

TOWARDS THE EFFICIENT UTILIZATION OF GEOTHERMAL RESOURCES

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ABSTRACT - Separated geothermal water from production wells at Wairakei, Ohaaki, Kawerau, Ngawha and other less developed fields in New Zealand, contains potentially valuable chemical constituents. In particular, the extraction of precipitated amorphous silica is discussed in terms of its strategic and beneficial value to expanded energy generation in geothermal development, removal of environmentally sensitive constituents and as a marketable commodity in its own right. The prospect of recovering other minerals thereby realising the full potential of geothermal resources is considered. Expectations regarding high temperature reinjection could be reviewed in consideration of alternative opportunities which have been advanced in recent years.

1.0 INTRODUCTION

The opportunities to better utilize New Zealand's geothermal resources, which contribute significantly to the nation's wealth are addressed in this paper. **The developments discussed here, represent a potential benefit to geothermal resource owners and operators, the community and end users of minerals which are identified as being of commercial value.** To date, chemical processing of geothermal water has not received much attention and engineering solutions have been provided to treat separated water. However, chemical processing would enable a valuable synergy to be obtained between geothermal power operation and protection of some natural waterways from separated geothermal water. **The opportunities are considered to fall into three categories:**

- i) Mineral Recovery.
- ii) Acceptable return of water to the environment.
- iii) Heat Recovery.

Established geothermal developments still involve a thermally inefficient process. Rejection temperatures for separated water at Wairakei, Ohaaki and Kawerau are 135°C, 155°C and 172°C respectively. In exploited water dominated geothermal resources, reject temperatures for separated water remain high to minimize a significant operating constraint with respect to amorphous silica deposition.

Other chemical constituents of geothermal water make treatment of it, a responsible task. For example, arsenic is perceived and by some parties is considered to be an environmentally sensitive constituent of separated geothermal water. With existing technology, responsible management of separated geothermal water usually involves reinjection. For example, Electricorp are

proceeding with high temperature reinjection of part of the total separated water flow from Wairakei in an attempt to reduce the impact of geothermal water flow to the Waikato river. Implementation of a reinjection scheme at Wairakei or elsewhere, pre-empts to a degree, the options of recovering minerals and extracting further energy. Reinjection also involves a considerable capital investment. The technologies believed important to the processing of large water streams have advanced significantly over recent years and have prompted reconsideration of the expectations of reinjection as a development strategy for the future development of geothermal resources.

2.0 MINERAL RECOVERY

2.1 Mineral Content of Geothermal Fluids at Wairakei, Ohaaki, Kawerau and Ngawha.

Table 1 and figure 1 show the principal chemical constituent concentrations contained and minerals and elements recoverable from separated geothermal water for Wairakei, Ohaaki, Kawerau and Ngawha production wells.

The net worth of these minerals is substantially less than that indicated by the gross value. However, the gross revenues roughly indicate the level of capital and operating costs which could be tolerated in each case. Estimates of the recoverable quantities of respective minerals were based on the following water flows from each field:

i) Wairakei	30 million tonnes.
ii) Ohaaki	9 million tonnes.
iii) Kawerau	7 million tonnes.
iv) Ngawha	10 million tonnes

Table 1. Potential Quantity and Value of Minerals from N.Z. Geothermal Water.

RESOURCE MINERAL	CHEMICAL SYMBOL	CONCENTRATION IN WATER mg/kg	QUANTITY tonnes/annum	GROSS VALUE \$NZ PER ANNUM millions
WAIRAKEI				
silica	SiO ₂	550	9000	9
Lithium	Li	10	300	26
Arsenic Trioxide	As ₄ O ₆	6	170	0.2
Boric Acid	H ₃ BO ₃	145	4200	4
OHAAKI				
silica	SiO ₂	700	4500	4.5
Lithium	Li	11.5	100	8.5
Arsenic Trioxide	As ₄ O ₆	6	50	0.1
Boric Acid	H ₃ BO ₃	225	2200	2
KAWERAU				
silica	SiO ₂	750	4500	4.5
Lithium	Li	7	45	4
Arsenic Trioxide	As ₄ O ₆	2.8	20	0.03
Boric Acid	H ₃ BO ₃	285	2000	2
NGAWHA				
Silica	SiO ₂	470	2700	2.7
Lithium	Li	10	100	8
Arsenic Trioxide	As ₄ O ₆	0.6	6	0.01
Boric Acid	H ₃ BO ₃	5700	57000	60

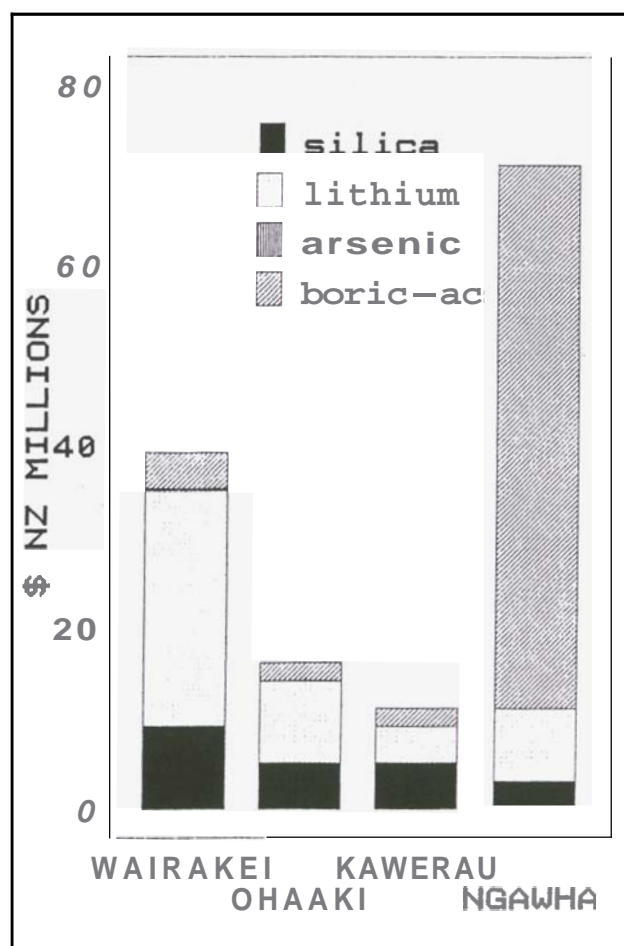


Figure 1. Estimated Gross Value per annum of Minerals from N.Z. Geothermal Fields - dependent on the removal of silica.

The potential commercial value of these minerals was based on quoted prices in the Chemical Marketing Reporter (1991) and market research conducted separately by Electricorp and Victoria University.

2.2 Recoverable Products.

A considerable amount of work has been carried out on the treatment of geothermal brines for the recovery of certain minerals, both in New Zealand and overseas (Buisson et. al., 1979; Crane, 1982; Mercado et. al., 1979; Recepoglu & Beker, 1991; Rothbaum & Anderton, 1975; Rothbaum & Buisson, 1977; Rothbaum & Middendorf, 1986; Thordarson et. al., 1987.). However, much of this' research and development focused on the removal of environmentally sensitive constituents with little effort being directed towards marketable products. The following discussion identifies some of the recoverable products and their market potential.

Amorphous Precipitated Silica

Nearly all energy extraction processes result in geothermal water becoming supersaturated with and depositing amorphous silica. The amorphous silica deposits in pipework, channels, pumps (where these are used), reinjection well casings and reservoir formation. It may take the form of a dense, vitreous deposit or have a lower bulk density, friable character. Whatever form these natural deposits take, investigations have shown that the silica **does** not have suitable physical and chemical characteristics to be of significant commercial value. When a newly formed supersaturated silica solution is allowed to stand the dissolved monomeric

silica polymerizes to form colloidal silica particles which can be further aggregated to form a precipitate. The precipitation process can be controlled to produce silicas with varying physical and chemical qualities which do have commercial significance. Precipitated silicas are an internationally traded commodity and industries which consume these products include; rubber, plastics, paper, paint, cement, ceramics, pharmaceuticals, pesticides and adhesives. A vast array of precipitated and other silicas are commercially manufactured from synthetic sources to suit these applications. The New Zealand situation demands that a concerted effort be made towards research with a specific end use in mind. It is considered that commercialization of the silica extraction process will require manufacture of a moderately valued precipitated silica which satisfies an application having a reasonably high demand. On this basis, a long term supply contract can be established with the end user, from which revenue can support the development of alternative forms of silica, if the need arises.

Research into amorphous silica extraction from geothermal water in New Zealand has been conducted over several years. DSIR (Rothbaum & Anderton, 1975; Shannon et. al., 1982) have developed laboratory and small field test rigs to extract arsenic and calcium rich precipitated silica with the objective of rendering water benign for environmental disposal. For a variety of reasons none of these developments were accepted as having commercial significance. It is understood that DSIR have conducted work on a potentially commercial type of silica which has low concentrations of adsorbed arsenic; an attractive characteristic in some applications.

A significant, coordinated research effort by Tasman Pulp & Paper Co. Ltd., and Victoria University has resulted in a commercial prototype pilot plant being built to extract several grades of silica which have performed well relative to commercial newsprint additives (Harper and Keyte, 1990). In particular, the process provides for control of arsenic adsorption, surface area, pore volume and structural morphology of the precipitated silica. The pilot plant is currently operating and has a proven production output of 500 kg/day of precipitated silica which when accumulated, is sufficient for full scale paper machine trials. The process is continuous and the plant has achieved a commercial number of hours. Important information regarding the reticulation of atmospherically separated water and precipitated silica slurry has been obtained. The benefits of combining this kind of research with a potential end user such as the paper industry have been considerable. It is understood that commercial decisions regarding the use of geothermal precipitated silica will be favourable if paper machine trials prove various silica products to be cost effective as additives to improve newsprint quality.

Precipitated silica of this type competes with other commercial additives at about NZ \$1000/tonne. It is

anticipated that the newsprint and filled grade paper industries could consume the total output of precipitated silica from the Wairakei and Kawerau geothermal fields.

The extraction of amorphous silica is strategic to the full utilization of geothermal resources. Silica removal is considered a necessary process prior to downstream chemical processing and reinjection of lower temperature geothermal water. It therefore paves the way for expanded energy extraction, reliable long term, low temperature reinjection and possibly safe environmental disposal to natural waterways. In some cases the treated geothermal water may become a useful industrial water source, thereby reducing the demand on surface water. The scale of the silica pilot plant built by Tasman Pulp & Paper Co. Ltd. brings the commercialization of silica extraction a step closer and the beneficial implications such an endeavour has for geothermal development can not be overemphasized. A commercial precipitated silica process must take into consideration the needs of an integrated geothermal development. It should therefore be able to receive water from conventional separator or binary cycle installations. Further, geothermal water which has been processed by a silica extraction plant should be of acceptable quality for low temperature reinjection, or surface disposal.

Lithium

The technology to extract lithium from various water sources exists and in situations where brine lithium concentrations are sufficiently concentrated, is considered economic, (Crozier, 1986). Lithium extraction has been attempted (Yanagase et. al., 1983) from geothermal water and various methods were reviewed by Rothbaum and Middendorf (1986). The latter review mentioned the use of membrane impregnated crown ethers, which were shown to be lithium selective, (Kimura et. al., 1985). Use of these immobilized materials has not yet been attempted on geothermal water. Pilot plant scale tests have been successfully conducted on other reject water streams of significant volume, (American Chemical Society, 1991). The potential production rate from both Wairakei and Ohaaki is over 300 tonnes per annum (lithium metal) which is estimated to have a value in excess of NZ \$30 million per annum. Production costs are sensitive to recovery techniques used and research supported by Electricorp is being conducted by DSIR and Victoria University to determine if alternative active substrates and or solvents can be used to enrich extractive media with lithium. These studies are also attending to the site specific characteristics of geothermal water which differ from commonly exploited brine sources rich in lithium. Investment in a more commercial approach to lithium recovery may be warranted in view of the knowledge which already exists with respect to selective lithium extractive chemicals and the fact that lithium has the highest potential value. Lithium is considered to be a

strategic metal for the future energy and materials industries. It finds application in refining of aluminium and is used in the manufacture of batteries. New Zealand has only a small demand for lithium and production from a commercial plant at Wairakei for example would represent a significant export industry.

Arsenic

Arsenic is the constituent of most environmental concern in the separated geothermal water from Wairakei, which flows to the Waikato river. Under average river flows the concentration of arsenic in the Waikato river after mixing is below the W.H.O. specification for potable water of 0.05 ppm (Aggett and Aspell, 1980). Nevertheless, in 1979 Electricorp (then, NZED) commissioned DSIR to develop a process to remove arsenic from geothermal water to obtain low concentrations. Research (Rothbaum and Anderton, 1975; Buisson et al., 1979.) culminated in the construction of a pilot plant which extracted 95 - 98% of the arsenic; however both the capital and operating costs were excessive, (Mills, 1984). This process produced a useful end product chemical. A process which removes arsenic but does not involve conversion to a useful chemical is considered feasible and may prove more economic within an integrated geothermal development. Such a process would require the ongoing controlled disposal of the resultant waste product.

Boron

Boron in geothermal water is present as boric acid and its dissociated anion, borate. At Wairakei, Ohaaki and Kawerau, the boron concentrations are low compared with that at Ngawha. For example, the boron concentration of the average Waikato river flow after mixing with the separated water from Wairakei is approximately 0.3ppm; a concentration considered acceptable for irrigation of boron sensitive plants such as citrus and possibly kiwifruit (Fellows, 1990). Development of Philippine geothermal resources has proceeded without significant environmental impact, upstream of major rice farming areas, despite boron concentrations of separated water being higher than those reported here for N.Z. waters; apart from Ngawha. Development at the Kizildere geothermal resource, in Turkey is constrained by boron concentrations of the separated water and complications with respect to reinjection, attributed to moderate silica concentrations, (Recepoglu & Beker, 1986.). Boron is not considered an environmentally sensitive constituent in the context of geothermal operations in New Zealand, outside Ngawha although the significance of quality irrigation water for the kiwifruit and other agricultural and horticultural industries is recognized.

Extraction of boron as boric acid or borax has been accomplished from brine sources (Kirk-Othmer, 1978.), but only at much higher concentrations than that contained in waters of geothermal resources in the Taupo Volcanic Zone. Methods to extract boron from

geothermal water have recently been reported for the Kizildere resource, in Turkey (Recepoglu & Beker, 1986.). The water at Ngawha is exceptional and development at this field could include a boric acid, borax process. It is unlikely that economic recovery of boric acid or borax could occur at Wairakei, Ohaaki or Kawerau with existing technology. However, processes which employ borate selective media, similar to the crown ethers previously discussed, could be used to reduce the concentration of boron in the more dilute separated water. Such processes represent a cost to overall energy and mineral extractive activities and would need to be compared with the capital and operating costs of a high temperature reinjection scheme. This cost could be acceptable to an integrated geothermal development which maintains surface disposal of separated water.

Precipitated Calcium Carbonate.

In its most abundant natural form limestone (calcium carbonate) finds application in many materials and industrial processes. Its abundance also means that it is available at a relatively low cost. However, precipitated calcium carbonate has special chemical and physical properties and has a greater value than limestone or finely ground calcium carbonate, although a narrower field of application. Specialist grades of paper can have several percent by weight of precipitated calcium carbonate. Precipitated calcium carbonate (PCC) has been shown to impart superior unprinted and printed optical properties to paper compared with even the finest ground calcium carbonates. PCC's have found increasing use as fillers for uncoated groundwood paper, (Bown, 1985).

Much experience has been gained over the years with calcite deposition in well casings after periods of production. Experimental work and field studies have established a good understanding of the conditions which give rise to supersaturated geothermal water with respect to calcium carbonate. This knowledge can also be used to promote precipitation of useful calcium carbonate downstream of silica precipitation.

Precious Metals.

Studies by DSIR have investigated the enrichment of scale deposits with gold and silver which are initially present in water at concentrations about 05 ppb. Enrichment was possible to ore grade concentrations but the annual recovery was low, (Electricorp, 1989). Efforts to recover these minerals are not considered as important at this stage relative to the minerals discussed above.

3.0 THE RETURN OF WATER TO THE ENVIRONMENT

The management of separated water from geothermal developments varies on a global basis. Factors which are considered to affect methods of handling separated water arise from geographical, environmental, scientific,

engineering and political considerations. Historically, the treatment of separated geothermal water has involved:

- i) Flow to holding ponds utilizing subsurface drainage and evaporation.
- ii) Flow to natural waterways.
- iii) ReInjection at depth, into and or on the boundaries of a geothermal reservoir.

High temperature reinjection of the separated water represents a relatively "dead investment" in terms of geothermal resource utilization. The best that can be expected from a reinjection system is that no impact on the productivity of the reservoir will occur. The worst case indicates that rapid thermal damage from the return of reinjection fluid to the production sector reduces reservoir productivity. Usually a middle ground is reached for which an optimum production and reinjection well configuration is established. This operational strategy requires a significant ongoing commitment to reinjection and production well drilling. Several geothermal power schemes have had to implement remedial measures after reinjection; e.g. Hatchobaru & Otake (Japan), Tiwi & Palinpinon (Philippines). Such an ongoing investment can have a significant impact on the economics of geothermal development.

Separated geothermal water is considered benign relative to most other chemical process streams and a significant volume has been discharged to the Waikato and other rivers from natural, surface thermal manifestations over many years. However, it has been recognized that additional separated water from geothermal power stations places a load on these rivers. Much of this concern has centred on arsenic which can accumulate in river sediments. A clear distinction between a perceived and real environmental problem with respect to other constituents of geothermal water is not apparent.

As part of a greater mineral and energy recovery scheme, the cost of processes which result in reduced concentrations or recovery of potentially sensitive environmental constituents is likely to be acceptable. If equivalent attention and investment are given to chemical processing of geothermal water as have been given to reinjection, a viable alternative to treatment of geothermal water may well result.

The capital cost of a reinjection system for a moderately sized geothermal development, say 100MWe, amounts to 30 - 35% of the total capital cost of the steam-water gathering system which represents tens of millions of dollars invested. Experience with reinjection has given emphasis to the need for "off-field" injection wherever possible, to minimize the return of separated water to the production sector. This development philosophy departs from the view that mass replacement via reinjection is necessary to provide a sustainable, exploitable resource. Rather, reinjection provides an environmentally acceptable solution to the treatment of separated water. It need not be considered a permanent

solution to the treatment of separated water, in view of the chemical process technologies discussed above.

4.0 HEAT RECOVERY.

Heat recovery opportunities are considered to be:

- i) Binary cycle electricity generation.
- ii) Direct Heat Utilization.

A small binary cycle plant (Ormat Turbines Ltd.) owned and operated by Bay of Plenty Electricity has generated approximately 2.4MWe on a continuous basis for a little over two years at the Kawerau geothermal field. The separated geothermal water can be conductively cooled to approximately 80°C which is of assistance to most mineral recovery processes. The importance of this technology is well illustrated by consideration of the extra power which becomes available from the various geothermal fields. It is estimated that at Wairakei and Kawerau the extra power amounts to 20 - 30 MW and 10 - 15 MWe respectively. The application of binary cycle power generation in conjunction with reinjection requires the removal of silica.

Direct heat applications at Wairakei, Ohaaki and Kawerau include:

- i) Lucerne drying; Ohaaki.
- ii) Timber drying; Ohaaki.
- iii) Prawn farming; Wairakei.
- iv) Horticulture - glasshouses; Kawerau.

Large scale use of separated water for direct heat applications would be assisted by the removal of silica.

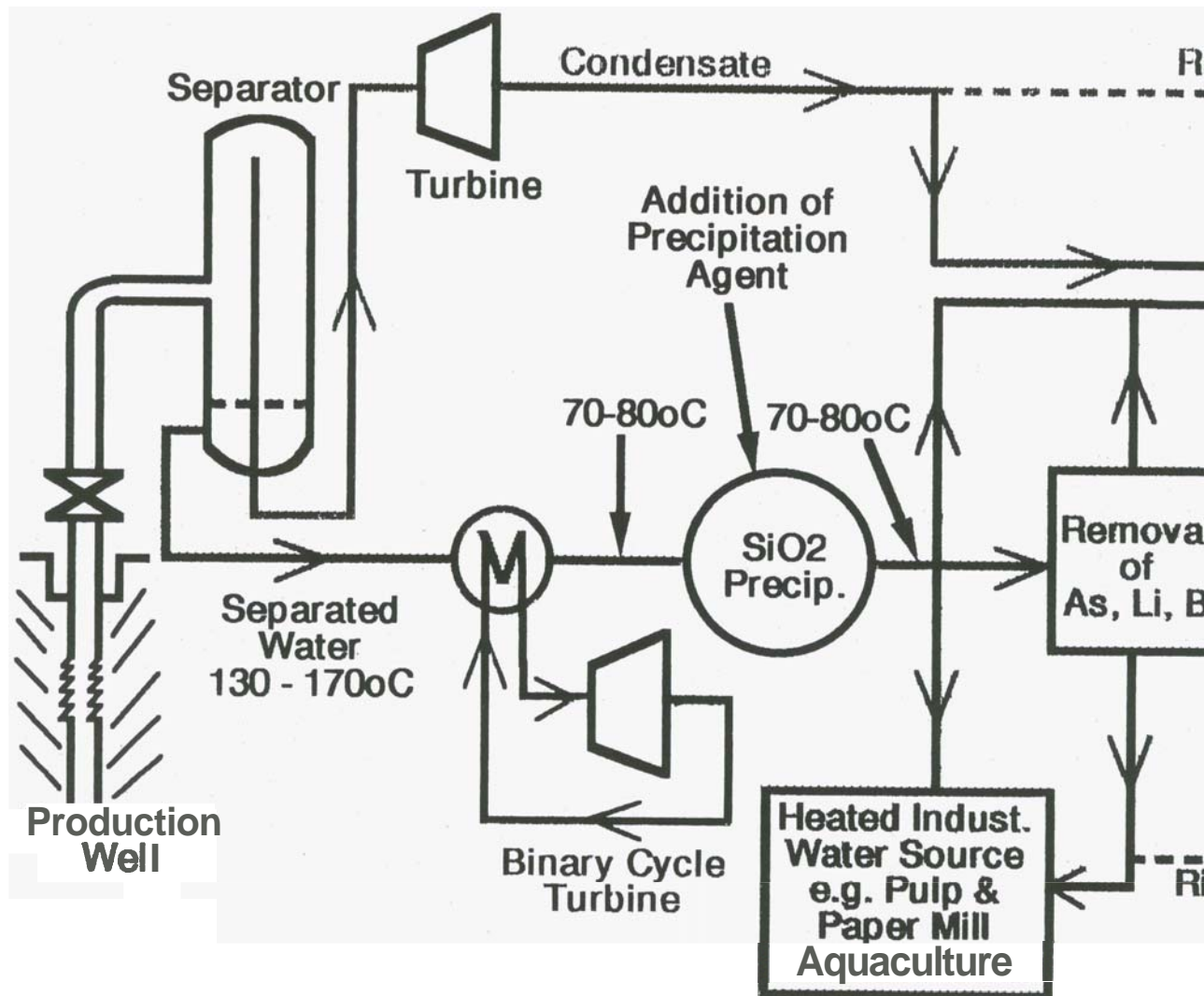
The implications of a reliable process to precipitate a commercially acceptable silica, or in some cases to simply remove silica are remarkable when put in the context of the wider development of water dominated geothermal resources. It is estimated that successful commercialization of the "precipitated silica process" will provide for the generation of 25% more power from any exploitable water dominated geothermal resource. This is equivalent to several hundred megawatts of additional generation, in terms of the current installed capacity worldwide.

5.0 CONCLUSIONS

The full potential of geothermal resources in New Zealand has not been realized. High temperature reinjection at Ohaaki and the scheme proposed for Wairakei have been introduced in recognition that this method of handling separated water reduces environmental impact. However the advances which have been made, both in New Zealand and overseas with respect to mineral recovery and removal of environmentally sensitive constituents indicates that treatment of separated water to facilitate low temperature reinjection and or replacement of water to the environment may be in the better interests of all concerned.

Schematic Diagram of an Integrated Geothermal Development

Figure 2



High temperature reinjection of separated water to avoid amorphous silica deposition significantly undervalues the potential benefit to be gained from geothermal resources. The technology to remove silica from lower temperature separated waters exists and should be advanced to a commercial scale to enable further electricity generation and mineral recovery.

The chemical processing of separated geothermal water to reduce the concentrations of arsenic and perhaps boron should be reconsidered in view of technological advances in the treatment of chemical process streams over recent years. A schematic diagram which illustrates the way in which the processes discussed above could be integrated, is shown in figure 2.

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