2020 ICI Virtual Technical Conference & 3D Expo

New Generation Colloidal Silica Binders

How They are Made

John Lea – Sales and Marketing Director, Geo40 Limited

Ken White – Business Development Manager – USA, Geo40

Introduction

Geo40 was established in 2010 as a progressive New Zealand technology company that brings together a stable of experts across a wide range of disciplines to make harvesting of minerals from hot geothermal water a reality. Geo40 has been able to achieve what nature has been doing all along, by emulating nature's own processes in harnessing valuable minerals from the earth through benign methods. In doing this they have created the next generation of sustainable, high quality mineral products. One of these products is colloidal silica.

Geothermal Energy Background

New Zealand is considered a world leader in renewable power generation with 95% of the power generated in New Zealand coming from renewable sources. Geothermal power generation makes up around 40% of the renewable power generation in New Zealand.

New Zealand sits on the “Ring of Fire” which is a large geothermally active 40,000 km (25,000 mi) horseshoe shape in the basin of the Pacific Ocean.

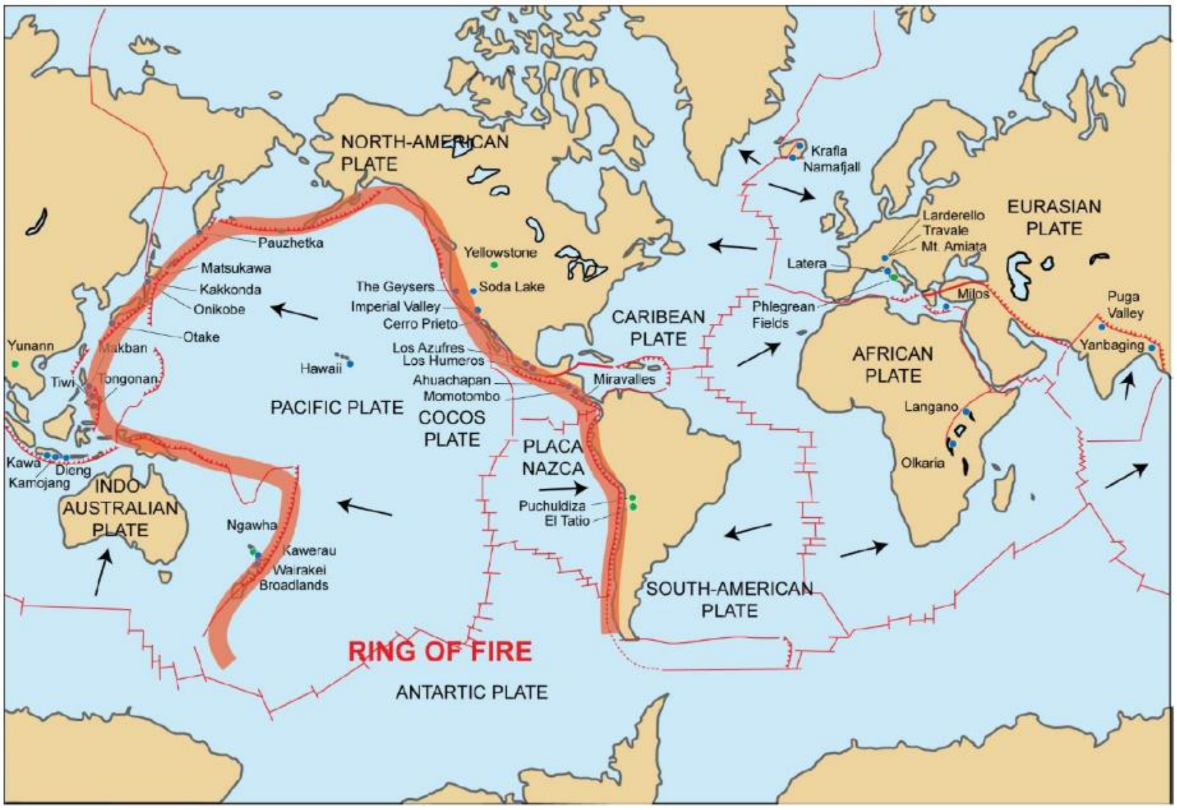


Figure 1: Map of the “Ring of Fire” and global tectonic plates

This geothermally active area stretches from New Zealand up through Papua New Guinea, Indonesia, Philippines, Japan and across to Alaska and down the west coast of USA and South America.

In this “Ring of Fire” the earth’s crust is thin and molten centre of the earth comes closer to the surface, often displaying itself in the form of volcanoes and bubbling hot pools and geysers.

Figure 2: A geyser bubbling with hot geothermal water in Yellowstone National Park, USA

Figure 3: Traditional Japanese Onsen heated by geothermal activity, Japan

In the 1950's, engineers became interested in harnessing the "free energy" created by this natural phenomenon and focussed on the steam created in geothermally active areas. In the 1960's the world's first renewable geothermal power station, utilising hot geothermal water brought up to the surface, was built at Wairakei in New Zealand. Since then, New Zealand has been at the forefront of geothermal power generation technology and its application as baseload renewable power generation source.

Around 80% of geothermal power generated globally utilises the New Zealand developed technology of drilling wells deep into the geothermal reservoir where hot geothermal water is then brought, under pressure, to the surface. Typically, this water, which has been heated by the earth's energy, is at 200°C - 350°C (392°F - 662°F). On the surface the power generator releases the pressure to create medium and low-pressure steam. This steam is piped from the geothermal field to the power station where it is used to generate electricity in steam turbines.

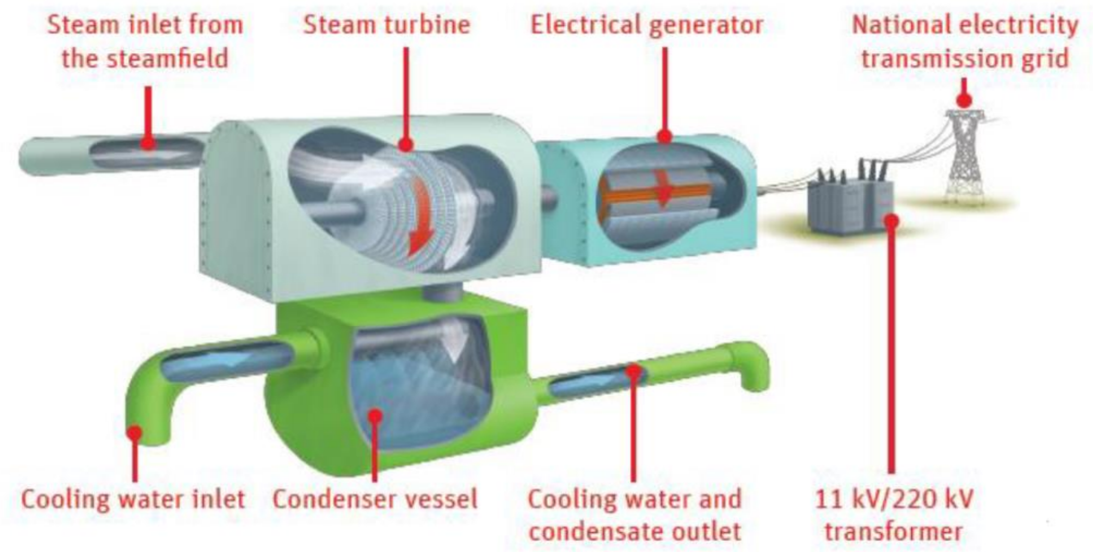


Figure 3: Geothermal steam used for power generation

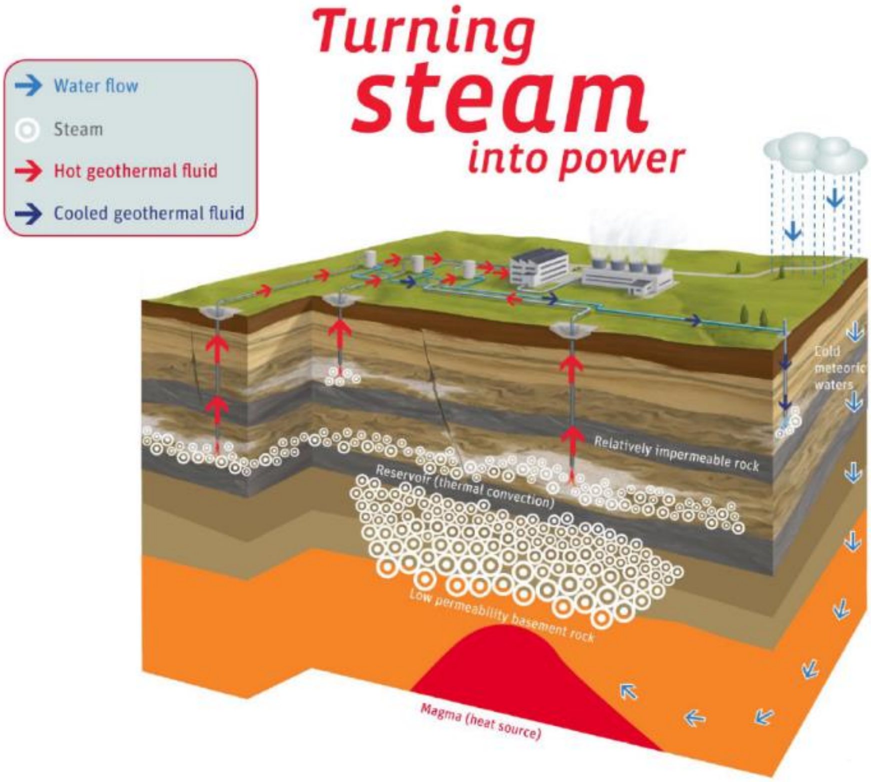


Figure 4: How geothermal energy is harnessed for geothermal power production

The naturally heated hot geothermal water, that is brought up to the surface, contains minerals that have been naturally dissolved deep under the ground. When the generator releases the pressure on the geothermal water it boils and creates steam energy and the result is the temperature of the water lowers. The combination of lower temperatures and decreased water volume (30% of the volume is taken off as steam) concentrates the minerals.

The most abundant mineral is dissolved silica. A key limitation to geothermal power generation is the level of dissolved silica and the temperature that this becomes saturated in the water. If the generator continues to take steam off and lower the water temperature below the saturation point of the silica, it will come out of solution and deposit silica scale into the steam separator and associated pipework. This must be avoided, so generators have to stop taking steam before this happens.

Despite this, silica scaling in geothermal power generation is a significant issue. Work carried out by Jacobs[1] for Geo40 has shown that silica management costs can be as high as 20% of a power plant's operating cost. Jacobs have also shown that up to 20% more power could be produced from reinjection water through the introduction of binary power plants if silica levels were able to be reduced.

[1] RZ015400-GE-RPT-001B Cost of Mitigation of Silica Scaling, Study 1

The majority of this scaling occurs in the pipework leading to and in the reinjection wells. This photograph is of a 450mm reinjection pipe at Coso geothermal power plant in California, USA, and shows the level of scaling after eight years of use. This is because the hot geothermal water is pumped to the far edge of the field and reinjected back into the reservoir, where it gets reheated to create the renewable loop for power generation. As it is pumped, localised surface cooling takes the fluid through the saturation point and scaling occurs.

Aside from silica, other important and valuable minerals are also contained in the water including lithium for batteries and rare earths for other specialised applications.

Geo40 was formed in 2010 to develop technologies for the benign harvesting of these minerals and turning them into important sustainably produced and competitively priced alternatives in the market.

Colloidal Silica (Silica Sol) – Basic Facts

Many of the properties of colloidal silica are counter intuitive. Oversimplifying, a solution of particles is stable at a pH above 9 or below 3.5. The particles are not dispersed but are stabilized because of steric or ionic repulsion. At neutral pH, the negatively charged particles destabilize and become reactive and gel or agglomerate or react with a surface. Dilution when adjusting pH can distance the particles and help maintain stability.

Most significant, is that the individualized particle size is measured in nano-meters or 10^{-9} meters. Colloidal silica for investment casting is produced to targeted particle sizes and particle distributions.

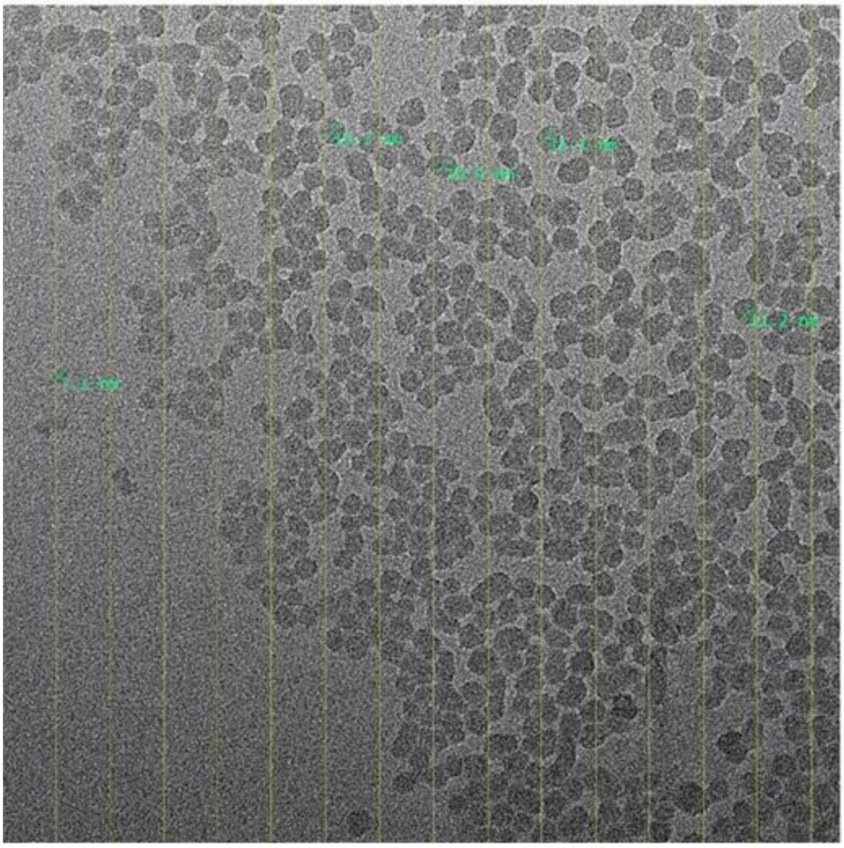


Figure 5: Transmission electron micrograph (TEM) of Geo40 10nm colloidal silica (sol)

For particles sizes below 10nm or 12nm, the particles are so small that when concentrated to 30% solids, the solution is still water clear as it does not refract light. Larger particles of 40nm or higher can be concentrated to 40% or 50% solids and are more easily seen and appear milky white. The particles when dried on a surface can be felt to the touch.

Figure 6: Geo40 colloidal silica at 30wt% concentration and various particle sizes

Surface area is what makes colloidal silica so unique. It was one of the original "nano" products making headlines today. A smaller particle size colloidal product (5 nm) can have a surface area of 625 square meters per gram (190,739 square feet per ounce or 4.25 acres per ounce!). To put this in perspective, approximately 2 teaspoons of colloidal silica would have the surface area of a football field. For colloidal silica, the relationship between surface area (SA) and particle size (PS) is: SA = 3125/PS

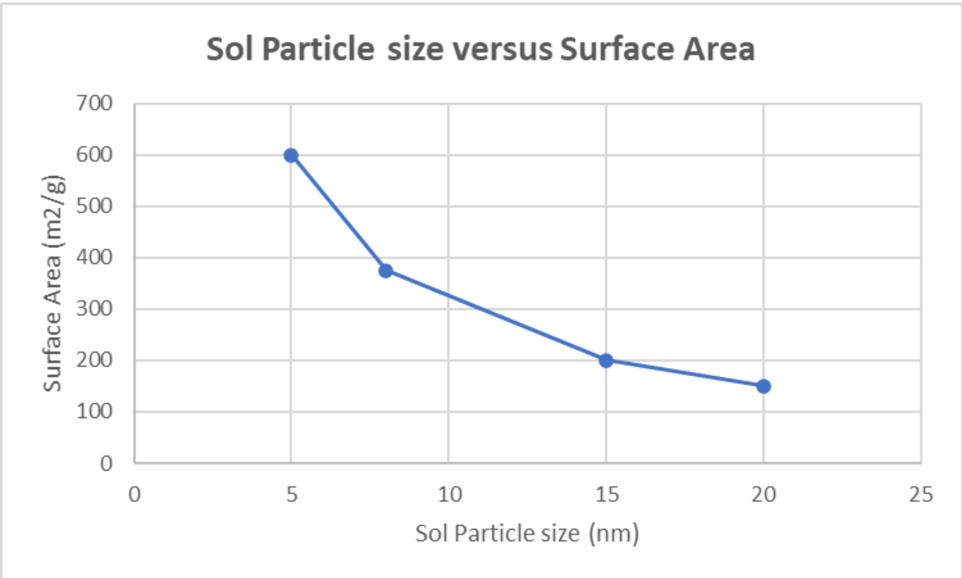


Figure 7: Plot of the effect of colloidal silica particle size on surface area

This combination of being a stable inert amorphous liquid, high surface area but easily becoming a reactive silica particle makes colloidal silica so unique and useful. Uses of colloidal silica are wide ranging including being an excellent binder, rigidizer, polishing agent, frictionizer, coagulant, anti-soilant, carrier, scratch preventer, densifier and many more. Only limited by your imagination.

Industrial Production of Colloidal Silica

Early patents date to the 1940s and 1950s with names like Iler, Bird, Alexander and others. The historic commercial process for making colloidal silica starts with the production of sodium silicate (Na_2SiO_3) through the melting of quartz sand and sodium carbonate (soda ash) in a natural gas heated or electrically heated liquid pool furnace at temperatures of around 1,600°C (2,912 °F). The sodium silicate glass is cooled and broken into chunks which are later dissolved with caustic in a high temperature, pressurized autoclave to form a concentrated liquid silicate solution with a pH between 10-12, depending on grade. Grades are defined by the ratio of silica (as SiO_2) to sodium (as Na_2O). Standard SiO_2/Na_2O ratios range from 1.6 to 3.3 with various silica concentrations.

Numerous different routes exist to make colloidal silica. Slightly simplified, the traditional process is to deionize sodium silicate (by membrane or direct resin contact), adjusting pH to be slightly alkaline, mix with heat to promote nucleation, add acid and additional deionized sodium silicate to grow particle size, wash to remove impurities, stabilize by adjusting pH and then concentrate (evaporation or ultrafiltration). For colloidal silica, the final product concentration can increase as the particle size increases. The smaller the particle size (2 - 150 nm are possible) the higher the surface (1560 to 60 square meters per gram).

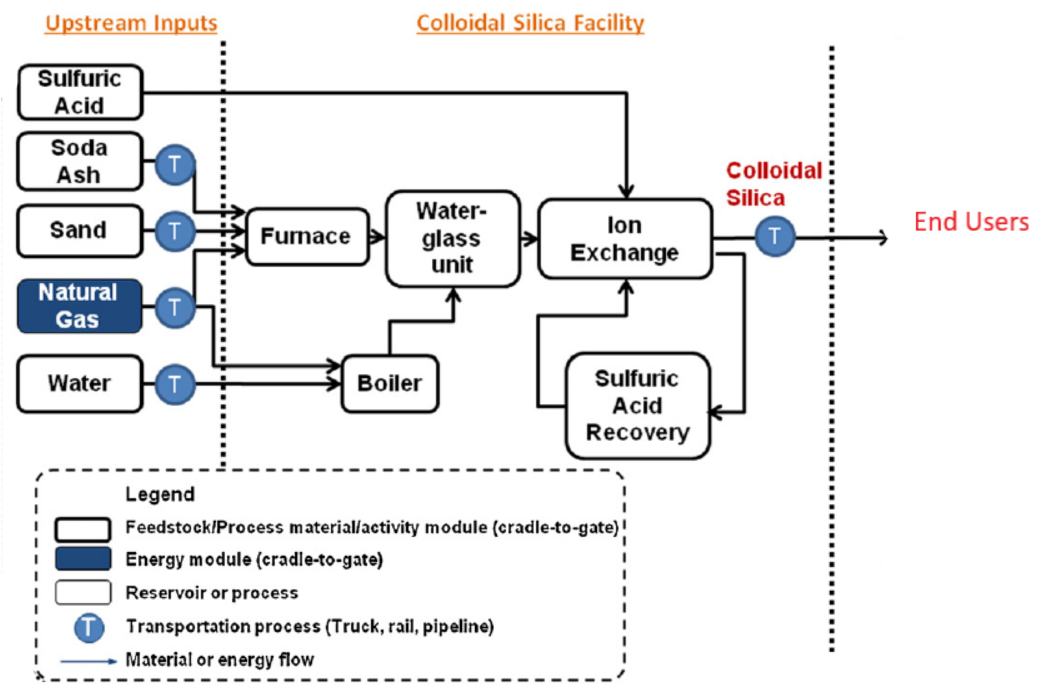


Figure 8: Typical colloidal silica manufacture from quartz sand

New Generation Sustainably Produced Colloidal Silica

In 2010, Geo40 recognised the opportunity to work with the geothermal power generators globally to reduce their maintenance costs for managing silica scaling by harvesting the pure dissolved silica and turning it into sustainably produced colloidal silica products.

Work started with literature searches and laboratory tests to determine the best methods for harvesting the silica. In 2014, the first large scale pilot plant was built on Contact Energy's Wairakei geothermal field in New Zealand.

Figure 9: The first pilot plant located at Contact Energy's Wairakei geothermal field in New Zealand

Further work was carried out over 2015 to refine the process and improve the colloidal silica production to make products with targeted particle sizes and distribution. The colloidal silica markets are differentiated by application and colloid size. Geo40 developed processes for producing a product range of 6nm 15wt%, 8nm 20wt%, 10nm 30wt%, 12nm 30wt% and 14nm 30wt% products. This resulted in Geo40's third patent application being filed. The Geo40 process was finalized on this process.

Following the successful work at Wairakei a simplified pilot plant was relocated to Kawerau in New Zealand where the process was tested on different geothermal water to ensure the robustness of the process. Further large-scale pilot plant trials were carried out at Mercury's Kawerau Geothermal plant, at the Ohaaki geothermal field in New Zealand and Kakkonda geothermal field in Japan.

Following successful pilot plant trials at Warakei, Kawerau and Ohaaki geothermal fields in New Zealand and Kakkonda geothermal field in Japan, Geo40 signed an agreement with Contact Energy in New Zealand for a staged commercialization of the technology at Contact Energy's Ohaaki geothermal field. The agreement was a three-way agreement with Contact Energy, Geo40 and with the local indigenous (Maori) landowners, Ngati Tahu Tribal Lands Trust.

In the agreement, there was a requirement for the outflow from the first commercial plant to feed an historic Maori hot spring (Ngawha). Historically, before geothermal development occurred in the area in the 1980s, the hot spring had flowed clear and had been used by generations of Maori or Tangata whenua (people of the land) for bathing and cooking. When the first geothermal development was established, the historic spring dried up. Flow was later restored to the spring from the power station, but the flow was high in silica and the spring flowed a milky white colour. On building the first plant and harvesting the silica in the water, the Geo40 process was able to supply hot geothermal water, now with lower silica, and restore the hot spring back to its original pristine natural beauty.

Figure 10: First commercial plant built in 2018 at Ohaaki, New Zealand

Figure 11: The top photographs show the hot spring before and after the first Geo40 plant was built, demonstrating the harvesting of the silica and supply of the hot geothermal outflow from

the plant to the hot spring. The top left photograph shows the hot spring before and the top right shows the hot spring after. The white areas in the second photograph show the natural white silica terraces cascading into the depths of the pool. The bottom two photographs show the overflow from the hot spring into the Waikato River, before and after the Geo40 process and how the white silica plume has disappeared.

How it is made

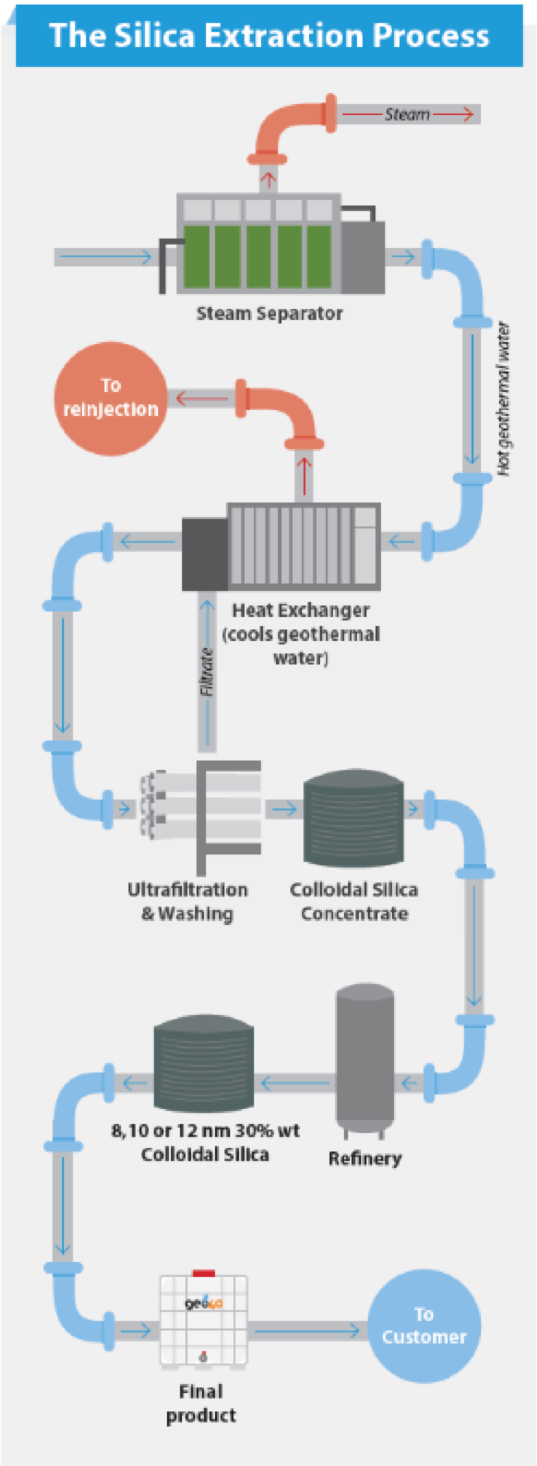


Figure 12: Geo40 process

The Geo40 process works on the treatment of geothermal water from the steam separator in a geothermal power plant. Water leaving the plant is close to silica saturation. Geo40 receives the water, cools it to below the saturation point. During the cooling stage the silica forms discrete colloidal silica particles that are around 1nm - 2nm in size. These particles are then aged and filtered out using a continuous ultrafiltration (UF) and washing circuit to concentrate the silica from its incoming concentration to a 4wt% solution. This concentrate is then further processed, using conventional technology, into sustainably produced and cost competitive, high quality colloidal silica products. Filtrate from the process is now low in silica and able to be used for further mineral extraction before being sent to cool the incoming geothermal water and be reheated and pumped to the reinjection wells at the edge of the geothermal field.

The hot filtrate water leaving the plant is low on silica and cannot cause further silica scaling in the pipework and reinjection wells, saving significant costs for the geothermal power generator. Before it gets reinjected back into the field, the hot low silica geothermal water can now also be used for direct heating opportunities or further power generation improving the efficiency of the renewable power being generated.

Geo40 is well advanced in technologies for removing the dissolved lithium in the geothermal water after the silica has been harvested. To date, near battery grade, sustainably produced and cost competitive, lithium carbonate has been produced from the lithium harvested.

Geo40 is now also exploring the sustainable and competitively priced harvesting of other minerals from the geothermal water before it is reinjected.

Next generation, sustainable production, and high quality

In current industrial processes for producing colloidal silica, large amounts of energy are required to get the silica from the quartz sand, dissolved into water so that it can be made into colloidal silica. Further processing and heat is required, including other chemicals in the process and for ion exchange resin regeneration.

In contrast, colloidal silica produced from geothermal sources utilises nature's own energy to dissolve the silica and other minerals in the underground spring water. The hot water is brought to the surface and used to generate renewable power. The Geo40 process utilises this renewable power in the plant for the further processing and finishing its products. Harvesting of the silica results in improved power plant efficiencies and opens up the opportunity for harnessing further green and renewable energy.

Figure 13: Photo of the next generation, sustainable, high quality colloidal silica

Geothermally harvested colloidal silica products are the "same but better" than industrially produced equivalents. They are the same in that they have been proven to perform as well in all applications, and in some applications, better than current industrially produced products. Current geothermally produced products are competing competitively in high quality precision investment casting applications, refractory fibre bonding and refractory casted production, catalyst production, enhanced oil recovery, electronic component production and as additives in concrete, adhesives and paints.

The “better” is coined as better for the environment and better for renewable geothermal power generation and a better choice for users. As the world moves to more environmentally responsible solutions, this must include looking at our manufacturing processes and seeing where we can utilise products that have a better environmental footprint. Minerals harvested from geothermal sources offer a next generation opportunity for sourcing quality sustainably harvested products at competitive prices.

Next stages

Geothermal power production is sustainable, renewable and baseload. Unlike solar and wind power, that rely on the wind blowing or the sun being out to generate power, geothermal power production is 24/7 and provides constant renewable baseload power generation.

Global geothermal power generation is growing fast, opening the opportunity to work in symbiosis with the industry to sustainably harvest minerals. The global geothermal power industry sees Geo40’s technology as “ground-breaking” and has the potential to change how geothermal power stations are built and run in the future.

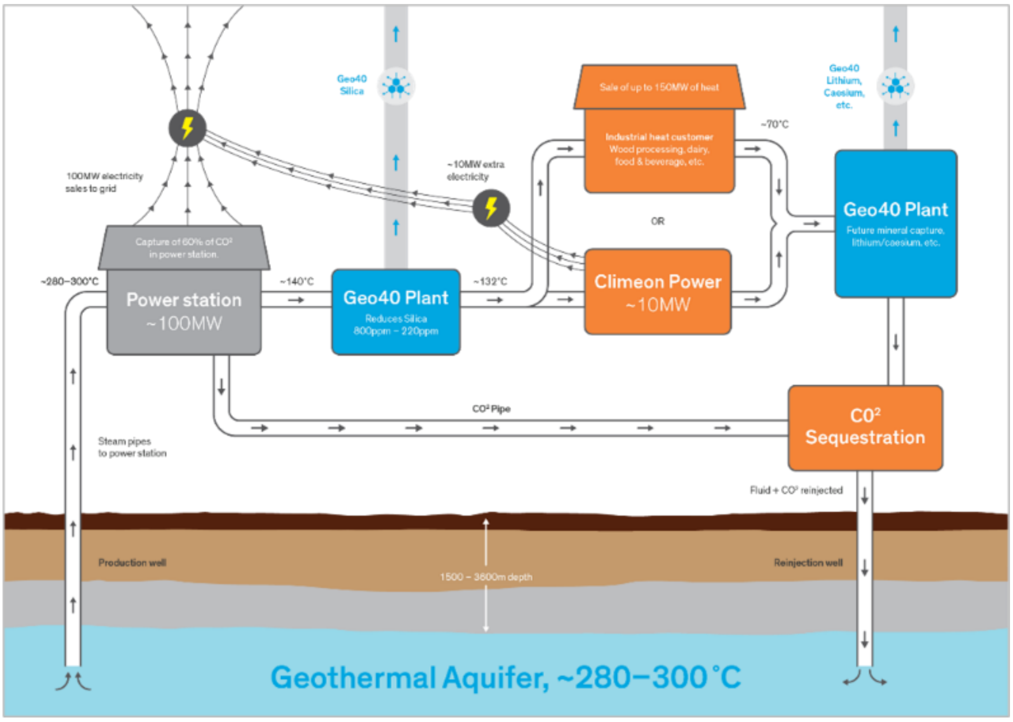


Figure 14: Diagram of Geo40 processes and added options when installed

1. Hot geothermal water is pumped to the surface from the geothermal aquifer.

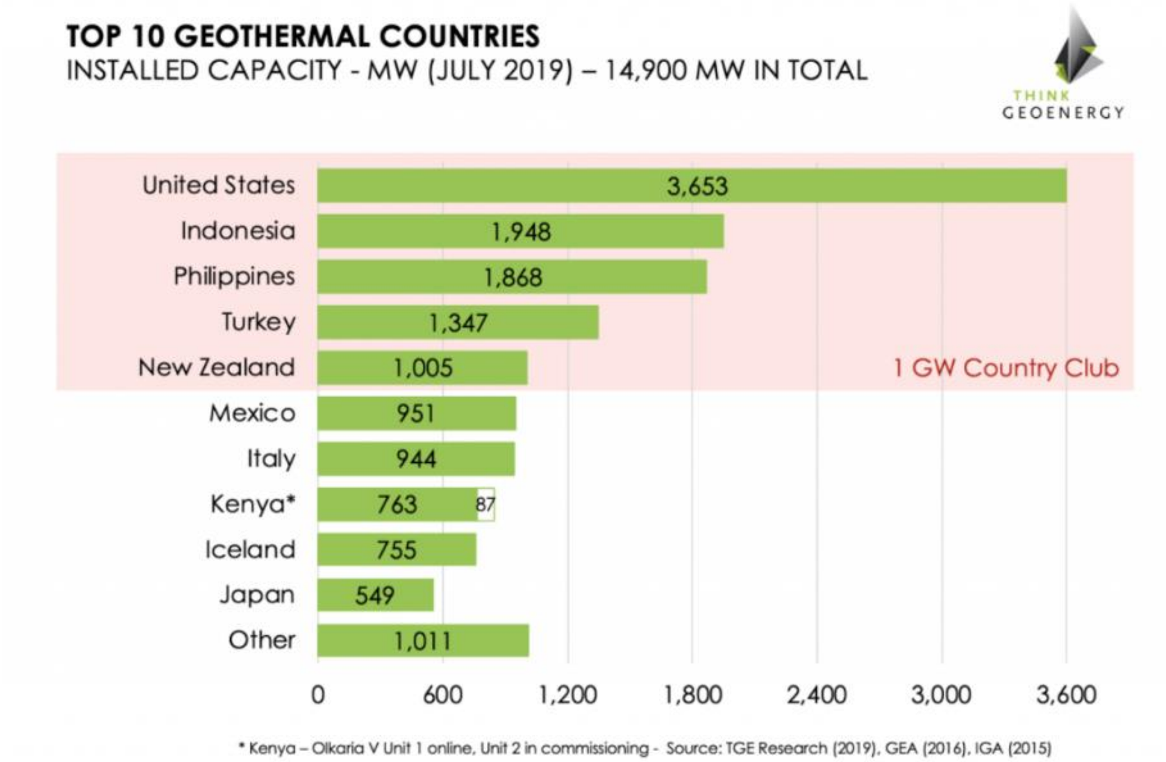
2. Hot geothermal water enters the power station. Geothermal operator generates electricity, from the steam, to sell into the grid.

3. Geothermal water flows on to the Geo40 plant. Silica is harvested, removing it from the water and allowing Geo40 to obtain silica and minerals to process into products.

4a. Geothermal water flows on to a partner plant, generating heat to sell to industrial heat customers, OR;

4b. Geothermal water flows on to a Climeon partner plant, generating an additional 10MW of electricity.

5. In the future, geothermal water flows on to another Geo40 plant, where lithium and caesium are harvested for Geo40 to sell.
6. Geothermal water flows on to a partner plant that enables carbon sequestration.
7. Geothermal water is reinjected back into the aquifer.



Global Geothermal Power Generation Capacity - 29 July 2019 (source: ThinkGeoEnergy)

Figure 15: Geothermal Power Generation capacity globally

Photo: New 5,000-10,000 metric tonne capacity colloidal silica plant under construction in NZ

Summary

Colloidal silica is an important component in investment casting. The nanoparticles of silica are used in the mould systems as a binder and to help provide a high-quality finished surface on castings. The technology used to produce current colloidal silica products used in investment casting was first developed in the 1940s and 1950s.

Over the years, binder systems have evolved to meet the more demanding requirements of investment casters and their customers. However, the base process for producing the majority of the nano sized colloidal silica particles has not changed much.

The process starts with silica in the form of quartz sand and uses high amounts of energy to first convert this to a more soluble form, called water glass, and then further energy to get the silica dissolved into water to process into the nano sized particles of colloidal silica. Further processing is required to grow the particles to the right size, particle distribution and trace mineral content.

For millions of years, nature has been doing this right under our feet. Heat from the earth’s core has been heating water under pressure in the earth’s crust and dissolving silica and other minerals. Nature’s forces have brought this water to the surface creating natural geysers and bubbling hot springs with the silica depositing out as natural silica terraces at these features all around the world.

The team at an innovative company in New Zealand, observed this phenomenon and in 2010 set about utilising this natural source of dissolved minerals to harvest and produce sustainable high-quality products.

The process involves working in symbiosis with the geothermal power industry to take hot geothermal water, used for renewable power generation, cool this as nature does and harvest the resulting minerals as they come out of solution in the water. Further processing, using conventional colloidal silica growth technologies has resulted in a new generation and sustainable way for producing sustainable, high-quality, and competitively priced colloidal silica-based binders for precision investment casting applications.

The added benefit of this has been an improvement in the economics and power output of renewable and sustainable geothermal power production.