Proceedings World Geothermal Congress 2015
Melbourne, Australia, 19-25 April 2015

From Waste to Wealth: Mineral Extraction from Geothermal Brines

Ed Mroczek[1], Melissa Climo[1], Ying Li[2], David Evans[1], Brian Carey[1] and Wei Gao[2]

[1]GNS Science, Private Bag 30-368, Lower Hutt 5040, New Zealand

[2]The University of Auckland, 20 Symonds Street, PB 92019, Auckland 1142, New Zealand

e.mroczek@gns.cri.nz

Keywords: New Zealand, mineral extraction, geothermal brines, silica, lithium, market drivers, regulatory framework, technologies, chemical composition

ABSTRACT

The composition and volume of geothermal fluids in New Zealand offers considerable potential for the extraction of various metals and minerals, as well as being a source of heat energy, steam and gases, and for use in generating electricity.

While extracting products from geothermal fluids is technically feasible, positive economics is the key driver for commercial success. However there is no assessment of this opportunity which identifies simple, cost-effective processing technologies, and provides a greater understanding of the economic viability and barriers for implementing such technologies.

The methodology that will be used to evaluate the commercial opportunities for New Zealand will be discussed. A suite of cross-disciplinary studies will integrate a range of information on the opportunities and barriers to the commercial recovery of a selection of products from geothermal fluids. These will include a technological, market and New Zealand regulatory review. The outcome will be the best technical options and economic models to assist in guiding future investment.

1. INTRODUCTION

Geothermal resources have important strategic value for New Zealand; able to directly supply both heat and electricity. The composition and volume of geothermal fluids in New Zealand also offers considerable potential for the extraction of various metals and minerals, as well as being a source of heat energy, steam and gases, and for use in generating electricity. Geothermal fluids are heated as they travel through rock bodies. They interact with the rocks and become increasingly saturated with various minerals and metals that could be saleable products. The presence of high concentrations of minerals in fluids has often been considered a major engineering challenge, with corrosion and scaling a significant issue in the electricity generation plants, direct use facilities and injection wells (Mroczek et al, 2011; Lichti, 2007; White et al 2000). However, this occurrence also offers a commercial opportunity through recovery and sale of bi-products. There are no costs associated with mining and physical processing of an ore, and no negative environmental impacts. Compared to other mining processes, there are no costs associated with dissolution of ore minerals into an aqueous phase because they are already in solution. Economic, social and environmental benefits will arise from creating new industry for New Zealand, developing world leading capabilities in processing technologies, and improving the productivity and value of the geothermal industry.

New Zealand-based researchers are undertaking a small study (2013 - 2015) to assess this opportunity and its barriers, as a springboard for future research and investment. While extracting products from geothermal fluids is technically feasible, positive economics is the key driver for commercial success. There is a need for an integrated assessment of this opportunity which identifies simple, cost-effective processing technologies, and provides a greater understanding of the economic viability, market drivers and regulatory barriers for implementing such technologies.

1.1 R&D Context

Recent industry and Government funded research in New Zealand has been directed on remediation and treatment of geothermal waters. This has included testing and development of processes for:

- carbon dioxide recovery (hydrogen sulphide removal) from geothermal gases;
- a bioreactor for removing hydrogen sulphide from condensate (Bierre and Fullerton, 2013);
- removal of arsenic from geothermal fluids (Mroczek et al. 2006)
- effective acid dosing methodology of geothermal brine for inhibiting silica scaling (Mroczek et al., 2010) ; and
- producing clean steam from geothermal steam for paper processing (Lind et al., 2013).

Little recent work has been done on the economic extraction of valuable minerals; for example lithium (Iwanaga et al. 2007; Mroczek et al., 2015) and silica (Borrmann et al., 2010).

However internationally, there is progress in this area. In the last decade the extraction of valuable compounds from geothermal brine has received impetus as part of the worldwide minerals commodity boom with two international conferences being held in 2005 (Russia) and 2006 (US). Lithium has been the focus of research in the US, and publically available reports from Simbol Materials suggest they are producing industrial quantities of lithium from their demonstration plant at the Salton Sea (myDesert.com, 2014).

1.2 Stakeholders

In New Zealand mineral/metal recovery is most likely feasible either by, or in partnership with, a geothermal energy development, for both practical and economic reasons. Geothermal plants are already permitted and are experienced in pumping, processing, handling and disposing of geothermal fluids. Extraction of minerals and other materials offer benefits to the geothermal industry in improving the economics of geothermal energy use by co-producing and marketing selected dissolved constituents. Mineral extraction would most likely consist of an additional treatment step added to existing plant facilities.

Geothermal mineral extraction would increase opportunities for regional growth and development, and additional employment. Māori groups, as geothermal resource owners, are in a position to directly benefit from geothermal research in New Zealand in supporting the development of their natural resource assets for, for example, electricity generation and direct uses, including mineral recovery.

2. MINERAL EXTRACTION

Bourcier et al. (2005) suggest that that silica, lithium, and zinc have the greatest potential to be economically extracted from geothermal brines. However, for low salinity New Zealand brines, zinc is not important. Other materials have, at times, been economic, but have lost their economic competitiveness, for example the zinc extraction plant built by CalEnergy in the late 1990s (Clutter et al., 2000) was abandoned in 2002. Previous published research on extraction of resources from geothermal fluids has included precious and platinum group metals, gold, silver, zinc, lead, copper, manganese, rare earth elements, silica, lithium, arsenic, antimony, boron, bromine, iodine, strontium and barium sulphate, precipitated calcium carbonate, calcium chloride, potash, table salt, sodium sulphate, and others (Gallup, 1998; Gilau and Stanasel, 2010; Harper et al., 1992; Harper et al., 1995; Bourcier et al. 2005; Mroczek et al. 2006). Additional saleable products could also include rubidium, cesium, elemental sulphur, sulphuric acid and carbon dioxide (Bourcier et al. 2005; Bloomquist, 2006; Hirowatari et al. 1997; Simsek, 2003; Monnery, 2005).

2.1 Silica

Silica is one of the biggest “problem” minerals in geothermal energy production, and potentially one of the most valuable minerals. Silica is a marketable commodity in its own right with a wide range of uses (Bergna, 1994; Bergna and Roberts, 2005), the major markets being glass, foundries, building products, and chemicals. However, the value and price for silica varies widely 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$1.3b, and growing over 5% annually (Freedonia, 2012). This market includes cosmetics and toiletries, chemicals, rubber, coatings and inks, electrical and electronic equipment. The revenue stream from silica from a 50MWe geothermal plant could provide US$10-12M per year (Bloomquist, 2006).

Of immediate benefit for a geothermal facility in removing silica are a reduction of operating and maintenance costs (through reduced scaling of pipes), and greater energy extraction (thus creating of a more cost competitive product; $/kWh). This can lead to millions of saved dollars for fewer production and injection wells, and increased production efficiency while operating and maintenance costs are reduced. For example, at Wairakei the Binary Plant cools fluid to 90°C, 40°C below the 130°C minimum temperature to avoid silica scaling. An additional 15MWe of generation is produced from the “waste” fluid, worth $10M at $80/MWe.hr, however the scaling results in extra maintenance and possibly some faster decline of injection capacity.

Silica research has been the abiding research interest in New Zealand since the 1980s (Mroczek et al, 2011). However extraction of silica is only one method to solve scaling problems and needs to provide economic benefits to compete against the chosen silica control method undertaken at three geothermal power stations (i.e. pH modification of brine). At least six different silica extraction methods have been tested in New Zealand, two at large $M pilot plant scale (Harper et al, 1995; Brown and Bacon, 2000), and a number of other extraction methods at overseas geothermal power stations (Harper et al, 1992). However, these have not been taken up by the commercial sponsors. There are many processes available to extract silica, but removal to the point of no further precipitation is crucial and a necessary catalyst for the extraction of other minerals and metals, or to utilize the waste heat and realize power generation efficiencies.

2.2 Lithium

Kennedy (1961) published experimental work proving the economic and technical viability of extraction of lithium using electrodialysis, an electrochemical technology then in its infancy. Other unpublished reports by Kennedy discussed the economic and technical aspects of concentration of water by evaporation and silica removal. Rothbaum and Middendorf (1986) published an alternative absorption method for lithium recovery based on earlier work at Hatchobaru (Yanagase et al., 1983). Although successful at the laboratory scale, this was not further investigated. None of these pioneering investigations were taken forward. Since then, lithium has increased in economic value. The expected annual growth rate between 2011 and 2025 from existing market applications is 7%, with an annual maximum rate as high as 10%, depending on the demand of the electronic and transportation sectors (Roskill, 2009).

2.3 CO_2

Effective chemical technologies exist for removal of poisonous and corrosive hydrogen sulphide from geothermal gas but these are expensive and only economic for electricity production in a stick regulatory environment, not for other uses such as horticulture. Attempts have been made to clean up offgas using less expensive biological based technologies, but ultimately the concentration of hydrogen sulphide cannot be reduced sufficiently at a low enough cost for horticultural use.

2.4 Trace elements

There are other minor and trace compounds in geothermal fluids, such as boron, gold and silver, the extraction of which have been investigated over the years (Seastres, 1989; Timperley and Mroczek, 1989) with no commercial outcome. However since those early attempts, the advent of new materials potentially offer more promise. These include SAMMS (self-assembled monolayers on mesoporous supports; a family of "designer" adsorbents made using molecular-engineering), modified micro- and meso-porous materials, selective membranes/absorbents, and nanopowders, such as titanium sponge (e.g. removal of cesium see Lin et al., 2001).

3. BARRIERS TO IMPLEMENTATION

Mineral extraction from brines is an international topic of interest. In 2005 and 2006 two international conferences specifically targeting mineral extraction from geothermal brines were convened. Core issues facing implementation internationally were identified by conference attendees and have not markedly changed. Barriers to implementation of commercially viable product recovery from geothermal fluids include (Bloomquist, 2006; Bloomquist and Povarov, 2008):

- lack of knowledge regarding the presence and potential uses for resources and technologies;
- technologies not yet developed and/or not economically viable;
- insufficient market drivers;
- removal of silica;
- availability of competitive product sources e.g. mines, quarries, salt lakes; and
- modest interest by geothermal electricity generators in diversifying their business, particularly "cascade" uses.

There is a need to examine these barriers in the New Zealand context, as well as identifying additional local obstacles such as potential regulatory hurdles.

4. FROM WASTE TO WEALTH

This research programme aims to provide a starting point for an information resource to determine the commercial potential and best technical options for encouraging future investment in technologies for the extraction of saleable products from geothermal fluids. The components of the programme are overviewed in Figure 1.

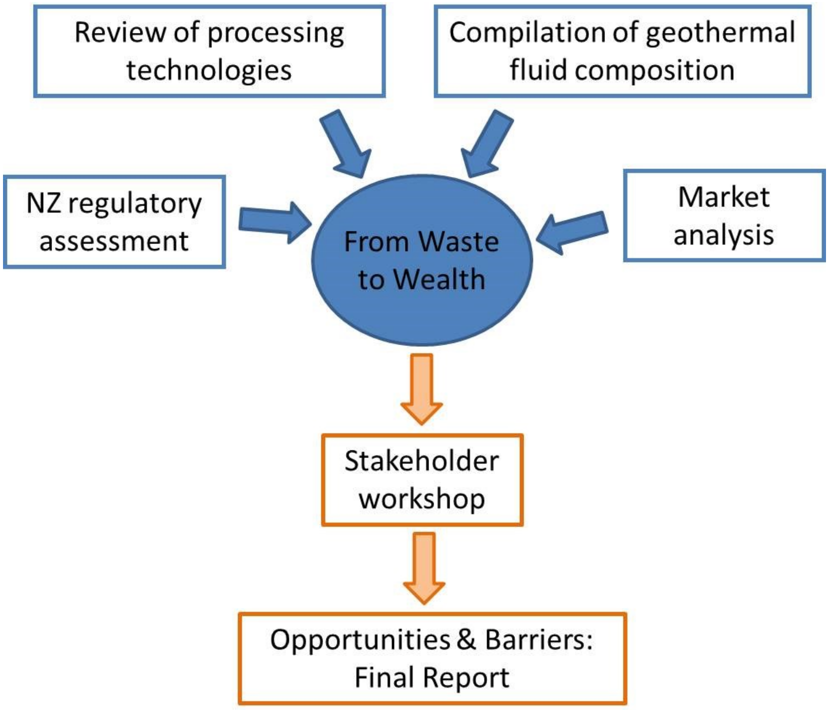

Figure 1: Overview of research programme components.

4.1 Geothermal Fluid Composition

Whilst chemical compositions of particular low enthalpy geothermal fields and surface features (e.g. springs) have been published (Reyes et al. 2010), there is not yet a compiled summary of the chemical composition of New Zealand's production geothermal fluids with sufficient detail to inform a big-picture view to economic mineral recovery potential. In Table 1 is a compilation of publically available information on selected metals and metalloids in high temperature well aqueous solutions in the geothermal systems of the Taupo Volcanic Zone (Central North Island) and Ngawha (Northland). Three major fields (Orakei Korako, Waimangu and Waiotapu) are protected geothermal systems and are not included in the list (WRC, 2014; BOPRC, 2008). In addition to published studies, unpublished data and reports held in GNS Science files and databases (GNS Science, 2014) were reviewed. Contact Energy Ltd provided recent unpublished data for Ohaaki, Tauhara and Wairakei and Mighty Power Ltd for Kawerau, Ngatamariki and Rotokawa. There is no recent compositional data for Mokai except that published by Giggenbach (1995).

A considerable amount of historical data (prior to 1990) was found for the major elemental compositions (Li, Na, K, Ca, Cl, B, SiO_2, SO_4 and HCO_3, as well as Rb, Cs and Mg) as these species are used to characterize and monitor the effects of geothermal production on reservoir composition and production problems such as scaling. Representative values are given in Table 1. In contrast very few studies that have investigated trace element compositions in geothermal fluids. However some studies have examined the flux of precious metals through geothermal systems, and have estimated that the flux is significant for certain locations in New Zealand; e.g. Simmons and Brown (2007) found Rotokawa to have the highest flux rates in the TVZ, 37-109kg/yr and 5200-11400kg/yr for gold and silver respectively. Several studies (e.g. Reyes et al. 2003) investigated the chemistry of scales and deposits on pipelines and found them to contain gold, silver, and a wide range of trace elements, however these are not always directly reflective of the water trace element composition chemistry so have limited use in this study.

Table 1: Representative water composition[1] of selected Taupo Volcanic Zone and Ngawha geothermal wells; values in mg/kg unless otherwise specified.

Location	Li	Na	K	Ca	Rb	Cs	Mg	Cl	SO_4	$tHCO_3$	B	SiO_2	Ag	Cu	Au
													µg/L	µg/L	µg/L
Wairakei	12.7	1217	194	19.0	2.2	1.3*	0.01	1991	42	<10	27	618	1.4-31.5	490-2360	0.03-2.1
Kawerau	6.3	789	119	2.2	0.7	0.6*	0.01	1028	69	315	57	954			
Rotokawa	7.9	633	175	2.2	2.1	1.6*	0.01	1099	13	112	30	1163			
Ngatamariki	9.1	892	183	3.7	1.6	1.7	0.06	1441	12	100	23	935			
Ohaaki	11.8	919	166	1.4	1.5	1.0*	0.01	1172	31	461	38	829	2.7-8		0.3-1.5
Mokai*	29.0	1783	487	13.3	4.9	6.1	0.03	3540	18	6	40	1070	250	-	0.6
Tauhara	15.1	1216	244	12.3	2.6	2.6	0.03	2186	36	38	38	809			
Ngawha	12.3	1043	82	7.2	0.3	0.8	0.27	1465	38	456	1063	461	0.4-19.1	750-4700	0.5-1
Rotorua	2.7	525	50	7.6	0.4	0.4	0.07	527	74	342	6	319			

[1] Well composition normalized to separation at 1bA; except for trace elements

* Indicative values from Giggenbach (1995)

4.2 Technology Review

The economic value of minerals present in New Zealand geothermal brine, particularly lithium, was recognized as early as 1957 (Kennedy, 1957; 1961), before the commissioning of the Wairakei Power Station in 1958. In the 55 years since there have been numerous studies published in New Zealand and internationally on the laboratory and field scale trials of extracting valuable products (Bloomquist and Povarov, 2008). Although these ideas have been published and studied, neither the competing technologies nor the inferences on the integrated economics of power production and extraction have been subject to a rigorous technical nor economic evaluation. Few processes have made it to a commercially viable industrial process. We are undertaking a technology review that includes silica and lithium, as well as other compounds present in the geothermal fluid (e.g. boron, precious metals, iodine, carbon dioxide, helium). We are endeavoring to uncover unpublished work in discussions with industry to summarize what has gone before and the outcomes; particularly identifying technologies and processes that have already been trialed.

4.2.1 Silica recovery – preliminary review

The advantages and disadvantages associated with the economic, technical and environmental factors for selected silica inhibition/control technologies were examined; e.g. the capital cost, operating cost per annum, revenue generated from silica sale per annum, feasibility and sustainability. The silica removal methods of lime softening, line mine, Mg ion addition, reverse osmosis and ultrafiltration were considered to be most beneficial and were further evaluated. Two methods, lime softening and ultrafiltration appeared to be best suited for large scale removal of silica from brine. Both have been successfully trialed in New Zealand (Rothbaum and Anderton, 1975; Harper et al., 1992; Brown and Bacon, 2009).

Lime softening is the addition of lime (calcium hydroxide) to remove silica as calcium silicates. The discharged water is "aged" first to ensure polymerization of silica, followed by the addition of slaked lime to rapidly precipitate a flocculent, hydrated calcium silicate gel that can be sent to a clarifier or filter.

In contrast the general process of ultrafiltration consists of cooling, ultrafiltration and diafiltration. Cooling induces polymerization which results in colloid formation and ultrafiltration permits the silica colloids to be concentrated (Bourcier et al, 2005). Diafiltration describes the use of dilution and additional ultrafiltration to remove, or lower, the concentration of salts and contaminants from solutions (Brown and Bacon, 2009). The purpose of ultrafiltration is to constrain the size of colloids within narrow limits (i.e. monodisperse) and control the impurity level for certain applications. In a three-stage process Brown and Bacon (2009) were able to prepare solutions to >30% silica by weight.

4.2.2 Lithium recovery – preliminary review

Many methods have also been proposed in the literature to salvage lithium such as ion exchange (Chitrakar et al., 2000, 2001), solvent extraction (Dang et al,. 1978) and high capacity membranes (Zhu et al, 2014). The adsorption methods especially those using the inorganic type spinel manganese oxides adsorbent appear to be some of the most promising methods for lithium recovery from seawater and salt lake brine and perhaps geothermal brine. The spinel manganese oxide adsorbents exhibit attractive characteristics including extremely high selectivity and capacity, low toxicity, low cost, high chemical stability and environmental friendly (Wang et al, 2009).

Another technique which offers the potential for commercialization would be the application of altered polycrystalline hydrated alumina like gibbsite. (Bauman and Burba, 2001, 1997, 1995). Ryabtsev et al. (2002) has also suggested a similar technique but employs the aluminium oxide adsorbent $LiCl \cdot 2Al(OH)_3 \cdot mH_2O$ in granulation with a chlorinated vinyl chloride resin (PVC).

4.2.3 CO_2 Recovery – preliminary review

Table 2 list some of those effective hydrogen sulfide abatement processes which enable the elimination of more than 90% of the existing hydrogen sulfide gas within the geothermal gas (Rodríguez et al., 2014). However at this H_2S concentration the gas would not be able to be used for horticultural purposes.

Table 2: summary table of hydrogen sulfide removal process

Process	Condenser Design	NH_3/H_2S ratio	Economics	Best suitable for	Comments
Dow Spec RT-2	Direct Contact Condenser	Low to Medium	High capital costs	Large units	Can treat both condensate and off-gas in down stream
BIOX	Surface Condenser and Direct Contact Condenser	High and low	Low capital and low operating costs	Small and large	Can treat both condensate and off-gas
Stretford	Surface condenser	Low	High capital costs	Large plants	Environmental issues associated with hazardous waste Treat off-gas only
LOCAT II	Surface condenser	Low	High capital costs	Large plants	Treat off-gas only
Xergy	Unspecified	High and low	Low capital and low operating costs	Small and large	New technology, few commercial practice Treat off-gas only

Xergy and BIOX are relatively more economical than other types of hydrogen sulfide abatement methods. However, they are newly developed technologies which have greater uncertainties for practical applications compared to competing technologies, such as LOCAT II, Stretford, etc.

Generally, the hydrogen sulfide removal technologies should be chosen based on the conditions of the actual geothermal plant, such as the plant scale, type of condenser (i.e. Tauhara, Poihipi, Mokai and Ngatamariki use surface condensers; Kawerau, Ohaaki and Wairakei and the new Te Mihi use contact condensers while Rotokawa Plants have both types), ammonia to hydrogen sulfide ratio within the geothermal gas, and whether it is also needed to treat the condensate or just needed to treat off-gas only.

4.3 Regulatory Framework

In New Zealand, geothermal resources are treated as water, and are covered by broad environmental management legislation, in particular the Resource Management Act 1991. However, there is a real possibility that a mineral in situ or in a geothermal fluid must be considered separately. One possibility is that the mineral is Crown-owned and therefore subject to the Crown Minerals Act 1991. Another possibility where minerals are in private ownership separately from the surface is that the mineral is owned by the mineral rights owner. A third is that the mineral is the property of the surface owner. Another again is that the mineral is personal property in the hands of the geothermal operator. A legal analysis of these questions will be undertaken in order to determine the implications for commercial operations, with particular regard to removing any barriers to mineral processing development. Conventional methods of legal analysis of legislation and case law are being used, and the situation will be evaluated under the existing legal settings and then under different reform options.

4.4 Market Drivers

A market analysis will be undertaken for products identified from the study of New Zealand's geothermal fluid composition and the technology review. This is likely to include (where available) market segments, market size and development (current and future), market growth rate, supply and demand, profitability, industry cost structures, pricing dynamics, competitive products, and key success factors. A summary report will indicate the markets, and thus products, with the most potential from geothermal fluids.

4.5 Recommendations for the Future

A workshop will be convened to present and discuss the findings from this suite of investigations. The workshop and integrated analysis would include investors, regional development agencies, Māori groups, geothermal industry and researchers. It is anticipated that a white paper from this workshop will be used to guide future research priorities. These might include:

- adapting novel technologies to New Zealand geothermal conditions;
- assessing economics including extraction costs (capital and operational);
- in depth assessment of markets and pricing/demand;
- financial modelling incorporating data on market pricing, capital and operating costs, process yields; and
- progressing selected technical projects to improve technical feasibility and economics.

5. CONCLUSION

The composition of New Zealand's geothermal fluids offers a potential commercial opportunity for the recovery and sale of a range of materials, such as silica, precious metals, various minerals and gases, but it is unclear what the best technical options for future investment are. While extracting products from geothermal fluids is technically feasible, positive economics is the key driver for commercial success. This work programme is a starting point for providing the necessary economic, market, regulatory and technical information to guide future investment.

ACKNOWLEDGEMENT

This work is funded by The New Zealand Ministry of Business, Innovation & Employment under contract C05X1307. The authors would like to thank Contact Energy Ltd and Mighty River Power Ltd for providing representative well fluid compositions.

6. REFERENCES

Bauman, W. C., and Burba, J. L.: Recovery of Lithium Values from Brines. U.S. Patents 6,280,693, 5,389,349 and 5,599,516, 5 pp (2001, 1997, 1995).

Bergna, H.E. (Editor): The Colloid Chemistry of Silica. *Advances in Chemistry Series*, American Chemical Society. (1994).

Bergna, H.E. and Roberts, W.O. (Editors): Colloidal Silica: Fundamentals and Applications. CRC Press. (2005).

Bierre, E. and Fullerton, R.: Full scale tubular bioreactor for hydrogen sulphide removal from geothermal power station condensing water. Proceedings AWA Oz Water conference (2013).

Bloomquist, G.R.: Economic Benefits of Mineral Extraction from Geothermal Brines. *International Mineral Extraction Conference* (2006).

Bloomquist, G.R. and Povarov, K.O. Mineral extraction-result studies of World Bank. Geothermal Resources Council Transactions, **32**, (2008), 375-378. http://pubs.geothermal-library.org/lib/grc/1028351.pdf

BOPRC (Bay of Plenty Regional Council). Regional Water and Land Plan. From http://www.boprc.govt.nz/media/31133/Plan-081201-BOPRegionalWaterAndLandPlanGeothermalResources.pdf, (2008).

Borrmann, T., Johnston, J. H., McFarlane, A. J., McBrearty, R.: Realizing Complete Silica Removal -- Moving Technology from the Laboratory to Pilot Scale. *Geothermal Resources Council Transactions* (2010).

Bourcier, W.L., Lin, M., Nix, G.: Recovery of Minerals and Metals from Geothermal Fluids. *LLNL UCRL-CONF-215135; Presented at 2003 SME Annual Meeting, Cincinnati OH, United States,* (2005).

Brown, K.L. and Bacon, L.G. Manufacture of silica sols from separated geothermal water. In: Proceedings World Geothermal Congress 2000, Kyushu-Tohoku, Japan. (2000).

Brown, K.L. and Bacon, L.G. Pilot plant experiments at Wairakei Power Station. Geothermics, 38, (2009), 64-71.

Chitrakar, R.; Kanoh, H.; Miyai, Y.; Ooi, K.: Synthesis of Spinel-Type Antimony Manganese Oxides and Their Li+ Extraction/ Ion Insertion Reactions. J. Mater. *Chem*, **10**, (2000), 2325.

Chitrakar, R.; Kanoh, H.; Miyai, Y.; Ooi, K.: Recovery of lithium from seawater using manganese oxide adsorbent ($H_{1.6}Mn_{1.6}O_4$) derived from $Li_{1.6}Mn_{1.6}O_4$, Ind. Eng. *Chem*, Res. 40 (2001) 2054–2058.

Clutter, T.; Davis, C.AMining economic benefits from geothermal brine. *Geo-heat Centre Bulletin.* (2000).

Dang, V. D.; Steinberg, M.: Preliminary Design and Analysis of Recovery of Lithium from Brine With The Use of a Selective Extractant. *Energy*, 3, (1978), 325.

Freedonia Group: Specialty Silicas to 2015 - Industry Market Research, Market Share, Market Size, Sales, Demand Forecast, Market Leaders, Company Profiles, Industry Trends. From: http://www.freedoniagroup.com/, (2012).

Gallup, D.: Geochemistry of Geothermal Fluids and Well Scales and potential for Mineral Recovery. *Ore Geology Reviews,* **12,** (2000), 225-236.

Giggenbach, W.F. Variations in the chemical and isotopic composition of fluids discharged from the Taupo Volcanic Zone, New Zealand. *Journal of Volcanology and Geothermal Research,* 68 (1995), 89-116.

Gilau, L.; Stanasel, O.: Experimental Study of Boron Recovery from Geothermal Water on Ion Exchange. *Proceedings World Geothermal Congress* (2010).

GNS Science. 2014. GNS Science Geothermal and Groundwater Database. http://ggw.gns.cri.nz/ggwdata/

Harper, R.T., Thain, I.A. and Johnston, J.H.: Towards the Efficient Utilization of Geothermal Resources. *Geothermics*, **21**, (1992), 641-651.

Harper, R.T., Thain, I.A. and Johnston, J.H.: An Integrated Approach to Realize Greater Value from High Temperature Geothermal Resources: A New Zealand Example. Proceeding World Geothermal Congress, Firenze, Italy. (1995).

Hirowatari, K.; Kusaba, S.; Takeuchi, K.; Fujioka, Y.: Production of Sulfuric Acid Using Thermo-Acidophilic Microorganisms for Use in Scale Prevention. *Geothermal Resources Council Transactions*, (1997).

Iwanaga, T., Watanabe, E., Mroczek, E. and Graham, D.: Lithium extraction from geothermal brines using an adsorption method after removal is silica using electrocoagulation. Abstract , p. 90 in *New Zealand Geothermal Workshop & New Zealand Geothermal Association Seminar : workshop handbook.* Auckland: Geothermal Institute, Auckland University. Proceedings of the New Zealand Geothermal Workshop *29,* (2007).

Kennedy, A.M.: An Assessment of the Economics of Lithium Recovery from Geothermal Fluid. D.L. 118/18-AMK; Dominion Laboratory Report. (1957).

Kennedy, A.M.: The recovery of lithium and other minerals from geothermal water at Wairakei. In: proc. of the UN Conf. on New Sources of Energy, Rome. Paper G/36, (1961), p 502.

Lichti, K.A.: Forgotten phenomenon of materials selection and use in geothermal energy applications. *Materials at High Temperatures*, 24, (2007), 351-36.

Lin Y., Fryxell, G.E., Wu, H. and Engelhard, M.: Selective Sorption of Cesium Using Self-Assembled Monolayers on Mesoporous Supports. *Environ. Sci. Technol*, **35, (**2001), 3962–3966.

Lind, L.; Mroczek, E.; Bromley, C.J.: Production of clean geothermal steam for direct use as process heat. p. 98-103 In: *Proceedings of the 3rd International Conference on Energy Process Engineering : transition to renewable energy systems.* Frankfurt: DECHEMA. (2013)

Monnery, W.: Geothermal Steam Economic H2S Abatement and Sulfur Recovery. *Proceedings World Geothermal Congress.* (2005).

Mroczek E., Graham, D. and Bacon, L.: The Removal of Arsenic and Silica from Geothermal Fluids by Electrocoagulation. *International Mineral Extraction Conference* (2006).

Mroczek, E., Bacon, L., Graham, D., Kotze, K. Pummer, B.: pH Modification Pilot Plant Trials. *Proceedings World Geothermal Congress* (2010).

Mroczek, E., Dedual, G., Graham, D., Bacon, L.: Lithium Extraction from Wairakei Geothermal Fluid using Electrodialysis pH Modification Pilot Plant Trials. *Proceeding World Geothermal Congress* (2015).

Mroczek, E., Graham, D. and Bacon, L. Silica Deposition Experiments: Past Work and Future Research Directions. Western Pacific Regional Branch (2011).

MyDesert.com. http://archive.desertsun.com/article/20140222/BUSINESS0302/302220055/Simbol-Materials-lithium-extraction-Salton-Sea (2014).

Reyes, A., Christenson, B. and Faure, K.: Sources of solutes and heat in low-enthalpy mineral waters and their relation to tectonic setting, *New Zealand. Journal of Volcanology and Geothermal Research,* 192, (2010), 117-141.

Reyes, A., Trompetter, W., Britten, K., and Searle, J.: Mineral deposits in the Rotokawa geothermal pipelines, New Zealand , *Journal of Volcanology and Geothermal Research*, **119,** (2003), 215-239.

Rodríguez E.; Harvey W.S.; Ásbjörnsson E.J.: Review of H_2S Abatement Methods in Geothermal Plants. *Proceedings 38th Workshop on Geothermal Reservoir Engineering*, (2014).

Roskill Information Services Ltd Report: Estimates. Roskill information cited by: http://www.orocobre.com.au/Lithium_ Market.htm (See also http://www.roskill.com/reports/ minor-and-light-metals/lithium (2009).

Rothbaum, H.P. and Middendorf, K.: Lithium extraction from Wairakei geothermal waters. *NZ Journal of Technology*, **2(4)**, (1986), 231-235.

Ryabtsev, A. D., Menzheres, L. T., and Ten, A. V.: Sorption of Lithium from Brine into Granular LiCl·2Al(OH)3·mH2O Sorbent under Dynamic Conditions. *Russian J. Appl. Chem.* **75**, (2002), 1069–1074.

Seastres, J, S.: Ore petrography and mineral chemistry of trace metals extracted from geothermal fluids at Rotokawa, Taupo Volcanic Zone. MSc Geology Thesis (1989) . University of Auckland.

Simmons, S. F., and Brown, K.L.: The flux of gold and related metals through a volcanic arc, Taupo Volcanic Zone, New Zealand. *Geology,* **35**, (2007), 1099-1102.

Simsek, S.: Present status and future development possibilities of Aydin-Denizli Geothermal Province. *Iceland Geothermal Conference.* (2003).

Timperley, M.H. and Mroczek, E.K. Gold in geothermal fluids. Technical note / Chemistry Division 89/18. (1989).

Wang, L.; Meng, C. and Ma W.: Study on Li+ uptake by lithium ion-sieve via the pH technique, Colloids Surfaces A: Physicochem. Eng. Aspects 334 (2009), p34–39.

White, S.P., Lichti, K. and Bacon, L.: Application of Chemical and Wellbore Modelling to the Corrosion and Scaling Properties of Ohaaki Deep Wells. *Proceedings World Geothermal Congress*, (2000).

WRC (Waikato Regional Council). From: http://www.waikatoregion.govt.nz/Environment/Natural-resources/Geothermal-resources/Classifying-geothermal-systems/.

Yanagase, K.; Yoshinage, T.; Kawano, K.; Matsuoka, T.: The Recovery of Lithium from Geothermal Water in the Hatchobaru Area of Kyushu, Japan. Bull. *Chem. Soc*, **56**, (1983), 2490.

Zhu,G.; Wang, P.; Qi, P.; Gao, C.: Adsorption and desorption properties of Li+ on PVC- $H_{1.6}Mn_{1.6}O_4$ lithium ion-sieve membrane. *Chemical Engineering Journal,* **235**, (2014), 340–348.