ALTA 2019 NOVEL LITHIUM PROCESSES PANEL DISCUSSION

May 2019

The panel discussion was held on Friday 24 May 2019, immediately following the Lithium Processing sessions at ALTA 2019 in Perth, Australia.

Panel Chair: Dr Chris Griffith (CG), ANSTO Minerals (Australia)

Panel Participants (left to right): Dylan van den Berg (DB), Hatch (Australia); Mike Dry (MD), Arithmetek Inc. (Canada); Goutam Das (GD), CSIRO (Australia); Marika Tiihonen (MT), Outotec (Finland); Grant Harman (GH), Lithium Consultants Australia (Australia); Adrian Griffin (AG), Lithium Australia (Australia); Alexandre Chagnes (AC), University of Lorraine (France)

***Editor's Note**: The contributions of the panel members and delegates are not presented verbatim, but rather have been paraphrased and condensed for clarity and brevity. They are not necessarily recorded in order but are grouped into major topics. Also, it is not feasible to include all contributions made during the discussions, and they are limited to some that are representative of the key points raised and debated.*

Sodium Sulphate Issue

CG (chair) opened the discussion by asking the panel whether there is any improvement that can be made to improve current processing - in particular, the sodium sulphate problem in conventional processes for lithium hydroxide or lithium carbonate production.

DB (panel) responded that the first option is to try to sell the sodium sulphate if there is market for it and accept a low or no margin for someone to take it. This may be feasible for a single plant, but for a number of plants starting up, finding a market will be a problem and disposal (long term) will be required. Since sodium sulphate is highly soluble, this will require an engineered facility, and a risk remains of release to the environment. So the best option is not to produce it.

CG (chair) in Western Australia (WA), asked about the feasibility of obtaining a permit for such a facility.

DB (panel) was unable to comment on the permit aspect. As a possible option, he has seen electrolysis being proposed to regenerate caustic and sulphuric acid which are concentrated and recycled. However, this is very energy intensive, and unlikely to be economic.

GH (panel) commented that the sodium sulphate issue is a common concern. Depending on the technology, the ratio of sodium sulphate to lithium carbonate produced in his experience will be the range of 2.2 to 4.5, so when you are visiting a plant, the white mountain you see is sodium sulphate, not lithium carbonate. Because of this problem, the Namaska project has adopted electrolysis and avoided sodium sulphate by-product.

CG (chair) added that to his knowledge there is a significant power advantage for chloride electrolysis with 1 kwh/m^2 versus 7 for sulphate. He raised the question of using HCl rather than sulfuric acid at the back end as it is a lot easier to dispose of a brine. Why not accept a slightly lower recovery in order to have an easier back end?

GD (panel) Regarding sodium sulphate as a dump product assumes that we cannot do anything productive with it. Why not look at it as an opportunity to convert it into a product? He is doing testwork along these lines for a plant, but he could not give any information. In response to a query from CG (chair), he added that the question as to whether it is economic depends on how your look at it.

Ahmad Ghahreman, Queen's University (Canada) (**floor**) another option is to mix potassium chloride ($200/t) and sodium sulphate ($100/t) to produce potassium sulphate f$400/t) which has more options for agriculture application than potassium chloride due to chloride sensitivity. The technology to do the conversion is known in Chile and Canada, and his group in Canada are looking into it for a project.

He also commented that while membrane separation technology is very interesting it comes with a cost in that the magnesium and calcium concentrations in the feed must be at ppb level.

De-Risking the Processing of Non-Spodumene Resources

CG (chair) raised the topic of de-risking the processing of non-spodumene resources and asked whether there were any further comments in addition to those already discussed during the conference sessions.

AG (panel) responded that Lithium Australia has done a lot of work on lepidolite and zinnwaldite. To some extent, the economics of these materials will probably revolve around the by-products which vary from one deposit to another. They found that there is a major water balance problem with respect to producing lithium carbonate in particular from lepidolite and zinnwaldite. They did find that precipitation of phosphate was a much better way to go because phosphate is so insoluble. It significantly reduced the recirculating load and the requirement for evaporation and crystallization. Also, you can take it straight to a cathode powder to produce an excellent battery without hydroxide or carbonate, which reduces the number of steps and facilitates going from non-spodumene material to cathode powder in a vertically integrated process, which is very attractive.

CG (chair) invited comments on the removal of problem elements cesium and rubidium in the processing of clays and micas, bearing in mind that clays yield a lower ratio of these elements to lithium than micas.

GH (panel) the current proven way of getting them out is as a mixed rubidium-cesium alum which is not generally regarded as a by-product but is put aside for possible future harvesting. There are also SX and IX options but he has never explored them. These resources contain many other potentially valuable elements such as indium and tantalum and projects are coming under pressure from governments to recover them in order to generate more revenue, which further complicates process development.

CG (chair) added that the main market for drilling fluid as cesium is cesium formate. At first sight this appears to be an opportunity for a valuable by-product. However, while you can recover cesium in a bleed stream, it is very difficult to realize the value of it as marketable cesium formate.

GH (panel) On one of his projects involving non-spodumene feed, they decided to adopt the indirect route using the safe proven 1950s route rather than risk an innovative process. However, due to the lime used by the laboratory they did not achieve battery grade lithium hydroxide. They then tried to source a pure form of limestone or lime, and this led to making it in the laboratory by crystallizing out calcium carbonate and passing it through a kiln. However, the minor impurities built up rapidly and de-risking was not achieved.

CG (chair) suggested that perhaps there is an opportunity to find a better SX extractant or IX resin.

Outotec Alkaline Leach Process

Jacques Eksteen (JE), Future Battery Industry CRC, Curtin University (Australia) (floor) added that the Outotec Process presented in the sessions, which uses a caustic leach and quick lime addition, is a very elegant route. Although the autoclave is an expensive item, the process is appealing as it avoids the big issue of sodium sulphate production. He stressed that the point at which lime is added in the flowsheet is quite important. If it is very close to the production of lithium hydroxide, and the lime is not pure, the whole last portion of the process is jeopardised. He believes that many companies produce good quality lime, particularly in Europe. He asked MT (panel) to confirm that his understanding of the Outotec flowsheet was correct

MT (panel) confirmed that the Outotec Process is comparable to any lithium carbonate-lime conversion plant, so the lime has to be very pure. Polishing with IX is included but it can only remove multi-valent metal impurities.

JE (floor) Asked about the comparative economics, in particular the opex. He said that while the sulphation kiln has been eliminated, an autoclave has been added which will affect the capex.

MT (panel) confirmed that they have carried out some comparisons with the sulphuric acid route and their alkaline based process appears to be somewhat more attractive. The lime and sodium carbonate additions are not excessive.

CG (chair) asked whether Outotec have any plans for more piloting, because the data appears to indicate that impurities were still building at the 300-hour mark?

MT (panel) advised that there are scenarios to be piloted and they may do more runs for clients which will also increase their in-house knowledge.

CG (chair) said that potassium appears to be still building in the crystallization data, and asked whether this is mainly due to the bleed ratio that was used.

MT (panel) responded that there is way out for potassium if required because it stays quite steady and concentrated mother solution can be recycled to the soda leaching area where potassium and sodium react equally and end up in the residue. So we don’t have to deal with it separately.

Ahmad Ghahreman (AG), Queen’s University (Canada) (floor) asked what is the residence time of the autoclave? He also noted that in the two pilot tests Outotec used quite fine concentrates, at PADs 80 um and 100 um, and asked what would the recovery be with medium sized spodumene concentrates in the high or medium size range?

MT (panel) advised that the effective residence time is close to one hour. With regard to the fine PAD figure, this is for the concentrate after calcination. The original size for the concentrate before calcination was around 80% 210 µm.

GD (panel) Added that you can adopt a bigger particle size for the calcination of spodumene using a higher temperature, otherwise grinding will be quite expensive. The conditions need to be manipulated to achieve the optimum energy consumption.

Stationary Storage Batteries

Simon Cobden (SC), Jord International (Australia) (floor) asked, in relation to a remote off-grid site, whether lithium ion batteries can be discharged right down to zero without affecting their life span, and whether could they can be used for stationary storage?

AC (panel) responded that lithium ion technology should not be discharged to less than 20% in order to maintain good cyclability. Lithium ion batteries can be used for stationary application because they are suitable for float charging. However, as this involves the battery being fully charged and at high voltage for a long time, it is possible to have a side reaction which produces carbon dioxide if the battery is not well balanced. But now lithium ion battery technology is significantly improved so that we can use it in stationary application without any problem as it requires a lower current density. There is still the problem of needing a huge amount of lithium due to the large number of batteries required. There are two options to overcome this. One is to reuse spent lithium ion batteries, such as from electric vehicles, for which the cyclability and current density are still sufficient for use in stationary storage. The second option is to drastically change the technology to such as electrolysis to produce hydrogen which can be stored and then used to produce electricity, or sodium ion batteries. Two years ago, France decide to produce sodium ion batteries industrially which paved the way to reuse them for stationary application. In his opinion, in the future, sodium ion batteries will be the dominant technology for stationary storage application rather that lithium ion.

AG (panel) agreed and emphasised that the chemistry of the battery makes a big difference. You can fully discharge lithium iron phosphate batteries, though I'm not advocating that anyone should do it.; you are much better off running them with a good battery management system. A lot of the technology involved in getting the battery right is in fact the electronics and not the chemistry - looking after all those charging and discharging cycles which makes an enormous difference to heat dissipation and the number of cycles you can get out of the battery. But if you look at the lithium iron phosphate battery for power storage application, you've got about 4% lithium in comparison with about 7% in an NMC battery. So the problem of the huge demand of lithium can at least be mitigated. And you can get a battery having about three times the numbers of cycles of NMC. So if you go for stationary storage, picking the right battery is the most important thing. If you pick a high-end lithium ion battery, lithium iron phosphate of course, it will be lot better than lead acid, apart from the new ones that CSIRO are making - which are quite remarkable.

JE (floor) added that there are a number of important considerations in stationary storage technology including the use of lithium iron phosphate to mitigate lithium usage as mentioned. Some recent applications include the use of vanadium redox flow batteries for the on-grid 50 MW 250 MW/H system to be installed at Port Augusta, SA; and the use of NMC technology for the off-grid 30 MW 11MW/H industrial storage system supplied by Kokam and constructed by Alinta Energy at Newman, WA. Important as these are, he believes that a key issue is the re-purposing of batteries to extend the life cycle before final deep discharge and recycling.

While there is a lot of talk on the NMC side around growth of electric vehicles, but we should not misjudge the market growth for stationary storage. If you look at Australia, Africa, and the Asian countries, there is a huge opportunity for stationary batteries plus PV. In Indonesia you have to provide power for communities on 7,000 islands, so the stationary storage market there is also potentially enormous.

AG (panel) Agreed with JE (floor) that we will see an uptake in stationary storage of about the same as for EVs, though there will be substitutes in all these fields. The required amount of lithium will be about the same, at total of about 3.5 m t LCE by 2030.

Alternative LIB Precursor Feed Chemicals

CG (chair) raised the issue of opportunities for alternative lithium ion battery precursor feed chemicals and asked whether there is a future where we can avoid lithium hydroxide.

AG (panel) responded that It depends on the source of the lithium salt. Certainly, there is no need to make lithium hydroxide or lithium carbonate from recycled feed; but if you are processing spodumene, it makes lot of sense. Lithium phosphate has a particular advantage for the production of lithium iron phosphate batteries as the value of both phosphorous and lithium is realized, whereas the phosphorus has to be taken out if used for NMC batteries. He added that VSPC are only focussing on lithium iron phosphate because we think there is a market for it and the chemistry is out of patent so a license to produce it is not needed. However, the VSPC technology can also be used to make any of the other products.

AC (panel) agreed that lithium phosphate is a very good chemical for lithium ion batteries and has a good future. His group has undertaken a lot of research on the next generation with cathodes for high voltage batteries using lithium cobalt phosphate mainly derived from lithium phosphate precursor.

CG (chair) asked whether there a reason why we just can't stop the processing spodumene at lithium sulphate and use that as a precursor. Is there a fundamental reason why it is not an appropriate precursor?

AG (panel) for some of the cathode manufacturing technologies that are done primarily by pyromet processes there are distinct advantages in using hydroxides. It revolves around the crystal structure you get in the spinel you produce which is a little bit better if you use hydroxide rather than carbonate which affects the quality of the battery delivered to the consumer. If you use pyromet there is probably no advantage of using lithium phosphate.

Lithium Iron Phosphate Batteries

Chris Chalwell (CC), Galan Lithium (Australia) (floor) said that Galan are currently proving up a brine resource at Hombre Muerto (Argentina). From a practical perspective, being remote, isolated, and at 4,000 m elevation, some of the processes discussed appear to be complicated and challenging. His question to the panel is whether the world is ready for thousands of tons of lithium phosphate, because it appears to be an easier product to make in an isolated place?

CG (chair) responded that there is some precedent for that with POSCO. Why they don't convert to phosphate on-site, is another matter. But none the less they take the phosphate back to Korea, so they have thought about that, but at the end of day you still need to transport phosphate, phosphoric acid, sodium phosphate, potassium phosphate to site. So you still have logistical issue. Having said that, he was unable to answer the question whether the world is ready to switch over to lithium iron phosphate.

AG (panel: reported that LFP is still around 30% of the market in China. It is not widely used in North America or the EU but is very popular in China. In fact, until recently, China had regulations saying that vehicles with lithium ion batteries must use LFP for safety considerations because they will not spontaneously combust. That is no longer the regulation. What they have done is to change to subsidising vehicles which have a high range. But this generally involves buying a top of the market vehicle, and Chinese consumers have switched to low range vehicles with LFP batteries which are much cheaper. The consequence is that today the quantity of LFP batteries being used in China is accelerating beyond other types. It is at 30% of the market and expanding. So maybe the world's not ready for it, but China is.

AG (floor) added that Europe and North America, governments require the EV battery producers to recycle the battery at the end-of-life. If you recycle an LFP battery you will lose money, but if you recycle NMC battery you will make money, which will likely discourage the world from embracing LFP batteries.

AG (panel) disagreed, as with their patented technology, dumping an LFP battery into oxalic acid results in the reprecipitation of the cathode powders in a single step.

CG (chair) added that the binder does tend to slow it down.

Saikat Sengupta (SS), Wood Mackenzie (Australia), floor: commented that the LFP battery used to be dominant in China because BYD, one of the biggest battery producers, primarily used to use LFP in their PHEV. But the ratio between NMC and LFP has now become 50%-50%. So, China seems to be moving towards NMC. One of the reasons is that the specific energy you can get from LFP is lower than for NMC and NCA. He asked AG (panel) whether when he said that LFP was the future he was referring to an improved LFP that can have a higher specific energy or the same as?

AG (panel) responded that he intended to say that LFP has a future rather than it is the future. He agreed with the 50%-50% ratio for BYD and added that he thought that CATL produces over 20% LFP. He said that the main difference is that that NMC delivers at a higher voltage than LFP but pointed out that the LFP voltage can be increased by adding a small amount of manganese to just about complete on energy density with NMC. However, they have found that quality control is more difficult. He added that you can definitely get a significantly higher operating temperature and many more duty cycles with LFP, which enhances range.

Alternative Battery Electrolytes

SS (floor) asked AC (panel) whether anyone is looking at a lithium fluoride battery given that the most positive redox potential in the electrochemical series is lithium at 3.07 and the least is fluorine, which would effectively produce 6 volts.

AC (panel) replied that today there are a few cathodes which can operate at 5 volts, not 6 volts, which are being researched but have not yet reached industrial scale. The problem is in the electrolyte rather that the cathode. Oxidation of electrolyte occurs because 5 volts is above the 4 volts stability limitation of current batteries. So today the challenge is the design of new electrolytes. For years, research was focussed on new cathodes, new electrodes, and new materials which can cycle at 5 volts. But the problem is that we don't have a good electrolyte and we don't know if the poor cyclability problem at 5 volts is due to the electrolyte or the of cathode.

CG (chair) asked who are the people round the world looking at alternative electrolytes?

AC (panel) said that there are a few groups including his own. But it is not easy since the physical chemistry is very complicated because in lithium ion battery you have cathode and also you have anode and if you want a good cyclability of the battery you need to form a very good passivative layer on the negative graphite electrode to avoid exfoliation of the graphene layers. This means that the electrolyte must be compatible with the positive side and the negative side and must exhibit a very high conductivity and a low viscosity at the same time, which is not easy.

JE (floor) reported there is a group at Deakin which may be the best leading group in Australia in terms of electrolyte development.

CG (chair) asked whether Australia is a world leader in terms of domestic storage?

JE (floor) advised that in terms of solar PV up-take, Australia is definitely a world leader. An example Magellan Power, Perth, who are building systems for Burkina Faso, Ivory Coast, and elsewhere in Africa, all high temperature areas which offer a potentially big market. Realistically, Australia's participation in the global NMC market for EVs will likely be limited to making precursors. The cathode production needs to be close to where the cars are manufactured in the EU, China and the USA. But when it comes to LFP and stationary storage Australia is going to have a good chance to compete.

Battery Recycling

Bernadette Currie (BC), Independent Consultant (Australia) (floor) asked how we can influence the commercial battery suppliers to adopt design-for-recycling to facilitate the use hydromet techniques to eventually recover the materials and help the circular economy.

DB (panel) responded that he is aware of a number of companies developing various recycling flowsheets, but variations in batteries is a challenge. From a positive viewpoint, current trends in technologies such as low-cost sensors, computer systems, and heap, and robots could facilitate the development of an automatic factory in which the various recycled battery types, could be recognized, identified and separated for processing. However, he acknowledged that this is the wrong way around compared with design-for recycle.

BC (floor) agreed that it is a reactive approach and hopes that something pro-reactive that can be done by designing the various parts of the battery to work well with the recycling process.

CG (chair) commented that ideally you should have a vision for recycling when you are actually designing the battery; however, the number of items involved in battery design and production is a significant challenge.

GD (panel) added that if you are recycling one type of battery, design-for-recycling makes sense; but if you are recycling a mixture of many batteries and devices it is difficult for a battery manufacturer to design for the recycling process which is undertaken by other companies.

MD (panel) added you are dealing with human nature as well. The story I have heard is that the early lithium ion battery suppliers made them visually identical to lead acid batteries so they could be used as direct replacements in their boats and motorbikes etc, which led to the two types being inadvertently mixed when sent for recycling, which caused major problems in the process.

Summary of Key Points

- Despite the 'conventional' spodumene to lithium hydroxide processes being well proven industrially, the production of problematic waste streams, such as sodium sulfate, remains a key challenge. Avoiding production of these waste streams or economically converting them to saleable by-products is a key opportunity for the industry.

- Non-spodumene feedstocks for the production of lithium carbonate and hydroxide is feasible but dealing with the varied and increased impurity suite (relative to spodumene) is challenging. Managing these impurities is one aspect but the other is realising the potential value in some of those impurities as part of that management strategy e.g. potassium sulfate, cesium (as formate) etc.

- Despite the intense interest in ‘lithium’, alternative process flowsheets for lithium carbonate and hydroxide are relatively scant and remains an area of considerable opportunity.

- LFP vs NMC LIB technologies have pros and cons, and ultimately it comes down to the application that is being proposed. There is no question that LFP production is less complex and for many applications, the lower cost and increased stability of LFP batteries counteracts their reduced energy density versus NMC batteries.

- The different LIB technologies pose a number of challenges such as more efficient and less costly(cathode) production, reduced dependence on lithium hydroxide as a chemical feedstock, increased energy density for EV applications, ease of recycling etc. Although not as readily acknowledged, new electrolyte development is a particularly challenging area.

The Editors acknowledge the work of the student volunteer from Curtin University, Huan Li, for compiling notes on the discussion.

Trends in Battery Technology is the featured topic for the ALTA 2020 Lithium Processing Forum and Panel, which will be held 29 May in Perth, Australia.

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ALTA Panel Notes