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Reykjanes Geothermal Field: Clarification of Brine for Reinjection and Production of Precipitated Silica.

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ABSTRACT

In the Reykjanes geothermal power plant, the steam is separated from brine at high pressure, and the hot brine disposed. Bottoming unit is now being developed in which the hot brine will be flashed in two stages and the medium and low-pressure steam used in a dual-stage turbine to generate 30 MW of electricity. The brine flowing at atmospheric pressure from the separators contains 940 mg/kg SiO_2, and silica will rapidly precipitate out of solution making it impossible to inject the brine into wells. A process for clarifying the brine for reinjection and production of precipitated silica was developed and tested in a pilot unit which can treat 20 kg/s of brine. In the process the brine is rapidly mixed with silica slurry in a solid contact reactor at optimal pH for silica precipitation. In the reactor the concentration of dissolved SiO_2 is reduced almost to saturation. The brine then flows into flocculation where the small silica particles are flocculated by adding alkali and with slow stirring. The flocculated silica is separated from the brine by settling in a clarifier. After dilution with condensate below silica saturation, the brine containing less than 20 mg/kg suspended silica particles is finally filtered in a drum filter and is then suitable for reinjection. The silica slurry which settles in the clarifier is recirculated to the solid contact reactor. Sufficient silica slurry is removed from the process to balance the precipitation of inflowing SiO_2 and at the same time keeping the slurry concentration high enough in the solid-contact reactor. The full-size process will handle 300 kg/s of brine and as a valuable byproduct, produce 14 tons per day of precipitated silica. The silica has great potential for various uses which are being investigated.

1. INTRODUCTION

HS-orka operates a 100 MW power plant in the Reykjanes geothermal field in Iceland. The plant is fed with steam from 1030 to 2800 m deep wells which tap 250 to 320 °C hot brine of seawater salinity from the geothermal reservoir. In the power plant, 2 x 85 kg/s of steam is separated from the brine at 18 bar separator pressure. The steam is used for powering two 50 MW turbines, and the exhaust steam is condensed at 40-45 °C in surface condensers. The non-condensable gas is extracted from the condenser and discharged through a chimney. The separated 207°C hot brine is now partly reinjected and partly disposed into the ocean. The energy content of the disposed brine is considerable and can be used to generate at least 30 MW of electricity.

Because of high silica concentration and high salinity, severe scaling will occur when the brine is flashed to lower temperature in a separator. The use of acid for scale mitigation, although effective, is considered unattractive and therefore a new separator technology was developed to control the silica scaling with critical nozzles and without use of chemicals in a combined vertical and horizontal separator. This new technology is described in two other papers at this convention, Lund et al. (2020) and Þórólfsson et al. (2020).

The brine flowing at atmospheric pressure from the separators contains 950 mg/kg SiO_2, and the dissolved silica rapidly precipitates out of solution making it challenging to handle the brine and impossible to inject the brine into wells. Precipitation and separation of silica from geothermal brine has been studied worldwide. Precipitation experiments were done at HS-orka Svartsengi plant with brine with similar chemistry, but lower salinity, Thordarson and Tomasson (1989) showed that the silica precipitation could be controlled by addition of alkali. Precipitation process for manufacturing silica for use as additive in paper was developed in Kawarau in New Zealand, Harper et al. (1992). Precipitation of silica in a crystallizer reactor clarifier has been successfully utilized in the highly saline fields of Salton Sea in California, Featherston et al. (1995). Other brine clarification processes have also been developed such as the use of cationic polymeric flocculants, Kato et al. (2000) and a process for silica precipitation without any chemicals which is used in Svartsengi by the Blue Lagoon, Hauksson (2003). Based on this experience the clarification of the Reykjanes brine for reinjection and production of precipitated silica was considered a viable option and a pilot process was designed and built and its testing and development is described in this paper.

2. BRINE CHEMISTRY

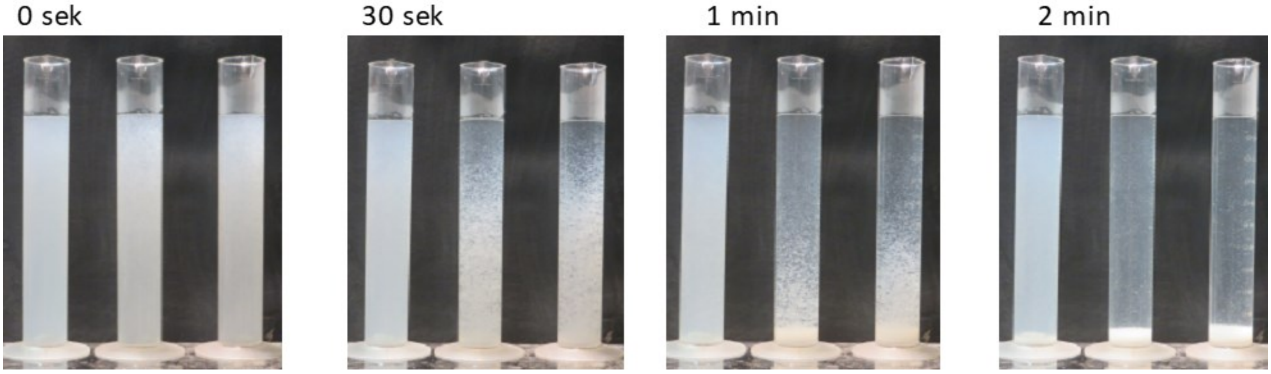
The brine in the Reykjanes reservoir is of seawater salinity. The chemical composition differs from that of seawater because of equilibrium with minerals in the rock at high temperature. Sodium (Na) and chloride (Cl) concentration of the brine in the reservoir is similar to seawater concentration, but the magnesium (Mg) and sulphate (SO_4) concentration are much lower while the calcium (Ca) and potassium (K) concentration is higher. Because of the high chloride content and high temperature, the solubility of metals such as iron (Fe), manganese (Mn), zinc (Zn) and lead (Pb) is considerable in the reservoir brine. The concentration of silica (SiO_2) is controlled by equilibrium with quartz in the rock at reservoir temperature. At separation pressure of 18 bar in the power plant the silica concentration is 750 mg/kg and below the amorphous silica solubility in the brine. When the brine is separated in the bottoming process to atmospheric pressure the silica concentration rises to 940 mg/kg, well above the solubility of silica. During initial tests of separators for the bottoming process, the silica precipitated rapidly out of solution and formed thick silica sludge inside the brine collection basin (Figure 1). The outflow from the basin was still highly silica supersaturated, and the silica which precipitated out of solution partly formed sludge in the discharge piping and was partly carried with the brine as suspended matter. If this is not dealt with properly it will affect the operation of the separator unit and the brine disposal channel which will need to be cleaned regularly with possible interruption of power production. Also, the disposed brine will contain suspended silica, and the brine cannot be injected into wells unless it is clarified. It was therefore decided to develop a brine clarification process which would make the brine injectable and yield precipitated silica as a byproduct as well as reduce the formation of sludge in the brine disposal system.

Figure 1: Silica sludge in brine collection basin after 56 days.

3. CHEMICAL TESTS

The clarification of brine occurs principally in two steps. First, the silica precipitates out of solution in a reactor were the concentration of dissolved silica is reduced, and the silica supersaturation minimized. In the second step the precipitated silica particles settle, and the brine is clarified. The size of reactor must allow sufficient holdup time so that the silica concentration approaches solubility of silica before it enters the clarifier. In the clarifier flocculant is added to the brine, and the small silica particles adhere and form big flocks of silica that rapidly settle out. As a preparation for the design of the experimental clarification process, chemical tests of the effluent brine were done to determine the precipitation rate of silica, size of precipitation tank, the concentration, and type of flocculant, settling rate of silica particles and size of the clarifier.

Samples of brine effluent were collected, and the flocculation of the brine was tested in the laboratory at site. It was soon evident that caustic soda is a suitable flocculant for Reykjanes brine and that the suspended silica can be removed from the brine by settling, see Figure 2. In the cylinder without NaOH the fine silica does not settle at all. When NaOH is added to the brine the suspended silica form flocks that settle very rapidly. Addition of hydrated lime ($Ca(OH)_2$) was also tested and had similar effect presumably because of the pH increase. Other flocculants tested, i.e. aluminum and magnesium were not beneficial.



0 sek

30 sek

1 min

2 min

Figure 2: Flocculation with 0 ppm, 35 ppm and 70 ppm NaOH.

Addition of 35 ppm of NaOH was sufficient for good flocculation and when more NaOH was added the clarity of the brine was somewhat improved. Further tests were done with different NaOH concentrations were aliquot of the brine was taken from the top of the jar after settling and the solids concentration determined gravimetrically. According to this experiment the NaOH added needs to be more than 10 mg/l NaOH to lower the suspended solids below 20 mg/l but increasing the NaOH concentration above 20 mg/l did not have much effect on the clarity (Figure 3). It was decided based on these results that 15 mg/l sodium hydroxide would be used for the flocculation in the pilot process. By slow stirring the flocks were bigger and settled more rapidly and optimal stirring time for the mixing of flocculant was 20 min. The settling rate of the flocks was approximately 6 m/h which was used to size area of the settling chamber in the clarifier.

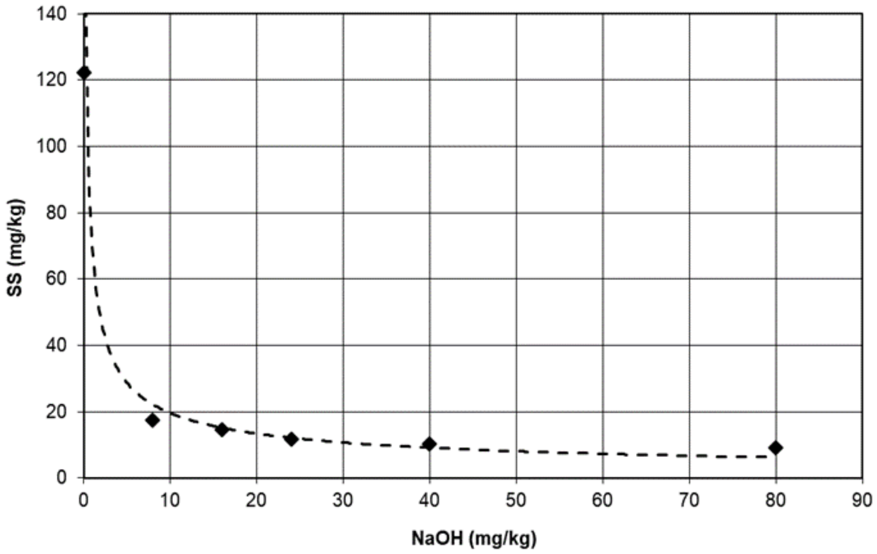


Figure 3: Effect of NaOH addition on brine clarity.

4. PILOT PROCESS

A brine clarification process capable of handling all the brine from the experimental separators was constructed. The flow diagram for the pilot process is shown in Figure 4. The brine from low-pressure separator entered the reactor through a barometric pipe. The brine level in the pipe was controlled and kept at 4 meters depth in the reactor. The temperature of the brine entering the tank was 108 °C, and it boiled in the reactor to 100 °C. The reactor volume was 40 m^3 and the holdup time at design flow of 20 l/s was 33 min. The precipitation of silica took place in the tank and the silica slurry was stirred by the up flow of steam in the tank and carried to the clarifier. The clarifier had two chambers. In the inner chamber, sodium hydroxide was mixed with the brine forming large silica flocks which settled out in the outer chamber. The settled silica slurry was pumped from the bottom with slurry pump to the reactor to increase the precipitation rate of the silica. The silica produced was withdrawn from the slurry line. The concentration of the silica in the recirculated slurry was controlled by the amount of slurry removed from the circulation. The diameter of the atmospheric tank was 4 meters, and the diameter of the clarifier was 6 meters. For 20 l/s flow the area loading (Q/A = flow divided by area) was approximately 3 m/h in the settling zone or 50% of the settling rate in bench-scale experiments. The installed pilot equipment is shown in Figures 5 and 6. The 30% NaOH was dosed from 1000-liter tanks with adjustable dosing pump. The slurry pump was flushed with condensate to avoid scale buildup and to protect the mechanical seal. The brine flow was measured in a weir box and also by accurate measurement of the diluting condensate flow and temperature of the mixture, and calculation of brine flow by heat balance. The slurry flow was measured volumetrically in a bucket.

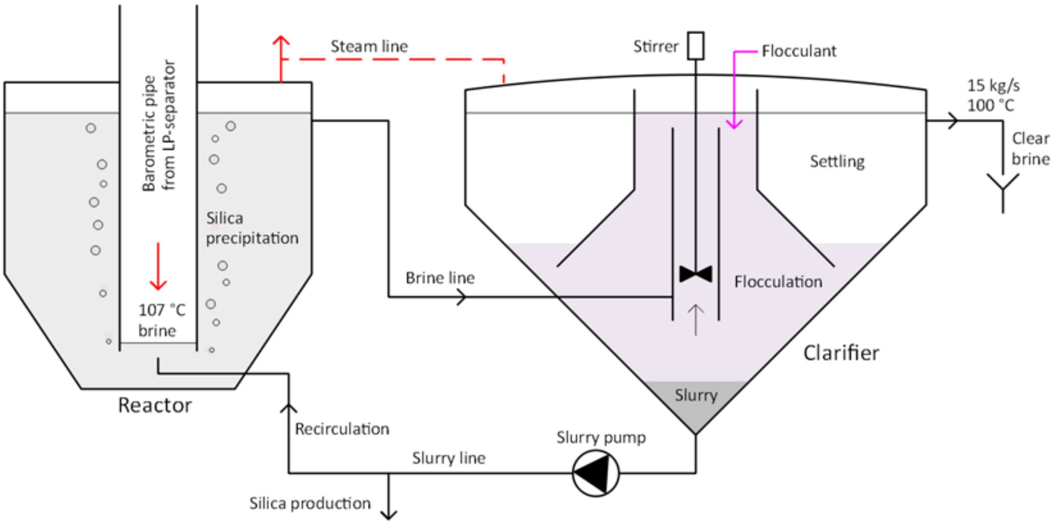


Figure 4: Flow diagram for the brine clarification pilot process.

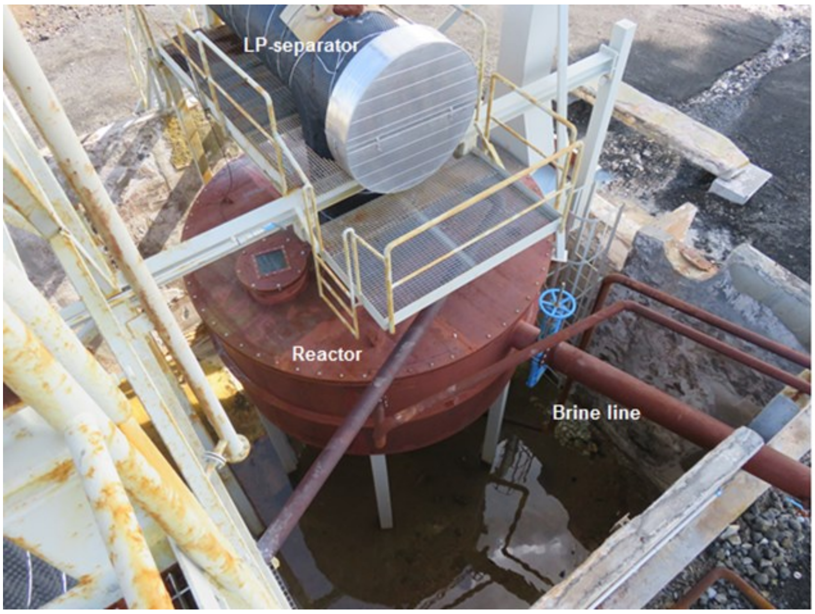


Figure 5: Reactor and LP separator

Figure 6: Clarifier and brine, slurry and steam lines from the reactor.

5. EXPERIMENTAL RUNS

Several experimental runs were done with different process parameters such as of flow, recirculation ratio, solids concentration in reactor, NaOH concentration in flocculator and stirring speed, etc.

5.1 Silica precipitation.

The concentration of dissolved SiO_2 in the inflowing brine after boiling to 100 °C was 940 mg/l in the reactor while the solubility of SiO_2 is only 356 mg/l at 100 °C. The silica precipitated rapidly out of solution in the reactor and formed solid silica particles. The experimental runs showed that the precipitation rate is highly affected by the concentration of silica slurry in the reactor. Without any slurry recirculation, the dissolved SiO_2 concentration in the brine only lowered to 600 mg/l, but when the slurry concentration was increased the precipitation rate increased, and the silica concentration got closer to silica saturation. This is shown in Figure 7, which shows the SiO_2 concentration in the reactor for different slurry concentrations. By keeping the silica slurry concentration above 6 vol% the concentration of dissolved silica could be lowered below 400 mg/l. The tests demonstrated that it is vital to keep the slurry concentration as high as possible in the reactor in order to increase the silica precipitation rate and reduce the silica supersaturation in the outflowing brine.

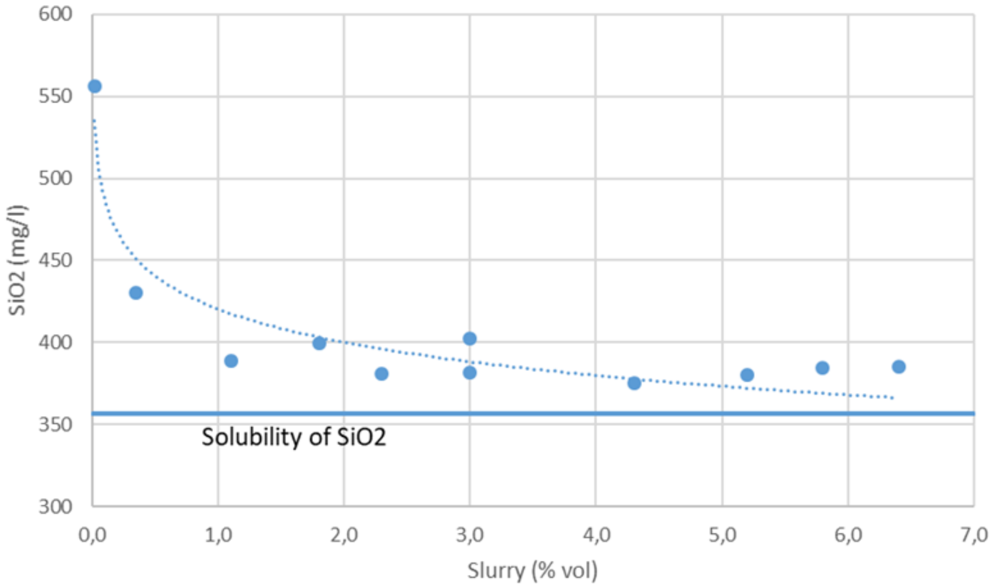


Figure 7: SiO_2 concentration vs. slurry concentration in reactor.

Dosing the alkali into the flocculating chamber of the clarifier increased the pH to 8.3. Some alkali is carried with the slurry collected at the bottom of the clarifier and recirculated to the reactor. The recirculation flow was 10-15% of the inflowing brine. The pH of the brine in the reactor was 7.0 without any recirculation, but with recirculation the pH became 7.3 - 7.6 depending on the recirculation ratio. The increase of pH positively affected the precipitation rate of silica but increasing the pH above pH 7.6 did not further increase the rate.

5.2 Clarification

The suspended solids concentration (SS) in the brine from the clarifier was measured gravimetrically by microfiltration and weighing. The target for the process was to lower the SS concentration in the brine for injection below 20 mg/l. This concentration could be obtained when the concentration of slurry in the circulated brine was below 1 vol%, but the SS concentration increased when the slurry concentration was increased (Figure 8). This counteracted the beneficial effect of increased slurry concentration on the precipitation rate of silica. At early stage in the process development, scaling tests were done with clarified brine which was pumped through pipe packed with basaltic gravel, Kristinsson (2017). Despite the clarification process removing 97% of the entering silica, the brine quality was not sufficient for it to be safely reinjected. This was experienced with the immediate scaling when the brine hit the gravel packing in the pipe. It was apparent that improvement of the processes is needed.

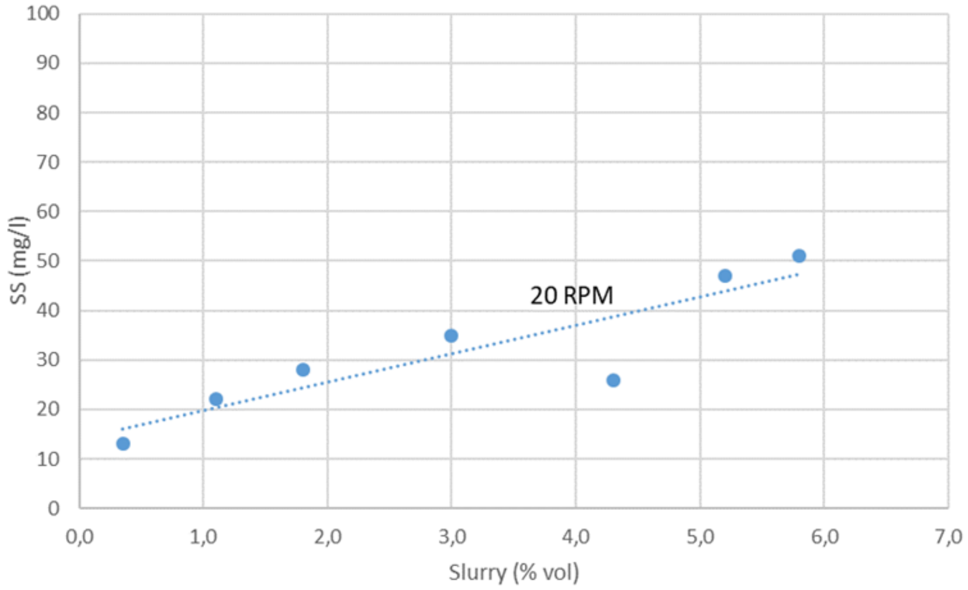


Figure 8: Suspended solids vs. slurry concentration in reactor.

The design of the reactor was changed, so that thick slurry was circulated within the reactor and separated from the brine before it flowed to the clarifier. The slurry in the reactor contained 15-25 vol% silica and was mixed immediately with the supersaturated brine flowing into the reactor from the LP separator. Because of the high slurry concentration minimal scaling occurred on the reactor surface. The concentration of silica in the recirculated slurry from the clarifier was less than 1 vol%. By this modification the silica concentration could be lowered to 400 mg/l, and the suspended solids in the outflow lowered below 20 mg/l.

To further reduce the SS concentration in the brine for reinjection, a secondary clarification process was considered. Clarification by centrifugal action was ruled out because of complexity and cost. An experimental secondary clarifying tank was installed which consisted of 40 ft insulated container. The brine from the primary clarifier was diluted by condensate to silica undersaturation and entered the secondary clarifier at one end and flowed out of the clarifier at the other. The secondary clarifier was able to reduce the suspended solids concentration to 10 mg/l but to lower it further, very low flow and small area loading (Q/A) was necessary. The efficiency of the secondary clarifier was somewhat better when the suspended solids concentration in the inflow was higher. Filtering of the brine from the experimental clarifier was tested. Drum filter with automatic backwash capable of filtering 15 l/s of brine and condensate mixture was installed (Figure 9). With filter fineness of 5 µm the suspended solids could be lowered to 10 mg/l. Some of the particles in the brine were seemingly too small to be efficiently removable by settling or filtration.

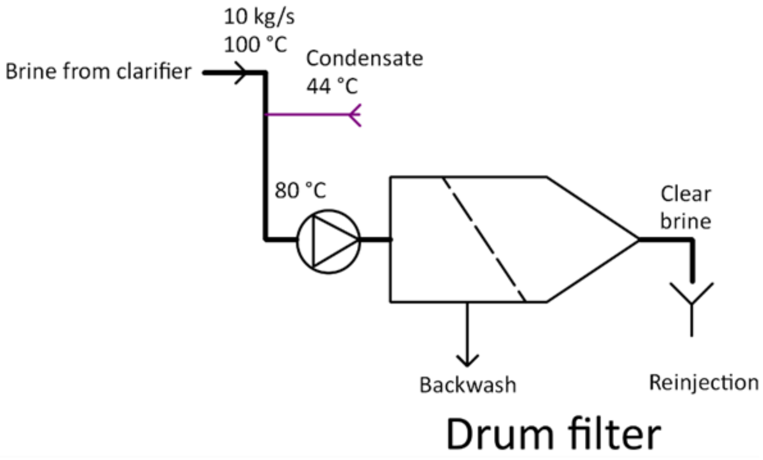


Figure 9: Flow diagram for the experimental drum filter with backwash.

6. PROPOSED FULL-SIZE PROCESS

The bottoming plant in Reykjanes will have two brine separating lines with brine flow of 2 x 150 l/s. Based on the findings in the pilot test runs, a full-size process was proposed (Figure 10). An atmospheric separator with diameter of 8 meters will be installed under the LP-separator. The barometric pipe from the separator will extend 4 meters into the brine. The steam will be separated from the brine in the AP-separator, and the brine will flow into a separate reactor tank with holdup time of 40 min and area loading (Q/A) of 7 m/h. Surry with solids concentration of 15 vol% will be circulated from the reactor bottom to the bottom of the atmospheric tank where it will mix with the inflowing brine. In the reactor, slurry particles will be separated from the brine, and the brine will flow from top of the reactor into the flocculating zone of the clarifier. Sodium hydroxide will be added to the brine under slow stirring to flocculate the small silica particles at a pH of 8.3. The consumption of sodium hydroxide for handling 300 l/s of brine is estimated to be 400 kg per day. The slurry collected in the clarifier will be recirculated from the clarifier bottom to the AP-separator where it mixes with the inflowing brine. The recirculation rate will be 10 % of the inflow. The brine will flow from the flocculating zone to the settling zone in the clarifier where the silica particles will be separated from the brine. The area load (Q/A) will need to be less than 3 m/h to separate the small particles carried with the brine. To reach this value the diameter of each 150 kg/s clarifier tank will need to be greater than 15 meters. The brine will finally be diluted to undersaturation with condensate and, if necessary, clarified in secondary clarifier or filtered for reinjection.

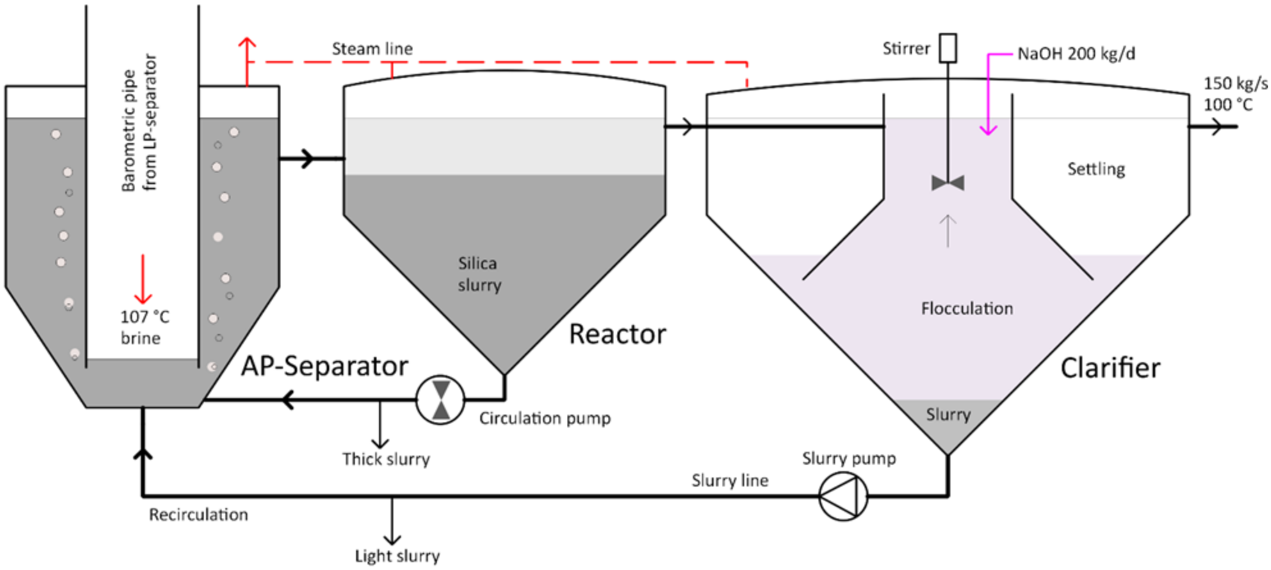


Figure 10: Full-size process for clarifying 150 kg/s of brine.

7. SILICA PRODUCTION

The brine silica concentration will be lowered from 940 to 400 mg/l in the process. Full-size process handling of 2 x 150 l/s brine will produce 14 tons per day of silica. At early stage in the process development, samples of the silica slurry were analyzed for surface area, porosity and other important parameters for powder manufacture and the potential commercial use of precipitated silica was screened, Hauksdóttir (2016). The analysis of the Reykjanes silica indicated some possibilities of producing marketable silica from the Reykjanes brine. Since then the process has been optimized, and various process parameters have been altered which will change the characteristics of the produced silica. The quality of the slurry will highly depend on where it is tapped off the process. The holdup time for the silica will be longest in the reactor which will yield thicker slurry with larger particle size and a lighter slurry with smaller particle size will be obtained from the recirculation line. The different quality may be suitable for different uses. Already studies of potential uses of the silica have been initiated. This includes, e.g. use for ferrosilicon manufacture, decoration in pottery, ingredients in cosmetic products or for use in spas to name only few.

8. CONCLUSION

The experiments showed that the silica could be removed from Reykjanes brine and the silica supersaturation and concentration of suspended solids lowered sufficiently for reinjection. Additional benefits will be better control of scaling in the disposal system and production of precipitated silica.

9. REFERENCES

Thordarson, H., and Tomasson, T. H.: Brine clarification at Svartsengi, Iceland: Effect of pH and temperature on the precipitation of silica and its properties. *Geothermics,* **18**, (1989), Pages 287-294.

Harper, R.T., Thain, I.A., and Johnston, J.H.: Towards the efficient utilization of geothermal resources. *Geothermics*, **21**, (1992), pp.641-651.

Featherstone, J., Butler, S., and Bonham, E.: Comparison of crystallizer reactor clarifier and pH mod process technologies used at the Salton Sea geothermal field. *Proceedings,* World Geothermal Congress, (1995), Florence, Italy, 18-31 May 1995, pp. 2391-2396.

Kato, K., Mogi, K., Ueda, A., and Ishumi, K.: Recovery of silica from the Sumikawa geothermal fluids by addition of cationic nitrogen-bearing reagents. *Proceedings,* World Geothermal Congress, (2000), Kyushu-Tohoku, Japan, May 28-June 10, pp. 2121-2124.

Hauksson, T.: Production of silica slurry in Svartsengi. Results of testing of an experimental separator and design of full-scale unit. *Developing work for the Blue Lagoon Ltd.* Reykjavik, Iceland. (2003), 5 p (In Icelandic).

Hauksdóttir, A.: Geothermal Energy: Silica precipitation and utilization. School of Science and Engineering Reykjavík University. *Thesis for Master of Science (M.Sc.) in Sustainable Energy Engineering.* (2016), 112 p.

Kristinsson, S. Þ.: Examining the reinjection potential of clarified geothermal brine at Reykjanes. *Project submitted in partial fulfillment of a Master Scientiarum degree in Chemical Engineering and Biotechnology.* Section of Chemistry and Chemical Engineering École Polytechniqe Fédérale de Lausanne. Switzerland, (2017).

Lund, Á.E., Hauksson, T., Þórólfsson, G., Jóhannesson, Þ., Gíslason, Þ., and Albertsson, A.: Reykjanes Geothermal Field: Control of Silica Scaling in Separator by Flashing of Brine in Critical Nozzles. *Proceedings,* World Geothermal Congress, (2020), Reykjavik, Iceland.

Þórófsson, G., Lund, Á.E., Hauksson, T., Jósefsson, V.A., Gíslason, Þ., and Albertsson, A.: Reykjanes Geothermal Field: Development of Combined Vertical and Horizontal Separator. *Proceedings,* World Geothermal Congress, (2020), Reykjavik, Iceland.