Review

Lithium recovery from brines: A vital raw material for green energies with a potential environmental impact in its mining and processing

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HIGHLIGHTS

- A strong increase in lithium mining is expected because of the battery industry.
- Energy storage is vital for electric mobility and intermittent energy sources.
- The largest lithium deposits are found in continental brines in desertic areas.
- Current mining practices are water intensive and produce large volumes of waste.
- Future technologies should analyse chemistry and geology of the individual deposits.

GRAPHICAL ABSTRACT
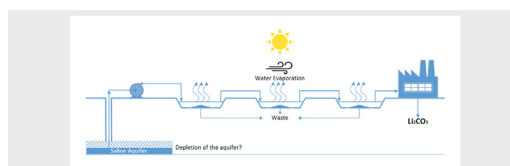
ABSTRACT

The electrification of our world is driving a strong increase in demand for lithium. Energy storage is paramount in electric and hybrid vehicles, in green but intermittent energy sources, and in smart grids in general. Lithium is a vital raw material for the build-up of both currently available lithium-ion batteries, and prospective next generation batteries such as lithium-air and lithium sulphur. The continued availability of lithium can only rely on a strong increase of mining and ore processing. It would be an inconsistency if the increased production of lithium for a more sustainable society would be associated with non-sustainable mining practices. Currently 2/3 of the world production of lithium is extracted from brines, a practice that evaporates on average half a million litres of brine per ton of lithium carbonate. Furthermore, the extraction is chemical intensive, extremely slow, and delivers large volumes of waste. This technology is heavily dependent on the geological structure of the deposits, brine chemical composition and both climate and weather conditions. Therefore, it is difficult to adapt from one successful exploitation to new deposits. A few years of simulations and piloting are needed before large scale production is achieved. Consequently, this technology is struggling with the current surge in demand. At time of writing, only 5 industrial scale facilities are in operation worldwide, highlighting the shortcomings in this technology. Both mining companies and academics are intensively searching for new technologies for lithium recovery from brines. However, focus on the chemistry of brine processing has left unattended the analysis of the sustainability of the overall process. Here we review both the current available technology and new proposed methodologies. We make a special focus on an overall sustainability analysis, with particular emphasis to the geological characteristics of deposits and water usage in relation to mining processes.

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Contents

1. Introduction

Lithium has been historically used in the production of ceramic and glass materials, greases, aluminium and others. In the last decade its demand has boosted because of its use in the lithium battery industry. According to the EU, lithium exceeds the threshold for economic importance and it is very close to the threshold of the supply risk (Report on Critical raw materials for the EU. Report of the Ad hoc Working Group on defining critical raw materials, 2014). A continuous and sharp increase in the demand for lithium is expected in coming years, since different types of lithium batteries are the most promising candidates to power electric or hybrid vehicles (Opitz et al., 2017; Evans, 2010). These batteries include both existing technologies, such as lithium-ion, as well as emerging battery technologies such as lithium-air or lithium-sulphur (Winter and Brodd, 2004; Bruce et al., 2012; Van Noorden, 2014; Arias et al., 2018).

While the general public largely associates lithium batteries to portable electronics and electric and hybrid vehicles, high capacity lithium batteries are also strong candidates for a possible solution for the storage of energy for the electrical power grid, *i.e.* smart grids. Large capacity batteries are needed for the accumulation of green energy, *i.e.* solar, wind and waves, which are all by nature intermittent energy sources (Brouwer et al., 2016; Pellow et al., 2015; Sternberg and Bardow, 2015; Bazán et al., 2018). In a world that is struggling to move forward towards a larger percentage of green energy, large capacity batteries or *energy banks* are a must. Indeed, if in a not so distant future we would like our energy matrix to rely to a large extent in renewable energies, energy banks will be needed to inject continuous power to the grid while these intermittent energy sources are either off or not working at their peak (night-time, no wind, no waves) (Brouwer et al., 2016; Pellow et al., 2015; Sternberg and Bardow, 2015). Finally, regardless of the energy source, large capacity batteries are also an alternative for energy accumulation in periods of low demand, allowing for this excess of energy to be re-injected into the grid at peaks of high demand (*e.g.* unusual cold or hot weather conditions, peak industry times, *etc.*) (Rahimi-Eichi et al., 2013).

Lithium is currently relatively inexpensive (about 15,000US$ for a ton of battery grade Li_2CO_3), but its price is likely to increase with demand (The Economist, 2016). Lithium is produced from lithium rich brines (dissolved lithium chloride) and hard rock ore (lithium minerals, spodumene, petalite and lepidolite). From lithium rich brines or salt lakes (called *salars*) comes by far the largest share of the worldwide lithium carbonate production and all worldwide lithium chloride production. Extraction from these salt lakes is the easiest and most cost-effective method (Kesler et al., 2012).

The viability of large scale production of many different types of lithium batteries with well varied characteristics and capacities is largely dependent on the availability of raw materials to build these batteries (Prior et al., 2013). Moreover, the diverse group of industries requiring large amounts of lithium salts, that up-to-date add up to roughly 65% of the worldwide lithium demand (Roskill's Information Services Ltd., 2016; Swain, 2017; British Geological Service, 2016), are also expected to keep growing, albeit at a slower pace, due to an increase in world population. In this context, the availability of lithium salts as a raw material can only rely on a strong increase of mining and ore processing.

An industrial mineral strongly associated to renewable and green energies, it would certainly be an inconsistency that the increased production of lithium salts would be associated with non-sustainable practices and contamination. Indeed, concern about mining practices is growing and many questions are being raised in particularly amongst the populations living within or close to the *Lithium Triangle* in South America. Therefore, it is of paramount importance to continue research in an attempt to answer the open questions regarding lithium mining and ore processing, while sustainable solutions should be sought to replace processes of known environmental impact. In this analysis article we aim to discuss the current situation regarding lithium mining and processing, including recently proposed new methodologies with a special focus on lithium from continental brines. We will discuss which are the open questions regarding mining operations, and we will present our interdisciplinary analysis of why we believe some of the proposed new methodologies might not be as sustainable as they present themselves to be, and might actually imply a harsher environmental impact than the currently used technology.

2. Lithium extraction

Lithium is relatively abundant on Earth, being the 25th more abundant element (Taylor and McLennan, 1985). Lithium is found in more than 150 minerals, in clays, in many continental brines, geothermal waters, and in sea water. Lithium concentration in sea water is very low, averaging 0.17 ppm (Vikström et al., 2013; Talens Peiró et al., 2013). Geothermal waters across the world show varying concentrations from 1 to 100 ppm (Kesler et al., 2012; Kunasz, 2006). While lithium deposits in all the above mentioned forms are worldwide widely distributed, only very few of them are large and/or concentrated enough to potentially allow for exploitation. A few high-grade lithium minerals and brines are the only current commercial lithium extraction operations (Kesler et al., 2012; Vikström et al., 2013; Kunasz, 2006).

Interest in recycling of lithium batteries has grown in recent years. However, recycling is still not economically attractive if compared to mining of the raw materials (Chen and Shen, 2017). Facilities for recycling are now available in the USA, Canada, Belgium, Germany, and Japan. However, lithium availability from recycling is insignificant

as compared to mined raw materials (U.S. Geological Survey, 2018; Jaskula, 2017).

Figures for lithium resources and reserves differ considerably accordingly to the source, although there is unanimously agreement that lithium resources in brine are much larger than those in hard rock (Kesler et al., 2012; Vikström et al., 2013; Kunasz, 2006; U.S. Geological Survey, 2018; Munk et al., 2016). The most recent figures from the US Geological Survey indicate total lithium resources (brine + hard rock) to be 54.1 Mtons (U.S. Geological Survey, 2018). In 2013, Vikström et al. reported estimated minimum and maximum resources for hard rock lithium at 12.8 Mtons and 30.7 Mtons respectively; while figures for brine deposits were reported as 21.3 Mtons and 65.3 Mtons, respectively for minimum and maximum estimates (Vikström et al., 2013).

2.1. Hard rock

Lithium in hard rock is extracted primarily from minerals occurring in pegmatite formations such as spodumene, petalite and lepidolite (Vikström et al., 2013). Extraction of lithium from hard rock ores, requires a wide range of hydrometallurgical processes, in marked contrast with lithium extraction from brines (Habashi, 1997). Exploitation is usually tailor-made for a given mineral, since these differ considerably in chemical compositions, and other properties (Vikström et al., 2013). Reported processes involve the crushing and heating of the ore in order to convert the lithium crystal phase from alpha to beta. This allows the lithium present in the ore to be displaced by sodium. The resulting concentrate is cooled and milled into a fine powder before being mixed with sulphuric acid and roasted again. A thickener-filter system then separates waste from the concentrated liquor, while precipitation removes magnesium and calcium from this solution. Finally, soda ash is added and lithium carbonate is crystallized, filtered and dried with purity close to 99% (Habashi, 1997; Barbosa et al., 2014; Hien-Dinh et al., 2015; Lee, 2015; Meshram et al., 2014).

Even though the cost for lithium extraction from rock is estimated to be roughly twice that of lithium extracted from brines, this methodology still persists. Australia is currently the number 1 worldwide lithium producer, since there is not enough offer for lithium from brines (U.S. Geological Survey, 2018; Jaskula, 2017). We already mentioned that total lithium resources in brine are much larger than those of hard rock. In addition, comparisons show that an average lithium brine deposit is larger than an average lithium hard rock deposit by a factor of 10 (1.45 Mton Li vs. 0.11 Mton Li) (Kesler et al., 2012). Despite these overwhelming differences, Kesler et al. suggest that pegmatites will remain to be exploited because of their wider geographical distribution, see below, and consequently a lesser susceptibility to supply disruption (Kesler et al., 2012).

2.2. Brines

Brines can be described as highly saline solutions, were total dissolved solids (mineral salts) show much higher values than in sea water, usually averaging 170–330 g L^{-1}. Brines can either be accessible directly from the surface, or deep under large saline expanses (salt lakes or salars) in very dry regions that allow salts to persist (Vikström et al., 2013). Lithium in brines is mixed with large quantities of NaCl (Kesler et al., 2012). The larger proportion of anions is given by Cl^{-}, with minor amounts of CO_3^{-2}, SO_4^{2-}, and different borates (Talens Peiró et al., 2013). Other than Na$^+$ and Li$^+$, cations present in brines include K$^+$, Mg^{2+}, and Ca^{2+}, amongst others (Kesler et al., 2012; Talens Peiró et al., 2013). The lithium content in mineable brines ranges from 0.01 to 0.2% (Vikström et al., 2013). It is interesting to point out that worldwide lithium brines are mostly concentrated in a small region of South America (Grosjean et al., 2012), often referred to as the Lithium Triangle. This region which extends between northwest Argentina, southwest Bolivia and northern Chile could potentially account for up to 80% of the world lithium resources in brines, with more precise figures yet to be determined by geological surveys (Houston et al., 2011). Second to the Lithium Triangle, China bears a large concentration of salt lakes in the Qinghai-Tibet plateau. Smaller deposits are found in the western United States and Northern Africa (Kesler et al., 2012).

A general schematic representation for the technology currently in use for lithium extraction from brines is given in Fig. 1A. The brine is pumped from beneath the crust on the salt lake into a series of large open air shallow evaporation ponds. The lithium brine is concentrated by solar evaporation and wind to a concentration of approximately 6000 ppm lithium, after which recovery takes place. This technology for lithium extraction is generally known as the evaporitic technology. It involves several steps of successive evaporation of the native brine in different ponds with concomitant precipitation and harvesting of salts of the other ions (Na, K, Mg) (Swain, 2017; Talens Peiró et al., 2013; Zhang et al., 2012; Choubey et al., 2016; Border and Sawyer, 2014; An et al., 2012). When lithium chloride in the evaporation ponds reaches an optimum concentration, the concentrated brine is pumped to a recovery or treatment plant. Chemical species that do not spontaneously precipitate in the ponds need to be removed by chemical treatment. Borates are usually removed by solvent extraction, while magnesium cations are removed by precipitation with lime (see below). The concentrated brine is then treated with sodium carbonate (soda ash), thereby precipitating lithium carbonate. Most often, primary lithium carbonate is redissolved and reprecipitated to reach the desired purity needed in battery grade. The specific details of the process differ, of course, in between different processing facilities, and are usually not revealed by exploiting companies.

Overall, these evaporation/precipitation steps take up between 12 and 24 months from the beginning of the extraction process (brine pump out of the underground aquifers). Because salar brines naturally occur at high altitude and in areas of extremely low rainfall (Munk et al., 2016; Castino et al., 2017), solar/wind evaporation is a cost-effective method for concentrating brines and precipitating salts. Lithium carbonate is a stable white powder, which is a key intermediary in the lithium market because it can be converted into specific industrial salts and chemicals, or processed into lithium metal. The evaporitic technology of extraction currently in use is a low cost/high margin process. In a general analysis, there is quite some general agreement that the current technology is relatively low-impact (British Geological Service, 2016), if compared, for example, to mining and processing of metals (gold, silver, lead, etc.) from ore which has led to several environmentalist groups to associate the verb mining as a synonym of strong contamination.

A small parenthesis regarding nomenclature needs to be made here. The words extraction and mining are primarily associated with the successful exploitation of a mineral deposit, i.e. the physical separation of ores from natural deposits. For lithium, this is equivalent to pumping out brine from underground deposits. After successful mining, ores need to be processed in order to obtain a certain mineral with a given degree of purity. In our case study, brine brought up to the surface, is a complex mixture of many ions, where lithium is only one minor component. Brines need to be processed in order for pure lithium salts to be produced. When some authors refer to new lithium extraction methodologies, it is actually meant new brine processing methodologies, i.e. processing methodologies different to the evaporitic technology. We believe there is plenty of room for improvement with regards to brine processing techniques, i.e. lithium salts capturing, recovery, separation or precipitation from brines. We understand that the first step for a successful production of lithium salts will still be pumping out brine, following pretty much the same methodology currently in use.

3. Geologic setting of the Puna Plateau and salar characteristics

In order to assess the sustainability of both the current and potential future technologies for lithium salts production, the whole process
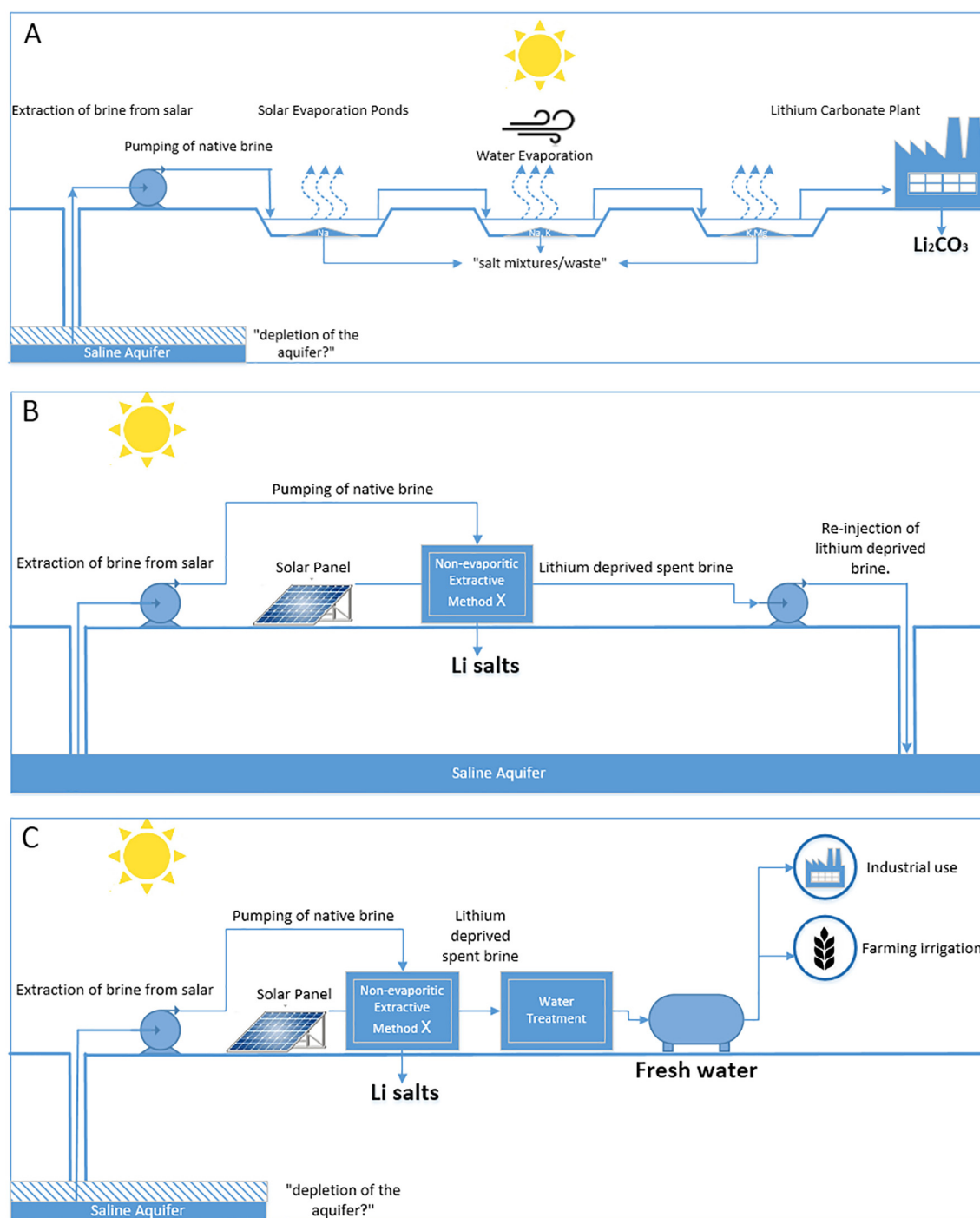
Fig. 1. Schematic representation of 3 different approaches to lithium extraction and processing. A-Current evaporitic technology, concentrates the native brine by solar and wind water evaporation, producing salt mixtures as waste, and potentially depleting the aquifers. B-Most newly proposed methodologies proposing a certain chemical/physico-chemical method to capture lithium, and suggesting the concomitant re-injection of large volumes of lithium deprived brine back to the underground aquifers. C-Our vision: Develop work on non-evaporitic extraction methodologies, followed by water treatment to produce fresh water and avoiding spent-brine re-injection.

involving mining, brine processing and waste production/disposal needs to be understood, and the impact of those processes in the specific geographical environment where brines are found needs to be assessed. Because the largest share of lithium resources in brines is located in the Lithium Triangle, in the Andean Highlands of South America, also known as *Puna*, we will describe the geological characteristics of these brine deposits. Most of what is known about salars in this region, is still transferable to lithium rich salars in other regions of the world.

The Puna Plateau region has an average elevation of 3700 m with broad depocentres separated by meridionally trending mountain ranges, with an elevation often higher than 6000 m. These sedimentary basins are presently internally drained and contain thick sequences of continental evaporites and clastic deposits (Alonso et al., 1991; Jordan and Alonso, 1987). Contraction in the region of the present-day plateau contributed to the formation of closed basins (Alonso et al., 1991; Horton, 2012; Strecker et al., 1989; Grier et al., 1991; Kraemer et al., 1999; Coutand et al., 2001; Marrett and Strecker, 2000; Carrapa et al.,

2005; Bossi et al., 2001; Alonso et al., 2006; Hilley and Strecker, 2005). The history of the Puna Plateau and its marginal basins documents the effects of tectonics and topography on atmospheric circulation pattern, the development of orographic barriers, and their influence on erosion and landscape evolution at various time-scales. Available sedimentologic, paleontologic and stable isotope data sets show a major shift from aridity towards increased humidity along the eastern border of the Puna Plateau in late Miocene to early Pliocene time due to the establishment of orographic barriers high enough to intercept moisture-bearing winds (Alonso et al., 2006).

The evolution of the Cenozoic basins of the Puna occurred in two distinct times. A first paleogene (Eocene) foreland of retro-arc, with exoreic drainage basins, in warm and humid climate, without formation of evaporites. This was followed by a second neogene stage (Miocene-Pliocene), with intra-arc/intra-plateau with endoreic arid basins, with volcaniclastic and evaporitic sedimentation development (Jordan and Alonso, 1987; Herrera et al., 2018). The height of the orographic barrier in east Puna, with altitudes that decrease from south to north and that produce the breaking of the moist winds of the Atlantic anticyclone, was decisive in the degree of aridity and it was maintained from the Neogene until the present time. The humidity of Puna decreases from north to south and from east to west, with maximum values of 350 mm in La Quiaca and minimum values of less than 50 mm in the south-western sector (Arizaro, Antofalla) (Alonso et al., 2006).

Salars of the central Andes constitute one of the world's major continental evaporite complexes that contain significant portions of known resources such as Li, B, K amongst other elements, and is often also referred to as the Evaporitic Puna Province (Alonso et al., 2006).

The Li-rich brine systems share six common characteristics that provide clues to deposit genesis while also serving as guidelines in the closed basins in arid regions: (1) arid climate; (2) closed basin containing a playa-lake or salar; (3) tectonically driven subsidence; (4) associated igneous and geothermal activity; (5) suitable lithium source-rocks; (6) one or more adequate aquifers; and (7) sufficient time to concentrate a brine (Munk et al., 2016; Bradley et al., 2013).

Salars consist of hard to soft saline crusts that overlie sequences of lacustrine sediments. We can identify five general types of salars: (1) zoned salars, consisting of an interior halite zone surrounded by a sulphate zone; (2) gypsums salars, consisting chiefly of gypsum and lesser amounts of other sulphate minerals, halite, and ulexite; (3) salars having crusts of silty halite that formed chiefly by capillary evaporation of near-surface ground water or brine in lacustrine sediments; (4) salars consisting chiefly of mud flats subjected to annual flooding and having thin ephemeral crusts of halite or sulphate minerals during dry seasons; and (5) salars with coarsely crystalline halite to a depth of as much as 160 m such as Salar Grande (North Chile) (Ericksen and Salas, 1990).

Salars basins in the Puna Plateau region of the Central Andes can also be classified in terms of two end members, "immature clastic" and "mature halite". This classification is based on (1) the relative amount of clastic sediment versus evaporite; (2) climatic and tectonic influences, as related to altitude and latitude; and (3) basin hydrology, which controls the influx of fresh water (Houston et al., 2011). The distinction between salar types is maintained even within the same basin, such as at Hombre Muerto, Argentina. Both types of salar may contain commercially valuable brine resources, and while it might be anticipated that mature salars contain more concentrated solutions, this is not always the case. Elements such as Li, K, and B may reach very high levels in immature salars and, of course, clastic deposits possess considerably higher porosities than halite (Houston et al., 2011).

Potentially important Li sources for brines include high-silica volcanic rocks, pre-existing evaporites and brines, hydrothermal clays, and hydrothermal fluids. The relative role of Li leaching from source rocks by low- and high-temperature fluids versus Li sourced in magmatic fluids themselves is not known and studies addressing this topic are scant.

Some authors suggest that Li is leached by groundwater from volcanic tuffs and that this process alone could account for Li in brines (Clayton Valley, Nevada) (Price et al., 2000). However, experimental weathering studies have shown that less than 10 μg/L Li are released from these volcanic rocks when exposed to water at ambient conditions (Jochens and Munk, 2011). Similar findings were reported from low-temperature leaching of Li from volcanic rocks near Salar del Hombre Muerto, Argentina (Godfrey et al., 2013). Risacher and Fritz (2009) concluded that Li and B in Andean salars are derived from the weathering of ignimbrites. Yu et al. (2013) demonstrated that playas in the Qaidam basin receive Li transported by streams that are ultimately sourced from upstream hydrothermal inputs.

It has also been hypothesized that Li could be sourced from alteration of volcanic rocks by hydrothermal fluids and/or from direct connection to differentiated magmatic sources. Moreover, volcanic glass contains elevated Li concentrations, suggesting that volcanic glass is a significant and readily available source of Li released to the environment via weathering processes, as well as in the fluid inclusions in minerals of erupted volcanic origin (Hofstra et al., 2013).

Geothermal activity played a significant role in the formation of Li-rich brines for several reasons: (1) it provides a hot water source for enhanced leaching of Li from source rocks; (2) it is also likely a direct source of Li from shallow magmatic brines and/or magmatic activity; (3) it may play a role in the concentration of Li through distillation or "steaming" of thermal waters in the shallow subsurface; (4) thermally driven circulation may be an effective means for advecting Li from source areas to regions of brine accumulation; and (5) it can result in the formation of the Li-rich clay mineral hectorite, which can in turn be a potential source of Li to brines if leaching and transport occur from the clay source (Munk et al., 2016).

In Puna there are several geothermal fields that are one of the important sources of Li, K, B, and other elements. Amongst those geothermal fields, one of the most studied is Cerro Tuzgle–Tocomar, where results suggest the presence of a 100–600 m thick shallow reservoir at variable depths (50 to 300 m from the surface) associated with 10 Ma volcanic deposits, and capped by sedimentary Miocene-Pliocene deposits (Coira, 1995). Recent evidence led to the conclusion that this reservoir constitutes the main geothermal reservoir and that it is in the Palaeozoic–Ordovician basement units, that is permeable because of intense fracturing, and that it is characterized by unevenly distributed secondary permeability. The reservoir is recharged by infiltration in the ridges above 4500 masl, where basement rocks are in outcrop (Giordano et al., 2013).

Even those who have shown evidence and argue that there is a continuous lithium recharge (Steinmetz, 2017; Eugster et al., 1978; Ide and Kunasz, 1989; Langbein, 1961), present recharge values that are several orders of magnitude lower than variations in lithium contents that are produced by full scale mining facilities upstream of the fluvial system of the basin. Therefore, in the context of mining, taking into consideration a time scale of no more than a century, lithium in brines should be considered a non-renewable resource. If a commercial scale exploitation producing 1000 tons yearly of Li_2CO_3 or more is active on a salar, the total amount of lithium will considerably decrease in the time span of the active exploitation (several decades).

A very important feature of salt deposits in the Puna is the relative significance of aquifer permeability which is controlled by both the geological characteristics and chemical composition of the aquifers (Houston et al., 2011). Conversion of brine resources to reserves will depend on the lithium concentrations in brine reservoirs, the extent to which brine can be recovered without dilution from recharge waters and degradation of salt-bearing reservoir rocks, and whether other brine constituents, including potassium, magnesium, bromine and boron, restrict processing or the capacity of production (Kesler et al., 2012).

4. Economic shortcomings of the evaporitic technology

Why should research be carried out to find out new brine processing methodologies? There are numerous strong reasons, both from an economic, and from a sustainability perspective.

We will first analyse some economic implications of the current methodology. Above all, the evaporitic process is an extremely slow process. After pumping from the underground reservoirs, brine is poured into huge shallow evaporation ponds and let to evaporate. A period of up to 24 months takes place before the concentrated brine can be processed in the fine recovery plant. There is not much that can be done to accelerate the evaporation process, rather than to *hope* for strong winds, and that rain is even more scarce than usual.

Secondly, associated with the slowness of the evaporation process, it is evident that the current methodology is strongly dependent on both general climate and particular weather conditions (Garrett, 2004; Lithium: Orocobre operations hit by Puna snowfall, n.d.). Solar irradiation, rain levels and wind strength will determine the rate of brine evaporation from the ponds. Evaluations assert that South American salars are subjected to climatic conditions which are more favourable to fast brine evaporation than Chinese salars (Kesler et al., 2012). However, even within the same region, such as within the Lithium Triangle, notorious differences are observed. The most obvious differences will appear depending on which side of the Andes the salar is located. Generally speaking, the western flank of the Andes is drier than the eastern flank. Moreover, there is also an important gradient of precipitations even east of the Andes (Houston et al., 2011; Castino et al., 2017; Alonso et al., 2006). As an example, Garret reports the evaporation rate for brine in Salar de Atacama (Chile) to be in the range of 3200 mm/year, compared with 2300 mm/year at Hombre Muerto (Argentina, 240 km away as the crow flies from Atacama), and 1800 mm/year at the Great Salt Lake and Clayton Valley (Garrett, 2004). In addition, at a single extraction facility, the efficiency and speed of the process will show variations on yearly basis (Lithium: Orocobre operations hit by Puna snowfall, n.d.), mostly depending on rain and wind changes.

Third, the efficiency of the current evaporitic technology is heavily dependent on brine composition (Kesler et al., 2012; Houston et al., 2011; Choubey et al., 2016). It is evident that the production yield of lithium carbonate per cubic metre of pumped brine will depend on the lithium concentration of the native brine. However, the efficiency of the process will also be strongly dependent on the composition of other ions which are present at low concentrations, and that do not spontaneously precipitate in the ponds before the concentrated brine is pumped to the fine recovery plant. The biggest problem reported today are magnesium cations, with big trouble being caused by borates, and sulphates as well. The ionic radii of Mg^{2+} and Li^+ are almost the same (Vikström et al., 2013; Mason and Moore, 1982). Therefore, some chemical properties of Mg^{2+} cations are extremely similar to those of Li^+, and thus $MgCO_3$ co-precipitates with Li_2CO_3 when Mg^{2+} concentration has not been heavily depleted in previous steps (Vikström et al., 2013). This property makes the extraction of lithium salts from magnesium rich brines extremely complicated.

Currently Mg^{2+} ions are precipitated by addition of calcium oxide (lime), which increases the pH and produces the precipitation of magnesium hydroxide usually at pH above 9. While calcium oxide has relatively low market prices, roughly at 130US\$/ton, its cost input in the overall extraction process increases considerably if Mg^{2+} concentration is too high. Moreover, magnesium hydroxide does not produce a crystalline precipitate. Instead, very small particles that flocculate are formed. These particles trap a relatively large amount of lithium rich brine. The more $Mg(OH)_2$ floccules that are produced, the more lithium rich brine that will be trapped and lost. If the native brine has a very large Mg^{2+} concentration the whole extraction process is rendered economically inviable, both because of the cost of lime and the larger amount of lithium rich brine that is lost. Finally, the permanent use of lime poses an added limitation, forcing the permanent transportation of chemicals towards isolated regions. As an example, if two or more of the about a dozen extraction projects currently at exploration/pilot scale stage in north-western Argentina were to start industrial level scale operations, calcium oxide produced in the area will no longer suffice. Larger supplies would have to be brought from further away, increasing the operational costs because of freight.

Forth, while no company releases exact figures of recovery rates, it is known in the lithium-brine business that the overall recovery yield is dependent on the total chemical composition of the brine. Different reports estimate average recovery values at around 70% of the lithium originally contained in the native brine, with some brines falling down to 50% or even lower recovery values (Jaskula, 2017; Garrett, 2004; Pure energy minerals, n.d.). Lithium is mostly lost because of entrapment/adsorption with salts that spontaneously precipitate in the ponds, and during treatment to eliminate Mg^{2+} (Song et al., 2017).

Overall, as a consequence of different salars showing different chemical compositions and sedimentary fills, as well as being subjected to diverse climatic conditions, the specific design of every mining and processing facility needs to be modelled in detail, and piloting needs to be carried out over many months, and sometimes even a few years, before large scale exploitation can start. This is not only a consequence of many of the specific operational details being protected by intellectual property rights and quite a good dose of industrial secrecy. Successful production from one salar does not necessarily assure success at others (Kesler et al., 2012). While this assertion holds true roughly for any mineral deposit, it is of paramount relevance for lithium in brines. Firstly because of the fluid nature of the deposit, that will produce a re-arrangement of the resource upon starting the exploitation. Secondly because there is overall very little knowledge on the subject, with only 5 fully active facilities worldwide. And last, because brine evaporation, unlike any other process is strongly weather and climate dependent. If the same company, successfully exploiting one deposit, were to start a new exploitation in a different salar, even within the same geographical region, for example within the Lithium Triangle, they would have to carry out careful and detailed feasibility studies in order to successfully adapt the process that previously demonstrated successful results. Together, prospection and piloting can take up to 10 years, again because of the fluid nature of the resource, and because piloting brine evaporation takes considerably longer than most other industrial processes. This lag time with no revenues is unfortunately a strong deterrent for investment. While the operational costs of the evaporitic technology are relatively low, the capital costs of building a facility are considerable. The last facility built in Argentina, with a capacity production of 17,500 tons of Li_2CO_3 yearly, was estimated at 250 million dollars (Brisbane firm wins \$250m to mine lithium to power world's phones, n.d.). In addition, this lag time is a synonym that lithium from brines is not a reliable source for coping with sudden surges in demand. As a consequence, the skyrocketing demand of lithium salts has taken the price of battery grade lithium carbonate from about 6000US\$ to roughly 15,000US\$ a ton from 2014 to 2016 (The Economist, 2016).

Table 1 lists all currently active lithium exploitation facilities from brine. There are only 8 active facilities worldwide, with 3 of them (the 3 Chinese plants) being only at piloting stage and not producing permanently (Song et al., 2017). In our humble understanding, this is a clear indication that there are both economic and technological important challenges with regards to lithium exploitation from brine.

Last but not least, we should stress two important frequent shortcomings in the discussion of lithium availability. First of all, the mixing of the concepts of *reserves* and *resources* (Vikström et al., 2013). A very general definition of reserve is the quantity that is currently available for exploitation with current technical and socioeconomic conditions. Reserves are what matters for production. Conversely, resources are broadly defined as the geologically measured deposits, which are not necessarily exploitable with current technologies or under the present socioeconomic conditions, because they could be in war zones, *etc.*, or

Table 1
Data for Li extraction facilities from brines. Only facilities currently producing are listed. Different sources cite different values for both Li$^+$ content and resources values. Facilities at piloting stage with a production capacity below 1000 tons/year of Li$_2$CO$_3$ were not listed.

Country	Deposit name	Resources (kilometric ton Li metal equivalent) (Garrett, 2004)	Operator name	Li$^+$ content/ppm	Current production capacity [Li$_2$CO$_3$ tons/year]
Argentina	Salar de Olaroz	1203	Sales de Jujuy	690	17,500
Argentina	Salar del Hombre Muerto	800	FMC Lithium	620	12,000 Li$_2$CO$_3$ + 7730 LiCl
Chile	Salar de Atacama	3000	Sociedad Quimica y Minera de Chile S.A.	1500	48,000 Li$_2$CO$_3$ + 6000 LiCl
Chile	Salar de Atacama	3000	Albemarle	1500	27,000 Li$_2$CO$_3$ + 4500 LiCl
China	Chaerhan Salt Lake	1000	Qinghai Lanke Lithium Industry	210–350	5000 (Li$_2$CO$_3$ + LiCl)
China	West Taijinar	2680	CITIC Guoan Lithium Science & Technology	100–300	5000 (Li$_2$CO$_3$ + LiOH)
China	Zhabuye	1000	Tibet Mineral Development	1000	5000
USA	Clayton Valley (Silver Peak)	300	Rockwood Holdings, Inc.	230	6000

exploitation might result economically inviable (Vikström et al., 2013). According to some, resources should be considered an academic figure, while only reserves are relevant for real supply in the near future (Vikström et al., 2013). Evidently, the classification of a deposit as either resource or reserves can change through time. For example, new technological developments might render the exploitation of more deposits economically viable. Conversely, a sharp decrease in international prices for a given mineral could convert some of the reserves in mere resources.

While many point out that the largest worldwide lithium resources are found in Uyuni salt lake, it is a known fact that no commercial scale exploitation has yet been stablished there. There is large agreement that the main problem in Uyuni (Vikström et al., 2013; An et al., 2012), and many of the Chinese salt lakes (Song et al., 2017), is the large Mg/Li ratio, which renders exploitation of the resource technically much more difficult and economically inviable with the present evaporitic/lime technology. The search for new lithium brine processing technologies aims at rendering economically viable the exploitation of these brine resources, as well as potentially even the exploitation of lithium resources in geothermal and oil fields which are considerably more diluted and under less arid climatic conditions.

Secondly, existing standards for resource/reserve reporting were draft and actually apply to solid phase mineral resources (Houston et al., 2011). Because the resource lithium is in a fluid state, it can actually move, mix and re-arrange itself relatively rapidly during the course of an active exploitation (Houston et al., 2011; Border and Sawyer, 2014), i.e. brines are a resource that changes through time.

5. Sustainability issues of the evaporitic technology

Beyond the economical driving force to look for new extraction technologies, there are 2 big questions regarding the overall sustainability of the whole process: water usage and waste generation/disposal. In close relation to these issues, rises the question of flora and fauna conservation.

It is of outmost importance to make a difference between the two different types of water that lithium mining from brines makes intensive use of. The first type of water corresponds to brine: high ionic strength of at least 170 g L^{-1} total dissolved solids (TDS), and most often TDS values around 300 g L^{-1}. The second type of water corresponds to fresh water: low salinity water, below 10 g L^{-1} TDS. Brine water is located within the limits of the salar. Fresh water is found in the border of the salar basin in free aquifers into alluvial fans and fluvial systems deposits. Water for industrial use is obtained from wells drilled and extracted from fresh water reservoirs, but that often are not suitable for human consumption either without further purification (King et al., 2012; Concha et al., 2010).

Evaporated water is originated exclusively in brine water, i.e. in order to precipitate the different salts and to obtain a Li$^+$ concentrated brine, up to 95% of the original brine water needs to be evaporated (Habashi, 1997). The volume of evaporated water is indeed huge. However, before we discuss these figures, we should strongly stress the

point that brine water as such is very far from being apt for either human or animal consumption. Aside from small scale, sodium chloride producers, which in turn also evaporate brine, no one was making use of brine water before lithium mining companies started exploitation. The total salts concentration in brine is on average 9 times higher than in sea water, and therefore, it is not suitable as drinking water, and it is of no use for irrigation either.

Brine water is often considered to be a static deposit. However, even in the absence of any exploitation, brine water is actually in dynamic equilibrium with the surroundings, with a slow turnover controlled by evaporation and by recharge from the scarce rains (Ahumada, 2014; Risacher et al., 2003; Corenthal et al., 2016).

The second controversy deals with fresh water. Mining companies have separate wells for their own supply of fresh water to be used in the different steps of the extraction/purification process. Some of this fresh water will even undergo a deionisation process. The highest consumption of fresh/deionised water will be in the preparation of the concentrated lime solution, and in the purification of lithium carbonate (washing, re-dissolution and re-precipitation of primary lithium carbonate). Data provided by Provincial and National Mining Offices in Argentina suggest that no less than 5 and up to 50 m^3 of fresh water are needed per ton of final battery grade Li$_2$CO$_3$ that is produced. This might not seem a huge volume, except it is being pumped out from very arid land.

It is very clear why both local populations and environmentalist groups are carefully watching the fresh water usage of the mining companies. However, there is also concern about the possible interaction of the different aquifers, i.e. brine water and fresh water, and in particular, what is going to happen if brine starts to get depleted by lithium mining.

There are extremely few reports discussing general trends about the hydrodynamic behaviour of lithium rich aquifers (brine water) (Houston et al., 2011; Border and Sawyer, 2014). Partial case studies are found in the NI-43 101 technical reports from mining companies managing active or prospective mining projects (King et al., 2012), and a few academic publications (Corenthal et al., 2016). Those same companies are surely in possession of much more detailed, though not reported, data about the hydrogeology of the basins where they are based. However, there is a serious lack of reported field measurements on the hydrodynamic behaviour and on water balances of fresh water aquifers surrounding the salars. To the best of our knowledge, there is no data to prove or disprove claims that lithium mining companies are drying out the Puna plateau. These claims are so far unsound (Izquierdo et al., 2015), and the lack of reported data does not allow a quantification and/or better assessing of the problem.

We can certainly assert that two different hydrodynamic systems co-exist, brine water, and fresh water. Secondly, there is large agreement that there is an interconnection between the two water systems (Houston et al., 2011; Border and Sawyer, 2014; King et al., 2012; Corenthal et al., 2016). However, in our understanding, the degree of interconnection of these systems will clearly be of different magnitude in different salars, and will also be dependent on the pumping rate/amount/location of pumping wells. Hydrogeological balances are most

often not released by mining companies. Moreover, even in the absence of active mining exploitations, datasets are incomplete and poorly understood. For example, no data has been released comparing natural evapotranspiration rates of the phreatic levels (*i.e.* in the absence of evaporation ponds, through the salt crust) and the evaporation rates where evaporation ponds are present, taking into account the whole salar basin. It is known however, that even in the absence of mining exploitations, these arid areas show a negative water balance, *i.e.* more water is discharged out of the basin (through evapotranspiration) than water influx *via* recharge waters and scarce precipitations (Corenthal et al., 2016).

Houston et al. (2011) and Border and Sawyer (2014) made very smart analyses to yield some light on this aquifer interconnection issue. Their analyses were made to assess the possibility of resource dilution in the event that large amounts of fresh water would permeate towards brine aquifers. A potential strong influx of fresh water into brine aquifers upon exploitation will dilute the resource, producing extracted brines of lower lithium content. According to the authors, mining companies should do their best attempt to avoid the interconnection of the fresh and brine aquifers, not only to preserve the environment, but to protect their reserves. We believe that this analysis is equally useful to analyse the potential scenario where fresh water is lost because of mining exploitations. According to these authors, the presence of intercalated or underlying beds of different permeability, sometimes allows the transmission of fresh waters from outside the salar margins through to the centre. Porosity and permeability are two fundamental concepts that characterize a salar. They are relevant to resource estimation, however, the porosity and permeability of the layers will eventually determine whether fresh waters from outside the salar might migrate towards the salar, and at which rate this will happen in the event of exploitation. The effective porosity of an aquifer relates to the volume of the pores which are in mutual contact and may thus be drained. In turn, the drainable porosity is the part of the porosity that may actually be drained during the pumping process. The permeability of mature salars is in clear contrast with that of immature salars. The first ones are more homogeneous and isotropic, while the latter are inhomogeneous and anisotropic (Houston et al., 2011).

Interestingly, evaporation of the superficial brine (the free phreatic level) will concentrate the brine and increase its density, producing its sinking through the aquifer. When brine extraction is begun, a redistribution of the resource starts to take place. This is because the fluid is being constantly stressed. Around each extraction well, the pumping will induce a cone of depression in the fluid around the pumping spot. The pumping rate as well as the permeability of the aquifer will determine the size and shape of this cone. Houston et al. assert that in mature salars high permeability and low drainable porosity values will yield a relatively flat depression cone, which extends laterally very rapidly. Conversely, in immature salars with low permeability and higher drainable porosity values, a much steep depression cone will be produced that deepens much faster than it extends laterally (Houston et al., 2011).

For both types of salars, the depression cone will eventually extend to the boundaries of the aquifer (usually the boundaries of the salar) after a period of time. And this is when it is of outmost importance whether the aquifer is surrounded by impermeable or permeable boundaries (lateral surfaces), and which are the permeability and porosity values of the different lithologic levels. If the boundaries are considered to be permeable, fresh water from outside the salar will flow towards the pumping pits/depression cones. Conversely, if the boundaries can be considered impermeable, the depression cone will propagate downwards, since no outside fluids can compensate the depleted brine. These are of course two extreme models. However, they are useful to give a very general idea of why the hydrogeological behaviour of a salar is not a simple issue. What will eventually define the amount of fresh water that can permeate towards the salar are the precise porosity values of both the salar lateral surfaces and the different lithologic levels

within the salar. These will determine at which rate external fluids will flow towards the salar.

Houston et al. (2011) assert that for a particular set of hydrogeological conditions (permeability of the boundaries, porosity of the strata, and distribution and abundance of fresh water in the margins of the salar) a nearly circular and larger salar, will exert less pressure on the fresh water aquifers than a salar displaying an *elongated* shape or of a much smaller size. This is because in the former case, it will take a long time for the depression cone to reach the boundaries of the salar.

Although we can certainly assert that many salars show several permeable stratigraphic levels and that brine extraction for mining purposes will cause the inflow of external fresh water to replace the volumes removed, the relevant question is to quantify the influx of fresh waters towards the salar. Two salars never show the same hydrogeological behaviour. Each salar is different, it displays different geological characteristics, with diverse permeability and porosity values for both the salar itself and the lateral surfaces around the salar, and fresh water sources are not equally abundant around the salars. Therefore, we believe that each salar should be studied individually. Independent and potentially different conclusions might be drawn out of the analysis of each specific case.

Strong lithium mining advocates, plainly argue that there is no connection between the two water systems, which we know it is not true, or they claim that the interconnection will not produce a significant depletion of fresh water levels. It is also claimed that the area of the evaporation ponds is considerable smaller as compared with the surface of the salar. In this context, the accelerated evaporation in the ponds, as compared with natural evaporation of the phreatic level through the salt crust should not be relevant, because it only happens in a small area. According to these claims, the only consequence of lithium mining will be the depletion of the lithium deposits after several decades of continuous exploitation, with no consequences to the hydrogeology of the fresh water courses. More cautious voices, argue that continuous field measurements and monitoring of both aquifers are needed (Houston et al., 2011; Border and Sawyer, 2014). And they venture that the potential depletion of either of the aquifers, and the influx of large volumes of fresh water towards the salar will depend on the rate of brine pumping and on the salar specific geological characteristics (Houston et al., 2011; Border and Sawyer, 2014). It is suggested that as long as mining companies stay below a certain maximum daily extraction volume, no big changes should be observed. Unfortunately, extremely little material has been published on this topic, with a lot of speculation and a long oral debate amongst industry professionals and environmentalists, which is not always backed-up by reported hydrogeological measurements (Izquierdo et al., 2015).

We must insist that the water issue is an open question, and neither the mining fundamentalists, nor the hard core environmentalists have yet shown conclusive evidence that either continuous brine pumping and evaporation is safe, nor that it is unsafe. Until further experimental field measurements are presented, a cautious approach is suggested. Any new extraction methodology that deals differently with water is worth being carefully studied and analysed. We insist once again that every case should be analysed separately.

The issue of waste production and disposal is better understood and quantified. There is unfortunately no doubt that the evaporitic process produces large volumes of waste. Currently, most of this waste is merely accumulated at the verge of the salar, except for the Mg-Ca residues which are sometimes used to consolidate precarious roads within the mining facility. Briefly, total dissolved solids in brine are very high. When brine is evaporated, all salts other than lithium carbonate end up as waste. Let us take the example of a native brine with TDS of 300 g L^{-1}, Li^+ content of 700 ppm and a recovery rate of 70%. Production of 1 ton of Li_2CO_3 by water evaporation will concomitantly produce over 115,041 kg of waste. Different Na and K salts will precipitate in the ponds in large amounts since they are the major cationic components in

the brine. Moreover, upon addition of calcium oxide, a precipitate composed of a mixture of $Mg(OH)_2$ and $CaSO_4$ is produced, which is currently very difficult to separate. While it is important to acknowledge that this waste is non-toxic, its volume will certainly call for waste management actions in years to come. If the said native brine is processed to produce 20,000 tons of Li_2CO_3 per year, after 10 years of continuous exploitation/production, an astounding figure of 2.3×10^7 tons of waste will have being produced. If we take an average volumetric density of 2 kg L^{-1} for the salts mixtures (density for carnallite is 1.598 g cm^{-3}, for NaCl is 2.17 g cm^{-3}, and similar values for other salts from the process) (Haynes, 2012), that mass will translate into a volume of $1.15 \times 10^7 \text{ m}^3$ of waste. If accumulated at ground level, and to a height of 1 m, it will occupy a terrain of 11.5 km^2.

Last but not least, a big question mark arises with regards to how the extraction process will affect local flora and fauna. For example, the dry arid land encircled by the Lithium Triangle is a *biodiversity hotspot* (Myers et al., 2000), with high levels of endemic species, unusual ecological and evolutionary phenomena, and global rarity (Izquierdo et al., 2015; Olson et al., 2001). The most obvious impact is related to fresh water availability. If lithium mining would affect the hydric balance in the region, this would in turn affect local flora and fauna, since water is the main limiting ecological factor in such an arid region. A less obvious potential impact, is related to the microbial activity in the vicinity of salars and in the salars themselves. Recently, the large occurrence of stromatolites has been reported in several locations within the Lithium Triangle (Albarracín et al., 2015; Farías et al., 2013). This region is one amongst the extremely few regions of the world were both fossil and live stromatolites are jointly found. Moreover, because of the harsh climatic and geographical conditions, such as extremely high salinity, and solar irradiation, in addition to extreme pH values and high arsenic content, these stromatolites are particularly interesting, since their study might shed a lot of light to the first appearance and early stages of life on Earth (Albarracín et al., 2015; Farías et al., 2013; Farías et al., 2014; Fernandez et al., 2016; Toneatti et al., 2017).

6. New technologies

In view of the current evaporitic technology, different alternatives have been proposed by both academic and industrial researchers. Many researchers have focused on improving lithium extraction procedures from concentrated brines, *i.e.* brines with a Li^+ concentration which is at least three times higher than the natural concentrations found in brine (An et al., 2012; Song et al., 2017; Alurralde & Mehta, n.d.). These are alternatives to Li_2CO_3 precipitation by addition of soda ash, the most classical procedure. It is generally understood that such high Li^+ concentrations have been reached by solar and wind brine evaporation. In the present discussion, we are interested, however, in analysing fully non-evaporitic technologies, and therefore we will not analyse at this time those valuable contributions.

An added advantage of non-evaporitic lithium capture methodologies is that they could potentially be applicable to more diluted lithium brines, such as geothermal or oilfield brines (Schaller et al., 2014). Solar evaporation might seem an inexpensive method, but is usually maladapted for these more diluted lithium sources. It relies on high solar irradiation and strong winds, and the ponds require very large areas of flat and inexpensive land for their construction. High lithium concentration brines which are found in salars very easily meet these requirements. But most geothermal or oilfields do not (Garrett, 2004).

Even before the recent lithium boom was started by the lithium battery industry, different authors proposed several alternatives to recover lithium from brines, avoiding altogether the need of brine evaporation or pre-concentration (Swain, 2017). The development of these technologies was driven by both the desire to overcome the limitations of the evaporitic technology in high altitude salt lakes and the search of techniques that might be applicable to more diluted brines which are more widely distributed around the globe. Garrett made a very throughout

listing of methods proposed up to 2004, and readers interested in the detailed methods are referred to that original work (Garrett, 2004).

There have been numerous reports of materials that are able to selectively adsorb lithium. Lithium has the ability to both being adsorb as well as to penetrate into non-stoichiometric crystalline networks of Mn, Ti and Al oxides and hydroxides. If Li^+ penetrates the crystalline network, it is usually at the expense of the liberation of H^+ into the solution from the said network. The adsorption capacity varies roughly between 3 and 40 mg Li/g material. Undoubtedly, most often reported absorptive or co-precipitation materials for lithium recovery are aluminium based compounds, with chemical structures close to alumina, aluminium hydroxide or aluminium chloride (Garrett, 2004). Lithium can be adsorbed onto the bulky gel-like structure of aluminium hydroxide related compounds. Goodenough was the first one to propose these types of compounds (Goodenough, n.d.). The basic principle has been upgraded in the form of ionic exchange resins using different forms of both amorphous and crystalline aluminium hydroxide and patented by several companies (Lee & Bauman, n.d.; Harrison et al., n.d.). Several patents based on similar principles have also been granted however with optimum operating conditions for brines that have previously undergone solar and wind evaporation to pre-concentrate the solutions in Li^+ (Alurralde & Mehta, n.d.; Burba, n.d.).

The precipitation of lithium from Dead Sea brines as lithium aluminate was reported as early as 1963 (Kaplan, 1963). By addition of different aluminium salts and ammonia, precipitation of lithium aluminate was achieved, which was then dissolved in sulphuric acid. Garrett (Garrett, 2004) makes a detailed account of results shown by different aluminium compounds on real brines. Overall, aluminium compounds usually show high values for lithium capturing from brines, with reports of at least 80% or more of the original lithium recovered. Results do vary however, depending on the lithium content, and whether magnesium concentrations are high or low. Moreover, usually very large eluent volumes are needed. This possesses two problems. Firstly, large volumes of fresh water are needed as eluents, and this water is usually scarce, at least around salt lakes, although it might not be a problem close to several geothermal fields. Secondly, after elution from the precipitate-ion exchange resins, lithium is more concentrated than in the original brine, but still quite diluted. Moreover, these aluminium compounds show a preferential attachment to lithium with respect to other cations, but non-negligible concentrations of other alkaline and earth alkaline elements are still present in the eluent. In some examples the amounts of aluminium compounds needed are higher in stoichiometric amounts than the lithium to be recovered, or very high amounts of acids and/or basis are needed for pH adjustment.

The details of the brine processing method used by FMC in Salar del Hombre Muerto have not been released. They claim however to have a particular extraction process that would allow them to work with a smaller area of evaporation ponds and be less reliant on solar evaporation (British Geological Service, 2016), since the brine would be treated in adsorbent beds that selectively capture lithium. Based on FMC patents, Garrett suggests that their technology could be based on alumina based ion exchangers (Garrett, 2004). As pumped-out brine would be treated on ionic-exchange columns, where LiCl would be concentrated roughly 4 times. A LiCl rich solution, deprived from most other ions would then be eluted from the columns. It is this solution that would, in turn, be poured into evaporation ponds for further concentration, *i.e.* the method *cannot* be classified as fully non-evaporitic. Moreover, in this particular method, the water that would be evaporated is not brine, but was originally fresh water, that would have been used to elute LiCl from the ionic exchange columns. There are no public reports on this methodology, other than the claims of the company that they use a different technology from everyone else's and that they are less reliant on solar evaporation, and therefore, we are limited to speculate on the said process.

The second large family of adsorbent materials are spinel types based on λ-MnO_2, to yield $Li_XMn_YO_4$ structures (Garrett, 2004). Li is

later liberated by acid treatment, whereby Li^+ is replaced by H^+ in the crystalline structure. These materials have been adapted to capture lithium by co-precipitation or in ion-exchangers. Manganese oxides have been proved to be extremely efficient for lithium recovery (Chitrakar et al., 2000a; Chitrakar et al., 2000b; Chitrakar et al., 2001; Chitrakar et al., 2012). pH titration studies suggested the formation of large numbers of uniform sorption sites having relatively high acidity. The uptake of Li^+ ions was found to be 37 mg g^{-1}, amongst the maximum for reported Li adsorbents (Chitrakar et al., 2000b).

Different chelating agents and H_2TiO_3 ion exchangers have been reported to recover lithium in ionic exchange columns from both natural and synthetic brines (Swain, 2017; Bukowsky et al., 1991). The possibility of using layered H_2TiO_3 as an ionic exchanger has also been revisited (Chitrakar et al., 2014). The adsorption of Li^+ by H_2TiO_3 follows the Langmuir model with an adsorption capacity of 32.6 mg g^{-1} at pH 6.5 from natural brines from Uyuni. The total amount of sodium, potassium, magnesium and calcium co-adsorbed was an order of magnitude below that of lithium, but still non-negligible. The authors suggested that the selectivity order originates from a size effect, although this would not explain the selection of Li^+ over Mg^{2+}. Abe and Chitrakar constructed a column of titanium(IV) antimonate cation exchanger, although their tests were performed with small liquid volumes (Abe and Chitrakar, 1987).

A few early reports proposed the use of chromatography to separate lithium from both concentrated and diluted brines (Dead Sea and hydrothermal). Rona and Schmuckler proposed the use of polyacrylamide gels. The difference in separation was most pronounced in the migration of univalent and bivalent metal ions (Rona and Schmuckler, 1973).

The possibility of using liquid-liquid extraction with organic solvents has also been put forward (Garrett, 2004; Song et al., 2017; Bukowsky and Uhlemann, 1993; Gabra and Torma, 1978). Several organic compounds can dissolve considerable amounts of LiCl with some selectivity with respect to NaCl and KCl, although there is not much of a difference when it comes to separation from $MgCl_2$ (Garrett, 2004). For example, LiCl solubility increases with decreasing molecular weight of alcohols, although the separation from other ions increases upon increasing the molecular weight of the alcohol (Garrett, 2004). Selective examples of solvents include β-diketones, alcohols up to 8 carbons, with n-butanol yielding the best results, neutral organophosphorus extractants, kerosene, and ionic liquids (Shi et al., 2016), amongst others (Song et al., 2017). In order to improve the selectivity of Li^+ vs. Mg^{2+} a drastic pH or brine composition change is required. Some authors have studied the synergistic effects of using two different extractants. For example Ma et al. studied a commercial ion-exchange chelating agent LIX54 (α-acetyl-m-dodecylacetophenone) and a neutral complexing agent (TOPO, tri-octyl-phosphine oxide) in a kerosene solution (Ma et al., 2000).

More recently, the boom in lithium demand launched a renovated wave of reports on new proposed methodologies for lithium recovery. Taking as a source of inspiration the reversible reaction of lithium insertion in cathodes in lithium-ion batteries, the use of electrochemistry for the selective capture of lithium has also been proposed. La Mantia et al. proposed to use a $LiFePO_4$ electrode for Li^+ capture, while chloride ions were captured in a Ag anode (Pasta et al., 2012). The idea is to use one of the commonly used materials in cathodes of lithium ion-batteries, where Li^+ ions are capable of intercalating when the Fe metallic centre is reduced. However, instead of working in organic media, as batteries do, the electrode is inserted in brine, while Li^+ is still selectively inserted into the cathode. The reaction is thermodynamically spontaneous. The authors proved that if the electrodes are first inserted in a sodium-rich brine (Li:Na = 1:100), the $LiFePO_4$ electrode captures Li^+ preferentially over Na^+. After the electrode is saturated in Li^+, the solution is changed for a LiCl low salinity solution, where the polarization of the electrodes is inverted. This is equivalent to the battery recharge step, and the Li^+ ions are liberated. Similarly to a real battery, this liberation reaction consumes energy, as opposed to the spontaneous Li^+ insertion. The final

solution is Li^+ rich, with a final Li:Na ratio of 5:1. Although these numbers show a considerable preference of the selective material towards Li over Na, the selection efficiency is still not high enough, and if the system would be scaled-up, a successive separation step would be needed to satisfy the required purity standards. In a subsequent article, the same group reported an improvement in selectivity, while they showed data that proves that the selectivity towards different cations is dependent on the current of the lithium intercalation step, with low currents being much more favourable to high purity Li^+ recovery vs. Na^+, K^+, and even Mg^{2+} (Trócoli et al., 2014). The same group has later proposed to optimize the technique by using nickel hexacyanoferrate as an alternative to silver as a chloride capturing electrode (Trócoli et al., 2015). In that system, the counter electrode is liberating Na^+ or K^+ cations to the brine solution, instead of capturing chloride. Later, the same authors also proposed the use of λ-MnO_2 as an alternative to $LiFePO_4$ for Li^+ intercalation (Trócoli et al., 2017). Finally the same group have later further investigated these systems, studying the performance of a flow-through electrochemical cell and the influence of electrochemical parameters (Palagonia et al., 2017). Alternatively, Lee et al. proposed to use a λ-MnO_2-Ag pair of electrodes (Lee et al., 2013). More recently, following the idea of a battery system in brine, Calvo et al. proposed to use a $Li_xMn_2O_2$ as a lithium recovery electrode coupled to a polypyrrole anode as a chloride capturing electrode (Marchini et al., 2016; Missoni et al., 2016). Calvo et al. were the only ones to demonstrate the excellent cycling ability of electrochemical systems for lithium recovery, with stability of the electrodes and the lithium capturing ability maintained for over 200 cycles. Moreover, the authors presented a full data set comprising several physico-chemical techniques that characterize the lithium insertion reaction (Marchini et al., 2016). Alternative electrode systems, following the same principle of reversible Li^+ insertion/desorption reactions have been proposed by other authors (Intaranont et al., 2014; Kim et al., 2015; Shin et al., 2015; Du et al., 2016).

A problem to be solved with all these battery like Li^+ capturing systems is the paradox between the low Li^+ molecular mass, 6.94 g mol^{-1} as compared to the active electrode materials, either 157.8 g mol^{-1} or 180.8 g mol^{-1}. In order to uptake 1 mol of Li^+, over 150 g of active electrode materials ($LiFePO_4$ or $LiMn_2O_4$) are needed. In addition, because these materials are non-conductive, a very thin layer needs to be deposited on a conductive, but otherwise inert material. Therefore, there is a very delicate equilibrium between building an electrode with as much as possible active material, so that more Li^+ can be recovered, and keeping the active layer relatively thin, so that the electric field is still transmitted across the non-conductive layer. Another possible alternative could be to build thicker electrodes by coating the current collector with a conductive slurry, which is a mixture of the battery material in a small particle size and conductive carbon. How thick electrodes could be built following this strategy is still an open question, since this strategy is hardly ever explored beyond 500 μm thicknesses, a value that would still require very large areas for the electrodes to recover significant amounts of lithium.

It is important to stress that while these electrode active materials might seem to be very similar to materials used in ionic exchange columns, the working principle of the battery like Li^+ capturing systems is completely different to selective adsorption. In battery like systems, Li^+ is inserted in the active material structure because a metallic centre has been reduced, and therefore, a positively charged species, Li^+, needs to compensate the charge of the whole chemical compound. In the second step, when the electrode potential is reversed, that same metallic centre is oxidized, the Li^+ ion is liberated. Therefore, battery like systems do not need acids or any other chemical reactants to elute LiCl from the active material, as it is the case with precipitants or ionic exchange resins (Lee & Bauman, n.d.; Harrison et al., n.d.; Burba, n.d.; Kaplan, 1963; Chitrakar et al., 2000a; Chitrakar et al., 2000b; Chitrakar et al., 2001; Chitrakar et al., 2012; Bukowsky et al., 1991; Chitrakar et al., 2014; Abe and Chitrakar, 1987). As in classical electrochemical systems, it can be considered that the reactants, are clean electrons.

Very recently Nisola et al. proposed a new type of 3D adsorbent filters for lithium capture. The authors reported the fabrication of electrospun composite nanofibers composed of a hydrophilic polyacrylonitrile (PAN) matrix infused with lithium ion sieves (LIS) $H_{1.6}Mn_{1.6}O_4$. These were employed as an adsorbent membrane filter in a continuous Li^+ mining process (Chung et al., 2017). Zhao et al., and Xu et al. proposed an electrochemical methodology close to electrodialysis, where Li^+ is selectively inserted into a $LiFePO_4$ electrode, and a membrane is used to help in the separation process (Jiang et al., 2014; Liu et al., 2015). Pontie et al. proposed to use nanofiltration for lithium separation, *i.e.* using membranes with pores in the nanometre scale and high pressure (Somrani et al., 2013). The authors achieved 85% separation for Li^+/Mg^{2+}, although they only obtained 85% separation for Li^+ from Na^+. The authors solved this limitation by separating Li^+ from Na^+ by dialysis, followed by the nanofiltration step.

6.1. A critical analysis of new extraction methodologies

New Li recovery methodologies propose different chemical or physico-chemical methods to capture Li^+ ions from the complex ionic mixture of the native brine, as detailed above. The listing of more than 30 pieces of work that we have just cited is certainly not exhaustive. We have shortlisted work with most promising results, and we have tried to highlight all the general chemical or physico-chemical techniques proposed so far with selective examples. Most reports on new lithium recovery methodologies describe experimental results at laboratory scale. While some authors estimate the cost of scaling up their proposed methodologies, there are extremely few reports on pilot scale results. Most Chinese salt lakes show large concentrations of either or both Mg^{2+} and sulphate, and the evaporitic technology with chemical precipitation of Mg^{2+} is particularly unsuitable for these chemical compositions. Therefore, driven by the unfavourable composition of many of their salt lakes, Chinese researchers and technologists have pioneered and taken big steps towards scaling up of new recovery methodologies (Song et al., 2017). A recent review discusses the technical challenges in attempting to set-up even pilot scale brine processing facilities in Chinese salt lakes (Song et al., 2017).

In addition, that a large proportion of studies have only been performed on artificial solutions attempting to mimic the real concentrations, but sometimes only including a few cations and anions, and disregarding other numerous minor components. Because Li^+ is only a minor component in brine, the effect of every other component, even if present in very diluted concentrations might also have an important effect on Li^+ recovery. Therefore, experiments performed on real brine samples (Chitrakar et al., 2012; Chitrakar et al., 2014; Marchini et al., 2016; Missoni et al., 2016) yield much more light on the potential real applications of any new recovery technology.

While scientific reports of laboratory scale results usually aim at proving concepts and the task of scaling up those concepts is left to engineers, when analysing lithium recovery from brine, scaling is of particularly paramount importance. We certainly do accept that a single research article cannot tackle all the technological questions opened by an individual piece of research. However, before those interesting ideas can be developed into a real life technological application, several aspects related to system scale-up have to be carefully considered. In what follows, we will not take into consideration the cost of scaling up, neither the capital, nor the operational costs. We will rather concentrate in the technical possibilities of scaling up and in the sustainability issues that might arise in the hypothetical large scale implementation of the new methodologies.

Let us take again the example of the deposit with a lithium concentration of 700 ppm, from where we wish to extract the equivalent of 20,000 tons of Li_2CO_3 on a yearly basis, now with a capturing efficiency of 90% of the lithium contained in the native brine. Different methodologies recover lithium in the form of salts other than carbonate, however to keep a coherent analysis we prefer to normalize all results to Li_2CO_3. A

simple chemical calculation shows that in order to produce that amount of lithium carbonate from the said brine, with the proposed efficiency, a hypothetical new technology would need to be able to process almost 6 million cubic metres of brine per year (5,965,079 m^3 per year). This is equivalent to processing an average of 16,343 m^3 of brine on a daily basis. There is no questioning that these are astoundingly big brine volumes.

Dealing with these large brine volumes is not a trivial matter for any technique. However, it is rather evident for us that some of the above mentioned techniques are maladapted to large volume processing. Although liquid-liquid extraction has been widely studied for lithium recovery (Song et al., 2017; Bukowsky and Uhlemann, 1993; Gabra and Torma, 1978; Shi et al., 2016), we believe that this is a technique which is particularly poorly suited for implementation in such a big scale. Selecting the right equipment has been a major technical and scientific challenge in the implementation of large scale liquid-liquid extraction. A mixed settler purposely-built for lithium recovery from brines showed a very large footprint, and liquid volume, while at the same time suffering from severe corrosion and long equilibrium time (Song et al., 2017). Centrifuge systems were proposed to reduce the large liquid volume and long equilibrium time, but these should be equally huge to mix-settlers, and would suffer from the same corrosion issues. Membrane extraction after mixing with the extractant could finally be a cheaper alternatively. However, a solvent resistant membrane is yet to be found. Finally, reciprocal extraction columns, such as those used in the petrochemical industry, could potentially present a solution here (Song et al., 2017). Even if the technical issues related to the huge footprint and volumes involved in liquid-liquid extraction were to be solved, yet another open question remains. What should be done with the equally huge organic solvent or ionic liquid volumes that would be used in the extraction? This is certainly a problem from a sustainability perspective.

For all other methodologies, analogies can be made with the same techniques which are currently applied in different large scale industrial processes. Therefore, it is reasonable to expect that they could be potentially scaled up and that the detailed engineering of the proposed processes can be worked out. Evidently, finding the right equipment and materials to deal with the highly corrosive nature of these brines, is one of the many issues that need to be solve in the scaling up project.

6.2. New technologies and spent brine

In our understanding, there is however one major shortcoming in the discussion of new recovery methodologies: what should be done with spent brine after lithium recovery? Most of the literature on the field completely ignores this question. Because the main driving force, at least for academic research, behind new brine processing technologies is the environmental impact of the current technology, it is most surprising that not a single written piece of research has raised the issue of the fate of millions of cubic metres of extremely saline spent brine.

Although there is a lack of written proposals for the fate of spent brines, there is an ongoing *unpublished* discussion. This is the proposition to re-inject spent brine back to the underground aquifers, *i.e.* back to the salar. This is for example what Pure Energy Minerals, authors of a patented method combining solvent extraction with electrochemistry (Zbranek et al., n.d.), and ERAMET, authors of a patented method for lithium adsorption by ionic exchange (Boualleg et al., n.d.-a; Boualleg et al., n.d.-b), propose in their web pages (Pure energy minerals, n.d.; ERAMET, n.d.). Moreover, brine re-injection is something that many authors of new published methodologies also propose in their conference presentations (Book of Abstracts 3rd International Workshop on Lithium, Industrial Minerals and Energy (IWLiME), 2017). And despite it is not explicitly said in research articles, the lack of discussion on this issue, somehow implies that the fate of spent brine is therefore re-injection.

This idea is schematically represented in Fig. 1B, where a generic non-evaporitic methodology is depicted. Since all of these new non-evaporitic methodologies are much more energy intensive than the evaporitic technology, authors usually stress the fact that most regions where salars are found are subjected to a particularly strong solar irradiation (Piacentini et al., 2003). This fact makes them ideally suitable for solar energy capture and its utilization to power lithium recovery methodologies, an idea with which we strongly agree.

If we analyse the subject of lithium mining from a broader perspective beyond the chemical processes needed to selectively capture lithium, we believe that there are many more issues to analyse than chemical specificity towards lithium of a given methodology. Either plainly ignoring the question of what to do with spent brine, or openly proposing to re-inject such an overwhelming volume of lithium-deprived brine back to the underground aquifers is a very dangerous oversimplification of the problem from an engineering, ecological and above all, geological point of view.

To the best of our knowledge, there are no reported precedents of re-injection of large volumes of brine or any other fluid in salt lakes. Some authors (British Geological Service, 2016; Kunasz, 2006) mention that residual brines, are sometimes re-injected back into salars upon lithium recovery, although no volumes are specified. Since these authors refer to the existing exploitations where the evaporitic technology is currently in use, we venture to say that the volumes that are re-injected are most likely minimal as compared to the originally extracted volumes, very likely not more than 5% of the initial volumes. Figures for these, as well as most other operational details are in general never reported. Moreover, knowing that their process is not fully reliant on solar/wind evaporation and that they use some sort of ion-exchange columns (British Geological Service, 2016; Garrett, 2004), it is strongly suspected that FMC re-injects at least a fraction of spent brine in their facility in Hombre Muerto, Argentina. Again, no figures about re-injection volumes have been reported.

Even if we let all sustainability issues aside for a moment, and we concentrate only on the technological aspects of lithium mining, re-injecting lithium deprived brine back into the salt lake, should be done with special care. Certainly, re-injection should take place as far away as possible from the aquifers from where the resource is being exploited to avoid its dilution. Even if re-injection is undertaken in different wells, which should ideally be compartmentalised from the extraction wells, it is known that in many cases a slow infiltration can happen (Horne, 1982) between the different aquifers and potential dilution from the valuable resource could take place through mixing with lithium deprived brine.

In the absence of precise reports from the extremely few facilities known to re-inject brine, our judgement that by re-injection the native brine will become more diluted in lithium is of course a hypothesis. This hypothesis is constructed based on fundamental concepts of solution chemistry, in addition to the knowledge that most salt lakes are either closed basins, or that they show a slow turnover of waters, and assuming that in the time frame of mining-exploitations lithium can be considered a non-renewable resource (Houston et al., 2011). In addition, Houston et al. (Houston et al., 2011) assert that the flow of fluids from outside the salar will certainly dilute the resource, and from this perspective, lithium-deprived-brine re-injection can be assimilated to the flow of an outside fluid. Moreover, important lessons can be withdrawn from the longest operating brine processing facility, the Clayton Valley in Nevada, USA. In operation since 1966, has been explored to depths of 300 m and is much more well-known than most other brine deposits in the world. The concentration of lithium in brine pumped considerably deep, at around 200 m, has been considerably diluted from an initial average value of 400 ppm at the beginning of exploitation to an average 166 ppm in 2004 (Kesler et al., 2012; Garrett, 2004).

Beyond the big question open from the engineering/exploitation perspective, more pressing issues arise from the perspective of the whole sustainability of the re-injection process. Firstly, all of the

techniques mentioned above are very likely to produce a treated brine that will leave behind, at the very least, traces of other chemical species which are exogenous to the native brine, such as aluminium (Lee & Bauman, n.d.; Harrison et al., n.d.; Kaplan, 1963), titanium (Bukowsky et al., 1991; Chitrakar et al., 2014), manganese (Song et al., 2017; Chitrakar et al., 2000a; Chitrakar et al., 2000b; Chitrakar et al., 2001; Chitrakar et al., 2012; Marchini et al., 2016; Missoni et al., 2016; Nishihama et al., 2011), iron derivatives (Pasta et al., 2012), phosphates (Chon et al., n.d.), silver (Pasta et al., 2012), pyrrole (Marchini et al., 2016; Missoni et al., 2016), organic solvents (Song et al., 2017; Bukowsky and Uhlemann, 1993; Gabra and Torma, 1978; Zbranek et al., n.d.), or ionic liquids (Shi et al., 2016), amongst others. In addition, the concomitant removal of certain chemical species together with the addition of exogenous ones could potentially change other properties of the brine, such as pH, and conductivity. For example, ion exchange reactions usually liberate H^+ upon lithium adsorption, and consequently the pH of spent brine might be reduced up to $pH = 4$ (Chitrakar et al., 2014). Sonoda et al. propose the addition of NaOH, in order to maintain the brine slightly alkaline for an optimum recovery process. In this case, the final spent brine will consequently show a pH value 1 unit higher than the native brine (Chitrakar et al., 2014). The effect of such changes on the delicate equilibrium of the salt lake system/playa complex is completely unknown. Moreover, despite the harsh conditions of the salt lakes, there is life in these extreme environments (Albarracín et al., 2015); and the ecosystem might be seriously affected by these chemical changes.

While there are no real case studies of brine re-injection back to salars, the SEDAR reports provide data on Vertical Electrical Sounding (VES-) surveys that were conducted at salt lakes' perimeter locations to explore potential shallow fresh water sources and to evaluate salar boundary conditions related to the brine/fresh water interface (King et al., 2012). This type of studies aims at avoiding the cross contamination of brine and fresh water at drilling/pumping spots.

The injection of large volumes of water in underground aquifers is, however, known in the oil industry. Large volumes of water are generated as a by-product of hydrocarbon exploitation. It is common practice to inject that water at underground locations either to stimulate secondary production, as well as in deep aquifers in order to discard wastewater. In this last scenario, the depth of the waste aquifer is of paramount importance in order to avoid contamination of superficial aquifers. While knowledge from the oil industry is a good starting point to evaluate the possibility of spent brine re-injection in the lithium industry, several differences have to be highlighted. Knowledge on the geological characteristics of oil fields is in general on different scales, because this is a much older and much more developed field. Oil fields are generally much larger than lithium exploitation, and both the volumes that are dealt with and the depths of many of the wells are of a different order of magnitude as compared to lithium exploitation. Most of the time, oil wells and wastewater wells in the oil industry are several kilometres deep, as opposed to wells which are usually not deeper than 300 m in the lithium industry.

Water injection is also well known in geothermal fields with very similar ends as in the oil industry: both improving the resource recovery and as residual deposits. Interestingly, a survey of water injection wells in Japan has shown a rapid and negative interference in 80% of production and re-injection wells (Horne, 1982).

Moreover, each evaporite basin presents unique and complex sedimentary fill characteristics. Attempts to re-inject brine into the underground aquifers might disrupt this whole stratigraphic structure. From an engineering perspective, it does not make sense to attempt re-injection of lithium deprived brine in the same stratigraphic level from where fresh brine is concomitantly being pump-out for processing. As stated above, this would imply the automatic dilution of the precious resource. Therefore, spent brine should be re-injected at a different stratigraphic level. However, which would be the consequences of trying to overfill a stratigraphic level while depleting another one?

Moreover, the different stratigraphic levels are somehow permeable and it is very likely that with time pump-out brine will end up being more diluted than at the beginning of the exploitation.

Is our previous knowledge from oil and geothermal energy industries on underground water injection a guarantee that we can automatically extrapolate results and a permission to re-inject brine into the salar straight away? The answer is a clear no. Particularly, if we consider that in many of the said cases, water is actually injected purposely to alter stationary/equilibrium conditions (secondary production). Therefore, it does not make sense to argue on one hand that brine is being re-injected to avoid alterations to the environment by depleting the brine deposits, and on the other hand purposely altering equilibrium conditions by severely disrupting the stratigraphic layered structure of a salar.

We believe that in the best scenario, previous knowledge on underground water injection should be taken as a departure point, and as a guide of which variables should be taken into consideration in order to assess the feasibility, and potentially the maximum flow rates at which spent brine might be re-injected. For example, porosity and permeability of the different stratigraphic levels are the first parameters to be studied before any injection project is judged feasible.

Moreover, considering that salt lake depict variable geological characteristics, it is impossible that any generic analysis can safely judge whether it is safe or not to re-inject large volumes of brine back to the underground aquifers for all salars indiscriminately. Lithium mining companies carry out individual and detailed studies in each individual salt lake before deciding whether exploitation is possible, economically viable, and which are the maximum native brine volumes that can be pump out on a daily basis. Following pretty much the same individual approach, specific and detailed studies should be carried out in each individual salt lake, in order to judge the possibility of re-injection and the maximum volumes and flows at which re-injection could be possible.

7. Water: from waste to resource

As we have just described, the evaporitic process consumes a large excess of water in one of the driest areas of the world (annual precipitations below 300 mm) (Castino et al., 2017). The exact amount of water evaporated per ton of extracted Li_2CO_3 and precise Li^+ recovery values will be dependent on the native brine composition (not only the absolute Li^+ content, but the ratio of Li^+ to other ions), and the details of the specific process used in the fine recovery plant. Because these are private exploitations exact figures are not released. Different authors estimate the amount of Li^+ that is recovered between 50 and 70% of the Li^+ contained in the native brine (British Geological Service, 2016). Taking the highest recovery, if we start with a native brine of composition, 700 ppm Li^+, it is easy to calculate that roughly 0.4 million L of brine water (383.5 m^3) are evaporated per ton of produced Li_2CO_3. If we think of an average extraction facility that produces 20,000 tons/year of Li_2CO_3, we arrive at the astounding figure of 7,669,388 m^3 of brine water being evaporated yearly at just one average lithium extraction facility.

Table 1 lists all known lithium brine extraction facilities worldwide, and summarizes their most relevant data. Reports indicate that at all those facilities evaporation of large brine volumes is carried out at some point of the process. If we estimate a 70% Li^+ recovery from the original native brine composition, and take the average Li^+ content listed in the table, we can easily estimate that 42.5 million m^3 of brine water are evaporated on a yearly basis, considering the 8 listed facilities together.

The volume of brine water that the evaporitic technology currently evaporates is certainly huge. Moreover, there is no experimental evidence that there has been an increase in precipitations anywhere in the vicinity of lithium exploitation facilities after exploitation started. Therefore, many consider that the current evaporitic technology is responsible for the *loss* of large volumes of water. We believe that this is

a statement open to discussion, following our extensive discussion above, see Section 5. The water that is currently lost is not fresh water, but brine water, *i.e.* water that is neither apt for drinking nor for irrigation purposes.

However, as we have also discussed, if one or more extraction facilities were to change their technology, or if a new plant would be built based on a new non-evaporitic technology, the volumes of lithium deprived brine that would be produced would be equally huge. What to do with that treated brine is neither a minor nor a trivial question. Some researchers and technologists propose to re-inject the spent brine back in the salt lake. We have discussed that this might not be possible and that the sustainability of such approach is far from being generally accepted.

A completely different approach might yet be possible. What if we were to try to recover that water and render it apt for human and/or animal use? This idea is schematized in Fig. 1C. It is certainly not a trivial matter how to desalinize that huge volume of brine water. We should however remember that salt lakes, in particularly those within the Lithium Triangle, are located at high altitude, in desertic environments with way over 300+ days of sunshine per year, resulting in extremely high sunshine irradiation (Piacentini et al., 2003), particularly convenient for solar driven technologies, either direct or indirect technologies. It is necessary to evaluate the feasibility, limits, and advantages of various available and emerging desalination technologies that can potentially be employed to treat highly saline brine, since on average, brine from these salt lakes is one order of magnitude more concentrated than seawater (Kaplan et al., 2017). The question arises, about which technologies, are best suited, or more easily adapted to obtain fresh water from brine. Therefore, if we were to find a technological and economically viable way of desalinizing, at least a certain proportion of the treated brine, the water recovered might produce very important changes in the standards of living of local populations. As an example, the water that can potentially be recovered from a facility producing 20,000 tons/year from a 700 ppm Li brine, with a 70% recovery rate is equivalent to the water household needs of 110,000 people in an average western country yearly (Food and Agriculture Organization of the United Nations, n.d.).

Primarily, water recovery will avoid the need of mining companies to pump out the already scarce fresh water for their own supply of process water. This will avoid the depletion of fresh water sources and potential conflicts with local populations which rely on that same water. Water amounts that are potentially recoverable are much larger than the fresh water needs of lithium mining companies. Therefore, we can think for example of the large area of currently desertic land that could be rendered useful for agricultural purposes provided that water would be desalinized to levels that made it apt for irrigation purposes. This is only an idea, no studies leading to its implementation have yet been reported. Moreover, using this recovered water for irrigation purposes could potentially be assimilated to keeping the water in the same basin (as opposed to evaporation). The natural infiltration of irrigation water could be considered a slower and less disruptive way of re-injecting that water back into the original aquifers. The water will be partly assimilated by crops, and partially permeate through the arid land, counteracting aquifers' depletion. This natural infiltration should be less disruptive to the natural fill characteristics than the forced daily re-injection of thousands of cubic metres of spent brine in a few dedicated wells. Of course, careful multidisciplinary studies of ecosystem change must be undertaken if abundant freshwater would be made available for irrigation.

Finally, we should once again recall that brines contain not only lithium, but also other potentially valuable resources. Most notably Mg, K, and borates are common to most brines, Cs and Rb have been reported at diluted levels in some salars (Garrett, 2004), and despite much lower market values Na salts should also be considered a resource. Concomitant recovery of these elements, together with lithium salts becomes vital in order to decrease the environmental impact of the mining

process. New methodologies should improve the eco-efficiency of raw materials extraction to turn the production process into a materials circle where waste from one process becomes the resource needed by another process, and where waste generation is avoided as much as possible. The simultaneous extraction of several raw materials from the same brine will decrease the total production cost, while decreasing the environmental impact.

The current technology discards most brine components other than lithium as waste. In addition, we have presented a discussion of why brine reinjection might not be a solution. Therefore, at this stage either the precipitated mixture of salts of the current technology, or a lithium deprived brine should be considered as waste, and therefore actions have to be envisioned to deal with such waste. Simultaneous extraction of several brine components at a single mining facility will therefore decrease the amount of generated waste, while decreasing the total salinity of brine water, facilitating the chances of water recovery after a non-evaporitic recovery methodology, as schematized in Fig. 1C. Indeed, our idea of recovering water after a non-evaporitic recovery methodology is much more sustainable if it does not imply the production of large volumes of waste that need to be discarded after water purification. For example, nowadays, some salars in the Lithium Triangle are exploited for lithium, others for borates, and yet different ones for NaCl. All of them evaporate water, and all of them produce waste. Extracting all these elements at the same location would decrease the amount of waste, reducing the environmental impact. Moreover, the environmental impact might yet be reduced if a smaller number of salars are subjected to exploitation, because several raw materials currently extracted at different facilities, could be extracted on the same spot.

8. Conclusions

Lithium is currently extracted from concentrated brines in desertic environments by a relatively inexpensive but extremely slow and relatively inefficient methodology consisting in brine evaporation in open air ponds where the different salts precipitate sequentially, with lithium carbonate being recovered from a concentrated brine in a fine treatment plant at the end of the evaporation process. This technology is only applicable to brines of certain compositions. Even for those brines where the technology is applicable a long period of piloting is needed before full scale processing can start, since the methodology is not directly transferable from one active facility to another one.

The slow pace of the process and the long period without production from the construction of a facility is a major concern to secure the supply of this raw material, which is vital for renewable energies. Despite a considerably cheaper cost for lithium extraction and processing from brines as compared to extraction and processing from hard rock, the latter persists because supply from brines is not sufficient. This methodology can certainly not cope with sudden changes in demand. While lithium mining involves relatively mild extraction procedures, with lower environmental impact than mining of metals, there are still important open questions regarding the overall impact of the mining process, particularly related to hydrological balances and waste generation. An already observed and the forecasted increased in lithium demand has therefore triggered research in new lithium recovery methodologies. Surprisingly, worldwide, only 5 full scale lithium carbonate production plants from brines were operational at time of writing this article. In the context of a boom in lithium demand, this overwhelming small number is a further indication that new brine processing methodologies are needed.

Different salars show different geological characteristics, with diverse permeability and porosity values. Moreover, because fresh water sources are not equally abundant around the different salars, we believe that each salar should be studied individually and that independent and potentially different conclusions might be drawn out of the analysis of each specific case.

It is important to work on dating the brines, as well as in the study of the development and evolution of the closed basin and hydrogeological models for these environments. In the basin evolution analysis, it is necessary to understand the transport and accumulation of sediments, as well as the precipitation of carbonates, sulphates and other evaporitic minerals, and to address the time factor for Li brines using a quantitative approach. In this scenario it will be possible to do models related to Li sources (isotope analyses), and their distribution in free and confined aquifers. A conceptual model of the catchment hydrology should be the first step. Quantification of parameters in both space and time is a must. Unfortunately, modelling variable density flows is not a trivial topic, and it is at the frontiers of knowledge (Houston et al., 2011).

A serious monitoring program of water levels both under and in the vicinity of the salar by governmental regulation agencies or independent academic institutions is certainly advised, to settle all current controversies between mining companies and environmentalists.

We have very briefly reviewed some very smart non-evaporitic Li recovery new methodologies. While some of the cited methodologies show very promising brine processing yields, there is a ubiquitous shortcoming to all of them: they do not tackle the issue of the fate of spent brines. Selective lithium recovery from native brines will produce immensely huge volumes of lithium deprived brine. This is not a secondary issue, and the possibility to effectively implement any of the said technologies will be tied up to finding ways to deal with those volumes of spent brine. While we do not completely discard re-injection into the underground aquifers altogether, the distinct and fragile sedimentary fills of the salars pose serious questions and very many essays will have to be carried out and the hydrogeological behaviour of the salar will have to be carefully modelled before any final decision can be taken regarding approval or dismissal of the re-injection idea. We must stress here once again that these analyses will have to be carried out individually for each salar, results and conclusions regarding re-injection are not to be extrapolated from one location to another one, even in neighbouring salars such as in the *Lithium Triangle*, in South America.

In this context, the whole picture of the mining, brine processing and waste disposal cycle should be analysed together. Brine re-injection is not necessarily *better*, or will produce less environmental impact than brine evaporation and the potential concomitant depletion of saline aquifers. For either of the two extreme alternatives, aquifer depletion or re-injection, more field experimental data and better hydrogeological modelling are needed in order to take informed decisions. And above all, the answer will certainly be dependent on the actual figures of pumping flow rate, volumes to be re-injected, and number of pumping/re-injection wells *vs.* total surface, geometry, and depths of each salar system. Blindly starting to re-inject huge volumes of spent brine might end up resulting in the cure being much worse than the disease.

From the analysis presented, in order to overcome the limitations of the evaporitic recovery technique, new lithium recovery methodologies should avoid altering the hydrological balance in the vicinity of the extraction facility while producing minimal waste. More efficient methodologies should be able to process brine much faster. Secondly, they should ideally be independent of climate and weather conditions and of brine chemical composition. If these requirements are met, many more brine deposits that are currently unexploitable with the evaporitic technology will become useful reserves. Moreover, replication of extraction facilities from one salar to another will become easier, without the need for long modelling and piloting.

The simultaneous recovery of other valuable components from brine, in addition to lithium salts, will help both to reduce the amount of generated waste, as well as to increase the cost effectiveness of the process, while contributing to a circular economy. Avoiding the need to carry large amounts of chemicals to isolated locations, will both decrease the processing costs and the environmental impact, by decreasing the amounts of generated waste and the use of petrol in transportation.

Finally, in a world that is slowly drying, new recovery methodologies should start looking at the water that is currently being evaporated as a potential resource, and in this context we certainly encourage the search and development of lithium recovery methodologies that attempt at water recovery as a by-product from lithium extraction.

Acknowledgments

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