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THE EVALUATION OF BRINE PROSPECTS AND THE REQUIREMENT FOR MODIFICATIONS TO FILING STANDARDS

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Abstract

The recent increase in demand for lithium has lead to the development of new brine prospects, particularly in the central Andes. The brines are hosted in closed basin aquifers of two types: mature, halite dominant, and immature, clastic dominant. The estimation of elemental resources in these salars depends on a detailed knowledge of aquifer geometry, porosity and brine grade. The geometry of the aquifers can be evaluated by classical geophysical and drilling techniques, but since the resource is a fluid, with the attendant problems of in-aquifer mixing and dilution, existing codes for filing resource and reserve estimates need modification. Total porosity is

relatively straightforward to measure, but effective porosity and specific yield, which are required to estimate the resource, are rather more difficult. Recovery factors are low compared with metalliferous and industrial mineral deposits due to reliance on pumping for extraction. These and related issues are discussed in-depth, and suggestions for changes to the reporting of resources and reserves are put forward for such brine prospects.

Introduction

Recent developments in the car industry have led to a boom in lithium exploration and development for the new generation of batteries that will power tomorrow's cars. In particular, one of the cheapest sources of lithium is the brines that contain the metal in solution. Such brines also contain other elements of commercial interest, most notably potassium and boron. As a result there has been a plethora of new exploration projects focused on the brines hosted in the aquifers of the inter-montane basins of the central Andes.

Most of the exploration is being carried out by junior mining companies with experience in metaliferous deposits, and the majority are attempting to comply with existing European, Canadian, or Australian stock market commission standards for reporting mineral resources and reserves. However, there is a fundamental problem for the companies attempting to comply with the existing standards: they apply to solid phase mineral resources, not to fluids. Since the resource is in a fluid state it has the propensity to move, mix and rearrange itself relatively rapidly during the course of a project lifetime. This is utterly unlike any other type of mineral resource, and hence requires a different approach to its investigation and evaluation. There are no standard methodologies for evaluating water resources, since water is usually considered to be in common ownership under the control of the state. Hence the requirement for new or modified filing standards.

Here, we review the requirements for brine resource/reserve evaluation, drawing on several examples from our experience in the central Andes.

Continental brine occurrence

Worldwide

Brines have been exploited on a relatively small scale at Silver Peak in Nevada, and Searles Lake, California for many years. However, the largest tonnages occur in the Andes of Chile, Argentina and Bolivia and in Western China and Tibet. The latter group, however, have complex chemistries, and the economic recovery of the contained Li, and associated elements is proving difficult. This is not the case in South America, where three operations (Soquimich and Chemetall in the Salar de Atacama, FMC in Hombre Muerto) are responsible for a very large percentage of the current world lithium supply. These sources together with more recent discoveries are expected to meet much of the massive demand for the electrification of motor vehicles (refs).

Basin and host aquifer formation in the Altiplano-Puna

The Altiplano-Puna is the second largest high altitude plateau in the world and is the focus of numerous brine bodies containing high concentrations of Li amongst several other species of economic interest. The Andes of western South America are the result of subduction processes as the Nazca plate descends beneath the South American plate (Figure 1). The central volcanic zone between 14°S and 28°S is the location of an extensive Neogene ignimbrite province (de Silva, 1989) that is underlain by one of the largest magma bodies in existence on earth, known as the Altiplano-Puna Magma Body (APMB) (Zandt et al., 2003; de Silva et al., 2006). Whilst the origin of the high Li concentrations in the brines of the Altiplano-Puna is considered to be intimately linked to volcanism (Ide and Kunasz, 1981), its precise origin remains speculative. The distribution of Li-bearing salar brine is roughly coincident with the APMB, but simple weathering of glass from these volcanic rocks as suggested by Kay et al. (2010) does not account for the very high Li/Mg ratios that characterize many of the Central Andean brines. The simplest way to produce brine with relatively low Mg concentrations relative to Li is to extract both elements from rocks at high temperatures which results in sequestration of Mg in smectites (Badaut and Risacher, 1983). Hydrothermal fluids can also introduce elevated alkalinity to groundwater which removes Mg from solution relative to Li as the water evaporates upon reaching the land surface. Weathering occurring at high temperatures may not be necessarily due to an unusually high heat flux, but to very low precipitation resulting in deep water tables allowing groundwater to be closer to a heat source (e.g., Gibert et al., 2009).

In the central Andes and Altiplano-Puna plateau, salt pans, known locally as *salares* form in closed topographic depressions (endorheic basins). Salars occur at all elevations from 1000 m to more than 4000 m above sea level (Figure 2). They generally represent the end product of a basin infill process that starts with the erosion of the surrounding relief, initially depositing colluvial talus and fan gravels, grading upwards into sheet sands, and playa silts and clays as the basin fills. There are many variants to this model and the tectonic and sedimentary processes that lead to the formation of such basins have been widely addressed in the literature both generally (Hardie et al., 1978; Reading, 1996; Warren, 1999; Einsele, 2000), and specifically with regard to the Altiplano-Puna (Ericksen and Salas, 1989; Alonso et al., 1991; Chong et al., 1999; Bobst et al., 2001; Risacher et al., 2003; Vinante and Alonso, 2006).

Structure controls the compartmentalization of many Andean basins. North-south aligned thrust faults, grabens and half grabens frequently create accommodation space, whilst transverse strike-slip faulting may assist with basin closure, offsetting basins against impermeable bedrock (Salfity, 1985; Marrett et al., 1994; Reijs and McClay, 2003). Volcanism also plays a significant role, both in basin infill (e.g. tuffs and ignimbrites), and in basin closure (e.g. volcanic necks and lava flows).

The latitude of the central Andes and its position under the subtropical high pressure belt for at least the last 55 million years (Hartley et al., 2005) has influenced both the type of sedimentary infill, and its architecture within the basins. Basin closure is thought to have occurred frequently around 14 Ma (Vandevoort et al., 1995), although the majority of evaporitic deposits appear to be less than 8 Ma (Alonso et al., 1991).

Recent evidence suggests that the Andes reached their current elevation around 6 Ma ago (Ghosh et al., 2006), and since that time the climate has been dominated by hyper-arid conditions (Hartley and Chong, 2001) allowing ample opportunity for evaporation of the influent water. However, during the same period there have also been excursions into wetter conditions (Fritz et al., 2004: Placzek et al., 2006; Rech et al., 2010), potentially allowing salt recycling. During the course of the aquifer formation, influent ground and surface waters have not always had the opportunity to escape from the basin, leading to the formation of temporary lakes or wetlands. Since the influent waters contained dissolved solutes as well as transported sediment load, evaporation resulted in the precipitation of salts, leading to the deposition of a wide range of evaporite deposits. Depending on the paleohydrological history of the basin, the deposition of evaporites may have taken place on more than one occasion, generating repeat sequences. There is a typical precipitation sequence starting with carbonate (typically calcite) as the first mineral precipitated, through sulphate (typically gypsum), to chloride (halite). Of course, natural salars rarely conform to this ideal. Asymmetry, gradational, and changing boundary positions due to climate change, tectonism, and sediment supply are normal.

Salar types

We recognize two types of host aquifers in the Altiplano-Puna: mature halite salars and immature clastic salars (Figure 3). A classification of salar types in the Altiplano-Puna is provided in Table 1.

Immature salars tend to be relatively small, and are more frequent at higher elevations and towards the wetter northern and eastern parts of the region. They are characterized by an alternating sequence of fine-grained sediments and evaporitic beds of halite and/or ulexite, representing the waxing and waning of sediment supply under a variable tectonic and climatic history. The contained brines often barely reach halite saturation, suggesting that the recent climate has not been severely hyper-arid, although the frequent occurrence of a thin surface halite crust attests to the contrary for current climatic conditions. The alternation of drier to wetter climates may lead to disequilibrium between evaporation rates and the brine concentration at a given time. The brines are normally fully saturated with respect to gypsum, leading to the widespread occurrence of gypsum (typically as selenite) throughout the sequence. Past dry climate intervals are evidenced by buried halite beds suggesting that decreased precipitation inflow and/or increased evaporation may have lead to brines saturated in halite. The presence of intercalated or underlying beds of different permeability sometimes allows the transmission of fresher waters from outside the salar margins through to the centre where there is a tendency for the density differential with the nucleus brine to allow its upward flow, providing that the confining bed has sufficient permeability to allow such leakage.

Mature salars tend to be larger and more common in the lower and drier parts of the region. They are characterized by a relatively uniform and thick sequence of halite deposited under varying subaqueous to subaerial conditions (Bobst et al., 2001). Nevertheless, ancient floods leading to widespread silty-clay deposits and volcanic fallout lead to relatively thin intercalated beds that can be recognized both in cores and geophysical logs. Such layers of varying permeability may lead to the transmission of fresher water from outside the salar margins to the edge of the nucleus where, once unconfined, float to the surface, dissolving halite in their ascent and leading to pipes and salt dolines at the surface (Figure 3). The contained brines are invariably halite saturated throughout the brine body, although the presence of multiple brine types, especially in the larger salars points to the hydrochemical variation of the contributing sub-basins.

The distinction between salar types is maintained, even within the same basin, as at Hombre Muerto where a mature sub-basin exists to the west and an immature sub-basin to the east. Both types of salars may contain commercially valuable brine resources, and whilst 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 (Table 1), and of course, clastic deposits possess considerably higher porosities than halite.

The pattern and distribution of crustal types may allow the identification of salar type in the field. Both types display the same range of features, from high reflectance re-solution crust, through salt polygons, to low-reflectance pinnacle halite, representing a progression from younger (< 1 yr) to older (> 10 yr) formation. However, immature salars tend to have a much larger proportion of their surface represented by re-solution crust, and relatively small areas of pinnacle halite, and this is readily identifiable on satellite imagery.

Porosity and permeability

There is considerable misunderstanding of the terminology related to porosity. Total porosity (P_t) relates to the volume of pores contained within a unit volume of aquifer material. Except in well-sorted sands some of the pores are isolated from each other and only the pores that are in mutual contact may be drained. This interconnected porosity is known as the effective (P_e). Assuming that the P_e is totally saturated, only part may be drained under gravity during the pumping process. This part of the porosity is known as the specific yield, or sometimes the drainable porosity (S_y). A portion of the fluid in the pores is retained as a result of adsorption and capillary forces and is known as specific retention (S_r). These parameters are related thus:

$$P_t > P_e \qquad\qquad P_e = S_y + S_r \qquad\qquad S_y \gtrless S_r$$

The relationship between S_y and S_r depends largely on lithology (Figure 4). In fine grained sediments $S_y << S_r$, whereas in coarser grained sediments $S_y >> S_r$. The determination of these pore parameters is probably the most challenging aspect of brine resource estimation.

Brine chemistry

The brines in the salar aquifers are thought to have evolved from the evaporation of dilute inflow waters, ultimately derived from precipitation. However, in some cases there might be a deep hydrothermal component (Orti and Alonso, 2000; Gibert et al., 2009). Concentration by evaporation leads to the development of chemical divides (Hardie and Eugster, 1970), which create differing end points depending on the original ionic ratios, especially for the $Ca-SO_4$ system. The initial ion ratios in the influent waters depend on their passage over and through the basin rocks, and if several catchments drain to the same salar, may result in multiple brine types within the aquifer. The Hardie-Eugster model interprets the chemical evolution in terms of a series of divides that lead to at least six alternative evolutionary pathways, although only two are common in the Altiplano-Puna. The exact concentration and density at saturation is dependent on the dissolved species, although empirical guidelines can be provided. The first mineral to precipitate is calcite, typically at concentrations of around 30 gm l^{-1} TDS (approximate density equivalent 1.03 gm cm^{-3}). This is usually followed by gypsum, typically at concentrations at about 200 gm l^{-1} (approximate density equivalent 1.15 gm cm^{-3}), or in alkaline conditions by magnesium-rich smectite (Badaut and Risacher, 1983). Halite saturation begins only at TDS concentrations of around 280 gm l^{-1} (approximate density equivalent 1.22 gm cm^{-3}), and a Na-Cl divide is rarely seen at concentrations of less than 320 gm l^{-1}.

The most common brine types in the Altiplano-Puna, based on data in Risacher et al. (2003) for northern Chile, Rettig et al. (1980) and Risacher and Fritz (1991) for Bolivia, Igarzábal (1984), and unpublished data for north-western Argentina, are $Na-Cl-SO_4$ and Na-Cl-Ca. The economically important elements Li, K and B are normally found to covary with Na and Cl, but there are some notable deviations. For example, at certain locations within several salars Li concentrations are much higher than expected, increasing beyond NaCl saturation (which results in halite precipitation). At Cl concentrations above about 160 gm l^{-1}, the Cl:Li ratio is typically >300. However, close to the mouth of the relatively dilute influent Rio Grande in the Salar de Uyuni, and again close to fresh water inflows at Hombre Muerto they drop to ca. 140. The reasons for these very high lithium concentrations so close to dilute inflows is currently unknown, but may involve recycling or geothermal sources.

The source of the salts and particularly the economic components such as Li, K and B are the subject of debate. Based on their geochemistry it appears that recycling of earlier deposits/salars seems to be a common factor in many salars (Risacher and Fritz, 1991; Orti and Alonso, 2000; Risacher et al., 2003; personal communication, Godfrey 2010), and this is supported by mass balance and accumulation rates analyzed in the Salar de Atacama (unpublished data). Mixing with pre-existing subsurface brines has also been suggested (Risacher et al., 2003), but neither of these hypotheses point to an ultimate source for the anomalous values of Li and other minor elements. Other explanations for the high values of Li and B include weathering of Neogene volcanic rocks (Rettig et al., 1980; Orti and Alonso, 2000; Kay et al., 2010), or Palaeozoic basement (Ortis and Alonso, 2000; Kasemann et al., 2004), and transport from hydrothermal volcanic activity (Orti and Alonso, 2000; Gibert et al., 2009; personal communication, Godfrey 2010).

Brine hydrology and water balance

The brine solution in all South American Altiplano Salars has been formed over many years ($10^4 – 10^5$ yr) in endorheic basins. Precipitation within the catchments drains towards the center of the basin either as surface or groundwater that contains dilute solutions of commercially interesting elements. Around the margins of the salar the drainage water is either close to the surface or may form open water lagoons. Extremely high rates of evaporation prevail in this marginal zone (Figure 5). Evaporation of the relatively fresh influent water causes concentration of the entrained dilute dissolved salts. Very small volumes of concentrated fluid then enter the salar nucleus and replace very small amounts of brine evaporated from the surface of the salar. Halite crusts are quite impermeable (Kampf et al., 2005), and within the nucleus of the salar the depth to brine is controlled by limited evaporation, the extinction depth for which is universally between 0.5-1.0 m (Houston, 2006).

Although the brine is generally considered to be static or "fossil", the system is actually in dynamic equilibrium, with a slow turnover controlled by evaporation. The dynamic aspect of these salars is also attested by the presence of dissolution pipes within their nuclei, combined with halite saturated brine bearing no indication of evaporation based on the stable isotopes of O and H (Fritz et al., 1978). Furthermore, within the brine body a density driven convection cell sometimes develops. Evaporation at the phreatic surface increases the brine density causing it to sink through the aquifer. This sinking manifests in reduced heads with depth in the centre of the salar. Correlative increasing heads with depth towards the edge of the brine body indicate return flow of brine to the surface.

The water balance of these salars is given by the following equation:

$$P + I_{SW} + I_{GW} - E_M - E_N = \Delta S$$

where P is precipitation over the salar, I_{SW} are surface water inputs, I_{GW} are groundwater inputs, E_M is the marginal evaporation, E_N is the nucleus evaporation and ΔS is the change in storage within the nucleus (manifested by increasing or decreasing brine levels).

By ignoring evaporation, since it does not remove salts from the system, the water balance can be converted to a mass balance thus:

$$P*C_1 + I_{SW}*C_2 + I_{GW}*C_3 = \Delta M*(1-P_t)$$

where C represents the concentration of the respective fluid, ΔM is the mass change in precipitated material and P_t is the total porosity of the precipitated material.

The transition from fresher waters to brine around the salar margin creates an interface in the subsurface that is governed by both layer permeability and the Ghyben-Hertzberg law. The latter states that within a homogeneous and isotropic medium, the depth to the interface is a function of the freshwater head and the ratio of the freshwater to brine fluid density. This inevitably leads to the expansion of the brine body at depth.

Brine body response to extraction

Immediately pumping (extraction) starts, redistribution of the resource begins since the fluid is being dynamically stressed. Pumping induces a cone of depression in the phreatic (water table) surface around the wellfield. The size and shape of the cone of depression depends on the physical properties (permeability and storage) of the aquifer, as well as the pumping rate and duration. Thus the cone of depression expands outwards (and downwards) over time until a new dynamic equilibrium becomes established, which may take many years before stabilizing.

The controlling factor for extraction rates is the permeability of the aquifer, with higher (lower) values being more (less) conducive to higher (lower) yields. The permeability of mature halite salars is very different from immature clastic salars. The former tend to be rather more homogeneous and isotropic, and the permeability is controlled by matrix porosity and in some zones by fissures. Unpublished data from the Salar de Atacama and Hombre Muerto indicate that fissures are most common at depths between 5-25 m in halite, and in these zones permeability may reach extremely high values (to 10^5 m d^{-1}), whereas matrix values in the upper 30 m are normally in the 10-30 m d^{-1} range. Below 30 m, the permeability of halite decreases significantly as a result of compaction, and crystal overgrowth. On the contrary, clastic sediments tend to be inhomogeneous and anisotropic, permeability being highly dependent on lithology. Fissures are largely absent, so that permeability may range anywhere between 10^{-2}-10^2 m d^{-1}, and declines only slightly with depth (over the likely depth range for extraction).

In mature halite salars the high permeability and relatively low S_y result in a flat cone that rapidly extends laterally (Figure 6A). Immature salars with relatively low permeability and higher S_y result in a steep cone that tends to deepen faster than it extends (Figure 6B). Almost inevitably, the cone will extend to the boundaries of the aquifer after a period of time, and what happens depends on the nature of the boundary. If it is permeable, off-salar fluids will flow inward (Figure 6A, solid line). On the other hand if the boundary is impermeable (Figures 6a and 6b, dashed lines) the cone will increase its downward rate of propagation.

In the event that off-salar fluids are drawn into the cone of depression, barren brine and/or "fresh" water may eventually migrate to the wells. This is exacerbated if the inflow is of a lower density, since the two fluids will tend to be immiscible, with the inflow floating over the resource brine. Ultimately the inflow may pool in the cone of depression creating problems with the extraction of the reserve brine.

A related extraction problem that occurs in both mature and immature salars is the ingress of fresh water at depth, as a result of higher permeability layers or beds (for example thin sand and gravel beds) extending into the salar (Figure 3). The fresh water in these beds is usually sourced from recharge outside the limits of the salar and transferred through the higher permeability bed as a result of an overlying confining layer. Where the confining layer feathers out the fresh water is released and tends to rise as a result of its density differential with the surrounding fluid. In halite, this may lead to the formation of solution pipes that reach the surface. The importance of this mechanism can be seen in Figure 7, where the rather concentrated in-situ brine has the potential to be somewhat diluted during pumping as a result of mixing with the fresh water that enters the well from thin sand horizons.

For a given set of hydrogeological conditions, and pumping rates, a larger and more nearly circular salar will be better able to support long term extraction than a smaller or elongate shape. In addition to aquifer size and shape, storage exerts control over the scale of the recoverable reserve. The ratio of extraction volume to storage volume will help to determine the life of a project. This is particularly important since it is not widely appreciated that a rule of thumb for the recovery factor of brine from an aquifer is only around one third.

Requirements for a brine evaluation

An in-situ brine resource evaluation should consist of three essential elements: the geometry of the host aquifer, the S_y of the host aquifer, and the concentration (grade) of the elements of interest in the brine. The product of the geometry and S_y determines the volume of the brine resource. The elemental resource is determined as the product of the brine volume and the grade of the element in the brine.

Host aquifer definition

Aquifer extent and depth, as well as boundary conditions (e.g. faulted, gradational) are necessary to establish the limits of the reservoir, and the possible interactions between the contained brine and surrounding groundwater. Within the nucleus of the salar, the lithological variations of the aquifer, and its hydrostratigraphy will control both brine storage and transmission. Initial studies often use geophysical techniques such as gravity or seismic, but inevitably drilling will be needed for a resource estimate. Drilling mature halite salars is considerably easier than immature clastic salars where unconsolidated, often overpressured formations create difficulties, and may require special techniques, such as sonic or triple-tube diamond rigs.

Drill sites within claim areas should be on a grid spacing to facilitate subsequent analysis. The size of the grid will depend on the type of aquifer (salar) and on the level of confidence required. Table 2 provides some guidelines that have been used in several investigations. The spacing may seem quite coarse when compared with industrial mineral exploration, but it is unlikely that horizontal changes in brine chemistry will be more rapid. As important is the vertical sampling interval for porosity and brine chemistry. Samples for both porosity and brine chemistry should be taken at the same localities so as to ensure compatibility during resource calculation. In some cases a vertical sample interval of 0.5 m has been chosen, but with increased experience it would appear that 1.5 m is acceptable for a Measured Resource, expanding to 5 m for an Inferred Resource, although this does depend on hydrogeological conditions, and should be reviewed based on exploratory data.

High core recoveries are essential in environments where rapid vertical changes in lithology may control both porosity and brine variations. Geological logging of the cores needs careful control to avoid subjective description bias in these environments. Once the holes are at full depth, geophysical logging will assist with hydrostratigraphic analysis. In this regard, the most useful tool is usually natural gamma, since electric logs are generally swamped by the extremely low resistivity of the brine.

Core sampling for the laboratory determination of porosity must be undertaken on undisturbed samples. These may be difficult to obtain in unconsolidated formations using conventional methods so that split spoons or Shelby tubes pushed ahead of the drill face may be necessary. On-site laboratory determination of P_t and P_e is not difficult using gravimetric methods, providing initial moisture loss is prevented after core extraction, and subsequently controlled to a stable weight in the laboratory. It is essential not to dry the cores at too high a temperature or gypsum will convert to anhydrite, and organic matter may incinerate creating erroneous measurements. Furthermore, due account must be taken of the salts precipitated during the drying process as a result of brine evaporation.

In a recent study, samples from lexan core barrels (9.4 cm diameter) were compared with split spoon cores (3.4 cm diameter), both obtained by sonic drilling. The resulting P_t determinations (Figure 8A) show wide scatter despite good correlation ($r = 0.65$; $p<0.001$). This scatter is partly a result of the depth difference between the lexan and split spoon cores (0.3 m) in a thin-bedded sequence with rapid alternations of lithology. The veracity of these measurements can be seen when compared with the geophysical log (N-Pt) in Figure 7.

The determination of P_e, S_y and S_r present special problems, and there are no standards for this. Two methods are in common use for the laboratory determination of P_e: liquid resaturation and helium injection. The former usually requires the initial drying of the sample and subsequent resaturation using formation brine or an inert liquid such as isopropyl alcohol, although fully saturated samples can be tested and then dried. The latter involves the injection of helium into the sample under controlled conditions. P_e is calculated using Archimedes principle and Boyle's law respectively. The results (Figure 8B) suggest that the liquid resaturation method may underestimate P_e in fine grained sediments as a result of extended drying times required. For S_y centrifuge techniques are used, but for reliable and repeatable results it is essential to control rotation speed to induce a moisture tension of ca. ⅓ atmospheric (the point at which gravitational flow effectively ceases in medium grained sediments) and temperature to $4^{o}C$ (Johnson, Prill and Morris, 1963; Lawrence, 1977). Independent checks on porosity may be made using resin impregnated cores, thin-sectioned and point counted under a microscope. Petrological inspection also allows the extent of grain disturbance and salt overgrowth to be estimated.

In some cases pumping tests have been used to determine S_y for the resource assessment. But it is essential to understand that whilst pumping tests on wells determine the S_y of the aquifer directly, the determination is made within the dewatered cone of depression (Walton, 1970; Bear, 1972). This is contrary to the source of the fluid being pumped at the same moment, which originates from the saturated zone below the cone of depression, hence precluding the use of pumping tests as a means of establishing the in-situ resource.

Neutron and density (gamma-gamma) logs provide a means of converting the point measurements determined in the laboratory to a continuous porosity profile, although it must be remembered that such logs determine P_t, even after calibration for the varying lithologies, so that algorithms for the conversion of P_t to P_e and S_y are required. Examples of such algorithms are shown in Figures 8c and 8d, for P_e and S_y respectively. Consequently, it is essential to provide a clear set of protocols with appropriate QA/QC procedures when reporting porosity determinations for resources and reserve calculations if their validity is to be assessed.

The permeability of the formations will be needed to assess well yields, and flow regimes under both natural and pumped conditions in order to estimate a recoverable reserve. An important consideration is that data will be required from outside the claims blocks since fluid movement is no respector of claim boundaries. Permeability within the aquifer may be established using pumping tests or laboratory determinations on core, although the former is likely to be better able to predict flows at field scale. Strictly speaking, permeability (k) is a function only of the matrix, with dimensions L^2, whereas flow through the aquifer is also controlled by the fluid density and viscosity, and should be properly termed hydraulic conductivity (K) with units of length per time. This becomes important during simulation modeling of recoverable reserves where changes in density enter the picture.

Brine body definition

The geometry of the brine body within the aquifer requires definition. The boundaries will be controlled by the transition zone to fresh water, which will conform to Ghyben –Herzberg principles. Time-domain electromagnetic or audio magneto-tellurics provide a means of establishing the approximate limits of the brine body, taking into account the uncertainties introduced as a result of the lack of a unique solution (Archie's Law: Archie, 1950).

Brine sampling needs to be undertaken to conform with the porosity sampling plan for the eventual resource estimate. Samples may be taken as either point samples or as zone samples using packer arrangements to isolate a section of the well. This becomes impossible in unstable formations where point sampling is the only option. Obtaining in-situ point samples may prove as challenging, or even more so than the porosity analysis. How can it be proved that the sample comes from the formation at a specific depth, rather than mixed with drilling fluid or overlying brines leaking around the drill rods or casing? Drilling dry using reverse circulation or sonic techniques is an obvious prerequisite, but may prove impracticable at depths greater than ca. 100 m, since the rods may get stuck. The use of a tracer in the drilling fluid and well water prior to sampling may assist in determining whether the sample is depth-specific or contaminated with over- (or under-) lying brines. A wellpoint pushed ahead into the formation will help, but during insertion of the wellpoint it will most likely fill with the mixed well fluid requiring either evacuation of the entire column above the wellpoint or low-flow pumping from within the wellpoint. If adequate core samples are available, the extraction of fluid from the matrix, after removing the potentially contaminated skin of the core, and centrifuging may provide sufficient uncontaminated in-situ sample for analysis (Figure 9A). Experiments recently conducted at the Salar de Olaroz in holes drilled without any fluid additives in unconsolidated clastic sediments have shown that where the casing closely follows the drill bit, samples bailed from within the casing are representative of in-situ brines (Figure 9B). Obtaining representative in-situ brine samples may thus not be so much of a problem as at first sight might be anticipated, but it is always necessary to check, and to be able to demonstrate the fact.

Certain parameters should be determined at the wellhead: temperature, density and pH as a minimum, since they may change during transit to the analytical laboratory. Brine analysis in the laboratory is not addressed here but it is noted that it is not as straightforward as for dilute waters, as several commercial laboratories have demonstrated, and a set of QA/QC procedures is essential to establish the validity of the results.

Once again, sampling outside the claim boundaries is required to investigate the grade/quality of fluids that may potentially get drawn into the reserve during extraction.

Putting it all together - in-situ resources

For a resource estimate, the aquifer geometry will be defined by the area of the claims and the depth determined from drilling results. Whilst this is required for valuation purposes, it should be recognized that this is only a convenience, since once extraction starts, resources may well be pulled in from outside this area. Where two properties are adjacent, this could lead to competitive extraction techniques, requiring some form of mutually acceptable compromise or arbitration.

It has been common practice in the past, for example at the mature salars of Atacama and Hombre Muerto to use P_e to define the resource, and to base the reserve evaluation on S_y. In mature salars, P_e is only slightly greater then S_y, so that the reserve base is only slightly less than the resource. The term “reserve base” when applied to a fluid is used to differentiate the potentially extractable volume from the actually extractable reserve, which depends on the ability of the hydraulic parameters to allow extraction by pumping (see below). Now that immature salars are being developed however, the use of P_e to determine the resource would lead to a significant difference between the reserve base and the resource: potentially by as much as an order of magnitude difference. Thus, we suggest that S_y be used to determine both the resource and the reserve in all salar types. This dilemma clearly compels the qualified person (QP) reporting the resource to ensure that sufficient detail and explanation be provided so that the result is not misleading.

Numerous modeling packages are available for resource estimation, but it is always necessary to consider how the data gets put together for these to work properly. Firstly, the model cell density should approximate that of the drill holes; increasing the cell density does not increase the precision of the estimate as some recently published work supposes. Secondly, the ideal method for calculating resource tonnages will be based on the derivative at each data point, so that:

$$G^{z,x,y} = P_e^{z,x,y} * C^{z,x,y} * b^{z,x,y}$$

where, $G^{z,x,y}$ is the unit volume tonnage, $P_e^{z,x,y}$ is the effective porosity, $C^{z,x,y}$ the elemental concentration, and $b^{z,x,y}$ the unit thickness (note that "unit" as used here is not a geological unit - it is the cell unit). The superscript z refers to depth, and x, y are horizontal coordinates. Since b and z values should ideally be equivalent across the claim area, the resource can be considered as a 3D matrix of j unit cells:

$$Resource = \sum_{z,x,y=1}^{j} G^{z,x,y}$$

It is tempting to average parameters for each well or lithologic unit, and sum the *n* well results across the claim area, but this results in:

$$Resource = \sum_{well=1}^{n} \left(\{[\sum_{z,x,y=1}^{k} P_e^{z,x,y}]/k\} * \{[\sum_{z,x,y=1}^{k} C^{z,x,y}]/k\} * \sum_{z,x,y=1}^{k} b^{z,x,y} \right)$$

where k is the number of depth samples. This will result in a mathematically different estimate, and is not the best use of the data.

However, in immature salars, it is likely that samples for different parameter evaluation (P_e, S_y, permeability, brine chemistry) may be separated by vertical distance up to several centimeters, and in cases where bed thicknesses are thin relative to the vertical sample interval may result in parameters at a specific depth interval being representative of different lithologies. Thus it may be necessary to break the resource down into a series of layers or zones. Since in thin bedded environments, lithology and flow tends to be near-horizontal, such zoning should not induce significant errors. Spatial analysis will then be carried out layer by layer. Since the vertical sampling interval may be of the order of 1 m, the maximum number of layers might rapidly approach or exceed 100, equal to the number of samples in the vertical direction. However, this is probably unwieldy, and we suggest that 10 m layer thicknesses are a reasonable compromise, although site-specific conditions must always be taken into consideration. This layer thickness proved to give useful results in the cases of the mature salars of Atacama and Hombre Muerto, but the more variable immature salars appear to require thinner layers to give the most useful results. The use of layer resource estimates is of benefit when considering reserves too, since over time there will be a tendency to exploit deeper and deeper layers as the cone of depression from the pumping wellfield expands.

Algorithms available for estimation of cell or layer tonnages are numerous, and well documented in the literature (e.g. Cressie, 1993) so that no review is necessary here. However, it is perhaps worth mentioning that Kriging has attracted widespread use, and approval for hydrogeological studies (e.g. de Marsily, 1986; Kitanidis, 1997).

Putting it all together - extractable reserve

The potentially extractable volume of brine (reserve base) is defined by the S_y of the aquifer, or the proportion drainable under gravity. As discussed above, coarser grained sediments and halite, present S_y only slightly less than P_e due to minor amounts of S_r. However, for fine grained sediments P_e diverges significantly from S_y (Figure 4) as a result of considerable S_r. Thus for the purpose of comparing resources and reserve base across different types of salar it is recommended that both the resource and the reserve base are calculated using S_y.

Only a relatively small proportion of the reserve base is extractable by pumping. Under any circumstances it is only possible to pump out a fraction of the fluid from an aquifer since the cone of depression around a well or wellfield can never lower the water level throughout the aquifer to its base. A rule of thumb for the recovery factor (the volume that can be pumped out) of an infinite aquifer is one third of the reserve base. In the mature salar example shown in Figure 6A, assuming a circular aquifer of radius 10 km, with an impermeable boundary, it would require 60 wells, spaced at 1.3 km, each pumping at 20 l s^{-1} for 25 years to extract 33% of the resource. For the immature salar in Figure 6B, the comparable number of wells would be almost

250, spaced at ca 600 m. Once well inefficiency, drawdown limitations, possible barren inflows and economics are entered into the equation, extraction of more than 33% is only possible under exceptional circumstances.

Many salar boundaries are permeable and extraction causes inflow to replace the volumes removed. Thus the brine body does not exist in isolation from its surroundings, so a broad understanding of the catchment characteristics is required in order to establish how the brine reservoir has become established, maintained, and will react to future changes as a result of pumping. A monitoring program to measure hydrometeorological parameters, surface water and groundwater flows, levels and quality is required to establish baseline conditions against which future changes can be compared. A conceptual model of the catchment hydrology is the first step. Quantification of the model parameters in space and time will allow a water balance to be established.

For the reserve analysis, it will be essential to build a digital flow simulation model, using one of several codes available on the market. Modelling variable density flow is a highly specialized subject, at the limit of current knowledge, and requires the services of experts in this field, who are not necessarily familiar with resource studies so that the integration of disciplines becomes paramount. Clearly, a well tested and documented code is to be preferred. The advantages and disdvantages of the various models are given for example in Spitz and Moreno (1996) and Simmons et al. (2010), and references therein, and are not considered in depth here. Two important points do need to be considered however: the requirement to simulate (reactive) solute transport and changes in brine density. The former are necessary to establish how grade may change over time and are in widespread use, especially for contaminant studies, but as far as we are aware no examples exist where solute movement has been linked to aquifer matrix dissolution, as might well be the case where dilute waters enter halite aquifers. This is an area that needs research. Variations in brine density cause flow in the same way as head does. Such variations are also problematic inasmuch as for small differentials (<0.01 gm cm^{-3}), two fluids are miscible, whereas at greater differential they are not. Thus whilst hydraulic conductivity values determined from pumping tests in the field and input to the model take care of small variations, large variations in density require two phase flow to be simulated. A similar situation occurs in coastal aquifers where seawater intrusion is explicitly modeled based on Ghyben-Herzberg principles, but the form of this, which often simulates a freshwater lens sitting in an oceanic island, is different from a brine body in a halite aquifer surrounded by freshwater. The latter being rarely modeled; to our knowledge only in the mature salars of Atacama and Hombre Muerto, although even here no comparison with a single phase model was ever attempted.

Finally, it should be clear from the preceding discussions that as a result of fluid reorganization, mixing, and inflows, a reserve estimate is not a static figure, even assuming that it could be calculated with precision. As extraction continues, the reserve will change, over and above (or below) the amount extracted. Thus, whilst it is obviously necessary to have a prediction for the tonnage over time, we question whether the use of a single reserve figure is the best way to approach the issue. Water resource engineers are used to dealing with unstable dynamics and we consider that this may also be a requirement for brine development.

Modifying standards

The existing codes for mineral resource/reserve reporting (JORC, 2004; NI 43-101, 2005; PERC, 2008) have all been prepared for solid phase minerals, and whilst they are broadly applicable to brine resources/reserves do not deal with them specifically. It can be seen from the foregoing review, that there are several important differences that arise when considering a fluid prospect.

The most important differences relate to the fluid nature of the prospect:

- Host aquifer property control – the resource is controlled by aquifer porosity, and the reserve by permeability,
- Brine body uniformity – because it is fluid the brine body is much more likely to have been homogenized during formation, at most a few brine types may occur relating to different source (catchment) areas,
- Fluid mixing – despite homogenization, dilute inflows can penetrate deeply into the aquifer and mix with the in-situ brine to cause grade variation during production,
- Influence from outside the claim area – during extraction, depending on the ratio of pumped to stored volume, extraction may rearrange the brine body necessitating investigation beyond the claim boundaries to assess the water balance and fluid properties throughout the catchment.

As a result the guidelines and requirements for reporting in the Codes may in part be inappropriate. The Contents of the Technical Report for NI 43-101 in particular require modification. Item 10, Deposit Types, does not translate well to brine prospects; there are no type deposits – aquifers form in an almost infinite variety of volcano-sedimentary deposits and structural settings. Here, we distinguish only mature and immature types. Thus we would prefer to see this chapter headed "Host Aquifer", containing all the investigations and interpretations relating to its geology, structure and physical properties. Item 11, Mineralization also does not translate well, implying as it does a fixed and time-invariant ore body. We would prefer to see this chapter headed “Brine Body”, containing information on grade, the existing geometry of the brine, and its relation to surrounding hydrogeology.

We also suggest that a new chapter is required to evaluate the water balance, and to investigate (or predict) what will happen to the resource during extraction. We suggest this chapter be called “Extraction Considerations”. Some consideration of the water balance and potential grade reorganization during extraction should be included in a resource statement. At the reserve level, this stage necessarily requires the formulation, calibration and running of a fluid flow digital simulation model to predict grades during project lifetimes. As previously discussed, this does not apply to a Mineral Reserve as defined by the current Codes, since a solid phase mineral deposit will not change within project lifetimes.

Given the different requirements for brine prospect evaluation, it becomes even more important to establish and document protocols for data acquisition and analysis. Such protocols should be included within the Technical Report so that third parties may be able to understand what was done, and to ensure that any due diligence be properly informed.

Since the concept of the Codes is based on transparency, materiality, impartiality and competence, we also recommend that specialized hydrogeological knowledge is applied to the investigation and reporting of these prospects.

Conclusion

Salars represent a relatively new and attractive source for elements such as lithium, potassium and boron. Existing operations at Silver Peak, Searles Lake, Salar de Atacama and Hombre Muerto are among the few examples that may provide guidelines for exploration and development of brine resources and reserves. Current reporting requirements are all aimed at solid phase mineral deposits and therefore not ideally suited to fluid brine prospects. The resulting variation in reporting standards lead to uncertainties and inconsistencies in project evaluation, which can be confusing for analysts and investors.

For any brine prospect the fundamental issues for evaluation are the host aquifer, and the brine body. The resource is estimated based on aquifer volume within the claim boundaries, its specific yield and brine grade. A reserve, in addition to economic and process aspects, requires estimation of extractable grade variation *as a result of in-aquifer mixing* with barren brine or fresh water.

Consequently we consider that the current requirements for disclosure and reporting of fluid mineral prospects need revision. It is essential, as we have shown, to be very clear which porosity parameter has been measured, and we recommend that the historical practice of using effective porosity to estimate the resource and specific yield as the base for the reserve evaluation be discontinued, and instead specific yield be used for both the resource and the reserve. We also believe that chapters on Host Aquifer and Brine Body should replace those of Deposit Type and Mineralization respectively, and a chapter on Extraction Considerations be added to both resource and reserve filing requirements for brines.

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Table 1

Selected salar types and brine chemistry in the Altiplano-Puna region (MAP = mean annual precipitation).

Salar	Area (km^2)	Elevation (m asl)	MAP (mm)	Salar type	Brine type	Cl ($gm\ l^{-1}$)	Li	K	B
Uyuni	10,000	3,653	150	Immature	Na-Cl-SO_4	190	0.42	8.7	0.24
Atacama	2,900	2,300	25	Mature	Na-Cl-Ca/SO_4	210	2.55	27.4	0.82
Olaroz-Cauchari	550	3,900	130	Immature	Na-Cl-SO_4	180	0.71	5.9	1.09
Huayatayoc-Salinas Grande	2,500	3,400	180	Immature	Na-Cl-Ca/SO_4	190	0.78	9.8	0.23
Rincon	280	3,740	63	Largely mature	Na-Cl-SO_4	195	0.40	7.5	0.33
Arizaro	1,600	3,500	50	Immature	Na-Cl-SO_4	190	0.08	4.0	0.12
Pocitos	435	3,660	60	Immature	Na-Cl-SO_4	170	0.09	4.8	1.32
Antofalla	540	3,580	-	?Immature	Na-Cl-SO_4	166	0.32	4.7	10.80
Hombre Muerto W	350	3,750	77	Mature	Na-Cl-SO_4	195	0.68	6.3	2.06
Hombre Muerto E	280	3,750	77	Immature	Na-Cl-SO_4	140	0.78	8.9	0.62
Maricunga	90	3,760	35	Mixed	Na-Cl-Ca/SO_4	204	1.05	8.9	0.79

Table 2

Suggested drill spacing in kilometers for different salar types and levels of resource definition

Salar type	Inferred	Indicated	Measured
Mature	10	7	3-4
Immature	7-10	5	2.5

Fig 1

Location map of the Altiplano-Puna and the principal physiographic features, including the Altiplano-Puna Magma Body (APMB) of de Silva et al., 2006.

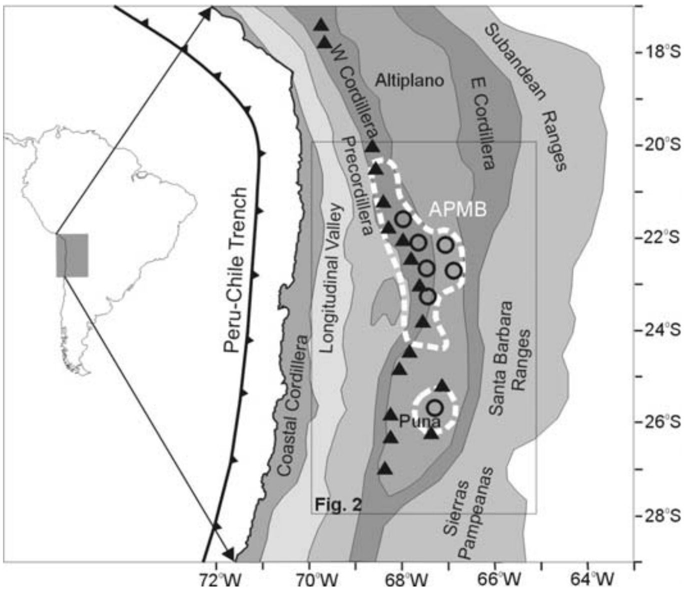

Fig 2

Digital elevation model (SRTM-90) of the central Andes, showing the location of the APMB (dashed line) of de Silva et al., 2006, and the location of selected lithium-rich salars.

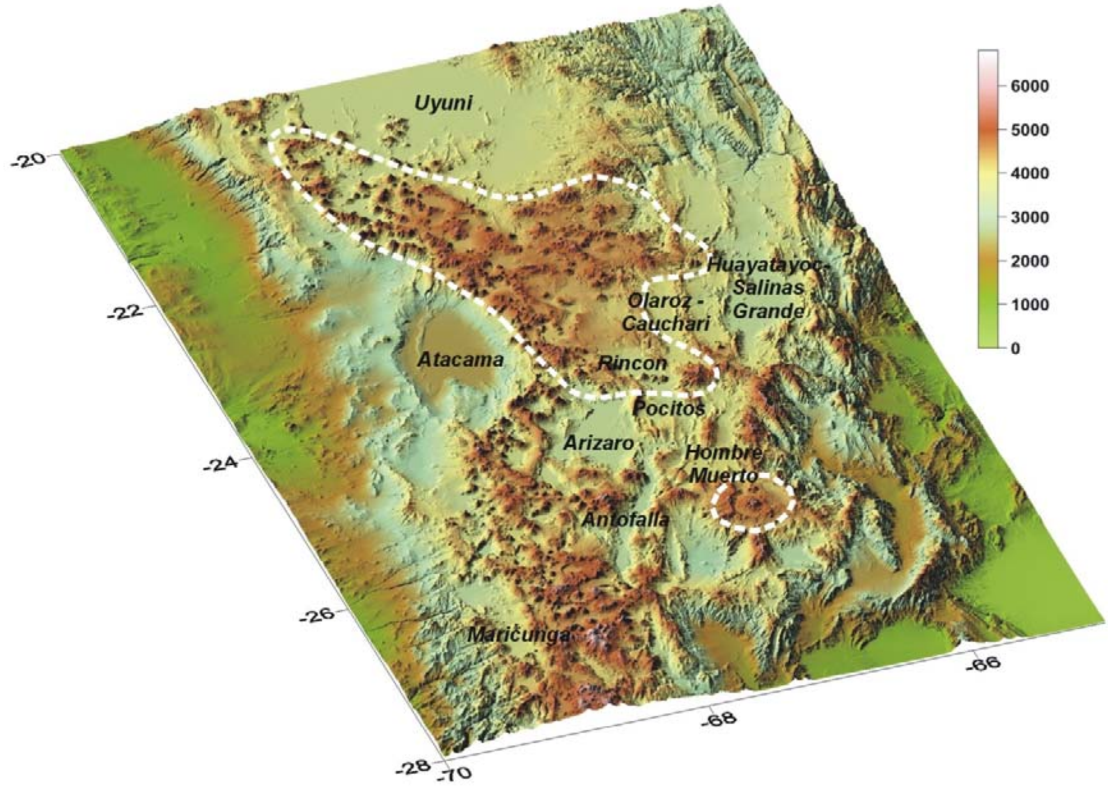

Fig 3

Block models of mature and immature salars showing the distribution of facies and main hydrological components. In the mature model, extension and recession of the marginal facies as a result of tectonism and climate variation lead to the possibility of dilute waters being transferred into the nucleus. In the immature model, whilst the marginal conditions have been simplified for clarity, the transmission of dilute waters into the nucleus is also possible. K refers to the hydraulic conductivity of the different units.

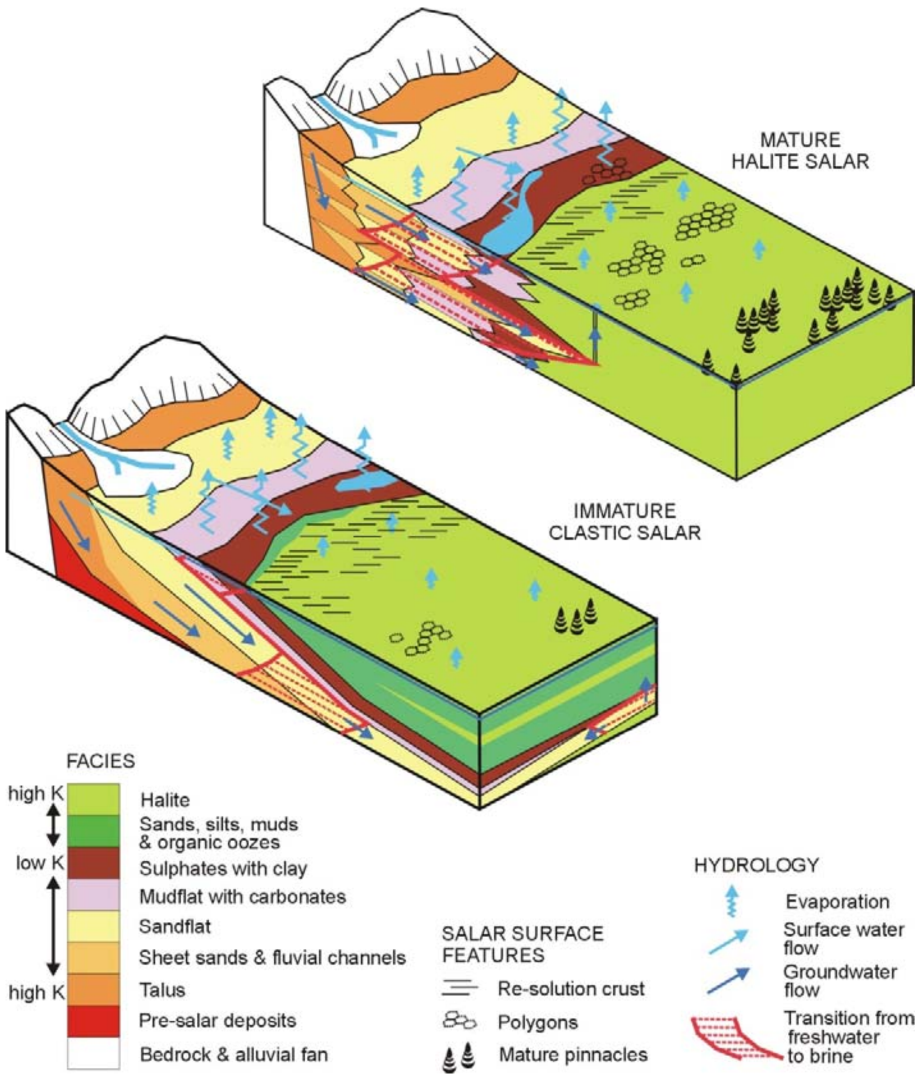

Fig 4

Porosity relations for sedimentary basins and salars. a) shows how grain-size affects the different components of porosity. Values are typical for largely unconsolidated sediments under lithostatic (normal) pressure, and within the upper 30 m of the crust. b) shows how porosity changes with depth for sands and halite. Although halite is generally considered to have almost no porosity below 30 m as a result of compaction and crystal overgrowth, open, brine filled fissures have been observed at depths of 100 m or more in several Andean salars.

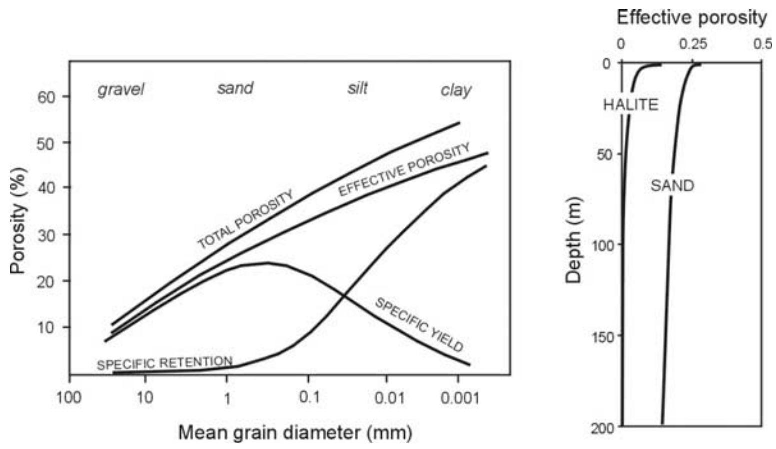

Fig 5

Evaporation relations for the salars (modified from Houston, 2006). a) shows the typical increase in evaporation as the water table comes close to the surface – note the difference in evaporation rates between dilute waters and brine. b) shows the influence of water table depth and brine for the marginal zones of salars. c) satellite image (bands 5,4,7 as RGB) of the Salar de Atacama, processed to reveal the main evaporating zone around the eastern margin.

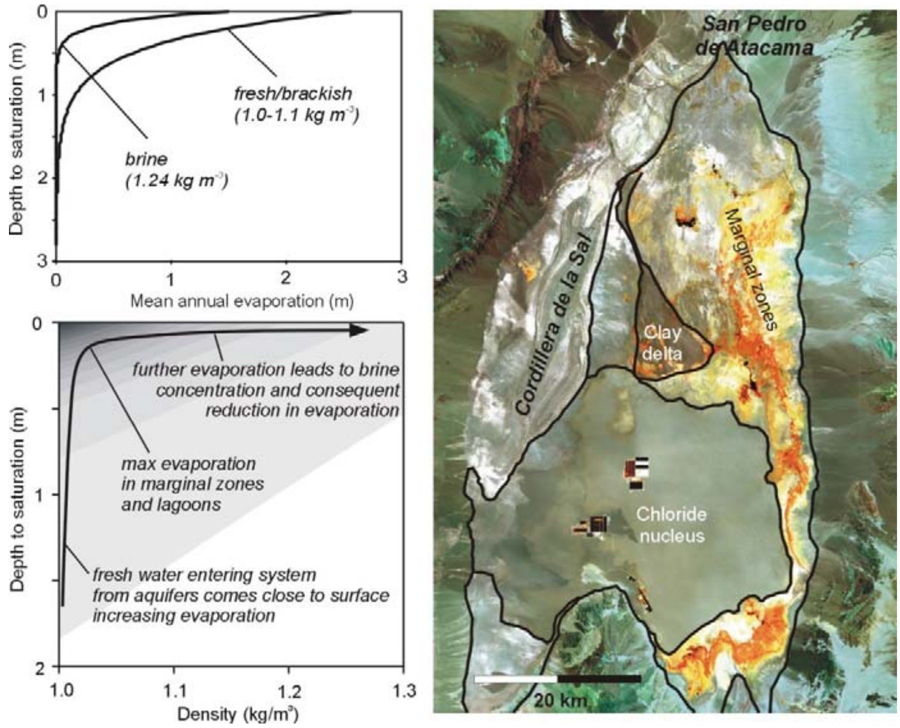

Fig 6

Drawdowns around three wells each pumping at 20 l s^{-1} for 25 years, and spaced 1 km apart in a 100 m deep aquifer, showing the differences that occur due to aquifer properties and extent. The solid lines represent the cone of depression that occurs in a horizontally infinite aquifer (i.e. extends beyond the bounds of the plots). The dashed line represents the cone of depression that occurs in an aquifer with impermeable boundaries at 0 and 20 kms (i.e. the edges of the plots).

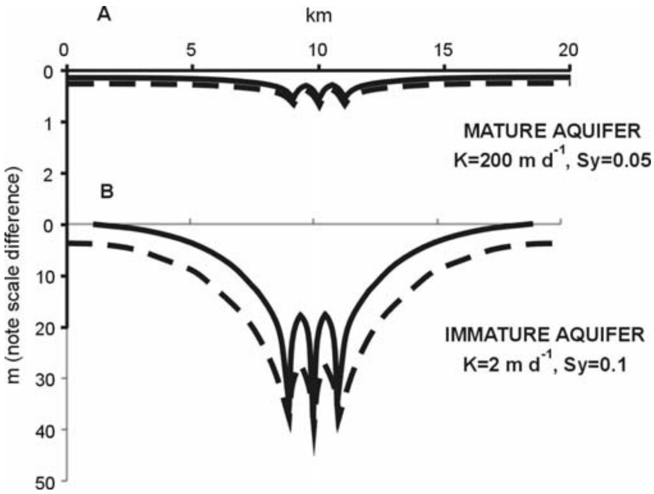

Fig 7

Data from a well in the Salar de Olaroz showing gamma log (GR), neutron porosity log (N-Pt), overlain with on-site lab determinations of P_t (grey dots), simplified lithological log, density and Ca – SO_4 concentrations. Two zones of relatively fresh water occur at 36 and 48-51 m depth, associated with thin higher porosity sand beds in a silty-clay unit. Such thin fresh water zones can result in significant lowering of grade during recovery as a result of their disproportionate contribution to the pumped fluid from higher permeability zones, potentially connected to off-salar recharge areas.

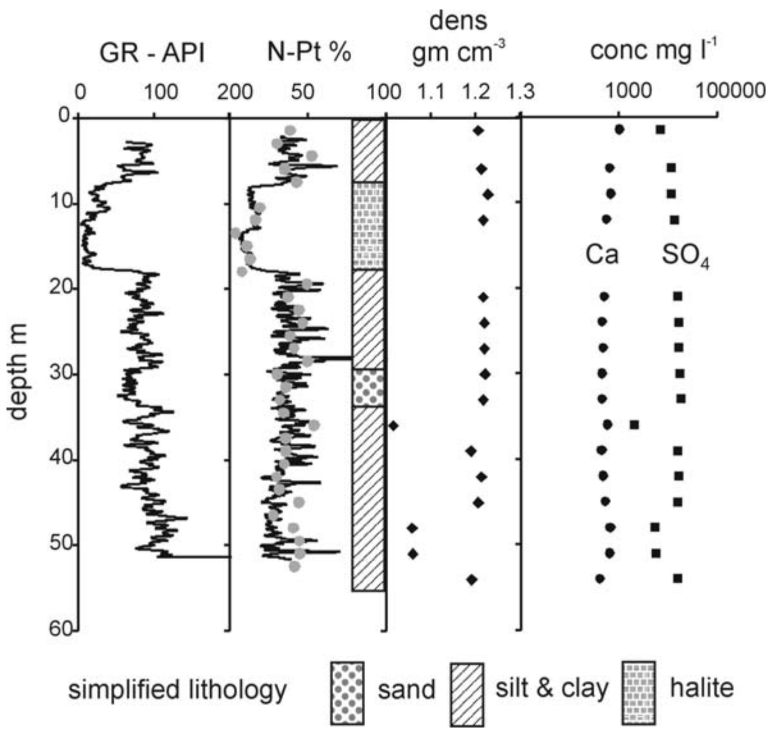

Fig 8

Porosity data from five wells drilled using sonic techniques in the Salar de Olaroz. A) Comparison of lexan and split spoon undisturbed samples separated by 0.3 m depth interval, and analysed by gravimetric methods, B) comparison of effective porosity determined by liquid resaturation and helium injection on same samples, C) comparison of total (split spoon) and effective (He injection) porosity on samples separated by 0.15 m depth interval, and D) effective porosity and specific yield on same samples.

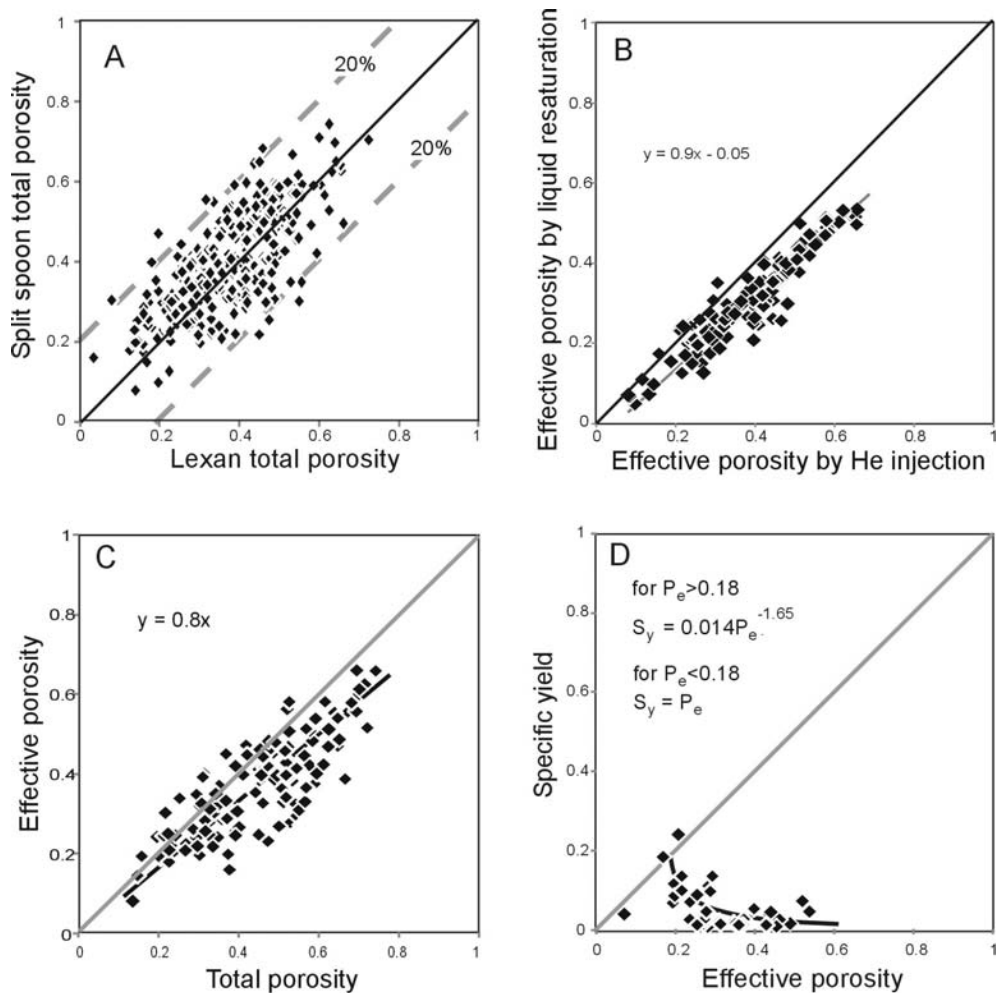

Fig 9

Validation of brine sample representativeness. A) Analytical results for pump-out sample versus pore fluid extraction from core sample, and B) point samples were taken every 1.5 m during drilling from a push-ahead wellpoint attached to the end of the drill rods and inserted inside the casing, which itself follows the drill bit closely. At 10 m and 38 m depth a series of samples were taken inside the casing and inside the drill rods (upper plot), as well as during the pump-out process (lower plot). In all cases the fluid concentrations were the same as the final point sample, regardless of whether the volume inside the rods was fully evacuated (10m sample lower plot), or only partially evacuated (38m sample lower plot). This confirms the precise origin of the sample, and indicates no contamination from over (or under) lying brines.