Technology review of mineral extraction from separated geothermal water

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EXECUTIVE SUMMARY

The possibility of extracting minerals from geothermal fluids was recognised many years ago. In Parliament in 1949 the Hansard records in the Supply Debate (p2511) the Hon Mr Broadfoot, MP for Waitomo, identifying “Thermal activity had been used for power purposes successfully in Italy, and if it were used in New Zealand there might be mineral by-products associated with it.” The ideas are not new.

This technology review is a component of a broader inquiry and update into the potential for the extraction of minerals from New Zealand separated geothermal water (SGW). The work is a part of a small Ministry of Business, Innovation and Employment funded research programme “From Waste to Wealth” (Contract No. C05X1307).

This report is a summary of the mineral extraction work undertaken in New Zealand, adding material from relevant overseas studies and the authors’ catalogue of techniques. A complementary technology review, which was not just limited to processing geothermal fluids, was undertaken in 2014 by Shirley Li at the University of Auckland in partial fulfilment for a Masters of Engineering.

This review identifies technologies and processes for removal of silica, lithium, boron and rubidium and cesium from New Zealand SGW.

The implicit assumption is that none of these extraction processes would be viable without ready access to the SGW and easy integration into an energy production process, as the cost for stand-alone production and disposal of fluid for the express purpose of minerals extraction is unlikely to be economically viable in the next few decades. Whether this could be achieved with existing infrastructure is a crucial point of discussion.

The most important mineral to extract is silica, as its removal holds the potential to improve energy generation efficiencies, which might encourage adoption by the energy companies and resource owners. Once removed, the geothermal fluid is in a condition where other dissolved minerals should be able to be extracted with less interference.

Silica

Extraction of silica has received significant attention in New Zealand and internationally. There are established and effective techniques that are suitable for silica extraction.

The five techniques discussed in more detail in this review are:

- Precipitation of calcium silicates
- Precipitation by cationic flocculants
- Precipitation as metal silicates
- Deposition onto seed particles
- Ultrafiltration

Given the level of development from trials and testing on silica that have already been undertaken, the barrier to extraction of this species is not a technical one.

It may be that silica extraction from SGW opens up opportunities for additional energy extraction, or it could offset costs associated with other silica control techniques currently in use, or it could be a prerequisite to the extraction of other species from the SGW. A cluster of processes, individually uneconomic on their own, may be the catalyst to move the technology from technically possible to adopted.

Lithium

Lithium is the species next after silica to receive the most research focus for extraction from SGW. Lithium compounds have many desirable properties in a number of industrial applications. The potential for lithium extraction was recognised in New Zealand in the late 1950s by Kennedy (1957; 1961). It is only more recently, over the last decade or two, with the increasing demand for lithium, that this species has received more attention for possible extraction from SGW.

The following methods are discussed in the report:

- Co-precipitation with aluminium hydroxide
- Manganese oxide (spinel) and cation exchange resins
- Electrodialysis
- Evaporation

There are a number of methods suitable for the continuous extraction of lithium. Presently only a few laboratory trials have been undertaken, with none being pilot tested, so there is no data to assess the extraction economics from geothermal fluids. The low concentration in New Zealand SGW (10-30 mg/L) compared to highly saline brines found elsewhere (200-5000 mg/L) could be an impediment. However, with geothermal heat available, concentration by evaporation might be achievable to assist secondary extraction viability. The likely oversupply of lithium for the next decade (Hill, 2015) may curtail investment in large plant, although possible supply constraints after that time might encourage investors to prepare ahead of these constraints by running trials with larger scale pilot plants.

Boron

Boron is of industrial importance and many methods exist for removing boron from fluid streams, both at high and at low concentrations. In the latter case this is often where boron may be present as an impurity with a higher value constituent. Reagent based extraction processes (e.g., addition of metal oxides such as lime) suitable for high boron concentrations (> 0.3%) are only efficient at < 30°C. Solvent extraction and ion-exchange and chelating resins are useful for extracting boron at lower concentrations. There have been no field trials or pilot tests of boron extraction from New Zealand SGW. The emphasis of a number of the international trials has been for environmental purposes, not for economic recovery; for example to enable surface discharge and subsequent irrigation use.

In New Zealand geothermal fluids, boron is present in low concentrations (40 mg/L), except at Ngawha (1000 mg/L), so enrichment technologies for each concentration range may be required.

Cesium and Rubidium

Of the minor components, both cesium and rubidium are the most valuable on a dollar per kilogram basis, and vary in concentration in New Zealand SGW between 1 and 6 mg/L. Successive extraction processes to remove silica, lithium and boron will leave the residual brine concentrations of these two constituents essentially intact. However, the small market for these metals and adequate world supply means that any process would need to be highly efficient and cheap. Methods for removing these metals include solvent extraction and ion-exchange.

KEYWORDS

Mineral extraction, geothermal fluid, New Zealand geothermal fields, technology review

1.0 INTRODUCTION

This review investigates publically available information and data on technologies that might be used to extract metals and minerals from geothermal fluids. A number of technologies have been trialled at a pilot scale, others at an experimental scale, and others are methods that appear to hold some promise.

This work is a component of a broader inquiry into the commercial potential in New Zealand for the extraction of minerals (for example silica, lithium) from geothermal fluids. The broader "From Waste to Wealth" research programme is a Ministry of Business, Innovation and Employment funded work programme (C05X1307, 2013-2015) that seeks to identify practical methods for the recovery of minerals, metals, gases and trace elements from geothermal fluids. This wider study also seeks to develop a greater understanding of the market drivers and the regulatory framework likely to influence the implementation of these technologies, as a springboard for future research and investment.

Companion reports are available for:

- Composition of minerals in geothermal fluids.
- Legal rights to minerals in geothermal fluids.
- Market drivers for minerals in geothermal fluids.

1.1 BACKGROUND

Geothermal fluids offer potential for the recovery and sale of a range of materials, such as silica, metals, various minerals and gases. In essence, this is mining of materials that are brought to the surface, in an aqueous phase, as part of the geothermal energy production processes.

There are a number of questions, such as:

- What are the technical options for extraction from the geothermal fluid streams and what are potential investment opportunities?
- Could economic, social and environmental benefits arise from creating industry around some of these minerals?
- Will New Zealand develop world leading capabilities in processing technologies and in so doing further improve geothermal energy productivity and industry value?

There are no costs associated with mining of the materials from the Earth, as the fluids containing the minerals are already brought to the surface as part of the geothermal energy production process. There are no costs associated with dissolution of ore minerals into a fluid, as the species in SGW are already in an aqueous and mobile phase. The volume of the geothermal fluids extracted in New Zealand's Central North Island geothermal fields is significant (in excess of 200,000 tonnes per day; Mroczek *et al.* (2015a)), and because they are associated with industrial scale energy developments, fluid production occurs on an almost continuous basis.

The concentration of the species differs between geothermal systems, however in the New Zealand geothermal fluids, the potentially valuable species of interest are generally at relatively low concentrations (Mroczek *et al*., 2015a).

The economic value of minerals present in New Zealand separated geothermal water (SGW), particularly lithium, was recognised as early as 1957, before the commissioning of the Wairakei Power Station (Kennedy, 1957; 1961) and was first mentioned as a possible resource for New Zealand by Hon Mr Broadfoot in Parliament in 1949. In subsequent years there have been studies published in the international literature on laboratory and field scale trials extracting various species. Few processes have however made it to a commercially viable industrial process, and as yet none in New Zealand.

There are five criteria to be considered when assessing the practicability of a mineral extraction process:

- Process feasibility – successful laboratory, field and pilot trials.
- Engineering practicality – easy integration into the existing power plant / energy development, including integration with the operation and maintenance of the energy development facilities.
- Downstream disposal – discharge water quality for surface disposal or injection.
- Capital and O&M costs.
- Product – market, value and offset costs (if any).

1.2 LITERATURE REVIEW

This literature review identifies technologies and processes for removal of silica, lithium, boron, cesium and rubidium from geothermal fluids. A complementary technology review, which was not just limited to processing geothermal fluids, was undertaken under the supervision of Professor Wei Gao in 2014 by Shirley Li at the University of Auckland in partial fulfilment for a Master of Engineering.

Where possible the emphasis has been on those processes that have been trialled on New Zealand geothermal fluids, with international results discussed where relevant, or if a promising technology was not trialled here.

It was not the intention to review all work undertaken, as the literature is vast.

2.0 SILICA

2.1 BACKGROUND

Managing silica and controlling silica deposition is a major consideration in effective geothermal energy production. This has arisen from energy producers seeking to avoid deposition in geothermal water pipelines and injection wells, and permeability loss in the reservoir where the geothermal water is returned to underground formations. Historically in New Zealand, silica scaling has been managed by ensuring that the temperature and dissolved silica concentration of the geothermal fluid was near the amorphous silica saturation solubility before injection (Ohaaki) or by surface disposal to rivers (Wairakei and Kawerau). These methods can limit the energy able to be extracted, and surface discharge seeking to avoid scaling can have environmental effects. To overcome this limitation, since 2008 three geothermal power plants in New Zealand have installed pH brine modification using sulphuric acid to delay silica deposition (Kawerau Geothermal Limited (2008), Nga Awa Purua (2010) and Te Mihi (2013)). This approach is not without its problems, but is considered more reliable and more easily implemented for the large water volumes involved in comparison to other methods that have been suggested; such as controlled precipitation, or brine aging, or dosing with organic silica inhibitors where the cooling at the power plant is undertaken in evaporative cooling towers, or brine dilution for binary cycle plants. The removal of dissolved solids to enable or increase generation is only practised at the Salton Sea geothermal power stations in the Imperial Valley, USA, where exotic and potentially deleterious scales deposit from the highly saline brines (Gallup, 2009). The silica extraction at Salton Sea is enhanced by the high total dissolved solids (TDS).

Silica extraction from geothermal brine is a method that could assist with scaling management. However, to be implemented it needs to provide additional economic benefits; be competitive with the pH modification silica control that has been adopted at three large New Zealand geothermal power stations since 2008 or the remixing implemented at Ngatamariki, Rotokawa and Te Huka binary plants. Furthermore, and quite importantly, the removal of silica to the point of no further precipitation (and even to near zero in some processes), is expected to be necessary to enable the extraction of other minerals and metals from the brine.

Silica is a marketable commodity in its own right with a range of uses. The markets include glass, foundries, building products, and chemicals (Hill, 2015). The value and price for silica varies, and is dependent on purity and physical properties. Precipitated and colloidal silica, which could be produced from geothermal fluids, are part of the specialty silica market, worth US$2B and growing over 5% annually (Hill, 2015; Hall *et al*., 2013). This market includes cosmetics, toiletries, chemicals, rubber, coatings, inks, and electronic equipment.

A number of silica extraction methods have been trialled both in New Zealand and at international geothermal power stations. In particular Harper *et al*. (1995) discussed a method for silica production for paper manufacture, and Brown and Bacon (2009) described a silica pilot plant at Wairakei processing 5 t/hr and operated by the Electricity Corporation of New Zealand (ECNZ) in the mid 1990s, that produced high quality silica sol. Although both were successfully tested at a large pilot plant scale, neither was taken up by their commercial sponsors.

2.2 SILICA CHEMISTRY IN SEPARATED GEOTHERMAL WATER

The chemistry of silica (SiO_2) in geothermal fluids is well understood (Brown, 2011). When geothermal fluid is brought to the surface for power production, the water contains an amount of dissolved silica that is dependent on the temperature of the reservoir. The hotter the water, the more dissolved silica it contains. As the temperature of the water is lowered during the extraction of steam for power production, the concentration of dissolved silica increases and often becomes greater than the equilibrium solubility of amorphous silica. Under these circumstances, solid silica would be expected to precipitate from the water. However, depending on the temperature, silica concentration and brine chemistry, the individual molecules of silica join together (nucleation) to form polymeric silica particles that remain suspended in solution. This is called a colloidal suspension and silica colloids can remain suspended in solution for years. The individual colloidal particles are very small in size, ranging from about 0.01 μm to 5.0 μm (1.0 μm = 1 millionth of a metre). If the colloidal particles are all of the same size, this is a "monodisperse" colloid. A solution containing particles of differing sizes is "polydisperse". Individual colloidal particles can come together to form larger clusters of particles. Such a process is called "agglomeration" or "flocculation".

Although colloidal silica can form a stable suspension, under certain circumstances it can also deposit very rapidly. The exact conditions required for deposition are not fully understood, but many factors are involved. These include such parameters as particle size, particle density, fluid flow conditions and the presence of other chemicals (Brown, 2011).

2.3 SILICA EXTRACTION TECHNOLOGIES

Geothermal silica extraction technologies fall into the following three broad groups, with some overlap:

Concentration and/or precipitation

- Seeding
- Reverse osmosis
- Ultrafiltration

Precipitation – physical processes

- Fluidised bed reactor

Precipitation – chemical processes

- Cation addition – inorganic salts
- Cationic polymer compounds
- Cation addition – electrocoagulation

At least six different silica extraction methods have been tested in New Zealand, two at a large pilot plant scale. Except for the direct deposition of dissolved silica onto seed particles, the silica extraction technologies rely on the initial polymerisation of the dissolved silica and the formation of colloidal particles, which can then be concentrated and/or precipitated using inorganic salts or cationic polymers. Controlling this process (paying attention to time, temperature, silica concentration, chemical additives and fluid chemistry) allows a monodisperse colloidal silica solution with a target particle size to be produced. This can be subsequently concentrated (e.g., ~ 30 wt%) to produce a silica sol (Brown and Bacon, 2000; 2009; Bourcier *et al*., 2006). Alternatively the colloidal solutions can be precipitated using various chemical flocculants to produce pure silica through to metal silicates (Harper *et al*., 1995; Gallup *et al*., 2003; Kato *et al*., 2003).

The end product quality and purity will depend at which point in the process cycle the silica is extracted and the method used. If the dissolved silica has already commenced polymerising, then control of particle size and agglomeration may not be possible; leading to a less valuable product with variable physical properties. Brown and Mroczek (1993) identified that geothermal silica would be unlikely to compete in the international silica market unless it was a high value product. This view is considered to continue to be relevant. A "no" value silica waste, or a low value silica product, is unlikely to be economic unless there are substantial downstream advantages achieved from additional mineral extraction and/or energy plant operating efficiencies. This type of economic analysis needs to be undertaken, but was not funded as part of the Waste to Wealth research contract.

In all processes seeking to produce silica from New Zealand SGW, the significant disadvantage is the relatively low concentration of silica in the brine, varying between 0.05% to 0.1 wt% silica (Mroczek *et al*., 2015a). The natural presence of other dissolved solids and trace contaminants, especially arsenic and antimony, can affect both product purity and properties. The pH at which the fastest polymerisation occurs also results in a negative charge on the growing colloid surface with cationic (metal) impurities adsorbed onto the particles. The surface charge is reduced by lowering the pH but this severely retards the polymerisation rate and affects the particle size (Brown, 2011).

Furthermore any waste stream must be able to be disposed of practically. The potential issue is with a fluid stream that is chemically or physically incompatible with the receiving formation; for example high suspended solids loading, or containing high concentrations of scaling chemicals (e.g., calcium or at high pH).

The material that follows is a brief description of the silica extraction process trialled in New Zealand (and similarly for the other species discussed in this report) together with cursory references to relevant overseas experience. The discussion excludes silica extraction at the Salton Sea in the US, where highly mineralised hypersaline brines require advanced brine processing methods not necessary for the New Zealand SGW (Gallup, 2009).

The authors are of the view that, given the level of development and the trials and testing already undertaken on silica, that the barrier to extracting this species is not technical, but rather economic. If silica extraction can be used to obtain additional energy production efficiencies or be offset against other silica control costs, then silica might start to be extracted from geothermal fluids. Also it could be economically viable to extract silica along with other species, such as lithium, from the brine or in an "integrated" process using some or all of the above processes (Harper *et al*., 1995; Bakane, 2013).

The sections that follow discuss six methods of silica extraction:

- Precipitation of calcium silicates
- Precipitation by cationic flocculants
- Precipitation as metal silicates and by cationic flocculants – Mitsubishi Materials Corporation
- Removal by electrocoagulation
- Removal by ultrafiltration
- Removal by deposition onto seed particles

2.3.1 Precipitation of calcium silicates

Rothbaum and Anderton (1976) developed a method for removal of silica and arsenic by precipitation of calcium silicate with lime (CaO). The lime is the source of the calcium and it also raises the pH. The latter is required to increase the negative surface charge on the colloid particle surfaces, which allows the calcium ion to adhere, coagulating the silica. An important focus of the work was removal of arsenic; Rothbaum (1985) maintained that if this species was removed there would be more opportunity for surface discharge of geothermal waters.

Rothbaum and Anderton (1976) experimental work (at 90°C) at Wairakei and Ohaaki showed that lime precipitates polymeric silica far more efficiently than dissolved silica, so it was necessary to age all fresh discharge waters. The aging was related inversely to the silica concentration, and varied between 30 and 150 minutes for the bores tested. Optimum operating conditions for water containing 1000 g/tonne silica involved adding 700 g/tonne lime. These conditions resulted in a 30% calcium silicate gel, which filtered well. Decreasing the lime concentration resulted in an increasingly silica rich calcium silicate. The ratio of SiO_2/CaO decreased from 1.75 to 1 on increasing the amount of CaO from 350 to 780 g/tonne. There were problems with the floc not settling, and at Wairakei addition of flocculant actually lengthened the settling rate. In subsequent work by Shannon *et al*. (1982) the dissolved air flotation (DAF) technique was tested for removing calcium silicate. DAF resulted in a calcium silicate with twice the solids content (20%) of that produced by settling and filtering together. The method was considerably more rapid than settling.

Harper *et al*. (1995) described work undertaken for Tasman Pulp and Paper Co. Ltd for extraction of precipitated silica from Kawarau geothermal fluid “under controlled precipitation and growth of the silica particles”. The physical properties of the silica were provided as well as representative analyses. The purity of the silica was a high 98%, with aluminium, calcium and sodium impurities, and a low arsenic content of 2 mg/kg. The properties and quality of the silica were such that it was of suitable quality for newsprint and “other industries”. At the time of their publication the research was continuing. No details are given in the paper except for those in the patent application (Harper *et al.*, 1993) and subsequently in Johnston (1999). The method involves allowing monomeric silica to polymerise and coagulating the colloidal silica with calcium chloride (200 to 400 g/tonne), followed by flocculating agents and surfactants (unspecified). The precipitated silica is removed as a slurry by DAF (minimum 90% efficiency) or using a thickener, and also by filtration. A portion of the precipitated silica is recycled to promote polymerisation. The desired type of silica is produced by controlling the following process conditions: - aging times, cooling rates, the final process temperature, chemical dosing rates and time of introduction into the polymerising brine. The chemical composition of the silica varied between 75 and 97% silica with the balance made up of calcium (reported as %CaO). Arsenic concentrations typically varied between 16 and 40 mg/kg (somewhat higher than reported by Harper *et al*. (1995)). However, the arsenic concentration in the product could be controlled at 9 mg/kg by quickly cooling the fluid. The floc particle size of an untreated slurry was distributed between 20 and 500 µm.

Norske Skog Tasman (NZ) Ltd now operate the mill and have not disclosed their plans for the extraction of precipitated silica. The process is technically viable and has been tested to the large pilot plant scale.

More recently Johnston and co-workers at Victoria University have investigated the precipitation of geothermal silica product which they call a “nano-structured calcium silicate” (Borrmann *et al.*, 2009; 2010). This process appears to build on their earlier work, but has only been field tested and not trialled on a pilot plant scale. Few details are disclosed in their patent application (Johnston *et al*., 2007), but it involves adding “spacer” compounds and additional precipitation of silica to strengthen the product. The uses listed are similar as for other calcium silicates and there is no indication as to the differences in properties or economics that could command an increased price or demand a premium over other calcium silicates. Borrmann *et al*. (2010) report that the silicates rapidly precipitated in both laboratory and fields trials. At a 1:1 Ca/Si ratio the particle size was ~ 30 μm and as there was no excess of calcium. Few impurities were precipitated with the silicate, which had “optimal pore volume and surface area properties”. These properties and impurities are not listed and no comparison was made with precipitated silica disclosed by Harper *et al*. (1995). A lower Ca/Si ratio of 0.4 was sufficient for complete removal of silica and if that was the only intention, was therefore seen as being the most economic. The particle size was 10 μm and they speculated that the waste stream may possibly be injected without removal of the silicate particulates. The properties of the lower ratio product were not tested except that the impurities were low (no analyses given) making it suitable to landfill. The molar 0.4 Ca/Si ratio is about the same as adding 400 g/tonne calcium chloride to Kawerau fluid (typical composition at that time) discussed earlier.

2.3.2 Precipitation by cationic flocculants

The first process utilising these chemicals in New Zealand was developed by Owers (1989). The method involved allowing silica to polymerise (between 30 minutes and 2 hours) and then precipitating the silica using an organic flocculating agent (Owers, 1989). A portion of the precipitated silica is recycled to act as seeding material in the fresh brine. The precipitated silica could be recovered by various techniques; separated by sedimentation into a thick slurry, which could be on sold as a slurry for further processing or filtered, washed and dried. Laboratory tests on Kawerau fluid gave a product that, after drying, had an acceptably low arsenic content (0.6 g/tonne) and mean particle size of 0.04 microns. Other major impurities were 2 kg/tonne sodium, 1.8 kg/tonne aluminium, 0.6 kg/tonne calcium and 0.3 kg/tonne iron. Product from a continuous flow pilot plant test at Ohaaki was more variable, with measured particle sizes between 2 and 26 microns, and arsenic concentrations between 1 and 4 g/tonne.

The effectiveness of these chemicals to precipitate colloidal silica was illustrated by Wilson (2009). The purpose was to desilicate Ngatamariki geothermal fluids prior to using the water as drilling fluid. A number of the cationic flocculants were trialled, as well as including others such as alum, which although very effective at precipitating silica was discounted because it was a more complicated process involving handling a solid form powder. Typically as dose increased, more colloidal silica precipitated. However there was a considerable difference between their effectiveness; showing that careful trials are required to select the appropriate chemical. For example the best performing chemical at higher concentration appeared to increase the concentration of silica in solution. Subsequent field trials confirmed that the preferred chemical could reduce the residual silica concentration down to the solubility of amorphous silica. The drilling programme was successfully undertaken using this process to produce drilling water. No properties or analyses of the precipitated silica were presented.

2.3.3 Precipitation as metal silicates and by cationic flocculants – Mitsubishi Materials Corporation

Ueda *et al*. (2003) reported field trials at Mokai for removal of silica by addition of quicklime (CaO) or cationic flocculant. The purpose was to assess the suitability of their Seed Addition Circulation System (SACS) technique to remove silica from brine at Mokai. Mokai brine had a silica concentration of 954 mg/L, similar to that at Ohaaki in the trials undertaken by Rothbaum and Anderton (1976). The SACS method was successfully trialled at a large pilot plant scale in continuous flow tests undertaken at Ohnuma and Sumikawa in Japan (Kato *et al*., 2003) and is discussed in greater detail below. Their results confirmed Rothbaum and Anderton's (1976) study that CaO reacts with the polymeric silica. Therefore, increasing the aging time or reducing the temperature increases the silica removal rate with less reagent added. After 15 minutes aging at 90°C 1.5 g/L of CaO was sufficient to remove all of the silica (Ca/Si = 1.7) and to reduce the silica below saturation 0.5 mg/L CaO (Ca/Si = 0.6). Addition of lime increased the pH to 11 however. Most of the deposits were amorphous Ca-Si-O with 38% SiO_2 and 23% CaO. Trace elemental concentration of the precipitates are not given, but increasing concentrations of CaO decreased the dissolved arsenic concentrations. At high pH and calcium concentrations (that is at high CaO), unavoidable co-precipitation of arsenic phases occurs and could be a major impediment if most of the silica is required to be removed (Gallup *et al*., 2003; Pascua *et al*., 2007). In contrast, the addition of cationic flocculant EC-004 (Daido Chemical Corporation), at up to 75 mg/L of a 1% solution, only the excess silica above the amorphous silica concentration precipitated. Their results were consistent with those observed in Japan. They concluded that their SACS technique would be equally effective for removing silica at Mokai and our view is for all other New Zealand SGW as well.

Kato *et al*. (2003) undertook a series of laboratory scale silica extraction experiments using various reagents at Ohnuma and Sumikawa Geothermal Fields. Their study is important in that the geothermal solution compositions are similar to that of SGW in New Zealand and the methodology, results, lessons and conclusions would also apply here.

The bench experiments used a considerable number of different reagents with pH adjustment to precipitate silica. This included silica gel, colloidal silica, metal chlorides (Ca, Fe, Mg and Al), clays, cements, calcium compounds (quicklime – CaO and slaked lime – $Ca(OH)_2$) and a number of cationic flocculants, including EC-004, which was used in the Mokai experiments discussed above. They also successfully trialled at the pilot plant scale (0.6 t/hr) continuous removal of excess silica using their SACS method and estimated the economics of their process. In the SACS method, flocculants (CaO or cationic reagent) are continuously added and the treatment of the brine (mixing, reaction and precipitation) occurs in a single vessel.

In the laboratory beaker tests, the minerals, silica gel and colloidal silica were not particularly effective at reducing the excess silica concentrations compared to the cements and the metal chlorides. The results for the latter were particularly interesting The dissolved silica concentrations were reduced close to amorphous silica solubility by adding 200 mg/L (to Ohnuma brine, with pH adjustment) of Fe and Ca chlorides, while for Mg and Al chlorides the dissolved silica concentrations remaining were lower than amorphous silica solubility; consistent with additional reaction with silica to form metal-silicate compounds. Although Mg and Al ions (pH> 9) were highly efficient in removing silica, considering that their compounds are expensive compared to calcium, Kato *et al.* (2003) concluded that addition of CaO, which did not require pH adjustment, was preferred for their SACS process. A number of SACS experiments were performed at Sumikawa using cationic flocculants. Importantly they found that after the initial precipitation the deposited silica was an effective seed in itself. This was also observed with the CaO seeding experiments. The composition of the silica precipitated with the cationic flocculants compared to that precipitated with CaO was pure will low metal content. No arsenic analyses were however reported.

2.3.4 Removal by electrocoagulation

Electrocoagulation is an electrochemical process that uses direct current to remove contaminants from wastewater. Electrocoagulation drastically reduces the use of chemical reagents. With a high degree of contaminant removal, there is greater potential for water reuse after electrocoagulation. Moreover, the process generates less sludge compared to other technologies and the residual concentrations in the effluents are lower, making them suitable for direct discharge (Chen, 2004). The technology accepts a wider range of wastewater with varied pH levels, is less complicated, readily available (e.g., http://www.waterrecycle.com.au/electro.htm) and cheaper than direct chemical dosing. The process is capable of significant self-regulation, more so than for the other water remediation processes.

Potapov *et al*. (2002) reported laboratory electrocoagulation experiments in geothermal fluids. Their purpose was to investigate silica removal with aluminium, stainless steel, copper and galvanised steel electrodes, and the effect of current strength, current density, voltage, temperature, pH, electrode separation and sedimentation rates. Their work showed that silica could be efficiently removed from geothermal fluids, with the rate of coagulation being fastest with aluminium electrodes. Power consumption decreased with increasing temperature but the process became less efficient at temperatures > 60°C, due to the formation of non-porous adhering scale on the aluminium surface.

Mroczek *et al*. (2006) recognised the potential of this technology to offer a simple and potentially more cost-effective method of removing arsenic from geothermal water using iron electrodes than more conventional chemical dosing methods. The iron electrodes also precipitate silica, but less efficiently than aluminium, the latter however does not efficiently precipitate the arsenic. The technique has been used on numerous occasions to prepare desilicated water for other purposes, such as the recently reported lithium extraction experiments (Mroczek *et al*., 2015b). This method is easy to scale up and is cheap to run, given that geothermal water is very conductive. However, unless a use can be found for the amorphous aluminium silicates, the technology may be better suited for smaller scale removal of arsenic and silica from geothermal water, which might be released as part of well testing or drilling.

2.3.5 Removal by ultrafiltration

Ultrafiltration is a continuous separation process that enables the suspended solids, in this case colloidal silica, to be concentrated (“retentate”) while the geothermal water (“permeate”) passes through a membrane filter to waste. The flow of liquid is parallel to the membrane, which reduces fouling. It was trialled in Japan and Hirowata *et al*. (1988) described a method involving ultrafiltration that was tested at a 5 tonne/hour pilot plant scale. The separated colloidal silica contained no arsenic. The recovered material could be manufactured into a zeolite (catalytic material).

A silica extraction pilot plant using this technique was commissioned at Wairakei by ECNZ and successfully ran in the mid 1990s, processing 5 t/hr of fluid (Brown and Bacon, 2000; 2009). The aim was to produce a high value silica sol which would be economic to extract and provide a commercial return. Privatisation of ECNZ and the subsequent formation of Contact Energy Ltd in 1996 resulted in this work, and the extraction of silica at that time, not being seen as core business. Funding was discontinued before completion of the project (Lew Bacon, Pers. Comm., 2015).

Very little detail and results are in the public domain, although the broad outline of the methodology is given (Brown and Bacon, 2000; 2009). The polymerisation and growth of the colloidal silica was carefully controlled in a series of aging tanks followed by concentration of the colloids in stages to greater than 30% silica. There was provision for chemical dosing to adjust pH and particularly for adding chemical dispersants, which avoided agglomeration of the silica colloids. Fouling of the membrane filters could not be avoided and these required weekly cleaning cycles. Brown and Bacon (2009) concluded that it was possible to produce silica sols of a predetermined size that compared favourably with commercial products. One sol analysis was provided. They said the purity was satisfactory, but that better results could be obtained with more washing out ("diafiltration") of the soluble salts during the concentration stages. In the analysis provided (25 wt% silica), the four highest contaminants (in g/kg = kg/tonne) were sodium 1.9, calcium 1, potassium 0.9 and aluminium 0.6. Of the deleterious species arsenic was a low 3 mg/kg and antimony higher at 80 mg/kg. Brown and Bacon (2009) did not disclose their economic analysis. However the largest operational cost was considered to be replacement of the ultrafilters, which ultimately have to be replaced as cleaning eventually becomes ineffective. Some years after the completion of this project, a personal contact at Akzo Nobel reported that the colloidal silica sol was most similar in properties to Bindzil 30/170. However, the high calcium and potassium (30-100x higher) meant that although the sol could be used in high temperature applications, the higher calcium and potassium meant that these applications were more limited than the Bindzil analogue. It appears this evaluation was not received (Lew Bacon, Pers. Comm., 2015), but it is a direction for future investigations; although other applications for silica sols may not be so sensitive to these contaminants.

Bourcier *et al*. (2006) described an ultrafiltration method for extracting colloidal silica at Mammoth Lakes in the US. The purpose was to develop a cost-effective method to extract marketable silica. The difference in the method to the ECNZ plant comes at the first stage, where the silica is concentrated from 250 mg/L to between 600-900 mg/L by reverse osmosis (RO). The permeate can then be used (for example) as a primary fluid for an evaporative cooler, with the concentrate either directed to injection (where it mixes with cooled water from the cooler) or to the silica extraction plant. The reason for this first step is that the low silica concentration means that the polymerisation kinetics forming the colloidal silica is very slow. This first dewatering step concentrates the silica to a level that allows more rapid extraction, either by precipitation by adding salts and polyelectrolytes, or further concentrated to a polydisperse colloidal solution by ultrafiltration. The low TDS of the water meant that high purity silica (99.6%) could be precipitated, although the trace contaminants were higher (e.g., As 162 mg/kg) than in the New Zealand precipitated silica. The results reported were based on field trials, although the intention was to carry out pilot plant tests as they stressed the importance of pilot testing to reduce the uncertainties in the economic analyses. Bourcier *et al.* (2006) believed this was the main impediment to commercialisation of silica extraction.

The subsequent pilot plant test utilising a 20 gallon/min plant was successfully completed at Mammoth Lakes and provided necessary data for the capital and operating cost estimates, as well as product properties (Roberts *et al*., 2009). The economic analyses showed favourable rates of return, greater than $0.01/kWh offset in cost of electrical power generation. Patent applications were published in 2009 (Bourcier and Bruton, 2009).

During 2013 / 2014 Environmetals Ltd set up a silica extraction plant at Wairakei with a capacity to process 200 tonnes/day of geothermal fluid. The plant process description and images of the plant can be found on their website (http://www.environmetals.co.nz). The process matches the description of the method outlined by Bourcier *et al*. (2006) and

Roberts *et al*. (2009); that is an RO dewatering step followed by concentration of silica by ultrafiltration. Information promoted on the company website identifies that the permeate can then be further passed through an ion exchange column to extract further elements; although if the RO is operating satisfactorily the permeate should be free of dissolved solids. The plant is able to process 150 tonnes/day and can be "easily disassembled so that it can be moved from one site to another". They estimate that the capital cost required to construct a plant capable of processing 20,000 tonnes/day of geothermal fluid to be NZ$41m with operating costs of approximately NZ$0.35/lb (US$0.27/lb, including transport cost of US$ 0.07/lb) of colloidal silica produced.

2.3.6 Reverse osmosis

New Zealand geothermal fields are high temperature and are therefore relatively high in silica (Mroczek *et al*., 2015a), so the silica polymerisation kinetics are sufficiently fast without the need for prior dewatering by RO. Avoiding silica fouling of the RO membranes is expected to be technically challenging. This may be why they were not utilised for the ECNZ pilot plant[1] and would also present more of a problem at other geothermal fields, where the silica concentrations are higher than in the Wairakei SGW.

Nevertheless solids removal by this widely implemented technology, used for desalinating seawater, could be implemented upstream given the prior removal of silica (Lew Bacon, Pers. Comm., 2015; Figure 1). This would concentrate up the residual species in the retentate fluid stream. Prior silica removal is necessary to avoid fouling of the RO filters and differs from Bourcier's *et al.* (2006) process where the silica is extracted from the RO retentate (concentrated fluid stream).

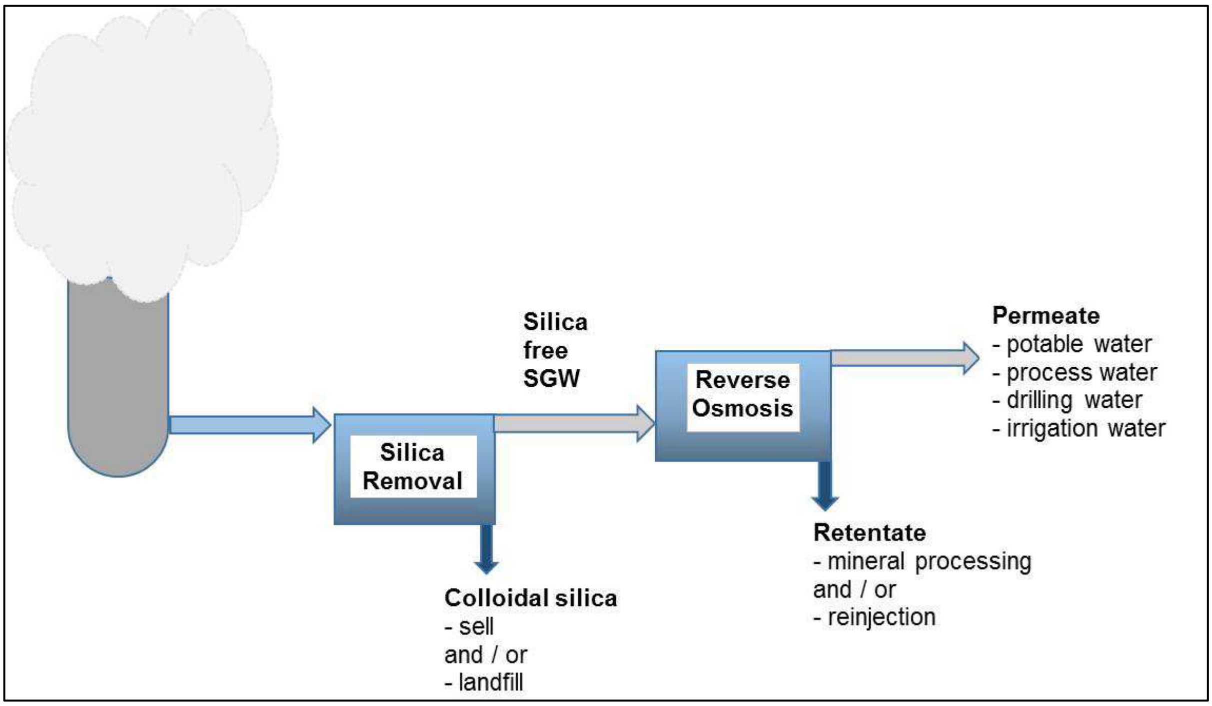

Figure 1 Bacon TDS removal process.

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[1] That and the need to not increase salinity

2.3.7 Removal by deposition onto seed particles

As illustrated in the examples above, deposition of dissolved silica onto seed particles is well known and can be particularly effective for reducing the concentration of excess silica above amorphous silica solubility. These seed particles, metal silicates or colloidal silica, are formed in situ, but there is also the option of introducing seed particles into the silica saturated solution. One such study has been reported by Sugita *et al*. (2003), showing the effectiveness of adding amorphous colloidal silica made from Onuma (*sic*) geothermal fluid, which was more effective than adding silica gel. The presence of seed means that the dissolved silica can precipitate onto the particles directly without the time required to form colloidal silica particles.

Desilication using a fluidised bed with naturally graded beach sand was successfully tested at Ohaaki (Grant-Taylor, 1981; Axtmann and Grant-Taylor, 1986). The bed vessel was 7.5 cm in diameter and about 3 m in height. It was able to remove over 75% of the supersaturated silica in 2.5 minutes (fluid residence time). The rate of removal was essentially independent of temperature, with all the silica depositing on the bed particles. Chemical analysis showed no detectible arsenic in the silica, and the silica was deposited with no adsorbed material. The silica could be ground off (with the bed particles being returned to the bed), giving a pure and uniform powder suitable for use in glass manufacture or as a (pozzolan) cement extender. The technique was later successfully used at Wairakei to measure the precipitation kinetics of amorphous silica and was found by the previous authors to be effective and fast method for reducing the concentration of excess silica (Carroll *et al*., 1998). The amorphous silica deposited on the sand grains contained 2 wt% aluminium.

A novel application of this technique was published by Siqueiros *et al*. (1992) where liquid fluidised bed served as a heat exchanger recovering heat from the brine as well as silica removal; with this arrangement avoiding scaling in the heat exchanger.

2.3.8 Recent work by Potapov and co-workers

In addition to their electrocoagulation work discussed above, Potapov and his co-workers have produced a series of papers on the production of geothermal silica using different methodologies, with a particular focus on evaluating the physical properties and identifying potential uses (Potapov *et al*., 2015). Other papers summarise their work on extracting silica using ultrafiltration and RO (Potapov *et al*., 2010) and include a review of world wide experience of mineral extraction from geothermal fluids (Potapov *et al*., 2006).

Interestingly, the sols prepared by ultrafiltration were more stable than those concentrated by RO. In the latter, the higher salt concentration destabilised the sol. These are important studies in showing the range of properties, the value of the silica extracted from the geothermal fluid and they confirm previous work undertaken elsewhere. However, as emphatically pointed out by Bourcier *et al*. (2006), ultimately the feasibility and economics of various extraction methods must be proven to potential investors by comprehensive pilot testing.

3.0 LITHIUM

Lithium is the species next after silica (excluding arsenic), to receive the most research focus for extraction from SGW. Lithium compounds have very desirable properties in many industrial applications, including high tech battery applications (Hill, 2015).

However it is with the increasing demand and price over the last decade (Hill, 2015) that this species is moving to a point that it may be considered economically viable for extraction from SGW.

3.1 LITHIUM IN GEOTHERMAL FLUID

Lithium in New Zealand geothermal fluids range in concentration between 3 and 29 mg/kg, with the highest concentrations found at Mokai (29), Tauhara (15) and Wairakei (13) (Mroczek *et al.*, 2015a). In contrast, the Salton Sea, which has the world's first and only operating large scale geothermal lithium extraction pilot plant, uses brines with ~ 200 mg/kg lithium. At the Salar de Uyuni in Bolivia and other saline lakes in South America, mining of lithium occurs from materials with up to 5000 mg/kg lithium. The higher concentration may not necessarily proportionately increase the economic extraction, due to high concentrations of impurities in the Salton Sea brines and South American saline lakes.

In geothermal solutions, lithium is highly soluble and usually remains in solution right through the geothermal energy production process; from fluid production from the reservoir through to injection back into the reservoir.

3.2 EXTRACTION OF LITHIUM

Due to the small size of the lithium ion and large hydrated radius, lithium has some special chemical properties relative to the other alkali metals; some of which are also found in SGW (sodium, potassium, rubidium and cesium). The chemistry resembles more that of magnesium and this forms the basis of many extraction processes. For example, lithium carbonate, the most used lithium salt and largest traded lithium commodity is of low solubility (inverse solubility with temperature). The chloride salt is highly soluble (double that of common salt) with strong affinity and reactivity with aluminates, which is the basis of many processes involving precipitation and absorption. This also explains the poor selectivity compared to the other alkali ions (when these are also present) with cation exchange resins.

Given the industrial importance of lithium, the processing literature is vast (Garrett, 2004; Tram and Luong, 2015) and is increasing. Lithium extraction technologies fall into the following three broad groups, with some overlap:

Absorption and then extraction into solutions

- Mg oxide spinels

Precipitation

- Aluminium hydroxide/chloride

Concentration – in solution

- Electrodialysis (LiCl)
- Evaporation

There has been no large scale pilot testing of lithium extraction in New Zealand, and only three small scale laboratory test have be reported in the public domain. Considerable press has been given to the lithium extraction pilot plant by Simbol Mining using geothermal fluids produced for the John L Featherstone (Hudson Ranch), Salton Sea geothermal power plant (USA). No information is provided on the technology used to extract the lithium. By searching the patents held by the CEO (Dr John Burba; http://www.simbolmaterials.com) an inference can be made that it is based on an aluminate (gibbsite) absorbent. The environmental discharge reporting for the John L Featherstone (Hudson Ranch) Geothermal power station (California Regional Water Quality Control Board, 2013) gives the average production fluid concentrations as; lithium – 228 mg/kg, silica – 437 mg/kg, iron – 1411 mg/kg, manganese – 1700 mg/kg and many other metal impurities at high concentrations. A significant portion of the silica (to amorphous silica saturation) will be removed as part of power generation using the crystallisation/clarification technology implemented at Salton Sea geothermal power stations. However, the residual silica and metals may need to be substantially reduced if the lithium is being extracted by passing the fluid through aluminate absorbents.

In 1994, Pacific Lithium was formed in New Zealand to extract lithium from seawater. This vision was not ultimately realised and the company moved into recycling lithium from batteries. However the authors of this report are aware that at that time the company also investigated the extraction of lithium from geothermal fluid. John Broome, a principal of the company at that time (Pers. Comm., 2014) identified that the reason the research was not pursued was the relatively small quantities of lithium available and the limited supply of geothermal fluid compared to the virtually unlimited seawater resource. He also indicated that their extraction technology was based on 1954 patents (no longer protected) for “lithium transport membranes” based on manganese spinels developed for medical applications.

Manganese oxide spinels have been the focus of intense research over the last 20 years. For example, a study by Chitrakar *et al*. (2014) investigated doped manganese spinel for lithium removal from Bolivian brine. We are not aware of any research undertaken in New Zealand except that published by Gary Burns (Victoria University of Wellington) as co-author with Brett Ammundsen, later CEO of Pacific Lithium (Ammundsen *et al*., 1996 and other papers).

3.2.1 Co-precipitation with aluminium hydroxide

Lithium extraction by co-precipitation with aluminium hydroxide was investigated in detail for Wairakei SGW by Rothbaum and Middendorf (1986). The experiments looked at the characteristics of the co-precipitation and how to maximise the extraction of lithium. They concluded that recoveries of 95% were achievable in a process operating at 30°C at a pH of 10. It was determined that with increasing temperature the extraction of lithium decreased. Numerous trials were conducted with silicated and desilicated SGW. The prior removal of silica was deemed essential for efficient co-precipitation, due to alumina silicate precipitation, which led to poor aluminium hydroxide recovery. The lithium extraction method was limited by the concentration of geothermal fluid within the aluminium hydroxide gel. This caused low lithium extraction values, with a maximum concentration of 51 ppm achieved.

In a subsequent unpublished report, Rothbaum (1990) investigated the precipitation of lithium aluminium silicates from Mokai and Wairakei waters for use in ceramics. It is a simpler process requiring no prior desilication. Although the Mokai waters have higher lithium, the amount extracted was proportionally lower than for the Wairakei water (45% vs. 75% recovery). Rothbaum (1990) speculated that this could be due to the higher salinity, which also caused the silica in brine separated at atmospheric pressure at Mokai to floc without chemical additives. The final washed Wairakei product contained 1.2% Li (as Li_2O) and Mokai contained 5%. If the waters were first desilicated, over 80% of the lithium in the Mokai water could be recovered by sodium aluminate addition. Of interest is that adding aluminium chloride solutions (which are cheaper and easier to handle, recycle and use than solid sodium aluminate) to Wairakei water resulted in lithium extraction efficiencies of only 30%, at best. However, for Mokai waters extraction efficiencies rose to 75% with no explanation able to be given. Rothbaum (1990) noted that almost all the rubidium and cesium remained in solution after lithium (and silica) extraction and that these could be removed by possible deposition on zeolites. Tram and Luong (2015) make the point that lithium mined from ores is used directly in ceramics and glasses without refining, whereas it is the lithium in brines that is extracted and purified for use in applications requiring a higher value product.

3.2.2 Manganese oxide spinels and cation exchange resins

Other methods that have been explored for the extraction of lithium from SGW are based on the use of adsorption methods and ion-exchange resins. Iwanaga *et al*. (2007), used manganese oxide (spinel structure) as the adsorption species for removing lithium from Wairakei brine. Pretreatment of fluid to remove silica was required and was achieved by the use of electrocoagulation using aluminium electrodes. Following the desilication, an effective extraction of 20% of the total lithium was obtained by the adsorption technology at room temperature. However, the values of total lithium extracted were not sufficient to encourage further commercial investigations.

Matsushita *et al*. (2013), recently presented data for lithium absorption from simulated SGW by manganese oxide spinel. The mineral absorbed 24 mg/g of lithium over 24 hours, but as their simulated brine contained 100 mg/L Li, they speculated that the actual uptake from SGW with lower lithium concentration would be much less. A kilogram of the oxide spinel would treat approximately two tonnes of Wairakei fluid, which would require a large facility to treat even a small portion of the flow, and the slow uptake would be a major impediment.

The need for use of actual geothermal fluid rather than simulated fluid for laboratory trials was illustrated by Park *et al*. (2012). They used a manganese oxide (spinel structure) absorbent to extract lithium from geothermal water from Hatchobaru (Kyushu, Japan). The water is very similar in composition to Wairakei (10 mg/L lithium, 30 mg/L boron, 3 mg/L arsenic). They found that the uptake of lithium absorption was inhibited by arsenic, which decomposed the structure of the absorbent with manganese present in the eluent. This inhibition became less pronounced with increasing pH, as the arsenic changed from a positively to a negatively charged species. They successfully removed lithium by first recirculating the geothermal fluid through a magnetite column and then passing it through the spinel. Wairakei water contains about 4 mg/L arsenic and this may explain the poor results seen by Iwanaga *et al*. (2007).

Rothbaum and Middendorf (1986) also reported ion exchange resin trials undertaken in 1964, which were unsuccessful due to the lack of sufficiently large selectivity of lithium with respect to sodium.

3.2.3 Electrodialysis

Electrodialysis is an electrochemical separation process in which ions are transferred through ion exchange membranes by means of direct current (Valero *et al*., 2011). The technology is now well developed for producing drinking water by desalinating large quantities of ”brackish” waters; for example desalination plants in Spain process up to

200,000 m^3/day. It is ideally suited for purifying water with TDS up to 12,000 mg/L (Valero *et al.*, 2011), which is greater mineralisation than found in New Zealand SGW. This type of plant should be able to be integrated into the backend of a geothermal power plant brine stream before it is injected. The permeate is however the waste product, where the concentration of dissolved minerals is of interest. Many processes using this technology have been developed for recycling or concentrating lithium (e.g., Ball and Boateng, 1987).

It is a technology that Kennedy (1961) used in the 1950s to concentrate the lithium in Wairakei fluids, but did not separate it from other constituents (e.g., sodium and potassium). Recently Mroczek *et al*. (2015b) undertook laboratory scale experiments, also utilising Wairakei brine, to evaluate the feasibility of larger scale field trials for concentrating the lithium in the SGW. Geothermal brine has a low concentration of magnesium, which is a distinct advantage in the carbonate precipitation stage. In their study, lithium specific membranes (e.g., DuPont Nafion) were not used, but they considered such membranes would provide a marked improvement for reducing the concurrent concentration of interfering impurities. The colloidal and dissolved silica can cause significant blocking within electrodialysis cells and can damage the membranes. This necessitated removal of silica prior to extraction of lithium. Any silica removal technology could have been used, but the silica was removed by electrocoagulation using aluminium electrodes. The electrocoagulation time was minimised to avoid lithium co-precipitation. The production of calcium sulphate can be detrimental to the performance of the membranes, as precipitation blocks active ion exchange sites. This interference can be removed by addition of either sodium polymetaphosphate or sodium oxalate. The chemical was typically added at the end of the electrocoagulation process, where the suspended silica floc would efficiently sweep down the insoluble calcium salts. Both chemicals were effective and caused no decrease in lithium concentration. Calcium removal did not appear to be necessary for processing Wairakei fluid.

Lithium extraction efficiencies were better than 80% and, normalised to relatively small 1 m^2 transfer surface area, was equivalent to extracting all of the lithium out of 250 kg per hour of Wairakei brine. A significant problem was the shorter than expected life of the membranes. The potential of the overall system as an industrial process could not be gauged from the small scale laboratory data. To test and understand if concentrating lithium from Wairakei fluid is economically viable, larger scale field pilot plant trials would have to be undertaken.

3.2.4 Evaporation

Solar evaporation of saline lake brines for concentrating lithium is a well-known method. Given the abundant geothermal heat it is surprising evaporation has not been trialled more extensively. Kennedy (1961) reported the use of a small vertical tube evaporator to concentrate Wairakei brine to 16 wt% NaCl. No attempt at prior removal of silica was made, which severely reduced the heat transfer rates. No solute concentrations were given, but they concluded it would be possible to recover all the salt and 90% of the potash by evaporation and fractional crystallisation before the brine became saturated with respect to lithium chloride. In an earlier study, Kennedy and Forrest (1960) reported the use of a single tube evaporator, and with no prior silica removal, concentrated the lithium 70x to 920 mg/kg, cesium to 99 mg/kg, rubidium to 144 mg/kg and calcium to 550 mg/kg. Dissolved silica reduced to 52 mg/kg with precipitation of a very hard adherent scale. Unpublished studies as part the electrodialysis work reported by Mroczek *et al*. (2015b) showed simple evaporation (immersed coil attached to a hot injection water supply) of desilicated water resulted in high concentrations of lithium (> 500 mg/kg) with significant crystallisation of sodium and potassium chlorides. The purpose was to increase the TDS in the brine prior to electrodialysis.

4.0 BORON

4.1 BORON IN GEOTHERMAL FLUID

Boron concentration in geothermal fluids ranges between 6 and 40 mg/kg, except at Ngawha where the concentration is significantly higher at 1063 mg/kg (Mroczek *et al.*, 2015a). Boron is present dissolved in water in combination with oxygen as boric acid $B(OH)_3$ at $pH < 7$. Above pH 7, the concentration of the tetrahydroxyborate oxyanion $B(OH)_4^-$ increases rapidly, which can affect the extraction efficiency. Like lithium, boron is highly soluble and is not removed from brine as part of the production operation. However, its slight solubility in steam means a very small portion is partitioned into the vapour phase on steam separation. The solubility in steam explains the high boron concentrations in steam condensates and this formed the basis of a boron extraction industry in Ladarello in Italy over the last couple of centuries (Wisniak, 2005).

Although boron is a necessary macronutrient, too much boron and possible boron pollution has always been an aspect for consideration in geothermal energy production. The element is a potent phytotoxin and is potentially a contaminant in surface and ground waters.

4.2 EXTRACTION OF BORON

Due to its toxicity the work on boron has been focussed more on removal for environmental reasons rather than for economic recovery.

The following technologies are the most used to remove boron:

Precipitation/Absorption

- Clays
- Lime, MgO and other metal oxides
- Electrocoagulation
- Chelating resins

Concentration

- Ion exchange
- RO
- Solvent extraction

Similar to lithium, for many of the above techniques the silica in the SGW would pose significant interference or would be co-precipitated with the boron. No boron extraction trials of New Zealand geothermal fluid are known, although Sheppard and Orange (1987) reported work on boron removal by addition of magnesium hydroxide to drainage waters from the Huntly West coal mine.

Many of the methods discussed below may have application in secondary extraction, although perhaps not appropriate as a primary means of removing boron from SGW due the large volume of water involved and possibly high operating and capital costs.

None of the papers reviewed presented any economic analysis by which to evaluate what methods might feasibly be implemented to extract boron from geothermal fluids.

4.2.1 Absorption

Yan *et al*. (2008) make the point that absorption by metal oxides (calcium, iron, aluminium, iron) and clays is only useful for concentrated boron solutions, whereas solvent extraction, RO and electro-deionisation (similar to electrodialysis except that an ion exchange membrane is also used) were better suited for removal of low concentrations of boron. It is likely for most New Zealand geothermal fluids that are low in boron, that reagent based processes (such as adding lime and magnesium oxide) will require high chemical dose rates (Rodionov *et al*., 1991).

Yan's *et al*. (2008) preferred method for removing boron from refined brine (40-400 mg/L) was with boron specific resins, as the boron oxyanion has poor retention in anion resins. Interestingly, their purpose was to refine brine containing 10000 mg/L of lithium as the presence of boron at even low concentrations was a major impediment to the production of lithium carbonate. They reported previous work on geothermal waters where Amberlite IRA 743 was used to remove boron from water containing 19 mg/L boron with 99% efficiency (see also Potapov *et al*. (2006)). They successfully trialled the boron specific resin XCS-800 and determined optimum removal conditions (e.g., flow rate, anion concentration, temperature and pH).

Many variations of the ion exchange removal method have been published. Kabay *et al*. (2013) used a hybrid method for removal of boron from geothermal fluid in Turkey (boron ~ 11.4 mg/L, but in a brine with a lower level of TDS (916 mg/L) compared to New Zealand SGW). The resin is mixed with the brine and then removed via ultrafiltration. Tornescu and Gilău (1997) and Gilău and Stănăşel (2010) used ion exchange resins to recover boron from Romanian geothermal fluids containing up to 24 mg/L boron from low temperature (< 120°C) bicarbonate springs, which are quite unlike the New Zealand geothermal fluid composition. Badruk *et al*. (1999a; 1999b) and Badruk and Kabay (2003) compared the effectiveness of various ion exchange resins to remove boron from Kizildere geothermal brine (30 mg/L) and, in a similar study, Koseoglu *et al*. (2015) did the same for Hachoubaru (*sic*) in Kyushu, Japan. Unsurprisingly, greater extraction efficiencies are achieved with greater amounts of resin, with what appears to be a relatively high 6 g resin /L being optimum for Hachoubaru brine. In these ion exchange methods, the boron on the resins must be eluted with dilute sulphuric (4%) acid solutions, with eluent concentrations up to 6 g/L boric, which can be concentrated to obtain high purity boric acid (Gilău and Stănăşel, 2010). This adds complexity and cost to any downstream processing if recovery is the purpose. The feasibility and cost of scaling up the large flows of geothermal fluid with this method is not known. Treating a considerably less mineralised fluid, for example a power station steam condensate (produced in a shell and tube condenser), for irrigation water may be possible with acidified waste eluent containing the boron being injected.

As part of their SACS process, Koichi Kato (Pers. Comm. in a presentation to GNS Science) showed that in Sumikawa geothermal brine, boron at 200 mg/L, with the prior removal of silica, could be reduced to near zero. The boron was recovered by adsorption onto boron selective resins (939 g in 24 hr continuous operation of their pilot plant). No further information is available.

Yilmaz *et al*. (2008) successfully trialled electrocoagulation for boron removal from Ilıca-Erzurum geothermal fluid (sodium bicarbonate chloride water at 52°C and boron 24 mg/L) and determined the optimum operating conditions (current density, pH and temperature). In their laboratory scale cell, for 1500 mL (24 mg/L boron) the removal efficiency was 96% at pH 8.0, electrolysis time of 30 min and current density of 6.0 mA/cm^2. The boron remaining was less than 1 mg/L and the effluent was suitable for irrigation.

Li as part of her Masters of Engineering programme has recently completed a series of extractions (as yet unpublished) on New Zealand geothermal solutions dosed with up to 1000 mg/kg boron. She used electrocoagulation, which simultaneously could also extract silica[2]. The boron extraction efficiency varied from 58% to 96% depending on pH and electrode material (iron was identified as better than aluminium). Recovery of the boron from the floc was not tested but would need to be undertaken to evaluate the viability of the process.

Badruk and Mordogan (2005) reported laboratory experiments involving extraction of boron from Kizildere brine (30 mg/L boron) by co-precipitation with alunite (potassium aluminium sulphate) and aluminium sulphate, using lime for pH control. They chose this precipitation and coagulation technique; suggesting it was economic compared to other methods and achieved essentially 100% removal of the boron at pH 11-12 with a precipitate of calcium aluminium sulphate. There is no discussion of co-precipitation of silica (415 mg/L in their brine). The brine would need to be acidified before being able to be used as irrigation water. The purpose of this and the previous study of Yilmaz *et al*. (2008) was the purification of water for irrigation and not for economic extraction of boron as a product for sale.

4.2.2 Solvent extraction

Boron-oxygen-carbon bonds can be very strong and this property allows the selective extraction of boron from brines by various organic solvents forming the basis of many industrial purification processes (Garrett, 1998). Rodionov *et al*. (1991) outline many advantages of these methods such as ease of automation and high purity of the produced product as well as some challenges such as complexity of the method and the loss of expensive reagents, which are partially soluble in the brine. Hydroxylated organic solvents were reported to have extraction efficiencies of 99%.

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[2] Also ultimately also lithium as found by Mroczek *et al*. (2015b).

5.0 CARBON DIOXIDE RECOVERY – REMOVAL OF HYDROGEN SULPHIDE

Effective chemical technologies exist for removal of hydrogen sulphide from geothermal gas streams but these are expensive and only implemented where demanded by the regulatory environment, such as is present in area of the Geysers in the USA. Rodríguez *et al*. (2014) summarised some of the hydrogen sulphide abatement processes which enable the elimination of more than 90% of the gas in a geothermal gas stream. Recently Gunnarsson *et al*. (2015) have described gas separation processes at Iceland and, although the CO_2 rich and H_2S gas streams are separated, they are ultimately both injected and not purified further. Mertoglu *et al*. (2015) reports that liquid carbon dioxide and dry ice production factories are integrated to Kizildere and Salavatli power plants with a production capacity of 240,000 tons/year. The reason this may be economic is that the offgas is very pure between 0.01-0.02% H_2S (Gunerhan and Coury, 2000) compared to 2% H_2S (by volume) in a typical New Zealand power station non condensable gas. This means that purifying the non-condensable gas can be accomplished relatively easily using technologies where quantities of H_2S are small.

One of the potential uses of a geothermal gas stream that is free from hydrogen sulphide is for CO_2 enrichment for enhanced plant growth in a glasshouse. At the residual H_2S concentrations achieved in the industrial abatement processes, the gas stream would still contain a too greater concentration of H_2S and would not be able to be used for horticultural purposes.

A wider technological and economic review of the H_2S abatement in geothermal gas streams to very low levels is a work stream for further investigation with a focus on producing a gas stream that can be used in horticulture. Building on the student report of Padilla (2007) on the use of gas from plants in El Salvador would be a good place to start.

6.0 RUBIDIUM AND CESIUM

These valuable elements are present in New Zealand geothermal water at concentrations from 1 to 6 mg/L. They are stable species, highly soluble as a chloride salt and remain in solution after all the other constituents of interest have been extracted. They can be concentrated to above 100 mg/L by simple evaporation.

Fractional precipitation, solvent extraction and ion exchange are commonly used to concentrate and extract these metals, the latter being perhaps the most useful and simplest to scale up.

Fractional precipitation is a method for separating elements or compounds with similar solubilities by means of their gradual precipitation from a solution. The concentration of the “precipitator” (e.g., oxalic acid, aluminium sulphate) and chemistry (e.g., pH) must be carefully controlled. The high cost of the precipitators and process complexity limits the wide application of this method (Zhang *et al.,* 2014).

A patent application assigned to Simbol Mining Inc uses a method based on precipitation of a tetrafluoroborate to extract these elements, including potassium, from geothermal fluid (Harrison *et al.,* 2014*)*.

Various absorbents have been trialled with some showing good extraction efficiencies. CsTreat (a selective hexacyanoferrate compound) displayed a very high sorption capacity of rubidium (238.1 mg/g), and a fairly high sorption capacity of cesium (43.7 mg/g) (Peterskova *et al.,* 2012). Often the application is the removal of radioactive cesium (Awual, 2014).

Solvent extraction is also an effective extraction method, especially phenol-alcohols and crown ethers, with cesium extraction rates better than 90% (Chun *et al*., 2001; Jianchen *et al*., 2005). The method would suffer the same problems as discussed for boron (complexity and loss of expensive reagents).

Given the vast world reserves and relatively small world demand (Hill, 2015; Butterman *et al*., 2004) any geothermal extraction method will need to be highly efficient and cheap.

Laboratory trials and developing extraction methods from a typical New Zealand brine composition is warranted.

7.0 FUTURE WORK

The following are possible future work streams. The work streams are grouped by species.

7.1 SILICA

The techniques for silica extraction from geothermal fluids are considered adequately characterised to the point that rough cost estimates should be able to be developed for large scale extraction plants. An outstanding but significant and important workstream is how these silica plants might be cogently integrated into an energy development.

There are at least two cases to consider:

- Where silica extraction is used instead of acidification (or other treatment process) and the geothermal fluid is all treated.
- Where a targeted high value silica is produced.

The methodologies should consider how these might occur for an existing energy development and for a new development.

7.2 LITHIUM

For lithium, there is an opportunity to pursue additional laboratory trials and then to select a methodology to be taken through to a pilot plant scale. At this point the economics of a large scale operation should be able to be estimated. With market pricing as it currently stands, the work on lithium should have a forward view of about a decade, at which time lithium supply is expected to become constrained.

7.3 BORON

Boron is another higher value constituent in brine at low concentration. There have been no published laboratory or field trials undertaken on SGW in New Zealand. The next step is to trial and evaluate extraction processes at a small scale in the laboratory and then, if sufficiently encouraging, follow up with trials at a larger pilot scale. In parallel with or ahead of the establishment of a larger pilot plant, estimates should be established for the economics of integration into an energy generation operation. Industrial boron extraction processes are sufficiently well established that these estimates should be able to be developed once the efficacy of boron extraction processes from New Zealand SGW are established.

7.4 RUBIDIUM AND CESIUM

For rubidium and cesium laboratory trials are necessary to evaluate which extraction process (if any) might be feasibly applied and scaled up to extract these constituents from New Zealand SGW.

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