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A tiny solution to a big problem: the use of nanobubbles in inhibiting silica scaling in geothermal systems

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ABSTRACT

The reduced production caused by scaling on pipes and within the geothermal reservoir poses a major problem for geothermal energy production. Calcium carbonate and sulfide scaling can occur in the production well of a geothermal plant, while silica scaling can occur in the injection well and parts of the geothermal reservoir. As the scale builds, the aperture through which geothermal fluids flow shrinks and flow is reduced. Silica scaling within the reservoir can permanently reduce its permeability. In general, scaling problems can be so severe as to partially or completely close a power plant. Common scaling removal techniques, such as reaming clogged pipes and acid washing, remove the scale but pose problems of their own. Reaming pipes can be effective in cased portions of the well, but this technique is ineffective if the slotted liner of the well is clogged. Acid washing can cause corrosion in the pipes and degrade their integrity. In this paper, we present an alternative scale reduction technique in the form of nanobubbles. These nano-scale bubbles have unique chemical and mechanical properties that may be advantageous in the removal of scale. Circulating nanobubbles through the geothermal system by injecting them into the geothermal fluid could either prevent scale from attaching to pipe walls or cavitate scale that has already built up, thus reducing the need for previously discussed removal techniques.

1. INTRODUCTION

Geothermal energy has the potential to provide reliable baseline power to communities and cities where there is a hot enough geothermal resource; it can also provide direct heat to a much wider geographic area via low temperature geothermal resources and ground source heat pumps. Despite this potential, there are many challenges associated with geothermal at every stage of production, from addressing issues while drilling to a reservoir (Carden et al., 1985) to preventing induced seismicity in enhanced geothermal systems (Khademian and Nakagawa, 2017). One such challenge is scaling, the deposition of minerals on the sides of fluid conduits in the geothermal system such as wellbores, surface pipes, and fractures in the reservoir itself. The most widely researched scaling phenomena occur in single flash and binary geothermal power plants, in which significant scaling can cause production to decrease so drastically that the plant faces partial or complete shut-down. Generally, different mineralogies of scale build at different locations in a geothermal system, based on the temperature and pressure conditions at each point in the system and the properties of the geothermal fluid. If we consider an electricity-producing power plant that utilizes a hydrothermal geothermal system, calcite and sulfides tend to accumulate in the production well, while silica scaling occurs in surface transport pipes, reinjection wells, and in the reservoir surrounding the reinjection well.

Current methods of removing and preventing scale include reaming and redrilling wells, replacing transport pipes, adding acids or polymers to the geothermal fluid, reinjecting fluid at high temperature, and letting cooling geothermal fluid stagnate and precipitate silica before reinjection. Each of these methods has proven effective at removing scale, but side effects such as corrosion, reduced power plant efficiency, and costliness, have prevented any one method from emerging as a consistently reliable scale reduction technique.

One possible solution is to use nanobubbles to prevent or remove scale. Nanobubbles are nano-scale bubbles of gas, liquid, or two-phase fluid that have unique physical and chemical properties attributed to their size (Bhushan et al., 2013). Nanobubbles are remarkably stable and can exist for several days in fluids and several hours on surfaces. Research has been conducted regarding the use of nanobubbles in more efficient coal flotation (Ahmed, S. 2013), treatment of contaminated water, and efficient intravenous delivery of medicine. The observed characteristics of nanobubbles suggest that, if injected into a geothermal fluid, they may be able to prevent scaling on pipe and fracture walls and transport scale particles to the surface for removal.

2. SILICA SCALING IN GEOTHERMAL SYSTEMS

Scaling is the accumulation of mineral particles on surfaces through which saturated fluid flows. Scaling in geothermal systems can occur in injection and production wells, surface transport pipes, and fractures in the geothermal reservoir. Different minerals are deposited as scale in different parts of a geothermal system, as shown in figure 1. In general, calcite scaling occurs in the production well as a result of pH changes caused by boiling processes as fluid rises to the surface. Sulfides may also precipitate in a geothermal system via boiling-derived pH changes and generally form at the top of the production well and in surface transport pipes. Both carbonate and sulfide scaling detract from the productivity and efficiency of geothermal systems, but silica scaling presents the most severe and most stubborn problem. Silica primarily accumulates in the transport pipes, heat exchangers, and injection wells of geothermal systems, as well as in the pore spaces and fractures of the geothermal reservoir around the bottom of the injection well.

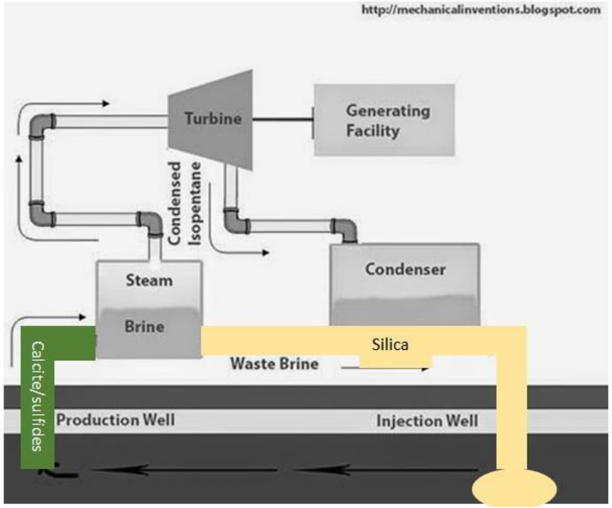
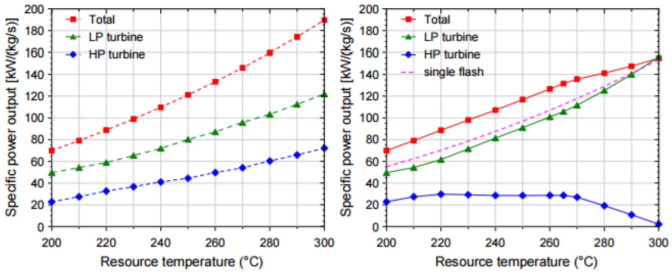


Figure 1: Diagram of a geothermal power plant with different scaling locations highlighted.

Silica scaling in pipes can be so severe as to reduce effective pipe diameter to a few centimeters, which reduces the efficiency of heat exchangers and causes pressure loss in the system. Scaling in the reservoir can reduce its permeability to the point where the fluid is unable to flow to the production well. Nugroho (Nugroho, 2011) analyzed the optimized power output of multiple types of geothermal power systems, and found that factoring silica scaling into the power output calculation significantly reduced the resulting output. An example of this analysis is shown in Figure 2.



(a) non silica constraint

(b) silica constraint

Figure 2: Graphs showing optimized specific power output of individual turbines in a double flash system. In scenario (a), silica scaling is ignored. In scenario (b), silica scaling is factored into the power output. (Ocampo, Valdez, and Schorr, 2014)

Ocampo et al. (Ocampo, Valdez, and Schorr, 2014) conducted a case study that addressed the scaling and corrosion problems at Cerro Prieto geothermal field in Mexico. Out of 160 active wells in the geothermal field, between 12 and 16 must be taken offline due to silica scaling – related maintenance, which includes cleaning and full workovers of the wells. The scaling problem in these wells causes an estimated 20% decrease in steam production. In order to maintain desired output, 1000t/h of steam production must replace the loss caused by scaling; this is primarily achieved by well repairs and the drilling of new wells. Unfortunately, as the dominant scale type in Cerro Prieto is silica, well repairs are costly and do not fully restore wells to their original production. In this study, sidetracking a well recovered 70% of steam production, deepening recovered 60% of production, and cleanouts were only able to recover 48% of steam production.

Whereas calcium carbonate is softer and can be reamed mechanically or dissolved using acid treatments, and sulfides are common but not ubiquitous in geothermal systems, silica is both ubiquitous and more difficult to remove. Highly concentrated dissolved silica is a characteristic of almost all known geothermal brines, and while calcium carbonate has a hardness of 3 on the Moh's hardness scale, silica scale can reach hardness values around 7, which makes reaming difficult and costly. Silica scale is also less reactive with acids than carbonate. Due to these properties, silica represents the most important scaling type to mitigate, and therefore the scaling processes and applications detailed below focus on silica.

2.1 Silica Scaling Processes

Silica scaling occurs via two major processes: Chemisorption, which describes the direct deposition of silica monomers onto surfaces, and polymerization, in which silica monomers bind to one another and form nano-scale polymer particles, as illustrated in Figure 3. Chemisorption occurs very slowly, while polymerization is often rapid (Kokhanenko, 2014).

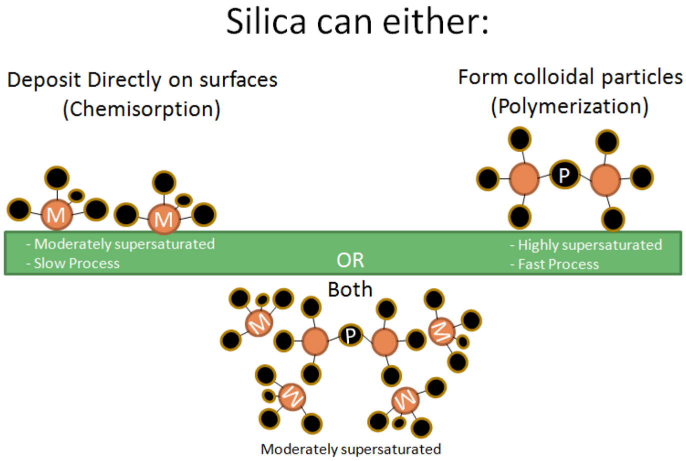


Figure 3: Depiction of chemisorption and polymerization processes of silica scaling on a surface.

The rate of silica scaling, and the process by which it occurs, is governed by the silica saturation index (SSI) as well as the hydrodynamic properties of the fluid. The SSI is determined by dividing the amount of dissolved silica in the geothermal brine by the silica saturation concentration of the fluid.

$$SSI = \frac{Actual\_silica\_concentraton}{Saturation\_silica\_concentraton}$$

When the SSI is greater than 1, the fluid can be considered silica supersaturated. At low levels of silica supersaturation, chemisorption is the dominant scaling process.

When the fluid exceeds a critical saturation level, polymerization takes over as the dominant scaling process, which commonly accelerates the overall scaling rate. Dunstall and Brown (Brown and Dunstall, 2000) found a direct correlation between colloidal particle size and scaling rate. Extensive polymerization creates large colloidal particles in the geothermal brine. It was concluded that these large particles have sufficient inertia to penetrate the flow boundary layer between the deposition surface and flowing brine and attach to the surface, whereas smaller particles lack this inertia and remain suspended in the flowing brine. If the rapid removal of dissolved silica from the fluid via polymerization reduces the SSI back to below the critical saturation level, chemisorption is resumed and silica monomers can bind either to existing surfaces or to the polymerized silica particles suspended in the brine.

2.2 Factors that Influence Silica Scaling

Certain conditions of the geothermal brine, pipes, and reservoir govern the rate of silica scaling. As polymerization is the more rapid scaling mechanism, and it is more likely to occur at higher saturation levels, conditions that increase the silica saturation level are likely to increase the scaling rate. Other conditions may increase the reaction rates of either polymerization or chemisorption by influencing kinetics. A selection of the major factors that govern the rate of silica scaling are as follows:

2.2.1 Temperature

Silica saturation is partially dependent on temperature. As temperature increases, silica solubility increases and thus, more silica can be dissolved in the geothermal fluid without exceeding the silica saturation line, as shown in Figure 4a (Chan, 1989). This lowers the SSI for a given fluid silica concentration and reduces scaling rate. Chigira and Watanabe (Chigira and Watanabe, 1994) designed an experiment to test the effect of temperature, pressure, pH, and flow velocity on the deposition of silica in a porous medium with a negative thermal gradient. They constructed a vertical reactor with seven separate sample vessels filled with a porous medium. Silica-rich solution was pumped through the column at a constant pore pressure and a negative thermal gradient was imposed on the apparatus. The hydraulic conductivity and silica concentration was measured for each sample to analyze the conditions of silica deposition. As seen in Figure 4b, sample 3 had a higher temperature than sample 4, and fluid in the sample 3 vessel had a higher concentration of silica but no silica deposition occurred within the porous matrix. Thus, silica concentrations in sample 3 fell below the silica solubility curve, but the concentration in sample 4 exceeded the curve and caused deposition.

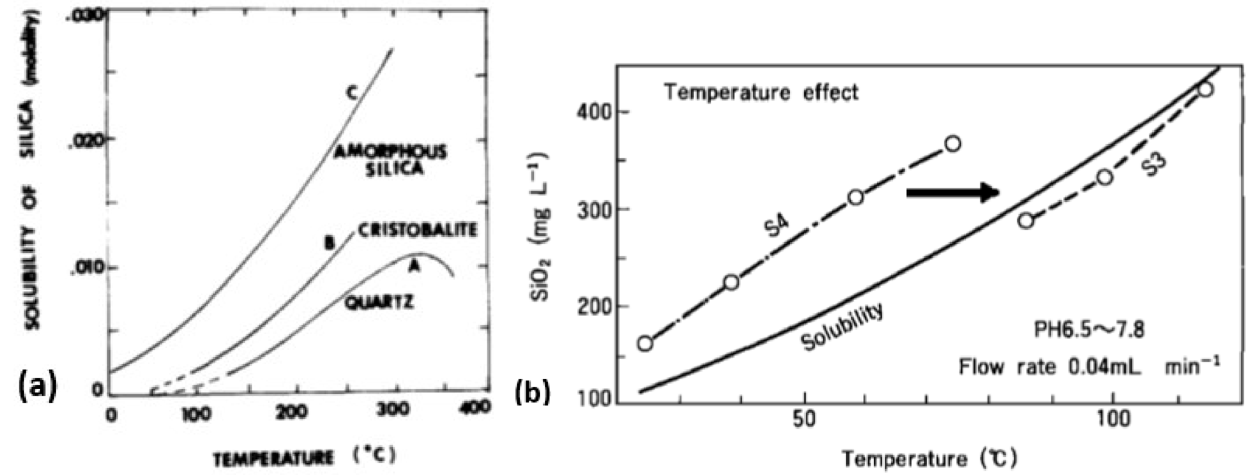


Figure 4: (a) Temperature – solubility curve for silica (Chan, 1989). (b) temperature effect of silica saturation as seen in samples S3 and S4 (Chigira and Watanabe, 1994).

2.2.2 Pressure

Silica solubility increases with increased pressure, although not as strongly as with temperature. The slope of the pressure - silica solubility curve is steeper than that of the solubility curve with temperature (Chan, 1989).

2.2.3 Silica Concentration

The SSI of the brine can be increased during fluid transport through pipes as well as during fluid flow through the geothermal reservoir. As the geothermal fluid is flashed in the surface workings of single flash geothermal power plants, a significant amount of water is evaporated into steam to turn the turbine. A majority of this steam is vented into the atmosphere via cooling towers. While producing a large amount of steam during flashing results in high energy production, it also significantly decreases the amount of 'solvent' water in the geothermal brine, which increases the fluid's silica concentration. Additionally, most rock on Earth contains a significant amount of silica. Particularly, lower stability mafic silicate minerals which are present in igneous intrusions - often the source of heat in geothermal reservoirs - are at risk of reaction with geothermal fluids. As geothermal fluids flow through reservoir rock, they pick up silica from that rock, which increases the amount of dissolved silica and thus the SSI of the fluid.

2.2.4 Fluid Residence Time on Surfaces

Silica deposition is more likely to occur when silica particles move slowly enough to come to rest on a surface and attach to it. Thus, the lower the flow rate at the fluid-surface contact, the more rapidly scale can form. Highly viscous fluids display a stronger "no-slip" condition on surfaces, so scaling may occur more rapidly from more viscous fluids. This effect is confirmed by Dunstall et al. (Dunstall, Zipfel, and Brown, 2000), who observed that silica scaling was more extensive at lower flow velocity.

2.2.5 Fluid Flow Regime

In an experiment by Dunstall et al. (Dunstall, Zipfel, and Brown, 2000), deposition of polymerized silica was induced on a cylindrical steel pipe in flowing brine. The most extensive silica deposition was observed at ~20 degrees away from the stagnation line, shown in Figure 5, which closely corresponds with the steepest slope in the fluid pressure coefficient and, thus, the zone of maximum fluid shear stress. It was concluded that the severity of silica scaling is directly correlated with fluid shear stress. Dunstall et. al. also noted that shear stress is determined by differentiating the skin friction function. Thus, the higher the skin friction gradient of a depositional surface in flowing brine, the higher the shear stress and extent of scaling.

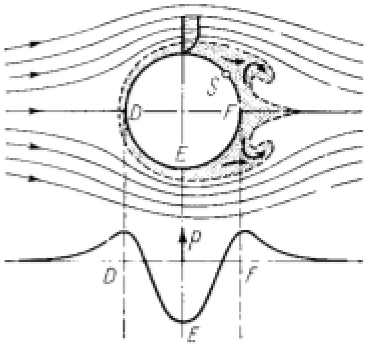


Figure 5: Diagram of fluid streamlines around a cylinder. Stagnation line is at location D (Dunstall, Zipfel, and Brown, 2000).

2.2.6 pH

The pH of the geothermal brine has a dual effect on the rate of silica scaling. Silica solubility is higher in fluids with high pH, and thus at a given dissolved silica content, a geothermal fluid with high pH has a lower SSI compared to a lower pH fluid. This lower SSI reduces the scaling rate. However, pH is directly correlated with the rate of the silica polymerization reaction, and at very low pH levels, this reaction can be significantly inhibited. Chan reported that the maximum silica precipitation rate occurs between pH values of 6 and 9 (Chan, 1989).

2.2.7 Surface Area to Fluid Mass Ratio (A/M Ratio)

Silica scaling rate is directly related to the ratio of surface area to fluid mass (A/M ratio). An extensive study on silica precipitation reaction kinetics by Rimstidt and Barnes (Rimstidt and Barnes, 1980) showed that systems with high A/M ratios had faster reaction rates than those with lower A/M ratios. It was concluded that "This means that very high concentrations of silica can be maintained in solution at low temperatures for relatively long periods of time provided the A/M ratio of the system is not increased" (Rimstidt and Barnes, 1980). If more surface area is exposed to a given amount of geothermal brine, there are more available nucleation sites at which scaling can occur. A/M ratio can be affected by the aperture of a fluid conduit; in geothermal reservoirs, narrow fractures contain less fluid mass at a given time than more open fractures and thus have a higher A/M ratio. Scaling is therefore more likely to occur most rapidly in the narrowest fractures. A/M ratio can also be varied by varying the surface roughness of pipes and fractures, as rougher surfaces have more surface area. Rimstidt and Barnes noted that as silica precipitates onto a surface, the surface roughness is increased (increasing A/M ratio) and consequently scaling reactions may accelerate.

3. PROPERTIES OF NANOBUBBLES

3.1 Chemical Properties of Nanobubbles

Nanobubbles are gaseous domains that are less than 50 microns in diameter and generally form at solid-liquid interfaces. They were first inferred to exist 20 years ago and were first imaged in 2000 to confirm their existence. Their ability to be imaged on the nanoscale has enabled researchers to conduct experiments within the last 15 years that were not feasible before. In their relatively short time of study, basic information has been gathered regarding their shape, size, and interaction with various environmental conditions.

Nanobubbles' existence seems to be paradoxical; their shape and size suggests that they should dissolve in microseconds, due to excessive Laplace pressure that is usually associated with a small diameter, as observed in macro- and microbubbles. However, when they attach to a solid surface, they display a uniquely large contact angle with the surface that enhances their stability. The larger contact angle results in a larger radius of curvature and a commensurate decrease in the Laplace pressure, which allows them to avoid dissolution. (Zhang, Maeda, and Craig, 2006) Whereas little bubbles dissolve and big bubbles rise, nanobubbles remain intact and stable, pinned to the three-phase contact line between a liquid and solid interface. Nanobubbles have been observed to survive for up to 5 days (Wejis, 2013) which has led them to be dubbed "superstable." Nanobubbles can increase particle hydrophobicity and have been used to increase bubble-particle attachment in froth flotation processes (Fan, Zhao, and Tao, 2012). It is hypothesized that they may also reduce the viscosity of fluids, although this has yet to be tested and experiments following this paper will investigate the possibility further. Nanobubbles' unique range of chemical properties has sparked interest in their possible use in various technological applications.

4. NANOBUBBLES IN FLUIDS

4.1 Slip Conditions

Geothermal scaling can be caused by geothermal brine encountering a long residence time on the surfaces of pipes, fractures, pores, and pore throats (Brown and Dunstall, 2000). Additionally, geothermal fluid is known to precipitate scale when subjected to high shear stress (Brown and Dunstall, 2000). At the nanoscale, shear stress is linked to slip length. By increasing the slip length of the pipe and fracture surfaces, the fluid will have a shorter residence time and less shear stress, reducing the opportunity for silica to be deposited on surfaces. Nanobubbles may be able to achieve this by acting as a layer between the surface and the fluid, increasing the slip length and decreasing the shear stress.

Nanobubbles existing on hydrophobic surfaces have been shown by several experiments and theoretical models to affect the slip condition. In some cases, nanobubbles have been shown to increase slip length (Wang and Bhushan, 2010), (Liet al., 2016), (Hyvalouma, Kunert, and Harting, 2011). In other studies, nanobubbles have decreased slip length and increased drag forces (Maali and Bhushan, 2013), (Steinberger et al., 2007). This discrepancy is largely attributed to the shape of the nanobubbles and the area of the surface that is covered by nanobubbles. The shape of nanobubbles is defined by their height and contact angle. Nanobubble shape has been shown to be affected by the roughness and wettability of surfaces (Yen, 2015).

Slip and no-slip boundary conditions exist where a flowing fluid contacts a surface, such as a pipe or fracture wall. A no-slip condition means that a fluid has zero velocity at the contact with the surface. In contrast, a slip condition means that a fluid has a velocity along the surface, limited friction with the surface, and thus a reduced surface residence time. Slip is measured as slip length (b), defined as the extrapolated distance from the surface where the tangential velocity is zero as shown in Figure 6 (Priezjev, Darhuber, and Troian, 2005). The main factors that affect slip length are surface roughness and the surface wettability (Priezjev, 2012), (Yen, 2015). These factors are interconnected and one influences the other.

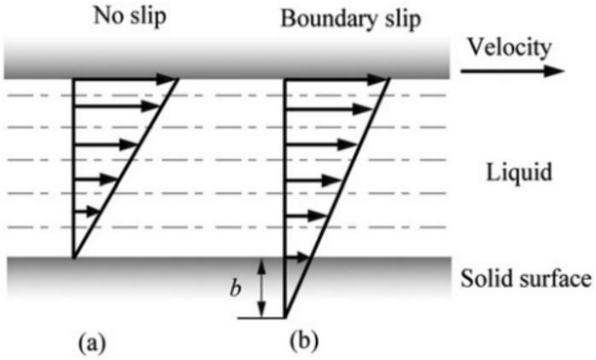


Figure 6: Diagram demonstrating no-slip and slip conditions. (a) No-slip boundary condition where the tangential velocity equals zero at the liquid contact with the surface. (b) A boundary slip conditions where the liquid's tangential velocity is greater than zero and "b" is the slip length (Wang and Bhushan, 2010).

When nanobubbles coat the sides of a rough surface, they can increase the slip length. For example, a typical slip length on a hydrophobic surface is 40-50 nm. Nanobubbles may increase slip lengths by 1 μm or more, significantly larger than a typical slip length (Priezjev, 2012). Nanobubbles added to a geothermal system could prevent silica molecules from accumulating on surfaces by increasing the slip length on fracture and pipe walls.

4.1.2 Contact Angle

The shape of nanobubbles is largely determined by the contact angle. The contact angle (Ө) is the outside angle between the surface and the tangent of the bubble as shown in Figure 7. The supplemental angle to the contact angle is called the protrusion angle, which is often the angle used in nanobubble studies. A large contact angle, or small protrusion angle, is required for slip length to be increased. The contact angle of the nanobubbles is affected by surface roughness and wettability.

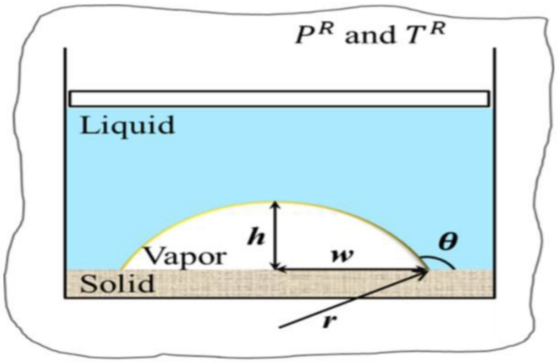


Figure 7: Diagram demonstrating the various parameters, width (w), height (h), radius (r), and contact angle (Ө), that determine the shape of a nanobubble. P^R and T^R are the pressure and temperature of the surrounding reservoir (Zargarzadeh and Elliott, 2016).

A rough surface increases friction, which decreases slip length and causes the fluid to have a longer residence time on surfaces. This longer residence time encourages silica scale to build in geothermal systems. Nanobubbles could fill in gaps on the surface, decreasing the roughness and thus the friction effect on the flowing fluid. An increase in the roughness of a surface has been shown to increase the contact angle of nanobubbles, causing a pinning effect that holds the nanobubbles stationary (Wang and Bhushan, 2010). Rough surfaces often exist on fractures so nanobubbles could be especially useful inside the geothermal reservoir. In contrast, nanobubbles on a smooth surface have a smaller contact angle, causing them to protrude above the surface and increase the friction and shear stress on the flow.

The wettability of a surface describes the surface's tendency to attract certain fluids over others (Bennett, 2016). The wettability is influenced by wall-fluid reactivity and surface roughness (Duffield, Sass, and Sorey, 1994). As the reactivity increases, the wettability decreases, causing a more hydrophobic surface. In contrast, as surface roughness increases, the wettability of a surface increases (Duffield, Sass, and Sorey, 1994). In the context of nanobubbles, wettability is often quantified by measuring the contact angle of the nanobubbles (Yen, 2015). Overall, as the wettability decreases, the nanobubble contact angle increases (Yen, 2015). Citing the wettability factors above, this means that small surface nanobubble contact angles exist where the wall-fluid reactivity is high and the surface roughness is low.

4.1.3 Height

The height of nanobubbles also influences the slip length, although the effect of height on slip length is also largely dependent on the density of nanobubble coverage. If only a few nanobubbles exist on a surface, then taller nanobubbles will create friction with the fluid and decrease slip length (Maali and Bhushan, 2013). For surfaces with sparse nanobubbles, a smaller height is optimal for reducing slip length. On a surface that is densely covered with nanobubbles, as the height of the nanobubbles increases, the slip length increases (Wang and Bhushan, 2010). In this case, the bubbles act as a "bubble mattress" that prevents the passing fluid from reacting with or encountering friction on the surface (Hyvalouma, Kunert, and Harting, 2011). This concept is shown in Figure 8, where the sphere could represent a silica particle in a geothermal flow. Taller nanobubbles would serve to further reduce the drag at the surface by decreasing the difference in velocity between the fluid at the surface and the fluid in the center of the flow as shown in the figure.

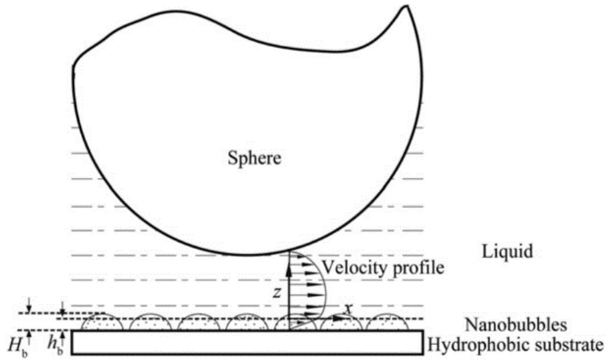


Figure 8: Schematic showing how nanobubbles can form a layer between the fluid and the surface. The nanobubbles increase the slip length and nanobubbles with larger height increase the slip length more (Wang and Bhushan, 2010).

4.1.4 Contact Angle, Density Distribution, and Slip Length

Hyvaluoma et al. conducted a theoretical study that attempted to qualitatively express the effects of the protrusion angle and density distribution of nanobubbles on the slip length using the lattice Boltzmann simulation method (Tester et al., 2006). Figure 9 shows the results of their simulation. The authors used a surface with microgrooves in their study, with groove widths at a ratio of one width unit to two length units, producing a width of 0.5 units (Tester et al., 2006).

The maximum slip length occurred when the protrusion angle was about 20° (a contact angle of 160°). As the contact angle decreased, the slip length decreased, in agreement with other studies. Conceptually, this result states that as the protrusion angle increases (decreasing the contact angle) the bubbles will bulge more and cause friction on the flowing fluid. They found that the bubbles with the largest height affected the flow the most, increasing the velocity of the flow (Hyvalouma, Kunert, and Harting, 2011).

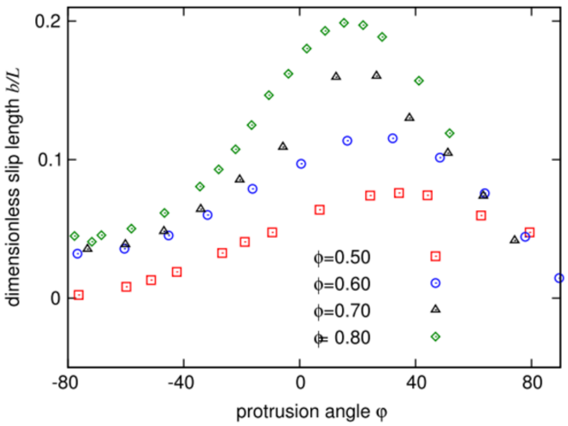


Figure 9: Slip length versus protrusion angle, varying the area covered by nanobubbles. As the coverage increases, the slip length increases. The longest slip length occurs when the protrusion angle is about 20° (a contact angle of 160°) (Hyvalouma, Kunert, and Harting, 2011).

Additionally, the largest slip length was associated with the largest surface coverage of nanobubbles. In this experiment, nanobubbles could act as a mechanism to smooth the rough surface or they could act as a "bubble mattress" that inhibits fluid reactions with the wall rock. If a surface is densely covered with nanobubbles, then taller nanobubbles further increase the slip length.

4.1.5 Density Distribution, Height, Coverage Area, Contact Angle, and Slip Length

Li et al. (2016) conducted an experiment to understand the properties of spontaneously formed surface nanobubbles and how they affected the slip length of a surface. Polystyrene (PS) coated silicon substrates were submerged in water for 40 to 50 minutes. The authors varied the contact angle, root-mean-squared (RMS) values of surface roughness, the film thickness, and the PS solution to create four different substrates. The authors changed the concentrations of PS to change the surface roughness. Tapping-mode atomic force microscopy (TM-AFM) was used to image the nanobubbles and determine the nanobubble measurements. Contact-mode AFM was used to measure the slip length and hydrodynamic force.

The authors found that nanobubbles differed in size and contact angle with each of the substrates. Substrate 4 had the thickest coverage of PS and thus the largest surface roughness. Substrate 4 exhibited the largest coverage density of nanobubbles, suggesting that nanobubbles are more likely to spontaneously form on rougher surfaces. This study suggests that nanobubbles may be more firmly attached to a rougher surface due to pinning. This substrate also had the largest slip length. Thus, Li et al. showed that nanobubbles can be more influential on the slip length of a rougher surface. (Li et al., 2010)

4.1.5 Nanobubbles, Slip Length, and Shear Stress

Slip length and shear stress in fluid flow are closely related. The shear stress in a fluid flow is developed when the fluid has varying velocities at different places along the flow. For instance, a fluid that is moving at the same velocity at every point in the flow has a relative velocity of zero and thus, zero shear stress (Sleigh and Noakes, 2009). However, fluids flowing through a pipe or in a fracture experience shear stress since the velocity at the contact with the surface of the pipe or fracture is less than the velocity in the center of the flow, as shown in Figure 10. This velocity difference creates a shear stress. Silica scaling can be correlated with a large shear stress (Brown and Dunstall, 2000). Therefore, the shear stress must be minimized to reduce silica scaling.

Additionally, an increase in the slip length on a surface can reduce the shear stress. Revisiting the diagram of the fluid flow velocities in Figure 10b, the shear stress can be thought of as the derivative of the velocity profile. Thus, the maximum shear stress would occur at the surface of the pipe, where the change in fluid velocity per unit of distance away from the surface is a maximum. Nanobubbles at the surface would increase the slip length which would "stretch" this profile and reduce the difference in velocity between the surface and the center of the flow, which would in turn reduce the shear along the surface.

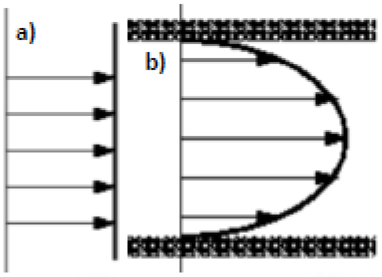


Figure 10: (a) Profile of fluid flowing with uniform velocity. There is no shear stress present. (b)Profile showing the velocity flow in a pipe. There is a velocity difference between the center and surface of the pipe, and thus there is shear stress (Sleigh and Noakes, 2009).

4.1.6 Pinning

Nanobubble pinning is closely linked to surface roughness and may enable nanobubbles to stay attached to a surface under high shear stress. Nanobubbles are pinned most effectively on nanoindents or "islands" on the surface of a fracture or pipe (Wang and Bhushan, 2010). A lack of pinning allows nanobubbles to coalesce, which creates larger bubbles that increase friction on the fluid. Additionally, a larger pinning force increases the contact angle as the nanobubble is held closer to the surface (Yen, 2015). Thus, it is necessary for nanobubbles to be immobile for them to increase the slip length (Wang and Bhushan, 2010).

An experiment was conducted by Wang and Bhushan to determine what factors affect nanobubble pinning. They utilized substrates with varying PS coating and imaged nanobubbles using TM-AFM. They tried to move nanobubbles along the surface by prodding them with a cantilever tip. They found that as the roughness of the substrates increased, the nanobubbles were more immobile (Wang and Bhushan, 2010). They found that at smaller amounts of nanobubble pinning, the nanobubbles would coalesce and create one large nanobubble. Three situations for nanobubble pinning are shown in Figure 11. Figure 11a shows a nanobubble pinned to a flat surface. This is when the nanobubble experiences the weakest pinning force. The second (Figure 11b) is a nanobubble situated in a nanoindent. The nanobubble is the most difficult to move, thus pinning is at a maximum. The third situation (Figure 11c) depicts a nanobubble attached to an island. The pinning force is larger than for a nanobubble on a flat surface but is not at a maximum.

This experiment shows that nanobubble pinning is stronger on rougher surfaces. The effects of pinning on the slip length have not been directly studied to date but it can be concluded that a stronger pinning force could contribute to a longer slip length since the nanobubbles will not coalesce to form larger bubbles. In addition, they will be deformed under high shear instead of being brushed off the surface.

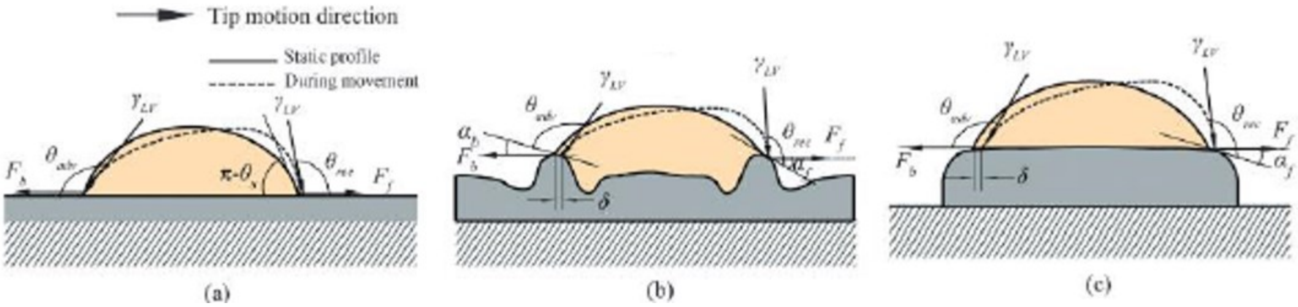


Figure 11: Schematic diagrams showing how nanobubbles can be pinned to different surface features. (a) A nanobubble pinned to a flat surface. (b) A nanobubble attached to a nanoindent. (c) A nanobubble pinned on an island. Θadv=contact angle before deformation; Θrec=contact angle after deformation; Ff, Fb=surface tension forces on the front and back of the nanobubble, respectively (Wang and Bhushan, 2010).

4.2 Conclusion and Application to Silica Scaling

Although these experiments were conducted with nanobubbles that spontaneously formed on the surface of varying materials, these principles may be applicable for nanobubbles that are injected into a geothermal reservoir. These nanobubbles could adhere to the sides of piping and fractures, creating the same slip conditions as discussed above. Brown and Dunstall (2000) showed that silica scaling occurs because of a long fluid residence time on the surface of pipes or fractures and a high shear stress, among other factors discussed below. Nanobubbles on the surface can increase the slip length and decrease the shear rate. This would help to prevent silica scaling by shortening the residence time of the fluid.

However, their effects are largely dependent on the wettability and surface roughness of the walls of pipes or fractures. These parameters affect nanobubble contact angle, height, and surface coverage which influence the slip length. It has been shown that nanobubbles with large contact angle and height that cover a larger area of the surface can increase the slip length, thus decreasing the shear stress. However, the nanobubbles must have a strong pinning force to withstand any existing fluid shear stress. The roughness of fractures in a geothermal reservoir and the potential for hydrophobicity in geothermal piping could be vital for injected nanobubbles to increase the slip length. By increasing the slip length, nanobubbles could prevent scaling in the geothermal reservoir.

5. NANOBUBBLE STABILITY AND EXISTENCE

5.1 Temperature Stability

Nanobubbles appear to be stable as the temperature of their environment varies. Yang et al. (Yang et al., 2007) increased the temperature of a vessel of water containing nanobubbles from 20 to 40 °C in intervals of 5 °C, and they found a dramatic increase in nanobubble density between 30 and 35 °C. They also found that the nanobubbles did not disappear when the water cooled down to ambient conditions within the time scale of the experiment. Another experiment showed nanobubbles to be stable up to boiling temperatures. Zhang et al 2014 (Zhang et al., 2014) used the solvent exchange method (utilizing an exothermic reaction between alcohol and water) to nucleate nanobubbles and atomic force microscopy (AFM) imaging to study nanobubble morphology during the increase in temperature. The liquid containing the nanobubbles was heated and from 37 °C to 74 °C and there was no observable change in size of the nanobubbles. The nanobubbles remained stable until visible bubbles began to form at 90 °C as the water began to boil. While these results are promising, research has yet to be conducted that studies nanobubble stability under conditions that specifically replicate geothermal environments.

5.2 Resistance to Solvents, Surfactants, and pH Changes

Nanobubbles also appear to be impervious to the addition of solvents that change the conditions of their liquid environment. Zhang et al. investigated the effect of surfactant solutions on the stability and morphology of deliberately formed nanobubbles. The experiment used Octadecyltrichlorosilane (OTS) Silicon as a substrate and the solvent exchange method to form the nanobubbles; AFM imaging was used as an observation tool. The results showed that surface nanobubbles on the OTS silicon substrate were stable when the cationic (cetyltrimethylammonium bromide (CTAB)), anionic (sodium dodecyl sulfate (SDS)) and nonionic (Tween 20) surfactant solutions were added. The only significant change observed was in the nanobubbles' morphology: the surface nanobubbles that were irregularly shaped at the three phase contact line in water became more spherical with the addition of each surfactant (Zhang, Maeda, and Craig, 2006).

In the same report, Zhang et al. examined the effect of the addition of salts, acids and bases on nanobubble morphology and stability and determined that the nanobubbles, once formed, were insensitive to the addition of salts, acids, and bases. They used NaCl (1 M), Na2SO3 (0.5 M), Na3PO4 (0.1 M), CH3COONa (1 M), and Ca(NO3)2 (0.25 M) salt solutions, as well as the acidic solutions, H2SO4 (0.1 M) and HCl (0.1 M) and basic solutions, KOH (0.01 M) and NaOH (0.01 M) (Zhang, Maeda, and Craig, 2006). Initial observations of TM-AFM images showed no difference in the stability or morphology of the nanobubbles between water and any of the solutions investigated (Zhang, Maeda, and Craig, 2006).

5.3 Evidence for Nanobubbles in Nature

Direct observation of nanobubbles in nature has not been reported or confirmed. It is likely for nanobubbles to form in hydrothermal conditions associated with mid to shallow geothermal environments as reported by Bejar et al. and Cheung Yec and Chun Zeng. Their research produced manganese silicate nanobubbles in an environment that replicated shallow geothermal reservoir conditions. Their experiments included aqueous solutions of silica, manganese and carbonate, which are commonly present in the geothermal environment. Additionally, the temperature of 180°C used in these studies falls within the temperature range of most shallow geothermal reservoirs. Thus, it is likely that nanobubbles would be stable in geothermal environments and applicable to the scope of this research paper.

There is strong evidence for the occurrence of nanobubble growth in deep geothermal environments during magma ascension and decompression as reported by Aubry et al. (Aubry, Sator, and Guillo, 2013). They observed the nucleation of a nanobubble by molecular dynamics simulation (MD) while investigating the vesicularity and noble gas fractionation of Mid Oceanic Ridge Basalt (MORB) degassing. In a MD simulation starting from an equilibrated CO2-bearing melt at 1873 K and 50 kbar (~9.5 wt.% CO2) and applying a sudden pressure drop from 50 to 5 kbar, simulations show the growth and development of a CO2 nanobubble after a few ns of running time. The experiment demonstrated the formation of a single CO2 nanobubble and "this size agrees with the vesicularity estimated by thermodynamics" (Aubry, Sator, and Guillo, 2013; 92). This experiment simulates the vesicularity of a degassing, CO2-saturated MORB. This study shows the formation of a CO2 nanobubble from a melt at 1873 K and a 50 to 5 kbar pressure drop.

This type of experiment may be applicable to deep geothermal reservoir exploration at mid ocean ridge settings such as Iceland. As pressure and temperature increase with depth, the conditions more accurately reflect Aubry et al's study, indicating that it may be more possible for a nanobubble to exist at this depth. As this study modeled the nucleation and existence of a CO2 nanobubble from a basalt degassing at very extreme P-T conditions, it is uncertain if the nanobubble would be preserved at shallower depths and how abundant nanobubbles nucleate from basalt degassing

6. PREVENTION OF SILICA SCALING

While there are many factors that govern the rate and extent of silica scaling (many of which we may not yet be aware), understanding the conditions that catalyze silica scaling can allow us to engineer the conditions in the geothermal system to prevent scale. Based on the previous analysis of scaling factors, we can construct an 'ideal' geothermal system in which silica scaling would be unlikely. In this system, the geothermal fluid would remain at a high temperature and pressure and thus be subjected to a small thermal gradient. The fluid would be low in silica concentration. Flow through pipes and fractures would be fast enough to prevent suspended particles falling out of the solution and slow enough to minimize fluid turbulence. The fluid would have a low viscosity and conduit walls would have a low surface roughness so that skin friction and thus fluid shear stress would be minimized. The fluid would have a pH that fell outside of the range of 6 to 9 to either increase silica solubility or inhibit the scaling reaction. Finally, the fluid conduits in the geothermal system would have a low A/M ratio, either due to reduced fluid contact with surfaces or wider diameter conduits.

While it may be impossible or impractical to engineer all of the aspects of the geothermal system, there is great promise in engineering a solution to scaling based on a limited combination of factors. In fact, many researchers have proposed solutions to scaling based on modifying the temperature, pH, and silica concentration of geothermal systems. Their methods are described in the following sections.

6.1 Keep Temperature High

Much research has been conducted in the investigation of engineering the factors that govern silica scaling rate so that scaling is prevented. Attempts have been made to prevent silica oversaturation by separating steam at high temperatures and re-injecting the brine before the temperature falls below the silica saturation temperature. This has been successful, however it reduces the utility of the geothermal fluid in that not as much heat can be extracted from the fluid as could potentially be useful (Brown, 2013).

6.2 Reduce or Raise pH

Scientists have attempted to inhibit the silica polymerization reaction by significantly decreasing the pH of the geothermal brine to 4.5-5. This is effective at preventing the formation of colloidal silica particles, but the low pH can lead to corrosion of the system's infrastructure. Treating the brine with sulfuric or hydrochloric acid also requires significant volumes of the additives, which can be costly, may pose environmental risks, and the low pH may cause other minerals to deposit.

As silica scaling occurs most rapidly between pH values of 6 and 9, and lowering the pH may have corrosive side effects, researchers have proposed using alkali to raise the pH of the brine above 9. Kawahara et al. (Kawahara, Shibata, and Kubota, 2013) conducted a feasibility study at the Kakkonda geothermal plant in Japan and concluded that intermittently adding alkali and a secondary additive (to prevent scaling of other minerals such as calcite) was the most appropriate scaling mitigation technique for Kakkonda. This technique has proved successful at inhibiting scaling; however, the alkali additive is costly.

6.3 Reduce Dissolved Silica Concentration

A possible silica scaling reduction technique is to leave silica-supersaturated water to fully polymerize in a holding tank before reinjection. As silica precipitates from the solution into large colloidal particles, the amount of dissolved silica in the brine decreases, which could prevent silica precipitation during reinjection. Yildirim and Simsek (Yildirim and Simsek, 2003) incorporated this method in their attempt to engineer the reinjection conditions of the brine at the Kizildere power plant in Turkey. They proposed letting the silica-enriched brine stagnate for an hour to reduce the dissolved silica concentration to a level equivalent to that of the reservoir fluid. A major drawback to this method is that in order for the fluid to take the time to age, the cycle rate of fluid through the geothermal system may be reduced and lead to reduced production.

6.4 Modify Fluid Shear Stress and Slip Conditions Using Nanobubbles

Nanobubbles may be used in a similar fashion to the previous methods that involve engineering the properties of the brine and its environment to inhibit scaling reactions. The chemical and mechanical properties discussed previously may qualify nanobubbles as an ideal additive that could combat multiple factors that encourage scaling. In this case, introducing nanobubbles into geothermal brine could minimize A/M ratio, minimize fluid residence time on surfaces, and modify the fluid flow regime to minimize the fluid shear stress at pipe and fracture walls. The properties of nanobubbles previously discussed indicate that they may be stable enough to exist at all points in the geothermal system that involve a liquid phase fluid.

The proposed application of nanobubbles would involve injecting the bubbles into the geothermal waste brine after steam separation. As the fluid travels through the pipes and injection well, nanobubbles could adhere to the walls of the pipes, pinned by the small fissures and islands that constitute the pipes' surface roughness. This would create a slip - boundary between the fluid and the pipe walls, which would increase the slip length and reduce the fluid shear stress. If introducing nanobubbles reduces the fluid viscosity, this may reduce the overall fluid shear stress at flow boundaries. Nanobubbles coating the walls of the pipe would also reduce the surface area over which deposition could occur, thus reducing the A/M ratio. As the fluid enters the geothermal reservoir, nanobubbles could attach to the rough walls of fractures, creating a similar slip condition scenario as in the pipes on a smaller scale. If the viscosity of the fluid is reduced, this could also allow for fluid to travel through fractures more efficiently.

Reducing the occurrence of scaling in the geothermal system reduces the opportunity for silica to leave the brine, which would cause the silica concentration of the brine to remain very high. It is likely that the brine would be saturated or supersaturated at some points in the system. Nanobubbles' application to flotation can be of use here: If polymerization occurs due to this supersaturation and colloidal silica particles are created in the brine, nanobubbles may attach to these particles and cause them to agglomerate and if a large enough, buoyant enough silica particle could be created, silica could be removed from the system via the solid separator.

7. CONCLUSION

Silica scaling is an issue that can cause severe depletion of a geothermal power plant's production since the scale can clog the pipes. Nanobubbles may be able to prevent or reduce silica scaling's effects due to their unique properties but there is still very little information about them and with each question that is answered, more are developed. Therefore, more research needs to be conducted with nanobubbles in varying environments to test their bulk properties and their ability to survive in different environments since there is currently little information about this.

The study of bulk properties of nanobubbles in a fluid has only just begun. These properties include their effects on fluid viscosity, thermal conductivity, and specific heat capacity, and how they interact when suspended in fluids. Each of these properties could greatly impact their usage as a scaling prevention method. If nanobubbles reduce geothermal brine viscosity, the brine could flow faster, reducing the potential for scaling to occur. An increased thermal conductivity could reduce friction coefficients and an increased specific heat capacity would reduce the variance in brine temperatures as it travels through the system, which could reduce the ability of silica scaling to occur. Additionally, nanobubbles' bulk properties may change in varying environments. More research should be conducted with nanobubbles in extreme temperatures and pressures similar to the conditions experienced in a geothermal well and with both nanobubbles made of different gases and fluids of different compositions. Each of these parameters could change how nanobubbles interact with and affect the fluid, which could have large impacts on their use for silica scaling. They could also be specifically tailored to different brine compositions by varying the gases that compose them to more efficiently reduce scaling.

We are currently in the beginning phases of testing the effects of nanobubbles on the previously mentioned fluid properties. By generating nanobubbles and introducing them to a sample of fluid that can be continuously monitored, we will be able to systematically test whether adding nanobubbles has an effect on any or all of these properties. As of the submittal of this paper, no results have been gleaned from these experiments and, subsequently, no analyses have attempted to quantify nanobubbles' effects on fluids, but once experiments have been conducted, the information can be used to better apply them to different environments. Further research may expand nanobubbles' use in preventing scaling to not only geothermal but also oil and gas, environmental remediation, and industrial scenarios, increasing the flow efficiency of a wide range of reactive fluids. In the context of geothermal, as research deepens our understanding of geothermal systems and technology improves, it will be possible to address an increasing number of the challenges that geothermal energy production currently faces. Using nanobubbles in geothermal energy systems could address the challenge of silica scaling, allowing more geothermal power plants to be constructed with a longer projected life span, which would increase the use of green energy and aid in the fight against climate change.

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