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MANUFACTURE OF SILICA SOLS FROM SEPARATED GEOTHERMAL WATER

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ABSTRACT

A purpose built pilot plant was constructed at the Wairakei Power Station to investigate the possibility of producing silica sols from geothermal water. The plant constructed was designed to process approximately 5000 litres per hour of geothermal water and consisted essentially of a heat exchanger, several aging tanks in series and a three stage ultrafiltration module. Provision was also made for chemical injection, for washing geothermal contaminants (diafiltration) from the concentrated sol and for independent control over the variables which determined not only the silica colloid particle size, but also the concentrated silica sol stability and final concentration.

Trials carried out during 1996 demonstrated that:

- Silica sols could be produced with predetermined particle sizes between approximately 10 and 70 nm and at concentrations up to 50% depending upon particle size
- Organic stabilising agents were essential to avoid gel formation
- Ultrafiltration provided a simple and efficient means of concentrating silica sols with reasonable down time for cleaning.
- Silica sols equivalent in particle size and quality to commercial silica sols can be produced successfully from Wairakei's separated geothermal water.

1. INTRODUCTION

The deposition of silica in geothermal power devlopments has traditionally limited the efficient use of geothermal energy. One possible solution to this problem is to remove the silica from the geothermal brine, which would then allow further utilisation of heat not normally available. In the past, the extraction of geothermal silica by different techniques (eg Rothbaum and Anderton 1975, Weres and Tsao 1981, Kindle et al, 1984, Axtmann and Grant Taylor 1986, Harper et al 1993) have not resulted in a commercial process Our aim was to produce a high value commercially acceptable silica product which would not only offset the cost of extraction, but also provide a commercial return. A further requirement was that any process did not constrain normal power station operations.

A very rudimentary market analysis suggested that silica sols would provide higher returns than other silica commodities. Such silica sols are concentrated solutions of colloidal silica where the colloid particles are constrained within narrow size limits (ie monodisperse), and where impurity levels are appropriate for the final application. A further requirement is the necessity to produce monodisperse sols with different average particle diameters. Typical uses of such sols are in refractory cements, polishes for silicon wafers, photographic coatings and as binders for catalytic materials.

Initial bench top experiments were conducted to determine:

- how to measure particle size
- how to control particle size distribution
- how to stabilise the particles to halt agglommeration
- how to concentrate the colloidal solution
- how to remove contaminants
- typical scale-up parameters for a larger pilot plant

These parameters were then used to design a small pilot plant that would provide sufficient sample for commercial evaluation and provide sufficient operational data.

2. METHODS

The conceptual design of this pilot plant was based on initial temperature control to regulate the particle size followed by ultra-filtration to concentrate the sol, incorporating diafiltration to remove contaminants. Initial field experiments at Wairakei had elucidated the silica polymerisation kinetics which allowed the design of the colloid growth section of the plant. The use of ultrafiltration is commonplace in New Zealand in dairy milk processing and this experience facilitated the selection of UF membranes.

2.1 Equipment

The essential elements of the pilot plant consisted of:

- a supply of separated geothermal water which was under-saturated with respect to amorphous silica
- a heat exchanger to reduce the temperature of the separated geothermal water from approximately 125°C to the selected silica sol "nucleation temperature"
- a series of temperature controlled ageing tanks to enable control of temperatures during colloid growth
- a 100 micron filter to remove suspended solids
- a three stage continuous ultrafiltration system to concentrate the pre-formed colloidal silica to a concentration of >30% silica by weight
- dosing pumps to enable pH adjustment and the addition of stabilising agents
- fresh water supply to enable the removal of geothermal salts
- ancillary equipment to enable mixing and circulation of chemicals for sterilising and cleaning the UF filters and pipe-work

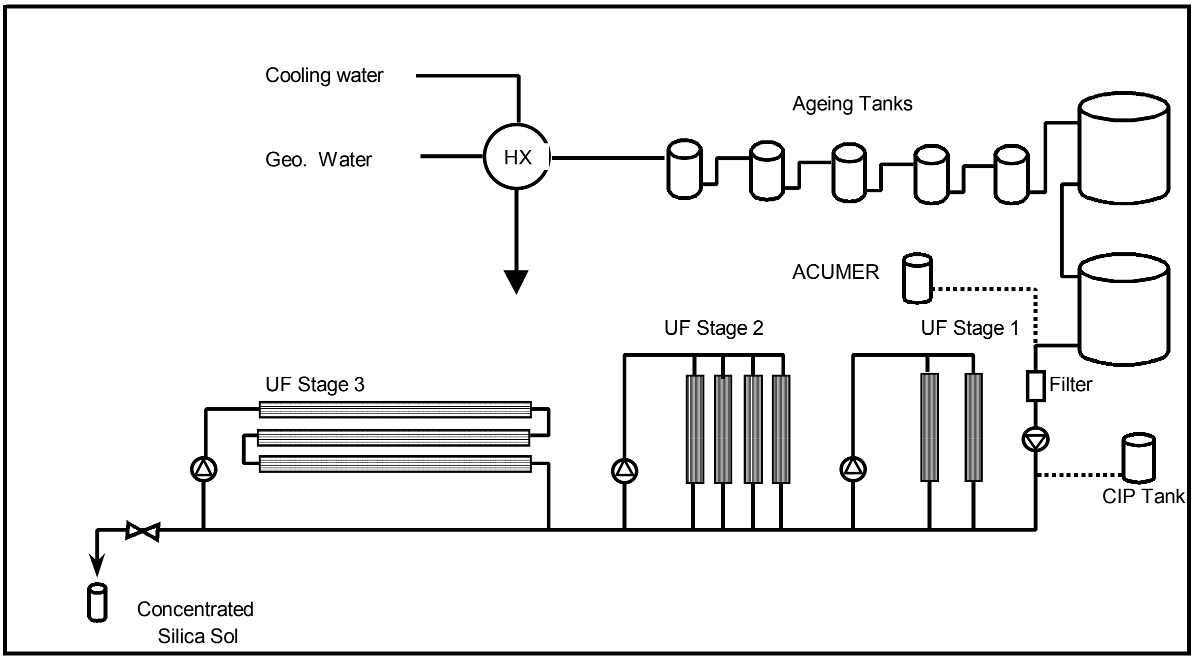

Figure 1. A schematic of the silica extraction pilot plant

2.2 Process Instrumentation and Control
A comprehensive computer based process control system enabled all process variables to be selected, measured and recorded.

2.3 Particle Size Control
The colloid particle size was determined by the "nucleation temperature". This is defined as the temperature to which geothermal water is reduced in the primary heat exchanger and the temperature at which initial ageing and hence particle growth commences. This process works in the following manner. The initial temperature drop provides a certain degree of oversaturation of the silica. This causes nucleation of individual silicic acid molecules to eventually form polymerised colloids. The chemical driving force for nucleation is the degree of supersaturation, and therefore the larger the degree of oversaturation, the greater the number of nuclei formed. Ageing and further *gradual* cooling by careful temperature control allows growth of the colloids already formed, rather than the formation of new nuclei. Cooling at higher rates runs the risk of further nucleation and a bimodal silica sol. Therefore, the nucleation temperature controls the **number** of particles that are formed, and the cooling regime which follows determines the final particle size. Thus a low nucleation temperature (20°C) produces a colloid size of approximately 10nm while a higher nucleation temperature of 70 °C produces a final particle size of about 60nm. The use of a stabiliser was considered essential to avoid potential particle agglomeration. For this purpose, we used ACUMER© 5000 produced by Rohm and Haas Ltd. This was dosed at a rate of less than 5 ppm.

2.4 Concentration of the colloid

Commercial silica sols are normally produced at concentrations ranging from 30 to 50% silica by weight. The challenge for producing similar products from geothermal water, involves not only the ability to control particle size but also to be able to concentrate sols from a very dilute 300 mg/l to more than 30%, equivalent to a concentration factor of >1000 times. Ultrafiltration (UF) has been used previously for the production of commercial silica sols, normally as a means of washing unwanted salts from concentrated sols. This is the first time, to the authors knowledge, that UF has been used for concentrating silica sols through such a high concentration factor for the purpose of producing a commercial product. Since an operational requirement was a continuous flow plant, as opposed to a batch process, a continuous flow ultrafiltration system was designed (Figure 1). This had three stages. The first two stages were designed to concentrate the silica colloid to a few percent. The final stage concentrated the solution to >30%. The actual final concentration of silica sol was controlled by a flow rated discharge valve. We decided on the use of hollow fibre cartridge membrane modules for stages 1 and 2 and tubular membranes for stage 3. The use of the more rugged tubular membranes for the higher silica concentrations in stage 3 provided for less fouling and easier cleaning of the membranes.

The primary problem with ultrafiltration techniques is membrane fouling. This results in declining membrane fluxes together with increasing membrane pressures. Membrane cleaning frequency is therefore a major economic consideration and the membrane pressure was continuously monitored to enable membrane performance to be measured and cleaning intervals to be optimised.

2.5 Stabilisation
Stabilisation of commercial silica sols is normally achieved through the use of stabilising cations such as ammonia or sodium in conjunction with a pH adjustment to about 8 to 10. This high pH maintains the high negative surface charge

needed to inhibit agglomeration. At Wairakei the initial separated geothermal water pH is approximately 8.5 and hence sufficiently alkaline to achieve stability of low concentration colloids during the ageing process. The organic stabiliser used was injected into the flow after ageing and prior to ultrafiltration. This was found to be sufficient to inhibit agglomeration during the process and provide ongoing stability over several years.

2.6 Diafiltration

The diafiltration or washing of unwanted salts from the concentrated geothermal silica sols was carried out using local potable water. The process could be used at any stage during the ultra-filtration process though clearly less fresh water and hence less time is required at higher sol concentrations. The inclusion of salts in the colloid matrix during particle growth was an inevitable consequence of using geothermal brine. This was ameliorated to some extent at Wairakei where low dissolved solids concentrations exist.

3. RESULTS

3.1 Particle Size

Particle size was measured by dynamic light scattering on a Leeds Northrup Microtrac UPA instrument. The results from the instrument compared favourably with known particle sizes of Du Pont standard sols.

Average particle sizes from about 10nm to about 70nm could be reproducibly manufactured. The size distribution was acceptably monodisperse and a typical example is shown in Figure 2. This can be contrasted with figures 3 and 4 and 5 which show unacceptable particle size distributions. The effect shown in figure 3 normally resulted from incomplete mixing of the flow, so that some particles grew faster than others, an effect due to non-plug flow. The bimodal distribution shown in Figure 4 probably resulted from a secondary nucleation where temperatures were decreased too rapidly during the ageing process. The effect shown in Figure 5 is probably due to agglommeration of the ~ 80nm primary particles to form agglomerates of ~ 2 µm.

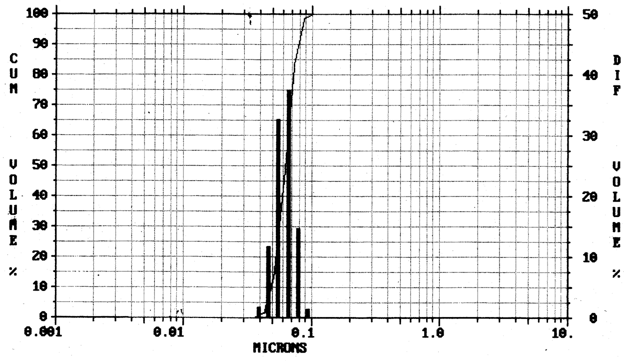

Figure 2 A normal monodisperse particle size distribution with average particle size ~ 62nm. The size scale is in µm.

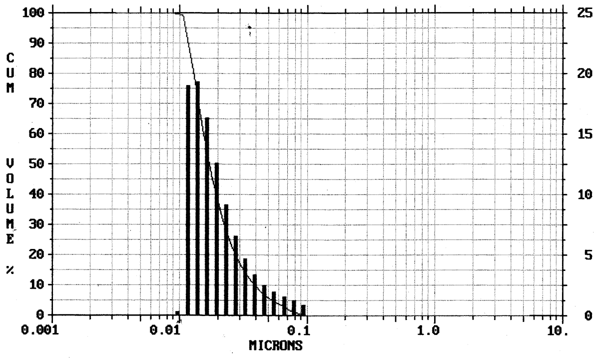

Figure 3. A skewed particle size distribution

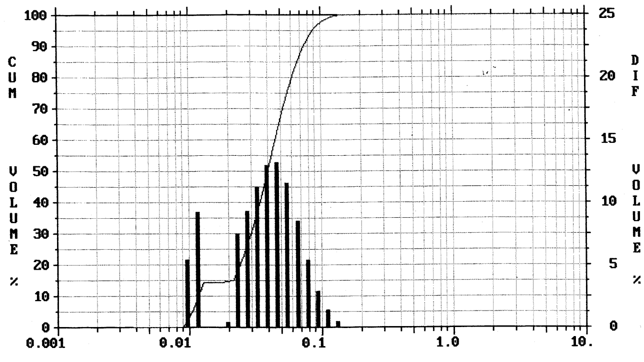

Figure 4 A bimodal distribution illustrating secondary nucleation

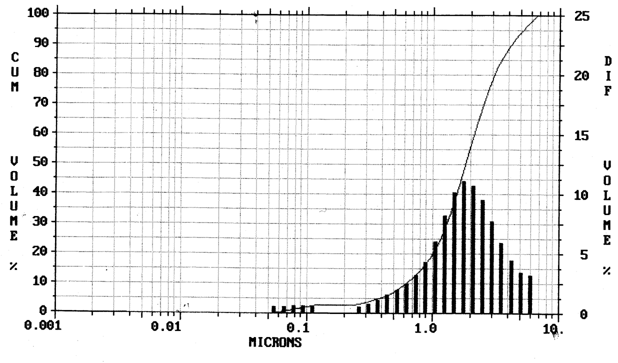

Figure 5. Agglomeration into larger particles

3.2 Silica sol analysis

A typical analysis measured by ICP-MS, and ICP-AES is shown in Table 1. For comparison, the original geothermal brine concentration is also given. Many of these constituents have little effect on the final use of the product. As can be seen from the table, the sol concentrates most of the ions in solution. This is due to the surface charge on the colloid. Some ions are preferentially adsorbed, such as Ca, Sb, Mg. Future work could consider the use of chelating agents, for instance, to reduce the adsorption of multivalent ions onto the colloid.

3.3 Pilot plant operation.

In general the designed pilot plant performed as anticipated. The plant operated successfully on an intermittent basis for 11 months.

It was found necessary to add two large ageing tanks to ensure complete polymerisation prior to ultrafiltration. In common with observations at Wairakei and other NZ geothermal fields, the silica scaling rate is maximised when both polymeric silica and available monomeric silica is present similtaneously at elevated temperatures.

Initial cleaning frequency was typically ~ 6 hours. This was deemed unsatisfactory. Installation of the extra ageing tanks decreased this to frequency to ~ 5 - 7 days. The main fouling occurred in the hollow fibre membranes in stages 1 and 2. A cleaning cycle utilised hot hydrofluoric acid at pH ~ 3 over a period of 1-2 hours.

At the larger particle sizes, the ACUMER stabiliser was not required. However, at the small particle sizes, gel formation is maximised, and on occasions when dosing inadvertantly ceased, the stage 3 ultrafiltration tubes became completely blocked with gel. Fortunately, the design which included the tubular membranes in stage 3 averted a costly replacement. During the entire operation of the pilot plant, there was very little silica scaling observed in any of the ageing tanks or on the permeate side of the ultrafilters. This is consistent with field observations in the general power plant which indicate that scaling rates are low at low temperatures when the silica is fully polymerised.

4.0 Discussion

The experiments proved that it is possible to produce silica sols that compare favourably with commercial products. One of the prime requirements of a commercial process is the ability to produce sols of predetermined particle size, which we were able to accomplish. The purity of the sols is satisfactory, but probably better results could be achieved with greater time for the diafiltration. Of particular concern is the amount of aluminium and calcium in our final product. The sols seemed to be stable once ACUMER was added, and this stability seems to have lasted – even for some of the smaller particle size sols. One problem noticed was the possibility of algae forming in the tanks and in the finished product. This problem was easily overcome by the addition of a small amount of biocide.

The economics of a full scale process were not easy to ascertain. However, the principal factors were recognised. Probably the largest operational cost is the replacement of the ultrafilters. These need replacing when they become blocked and cannot be satisfactorily cleaned. This is a gradual process, and we never reached this stage in our experiments. Consequently, we can only estimate the likely lifetime of the filters. We achieved a reasonable cleaning frequency in our apparatus, and so operational downtime is not a significant problem. Added chemicals are not expensive. The ultrafiltration units are expensive, and a plant for any reasonable throughput would require large areas of land for the ageing tanks. The rest of the equipment is not excessively expensive.

Table 1. Analyses (ppm) of feed geothermal water and concentrated silica sol

	Raw Geothermal Fluid	Produced silica sol (JSR/03)
SiO2	490	250,000
Cl	1688	NA
Na	960	1960
K	144	900
Li	9	10
Ca	15	1050
SO4	34	NA
B	22	100
F	12	NA
Br	4.7	NA
Rb	1.8	20
Cs	2	40
As	4.5	3
Sb	0.1	80
Al	0.3	550
Mg	0.005	10
Fe	< 0.1	3
PH	8.7	8.4
Density (g/ml)	NA	1.32
particle size	NA	48nm

The advantage of a geothermal source, is that the colloidal silica is very cheap. In the normal commercial process, silica from quartz sands is dissolved in alkali and then acidified to produce saturated conditions. This produces a very concentrated product, but chemical costs are greater. The geothermal process produces a very dilute solution, and ultrafiltration is then required to concentrate the product.

The removal of silica from the brine allows a large range of downstream processes. Other mineral extraction processes become much easier when the silica is removed and heat exchangers can also be much more easily utilised without the threat of silica deposition.

5. REFERENCES

Axtmann, R.C. and Grant Taylor, D. (1986). Desilication of Geothermal Waste Waters in Fluidized Beds. *Geothermics*, Vol 15, 185-191Harper, R., Johnston, J. and Wiseman, N. (1993). The controlled precipitation and use of amorphous silica from geothermal fluid or aqueous media having a silicic acid concentration. *NZ Patent* 232170/228472

Kindle C.H., Mercer, B.W., Elmore, R.P., Blair, S.C., and Meyers D.A. (1984). Geothermal injection treatment. *Pacific Northwest Laboratory Report* No PNL - 4767

Rothbaum H.P. and Anderton B.H. (1976). Removal of silica and arsenic from geothermal discharge waters by precipitation of useful calcium silicatres. *Proceedings of the Second United Nations Symposium on the Development and Use of Geothermal Resources.* San Fransisco, 1417 - 1425

Weres, O. and Tsao, L. (1981). Chemistry of silica in Cerro Prieto Brines. *Geothermics*, Vol 10, 255 - 276