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REVIEW

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Chemical stimulation of geothermal reservoirs using retarded acid systems: current developments and potential directions

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Abstract

Stimulation techniques to enhance fluid pathways are an important tool to make geothermal projects economically feasible. So far, hydraulic stimulation is used almost exclusively for reservoir-wide improvement of the permeability, but induced seismicity poses a challenge. Chemical stimulation on the other hand has been limited to the close vicinity of the borehole and has barely been considered for the creation of enhanced geothermal reservoirs. However, retardation mechanisms reducing the chemical reaction rate can be used to increase the radius of the chemical stimulation thus enabling a reservoir-wide enhancement of fluid pathways. In this work, we review the technologies of retardation mechanisms for chemical stimulation in geothermal systems and identify five groups of retardation techniques: (i) causing impaired mobility of the acid, e.g., by gelling agents; (ii) causing an impaired dissociation, e.g., by the in-situ generation of the reactive compounds; (iii) blocking the mineral surface area, e.g., by alternating injections of pad fluids and acids; (iv) reducing the reaction rate constant, e.g., by cooling; and (v) changing the chemical equilibrium through chelating agents. We found that most applications are currently based on the use of impaired dissociation, but present research focuses on the development and application of chelating agents. Most of these retardation techniques are adopted from the hydrocarbon industry, but there are several techniques that have not been applied in the geothermal context so far for various reasons. We identify a distinctive lack of in-depth descriptions of the retardation techniques in various studies—mostly to protect intellectual property. However, in the light of public concern regarding fracking techniques and to independently assess potential environmental hazards, scientific examination of proposed techniques is indispensable.

Keywords: Geothermics, Chemical stimulation, Retardation, Penetration depth, EGS

Introduction

Geothermal energy is a base-load capable, renewable energy source and thus an excellent complement to solar and wind energy (Xu et al. 2022). However, geothermal production wells need flow rates of $50\,L\,s^{-1}$ to $100\,L\,s^{-1}$ for the economic feasibility of geothermal power plants (Li et al. 2022). At many locations, the natural permeability is too low to achieve such flow rates and stimulation is necessary to increase it, creating an enhanced geothermal system (EGS) (Huenges 2016). In contrast to natural, hydrothermal reservoirs, which were used as early as 1904 (Burgassi 1999), EGS are much less mature as their development is about a hundred years shorter (Spada et al. 2021). At the current state of the art, successful reservoir stimulation cannot be achieved without severe efforts and high costs (Hackstein and Madlener 2021). In addition, although geothermal projects generally suffer from high initial costs, they are even higher for EGS (Goldstein et al. 2011). Induced seismicity during hydraulic stimulation of reservoirs has caused public outrage and costly stops of projects. Therefore, further research on stimulation techniques is necessary to make EGS more feasible and extend the list of possible geothermal projects.

Current stimulation techniques include hydraulic, thermal, and chemical stimulation. The latter is mostly restricted to the removal of formation damage in the vicinity of the borehole due to its short penetration depth caused by the comparably fast reaction between acid and rock. Depending on the acid and rock properties, the radial penetration depth of chemical stimulation amounts to only several centimeters (Singh and Quraishi 2015) or some meters (Schumacher and Schulz 2013). Various retardation techniques to increase this penetration depth were invented by the hydrocarbon industry and many of them were adopted for geothermal applications. Retarding the chemical reaction can improve the well rejuvenation when formation damage is removed (Gomez et al. 2009) and even enable a chemically stimulated EGS. There are attempts to develop such reservoir-wide chemical stimulation techniques to replace or accompany hydraulic stimulation and hence reduce the potential seismic hazard (Mella et al. 2006; Grifka 2023). In addition, retarded acid systems protect the wellbore casing by reducing the corrosivity (e.g., Mahmoud and Gomaa 2022).

In this work, we review retardation methods currently applied in or developed for geothermal applications with the aim of an extended penetration depth for improved well rejuvenation or even reservoir-wide chemical stimulation. This explicitly excludes works applying acid stimulation without retardation (e.g., Schulz et al. 2022; Brehme et al. 2024). Reviews on general chemical stimulation with geothermal context can be found in Portier et al. (2007), Huenges (2016), Charalambous (2021), Li et al. (2022). Publications included in this article fulfilled the following conditions: only works published since 2000 and written in English were considered. This literature review covers publications of the type of research article, conference paper, dissertation, and report. The content of the publications had to address laboratory or field experiments regarding chemical stimulation for geothermal applications. Works only based on numerical modeling, addressing scaling prevention, or hydrocarbon reservoirs were excluded. In addition, publications describing the same experiment or field case as another publication were removed from the pool. The articles that were checked for these conditions were collected by a keyword search using 'geothermics'/'geothermal', 'acidizing', and one of the following keywords to cover the different retardation mechanisms: 'retardation', 'retarded acid system', 'delayed', 'penetration', 'slow', 'reaction', 'surfactant', 'gelled', 'viscosity', 'in-situ', and 'chelating'. The reference lists and citing literature of these publications as well as of relevant reviews were evaluated to broaden the field of studies considered. The search resulted in only 32 different publications fulfilling the above criteria (Table 1). Some works are cited in several sections as different retardation mechanisms were used

Table 1 List of publications with retardation mechanisms in a geothermal context. The scale (field scale, laboratory scale and modeling) and the retardation technique for each publication are given as well as the type of publication

Authors	Date	Publication type	Scale	Rock type	Retardation technique
Akin et al.	2015	Conference paper	Field	Metamorphic rocks	Quenching, retarder
Alcalá	2012	Report	Field	Sandstone[a], Volcanic rock[a,b]	In-situ production
Barrios et al.	2011	Conference paper	Field	Volcanic rocks	In-situ production, quenching
Cobos and Søgaard	2021	Paper	Laboratory	Sandstone	Chelating agent
Cobos and Søgaard	2022	Paper	Laboratory	Sandstone	Chelating agent
Eker et al.	2017	Conference paper	Field	Metamorphic rocks	Quenching, corrosion inhibitor
Elsayed et al.	2023	Paper	Laboratory	Limestone	Gelled acid
Feng et al.	2021	Conference paper	Field, laboratory	Carbonates	Gelled acid, multistage alternate injection
Flores-Armenta	2010	Conference paper	Field	Volcanic rocks	In-situ production
Goh et al.	2020	Conference paper	Field	Sediments[c]	Weak acid, quenching, organic acid
Gomez et al.	2009	Conference paper	Field	Volcanic rocks	In-situ production
Grifka et al.	2023	Paper	Laboratory	Carbonates	Weak acid, organic acid, chelating agent
Grifka	2023	Dissertation	Laboratory, modeling	Carbonates, sandstone	In-situ production
Lim et al.	2011	Conference paper	Field	Sediments[c]	Gelled acid, quenching
Lummer and Gerdes	2019	Paper	Field, laboratory	Granite	Natural retardation
Madirisha et al.	2022	Paper	Laboratory	Clay Minerals	Chelating agent
Mella et al.	2006	Paper	Laboratory, modeling	Limestone	Chelating agent
Monette and Nguyen	2023	Paper	Laboratory	Limestone	Aqueous phase retarded acid system
Nami et al.	2008	Conference paper	Field	Granite	In-situ production
Pasikki et al.	2006	Conference paper	Field	Volcanic rocks	In-situ production, quenching
Pasikki et al.	2010	Conference paper	Field	Volcanic rocks	In-situ production, quenching
Portier et al.	2009	Paper	Field	Granite	Chelating agent
Rose et al.	2007	Conference paper	Laboratory, modeling	Limestone, glass	Chelating agent
Salalá et al.	2021	Conference paper	Laboratory	Volcanic rocks, granite	Chelating agent
Salalá et al.	2023	Paper	Laboratory	Volcanic rocks	Chelating agent
Salalá et al.	2024	Paper	Laboratory	Volcanic rocks	Chelating agent
Samouei et al	2022	Conference paper	Laboratory	Carbonates	Retarder
Schumacher and Schulz	2013	Paper	Field	Carbonates	Weak acid, organic acid
Silin et al.	2022	Paper	Laboratory	Carbonates	Organic acid
Takahashi et al.	2023	Paper	Laboratory	Granite	Chelating agent
Watanabe et al.	2021	Paper	Laboratory	Granite	Chelating agent
Zemach et al.	2013	Report	Field	Metamorphic rocks	Chelating agent

[a] Gutiérrez-Negrín et al. (2010), [b]Barrios et al. (2011), [c]Milicich et al. (2016)

together. To give a clear view of the available methods, the articles are grouped by their respective retardation mechanism as resulting from the following description of the kinetic process involved in rock dissolution.

The penetration depth of the acid and thus the range of the stimulation depend on the rate of the reaction between acid and rock. In a fast reaction, the acid is spent before it can penetrate the rock significantly. When the reaction is slow, the acid can flow deeper into the formation before it is spent. The reaction between acid and rock is a heterogeneous one and thus consists of several transport steps and the surface reaction itself (Brantley 2005). Each step can be used as a point of action to slow the overall reaction down and thereby increase the penetration depth.

The transport steps are highly influenced by the flow velocity and the substance mobility. The penetration depth can be increased by a higher flow velocity, which accelerates the transport of the acid into the formation compared to the surface reaction (e.g., Akin et al. 2015; Goh et al. 2020). This practice is more on the mechanical side not influencing the stimulation fluid and is not further discussed in this work as it is outside the scope of this work. However, the transport steps can be influenced by impaired substance mobility as well (discussed in section "Impaired mobility"). In addition, the simple unavailability of the attacking particles (mostly hydrogen ions) achieved by impaired dissociation of the acid can reduce the reaction rate (discussed in section "Impaired dissociation").

The rate r of the surface reaction follows the rate law

$$r = A_{surf}\,k\left(1 - \left(\frac{\mathrm{IAP}}{K_{eq}}\right)\right) \tag{1}$$

and depends on the available surface area A_{surf}, the reaction rate constant k, the chemical equilibrium in the form of the ion activity product IAP, and the equilibrium constant of the ions K_{eq} (Lasaga 1998). When the surface area is obstructed, the reaction is slowed down (discussed in section "Obstructed surface area"), and when the chemical equilibrium is shifted, the reaction can go on longer than it would without the removal of the reaction products (discussed in section "Change in the chemical equilibrium"). The reaction rate constant k itself depends on the temperature T and the substance as given by the Arrhenius equation

$$k = A\exp(-E_a/(RT)) \tag{2}$$

with the substance specific pre-exponential factor A and activation energy E_a as well as the ideal gas constant R. The reaction rate constant can thus be reduced by a reduction of the temperature or by an appropriate choice of substances (discussed in section "Reduction in reaction rate constant").

Retardation mechanisms applied in geothermal context

Impaired mobility

Two different techniques were found in the context of geothermal applications to impair the mobility of the acid and thus retard the reaction. The first one is a change in viscosity due to gelling agents. The gelling of acids creates a temporary diffusion barrier to slow down the diffusion of the acid to the rock surface (Singh and Quraishi 2015). This technique was used during well treatment in two different case studies, one in Tayun, China

(Feng et al. 2021) and one in the Kawerau geothermal field, New Zealand (Lim et al. 2011). Both stimulations were successful as regarded by the respective authors. A recent study in the laboratory aimed to further investigate and develop the application of gelled acids (Elsayed et al. 2023). However, the increase in viscosity brings its challenges. The injectivity of gelled acids can be greatly reduced and their applicability in matrix acidizing is thereby degraded (Sayed et al. 2018). Therefore, Feng et al. (2021) used the gelled acid for fracture acidizing, not matrix acidizing. In the other case, the acid treatment was only used to dissolve scaling (Lim et al. 2011). Both case studies also apply other techniques in combination with the increased viscosity that reduce the overall reaction rate as will be shown below.

The second technique to reduce the mobility of the acid and thus reduce the reaction is an aqueous phase retarded acid system developed by Monette and Nguyen (2023). This system was not solely developed for geothermal applications but for well-stimulation in different fields. The hydrochloric acid of the system is retarded by an additive, that is not further specified but acts by impairing the mobility of the hydrogen ions. The new technique from Monette and Nguyen (2023) is still tested on the laboratory scale and has not been applied in the field yet.

There also exist mechanical approaches to divert the acid into the target zone and avoid leakage of the acid (e.g., Shehata et al. 2024), but these techniques do not apply retarded acids. Therefore, they are not within the scope of this work.

Impaired dissociation

An alternative to reducing the mobility of the hydrogen ions to slow down the reaction is a delay in the dissociation of the acid. Due to an impaired dissociation, the hydrogen ions are unavailable at first and the fluid has thus more time to penetrate the reservoir formation before the hydrogen ions can attack the rock.

Weak acids do not dissociate completely like strong acids do. However, they can dissociate further when the chemical equilibrium is changed due to the reaction of the hydrogen ions with the rock. The reaction of weak acids with the rock is therefore slowed down but lasts longer compared to the reaction of strong acids, such as hydrochloric acid (Buijse et al. 2003). Weak organic acids are used in geothermal well stimulation, however, not as pure or main stimulation fluid but rather in combination with strong mineral acids, such as hydrochloric and hydrofluoric acid. Formic acid was already applied at the Kawerau Geothermal Field in New Zealand (Goh et al. 2020) and acetic as well as citric acid were used in the South German Molasse Basin in Germany (Schumacher and Schulz 2013). Citric acid was also tested as a pure stimulation fluid without the addition of strong acids, but the experiments are still on a laboratory scale (Grifka et al. 2023). Due to their slowed reaction, organic acids are not only used to increase the penetration depth but also for high-temperature applications when mineral acids cannot be inhibited anymore (Kalfayan 2008). However, organic acids are more expensive and their reaction products are less soluble compared to the ones from inorganic acids (Chang et al. 2008). There are likely other cases, where these or other organic acids were used to stimulate geothermal wells. As the search criteria for this review were centered on retardation, but organic acids are not solely used for this purpose, the listing above is bound to be incomplete but sufficient for the scope of this work.

The dissociation can also be delayed by in-situ production of the acid. The educt itself, which releases the acid once it is in the reservoir, does not react with the reservoir rock as it cannot dissociate and release its hydrogen ions. However, in contact with the water in the reservoir, it decomposes to release the acid, so that the dissociation can start. Sandstone acid is an acid system based on organo phosphonic acid that generates hydrofluoric acid in-situ (Pasikki et al. 2006). It is likely that the sandstone acid and retarded phosphonic hydrofluoric acid (RPHF) are the same or at least very similar stimulation fluids as RPHF is also created from phosphonic acid and hydrofluoric acid (Barrios et al. 2011), sometimes in addition with hydrochloric acid (Alcalá 2012). Detailed mechanisms or exact formulations of the two stimulation fluids were not provided in the respective publications. Regardless, the phosphonic acid-based systems have often been applied in geothermal well stimulation in El Salvador (Gomez et al. 2009; Barrios et al. 2011; Alcalá 2012), Nicaragua (Gomez et al. 2009), the Philippines (Barrios et al. 2011) and Indonesia (Pasikki et al. 2006, 2010). Another retarded version of hydrofluoric acid is organic clay acid (OCA) produced by Schlumberger, which consists of an organic acid as well as fluoroboric acid that undergoes hydrolysis in the reservoir to release the hydrofluoric acid (Jaramillo et al. 2010). OCA was applied in France (Nami et al. 2008) and Mexico (Flores-Armenta 2010). This type of ester-based retarded acid system that releases the acid in the reservoir by hydrolysis is also applied with other acids like methyl acetate in the hydrocarbon industry (Zimin 2021), but no other instances are known for geothermal applications. However, esters have a lot of potential as the hydrolysis reaction can be influenced by molecular design for an appropriate reaction speed to regulate the penetration depth (Nottebohm et al. 2012) and should be considered for future developments of retarded acid systems. Citric acid was already investigated as a basis for an ester-retarded stimulation fluid but has not yet been tested in full (Grifka 2023). Possible further candidates besides esters for in-situ production of acids are carbamates (Cao et al. 2018) and amides (Schaffer et al. 2016). However, both substance groups were not yet tested regarding stimulation through acid production but only for tracer applications. Theoretically, the possible penetration depth would increase from esters to carbamates to amides due to their respective reactivity.

Obstructed surface area

Similar to the impaired mobility, the reaction can be retarded when the surface is blocked. Here, only the mobility in one direction is reduced, but it is the crucial direction. The obstructed surface has the same effect as the impaired mobility in as much that the hydrogen ions cannot reach the rock surface and react with it.

The multistage alternate injection of pad fluid and acid in the process of acid fracturing is common in the hydrocarbon industry (e.g., Mou and Zhang 2015), but one case from geothermal applications was also found (Feng et al. 2021). In this form of acid fracturing, the injection of pad fluid and acid is alternated multiple times. The viscosity of the pad fluid is much higher than the one of the acid, even if the acid is gelled, and the acid is not able to spread or leak off to the sides when penetrating the pad fluid like a finger (Wang et al. 2022). Thus, the acid flows to the front of the fracture, and the penetration depth of the live acid increases.

Reduction in reaction rate constant

The reaction between acid and rock can also be retarded by reducing the reaction rate constant, so that the surface reaction is slowed down. The Arrhenius equation (Eq. 2) states that the reaction rate constant depends on the temperature and on substance specific properties, so that it can be reduced by a reduction of temperature and a change of the acid. As a rule of thumb, the reaction rate halves for a reduction in the temperature of 10 °C. Although the deliberate reduction of the temperature in the context of geothermal applications seems odd, it is a widely used technique found in five different countries to quench the well with cold water to reduce the downhole temperature (Pasikki et al. 2006, 2010; Lim et al. 2011; Barrios et al. 2011; Akin et al. 2015; Eker et al. 2017; Goh et al. 2020). It is not only applied to slow down the reaction rate but to reduce the corrosiveness of the acids as well which is also temperature dependent (Pasikki et al. 2006; Barrios et al. 2011).

Substances for chemical stimulation which are applied for their lower reaction rate constants compared to the conventional mineral acids include the organic acids already mentioned above (Schumacher and Schulz 2013; Goh et al. 2020; Silin et al. 2022; Grifka et al. 2023) as well as chelating agents (Watanabe et al. 2021). Due to their slower reaction rates and different mechanisms, they can penetrate deeper into the reservoir. However, their reaction capacity is not large enough, so that they are often combined with other methods like in-situ production as described above (Grifka 2023).

Since chelating agents are mainly applied for a second important property, their current application in geothermics is described in the next section.

Change in the chemical equilibrium

The reaction rate depends on the chemical equilibrium, as shown in Eq. 1. The more ions are dissolved in the water, the more the reaction is slowed down. Chelating agents can form strong complexes by binding a central atom, usually a metal ion. The presence of complexes increases the solubility of the respective central ion species, since the complexed ions do not contribute to the concentration of the respective hydrated ions (Koretsky 2000). Therefore, the chelating agents applied for chemical stimulation at geothermal facilities not only dissolve the rock but can also bind the dissolved material. The shift in the chemical equilibrium caused by the formation of these complexes allows a dissolution further away from the injection well in the reservoir formation. Without the chelating agents, only a saturated stimulation fluid would reach the deeper parts and the rock would not be dissolved. Due to the complexation by the chelating agents, it takes longer to reach saturation in the stimulation fluid.

The chelating agents that are applied in the geothermal context are nitrilo-triacetic acid NTA (Mella et al. 2006; Rose et al. 2007; Portier et al. 2009), sulfophthalic acid SPA (Zemach et al. 2013), ethylenediaminetetraacetic acid EDTA (Mella et al. 2006; Cobos and Søgaard 2022), hydroxyethylenediaminetetraacetic acid HEDTA (Salalá et al. 2021), different aminopolycarboxylic acids called BCA (Madirisha et al. 2022), *N*, *N*-bis(carboxymethyl)-L-glutamic acid GLDA (Salalá et al. 2021; Watanabe et al. 2021; Salalá et al. 2023; Takahashi et al. 2023; Salalá et al. 2024) and citric acid (Cobos and Søgaard 2021; Grifka et al. 2023). Only NTA and SPA were applied in the field and SPA only in combination with a hydraulic stimulation (Zemach et al. 2013). However, NTA is considered carcinogenic (Cobos and Søgaard 2021). Therefore, a lot of research on the laboratory scale is conducted to replace NTA as can be seen by all the other studies cited above. The goal is often to find an environmentally friendly replacement (e.g., Salalá et al. 2021; Watanabe et al. 2021; Grifka 2023; Salalá et al. 2024), leaving EDTA and HEDTA out of the running as they are not biodegradable (Sýkora et al. 2001; Cobos and Søgaard 2021).

Others

In many of the cited works, details of the exact composition or the retardation mechanism were not given. This is probably due to two reasons: in some cases, the method is extremely well-known from the hydrocarbon industry and an explanation does not seem to be necessary. In other cases, the maintained silence seems rather to protect business secrets, especially when the work is written by one firm or another. In case of the first reason, information was often found in other publications and was given above alongside with the cases of geothermal application. The others are given here for completeness, although not much information can be drawn from them.

Lummer and Gerdes (2019) presented two naturally retarded acid systems, which they labeled SSB-007 and SFB-007. They were successfully tested in the laboratory and the field, but neither the composition, the underlying acid nor the retardation mechanism is given. In a similar manner, Samouei et al. (2022) tested six different retarder systems for hydrochloric acid in the laboratory without giving details. Akin et al. (2015) have applied a retarder in the field but did not give the name maybe, because it is commonly used for that purpose. Quite often also a corrosion inhibitor is used to retard the reaction (e.g., Eker et al. 2017).

Further retardation mechanisms applied in the hydrocarbon industry

Although most of the techniques for retardation described above are adaptions from the hydrocarbon industry, not all methods applied there are also used in geothermal applications. In the following, these retardation methods from the hydrocarbon industry are described, although the list makes no claim to completeness.

While gelled acids were transferred to geothermal wells, there was no application found of emulsified acids that also increased the viscosity and created a temporary diffusion barrier (Singh and Quraishi 2015). This may be due to the added complexity of the stimulation fluid as extensive mixing procedures are required in the field (Monette and Nguyen 2023). A similar method of enclosing the acid is the physical encapsulation, for example, by nanoparticles (e.g., Singh et al. 2019). This method also ensures deep penetration of the acid, while the stability of the mixture is not as problematic as for emulsified acids.

From the group of methods to impair the dissociation of the acid, Sayed et al. (2018) recently proposed a new mechanism for hydrocarbon well stimulation that relies on a reduction of the free water in the system to prevent complete dissociation of the acid. This is achieved by an organic compound that is readily soluble in a conventional mineral acid like hydrochloric acid. The retardation is comparable to the one of gelled or emulsified acid systems, while it does not suffer from the drawback of elevated viscosity (Sayed et al. 2018).

Finally, from the group of blocked surface area, there is the surfactant retardation. Here, oil-wetting surfactants are applied to coat the pore surface, thereby preventing or slowing down the reaction (Kalfayan 2008).

Conclusion

In this work, the techniques for reaction retardation that are applied in geothermal reservoirs were reviewed. Retarded acid systems do not damage the wellbore casing by providing corrosion protection for all components (Mahmoud and Gomaa 2022). In addition, the retardation of the dissolution reaction enables a deeper penetration of the acid into the reservoir formation and thus increases the range of the stimulated area. This can be useful when the reservoir rock is easily dissolvable and the penetration depth of classic stimulation is thus only a few centimeters or when the formation damage is so extensive that it cannot be completely removed by chemical stimulation with a normal range. The extreme case of this increased stimulation range of the chemical stimulation is the intention to replace hydraulic stimulation (Mella et al. 2006) and enable reservoir-wide chemical stimulation on the basis of retardation (Grifka 2023).

The retardation methods that are already applied in the field include the use of gelled acids to decrease the mobility of the hydrogen ions, the retardation of the dissociation either by weak acids or in-situ production of the acid, multistage alternate injection to reduce leak off and block the surface area, quenching of the well to reduce the reaction rate constant or usage of substances like organic acids with naturally lower reaction rate constants, and the shift of the chemical equilibrium by chelating agents (see Table 1). In addition, retarder and inhibitor substances are used for retardation.

Besides the already existing techniques applied in the field, much research is done to refine these methods or develop new ones. A new aqueous phase retarded acid system was presented (Monette and Nguyen 2023) and individual cases to develop new retarder substances (Samouei et al. 2022) and new substances for in-situ production (Grifka 2023) were found. However, by far most works presenting research on the laboratory scale are about the development of new chelating agents. One-third of the works presented in this article investigated chelating agents.

Although there is a great variety of retardation mechanisms that are applied to or researched for geothermal reservoirs, there are some methods from the hydrocarbon industry that were seemingly not adopted for geothermal applications. These include the use of emulsified or physically encapsulated acids (Singh and Quraishi 2015; Singh et al. 2019), the application of oil-wetting surfactants to block the surface area (Kalfayan 2008), and a method to reduce the free water in the system to retard the dissociation (Sayed et al. 2018).

When evaluating the literature that was found on retardation mechanisms, it is interesting to see that deeper penetration is rarely the goal of their application. Sometimes retardation is necessary for high-temperature application (e.g., Samouei et al. 2022), most often deeper penetration is more of a side effect and the goal is the safe application of the acids in reservoirs containing clay (e.g., Madirisha et al. 2022) or more even dissolution patterns (e.g., Mella et al. 2006). Thus, the implications of retarded dissolution and possibilities of deeper acid penetration into the reservoir formation are often going unnoticed. Only two works were striving to find a technical solution to replace hydraulic stimulation with chemical stimulation to avoid the hazards of induced seismicity (Mella et al. 2006; Grifka 2023). Another issue with the reviewed literature is the big portion of conference papers which are often lacking detailed descriptions of the techniques and theoretical background information to illustrate the underlying mechanisms of the retardation. Presumably, a lot of information is getting lost due to this way of communication and preservation which hinders ongoing research. The secrecy of the corporations with their methods, although understandable, is not helping with that either.

In light of these problems, this article gives an overview of existing methods for retardation in the geothermal context and also highlights methods from the hydrocarbon industry that might still be adapted in the future. However, there must be better coverage of future research including detailed method descriptions and proper research articles. In addition, techniques that are already applied in the industry but not covered in the scientific literature should be revised. Although the maintaining of business secrets is understandable, environmental safety cannot be independently examined and public concern regarding groundwater pollution needs to be seriously addressed. Independent scientific examinations of proposed techniques are required to avoid environmental hazards and public harm. Failures from chemical stimulation techniques in hydrocarbon production, which led to the banning of several methods in Europe and other parts of the world, may not be repeated for geothermal reservoirs. On the other hand, chemical stimulation of geothermal reservoirs using retarded acid systems shows promising results at the laboratory scale and in a few field applications as described in this article. Further research, especially at the field scale, is required as relevant time and space conditions can barely be reproduced at the laboratory scale. The usage of underground research facilities, which are already applied when testing hydraulic stimulation, can help with this and close the gap between the vast research done on the laboratory scale and field applications.

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