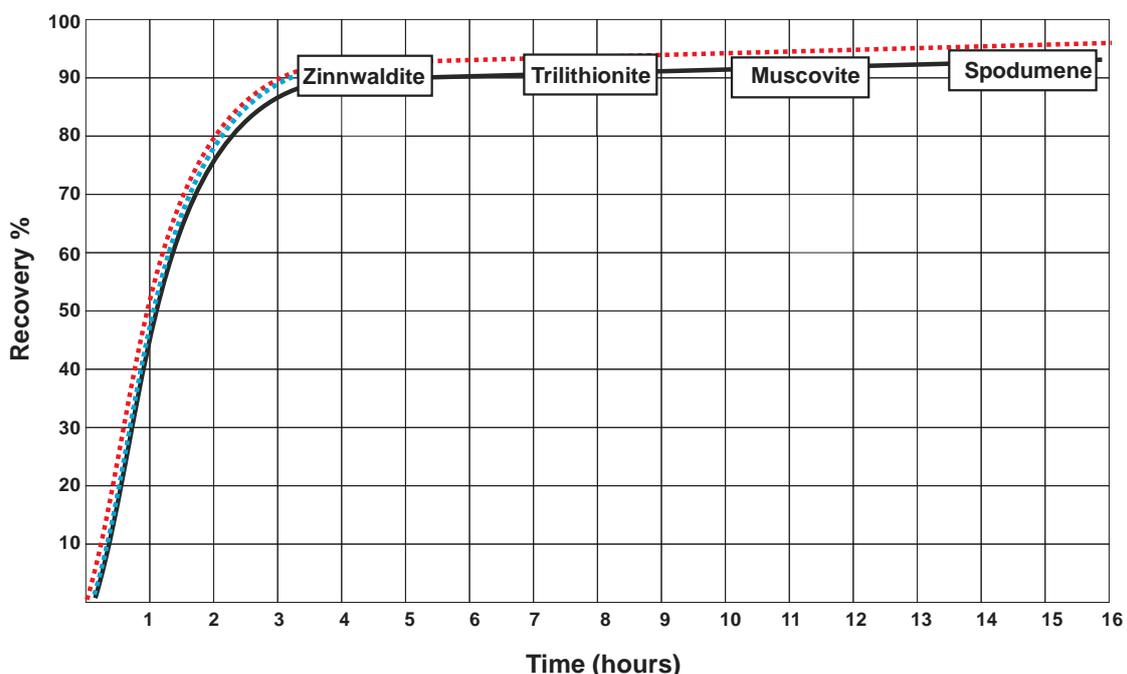


Figure 4. Optimised extraction rates for lithium, from various silicates, in bespoke Sileach™ lixivants.

While the time it takes to leach lithium from a mica lattice in sulphuric acid varies from one mica to another, the Sileach™ process completely deconstructs the crystal lattice of most micas, and extracts more than 90% of the metal values, within four hours (see Figure 4).

Lithium micas contain abundant potassium oxide ('K₂O'), generally in the order of 9 to 10%. Indeed, so high is the concentration of K₂O that they could well be considered potassium ores with a lithium by-product credit. It is these high levels of by-product credits, combined with the low-energy requirements of the Sileach™ process, that enhance the viability of micas. Similarly, a number of other silicates may be considered sources of lithium ore. They include amphiboles, pyroxenes, tourmalines, jadarite and some rare examples of lithium-bearing feldspars. With all of these minerals, the Sileach™ process lixivants can be designed to achieve optimum extraction rates.

Thus, the Sileach™ process allows the production of low-cost lithium chemicals from not only spodumene but also all other lithium-bearing silicates.

CATHODE MATERIALS – STRETCHING THE ENVELOPE

In relatively recent times, a wide range of battery technologies has evolved (Figure 5).

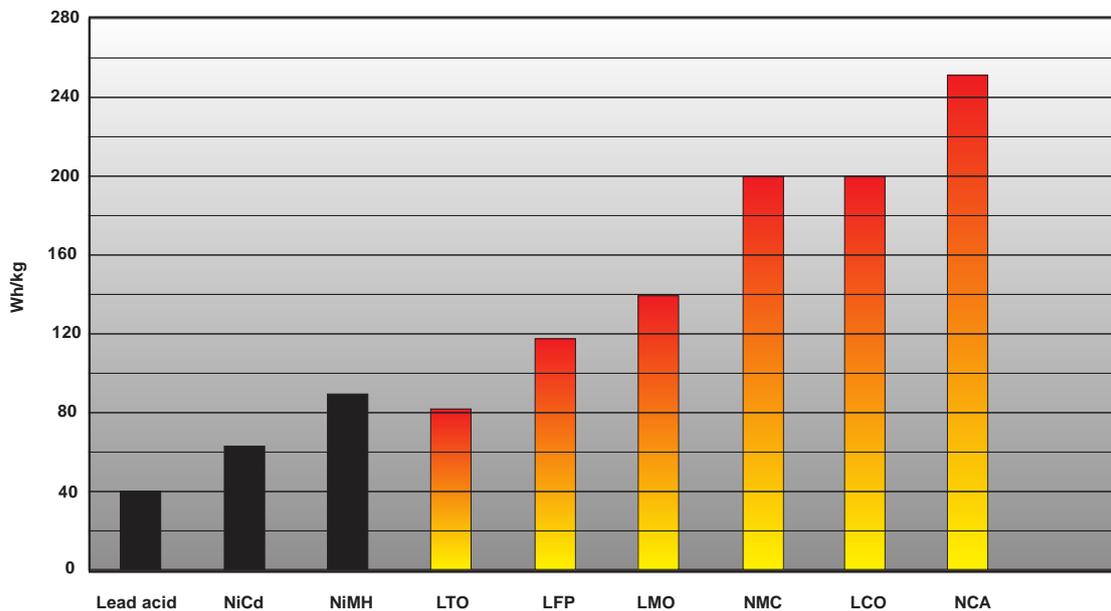


Figure 5. Comparative specific energies of common battery technologies [source: Battery University, http://batteryuniversity.com/learn/article/types_of_lithium_ion].

The plethora of lithium ion ('Li-ion') battery types currently produced includes the following.

- Lithium/titanium oxide (LTO)
- Lithium/iron phosphate (LFP)
- Lithium/manganese oxide (LMO)
- Lithium/nickel-manganese-cobalt (NMC)
- Lithium/cobalt oxide (LCO)
- Lithium/nickel cobalt aluminium

Li-ion batteries of the highest capacity have in common the use of cobalt in their cathodes.

In terms of global cobalt supply, the battery industry has been taking a progressively larger share, with demand now at an all-time high. Supply relates to copper and nickel production, with cobalt a by-product of this. Thus, it is very difficult to increase the availability of cobalt without expanding nickel and copper production. In a depressed commodity cycle, as is the case at present, consumption compared to availability must be approaching a tipping point. Further, the battery industry's demand for cobalt as a cathode material must compete with demand for the use of cobalt in specialty metals, among them the high-tech alloys required for specialist applications, including high-speed steel tooling, turbine blades and military applications. Further, most cobalt originates from the war-torn states of central Africa, where child labour is rife and the ore often used as currency for arms trading. From an ethical standpoint, sourcing cobalt from these zones is subject to increasing scrutiny and it may eventually be outlawed by a number of governments.

The battery industry's response to the cobalt tipping point should be twofold; it needs to develop both:

- early – and efficient – recycling practices, and
- alternatives to cathodes containing cobalt.

At present, only about 4.2% of the Li-ion batteries consumed in Australia are recycled (ABRI, 2014) and it seems this is not far from the global average. Recycling involves many practical difficulties and any expansion is unlikely until such time as the market approaches saturation and a significant number of batteries exceed their useful life. Neither scenario is likely in the near term, so new battery production will continue to outstrip recycling capabilities.

Recycling of battery materials is not limited to the potential extraction of cobalt. That said, cobalt is presently the most valuable component of many Li-ion batteries. Other cathode metals can be recycled too, of course, as can the lithium in the anodes and electrolytes (Hanisch, 2015).

In the short term, development of cobalt-free cathodes could be the solution to an otherwise potentially severe restriction in the battery supply chain. In particular, the lithium/sulphur ('Li-S') battery, with a cathode of graphite and sulphur, shows huge promise. The Li-S configuration not only eliminates the

requirement for cobalt but may also carry up to five times the charge density of competitive cobalt-based batteries (Beetz, 2014). The downside is controlling heat dissipation during the charging cycle. That consideration aside, Li-S is the only battery type with sufficient capacity to drive an attempt at global circumnavigation by a zero-fuel aircraft. (The *Solar Impulse*, a Swiss long-range experimental solar-powered aircraft can fly at night on batteries charged during daylight hours. It has so far set a duration record of 116 hours aloft without refuelling.)

WHERE NEXT FOR LITHIUM BATTERIES?

Technology can help maintain lithium supply

Clearly, hard-rock lithium projects need to adapt their processing routes to remain competitive with brine lithium producers. Further, the amount of lithium chemicals produced from spodumene and other lithium silicates needs to be increased. The technology to fulfill both aims is now available, in the form of the Sileach™ process, which has the potential to commercialise the recovery of lithium not just from spodumene but also from a wide range of other silicates, thereby broadening global resource inventories.

Cathode substitution to alleviate reliance on cobalt

Improved cathode technology involving cobalt substitutes, coupled with vastly improved lithium battery performance, is likely to overcome cobalt supply difficulties. Li-S batteries, for example, with a cathode of graphite and sulphur, already significantly outperform Li-ion batteries incorporating cobalt alloy cathodes. Indeed, the Li-S configuration, as well as being a prime contender in resolving cobalt supply issues, may even come to dominate the portable energy storage space in due course. While commercialisation of Li-S cells is in its infancy, the potential to substitute a cathode material costing US\$200/tonne (sulphur) for one costing US\$24,000/tonne (cobalt) while achieving a fivefold increase in efficiency (Hagen *et al*, 2015; Oxis, 2016) is beguiling.

Recycling

Market saturation, end-of-cycle disposal and cost incentives are required to make widespread recycling of lithium batteries viable. Many aspects must be considered as the industry matures and approaches steady state (Gains, 2014). Even so, matching the +90% recycling rates achieved in the lead-acid battery business may prove difficult. Moreover, the fact that almost 90% of Li-ion batteries are sold with, or in, the products they power – and are thus disposed of still within their ‘hosts’ – is another significant challenge (Lithium Australia NL, April 2016).

The many and varied components of current lithium batteries include casings, anodes, cathodes, electrolyte, separators and, often, organic solvents. While the value of the contained lithium is relatively small, the cathodes in most instances represent the highest component value. Periods of high metal prices, or shortages in the supply of cathode metals (cobalt in particular), are commercial imperatives for recycling. Indeed, the metal concentrations in the

recycled material may prove a most competitive source of new materials, removing much of the industry's reliance on freshly mined metals. However, a major shift towards Li-S batteries could diminish the value of any retrievable metals within other types of lithium batteries and make their recycling less attractive commercially; that said, recycling remains imperative from an environmental point of view.

Only time will reveal the extent to which lithium batteries can be recycled. Lithium Australia is researching the extent to which the metal species within such batteries can be reclaimed, effectively treating them as the ore feed to a hydrometallurgical circuit.

CONCLUSIONS

- While there is no shortage of primary lithium resources, integrated flowsheets like the Sileach™ process will enable supply of competitively priced lithium chemicals to the battery industry in the long term. Other lithium silicates can supplement spodumene feed sources, and the brine producers will continue on a similar cost basis to the new generation of hard-rock producers.
- Supply constraints on cobalt can be alleviated by the use of alternative cathode technology, which has the potential to deliver better battery performance at a lower price.
- Effective lithium battery recycling will result from a maturing of the lithium battery industry and stable supplies of end-of-life product. Such market conditions are yet to be met, and the great variety of current battery chemistries makes designing efficient recycling plants a real challenge. In the short term, recycling will be driven by cobalt shortages. Later, as the industry phases out cobalt cathodes, environmental considerations will create the overriding imperative for recycling.

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