



Potential environmental impacts from techniques to enhance rock permeability

Chief Scientist's Group research report

November 2022

We are the Environment Agency. We protect and improve the environment.

We help people and wildlife adapt to climate change and reduce its impacts, including flooding, drought, sea level rise and coastal erosion.

We improve the quality of our water, land and air by tackling pollution. We work with businesses to help them comply with environmental regulations. A healthy and diverse environment enhances people's lives and contributes to economic growth.

We can't do this alone. We work as part of the Defra group (Department for Environment, Food & Rural Affairs), with the rest of government, local councils, businesses, civil society groups and local communities to create a better place for people and wildlife.

Published by:

Environment Agency Horizon House, Deanery Road, Bristol BS1 5AH

www.gov.uk/environment-agency

© Environment Agency 2022

All rights reserved. This document may be reproduced with prior permission of the Environment Agency.

Further copies of this report are available from our publications catalogue: <u>www.gov.uk/government/publications</u> or our National Customer Contact Centre: 03708 506 506

Email: <u>enquiries@environment-</u> agency.gov.uk Author(s): Peter Sawyer Rachel Gavey Marie Grand Xiaojing Wang Simon Haworth

Keywords: Reservoir, permeability enhancement, acid, oil, gas, geothermal

Research contractor: WSS Energy Consulting Limited Export House Wolsey Walk Woking GU21 6QX

Environment Agency's Project Manager: Sian Loveless

Project number: SC210002

Contents

Executive summary	7
1. Introduction	9
2. Methodology	11
3. Overview of acid-based techniques	13
3.1. Fluids, chemicals and reactions	15
4. Matrix acidising	26
4.1. Technology application	26
4.2. Fluids and chemicals	26
4.3. Operational parameters	26
4.4. Subsurface impact	34
4.5. Geological applicability to England	35
4.6. Environmental impact	36
4.7. Knowledge gaps	37
5. Acid fracturing	38
5.1. Technology application	38
5.2. Fluids and chemicals	38
5.3. Operational parameters	39
5.4. Subsurface impact	43
5.5. Geological applicability to England	44
5.6. Environmental impact	45
5.7. Knowledge gaps	48
6. Fluidic oscillation	49
6.1. Technology application	49
6.2. Fluids and chemicals	49
6.3. Operational parameters	50
6.4. Subsurface impact	51
6.5. Geological applicability to England	51
6.6. Environmental impact	51
6.7. Knowledge gaps	52
7. Energised fluids and foams	53
7.1. Technology application	54
7.2. Fluids and chemicals	55
7.3. Operational parameters	57
7.4. Subsurface impact	58
7.5. Geological applicability to England	59

7.6. Environmental impact	60
7.7. Knowledge gaps	61
8. CO ₂ fracturing (liquid-CO ₂ and super critical-CO ₂)	63
8.1. Technology application	64
8.2. Fluids and chemicals	65
8.3. Operational parameters	66
8.4. Subsurface impact	67
8.5. Geological applicability to England	67
8.6. Environmental impact	67
8.7. Knowledge gaps	68
9. Gelled propane/LPG fracturing	69
9.1. Technology application	69
9.2. Fluids and chemicals	70
9.3. Operational parameters	70
9.4. Subsurface impact	71
9.5. Geological applicability to England	71
9.6. Environmental impact	72
9.7. Knowledge gaps	73
10. Narrow diameter multilateral drilling	74
10.1. Technology application	74
10.2. Fluids and chemicals	75
10.3. Subsurface impact	75
10.4. Geological applicability to England	76
10.5. Environmental impact	76
10.6. Knowledge gaps	77
11. Shock fracturing	78
11.1. Technology application	78
11.2. Fluids and chemicals	78
11.3. Operational parameters	79
11.4. Subsurface impact	79
11.5. Geological applicability to England	80
11.6. Environmental impact	80
11.7. Knowledge gaps	80
12. Propellant fracturing	81
12.1. Technology application	81
12.2. Fluids and chemicals	81
12.3. Operational parameters	82

12.4. Subsurface impact	82
12.5. Geological applicability to England	82
12.6. Environmental impact	82
12.7. Knowledge gaps	83
13. Low volume hydraulic fracturing	84
13.1. Technology application	85
13.2. Fluids and chemicals	85
13.3. Operational parameters	85
13.4. Subsurface impact	86
13.5. Geological applicability to England	87
13.6. Environmental impact	88
13.7. Knowledge gaps	89
14. Permeability enhancement of enhanced geothermal systems	90
14.1. Technology application	90
14.2. Fluids and chemicals	91
14.3. Operational parameters	91
14.4. Subsurface impact	92
14.5. Geological applicability to England	92
14.6. Environmental impact	92
14.7. Knowledge gaps	93
References	94

Research at the Environment Agency

Scientific research and analysis underpins everything the Environment Agency does. It helps us to understand and manage the environment effectively. Our own experts work with leading scientific organisations, universities and other parts of the Defra group to bring the best knowledge to bear on the environmental problems that we face now and in the future. Our scientific work is published as summaries and reports, freely available to all.

This report is the result of research commissioned by the Environment Agency's Chief Scientist's Group.

You can find out more about our current science programmes at https://www.gov.uk/government/organisations/environment-agency/about/research

If you have any comments or questions about this report or the Environment Agency's other scientific work, please contact <u>research@environment-agency.gov.uk</u>.

Dr Robert Bradbrune Chief Scientist

Executive summary

Permeability enhancing techniques can be used to increase the productivity of oil and gas or geothermal, reservoirs or wells in a range of geological formations. This report was commissioned to provide a better understanding of reservoir permeability enhancement techniques that could be used in England, and their potential environmental impacts. These techniques can be used in conventional reservoirs (in which permeability is high enough for oil and gas to flow easily to the wellbore and be extracted such as sandstone or carbonates) or unconventional reservoirs (low permeability rock formations such as shales, coal or tight sandstone). Techniques include those with an established history of use in England as well as emerging techniques that have been used elsewhere and could be considered for use in England in the future.

The report summarises permeability enhancing techniques, outlining their purpose, suitability for use in particular rock formations, common chemicals and proppants used, pressures applied, frequency of application, infrastructure, surface operations and limitations. It discusses potential environmental impacts and important knowledge gaps associated with each technique.

Permeability enhancing techniques are often applicable to specific geological and reservoir conditions. The economic feasibility of using techniques depends on many factors. As such, it is difficult to identify which techniques are applicable and likely to be considered for use in England. Semi-structured interviews with onshore oil and gas and geothermal operators and service providers suggest that matrix acidising and low-volume hydraulic fracturing are the most likely techniques to be used in the near future, with supply chain and cost challenges thought likely to prevent the adoption of more novel techniques.

The main risk to the environment from reservoir permeability enhancing techniques arises from the chemicals used being released to groundwater. This could be through existing fractures, fractures created as part of the permeability enhancement operation, surface leaks or spills or through failures in well integrity. Permeability enhancement uses a large range of chemicals, some of which are inert and some of which can be toxic. However, any chemicals used are subject to rigorous controls as part of the permitting process.

There is a low risk of chemicals being released to groundwater if good operational practice is followed and the permeability enhancement operation is modelled using good reservoir and geological data that takes into account existing fracture networks, caprock integrity and the extent of geological faulting. The low volumes of fluids used in comparison to high volume shale permeability enhancement operations further reduces the risk of long fracture propagation and connection with existing fracture systems.

Knowledge gaps which would further reduce risk for techniques likely to be used in England include in better understanding the long-term behaviour of chemicals under fieldspecific reservoir conditions and when used in combination with other chemcials. In addition, a record of the techniques that have been applied in England, and the results of these technique applications, would provide important information for understanding these techniques and their possible environmental impacts. It is recommended that historical data from previous operations in England is made available to develop the research base.

1. Introduction

Permeability enhancing techniques are commonly used to increase well productivity in the oil and gas industry, with some techniques also used for geothermal development. The objective of this report is to better understand the physical and chemical processes involved in these techniques, and to identify the potential environmental impacts. These techniques can be used in conventional reservoirs (in which permeability is high enough for oil and gas to flow easily to the wellbore and be extracted such as sandstone or carbonates) or unconventional reservoirs (low permeability rock formations such as shales, coal or tight sandstone). Understanding the potential impact of these techniques helps with environmental decision-making and allows appropriate risk-based monitoring and management strategies to be implemented that reflect the available evidence.

Rock permeability can be enhanced when rock is subjected to a force which produces deformation or failure. The strength of rock is defined as the stress that the rock can bear under a given set of deformation conditions. Rock strength depends on intrinsic properties such as cohesion and friction, but strength is profoundly influenced by external factors such as applied stress, loading and unloading cycles, and presence of water, and is not a unique value. Failure of the rock occurs when the rock cannot sustain the forces applied and its strength has been exceeded. Failure can occur in different ways, either as brittle failure or ductile failure.

Permeability can also be enhanced chemically through the injection of acid, which dissolves the rock matrix rather than creating fractures. Some of these techniques have very local (<1m from the wellbore) effects on the rock properties, and are principally used to remove near-wellbore damage caused to the formation by drilling or completing (preparing the well for production) the well. Other chemical methods are designed to penetrate the rock over a greater distance to increase flow to the wellbore through formations where unfractured flow rates may prove to be too low to be economic.

Potential environmental impacts related to permeability enhancement can be due to:

- the use of hazardous chemicals and the associated impact on groundwater, including deep saline aquifers and/or deep sourced springs through the transport of fluids through faults, fractures or well casing
- surface leaks and spills of hazardous chemicals due to poor operational practices
- the release of methane or other gases during the technique application

This report is an overview of permeability enhancing techniques that have been, or could be, used in England. It provides an understanding of the types of chemicals used and their waste products, the changes in mechanical strength of the rock and the pathways created, the impacts of any induced seismicity and, finally, identifies environmental impacts. Regardless of which technique is considered for use by an operator in England, the substances that operators are permitted to inject and the formations that they target are subject to rigorous controls through the environmental permitting process. High volume hydraulic fracturing for shale gas is not included in this overview due to the volume of existing literature on the topic, and the implementation of a UK Government Moratorium on this technique at the time of commissioning the report (October 2021).

2. Methodology

The project used a structured literature review to answer 8 guiding research questions:

- 1. What is the purpose of the technique and what is it used for (for example, oil and gas, geothermal or other industry)?
- 2. What are the suitable rocks and conditions that it can be used in (for example, temperature/pressure/composition/permeability)?
- 3. What are the common chemicals and proppants used, concentrations and volumes (including other chemicals such as inhibitors and sequestering agents) and the range of water volume typically used for the technique?
- 4. What are the common pressures applied (absolute and in relation to rock fracture strength)?
- 5. How often is the technique applied?
- 6. What are the specific infrastructure and surface operations, including waste management and waste class (for example, hazardous, non-hazardous, inert)?
- 7. Are there any technique limitations?
- 8. Are there any potential environmental impacts that could result from using the technique?

An extensive list of rock permeability enhancing techniques was identified using project team knowledge combined with an initial literature search. Techniques to be investigated in the project were selected through discussions with the Environment Agency steering group. If it was not clear if a technique should be included in the project scope, further research was carried out to provide sufficient evidence to make this decision. In addition to techniques that were considered likely to be used in reservoirs in England, background information was also provided on some techniques that were less well known or not routinely used. High volume hydraulic fracturing for shale gas is not included in the overview due to the volume of existing literature on the topic, and the implementation of the UK Government Moratorium on this technique at the time of commissioning the report (October 2021).

The research protocol used a literature review supported by semi-structured interviews with industry experts. The literature review primarily used peer-reviewed technical publications and other available literature for supplementary information. The literature search used the Google Scholar database for technical publications, with search strings developed for each technique and then varied to progressively find environmental impacts once the technique had been sufficiently defined. The search was limited to publications in English, with no limit set on publication date. Additional information was found through recommendations from the Environment Agency, geographic-based searches for data from overseas regulatory bodies and academia and through reviewing suggestions from oil and gas service companies and technique vendors following interviews.

An interview programme with operators in England, service companies and academia was used to provide additional context and to determine which techniques were likely to be considered for use in England. Eight interviews were conducted using a semi-structured format, with each interview lasting between 45 and 60 minutes. Interviewees were asked to provide professional opinions based on their area of expertise. The questions covered interviewee opinions on the techniques being investigated, whether they would consider them applicable to the English operating environment, their experience of different techniques and their opinions on barriers and enablers for using different permeability enhancing techniques in England.

Information from the literature review and interviews was combined and used to answer the research questions. Knowledge gaps were identified from the evidence or provided by the research team. This report provides an overview of each of the techniques, rather than in-depth analysis. In the interests of brevity, sources for additional information are signposted throughout the report rather than included in full.

Limitations in this report are related to the literature available. While literature case studies provide information on specific field conditions, they may be missing geological or operational data, and the analogue with English oil and gas fields is often indirect. Data on chemicals is often incomplete because specific chemical formulations are often proprietary or not released. For emerging techniques there is often little data available as few field trials have taken place. The use of very mature techniques is well established and so there is often little recent data as research interest is limited.

3. Overview of acid-based techniques

Acid-based techniques are used to increase or restore fluid recovery from a production well or to increase flow from an injection well for oil and gas and geothermal applications. Using acid reduces near-wellbore damage or 'skin' which may occur during or after well operations. Wellbore damage can occur for a variety of reasons such as hydration or swelling of clay minerals, low-permeability mud-cakes, precipitation of scales and plugging by materials from drilling mud. The acid-based technique restores or increases the initial formation permeability and porosity. The main types of acidising operations are described below.

- 1. **Acid wash**: a wellbore acid treatment designed to remove scale or similar deposits from perforations and well-completion components. Acid-wash treatments generally do not include injection of treatment fluid into the reservoir formation (SCHLUMBERGER, 2021).
- 2. Acid squeeze: the application of pump pressure to force the treatment fluid into a planned treatment zone within the formation. In most cases, a squeeze treatment will be performed at downhole injection pressure below that of the formation fracture pressure and penetrate from 0.3m to 1.5m maximum in the formation (SCHLUMBERGER, 2021).
- 3. **Matrix acidising**: acid solution is injected into the formation in order to dissolve some of the minerals to recover the permeability of sandstones by removing well damage or 'skin', or to increase the permeability of carbonates near the wellbore by removing scale and/or by creating new irregularly shaped channels called wormholes (AL-MAHASNEH, et al., 2021).
- 4. **Acid fracturing**: aims to create new pathways or fractures in the formation to enhance flow. Fractures may be created mechanically first, by applying pressures greater than the formation fracture pressure, followed by injecting acid into fractures, or gelled acid may be used at higher pressure to create fractures (GUO, et al., 2017).
- 5. **Well soaking**: is a process in which formation damage can be removed by soaking the wellbore with mud acid, aromatic solvents or other chemicals depending on the type of damage (MALATE, et al., 1998).

Matrix acidising and acid fracturing are the techniques most commonly used for permeability enhancement and are the focus of this section.

Achieving a reliable long-term production increase from acidising requires a thorough understanding of the formation mineralogy (PORTIER, et al., 2007). Table 1 summarises characteristics of different well acid-based techniques.

Table 1: Characteristics of acid-based permeability enhancement operations – chemicals described in section 3.1 (CROWE, et al., 1992), (KHAMIS, 2016), (VAN HONG & BEN MAHMUD, 2018), (GOMEZ, 2006), (XU, et al., 2003), (MALATE, et al., 1998), (MALATE, et al., 1999), (PORTIER, et al., 2007) (ABDULLAH, et al., 2016), (HOUSEWORTH, 2016), (KRISTSANAPHAK, et al., 2010)

Operation	Duration of the treatment	Volume of acid treatment injected (m ³ or m ³ /s of open hole)	Chemical concentration	Treatment pressure compared with formation pressure	Penetration
Acid wash or 'maintenance'	Minutes	0.001 to 0.1m ³ /s	Acid 3 to18% Additives 2.6 %	Below	In and near wellbore
Acid squeeze	Minutes	~0.0125m³/s	Hydrochloric acid (HCl) 15 to 28 %	Below	Up to 1.5m
Matrix acidising	A few minutes (skin damage removal) to a few hours (full impact of spent acid after more than 24 h)	Up to 0.1m³/s	Acid 3 to18 % Additives 3 %	Below	0.3m in sandstone and may be up to 6m into carbonate
Acid fracturing	A few minutes to a few hours	0.016 to 0.25m³/s	Acid 3 to 28% Additives 9%	Above	~10 to 250m
Well soaking	Hours	0.1 to 0.13m³/s	HCl 10% + 5% hydrofluoric acid (HF)	Below	Near wellbore
Fluidic oscillation	Minutes to hours	Variable and non- invasive, can be used in conjunction with acid treatment: 0.45m ³ to 27m ³ + nitrogen	Similar to matrix acidising if used in combination	Below	Up to 1m

	(N) (1,982 to 2,831m ³)			
--	-------------------------------------	--	--	--

3.1. Fluids, chemicals and reactions

There are more than 200 different chemicals that can be used in acidising, with acid concentrations ranging from 5 to 28%, the remainder being water. If the acidising fluids are introduced into the well in the right proportions and order, and sufficient time and conditions are allowed for reactions to proceed, then the original acids are used up during the acidisation process and fully neutralised through downhole reactions. If not, the waste returns can still be highly acidic, in the range of pH 0 to 3.

Acid fluids can be classified into 3 types: mineral acids, organic acids and retarded acids. Different acids are applied to different rock types for different treatment purposes (GUO, et al., 2017). Mineral acids like hydrochloric (HCI) acid are commonly used for their low cost and fast action on carbonate rock types. They can be mixed with hydrofluoric (HF) acid for sandstone acidising. Organic acids are less corrosive and have a slower reaction time with the rock compared to mineral acids. This retards the action of acid, allowing greater penetration into the formation, and suits higher temperatures. Retarded acids comprise mineral and organic acids to form gelled and emulsified acids which will further retard the reaction. The most common acids, along with their advantages and limitations, are shown in Table 2.

Table 2: Most common acid types used in acid based permeability enhancement techniques and their advantages and limitations (GUO, et al., 2017), (KHAMIS, 2016), (GIROUD, et al., 2012), (PORTIER, et al., 2007), (ECONOMIDES & NOLTE, 2000), (BURGOS, et al., 2005)

Acid name	Туре	Advantage	Limitations
Hydrochloric, HCl	Mineral	Cost effective. Fast reaction with calcium carbonate (CaCO ₃) minerals. No impurities. Used for pre-flush in sandstones containing calcium carbonate.	Slow reaction with dolomite (CaMg(CO ₃) ₂). Does not dissolve quartz (SiO ₂) and clays in sandstone formations. Reaction can be too fast, limiting penetration, particularly at high temperatures (>120°C).
Hydrofluoric, HF (can be created by mixing HCI and		Dissolves most minerals to a certain extent.	Precipitation of calcium fluoride (CaF ₂) that plugs pore spaces. Only used in

ammonium fluoride (NH ₄ F) and injecting directly down the well or be created at greater depth from hydrolysis of fluoboric acid, HBF ₄)		Main reason for use is to dissolve clay. Used as retardant when produced at greater depth from HBF ₄ .	formations with less than 20% calcium carbonate (CaCO ₃). Complex reactions in sandstones. Need additives, corrosion inhibitor.
Acetic, CH ₃ COOH (also produced from hydrolysis of methyl acetate, C ₃ H ₆ O ₂)		Used with or without HCI (mainly to retard acid reaction. Typical concentrations: acetic 15% + formic 10%). Used for high	
Chloroacetic, CICH ₂ COOH	Organic	temperature wells and wells containing hydrogen sulphide (H ₂ S). Reversible reactions. Less corrosive. Better at high temperatures to avoid corrosion (above 200°C). Minimises potential asphaltene production from crude/acid contact.	More expensive. Salts can cause damage in formation and the well. May require special corrosion inhibitors. Formic acid strength should be limited to 9% to 10% to avoid calcium formate (Ca(HCOO) ₂) reprecipitation.
Citric, C ₆ H ₈ O ₇	Organic	Widely available and can also sequester soluble iron (Fe) to prevent polymer crosslinking.	As above and is less reactive.
Fluoboric, HBF₄	Mixture	Hydrolyses water, used to form HF in-situ and retard acid reaction for deeper formation penetration.	

HCl is the most commonly used acid for carbonate treatment as the main readily HClsoluble minerals are those found in carbonates - calcite, dolomite, and siderite (FeCO₃). This reaction also does not generate precipitates. Acid reaction with carbonates is usually considered 'non damaging' and the acid reaction provides gas assist as carbon dioxide (CO₂) is generated in the reaction. Gas assist improves fluid flowback and well recovery in reservoirs with low pressure (GARROUCH & JENNINGS Jr, 2017).

Sandstone acidising is routinely used to remove skin damage in oil and gas wells and in high temperature water-bearing sandstone reservoirs for geothermal wells. Siliceous (containing silica) minerals are dissolved by HF. Chemical reactions become significantly more complex with this acid as compared to HCI when carbonate minerals are present. Quartz, clays and feldspars are the main targets of sandstone acidising. The acid reactions can create precipitates that may cause plugging of voids, therefore further chemicals are used to mitigate their precipitation.

The most common primary and secondary chemical reactions in acid treatments are shown in Table 3.

Table 3: Chemical reactions for different	ent minerals treated v	with HCI or mud acid ((HCI+HF)
(GIROUD, et al., 2012)			

Mineral - (Acid(s) used)	Chemical reaction(s) with acid used
Calcite - (HCI)	$2\text{HCI} + \text{CaCO}_3 \rightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2$
Dolomite - (HCl)	$4\text{HCl} + \text{CaMg}(\text{CO}_3)_2 \rightarrow \text{CaCl}_2 + \text{MgCl}_2 + 2\text{H}_2\text{O} + 2\text{CO}_2$
Siderite - (HCI)	$2\text{HCI} + \text{FeCO}_3 \rightarrow \text{FeCI}_2 + \text{H2O} + \text{CO}_2$
Montmorillonite clay (Bentonite) - (HF/HCL)	Al ₄ Si ₈ O ₂₀ (OH) ₄ + 40HF + 4H ⁺ ↔ 4AlF ₂ + 8SiF ₄ (silicon tetrafluoride) + 24H ₂ O
Kaolinite clay - (HF/HCI)	Al₄Si₄O10(OH)8 + 24HF + 4H⁺ ↔ 4AlF2 + 4SiF4 + 18H2O
Illite clay - (HF/HCI)	K _{0.6} Mg _{0.25} Al _{2.3} Si _{3.5} O ₁₀ (OH) ₂ + 18.6HF + $3.4H^+ \leftrightarrow 0.6K^+ + 0.25Mg^{++} + 2.3AlF_2 + 3.5SiF_4 + 12H_2O$
Feldspar – (HCl/HF)	(Mg, Na or K) KAlSi ₃ O ₈ + 14HF + 2H ⁺ \leftrightarrow K ⁺ + AlF ₂ ⁺ + 3SiF ₄ + 8H ₂ O
Quartz (HCI/HF)	SiO₂ + 4HF ↔ SiF₄ + 2H₂O
	SiF ₄ + 2HF \leftrightarrow H ₂ SiF ₆ (fluosilicic acid)

Table 4 lists the quantities of different by-products of the reaction of 15% HCl with carbonates. Calcium chloride (CaCl₂) and magnesium chloride (MgCl₂) are highly soluble in spent acid (acid that is largely chemically reacted, neutralised, and converted to inert materials) and present no risk of reprecipitation.

Table 4: Example of quantities of by-products created by the reaction of 15% HCl and limestone (ECONOMIDES & NOLTE, 2000)

НСІ	CaCO ₃	CO ₂	H ₂ O	CaCl ₂
3,750 L	840kg	190m ³	0.155m ³	960kg

A range of aluminium (AI) complexes (SiF₆ ²⁻, AIF²⁺, AIF₂⁺, AIF₃, AIF₄⁻) can be produced from sandstone acidising when HF is used. At high temperatures (>90°C) they can combine with free sodium (Na), potassium (K) and calcium (Ca) to form amorphous silica (Si): sodium fluosilicate (Na₂SiF₆), sodium fluoaluminate (Na₃AIF₆), potassium fluosilicate (K₂SiF₆) and calcium fluosilicate (CaSiF₆).

Figure 1 shows the types of reactions occurring when a sandstone formation is exposed to mud acid (a mixture of HF and HCl acid). When the sandstone formation is treated with the mud acid, usually 3 groups of reactions take place. The primary reaction occurs close to the wellbore, which results in the formation of Al and Si fluorides. In these reactions, minerals are usually dissolved rapidly and without any precipitation. Away from the wellbore, the secondary reaction takes place in which these primary products react further to form silica gel (slow reaction), which is a precipitate (represented by down arrows on Figure 1). At a greater distance from the injection zone, additional silica gel precipitates due to tertiary reactions. The sandstone acidising treatment may fail due to the rapid kinetics of the secondary and tertiary reactions at higher temperatures.



Figure 1: Sandstone acidising reactions – x axis is scale-less distance from wellbore, y axis is vertical treated zone thickness (AL-HARTY, et al., 2008)

These precipitants have varying degrees of solubility and can reduce permeability and injectivity rate. In sandstone acidising of deep geothermal wells using HF (5%), modelled and field data showed that precipitation occurred from the wellbore up to a 20m radius around the well (XU, et al., 2003).

Much of the design of a sandstone acid treatment is aimed at removing any risk of precipitation (CROWE, et al., 1992) by introducing different stages in acidising (pre-flush, main stage, post flush) and preventing contamination to other formations by adding other chemicals (for example, diverters) and mechanical barriers (for example, packers). Service companies have their own proprietary formulations for acid treatments and will design tailored treatments and fluid options depending on the formation, well equipment and local context. Further chemical reactions in sandstone acidising are discussed in (HE, 2013).

Acid retardants

HCl and HF both react quickly with carbonates and silicates. To increase diffusivity, conductivity and penetration, it is often desirable to retard the acid reaction (PORTIER, et al., 2007). Table 5 lists the methods and chemicals used to slow the acidising process.

The 2 most common organic acids used in acidising treatments are acetic acid (CH₃COOH) and formic acid (HCOOH). Either can be used as a component in retardedacid systems to prevent clay swelling in the formation from high temperatures (GUO, et al., 2017).

An acid system applicable for moderate to deep penetration can also use an organic phosphonic acid complex (HEDP - hydroxyethylidene diphosphonic acid) instead of HCl to hydrolyse NH₄HF₂.

Table 5: Most common acid retardants and their characteristics (PORTIER, et al., 2007), (CROWE, et al., 1992)

Acid retardants	Action	Purpose
Oil-based solvents (for example, diesel)	Emulsifies aqueous acid. Most common retardant up to 150°C. N ₂ can be added for more homogenous dissolution pattern.	Slowing reaction.
Alcohol and gels	Dissolves acid in non-aqueous solution.	Increasing viscosity.
Gelling agents	Limited to lower temperature (degrades rapidly in acid solution at temperatures above 55°C). Gelling agents for thickening acid have been shown to be ineffective in geothermal liner completions.	Increasing viscosity of the resulting 'gelled acid', used to retard acid reaction rate in treatments such as acid fracturing (also decreasing leak-off ¹ rate) and matrix acidising.
Methyl acetate (C ₃ H ₆ O ₂) injection	Hydrolyses slowly at very high temperatures to produce acetic acid (CH ₃ COOH).	Slowing in-situ reaction, increasing depth of penetration in formation.
Fluoboric acid (HBF4)	Hydrolyses slowly, able to generate HF at greater depth of penetration and induces longer reaction HBF4 + H2O -> HBF3OH + HF.	Greater depth of penetration and maximum dissolution of fine sediments.

¹ A leak-off test is performed to test the strength or pressure containment of the cement shoe – part of a drilling operation – to help ensure that the new hole has been securely isolated from what has been cased off

Foams (N₂/CO₂)	Retards the acid reaction.	Etching occurs further from the wellbore.

Other chemicals

Chelating agents (or sequestering agents) are negatively charged organic molecules that can combine with metal ions. They are used to prevent precipitation of metal containing materials (for example, iron hydroxide (Fe(OH)₂), iron sulphide (FeS), aluminium Al³⁺) as the acid is spent in the formation at pH levels <4. They can also combine with calcium to remove or prevent scaling during acid treatments (FRENIER, et al., 2000). The dissolution mechanisms are difficult to study due to the complexities of the systems. (FREDD & FOGLER, 1998) and (ALMUBARAK & NG, 2017) review the chemical reactions and characteristics of these agents as well as necessary combinations with other chemicals to prevent formation of by-products such as hydrogen sulphide (H₂S).

Two types of chelating agents are polycarboxylic acids, including polyaminopolycarboxylic acids and phosphonates. Their characteristics are shown in Table 6. Chelating agents which are used for scale removal such as etheylenediaminetetraacetic acid and nitrilotriaetic acid (EDTA and NTA) do not usually perform dissolution as fast as strong mineral acids, but the slower rate allows a balanced path and a more evenly dissolved calcite along the wellbore and in all available fractures. Their volumes represent 0.3 to 0.6% of total treatment fluid volumes in carbonates and sandstones. Their utilisation and time of reaction in operations takes a few minutes to a few hours ((AL-MAHASNEH, et al., 2021), (BRANNON, et al., 1987)).

In geothermal wells, the most promising mineral dissolution agent for the Coso geothermal field (a rhylotic lava dome) in the USA was nitrilotriacetate (NTA). Operations lasted 4 hours to give the chelating agent time to act on the problematic calcite. The milky brine produced was completely complexed with calcium (calcium formed ion couplets with anions such as bicarbonate and/or citrate) (PORTIER, et al., 2007).

Diverters ensure a good sweep efficiency or divert flow from high permeability zones into low permeability zones (preventing acids from taking the path of least resistance instead of targeting the zone of damage or formation of interest). Effective acid diversion also reduces acid volumes needed (McLEOD, 2017). Diverters are classified as mechanical, chemical or particulate. Their applicability depends on the specific reservoir conditions.

Diverting agents should ideally be either degradable or partially soluble in the produced oil or water to prevent them from impeding the flow of fluids from the reservoir into the wellbore once the treatment is completed. Before diverters are used in the field, they must be tested in lab conditions which simulate the specific field conditions. A degradation test is used to examine the ability of the diverter to retain integrity during pumping time but fully degrade after a few hours. The compatibility test is conducted to ensure that no

precipitation will occur when diverters come into contact with formation fluids. A fluid loss test is used to ensure the diverters can plug a conductive slot at an elevated temperature (ALJAWAD & ALJULAIH, 2019).

Table 6: Most common chelating agents and their characteristics (FREDD & FOGLER, 1998), (ALMUBARAK & NG, 2017), (PORTIER, et al., 2007) (FRENIER, et al., 2000), (AL-MAHASNEH, et al., 2021)

Chelating agents	Characteristics
EDTA (Ethylenediaminetetraacetic	Work better than citric/acetic acid
acids)	 Less thermally stable than NTA, maximum temperature 200°C
	Not readily biodegradable in lab tests
	Low solubility in HCI
NTA (Nitrilotriacetic acid)	 Can be used at temperatures as high as 290°
	 Not as stable as EDTA or DTPA for iron
	 Soluble and biodegradable but potentially carcinogenic
DTPA (diethylenetriamine- pentaacetic acids)	 Same family as EDTA, more effective at removing barium sulphate scaling/deposits (BaSO₄)
HEDTA (hydroxyethyl- enediaminetriacetic acids)	 Less thermally stable than NTA, maximum temperature 200°C
	 Controls iron precipitation to at least 150°C
	High solubility of salts in acid over wide pH range
	Not biodegradable
HEIDA (Hydroxyothyliminodiacotic	More rapidly biodegradable than NTA
acid)	 Controls iron precipitation to at least 150°C
	High solubility of salts in acid over wide pH range
	Not as effective as HEDTA in all conditions

Organic clay acid for high	 Stabilises clays and fines without the adverse effects
temperature (OCA-HT)	of conventional acid systems
	Combats sludging

The most commonly used diverter is oil soluble resin (OSR) which quickly dissolves in produced oil after treatment. Acting as a particulate diverter, sodium benzoate salt in HCI will create benzoic acid which is soluble in water and will be dissolved in the injection water with added surfactants (ECONOMIDES & NOLTE, 2000). Foamed acid is a better means of diversion in gas wells as solid diverters are difficult to flush from the well.

The term 'self-diverting acid' can refer to a mixture of HCI with a gelling agent and a pH sensitive crosslinker. It was originally developed for acid fracturing but is also used in matrix acidising. These are better for fractured formations and in long, open intervals (ECONOMIDES & NOLTE, 2000).

Chemicals used in diverting agents and a list of other common substances used in acidbased permeability enhancement techniques is found in Table 7.

Table 7: Chemical additives and substances used in acid based permeability enhancement techniques and examples of volumes used (CZUPSKI, et al., 2020), (AL-MAHASNEH, et al., 2021), (ALMUBARAK, et al., 2017), (BRANNON, et al., 1987), (PORTIER, et al., 2007), (BURGOS, et al., 2005), (BUIJSE & GLASBERGEN, 2005), (TAMALMANI & HUSIN, 2020), (ECONOMIDES, et al., 2013) (KAHRILAS, et al., 2015))

Туре		Purpose	Concentration	
Diverting agent	Nitrogen foam, oil soluble resin, organic resin, liquid polymer, benzoic acid, wax beads, rock salt, naphthalene (not used in water injection wells), ammonium chloride + hydroxyethylcellulose (HEC).	See section above.	0.1 to 3% depending on formation permeability and product used.	
Chelating agents	See section above.	See section above.	~0.3 to 0.6%.	
Solvent	Xylene.	Used in pre-flush to clean or displace crude oil.	0.005m³/s.	

Corrosion inhibitors	Isopropanol acetaldehyde, propargyl alcohol, pyridine, c10- c16 alkyl derivatives, plant-based inorganic and organic (flavonoids, alkaloids and by- products of plants).	Pipe corrosion prevention by diluted acid. Always necessary if water is >63% in weight in acid composition.	~0.1 to 0.4%.
Iron (Fe₂⁺) control	Citric acid, thioglycolic acid, chelatants.	Prevent precipitation of metal oxides and formation of amorphous silica residue.	See chelatants.
Biocide	Glutaraldehyde, 2,2- dibromo-3- nitrilopropionamide (DBNPA).	Bacterial control.	0.0005 to 0.05%.
Gelling agent	Guar/xanthan gum (up to 110°C), or synthetic polymer like hydroxyethyl cellulose (HEC) up to 230°C.	Thickens to suspend proppants. Controls dominant wormhole growth in matrix acidising and limit acid leak off in acid fracturing.	2%.
Clay stabiliser/ control	Polyquaternary amine. Ammonium chloride (NH₄CI). Potassium chloride.	Most effective when added to over-flush stage only. Can be used in pre- flush to displace clay from contact with HCI/HF.	~0.02 to 3%.
Surfactant	Ethanol, isopropyl alcohol, 20- butoxyethanol. Natural biogenic surfactant (WAN, 2017).	Decreases surface tension to increase recovery.	~0.05 to 0.5%.

Mutual solvent	Ethylene glycol monobutyl ether (EGMBE).	Improves clean-up and wettability of particles in sandstones. Improves solubility of corrosion inhibitors in spent acid.	10% during over-flush.
	alcohol).		25% max.
	Isopropyl alcohol (IPA).		20% max.
Proppant	Silica, quartz, sand, ceramics, sintered bauxite, hydroxypropyl polymer gel (stable at high temperature) and calcium carbonate.	Keeps fractures open if used in combination with acid fracturing. Can act as fluid loss additives in acid fracturing.	1 to 3%.
Breaker	Ammonium persulfate, magnesium peroxide.	Promotes breakdown of gel polymer.	0.0023kg/m ³ .
Oxygen and hydrogen sulphide (H ₂ S) scavenger	Ammonium bisulphide. Chlorites/chlorine dioxide.	Removes oxygen from fluid to reduce pipe corrosion. Prevent iron sulphide precipitation.	
Crosslinker	Borate salts, FeCl₃.	Maximises fluid viscosity at high temperatures.	~0.45%.
pH adjustment	Potassium, sodium hydroxide, carbonate.	Maintain efficiency of other compounds like crosslinker.	
Nitrogen		Add to acid treatment to clean the well, use as diverter, displace treatment chemicals out or into formation in final flush.	

4. Matrix acidising

Matrix acidising (also called 'matrix treatment', 'maintenance acidising' or 'routine acidising' (LONG, et al., 2015) is a technique to pump acid and other treatment fluids below the fracture pressure of formations. Acid penetration is commonly up to 0.3m in sandstone and up to 6m into carbonate. The objectives of matrix acidising are to:

- remove skin damage that restricts injectivity, production due to near-wellbore changes in permeability, plugging of perforations or gravel packs (caused by mud and cement damage, mechanical damage from drilling, damage from perforating guns, scale and siliceous particles deposition, amorphous silica in geothermal wells, paraffin and asphaltene depositions, water blocks, gas blocks, acid sludges and emulsions)
- enhance permeability and injectivity into the formation through matrix dissolution and the creation of wormholes, connecting the formation to the wellbore (GUO, et al., 2017), (HEGAZY, et al., 2009), (KHAMIS, 2016)

4.1. Technology application

Matrix acidising is widely used and was initially applied in carbonate reservoirs to enhance permeability in limestones, dolomite formations or formations presenting above 85% acid solubility. It has been extended to more complex mineralogy like sandstones even though results can vary. It is a relatively simple permeability enhancing technique and is a cost-effective method to significantly improve the well productivity (GOMEZ, 2006).

In sandstones, matrix treatments restore or improve the natural formation permeability around the wellbore by removing formation damage, by dissolving material plugging the pores or by enlarging the pore spaces. In carbonates, matrix treatment creates new, highly conductive channels (wormholes) that bypass damage. Because of these differences, the selection criteria for the treating fluid are also distinct (SCHLUMBERGER, 2021).

4.2. Fluids and chemicals

Fluids and chemicals for matrix acidising are reviewed in section 3.1.

4.3. Operational parameters

Treatment preparation and results depend on many factors. There is no single model to estimate the depth of acid penetration, which can result in process inaccuracy (KHAMIS, 2016).

Infrastructure and surface operations

A rubber-lined tank is used to store concentrated acid on the wellsite. As some acid additives attack or degrade rubber, acid treatment fluids are not generally mixed or transported in acid tanks, but are instead mixed in special batch tanks or continuously mixed as the treatment is pumped (SCHLUMBERGER, 2021), (KHAMIS, 2016) (see Figure 2).



Figure 2: Left: Schematic representation of matrix acidising surface set-up, with diverters used to target treatment volumes into different geological zones (red) (ABDOLLAHI, et al., 2021). Right: A CT scan of pathways created in a 0.5 x 0.4 m carbonate block in laboratory conditions, (AIDAGULOV, et al., 2018)

Separate tanks or containers are used to isolate the initial produced fluids (spent acid and produced water). The spent acid will typically have a pH of 2 to 3 or greater, approaching neutral pH. These fluids can be further neutralised to a pH >4.5 before they are introduced to the produced water treatment equipment, if necessary. Once neutralised, the spent acid and produced water can be handled with other produced water at the production site and be used for reinjection.

Process design and sequences

The design process is a systematic approach to estimate and calculate injection pressure and rate, volumes, and concentrations with regards to the formation characteristics, well condition and desired effect.

The total volume or weight of water and chemicals used in matrix acidising are usually lower than in acid fracturing. Treatments between 30,000 and 300,000kg for matrix acidising are common, compared with 700,000kg for acid fracturing (ABDULLAH, et al., 2016).

Carbonate acidising

Limestone and dolomite formations can easily be stimulated with acid formulations. Unlike sandstone acidising, the goal of carbonate acidising is usually to bypass the damage rather than dissolve it.

In carbonate treatments, reservoir temperature, pumping rate and fluid type become more significant because these parameters directly affect the reactivity of the treating fluid with the reservoir rock (GOMEZ, 2006), (PORTIER, et al., 2007), (BRANNON, et al., 1987).

HCl is typically used for carbonate acidising with a minimum 15 to 28% HCl (ABDOLLAHI, et al., 2021). However, it is not suitable to use HCl for some field conditions, such as where there are incompatible crudes, low temperatures, high temperatures, risk of corrosion, sour conditions (high concentrations of H₂S) and in high porosity formations. In these conditions, other formulations are used, such as emulsions or organic acids. Suspending agents or solvents can also be used if required by the type of damage. The high reactivity of acid with limestones and high-temperature dolomites results in the creation of 'wormholes', which considerably increase the apparent permeability around the wellbore. When wormholes extend beyond the damaged zone or connect with natural fissures in the formation, a negative skin effect is obtained². As in sandstone acidising, proper placement of the acid over the whole interval is necessary for successful treatment and usually requires using placement techniques. Foam diversion and self-diverting acid are 2 methods that are increasingly used, with good results (ECONOMIDES & NOLTE, 2000). The optimum injection volumes and rates in carbonates is the rate at which the dominant wormholes will be formed (KHAMIS, 2016).

A carbonate treatment consists of alternating stages of the main fluid and diverter. Characteristics of the treatments for carbonate are summarised in Table 8.

Steps	Volumes (m³ or m³/s)	Application	Chemicals	
1. Wellbore cleanout or 'pickling'	10'sm³.	To mainly remove the tubing mill scale and rust, and dissolve wellbore	10 to 15% HCl + corrosion inhibitors, mutual	

Table 8: Different treatment steps of carbonate matrix acidis	ing (GARROUCH & JENNINGS
Jr, 2017)	

² Negative skin occurs when there is a localised increase in permeability in the vicinity of the wellbore

		deposits. Corrosion inhibitors may easily adhere on cleaned tubing surfaces, minimising acid reaction with the tubulars during the main acid treatment stage.	solvents (chemical additives that are soluble in oil, water and acid- based treatment fluids), surfactants and iron control additives.
2. Pre-flush	0.01 to 0.04m³/s.	To condition formation to receive acid treatment.	Acid and additives compatible with the reservoir (see Table 7).
3. Main acid treatment	0.01 to 0.05m ³ /s. Depends on damage and acid used (use of organic acid requires larger volumes).	To induce wormholes.	HCI 15 to 28%. Usually formic 10% or acetic 10% for high temperature borehole >200°C. Mix of HCI and organic acid. Gelled acid. Nitrogen can be added.
4. Diverter	5m ³ .	To ensure uniform injection profile. Most challenging to define which diversion.	For example, benzoic acid flakes.
Repeat 1, 2, or repeat 1,2, 3			
5. Over-flush	0.01 to 0.03m³/s.	Brine or seawater to displace insoluble reactant products completely into formation and break down any plugging material.	

6. Displacement	For complete displacement of over- flush fluids into formation and facilitate fluids, spent acid, gel residuals flow- back.	Nitrogen is recommended for low-pressure wells with a pressure gradient below 0.46psi/ft (ECONOMIDES & NOLTE, 2000).

Sandstone acidising

For sandstone treatments, knowledge of the extent, type of damage, location, origin, reservoir mineralogy (petrographic study) and compatibility of the treating fluid with the formation are especially important. Live HF acid usually penetrates only about 0.08 to 0.30m into the sandstone before spending. If acid can easily reach nearby plugging solids, small volumes of 300 to 600L/m of HF-type acid can dissolve this damage. However, with more severe damage, more time and volume is needed to reach the plugging solids (McLEOD, 2017).

In terms of composition, a typical 5% HCl to 3% HF mud acid solution can be prepared for sandstone acidising. The cleaner the sandstone (lower silt and clay content) and the higher the permeability (Table 9), the lower the HCl/HF ratio, and the more aggressive the treatment can be. Typically, the HCl/HF ratio is either 4/1, 6/1, or 9/1. A higher volume of weak acid must be pumped to obtain the same results as a smaller volume of a stronger acid. This is an important consideration when designing treatments for environmentally sensitive areas, where disposing of spent acids can create problems (PORTIER, et al., 2007).

Table 9: General acid composition and concentrations guidelines for the chemicaltreatment of sandstones according to the mineralogy, permeability and temperature of thetreated formation (PORTIER, et al., 2007)

Temp	Rock mineralogy (%)	eralogy (%) Roc >100md		ck permeability			
(deg C)				20 to 100md		<20md	
		HCI (%)	HF (%)	HCI (%)	HF (%)	HCI (%)	HF (%)
<100	High quartz (>80), low clay (<10)	12	3	10	2	6	1.5
	High clay (>10), low silt (<10)	7.5	3	6	1	4	0.5

	High clay (>10), high silt (>10)	10	1.5	8	1	6	0.5
	Low clay (<10), high silt (>10)	12	1.5	10	1	8	0.5
>100	High quartz (>80), low clay (<10)	10	2	6	1.5	6	1
	High clay (>10), low silt (<10)	6	1	4	0.5	4	0.5
	High clay (>10), high silt (>10)	8	1	6	0.5	6	0.5
	Low clay (<10), high silt (>10)	10	1	8	0.5	8	0.5

Further acid composition and concentration guidelines relating to mineralogy, temperature and depth are given by (KALFAYAN & METCALF, 2000).

Post-acidising problems with migration of fines in sandstones can be reduced by bringing a well on to production slowly after acidising, that is, increasing flow gradually (for example, over one to two weeks), rather than maximising return production right away (PORTIER, et al., 2007).

In general, sandstone matrix acidising follows similar steps to carbonate treatment but is chemically adjusted due to the low solubility of minerals and complex reactions. Characteristics of the treatments for sandstones are summarised in Table 10.

Table 10: Different treatment steps of sandstone matrix acidising (PORTIER, et al., 2007) (VAN HONG & BEN MAHMUD, 2018) (KALFAYAN & METCALF, 2000) (BRANNON, et al., 1987) (KALYA & BALAKOTAIAH, 2007) (ECONOMIDES & NOLTE, 2000)

Steps	Volume (m³ or m³/s)	Application	Chemicals	
1. Optional well soaking	~ 8m ³ .	Removes scaling in geothermal wells behind liners.	Mainly acid composition.	
2. Crude displacement	0.05m³/s.	Prevents oil sludging by acid.	Xylene, toluene.	
3. Formation water displacement		Prevents scale deposition from HCO ₃ and SO ₄ content.	Sandstone: 3% NH₄Cl. If carbonate present: 2% KCl and 3% NaCl.	

4. Acetic acid stage	0.05 to 0.02m³/s.		10% acetic acid.
5. Pre-flush	0.01 to 0.04m ³ /s.	Removes asphaltenes. In sandstones, displaces the formation brines, usually containing K, Na, or Ca ions, away from the wellbore so there will be no mixing with HF acids and decreases the probability of precipitates (see section on chemicals). Dissolves as much of the calcareous material as possible with HCl, prior to injection of the HF acid to minimise CaF ₂ (calcium fluoride) precipitation. Ammonium chloride (NH ₄ Cl) can be used in brine to displace Na, K, or Ca in clays and prevent contact with mud acid (affect 0.75m from the wellbore).	5% NH₄CL, 3-15% HCI.
6. Main flush	0.005 to 0.05m³/s.	Dissolves the silicates, quartz, feldspar, clay as well as undissolved carbonates after pre-flush.	0 to 3% HF and 3 to 13.5% HCI. N₂ 50%, acid 50%.
7. Over-flush	0.01 to 0.03 m³/s.	Maintaining low pH to spend acid deeper in the formation. To flush spent acid to keep the wettability in its original state and clean the formation. Minimum volume should be volume of the tubing plus twice the volume of the well bore below the tubing.	3 to 7% NH ₄ Cl, N ₂ (gas wells following a weak acid or water over-flush, 10s to 100s of thousands of standard cubic feet (300-3,000m ³), diesel (oil wells), 3 to10% HCl, 15% acetic acid, 3% ammonium chloride, xylene.

8. Diverter	5m ³ (for example, benzoic acid flakes).	When long intervals are treated, diversion stages are pumped after the over-flush and before the next stage of pre-flush. Some diversion techniques (for example, ball sealers, rock salt) are not suitable for use in sandstone acidising.	
Repeat steps 2-7 if needed			
9. Final flush		Same as over-flush.	3 to 7% NH₄Cl, diesel, HCl.

Coiled tubing (CT)

CT is often used to mechanically place treating fluids and is most useful in matrix and wellbore treatment (PORTIER, et al., 2007). CT can be cleaned of rust, scale and other deposits, a process known as 'pickling' by 10% HCl to provide a clean fluid conduit in the production tubing. Pressure variations during acid injection can be accurately monitored with a coiled tubing/annular pressure recorder to optimise chemical concentration and volumes used during the treatment (BRANNON, et al., 1987). Treatment fluids are injected and maintained under pressure inside the reservoir for a period of time, after which the well is swabbed and returned to production.

Flowback and clean-up techniques

Flowback prevents solid precipitation that could cause plugging immediately after the overflush. The additives that are injected are produced back at the surface (in water or oil) when the well is returned to production after the treatment.

The majority of flowback and produced water is composed of naturally occurring formation brines. It is unknown how much of the acidising chemicals are returned to the surface, but recent data submitted by operators in the US shows that the volume of recovered fluids collected after matrix acidising is 50 to 60% (LONG, et al., 2015).

Geothermal applications

Acid treatments are used to periodically remove scale from geothermal wells. This is used extensively in geothermal fields in the Philippines, El Salvador, and in the USA. The well injectivity of treated reservoirs increased by a factor of 2 to 10 (PORTIER, et al., 2007). At the Larderello geothermal field in Italy, field tests preceded by various laboratory tests

have shown good results on 5 deep wells for reservoir rocks composed of phyllites, hornfels and granites.

Treatment volumes, injection rates, acid placement techniques, acid system selection and evaluation of the results all follow the same criteria as for oil wells (Table 11). The important difference for geothermal wells is the formation temperature. High temperatures reduce the efficiency of corrosion inhibitors and increase the acid/rock reaction rate. The high acid/rock reaction rate requires the use of a retarded acid system to ensure acid will not all be spent immediately next to the wellbore but will penetrate deeper into the formation. Protecting the steel casing against corrosion is a challenge. This requires careful selection of acid fluids and inhibitors, while cooling the well by injecting a large volume of water pre-flush (PORTIER, et al., 2007).

Table 11: Example of fluid acidisation on a 600m sandstone section of a geothermal well, in
addition to a corrosion inhibitor when needed (GIROUD, et al., 2012)

Fluid	Volume m ³	Duration	Flow rate m ³ /s
Cold fresh water to cool down the well	2,000		0.012, 0.022, 0.028
Pre flush: Deoxygenated water with 15% HCI	25	15 min	0.022
Main flush: Regular mud acid at 12/3 (wt %) (12% HCI, 3% HF)	200	2.5 hrs	0.025
Post flush: Cold deoxygenated water	2,000		22, 28

4.4. Subsurface impact

Wormholing in carbonates

Wormholing in carbonate rocks is a complex 3-D phenomenon. Mechanical models aim to predict the parameters for optimum injection rate to obtain a radial dissolution pattern (KALYA & BALAKOTAIAH, 2007).

(GDANSKY, 1999) and (BUIJSE & GLASBERGEN, 2005) used laboratory experiments to develop models for the effect of different acid volumes and application rates on wormhole development in carbonates for different permeability, porosity, temperature, skin damage and oil viscosity. (GLASBERGEN, et al., 2005) performed field validation of the existing

models. Using a conventional volume of treatment fluid (~18m³), penetration of the wormholes was a maximum of 2m. Longer wormholes can be created with viscous additives or acid jetting.

Effect of acidising on porosity and permeability

The effect of acidising on porosity and permeability varies and remains an inexact science, particularly for sandstone acidising. (KALFAYAN & METCALF, 2000) reported a 100% permeability increase after a successful treatment on sandstone with organic acid and 6% hydrofluoric acid (HF).

4.5. Geological applicability to England

Matrix acidising is applicable to most formations in England to reduce skin factor or to increase permeability. Geological formations that may contain oil and gas deposits, such as the Bridport Sand Formation contain calcareous layers. The fluvial Sherwood Sandstone Group contains various types of clay and carbonate cements which will require specific sandstone acidising formulations for oil and gas to be recovered efficiently. Limestones of the Cornbrash Formation and Great Oolite Group may have more straightforward carbonate compositions.

Matrix acidising can also be used for geothermal wells in sedimentary rocks or granite (BUSBY, et al., 2011). Elevated temperatures are observed in eastern and southern England attributed to the thicker Permo-Triassic-aged sandstones and thermal blanketing of Triassic and Jurassic argillaceous rocks. Acid treatment composition would have to be tailored to high temperatures and deeper reservoirs (for example, >3,000m and >100°C in Cornwall).

4.6. Environmental impact

A summary of the environmental impacts for matrix acidising is shown in Table 12. The main environmental challenges for acidising techniques result from complex waste products and the chemicals used. The risk of each chemical used depends on the environmental exposure, toxicity, fate and transport, transformation, and cumulative effects with other chemicals. There is little information available for many of these factors. Given that the migration extent of acids in the subsurface is limited by relatively rapid reactions, the most likely source of water contamination comes from improper handling of wastewater at the surface.

(ABDULLAH, et al., 2016) and (SUN, et al., 2019) outline potential environmental risks related to fluids, in particular for surface and groundwater contamination:

- Handling of chemicals (including hydrocarbons used in permeability enhancement), flowback and produced water that might include brine and naturally occurring radioactive material (NORM) from the geological formation, including spills during mixing, onsite treatment or transport to off-site facilities and leaks from surface infrastructure. This could also result in effects on human health due to chemical exposure.
- Reusing or disposing of treated wastewater: poorly sited disposal, failure to ensure all acids are neutralised prior to discharge, poor wastewater treatment.

The identification, toxicity, biodegradability and bioaccumulation potential of many of the chemicals used in well maintenance and permeability enhancement using acid treatment have been discussed in detail in an independent assessment in California (LONG, et al., 2015) and by (ABDULLAH, et al., 2016).

In addition to wastewater handling hazards, there are potential contamination pathways in the subsurface from matrix acidising, including fluids leaking through the well casing. It is very unlikely for wormhole pathways to reach an aquifer because they do not extend far from the wellbore (ABDULLAH, et al., 2016).

Source	Pathway	Receptor
Acids	Surface spills.	Groundwater, surface water, personnel.
	Lateral connections with aquifers (depends on geological setting).	Deep aquifers, groundwater.
	Well integrity (cement quality, condition of casing and tubing and the impact of corrosive fluids).	Groundwater.

Table 12: Summary of potential environmental impacts for matrix acidising
	Existing permeable fractures.	Groundwater.
Waste (reaction products)	Disposal.	Surface water,
	Handling, spills.	groundwater, personnel.
	Existing permeable	
	fractures.	
	Lateral connections	
	(depends on geological	
	setting).	

4.7. Knowledge gaps

Models for reactive transport modelling to prevent precipitation and silica scaling in acidising geothermal wells are being improved and will be calibrated in the field (XU, et al., 2003). (SHAFIQ & MAHMUD, 2017) provide a table of acid systems which are still being researched to address the limitations of matrix acidising (that is, expensive at high temperatures, fast spending of acid, lack of penetration, precipitation reactions due to complex mineralogy, corrosion of pipelines).

Improving the quantification of the acid-rock reactions and fracture presence would help further assess the fate of what is not produced back to surface.

5. Acid fracturing

Acid fracturing is also called 'fracture acidising', 'acid fracking' or 'acid-fracture treatment'. Fracturing treatments are defined as treatments in which the injection rate of the fluid is larger than the fluid leak-off into the matrix of the formation. This increases the pressure beyond the fracture strength of the rock.

The aim of acid fracturing is to change the future flow pattern of the reservoir from radial to linear and to effectively create new pathways that increase production. Due to the acid distribution in the fracture and rock heterogeneity, the reaction and etching on rock surfaces can be uneven, which leads to small, open channels after fracture closure. These channels can provide higher conductivity compared to the original matrix permeability, as shown in Figure 3.



Figure 3: Conductivity in acid fractures (GUO, et al., 2017)

5.1. Technology application

Acid fracturing has increased in use since the 1990s and is widely used for enhancing permeability of limestone, dolomite or formations presenting more than 85% acid solubility. It is suitable for formations with low permeability (< 8md).

The technique can also be applied in shale gas formations when the content of carbonate minerals in shale is between 10% and 30%. If the shale has a high carbonate mineral content (>30%), the effect of acid-etching is not easily controlled, so the technique of acid fracturing should be carried out with caution (GUO, et al., 2017). Shale acid fracturing is discussed in more detail in (ALJAWAD & ALJULAIH, 2019).

5.2. Fluids and chemicals

Fluid and chemicals used for acid fracturing are the same as those used for other acidbased techniques and are reviewed in section 3.1.

5.3. Operational parameters

Infrastructure and surface operations

In general, hydraulic and acid fracture fluids are broadly similar in terms of chemical composition and surface set-up (Figure 4). The difference in infrastructure between matrix acidising and acid fracturing is that fracturing requires higher volumes of treatment fluid and therefore more vehicles, and the addition of a fracturing blender – a sealed tank in which the acid is mixed with other fluids.



Figure 4: Fracturing equipment surface set-up (ICOTA, 2022)

Process design and sequences

Acid fracturing is applied by pumping a viscous pad (a viscous nonreactive fluid or 'pad') that creates the fractures which are then acidised. Acid is injected into the newly opened fractures and etches their surfaces. Minerals sealing the fractures (scale) are dissolved and removed. Unlike hydraulic fracturing, proppants are not used to keep fractures open. Instead, when pumping stops, fractures will close but the etching and dissolution have generated new pathways along the existing fracture.

The conductivity of acid fractures depends on the remaining open channels, which strongly depends on acid distribution in the fractures, acid penetration depth, acid leak-off through fractures' walls and reaction rate of acid with carbonate rock. To achieve better performance of acid fracturing treatments the acid needs to be allowed to penetrate deeply into the fractures with enough time for the acid to react with fracture surfaces and acid leak-off through fracture surfaces controlled (GUO, et al., 2017).

Fractures can also be created when gelled acids are used. Some related techniques, like hydro jet fracture acidising (or acid jetting) with squeeze, may involve a mix of acid fracturing and matrix acidising. The fluids and chemicals used are similar in all applications.

The design of any acid treatment needs a thorough evaluation of the characteristics of the targeted formation. The composition, permeability, porosity, and strength of the rock must be determined, along with formation temperature and pressure and the properties of reservoir fluids.

A common mixture of 15% HCl and 10% acetic acid is used for acid fracturing carbonates with added corrosion inhibitors (~0.4%). Gelled organic acid will also contain gelling polymer (2%), crosslinker (0.45%), and breaker (0.2%) (BUIJSE & GLASBERGEN, 2005). Additives are further described in Table 7. If the acid used is too weak it will generate dissolved CO₂ and carbonic acid (H₂CO₃) which increases pH and does not allow the acid to spend (BURGOS, et al., 2005).

The different acid fracture fluid systems are:

- HCl based: straight, crosslinked gel, linear gel, emulsified, VES (viscoelastic surfactant-based acid)
- foamed/energised acid
- organic acid

Each have specific advantages and limitations which are discussed in (ALJAWAD & ALJULAIH, 2019).

Acid is pumped at high rates, usually between 0.01 and 0.05 m³/s and up to 0.2 to 0.25m³/s in open hole conditions (PORTIER, et al., 2007), (BUIJSE & GLASBERGEN, 2005). Acid fracturing treatments comprise several stages. The duration of the whole treatment varies, but averages 30 minutes to 1 hour. Typical acid fracturing pumping schedules for different formation types are shown in Table 13 and Table 14.

Table 13: Typical acid fracturing pumping schedule for oil bearing limestones (BURGOSand others, 2005)

Stage	Fluid	Volume (m³)	Cumulative volume (m³)	Pump rate (m³/s)
1	Organic acid	0.8	0.8	0.005
2	Linear gel (cooldown)	22.3	23.1	0.005 to 0.048
3	Crosslinked pad	31.8	54.9	0.048
4	Gelled organic acid	35.0	89.9	0.048
5	Crosslinked pad	15.9	105.7	0.048
6	Gelled organic acid	31.8	140.7	0.048
7	Crosslinked pad	15.9	156.6	0.048
8	Gelled organic acid	35.0	191.6	0.048
9	Linear gel	31.8	223.4	0.048 to 0.053
10	Organic acid	27.0	250.4	0.011 to 0.053
11	Organic acid	6.4	256.8	0.011
12	Treatment water (overflush)	8.0	264.8	0.011
13	Linear gel (displacement)	25.6	290.3	0.011

Table 14: Typical acid fracturing pumping schedule for dolomites (GLASBERGEN and
others, 2005)

Stage	Stage Fluid name		Pump rate	Diverter	Pump time
		volume (m ³)	(m³/s)	balls	(s)
1	Seawater	5.5	0.001	-	5241
2	HCI 22 %	63.7	0.016	-	3819
3	HCI 22 %	23.9	0.030	50	770
4	Emulsified acid 22 %	63.8	0.046	133	1400
5	HCI 22 %	23.6	0.048	-	489
6	Emulsified acid 22 %	64.0	0.047	100	1360
7	HCL 22 %	23.9	0.042	-	561
8	Emulsified acid 22 %	63.8	0.038	100	1641
9	HCL 22 %	23.8	0.035	-	658
10	Emulsified acid 22 %	63.8	0.034	100	1850
11	HCI 22 %	24.0	0.034	-	691
12	Emulsified acid 22 %	63.5	0.044	100	1418
13	HCI 22 %	79.4	0.041	125	1918
14	Diesel	60.8	0.038	-	1591
15	15 Diesel 4.7		0.042	-	111
16 Shut-in		0	0	-	900

Simulations show that the highest production following acid fracturing corresponds with the greatest penetration. Deeper penetration of an etched fracture and prevention of premature wormholing (and early spending of acid) can be achieved by increasing the acid volume, modifying the injection rate and acid concentration, including the pad fluid and/or applying retardation methods using different acid systems (PORTIER, et al., 2007), (ECONOMIDES & NOLTE, 2000).

In larger open-hole conditions, acid diversion is important, otherwise only the interval which breaks down or fractures first will be treated. Diversion can be achieved with packers, viscous pre-flush or chemically retarded acid for selective etching. Proppant-like sintered bauxite, hydroxypropyl polymer gel (stable at high temperature) and CaCO₃ can also be added to prevent fluid loss (PORTIER, et al., 2007).

5.4. Subsurface impact

The aim of this technique is to produce a fracture that is continuously conductive from the wellbore all the way to the tip of the fracture to provide maximum production enhancement from the surrounding rock. In deeper rocks, a vertical fracture forms which then extends laterally along the path of least resistance. If the pump rate exceeds the rate at which fluid leaks off through the fracture faces, and pressure remains above parting pressure at the fracture tip, the fracture continues to extend horizontally in both directions from the wellbore.

One of the most important parameters that affects fracture conductivity that can be adjusted to optimise the treatment design is the injection rate (UGURSAL, et al., 2018). Models (for example, Schlumberger 'FracCade') are used to evaluate the effect of injection rate and are calibrated by pre-injectivity breakdown tests in the field (incremental testing of the rock breakdown pressure). Many acid fracture models exist and are listed in (ALJAWAD & ALJULAIH, 2019).

Different fracture length and conductivities can be produced using different acid compositions, volumes and injection rates. A typical range of fracture length that preserve conductivity is between 10 and 100m for a tight³ formation (1md permeability) (ECONOMIDES & NOLTE, 2000).

³ Natural gas which is produced from reservoir rocks with low permeability



Figure 5: Simulated etched width for 13/9% acetic/formic acid and for 15% HCl in a carbonate formation. The acid volumes are such that the total carbonate dissolving capacity of the 2 acid systems are the same (BURGOS, et al., 2005).

When a natural fracture system exists within the formation it is more difficult to predict fracture distribution across the reservoir (SKINNER, 2021).

Geophysical logs (for example, dipole sonic, microseismic and tilt meters) as well as indirect monitoring of pressure, temperature (in vertical wells) and production tests can be used to monitor fracture location in the well, fracture direction, length and height in the stimulated reservoir, and overlying cap rock integrity following a fracturing simulation (WEITAN, et al., 2007) (KING, 2012).

Fracturing provides an improved delivery system to get fluids produced from the formation into the wellbore. Therefore, enhanced permeability refers to enhanced fracture conductivity and improved bulk permeability of the formation.

5.5. Geological applicability to England

In England, acid fracturing could be used to increase permeability in most carbonate fields for oil and gas production (for example, the Jurassic-aged Cornbrash Formation limestones in the Wessex basin) or potentially for geothermal applications (for example, the Carboniferous-aged limestones in the East Midlands).

5.6. Environmental impact

In addition to wastewater handling hazards and well integrity issues (reviewed in section 4.6 for matrix acidising), there are other potential contamination pathways in the subsurface from acid fracturing. They include (ABDULLAH, et al., 2016):

- Fracture formation: potential pathway for acid fluids from reservoirs into aquifers. However, the risk of connecting to the receptors is low due to the maximum likely extent of the fractures created (100m) and likely presence of low permeability units in the overburden, particularly for conventional reservoirs that must have a cap rock (KING, 2012).
- Fractures connecting to permeable faults that extend from the reservoir into the aquifer. In most cases faults of this size will be identified, although this will depend on the seismic resolution which is controlled by the acquisition parameters, quality of data and processing.
- Fluids leaking through the well casing; well cement integrity and casing barriers integrity issues stand for all acidising techniques.
- Fluid leaking through wells if a fracture intersects another offset well or abandoned coal mine.
- New pathways (activating faults/well integrity damage) through seismicity which can be induced in several ways:
 - $\circ\;$ during fracturing, where micro-seismic events are minor and difficult to sense at the surface
 - withdrawal of fluids from a reservoir which causes pore pressure changes and contraction of the rock which itself induces stress changes in the surrounding rock

Modelling suggests that acid fracturing is unlikely to result in contamination of aquifers through subsurface pathways. Deep acid fracturing operations are unlikely to produce fractures and conduits that intersect freshwater aquifers due to the separation distance. (ALJAWAD & ALJULAIH, 2019) and (KING, 2012) also demonstrated that the chance of fluids leaking through casing into freshwater aquifers for different scenarios of acid fracturing is very low, as wellbores usually contain layers of casing.

(KING, 2012) also provided estimations of the risks related to hydraulic fracturing that also apply to acid fracturing techniques by investigating thousands of well data operations in the US. Some of those risks and their estimation are listed below:

• The potential for chemical contamination of underground or surface sources of fresh water from the specific act of fracturing, applied in adequately constructed wells with pay zone depth of greater than 610m is less than one in a million

fracturing operations due to the self-limiting nature of fracturing leak off and the numerous fracture barriers overlying deeper formations.

- Height of fracture growth in deep wells is usually a few hundred feet (about 100m) above the targeted hydrocarbon zone but thousands of feet (more than 300m) below the deepest freshwater formation (documented by downhole microseismic, tilt meters, tracers, logging and other methods).
- For targeted hydrocarbon plays of less than 600m depth, regulators with knowledge of local geological systems may need to set specific limits on well depth, volume, rate, and/or type of fluid.
- Research and experience has identified that well integrity failure presents the highest risk of pollution of shallower aquifers. However, with proper well construction there was no documented case of fracturing chemical migration to a fresh water aquifer or to the surface from a zone deeper than 600m. Cases of suspected contamination by chemicals in shallower zones are known, with many, if not all, linked to poor isolation of the well during the well construction phase.

The reaction of strong acids with the rock minerals, corrosion products, petroleum, and other injected chemicals can also release contaminants of concern, such as H_2S from acid reaction with iron sulphides (FeS), which have not been characterised or quantified. H_2S can be released into the subsurface if well integrity is compromised or brought back in the flowback process and produced water (LONG, et al., 2015). H_2S can also be created in the treated reservoirs by the presence of bacteria in the water introduced from the surface. Proper monitoring and mitigations (for example, using chelating agents combined with certain additives as discussed in the Table 6) will minimise the risk of souring (introduction of H_2S) (NENGKODA, et al., 2011), (ALMUBARAK & NG, 2017).

Potential developments to reduce environmental risks from acidising and other treatment techniques using less harmful chemicals, could be:

Traditional chelating agents such as EDTA, HEDTA and NTA have low ٠ biodegradability and can pose health hazards (ALJAWAD & ALJULAIH, 2019). However, EDTA-type chelating agents can be degraded by chemical/photochemical methods (for example, agrobacterium species are capable of degrading EDTA). Therefore, the final fate of these materials in the environment is not clear. Ecotoxicology values of Na HEDTA and Na HEIDA were identified using North Sea water in laboratory experiments. The experiments reproduced a carbonate acidised using Fe-contaminated-HCI (sample powdered with CaCO₃) under reservoir and surface temperature (20 to 90°C). Results showed that neither material is considered to have any acute toxic characteristics (FRENIER, et al., 2000). Glutamic di-acetic acid (GLDA) is a good solvent and is also non-toxic and biodegradable, making it a suitable alternative (ALJAWAD & ALJULAIH, 2019). In the UK, oil and gas reservoir temperatures of existing fields are up to 70°C so the use of biodegradable chelating agents like HEIDA could be considered (up to 150°C).

- Currently, VES is widely used and considered to be an environmentally friendly system (ALKHOWAILDI, et al., 2016). It is polymer free and does not require metal cross-linkers or breakers where these additives are considered hazardous. Also, a degradable polymer based on lactic or glycolic acid has been suggested as a green alternative as well as a hydraulic gel made of polyacrylamide, which does not require a metal cross-linker (ALJAWAD & ALJULAIH, 2019).
- There is ongoing research on more environmentally friendly alternatives for corrosion inhibitors such as Chromolaena odorata, which is extracted from plant leaves, and Tridax procumbens, which is a common weed. Studies also showed that using gelatin as an inhibitor during acidising is effective. Gelatin is nontoxic and extracted from skin, bones, and animal tissue (ALJAWAD & ALJULAIH, 2019).
- (WAN, 2017) has recently discovered a promising natural biogenic surfactant (NBS) contained in the Earth's subsurface sediments that is inexpensive and abundant.
- Highly specialised proteins (enzyme-G) produced by living cells from plant tissues can be used as a breaker and mixed with HCl to clean out and stimulate wells with a more alkali/eco-friendly protocol (RAMANA MURTHY, et al., 2019).

Source	Pathway	Receptor	
	Surface spills.	Groundwater, surface water, personnel.	
Acids	Well integrity (cement quality, condition of casing and tubing and the impact of corrosive fluids).	Groundwater.	
	Existing permeable fractures and connection between new and existing fractures.	Groundwater.	
	Lateral connections with aquifers (depends on geological setting).	Deep aquifers, groundwater.	
	Disposal.		
Waste	Handling, spills.		
products)	Existing permeable fractures and connection between new and existing fractures.	Surface water, groundwater, personnel.	
	Lateral connections with aquifers (depends on geological setting).		

Table 15: Summary of potential environmental impacts for acid fracturing

5.7. Knowledge gaps

As for matrix acidising, improving the quantification of the acid-rock reactions and fracture presence would help further assess the fate of chemicals that do not flow back to the surface.

The monitoring of the extent of fractures created and their connectivity to other active fractures is currently available through various techniques but they have limitations. They are summarised in (KING, 2012).

6. Fluidic oscillation

Fluidic oscillation (or pulse-jetting) is primarily a downhole cleaning device that carries out mechanical permeability enhancement using a treatment fluid. Permeability is increased in a damaged formation by subjecting it to alternating bursts of pressure waves generated by pumping fluids through a fluidic oscillator.

6.1. Technology application

Fluidic oscillation (FO) is an alternative technique to acid treatment or other permeability enhancement techniques. FO has successfully been used in North America, Africa and the UK sector of the North Sea (HOWARD, et al., 2013).

It can be used in most formations, from very low to high permeability, and for formations where the uncertainty regarding rock mineralogy prevents conventional acid permeability enhancing techniques being used.

Fluidic oscillation can be used for (WEBB, et al., 2006), (BONAPACE, et al., 2011):

- removing scale and other deposits from the near-wellbore area, perforations and screens (perforation-tunnel damage, formation fines, mud and cement damage, drilling damage, water and gas blocks, and asphaltene/paraffin deposits)
- primary permeability enhancement of high permeability formations (to optimise initial production from high permeable zones)
- preparation for treatment, gravel packing (used to prevent production of sand), and frac packing (a completion technique that merges hydraulic fracturing and gravel packing)
- alteration of the injection profiles for water re-injection wells caused by nearwellbore scaling or damage
- accurate placement of treating chemicals

6.2. Fluids and chemicals

Fluids, and volumes used will be similar to those used in near-wellbore acidising techniques reviewed in section 3.1.

6.3. Operational parameters

Infrastructure and surface operations

The fluidic oscillator is a small device placed downhole using coiled tubing. When used in conjunction with acid permeability enhancement the surface set-up is the same as matrix acidising.

Design

The FO device is based on a technology that generates bursts of fluids. The FO tool creates pressure waves within the wellbore and formation fluids that break up near-wellbore damage to restore and enhance the permeability of the near-wellbore area. As the damage is removed, and the original permeability is restored, the pressure waves can penetrate deeper into the formation matrix for more complete damage removal.

The greater the contact area with the formation, the greater the action of the fluid. A small amount of acid/solvent blend can be pumped to wash the damage materials out of the well bore. FO tools can be stacked to offer different jet directions and an increased flow rate (WEBB, et al., 2006), (HEGAZY, et al., 2009), (HOWARD, et al., 2013) (Figure 6).

FOs have no moving parts and polymer seals, so any clean fluid can be pumped through them without compromising the treating effects or reliability. Fluids can be water-based, hydrocarbon-based, acid, foamed-CO₂ or foamed-N₂ using surfactant (reviewed in Table 7) (GUTIERREZ, et al., 2008).

The major difference between FO and a conventional jetting-nozzle run (a common squeeze of treatment fluid through perforation on coiled tubing) is that FO uses repeated bursts at a high frequency rather than a continuous jet.



Figure 6: Left: Fluidic oscillator tools, from 0.03 to 0.07m in diameter, in stacked assembly (HOWARD, et al., 2013). Right: The mechanism of obstacle removal from near-wellbore with FO. The arrows represent the direction of the burst of fluids (from formation or added as treatment) (KRISTSANAPHAK, et al., 2010).

The type of damage or scaling is first analysed (samples taken from production lines) and a treatment fluid may be added in combination with the use of the FO tool depending on the type of damage or scaling. An acid treatment will be similar to matrix acidising. Examples of treatment composition, steps and volumes are given by (HEGAZY, et al., 2009), (KRISTSANAPHAK, et al., 2010) and (ERMAKOV, et al., 2020) for high pressure, high temperature (HPHT) formations.

The fluidic oscillator tool operates at an optimal pressure drop of approximately 14MPa and oscillates at frequencies from 200 to 700Hz. Pumped volumes of combined treatment vary depending on the formation and depth. An average of 0.45m³ per metre perforated, at an injection rate of 0.001 to 0.008m³/s will create a radius of penetration of about 0.60m to 1m ((BONAPACE, et al., 2011), (GUTIERREZ, et al., 2008)).

6.4. Subsurface impact

Increased production from the application of FO with coiled tubing is between 30 and 360% (BONAPACE, et al., 2011). FO is a tool which enhances near-wellbore cleanup rather than creating long fractures.

6.5. Geological applicability to England

Fluidic oscillation is applicable to formation damage observed from drilling in most current producing reservoirs in England. It can be used at high temperatures and depths which also makes it a potentially attractive candidate for scale removal in deep geothermal wells.

6.6. Environmental impact

Chemical hazards and well integrity potential failures apply to this technique and are discussed in the acid section. No specific research on the potential subsurface or environmental impact of this technique has been found, but as formation damage occurs in any permeability enhancing application the following table of potential environmental impacts could be applied to this technique as well.

Source	Pathway	Receptor
Acids	Surface spills	Groundwater, surface water, personnel
	Well integrity (cement quality, condition of casing and tubing and the impact of corrosive fluids)	Groundwater
	Existing permeable fractures	Groundwater
Waste (reaction products)	Disposal	

Table	16: Su	mmary o	f potential	environme	ental impacts	of fluidic	oscillation
		·····		•••••••••••••••••••••••••••••••••••••••		•••••••	

Handling, spills	Surface water, groundwater, personnel
Existing permeable fractures	
Lateral connections (depends on geological setting)	

6.7. Knowledge gaps

There is research simulating the 3D effect of fluidic oscillator waves and improvements are constantly being made to upgrade FO tools (HOWARD, et al., 2013). No research was found on the structural impact of FO on specific geology and mineralogy, or environmental impacts.

7. Energised fluids and foams

Growing interest in tight and ultra-tight unconventional formations with high clay contents led to the development of energised fluid and foam systems (BARATI & LIANG, 2014). These were first used in North America to improve the permeability of low permeability and water sensitive formations through creating fractures, including in shales and coalbed methane (AL-DHAMEN & SORIANO, 2015). They are attractive because the water content in energised fluids and foam systems is small, reducing the damage potential to water-sensitive formations. Foam and energised fluid systems are also used in depleted reservoirs because the foam flows back faster and initial post-treatment production is increased.

Although volumes of foams equivalent to high-volume hydraulic fracturing could theoretically be used in shale formations instead of hydraulic fracturing, the process is expensive and and is therefore very unlikely to be considered. From interviews with service companies the most likely applications in England were thought to be for low-volume (less than $200m^3$) fracturing of depleted wells in conventional formations to improve near-wellbore permeability using CO₂ or N₂. For these applications, the extent of the fracture network would be similar to that caused by low-volume hydraulic fracturing as described in section 13.

Energised fluids and foams are fracturing fluids defined as fluids with one or more compressible gas component, such as CO₂, N₂ or any combination of gases, dispersed in a small volume of liquid (KARADKAR, et al., 2018).

The physical properties of energised fluids and foams can be modified through a range of parameters, including temperature, pressure, surfactant and phase compositions. These parameters can be varied to obtain the most suitable fluid/foam system for a specific field application.

- The first foam-based fracturing fluid: N₂ + water + foaming agent. The sand-liquid ratio was 120 to 240kg/m³, which is mainly suitable for low pressure gas wells (LI, et al., 2021).
- Second-generation fracturing fluid: water + foaming agent + polymer. To increase viscosity and stability of fracturing fluid, N₂ or CO₂ was used, and the sand-liquid ratio is 480 to 600kg/m³, which is mainly applied in high-pressure gas wells.
- Third-generation fracturing fluid: water + foaming agent + polymer + crosslinking agent. In this stage, N₂ or CO₂ foam was used as the fracturing fluid system, and the sand-liquid ratio was 600kg/m³, which is mainly used for large-scale fracturing of high-temperature and deep gas wells.
- In the fourth-generation, a constant-internal-phase technique was used to increase the sand-liquid ratio through more precise control of operational parameters rather than using additional chemicals or additives.

• The latest developments in the foam fracturing process include clean fracturing fluid systems (for example, surfactants synthesised from erucic acid from rapeseed oil production) and silicon dioxide nanoparticle-stabilised foams. Ultra-dry foam (up to 99% foam quality) is currently being developed in the laboratory (ABDELAAL, et al., 2021). However, no relevant field tests have yet been carried out.

7.1. Technology application

Energised fluids and foams have been widely applied globally, with all major service companies offering foam systems as part of their portfolio.

Energised fluids, foams and variations

A fluid-fluid mixture is a system where 2 or more fluids with different physical properties are mixed but not combined chemically due to immiscibility. The continuous fluid is known as the 'ambient phase' and the suspended fluids are known as 'dispersed phases'. Depending on the nature of the dispersed phases, the mixture is classified as an emulsion (liquid) or a foam (gas) (ABDELAAL, et al., 2021), (FAROUGHI, et al., 2018). High gas volume fraction mixtures are called 'foam' and the low gas dispersed volume fraction mixtures are called 'foam' and the low gas dispersed volume fraction mixtures are called 'foam' and the low gas dispersed volume fraction mixtures are called 'foam' and the low gas dispersed volume fraction mixtures are called fluids' (ABDELAAL, et al., 2021), (FAROUGHI, et al., 2018). The term 'energised fluids' was used initially because it has energy to flow back by itself without a pump or reservoir driving energy. Therefore, the energised fluid terminology also includes foams (ABDELAAL, et al., 2021), (FAROUGHI, et al., 2018). Figure 7 shows the classification of gas-liquid mixture based on gas volume fraction called foam quality (ψ) as given by:



 $FoamQuality = \frac{GasVolume}{TotalVolume} \times 100$



A summary of main foam systems reported as fracturing fluids (BARATI & LIANG, 2014) is shown below:

- N₂ foam using HPG (hydroxypropyl guar (guar gum-or hydrophilic polysaccharide is used in oil well drilling muds to regulate viscosity)) solutions and a foaming surfactant as shown in Table 17
- N2 foam using slickwater (a type of fracking fluid) and a foaming agent
- N₂ and CO₂ foams using crosslinked guar solutions
- N₂ and CO₂ foaming of the VES gels
- CO₂ foam using HPG solutions and a foaming agent
- CO2 foam using slickwater and a foaming agent
- CO₂ foams with no gelling agent
- CO₂ foam with zirconate crosslinked carboxymethylhydroxypropyl-guar (CMHPG) with or without methanol
- Polyemulsions: emulsified hydrocarbon such as condensate or diesel as an external phase with water

There are limited reports on the field applications of energised fluids and foams after 2015. This might be explained by the decreased oil price, the relatively high cost of these systems and less research interest as the technique is more widely applied.

7.2. Fluids and chemicals

The gas phase of an energised fluid or foam can be CO_2 , N_2 or a combination of both. The 2 gases have different properties and therefore will result in different fracture treatment parameters (OUSSOLTSEV, et al., 2008). N_2 is more commonly used because it is an inert gas and more widely available (WANNIARACHCHI, et al., 2015). The selection of the liquid phase depends on economic constraints and a range of reservoir conditions including permeability, water availability, clay content, temperature. (WANNIARACHCHI, et al., 2015).

Table 17: Summary of the main types of foam-based systems with constituents
(ABDELAAL, et al., 2021)

Type of foam	Main constituents
Water-based foam	Water + foaming surfactant + N ₂ (gas) or CO ₂ (gas)
CO ₂ -based foam	CO ₂ (liquid) + foaming surfactant + N ₂ (gas)

Acid-based foam	Acid (same acids as used in acid permeability enhancement) + foaming surfactant + N ₂ (gas)
Alcohol-based foam	Methanol + foaming surfactant + N ₂ (gas)
Hydrocarbon-based foam	Hydrocarbon + foaming surfactant + N ₂ (gas)

Foam-based fracturing fluids are non-Newtonian fluids. Their rheological properties change due to different parameters such as pressure, temperature, foam texture, foam quality and foam channel-wall interactions, shear rate, gas type and foaming agent (ABDELAAL, et al., 2021).

Foams are intrinsically and thermodynamically unstable due to large interfacial energy and surface tension between the constituents. For energised fluid and foam systems, the choice of the surfactant, which allows bubble formation, is particularly important and often challenging for reservoir-specific applications (AHMED, et al., 2019). The lifetime of the foam can be increased by increasing the surfactant concentration (FAROUGHI, et al., 2018). Detailed and structured information on various surfactants and volume applied is very scarce. Most of the pilot tests were carried out in the Barnett and Marcellus shales in the USA, using conventional surfactants (as shown in Table 18) which include non-ionic alcohol ethoxylate surfactants and amphoteric and cationic surfactants (AHMED, et al., 2019).

Table 18 summarises the commonly used surfactants for CO₂-foam enhanced oil recovery (EOR) applications, some of which are also applicable to CO₂-foam fracturing. The design, evaluation and optimisation of surfactants that can meet the requirement of targeted reservoirs and provide a satisfactory performance is an area of ongoing research.

In addition to surfactants, chemical breakers, biocide and additive-scale inhibitors are also added. These chemicals are described in more detail in the acid-based techniques in section 3.

Table 18: Summary of common surfactants used for CO₂-foam EOR and their potential environmental impact (CLARK & SANTISO, 2018)

Classification	Surfactant	Environmental impact
Anionic	Bis(2-ethylhexyl) sulfosuccinate (AOT)	Toxic to microorganisms
	Ammonium alkyl ether sulfate	Toxic to aquatic life
	Alpha olefin sulfonate (AOS)	Toxic to aquatic life

	Sodium olefin sulfonate	Toxic to aquatic life
	FomaxII & FomaxVII	Both unknown
	Nonylphenol ethoxylate sulfonate (NPES)	Toxic to aquatic life
	Sodium dodecyl benzene sulfonate (SDBS)	Toxic to aquatic life
	Sodium dodecyl sulfate (SDS)	Toxic to aquatic life and microorganisms
	Sodium dodecyl sulfonate	Toxic to aquatic life
Nonionic	Alkyl polyglycosides (APG)	Nontoxic
	Solvay N70K-T	Unknown
	Neodol 25-7™	Toxic to aquatic life
	Surfonic N120™	Toxic to aquatic life
	Triton X-100™	Toxic to aquatic life
	Tween 80	Nontoxic

7.3. Operational parameters

In field operations, the effectiveness of energised fluids and foams depends on foam stability and proppant carrying capacity (ABDELAAL, et al., 2021). Because foam is thermodynamically metastable, it can be difficult to stabilise during field operations (ABDELAAL, et al., 2021). There are a range of parameters that can affect foam stability, including surfactant type, reservoir fluid types and properties, placement method, injected gas types and properties and reservoir characteristics. The presence of oil will adversely affect foam stability, therefore oil saturation within the reservoir ideally should be as low as possible.

Due to the short lifetime of foam, it must be produced at the fracturing site just before the initiation of fracture fluid injection. Therefore, the chemicals and the main fluid phases (liquid phase and gas phase) must be stored on-site (WANNIARACHCHI, et al., 2015). When CO₂ is used, it is injected in the liquid state to form an emulsion when below 31°C (AL-DHAMEN & SORIANO, 2015). High-pressure N₂ or CO₂ is added just before the wellhead and dilutes the overall sand concentration (AL-DHAMEN & SORIANO, 2015).

Infrastructure and surface operations

The main surface equipment for energised fluids and foams fracturing is shown in Figure 8 (CO₂ foam is used for illustration).

- The foam stabiliser, crosslinking agent and other reagents are prepared and injected into the sand mixer through the pipeline. The surface mixer will need to be able to handle high proppant concentrations (30% to 40%) (AL-DHAMEN & SORIANO, 2015). Standard field blending equipment can handle proppant concentrations of approximately 57kg/m³ at low fluid rates, and higher concentrations are possible for short periods (AL-DHAMEN & SORIANO, 2015).
- The solution and sand are then evenly mixed in the sand mixer. After the mixing is completed, the mixture is pumped into the wellhead by the fracturing pump truck. CO₂ stored in the CO₂ tanker (in liquid phase) is injected into the pump truck through the pipeline and pumped to the wellhead. Liquid CO₂ and the liquid mixed with the reagent are pumped out into the well by the fracturing pump trucks at a controlled flow rate so that they remain a consistent mixture. During the downhole injection, the temperature of the mixed liquid gradually increases, and CO₂ begins to transform into a gaseous phase to form a gas-liquid 2-phase mixture, wherein CO₂ is in the gaseous phase and the additive solution in the liquid phase. The gas-liquid 2-phase fluid finally forms a CO₂ foam fracturing fluid before reaching the area to be fractured.
- After the treatment, when pressure is lowered to induce fluid returns, CO₂ flows back as gas, together with the fracturing fluids. Recent trial applications have been for multiple-stage wells, with each stage taking approximately 1,800 seconds to complete.



Figure 8: Main surface equipment for CO₂ foam fracturing (LI, et al., 2021)

7.4. Subsurface impact

In 2013, researchers from the University of Austin, Texas (RIBEIRO & SHARMA, 2013) reported on the modelled fracture propagation results of 6 different fracturing fluid

systems, including 3 foams: CO₂-foam 0.3 (30% CO₂), CO₂-foam 0.7 (70% CO₂), and N2foam 0.7 (70% N2). Using different modelling techniques, the research provided detailed simulation results and concluded that CO₂-foam 0.7 outperformed all other fluid samples when it comes to well productivity enhancement. This conclusion is consistent with observations made by other researchers during recent field applications in Saudi Arabia where 198,129kg of liquid CO₂ was pumped downhole (AL-DHAMEN & SORIANO, 2015) and in Montney, Canada, where CO₂ was used for enhancing the permeability of shale formations (KONG, et al., 2016).

7.5. Geological applicability to England

Generally, energised fluids and foams are suitable to stimulate under-pressured and under-saturated reservoirs and water-sensitive formations (KARADKAR, et al., 2018), (GUPTA, 2010), (ABDELAAL, et al., 2021).

(WARNOCK, et al., 1985) reported that CO_2 -foam systems have been successfully applied to low permeability oil and gas sands and carbonates at depths of 885m to 4,267m, reservoir temperatures of 48°C to 188°C, and reservoir pressures of 7MPa to 91MPa. Because of the high density of the water/CO₂ mixture, CO₂ foam can be used in deep, hot formations without prohibitive wellhead treating pressures. Examples of different field characteristics where CO₂-foam treatments have been applied are shown in Table 19. There is no evidence from the literature review that foams or energised fluids have been used in England to date. Volumes of CO₂ used are not widely reported, however practical logistical limitations (sourcing, transport and storage of CO₂) and the type of operation likely to be used will limit volumes to below 200 tonnes in the conventional formations encountered in England.

Field/well type⁴	Zone (rock type)	Depth (m)	Porosity (%)	Water saturation (%)	Perm. (mD)*	P (MPa) *	T (°C)*
Arkana (LA)/gas	Haynesville (sandstone)	3,215 to 3,321	8.8	38	0.05	43.6	127

Table 19: Characteristics of fields/zones where CO ₂ -foam treatments have been applied
WARNOCK, et al., 1985)

⁴ States of the United States of America: LA = Louisiana, AR = Arkansas, TX = Texas

Arkana Trend (LA)/oil	Pettet (limestone)	1,643 to 1,967	14.9	43	3.80	20.0	74
Dorcheat Macedonia (AR)/gas	Cotton Valley (sandstone)	2,112 to 2,703	12.7	45	0.10	27.6	107
Greenwood Waskom (LA)/gas	Hosston (sandstone)	1,957	12.0	52	0.10	21.2	85
Mira (LA)/oil	Woodbine (sandstone)	887	19.0	35	5.00	7.0	49
N.E.Bethany (TX)/gas	Cotton Valley (sandstone)	1,932 to 2,493	10.9	45	0.10	25.9	96
Shongaloo (LA)/gas	Haynesville (sandstone)	3,136	21.0	35	10.00	25.5	121
Vernon (LA)/gas	Cotton Valley (sandstone)	3,544 to 4,415	11.1	48	0.05	91.0	188
Winnsboro (TX)/gas	Travis Peak (sandstone)	2,591 to 2,891	9.7	28	0.10	30.1	104

*Perm = estimated permeability, P = reservoir maximum pressure, T = reservoir maximum temperature

7.6. Environmental impact

No literature was found to assess the environmental impact of energised fluids or foam systems. However, the potential risk of the additives used to stabilise the CO₂ foams should be considered.

The environmental impacts of surfactant and nanoparticles used in CO₂ foam for EOR highlighted by (CLARK & SANTISO, 2018) could apply to the foams used for fracturing, if nanoparticles are used. The potential environmental impact of various surfactants is provided in Table 20. Nanoparticle additives also pose potential environmental risks, for example, the toxicity of silica nanoparticles is poorly understood. Recent studies have

found that silica nanoparticles exhibit cytotoxicity depending on the particle size and level of exposure; other experiments have shown that silica nanoparticles can lead to liver and kidney injury, among other harmful effects (CLARK & SANTISO, 2018).

In addition, research has highlighted the importance of surfactant degradation. Anaerobic degradation, in the case of fracturing, is not well understood (CLARK & SANTISO, 2018). Although there is some information on the degradation of surfactants under ideal anaerobic condition, the overall understanding of how various environmental conditions relate to the degradation rate is still limited.

Source	Pathway	Receptor
	Surface spills	Groundwater, surface water, personnel
CO₂ foams, nanoparticles	Well integrity (cement quality, condition of casing and tubing and the impact of corrosive fluids)	Groundwater
,	Existing permeable fractures and connection between new and existing fractures	Surface water, groundwater, personnel
	Lateral connections with aquifers (depends on geological setting)	Deep aquifers, groundwater
	Disposal	Surface water, groundwater,
	Handling, spills	personnel
Waste (reaction products)	Existing permeable fractures and connection between new and existing fractures	
	Lateral connections (depends on geological setting)	
CO ₂ and N2	Pump priming and de- priming, leaks in pressure systems	Atmosphere, personnel
	Post-operational flow-back and venting	Atmosphere, personnel

Table 20: Summary of potential environmental impacts for energised fluids and foams

7.7. Knowledge gaps

The potential environmental impact of energised fluids and foams is a knowledge gap. More studies are needed to understand the subsurface effects of injecting large quantities of surfactants and nanoparticles underground. Long-term research programmes are needed to better understand chemical degradation carried out by microorganisms and how this changes with reservoir pH, temperature, water content and nutrients.

8. CO₂ fracturing (liquid-CO₂ and super critical-CO₂)

Fracturing with pure CO₂ has gained considerable research interest in recent years, especially the use of supercritical CO₂ as a fracturing fluid. CO₂ will be in a supercritical state at temperatures exceeding 31.26°C and pressures of greater than 7.28MPa, with fundamentally different properties from gaseous and liquid CO₂:

- The viscosity of supercritical CO₂ is close to that of a gas, but the density is close to that of a liquid. It has high mobility and a strong capacity to dissolve non-polar solutes (LIU, et al., 2014).
- In a supercritical state, CO₂ has very small inter-molecular forces and zero surface tension.

The main difference between the liquid and supercritical CO₂ techniques is that the fracturing fluid in supercritical CO₂ starts with a higher initial temperature, therefore it can reach the critical temperature and transform to supercritical state at the wellbore (LIU, et al., 2014). Generally, CO₂ would meet the supercritical condition when the reservoir is deeper than 750m (XIE, et al., 2021). Many researchers argue that CO₂ has the potential to increase hydrocarbon production while lowering environmental impacts (MIDDLETON, et al., 2015):

- additional fracture propagation due to its isenthalpic (a process that proceeds without any change in enthalpy) expansion
- hydrocarbon miscibility with CO₂, minimising flow blocking in small pores
- the potential exchange of CO₂ with methane adsorbed in organic-rich regions of the formation (desorption)
- CO₂ fracturing offers the potential for carbon capture utilisation and storage (CCUS) due to CO₂ preferentially displacing adsorbed methane (Figure 9)



Figure 9: Illustration of a fracturing system highlighting induced and natural fractures and 3 primary gas-in-place origins of methane. CO_2 as a fracturing fluid would be able to extract gas more efficiently from (1) & (2) because CO_2 is miscible with hydrocarbon and from (3) because CO_2 can exchange with methane that is sorbed to kerogen (MIDDLETON, et al., 2015)

8.1. Technology application

Liquid CO₂ (L-CO₂)-based fracturing fluid was first applied in the glauconite sandstone reservoir in Canada in 1981 (ZHANG (a), et al., 2019). In 1982, Bullen proposed that L-CO₂ could work well in low-pressure, low-permeability and strong water locking/water sensitive formations and it was applied extensively in the tight gas development in the USA and Canada (BULLEN & LILLIES, 1983). In the 1980s, the process was further developed by Canadian FracMaster and had some commercial success in Canada and subsequently in the USA (via American FracMaster) (WAN, 2017). Since then, L-CO₂ fracturing has been tested and applied in more than 1,000 wells in a variety of formations, including in Galbraith in the USA, the Glauconite gas reservoir in Canada and Ordos Basin in China, with permeability values from 0.1mD to 10D, depths over 3,000m and bottomhole temperatures from 10°C to 110°C (GUPTA, 2003) (ZHANG (a), et al., 2019).

Supercritical CO₂ (Sc-CO₂) fracturing is an emerging concept with only a small number of field trials, carried out in China, in recent years. To date, there has been no commercial field scale application of Sc-CO₂ fracturing.

Overall L-CO₂ is at a demonstration stage, and Sc-CO₂ is at a validation stage.

8.2. Fluids and chemicals

Both L-CO₂ fracturing and Sc-CO₂ fracturing use 100% CO₂ as the fracturing agent. Thickening chemicals are required to enhance the viscosity of CO₂ and overcome poor proppant carrying capability. The development of CO₂ fracturing fluid thickener is a challenging research and development area, in particular there is a lack of an effective high-temperature resistant thickener (LI, et al., 2021).

Polymer thickeners is one family of thickening chemicals. Fluoropolymers, hydrocarbon polymers, siloxane polymers and, more recently reported synthesised epoxy ether-based polymers, have all attracted interest from researchers (LI, et al., 2019). Table 21 provides more examples of different polymer thickeners that are being researched.

Agent	Solution wt %	Thickening result (mPa/s)
Vinyl benzoate/heptadecafluorodecyl acrylate co-polymers	5	483 times
Poly (1-decene), Poly (iso-butyl vinyl ether), Poly (ethyl vinyl ether)	0.81 to 5	(0.07 to 0.18))
Polydimethylsiloxanes	8 to18	4 to 20 times
Fluoropolymer & surfactant	0.25 to1.5	(1.3 to 9.3)
Amphiphilic surfactant	3	(8.2 to 20)
Poly (vinyl ethyl ether) and poly (1-decene)	0.56 to 0.81	13 to 14 times
Fluorinated-di-chain-surfactant	1 to 10	1 to 2 times

Table 21: CO₂ thickeners, concentrations and enhanced viscosities (HOU, et al., 2021)

There is ongoing research on small molecule thickeners, which has identified several options with mixed results in the laboratory environment, including trialkyltin fluorides and semi-fluorinated trialkyltin fluorides, hydroxyaluminum disoaps and fluorinated hydroxyaluminum disoaps, fluorinated urea and divalent metal cations that are capable of increasing CO₂ viscosity by 50% to 500% (LEE, et al., 2014), (LEE, 2016). However, no field test data is currently available for application of small molecule thickeners (LI, et al., 2021).

8.3. Operational parameters

Referring to Figure 10, for L-CO₂ operations, CO₂ is stored in storage tanks in liquid state (Point 1). It is then pressurised by a booster pump and injected into a high-pressure pump (Point 2). At the outlet of the high-pressure pump, liquid CO₂ reaches the required pressure for the fracturing operation (Point 3). It is then injected to the wellbore, during which its temperature and pressure further increase (Point 4). After CO₂ contacts with the reservoir and enters the fracture, its pressure will slightly decrease but temperature will significantly increase. At this point, CO₂ is in a supercritical state (Point 5). After the fracturing is completed and the backflow begins, the CO₂ pressure drops rapidly and flows back to the surface in a gaseous phase (Point 6).

For Sc-CO₂ operations, CO₂ is stored in storage tanks in liquid state and mixed with the proppant (Point 1). At this stage, both the temperature and the pressure of CO₂ are higher than the initial point of CO₂ for L-CO₂ operations (LI, et al., 2021). The mixture is then sent to the high-pressure pump to pressurise (Point 2). For shallow wells, the heating device will increase the temperature of CO₂ (Point 3). Liquid CO₂ is then injected to the wellbore, similar to the L-CO₂ process, with the increased temperature and pressure, CO₂ will change to a supercritical state (Point 4). After CO₂ contacts the reservoir and enters the fracture, its pressure will decrease but temperature will increase, with CO₂ still in a supercritical state (Point 5). When the flowback starts, the CO₂ pressure drops rapidly and flows back to the surface in a gaseous phase (Point 6).

Both techniques may also incorporate a high-pressure sand blender on the surface where proppant is mixed with the CO_2 . Alternatively, the CO_2 will be followed by a conventional proppant slurry in a subsequent stage to keep the fractures from closing.



Figure 10: Phase change of CO₂ in L-CO₂ fracturing (left) and phase change of CO₂ in Sc-CO₂ fracturing (right) (LI, et al., 2021)

Infrastructure and surface operations

The equipment used in both L-CO₂ and Sc-CO₂ fracturing operations are similar, and include CO₂ storage tanks, an airtight sand blender, a high-pressure pump and manifold trucks. For Sc-CO₂ applications in shallow wells where CO₂ cannot reach the critical temperature of 31.26°C, a heating device is required at the surface (LIU, et al., 2014).

Uniform and rapid heating of CO₂ is an operational challenge yet to be solved by the industry (LIU, et al., 2014).

8.4. Subsurface impact

Results from simulation studies (ZHANG, et al., 2017), (ZHANG (b), et al., 2019) have demonstrated that Sc-CO₂ has a fracturing effect in both horizontal and vertical directions, with higher density, larger extension length and more secondary fractures than is achieved with high volume hydraulic fracturing. It is accompanied by a 3-dimensional fracture network volume, better communication with natural fractures, and greater potential of improving fracture conductivity. These observations were verified by micro-seismic monitoring during the 2011 pilot test by Yanchang Petroleum in China (WANG, et al., 2020). This work also showed that compared to high volume hydraulic fracturing, fractures from Sc-CO₂ are radially distributed and have much more complex density and spatial complexity, which foster the development of a 3D fracture network and easily forms branch fractures (WANG, et al., 2020).

If CO₂ is proven to be an effective fracturing fluid, then shale gas formations could potentially become an option for Carbon Capture Use and Storage (CCUS), providing it can be demonstrated that CO₂ can be safely stored in these formations (MIDDLETON, et al., 2015).

8.5. Geological applicability to England

No reported geological or geochemical limitations that would prevent the application of L-CO₂ or Sc-CO₂ fracturing technologies in England were found. However, for CO₂ to maintain a supercritical state at the wellbore during Sc-CO₂ operation, the reservoir needs to have a suitable in-situ temperature and pressure that would enable the critical conditions of CO₂. In general, over-pressured reservoirs (that is where a subsurface pressure exceeds the hydrostatic pressure at a given depth) with depth greater than 750m are considered suitable (XIE, et al., 2021). This may preclude the use of the technique in depleted or low-pressure reservoirs.

8.6. Environmental impact

Currently, environmental impact assessments of CO₂-based fracturing fluids are focused on the positive impact of eliminating large volumes of surface and groundwater abstraction, minimising wastewater management and reducing life cycle greenhouse gas (GHG) emissions. As the technique is immature and at field-trial status there is limited life cycle analysis or environmental impact data in the public domain (WILKINS, et al., 2016).

Table 22: Summary of environmental	impacts for CO ₂ fracturing
------------------------------------	--

Source	Pathway	Receptor
Liquid CO ₂	Handling, offsite transport, spills	Groundwater, surface water, personnel, atmosphere
	Well integrity (cement quality, condition of casing and tubing and the impact of corrosive fluids)	Groundwater
	Lateral connections with aquifers (depends on geological setting)	Deep aquifers, groundwater
	Existing permeable fractures and connection between new and existing fractures	Groundwater
Gaseous CO ₂	Pump priming and de- priming, leaks from pressure systems, flowback	Atmosphere, personnel
Waste (reaction products)	Disposal	Surface water, groundwater, personnel, atmosphere
	Existing permeable fractures and connection between new and existing fractures	
	Lateral connections (depends on geological setting)	

8.7. Knowledge gaps

As a technique which has only had a limited number of field trials, information on fracture networks (extent and complexity) in field conditions has not been gathered. Laboratory experiments suggest that the fracture extent will be similar to high-volume hydraulic fracturing with a greater fracture complexity, however this needs to be proven. Environmental studies or evidence of other environmental impacts is similarly underdeveloped.

9. Gelled propane/LPG fracturing

Liquefied petroleum gas (LPG) is a mixture of petroleum gases that remain in a liquid state at ambient temperature and pressure. LPG fracturing is a reservoir permeability enhancing technique where propane, usually gelled before fracturing, is mostly used as a standard high-pressure fracturing fluid to deliver proppant and fracture the rock formation (KALAM, et al., 2021). It is considered a promising alternative to hydraulic fracturing due to its high volatility, low viscosity, low surface tension, high solubility in hydrocarbons and high recovery potential (KUMAR, et al., 2017), (KALAM, et al., 2021), (ROGALA, et al., 2012). However, the cost of the technique versus slickwater fracturing has prevented its uptake.

The main advantage of LPG fracturing is that it can be used in water-sensitive formations where conventional hydraulic fracturing can cause damage to the reservoir, such as water locking, polymer residues and clay swelling.

The literature review suggests that there are few ongoing LPG fracturing operations worldwide. This is due to GasFrac Energy Services Inc. (GasFrac), the pioneer of its proprietary LPG fracturing technology ceasing trading, as well as the high cost of the technique and the potential safety issues caused by having a highly flammable fracturing fluid in an operational environment.

9.1. Technology application

Research into LPG for reservoir permeability enhancement started in the 1970s (KALAM, et al., 2021). The technology was developed for, and applied to, conventional reservoirs before being adapted to unconventional reservoirs (MORIDIS, 2017), (KALAM, et al., 2021), including tight (low permeability) sands.

There is a technology variant, developed and promoted by Houston-based EcopStim, in which LPG is liquefied but not gelled (MORIDIS, 2017). In 2015, EcopStim announced its non-flammable, non-toxic LPG fluid, based on light alkanes (low molecular weight alkanes), approved by the US Food and Drug Administration for human ingestion and exposure (GANDOSSI & ESTORFF, 2015). This variant uses buoyant proppants such as fine sand and carbon fullerenes (carbon atoms with hollow shapes) (MOJID, et al., 2021) and completely avoids the use of chemical additives (GANDOSSI & ESTORFF, 2015). Since then, there has been little indication of further development.

Gelled LPG fracturing was successfully deployed globally until 2015 but has not been widely used since. It is estimated that the LPG fracturing operations performed by GasFrac have consumed a total of 206,793m³ propane and 4.34 x10⁷kg proppant (JIN, et al., 2017).

9.2. Fluids and chemicals

In LPG waterless fracturing, 100% LPG is used as fracturing fluid (CUI, et al., 2017). LPG has a high degree of purity and results in a very predictable fracturing performance (KALAM, et al., 2021). Similar to oil-based fluid, the LPG gel is prepared by thickening and cross-linking of alkyl phosphate and an aluminium complex with higher sand carrying capacity. The LPG density is 510kg/m³ (49% lower than water), and the gel breaking fluid has a viscosity of 0.1mPa.s (about 10% of water viscosity) and surface tension of 7.6mN/m (about 10% of water) (CUI, et al., 2017).

The proprietary LPG gel from GasFrac comprised predominantly liquid propane (converted into a gel) with phosphate ester and FeS. In addition, magnesium oxide (MgO) is added to delay the breakdown of the LPG gel (WILSON, 2013). 95% pure propane is the most commonly used LPG. Propane has a critical temperature of 100°C which limits its use above this temperature. For applications about 100°C, commercial butane, with a critical temperature of 176°C, is mixed with propane to achieve the desired performance (VAJPAYEE, et al., n.d.).

In addition, inert gases such as nitrogen are often used to purify LPG system components to prevent them from exploding, pushing the mixed gas from the storage tank through the pipes (SONI, 2014), (JIN, et al., 2017).

9.3. Operational parameters

To maintain propane as a liquid, it is stored at an ambient temperature of 21°C with a minimum storage pressure of 0.86MPa (SONI, 2014). When using propane as fracturing fluid, it is stored, gelled, and proppant blended at a constant pressure of 1.93MPa within the surface equipment (VAJPAYEE, et al., n.d.), (KALAM, et al., 2021).

During the process, the propane-based gel is pumped into the wellbore at low temperature and high pressure in liquid state. The high pressure forces the fluid to fracture the formation and penetrate into the reservoir matrix, creating microfractures in the formation (SONI, 2014), (KUMAR, et al., 2017). The decreased pressure and increased temperature as a result of fracturing will turn the gel into a vapour. It then moves up to the surface where it can be collected and reused.

For LPG fracturing services provided historically by GasFrac (no longer trading), the maximum consumption of proppant was 800 tons (about 726 tonnes), the highest working pressure was 90MPa, and the highest propane processing rate 0.133m³/s (JIN, et al., 2017). A review of 3 different LPG fracturing operations in sandstone formations showed that an average of 100m³ of LPG was typically used (TUDOR, et al., 2009).

Infrastructure and surface operations

LPG fracturing infrastructure consists of:

- propane and nitrogen tankers to store propane and nitrogen respectively
- boosters to increase the pressure of fluids coming from the discharge of tankers up to 1.99MPa
- pumps to increase the pressure to more than 49.9MPa
- remote monitoring system and control centre van for real time monitoring
- a blending system to mix gel (propane and chemicals) and proppant
- fire safety trucks

Gelling agent is mixed to maintain the viscosity requirement. By cooling the LPG mixture before introducing it into the fracture system, reduced pressures are needed. This minimises the potential for explosions or damage to the fracturing system which can be caused by high pressures (SONI, 2014).

During LPG fracturing, there is low energy consumption because the density and viscosity of the fluid are low (MOJID, et al., 2021).

9.4. Subsurface impact

There is limited information on fractures and fracture networks created by LPG fracturing. It has been reported that the effective length of fracture of LPG fracturing is above 100m (MOJID, et al., 2021). An experiment carried out in 2018 (ZHANG, et al., 2018) on 4 large scale true tri-axial fracturing simulation experiments on shale outcrops concluded that LPG fracturing creates a complex fracture network by activating discontinuities' long fracture length and creates a larger stimulated reservoir volume (SRV) than hydraulic fracturing. As LPG is a hydrocarbon, there is no water phase trapping and clay expansion, an advantage compared to water-based permeability enhancing techniques (MOJID, et al., 2021).

9.5. Geological applicability to England

LPG fracturing could be used in a wide range of reservoirs and formations, including tight oil, tight gas and condensate oil reservoirs with formation temperatures of 12°C to 150°C (CUI, et al., 2017), maximum operating depth is 4,000m true vertical depth (mTVD) (ZORANOC, n.d.). In summary, no obvious geological or geochemical characteristics limit the application of LPG fracturing technology (MOJID, et al., 2021). The supply chain for LPG fracturing is not well established, so practical rather than geological considerations are likely to hinder its use in England.

9.6. Environmental impact

Little research or quantitative evidence was found regarding the potential environmental impacts of LPG fracturing on subsurface soil and groundwater. The length of fractures created are suggested by (SONI, 2014) to be similar to equivalent volume hydraulic fracturing and can be modelled with LPG being treated as a viscous fluid.

Kumar et al. (KUMAR, et al., 2017) provided some qualitative assessments of the impact of LPG fracturing. LPG is electrically neutral, lacks friction and does not dissolve salts, heavy metals or radioactive compounds. Therefore, it has been argued that LPG does not return potentially hazardous dissolved elements to the surface in produced or flowback water. If natural gas is present, propane and methane in combination will become a unique liquid vapour saturation and return to the surface at ambient conditions and can then be separated.

In addition, the phosphate ester, FeS and MgO used during the operation will remain in the well (WILSON, 2013). Although GasFrac claims that these chemicals are non-toxic in the quantities used for fracturing (WILSON, 2013), there is no evidence to support this or any study looking into the potential environmental impact of LPG fracturing.

The most significant issue with LPG fracturing is operational safety. LPG is highly flammable and must be stored carefully in high pressure tanks. In 2011, a fire broke out during the LPG gel fracturing process at a well in Alberta, Canada, operated by Husky Energy, and 3 workers suffered non-life-threatening burns. The cause of the incident was an undetected propane leak (WILSON, 2013).

LPG poses health hazards to animals and humans as it is denser than air. Therefore, it can accumulate and persist at close to ground level (MOJID, et al., 2021).

Heptafluoropropane (a fluorinated form of propane used in fire suppression systems and considered for use in LPG fracturing to mitigate the fire hazard) is a very stable hydrocarbon but is also a greenhouse gas (GANDOSSI & ESTORFF, 2015). It was considered for use in 2014, however it has failed to gain any industry traction or deployments.

Source	Pathway	Receptor
	Surface spills, pressure vessel rupture, leaks	Groundwater, surface water, personnel, wildlife, atmosphere
LPG	Well integrity (cement quality, condition of casing and tubing failure)	Groundwater
	Existing permeable fractures and connection between new and existing fractures	Surface water Groundwater, personnel

Table 23: Summary of potential environmental impacts for gelled propane/LPG fracturing
	Lateral connections with aquifers (depends on geological setting)	Deep aquifers, groundwater
	Disposal	Surface water, groundwater, personnel
	Handling, spills	
Waste (reaction products)	Existing permeable	
	between new and existing	
	fractures	
	Lateral connections	
	(depends on geological	
	setting)	

9.7. Knowledge gaps

There is limited evidence on potential environmental impacts of this technique recorded in the literature reviewed. The technique has largely been surpassed by hydraulic fracturing and there is very little research interest currently. Should the technique be re-assessed in the future, knowledge gaps relating to reliably modelling the fracture length and geometry compared to hydraulic fracturing may need to be addressed.

10. Narrow diameter multilateral drilling

Narrow diameter multilateral drilling (NDMD) creates regularly spaced narrow boreholes (typically below 50mm) no longer than 12m in length off the wellbore using either acid or small drilling heads. The technique is also known as multilateral stimulation technique (MST), multilateral drilling stimulation technique (MDST) and fishbones. The technology is deployed with an open hole liner as part of a standard rig operation. Fishbones A/S, a company headquartered in Norway, is the pioneer of this technique.

10.1. Technology application

NDMD can be used in naturally fractured carbonates, layered carbonates, chalk, layered sandstones and coal bed methane in oil producing, gas producing and water injector wells.

NDMD is designed for horizontal wells in reservoirs with limited thickness and low permeability. It can also be used in reservoirs with thin sand and shale sequences where vertical communication between permeable layers is poor and where high fracture precision is required to avoid producing water or gas from formations outside the target areas (Oil and Gas Authority, 2017).

NDMD is carried out once the wellbore has been drilled and completed without casing. An open hole liner with a fishbone assembly is run downhole and activated to create laterals perpendicular to the main well (PRISKILA, 2014). This technique does not require additional fluids or pumps and has no additional equipment (VELDKAMP & BOXEM, 2015) (SOLHAUG, 2019).

The first NDMD installation was in November 2013 in a coal-bed methane formation in Sumatra, Indonesia. By 2019, 23 installations had been completed and Fishbones A/S aimed to have more than 100 installations by 2021.

There are 2 variations of the technique:

- Fishbone jetting: Pressure differences across the liner allow the small tubes/needles to be pushed out into the reservoir. For calcareous reservoirs, the needle heads spray acid to penetrate the formation through erosion and acid chemical dissolution (Fishbones A/S, 2021).
- Fishbone drilling: Turbines powered by fluid circulation in the well drive drill bits drill out into the reservoir. This is considered a permanent completion, however, Fishbones A/S does have methods for removing the needles if required (PRISKILA, 2014).

Fishbone jetting technology has been successfully used in multiple applications globally and the drilling technology was trialled in Norway in 2015 in a tight sandstone formation at 3,780m to 4,241m bsl (below sea level) with permeabilities ranging from 0 to 10mD (TORVUND, et al., 2016). It has also been used in a tight limestone formation within the Austin Chalk, Texas (RICE, 2016). It has not been used onshore in England.

10.2. Fluids and chemicals

Fishbone jetting uses 5% to 28% HCl in carbonate reservoirs. The spent acid is circulated back to the surface similar to other acid-based techniques. The volume of acid used depends on each operation, with a case study developed by the technology developer suggesting 140m³ of fluid used over a 5-hour operation (JORGENSEN, 2014).

For fishbone drilling, standard drilling fluids are used to drive the drilling turbines, with the fluid then circulated back to the surface and disposed of through conventional routes.

10.3. Subsurface impact

For fishbone jetting, needles penetrate up to 12m into the formation. Each sub⁵ contains 4 needles with flexibility in the number and spacing of subs used (Fishbones A/S, 2021). The technique does not aim to create new fractures, but to drill narrow diameter holes of a controlled length.

For fishbone drilling, each sub contains 3 laterals and there is flexibility in the number and spacing (Fishbones A/S, 2021). Up to 100 laterals 12 to 24m long can be created within the near-wellbore formation (VELDKAMP & BOXEM, 2015).



⁵ A short, threaded piece of pipe used to adapt parts of the drilling string that cannot otherwise be screwed together.

Figure 11: Schematic of a fishbone assembly with the titanium needles (green) extending into the reservoir away from the fishbone assembly (www.Fishbones.as)

A case study from the Middle East found that within a fractured limestone formation fishbones increased the productivity index⁶ (PI) by more than 4 times and more than doubled the flow rate (SOLHAUG, 2019).

10.4. Geological applicability to England

Fishbone jetting could be used in conventional carbonate reservoirs in England or in formations where acidising techniques would also be considered.

Fishbone drilling could be used for drilling in the radiothermal granites in the south-west (Cornwall) and northern England (Lake District and Weardale) as well as the Sherwood Sandstone Group and Bridport Sandstone Formation. The manufacturer states that they are designed to use in sandstone and basement rocks and the pressure and temperature conditions expected would be well within the limits of the technology.

10.5. Environmental impact

The environmental impact of fishbones (jetting or drilling) has not been subject to peerreviewed study. For fishbone jetting, the chemicals used are similar to acidising operations, with HCl used to penetrate the formation. For fishbone drilling, the drilling turbines are powered by conventional drilling fluids. Compared to acid fracturing, fishbone jetting produces holes of a defined length which are limited by the length of the titanium needles (12m). The fluid pressure at the tip of the jet is typically 20.7MPa, however the fluid is circulated from the well and no fractures are created.

drilling	Table 24. Summary of potential environmental impact for narrow diameter multi-lateral
	drilling

Source	Pathway	Receptor
	Surface spills, leakage	Groundwater, surface water, personnel
Acids (if used)	Well integrity (cement quality, condition of casing and tubing failure)	Groundwater

⁶ PI is the ratio of the total liquid surface flowrate to the pressure drawdown at the midpoint of the producing interval.

	Existing permeable fractures	Surface water, groundwater, personnel
	Lateral connections (depends on geological setting)	Surface water, groundwater, personnel
	Disposal	Surface water, groundwater, personnel
	Handling, spills	
waste (reaction products)	Existing permeable fractures	
	Lateral connections (depends on geological setting)	

10.6. Knowledge gaps

There are no reported adverse environmental impacts of this technique to date (VELDKAMP & BOXEM, 2015). This is consistent with its status as a relatively new technology that uses low volumes of standard oilfield chemicals and surface equipment (drill rig and pumping system) and which does not use sufficient pressure to create new fractures in the formation.

11. Shock fracturing

Shock fracturing, also known as 'jet perforation', 'explosive shaped charges' or 'concussive fracturing', involves using shaped charges to perforate the target formation. Once detonated, a high energy jet from the explosive shaped charge shoots through the casing and cement and into the formation, creating a fracture in the reservoir rock (ASUEILIMAN & ADETONA, 2013). Shock fracturing is a near-wellbore technique rather than a technique which develops a deep and extensive fracture network.

11.1. Technology application

Shock fracturing was first developed for use in the oil and gas industry in the 1950s (ALSHMLH, 2020). This technique is a development of the well perforating technique used in oil and gas wells and therefore most forms of shaped charge perforation are considered mature technologies (ALSHMLH, 2020). There are 2 variations of the technique which differ in how the explosive is conveyed into the wellbore rather than being fundamentally different in terms of reservoir impact.

Wireline conveyed

Wireline conveyed charges are run into the well on an electric cable and are detonated by running a current along the cable.

Tubing conveyed

Tubing conveyed charges have a perforating gun mounted on the end of the drill pipe string, production tubing or coiled tubing and this is lowered into the wellbore prior to detonation. After detonation, the gun can be pulled back out of the well or detached and dropped into the wellbore sump below the perforation (ASUEILIMAN & ADETONA, 2013).

11.2. Fluids and chemicals

This technique uses explosives that pose a risk to those that handle them (ALSHMLH, 2020). Primary high explosives are used as initiators, for example, lead styphnate and lead azide (ALSHMLH, 2020). The secondary explosives used are typically HMX (Cyclotetramethylene tetranitramine), RDX (Cyclotrimethylene trinitramine), PYX (Bis(picrylamino)- 3,5-dinitropyridine) and HNS (Hexanitrostilbene) and vary in thermal stability. Therefore, downhole temperatures need to be considered when deciding on the explosive type to use for secondary explosives (ALSHMLH, 2020).

Secondary charges typically contain 0.06kg to 0.32kg of explosive, but some open-hole guns may contain charges with 0.90kg or more of explosive.

11.3. Operational parameters

Detonation of explosives typically produces peak pressures between 3.4×10^4 MPa and 9.9×10^5 MPa over 1×10^{-5} to 1×10^{-6} seconds (KRILOV, et al., 2008).

Infrastructure and surface operations

The shaped charges are lowered into the well via an electric cable or mounted onto the end of the drill pipe string, production tubing or coiled tubing and detonated via perforating guns. If the intention is to detach the gun and leave it in the wellbore sump after firing, then this will have to be taken into consideration when the initial drilling takes place.

Some techniques require surface pressure control equipment to allow for the equipment to be run in and out of the well (ALSHMLH, 2020). If the aim is to develop an underbalance within the well, anchors are required for the tubing conveyed or wirelines guns to prevent them from being blown up the hole. It can also be necessary to isolate lower zones to allow for the next zone to be perforated.

11.4. Subsurface impact

When detonated, the charge produces a high velocity jet that penetrates the formation by 0.08m to 0.46m and produces a perforation that tapers along its length (KING, 1987; ALSHMLH, 2020). The length of the perforation depends on charge weight, charge type, rock strength, gun clearance and fluid (ALSHMLH, 2020). Most perforations are designed for maximum length of perforation at the expense of the diameter of the perforation. A large number of fractures are produced, with the distribution of fractures typically being irregular (KRILOV, et al., 2008).

The perforation process alters the formation within a 0.006m to 0.013m diameter around the produced tunnel. This zone of altered, compacted or crushed rock can have permeability reductions of 80% compared to the unaltered formation (ASUEILIMAN & ADETONA, 2013). The permeability around the perforated zone can decrease by more than 50% and the porosity by nearly 25% (ALSHMLH, 2020). There are techniques to reduce the damage caused, but it cannot be entirely avoided.

To try and combat the formation damage from conventional shaped charges, charges containing propellant have been developed. The addition of a propellant cap to the shaped charge has been observed to increase entry hole diameter, deepen fracture length, and enlarge perforation tunnel volume. The result is a cleaner perforation with higher permeability and less skin than conventional charges without propellant. The composite perforating system has been used on more than 2,000 vertical wells where production was increased by 28% on average (ALBERT, et al., 2018).

11.5. Geological applicability to England

Shock fracturing may be best applied in more permeable sandstone reservoirs (for example, Sherwood Sandstone Group, Collyhurst Sandstone Formation) as using an underbalance (where pressure in the wellbore is kept lower than static pressure of the formation) to clean perforations works best within porous clastic reservoirs. It is not known whether this technique would work well in basement rocks, so it may not be applicable for drilling in the radiothermal granites in the south-west (Cornwall) and northern England (Lake District and Weardale). The depth of these reservoirs would make conveying the explosives to the target wellbore section operationally challenging.

11.6. Environmental impact

No water is used with this technique so there are no requirements to deal with wastewater production as is the case with hydraulic fracturing. There is also no requirement for specialised pumping equipment as there is with acidisation techniques.

There are no additional chemicals or additives required, limiting the waste products produced and the need for surface infrastructure to transport waste for treatment.

Source	Pathway	Receptor
Explosives	Handling, offsite transport,	Groundwater, surface water,
Propellant	spills, pipe leakage	personnel

Table 25. Summary of potential environmental impacts for shock fracturing

11.7. Knowledge gaps

There are no known major environmental impacts of this technique recorded in the literature reviewed.

12. Propellant fracturing

This technique uses deflagration (the action of heating a substance until it burns away rapidly) of flammable and explosive materials to generate fractures within the reservoir, rather than detonation (a chemical reaction).

12.1. Technology application

The application varies according to the type of propellant. Some techniques require the formation to be already perforated, whereas others act as the perforator.

A variation of the technique, high energy gas fracturing (HEGF) transports propellants to the target area by wireline. Once ignited, the propellant releases gas that is contained in a column of fluid in the well, producing a pressure pulse that creates multiple fractures up to 15m in the direction of the well perforations (GANDOSSI, 2016).

Most propellant fracturing techniques are mature, but some are still under development, for example, dry fracturing explosive propellant system (EPS). This technique is commercially available and has been used in the US, Canada, Russia and China but is not used in Europe (KRILOV, et al., 2008).

HEGF is reported to have been successful in many lithologies including shale (GANDOSSI, 2016). This technique can be used in both water and air-filled boreholes, which can be important for reservoir intervals that contain swelling clays (FOURNEY, et al., 1983).

Propellants have been developed and successfully used in hundreds of wells in sandstone, limestone, shale, and coal formations (WANG, et al., 2016).

12.2. Fluids and chemicals

The main component of most propellants is nitrocellulose (KRILOV, et al., 2008), a solid low-explosive compound also used as a rocket propellant and as the main component of modern smokeless gunpowder with the chemical formula $C_6H_7O_2(OH)_3$.

As the force of the propellants deflagrating can push the wellbore fluids into the formation, it is important that the wellbore fluids are carefully chosen to prevent formation damage, as would be the case for any permeability enhancing technique (SALAZAR, et al., 2002). A hydrostatic pressure head of water or other wellbore fluid is required to contain and direct the force of the explosion into the formation, and this will typically be achieved by using water or a standard drilling mud.

12.3. Operational parameters

A hydrostatic pressure of approximately 3.4MPa is required when igniting propellants to obtain desirable burn characteristics (SALAZAR, et al., 2002).

Peak pressures of 9.9MPa to 99.9MPa are generated over 1×10^{-7} to 1×10^{-6} seconds (KRILOV, et al., 2008). The near-wellbore zone is subjected to temperatures in the range of 1,700°C to 4,700°C (SALAZAR, et al., 2002).

The peak pressures and burn characteristics produced are dependent on wellbore diameter, geometry, perforation area, formation properties and confining fluid compressibility (SALAZAR, et al., 2002).

Propellant fracturing requires the handling of explosive materials. At ambient conditions, the propellant material is effectively inert and will not burn properly without some type of confinement to allow the gas pressure to accelerate (SALAZAR, et al., 2002). There is minimal onsite equipment required, with the exception of a wireline unit (GANDOSSI, 2016).

12.4. Subsurface impact

The size, length and distribution of fractures produced is dependent on multiple variables, but fractures generally extend from below a metre to a couple of tens of metres. In moderately compacted sandstones, propellant (packaged for wireline deployment on a tool between 0.3m and 1.2m long) can create 3 to 10 fractures, 0.0005m to 0.0015m wide and 2m to 6m long (KRILOV, et al., 2008).

Laboratory experiments (SALAZAR, et al., 2002) show that vertical fractures can be constrained from propagating into layers with higher strength values; in testing, layers with unconfined compressive strength (UCS) of 241MPa and 275MPa constrained the fractures that developed in a block with a UCS of ~102MPa (PAGE & MISKIMINS, 2009).

12.5. Geological applicability to England

Propellant fracturing has mainly been applied to enhance production in sandstone and carbonate formations in vertical wells. The technique has not been applied in basement rocks so applicability to south-west granites (Cornwall) and northern England (Lake District and Weardale) is unknown.

12.6. Environmental impact

There is limited water use with this technique, therefore there is no requirement to deal with high volumes of wastewater as can be the case with other techniques. There is also no requirement for specialised pumping equipment as there is with acidisation techniques.

There are no additional chemicals or additives required, limiting the waste products produced and the need for surface infrastructure to transport waste for treatment. The propellant is provided packaged in a solid cardboard enclosed block in sealed packaging, therefore the risk of propellant entering the environment is very limited. Nitrocellulose is likely to be non-toxic for most monogastric mammalian species (QUINN, 2015) and is virtually non-soluble in water, therefore the risk of washout or leaching into surface or groundwater is very low.

Following the initiation of the nitrocellulose propellant charge, the gases produced are carbon monoxide, methane and hydrogen sulphide (US Environmental Protection Agency, 2022), which are vented to surface or dissolved in the fluid used to provide the hydrostatic head. Other propellants may also be used, however the gases produced are similar.

Table 26. Summary of potential environmental impact for propellant fracturing

Source	Pathway	Receptor
Propellant	Handling, offsite transport, storage	Groundwater, surface water
Propellant gases	Transport through wellbore to surface	Personnel at surface

12.7. Knowledge gaps

There are no known major environmental impacts of this technique recorded in the literature reviewed.

13. Low volume hydraulic fracturing

Low volume hydraulic fracturing is a technique for improving the permeability of sandstone reservoirs. The technique has developed since the 1930s, when it was observed that acid injection into limestone reservoirs above the fracture pressure resulted in permanent channels being left in the near-wellbore region. Over time, the technique evolved for use in sandstone reservoirs using a blend of crude oil, petrol and sand. These were superseded in 1953 when water was used as the fracturing liquid instead of petroleum products. In addition to water, proppants (commonly sand) are used to keep the fractures open and other chemicals are used, mainly to enhance the proppant carrying capacity of the water or to change the fluid viscosity (MONTGOMERY & SMITH, 2010).

Low volume hydraulic fracturing is closely related to acid permeability enhancing techniques (described elsewhere in this report) and requires the fluid used to be injected at a pressure higher than the fracture pressure of the reservoir rock. Low volume hydraulic fracturing for oil and gas production aims to create new fractures in rock, which when held open with proppant, allow the passage of oil or gas, while acid techniques depend on acid etching to form permanent fissures. There is no consistent definition for low volume hydraulic fracturing, which can lead to confusion as to whether a permeability enhancing operation is hydraulic fracturing.

As required by section 4A of the Petroleum Act 1998 (inserted by section 50 Infrastructure Act 2015), (HMG, 2017) all well consents issued on or after 6 April 2016 contain a requirement that the licensee obtain consent from the Secretary of State ('hydraulic fracturing consent' or 'HFC') before carrying out any associated hydraulic fracturing as defined in section 4B of that Act. On 2 November 2019 the UK Government announced that it would "take a presumption against issuing any further hydraulic fracturing consents" in England. Associated hydraulic fracturing means hydraulic fracturing of shale or strata encased in shale, which is carried out in connection with the use of the relevant well to search or bore for or get petroleum. It involves, or is expected to involve, the injection of more than 1,000m³ of fluid at each stage, or expected stage, of the hydraulic fracturing, or more than 10,000m³ of fluid in total.

Although there is a moratorium on high volume hydraulic fracturing for shale resource development, lower volume hydraulic fracturing is still a permeability enhancing technique available to onshore operators in England.

Within the English operational context in conventional formations a low volume hydraulic fracturing operation could be expected to use approximately from 150m³ of fluid (based on the most recent hydraulic fracturing operation in England) to approximately 2,600m³ of fluid in total (based on the median for US analogue wells).

13.1. Technology application

Broadly speaking, low volume hydraulic fracturing is mainly applicable to tight sandstone reservoirs. Matrix acidising is more likely to be used for carbonate formations or for the near-wellbore clean-up of sandstone reservoirs, given acids have limited effect on sandstone formations.

Low volume hydraulic fracturing reached maturity in the mid-1950s, when over 3,000 wells in conventional reservoirs were being hydraulically fractured in the USA per month as a routine step in the well completion process. From the literature review, there is no data available on how often the technique has been used onshore in England and in which reservoirs.

13.2. Fluids and chemicals

The engineering principles are very similar to high volume hydraulic fracturing, which has been used extensively to target US shale formations. While both techniques use similar equipment, fluids and proppants, the difference is in the volumes of fluids used. Data from the US showed that for broadly similar well geometries (that is, vertical wells in conventional formations) to the English context (vertical and directional wells) median water used was below 2,600m³ per well (GALLEGOS, et al., 2015).

Fluid compositions used by operators in England will be similar to those used in unconventional resource development in the USA, subject to their use being permitted in England. The US Environmental Protection Agency (U.S. EPA, 2016) has carried out a comprehensive review of fluids and chemicals used in hydraulic fracturing. A broader global review of trends in hydraulic fracturing fluids and chemicals, including trends towards less environmentally harmful additives was carried out by (AL-MUNTASHERI, 2014).

13.3. Operational parameters

Infrastructure and surface operations

Performing a low volume hydraulic fracturing operation requires additional equipment to be temporarily present on the wellsite. Figure 12 shows the equipment spread for Egdon Resources 2021 'proppant squeeze' operation at the Wressle Oil Field Development near Scunthorpe in North Lincolnshire.



Figure 12: Surface equipment set-up for low volume hydraulic fracturing (Lincolnite, 2021)

Equipment required comprises fluid, proppant and chemical storage, truck-based mixing units to mix proppants and water, a truck-based hydraulic fracturing pump and containerised test and control equipment.

The entire operation, including mobilisation and demobilisation from site typically takes 2 weeks. The duration of the low volume hydraulic fracturing operation is typically completed in under one day.

13.4. Subsurface impact

Determining the subsurface impact of low volume hydraulic fracturing is challenging, given that research with the necessary micro-seismic or tracer technologies has focused on US shale formations, where high-volume multi-stage hydraulic fracturing is used. Research based on US data (DAVIES, et al., 2012) shows that the largest vertical fracture created by high volume hydraulic fracturing in US unconventional reservoirs (from a horizontal well) was 536m, and the probability that a vertical fracture extends more than 350m is approximately 1%. Fracture lengths caused by low volume hydraulic fracturing would be considerably shorter due to the far smaller volume of fracturing fluid used. Fracture lengths for low volume fracturing can only be estimated using industry software based on a good understanding of specific reservoir conditions due to the complexity of hydraulic fracturing models.

No data was found in the literature providing case studies on the subsurface impact and fracture extent caused by low volume hydraulic fracturing in England. To understand the likely fracture extent, a study based on the specific reservoir conditions in question would need to be carried out using industry software.

13.5. Geological applicability to England

The Royal Society and The Royal Academy of Engineering (The Royal Society, 2012) suggests that approximately 10% of the UK's 2,000 onshore wells have been hydraulically fractured. However, the source of this data is unclear and is likely to include other production techniques such as water injection for improved oil recovery (ZALUCKA, et al., 2021), which have been used extensively in the UK's largest onshore oilfield at Wytch Farm.

Low volume hydraulic fracturing in England was most recently applied by Egdon Resources in 2021 to increase productivity from the Ashover Grit formation, a mediumcoarse grained sandstone with median permeability of 0.04mD (ABESSER, et al., 2005). The operation in this case was described as a 'proppant squeeze' and used 150m³ of liquid to perform the operation.

A similar operation in Germany on the Söhlingen Z16 well (targeting the Dethlinger Sandstone – late Rotliegend) in 2008 used $824m^3$ of liquid, $1.7x10^5$ kg of proppant and $3.8x10^4$ kg of additives (Umwelt Bundes Amt, 2012).

Figure 13 shows the relationship between source rock permeability and the hydraulic fracturing approach used for both oil and gas resource types in the US.



Figure 13: Applicability of hydraulic fracturing to rocks of different permeabilities, with 'massive fracturing' being equivalent to high volume hydraulic fracturing as defined in England (KLEINBERG & BOAK, 2018)

For producing reservoirs in England, low volume fracturing is likely to be pursued to improve the production rate from existing conventional fields and to remove near-wellbore

skin damage. Fracturing operations to access shale resources would use high volume hydraulic fracturing and are currently not able to be permitted.

13.6. Environmental impact

No studies were found which specifically address the environmental impact of low volume hydraulic fracturing. There is a considerable body of work related to the environmental impact of hydraulic fracturing, however most of the work completed to date has been either focused on high volume hydraulic fracturing for shale gas development in the US, for example (U.S. EPA, 2016) or preparatory work related to the shale potential of Europe. (TORRES, et al., 2016) contains a review of risk assessment techniques and main environmental findings for onshore unconventional oil and gas production. The British Geological Survey has developed a methodology to help in the preliminary assessment of risks to groundwater from subsurface oil and gas activities for England (British Geological Survey, 2019), which is available to the Environment Agency and external users.

Source	Pathway	Receptor
Chemicals	Handling and spills	Groundwater, surface water, personnel
	Well integrity (cement quality, condition of casing and tubing integrity)	Groundwater
	Existing permeable fractures	Surface water, groundwater, personnel
	New fractures connecting with existing fractures	Surface water Groundwater, personnel
	Lateral connections (depends on geological setting)	Deep aquifers, groundwater
Waste (reaction products)	Disposal	Surface water,
	Handling, spills	groundwater, personnel
	Existing permeable fractures and connection between new and existing fractures	
	Lateral connections (depends on geological setting)	

Table 27: Summary of environmental impacts for low volume hydraulic fracturing

13.7. Knowledge gaps

It has been suggested (DAVIES, et al., 2012) that further work to increase confidence in fracture propagation height and extent, based on data gained during fracturing operations, would allow a better understanding of several relationships between fracture height and variables such as the rock type, stress regime, fluid volumes and pumping time. Although these recommendations were targeted at shale developments, they would also be applicable to low volume hydraulic fracturing in England where field data is largely absent from the literature.

14. Permeability enhancement of enhanced geothermal systems

Unlike conventional geothermal systems, where reservoir permeability and existing fracture networks are sufficient to allow natural fluid flow from the formation to the wellbore, enhanced geothermal systems (EGS) are geothermal reservoirs comprising low permeability conductive rocks in which fluid connectivity is created through hydraulic, thermal or chemical permeability enhancement (HUENGES, 2016). Permeability enhancement is therefore necessary to allow EGS resources to be developed. Techniques used are largely variations of reservoir permeability enhancing techniques developed for the oil and gas industry.

Permeability enhancement mechanisms for EGS depend on whether the reservoir contains natural fractures (which require permeability enhancement to re-open or expand) or are free from fractures (requiring permeability enhancement to create new fractures).

14.1. Technology application

There are 4 different mechanisms for permeability enhancement of EGS reservoirs (LI & WANG, 2021).

- Pure tensile fracture mode. High downhole pressures (103.6MPa was used in the Cooper Basin Habanero-1 well) are used to create a fracture in an intact rock.
- Hydro-shearing mode. Existing fractures are re-opened using pressures below the minimal principal stress (Hijiori, Basel, Rosemanowes, Faklenberg and Le Mayet EGS developments). Hydro-shearing is thought to be the dominant technique used to date in this emerging industry.
- Mixed tensile and shear fracture mode. A complex fracture network is created by both creating new fractures and re-activating existing fractures.
- Cooling-induced cross tensile fracture mode. The temperature difference between the reservoir rock and working fluid creates complex new fracture networks in brittle rocks. This has been observed experimentally rather than developed as a permeability enhancement technique (GHASSEMI, 2012).

The hydraulic fracturing techniques used in EGS can be considered mature, given they originated in the oil and gas industry. The application of the techniques specifically for EGS is still developing, given that EGS was only pursued commercially from the late 1980s onwards and projects are at demonstration or early commercial stage currently.

(LI & WANG, 2021) contains considerable detail on the permeability enhancement techniques used for almost all global EGS projects.

14.2. Fluids and chemicals

The permeability enhancing fluid and additives used for EGS applications are derived from oil and gas industry fluids and additives. Freshwater is commonly used, however formation water, CO₂ or N₂ have also been considered for use. Proppants are not commonly used as they can block natural fractures, are not necessary in granite, and current proppants may not be capable of withstanding the pressures, temperatures and reactive chemical environments encountered in EGS (MCCLURE & HORNE, 2013). If proppants were to be used, they would be carried in oilfield-derived fracturing fluids. Volumes of water injected vary considerably depending by site, with a range of 13,000 to 58,000m³ and an average of 27,000m³ suggested by (CLARK, et al., 2011). Wellhead pressures show a similarly broad range, ranging from 2.2 to 89.2MPa with a median wellhead pressure of 21MPa across 17 different projects (LI & WANG, 2021).

Standard oilfield chemicals such as acids and cross-linked gels (ZIMMERMANN, et al., 2010) as well as friction reducers (BROWN, et al., 2012) may also be used, depending on specific reservoir conditions. However, as the industry is still developing, approaches are experimental and results inconsistent. For permeability enhancement operations where existing fractures need to be bypassed, thermo-degradable isolation materials have been developed. These are a type of ground polymer which biodegrade in the reservoir (CLADOUHOS, et al., 2012). No information is available on their chemical composition.

14.3. Operational parameters



Infrastructure and surface operations

Figure 14: Surface equipment set-up for an EGS permeability enhancement operation, Canada (Sask Today, 2020)

Permeability enhancement of EGS reservoirs requires the use of hydraulic fracturing equipment, namely frac trucks, pumps, mixers, manifolds, water storage, chemical storage and proppant storage. A typical equipment spread is shown in Figure 14.

14.4. Subsurface impact

From a review of existing EGS projects (MCCLURE & HORNE, 2013) suggested that new fractures initiate from open or sliding natural fractures which are connected to the wellbore and then propagate through the formation. Fracture extent and size therefore depend on the size of the existing natural fractures in the reservoir, which can only be determined through fracture modelling and fracture network mapping.

A comprehensive review of fault mechanisms and permeability enhancement techniques for all global EGS projects is detailed by (LI & WANG, 2021).

The size, length and complexity of fractures produced depend on multiple variables, but fractures generally extend from less than 50m to hundreds of metres from the wellbore. EGS developments may seek to link anthropogenic fractures with existing fractures to establish circulatory flow between injection and producing geothermal wells. In this case, the subsurface impact would be modelled based on a detailed understanding of the existing fracture network. Fracture modelling of granitic basements, similar to those found in England, has been carried out (HOFMANN, et al., 2016).

14.5. Geological applicability to England

The main resources for EGS in England (Atkins, 2013) are the radiothermal granites in the south-west (Cornwall) and northern England (Lake District and Weardale).

14.6. Environmental impact

Induced seismicity remains a significant challenge for EGS developments, due to permeability enhancement or fluid circulation or withdrawal during the operational phase. (GAUCHER, et al., 2015) provide a comprehensive overview of forecasting approaches to mitigate and better understand induced seismicity.

Research on other environmental impacts specific to EGS is very limited and has been tangentially suggested in the literature and outlined in (Environment Agency, 2021). Potential environmental impacts common to other reservoir permeability enhancing techniques include surface leaks of reservoir and permeability enhancing fluid, the use of groundwater resource (IDAHO NATIONAL LABORATORY, 2006) and contamination of aquifers due to well integrity failure (IOANNOU & FALCONE, 2020). Flow-back water may be high in dissolved minerals and naturally occurring radioactive materials (NORM) and therefore potentially more harmful than shallower well permeability enhancement flow-back fluid (IDAHO NATIONAL LABORATORY, 2006).

Passage of permeability enhancing fluids from EGS reservoirs to groundwater aquifers has not been studied in detail, due to the improbability of water transport from a potentially 5km deep basement formation through intermediate formations to groundwater aquifers where the risk has been considered to be low (MANNVIT, 2013). EGS developments in carboniferous rocks, for example, Balmatt in Belgium, have used acid techniques to stimulate wells in fractured carboniferous limestone rather than in granite basement formations (DOUZIECH, et al., 2020).

Source	Pathway	Receptor
Seismicity	Formation and overburden	Surface infrastructure
Chemicals	Handling and spills	Groundwater, surface water, personnel
	Well integrity (cement quality, condition of casing and tubing integrity)	Groundwater
	Existing permeable fractures	Surface water, groundwater, personnel
	New fractures connecting with existing fractures	Surface water Groundwater, personnel
Waste (reaction products)	Disposal	Groundwater, surface water

Table 28: Summar	y of potential environmenta	I impacts summary for EGS
------------------	-----------------------------	---------------------------

14.7. Knowledge gaps

EGS developments are still at a pilot or early commercial stage, with a small number of projects. While there has been research into the environmental impacts during the operational stage, specific research into the environmental impacts of EGS reservoir permeability enhancement is very limited, with the main environmental impact identified during the permeability enhancement stage being induced seismicity (Environment Agency, 2021). With regards to permeability enhancement fluids and chemical interactions, more research into specific environmental impacts should be expected as more projects are developed.

References

ABDELAAL, A., ALJAWAD, M., ALYOUSEF, Z. AND ALMAJID, M., 2021. A review of foam-based fracturing fluids applications: from lab studies to field implementations. Natural Gas Science and Engineering, Volume 95.

ABDOLLAHI, R., ESFANDYARI, H., PARI, M. AND DAVARPANAH, A., 2021. Conventional diverting techniques and novel fibre-assisted self-diverting system in carbonate reservoir acidising with successful case studies. Petroleum Research, 6(3), pp. 247-256.

ABDULLAH, K., MALLOY, T. AND STENSTROM, M., 2016. Toxicity of acidization fluids used in California oil exploration. Toxicological & Environmental Chemistry, pp. 1-17.

ABESSER, C., SHAND, P. AND INGRAM, J., 2005. Baseline Report Series: 18. The Millstone Grit of Northern England, s.l.: British Geological Society.

AHMED, S., HANAMERTANI, A. AND HASHMET, M., 2019. Exploitation of unconventional oil and gas resources - hydraulic fracturing and other recovery and assessment techniques. Online: IntechOpen.

AIDAGULOV, G., QIU, X., BRADY, D. AND ABBAD, M., 2018. New Insights into Carbonate Matrix Stimulation From High-Resolution 3D Images of Wormholes Obtained in Radial Acidizing Experiments. Damman, SPE.

ALBERT, L. AND OTHERS, 2018. Integrating Propellant and Shaped Charges to Improve Frac Efficiency. Texas, Society of Petroleum Engineers Liquids-Rich Basins Conference.

AL-DHAMEN, M. AND SORIANO, E., 2015. Increased well productivity from the use of carbon dioxide to foam fracturing fluids during a refracturing treatment in Saudi Arabia. Quito, Ecuador, SPE.

AL-HARTY, S. AND OTHERS, 2008. Options for high-temperature well simulation. Oilfield review, 20(4), pp. 52-62.

ALJAWAD, M. AND ALJULAIH, H., 2019. Integration of field, laboratory, and modeling aspects of acid fracturing: A comprehensive review. Journal of Petroleum Science and Engineering, Volume 181, pp. 106-158.

ALKHOWAILDI, M., AL-DRIWEESH, S., ABBAD, E. AND ABDRABALNADI, H., 2016. Eco-friendly hydraulic fracturing fluid: field deployment and performance evaluation in Saudi Arabia's tight gas reservoirs. Beijing, China, Society of Petroleum Engineers - SPE Asia Pacific Hydraulic Fracturing Conference.

AL-MAHASNEH, M., AL RABADI, S. AND KHASWANEH, H., 2021. Assessment of oil producing wells by means of stimulation approach through matrix acidising: a case study in the Azraq region. Journal of Petroleum Exploration and Production Technology, Volume 11, pp. 3479-3491.

ALMUBARAK, T., HONG, N. AND NASR-EL-DIN, H., 2017. Chelating Agents in Productivity Enhancement: A Review. Oklahoma, SPE.

ALMUBARAK, T. AND NG, J., 2017. Oilfield scale removal by chelating agents: an aminopolycarboxylic acids review. Bakersfield, California, 23 April 2017, SPE Western Regional Meeting.

AL-MUNTASHERI, G., 2014. A Critical Review of Hydraulic Fracturing Fluids for Moderate to Ultralow Permeability Formations Over the Last Decade. Denver, SPE Production & Operations.

ALSHMLH, N., 2020. Traditional perforations and upcoming laser perforation technology in oil and gas wells. s.l.:Politecnico Di Torino.

ASUEILIMAN, L.O. AND ADETONA, O.O., 2013. Effect of Perforation Job on Formation Damage. International Journal of Engineering Research and Technology (IJERT), 2(10), pp. 119-125.

ATKINS, 2013. Deep Geothermal Review Study, s.l.: Department of Energy & Climate Change.

BARATI, R. AND LIANG, J., 2014. A review of fracturing fluid systems used for hydraulic fracturing of oil and gas wells. Journal of Applied Polymer Science, 131(16), p. 40735.

BONAPACE, J., RIMONDI, G., BUSTAMENTE, M. AND QUINTAVALA, R., 2011. Stimulation with coiled tubing and fluidic oscillation: Applications in wells with low production (marginal profitability) in San Jorge Gulf Area - Argentina: Case History. Lima, Peru, Exploration, Exploitation, Processing and Transport of Hydrocarbons - VII INGEPET.

BRANNON, D.H., NETTERS, C.K. AND GRIMMER, P.J., 1987. Matrix Acidizing Design and Quality Control Techniques Prove Successful in Main Pass Area Sandstone, s.l.: SPE.

BRANNON, D., NETTERS, C. AND GRIMMER, P., 1987. Matrix acidising design and quality- Control techniques prove successful in main pass area sandstone. Journal of Petroleum Technology, 39(8), pp. 931-942.

BRITISH GEOLOGICAL SURVEY, 2019. 3D groundwater vulnerability - summary. [Online]

Available at: <u>https://www.gov.uk/government/publications/3d-groundwater-vulnerability/3d-groundwater-vulnerability-summary [Accessed 12 August 2022].</u>

BROWN, D., DUCHANE, D., HEIKEN, G. AND HRISCU, V., 2012. Mining the Earth's Heat: Hot Dry Rock Geothermal Energy. 1 ed. Heidelberg: Springer Berlin.

BUIJSE, M. AND GLASBERGEN, G., 2005. A semi-empirical model to calculate wormhole growth in carbonate acidising. Dallas, Texas, USA, Society of Petroleum Egineers - SPE Annual Technical Conference and Exhibition.

BULLEN, R. AND LILLIES, A., 1983. Carbon dioxide fracturing process and apparatus. USA, Patent No. US 4374545.

BURGOS, G., BUIJSE, M. AND FONSECA, E., 2005. Acid fracturing in Lake Maracaibo: How continuous improvements kept on raising the expectation bar. Dallas, Society of Petroleum Engineers.

BUSBY, J., KINGDON, A. AND WILLIAMS, J., 2011. The measured shallow temperature field in Britain, Nottingham: British Geological Survey.

CLADOUHOS, T. AND OTHERS, 2012. Stimulation Results From the Newberry Volcano EGS Demonstration. GRC Transactions, Volume 37.

CLARK, C.E., HARTO, C.B., SULLIVAN, J. AND WANG, M., 2011. Water Use in the Development and Operation of Geothermal Power Plants, s.l.: Argonne National Laboratory.

CLARK, J. AND SANTISO, E., 2018. Carbon Sequestration through CO₂ Foam-Enhanced Oil Recovery: A Green Chemistry Perspective. Engineering, Volume 4, pp. 336-342.

CROWE, C., MASMONTEIL, J. AND THOMAS, R., 1992. Trends in matrix acidising. Oilfield Review (Netherlands), Volume 4, pp. 24-40.

CUI, W., CUI, M., WANG, C. AND LIANG, C., 2017. Waterless stimulation for unconventional resources: an alternative to conventional water-based fracturing techniques. Abu Dhabi, UAE, SPE.

CZUPSKI, M., KASZA, P. AND LESNIAK, L., 2020. Development of Selective Acidizing Technology for an Oil Field in the Zechstein Main Dolomite. Energies, 13(5940).

DAVIES, R. AND OTHERS, 2012. Hydraulic fractures: How far can they go? Marine and Petroleum Geology, Volume 37, pp. 1-6.

DOUZIECH, M. AND OTHERS, 2020. Generation of simplified parametrised models for a selection of GEOENVI geothermal installation categories, s.l.: EU.

ECONOMIDES, M., HILL, A., EHLIG-ECONOMIDES, C. AND ZHU, D., 2013. Petroleum production systems. 2nd ed. Upper Saddle river, NJ: Prentice Hall.

ECONOMIDES, M. AND NOLTE, K., 2000. Reservoir Stimulation. 3rd ed. Chichester: John Wiley & Sons.

ENVIRONMENT AGENCY, 2021. Low carbon subsurface technologies: identifying potential environmental impacts, Bristol: Environment Agency.

ERMAKOV, K., HAMPSON, R. AND BARCLAY, D., 2020. Using fluidic oscillation technology with coiled tubing to cleanout scale from a high-pressure/extreme-temperature well beyond the limits of an HPHT motor: A case study from the UK North Sea. The

Woodlands, Texas, USA, Society of Petroleum Engineers - SPE/ICoTA Well Intervention Conference and Exhibition.

FAROUGHI, S., PRUVOT, A.-C. AND MCANDREW, J., 2018. The rheological behavior of energized fluids and foams with application to hydraulic fracturing: review. Petroleum Science and Engineering, Volume 163, pp. 243-263.

Fishbones A/S, 2021. Fishbones AS. [Online] Available at: <u>https://www.fishbones.as/jetting</u> [Accessed 8 August 2022].

FOURNEY, W. L., BARKER, D.B. AND HOLLOWAY, D.C., 1983. Model studies of well stimulation using propellant charges. International Journal of Rock Mechanics, 2(20), pp. 91-101.

FREDD, C. AND FOGLER, H., 1998. The influence of chelating agents on the kinetics of calcite dissolution. Journal of Colloid and Interface Science, Volume 204, pp. 187-197.

FRENIER, W., WILSON, D., CRUMP, D. AND JONES, L., 2000. Use of highly acid-soluble chelating agents in well stimulation services. Dallas, Society of Petroleum Engineers.

GALLEGOS, T., VARELA, B. AND ENGLE, M., 2015. Hydraulic fracturing water use variability in the United States and potential environmental impacts, s.l.: Water Resources Research.

GANDOSSI, L., 2016. An overview of hydraulic fracturing and other formation stimulation technologies for shale gas production, Luxembourg: Publications Office of the European Union.

GANDOSSI, L. AND ESTORFF, U., 2015. An overview of hydraulic fracturing and other formation stimulation technologies for shale gas production, s.l.: JRC Science Hub.

GARROUCH, A. AND JENNINGS, A.R., 2017. A contemporary approach to carbonate matrix acidizing. Journal of Petroleum Science and Engineering, Volume 158, pp. 129-143.

GAUCHER, E. AND OTHERS, 2015. Induced seismicity in geothermal reservoirs: A review of foreasting approaches. Renewable and Sustainable Energy Reviews, Issue 52, pp. 1473-1490.

GDANSKY, R., 1999. A fundamentally new model of acid wormholing in carbonates. The Hague, Society of Petroleum Engineers - SPE European Formation Damage Conference.

GHASSEMI, A., 2012. A review of some rock mechanics issues in geothermal reservoir development. Geotechnical and Geological Engineering, pp. 647-64.

GIROUD, N., VUATAZ, F. AND SCHILL, E., 2012. Geothermal reservoir of the EGS pilot plant at Soultz-sous-Forêts (France): Monitoring of the exploitation and prediction of its behaviour, Steinmaur: Deep Heat Mining Association.

GLASBERGEN, G., VAN BATENBURG, D. AND VAN DOMELEN, M.G.R., 2005. Field validation of acidzing wormholes models. Scheveningen - The Netherlands, Society of Petroleum Engineers - SPE European Formation Damage Conference.

GOMEZ, J., 2006. Design, set-up, and testing of a matrix apparatus. Unpublished MSc. thesis., Houston: Texas A&M University.

GUO, B., LIU, X. AND TAN, X., 2017. Acidizing. In: Petroleum Production Engineering (2nd Ed.). Houston: Gulf Professional Publishing, pp. 367-387.

GUPTA, D., 2003. Field application of unconventional foam technology: extension of liquid CO2 technology. Denver, Colorado, USA, SPE.

GUPTA, D., 2010. Unconventional fracturing fluids: what, where and why, s.l.: Tomball Technology Center.

GUTIERREZ, J., CALLAROTTI, G., AKRICH, O. AND MONROY, R., 2008. Stimulation with coiled tubing and fluidic oscillation. The Woodlands, Texas, USA, Society of Petroleum Engineers - SPE/CoTA Coiled Tubing and Well Intervention Conference.

HEGAZY, A., CONRAD, B., WAHEED, A. AND SANAD, O., 2009. Fluidic oscillation technique in conjunction with acid stimulation improves gas wells productivity. Scheveningen, The Netherlands, Society of Petroleum Engineers - SPE 8th European Formation Damage Conference.

HE, S., 2013. Study on damage and solution of acidizing technology in sandstone. Advanced Materials Research, Volume 631-632, pp. 729-732.

HMG, 2017. Hydraulic Fracturing Consent: Guidance on application for hydraulic fracturing consent (HFC) under section 4A of the Petroluem Act 1998 (inserted by section 50 of the Infrastructure Act 2015). [Online]

Available at:

https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment data/file/591631/Hydraulic_Fracturing_Consent_Guidance.pdf [Accessed 9 June 2022]. [Accessed 8 August 2022].

HOFMANN, H., BABADAGLI, T., YOON, J. AND BLOCHER, G., 2016. A hybrid discrete/finite element modeling study of complex hydraulic fracture development for enhanced geothermal systems (EGS) in granitic basements. Geothermics, Volume 64, pp. 362-381.

HOU, L. AND OTHERS, 2021. Review of fundamental studies of CO2 fracturing: fracture propagation, propping and permeating. Journal of Petroleum Science and Engineering, Volume 205, p. 108823.

HOUSEWORTH, J., 2016. Advanced well stimulation technologies, Berkeley: California Council on Science and Technology.

HOWARD, R., MARTINEZ, I. AND HUNTER, T., 2013. Successful case histories for the next generation 3D CFD-derived fluidic oscillator. The Woodlands, Texas, USA, Society of Petroleum Engineers - SPE/CoTA Coiled Tubing and Well Intervention Conference and Exhibition.

HUENGES, E., 2016. Enhanced geothermal systems: review and status of research and development. Geothermal Power Generation, pp. 743-61.

ICOTA, 2022. Stimulation. [Online] Available at: <u>https://icota.com/technical/stimulation</u> [Accessed 20 November 2021]. [Accessed 8 August 2022].

IDAHO NATIONAL LABORATORY, 2006. Impact of Enhanced Geothermal Systems (EGS) on the United States in the 21st Century, s.l.: Idaho National Laboratory.

IOANNOU, A. AND FALCONE, G., 2020. Synthesis of Environmental Factors, Glasgow: CROWDTHERMAL.

JIN, F. AND OTHERS, 2017. Green fracturing technology of shale gas: LPG waterless fracturing technology and its feasibility in China. Buenos Aires, Argentina, SPE.

JORGENSEN, T., 2014. Liner-Based Stimulation Technology Without Fracturing Proven in Field. Journal of Petroleum Technology, pp. 28-31.

KAHRILAS, G., BLOTEVOGEL, J., STEWART, P. AND BORCH, T., 2015. Biocides in hydraulic fracturing fluids: A critical review of their usage, mobility, degradation, and toxicity. Environmental science and technology, Volume 49, pp. 16-32.

KALAM, S. AND OTHERS, 2021. A review on non-aqueous fracturing techniques in unconventional reservoirs. Natural Gas Science and Engineering, Volume 95, p. 104223.

KALFAYAN, L. AND METCALF, A., 2000. Successful sandstone acid design case histories: exceptions to conventional wisdom. Dallas, Texas, USA, Society of Petroleum Engineers - SPE Annual Technical Conference and Exhibition.

KALYA, N. AND BALAKOTAIAH, V., 2007. Modeling and analysis of wormhole formation in reactive dissolution of carbonate rocks. Chemical Engineering Science, Volume 62, pp. 919-928.

KARADKAR, P., BATAWEEL, M., BULEKBAY, A. AND ALSHAIKH, A., 2018. Energised fluids for upstream production enhancement: a review. Dammam, Saudi Arabia, SPE.

KHAMIS, M., 2016. Acid types and reactions with different rocks, Riyadh: King Saud University.

KING, G., 2012. Hydraulic fracturing 101: What every representative, environmentalist, regulator, reporter, investor, university researcher, neighbor and engineer should know about estimationg frac risk and improving frac performance in unconventional gas and oil

wells. The Woodlands, Texas, USA, Society of Petroleum Engineers - SPE Hydraulic Fracturing Technology Conference.

KING, G.E., 1987. Selecting a Perforating System. Journal of Petroleum Technology, 3(39), pp. 261-262.

KLEINBERG, R. AND BOAK, J., 2018. Unconventional Fossil Fuels Nomenclature. Oklahoma Geology Notes, July, pp. 20-25.

KONG, B., WANG, S., CHEN, S. AND DONG, K., 2016. Minimise formation damage in water-sensitive unconventional reservoirs by using energised fracturing fluid. Lafayette, Louisiana, USA, SPE.

KRILOV, Z., KAVEDZIJA, B. AND BUKOVAC, T., 2008. Advanced well stimulation method applying a propellant based technology. Wiertnictwo, Nafta, Gaz, 2(25), pp. 405-416.

KRISTSANAPHAK, K., TIRICHINE, S. AND KAMMOURRIEH, M., 2010. A successful application of near-wellbore stimulation using fluidic-oscillation technique in North Africa. Beijing, Society of Petroleum Engineers-Proceedings of International Oil and Gas Conference and Exhibition in China.

KUMAR, N., RAJPUT, S. AND GAUTHAM, K., 2017. Propane fracturing: a waterless approach, safety considerations and its prospects in India. Mumbai, India, SPE.

LEE, J., 2016. Small molecule associative CO₂ thickeners for improved mobility control, Pittsburgh, PA, USA: University of Pittsburgh.

LEE, J. AND OTHERS, 2014. Development of small molecule CO₂ thickeners for EOR and fracturing. Tulsa, OKlahoma, USA, SPE.

Lincolnite, T., 2021. Mission complete: controversial fracking operation at oil field near Scunthorpe. [Online]

Available at: <u>https://thelincolnite.co.uk/2021/07/mission-complete-controversial-fracking-operation-at-oil-field-near-scunthorpe/</u>

[Accessed 8 January 2022]. [Accessed 8 August 2022].

LI, N. AND OTHERS, 2021. Fracturing technology with carbon dioxide: A review. Journal of Petroleum Science and Engineering, Volume 205.

LI, Q. AND OTHERS, 2019. Effect of a modified silicone as a thickener on rheology of liquid CO₂ and its fracturing capacity. Polymers, Volume 11, p. 540.

LI, S. AND WANG, S., 2021. Stimulation mechanism and design of enhanced geothermal systems: A comprehensive review. Renewable and Sustainable Energy Reviews, Volume 155, p. 111914.

LIU, H. AND OTHERS, 2014. Fracturing with carbon dioxide: Application status and development trend. Petroleum Exploration and Development, August, 41(4), pp. 513-519.

LONG, J. AND OTHERS, 2015. An independent scientific assessment of well stimulation in California - Vol II - Potential environmental impact of hydraulic fracturing and acid stimulations, Berkeley: California Council on Science and Technology & Lawrence Berkeley National Laboratory.

MALATE, R. AND OTHERS, 1998. Matrix stimulation treatment of geothermal wells using sandstone acid. 23rd Workshop on geothermal reservoir engineering. Stanford, California, Stanford University.

MALATE, R. AND OTHERS, 1999. Wellbore soaking: a novel acid treatment of geothermal injection wells. 24th Workshop on geothermal reservoir engineering. Stanford, California, Stanford University.

MANNVIT, 2013. Environmental Study on Geothermal Power, Reykjavík: Mannvit.

MCCLURE, M. AND HORNE, R., 2013. An investigation of stimulation mechanisms in Enhanced Geothermal Systems. International Journal of Rock Mechanics and Mining Sciences, Volume 72, pp. 242-260.

McLEOD, H.O., 2017. Petroleum Engineering Handbook - Volume IV - Production Operations Engineering. Houston: Society of Petroleum Engineers.

MIDDLETON, R. AND OTHERS, 2015. Shale gas and non-aqueous fracturing fluids: opportunities and challenges for supercritical CO₂. Applied Energy, Volume 147, pp. 500-509.

MOJID, M. AND OTHERS., 2021. A state-of-art review on waterless gas shale fracturing technologies. Petroleum Science and Engineering, Volume 196, p. 108048.

MONTGOMERY, C. AND SMITH, M., 2010. Hydraulic Fracturing: History of an Enduring Technology. Journal of Petroleum Technology, 62(12), pp. 26-40.

MORIDIS, G., 2017. Literature Review and Analysis of Waterless Fracturing Methods, Berkeley, California, USA: Lawrence Berkeley National Laboratory.

NENGKODA, A. AND OTHERS, 2011. Trending of H2S from reservoir after acidizing from well contained SRB bacteria: souring case study in Southern Oman. Doha, Qatar, Society of Petroleum Engineers - SPE Projects and Facilities Challenges Conference.

OIL AND GAS AUTHORITY, 2017. OGA Southern North Sea Tight Gas Stimulation, Aberdeen: Oil and Gas Authority.

OUSSOLTSEV, D. AND OTHERS, 2008. Foam fracturing: new stimulation edge in Western Siberia. Moscow, Russia, SPE.

PAGE, J.C. AND MISKIMINS, J.L., 2009. A comparison of hydraulic and propellant fracture propagation in a shale gas reservoir. Journal of Canadian Petroleum Technology, 05(48), pp. 26-30.

PORTIER, S., ANDRE, L. AND VUATAZ, F., 2007. Review on chemical stimulation techniques in oil industry and applications to geothermal system, Neuchatel: CREGE.

PRISKILA, L.M., 2014. Evaluation of Fishbone Lateral Stimulation: A Simulation Study. s.l.:Norwegian University of Science and Technology.

QUINN, M.J., 2015. Wildlife Toxicity Assessments for Chemicals of Military Concern. s.I.:Elsevier.

RAMANA MURTHY, R., KATARI, N., SATYA SREE, N. AND JONNALAGADDA, S., 2019. A novel protocol for reviving of oil and natural gas wells. Petroleum Research, 4(3), pp. 276-281.

RIBEIRO, L. AND SHARMA, M., 2013. Fluid selection for energised fracture treatments. The Woodlands, Texas, USA, SPE.

RICE, K., 2016. Multilateral stimulation technology - a new approach to stimulating/revitalizing production in carbonate reservoirs. San Antonio, AAPG Geosciences Technology Workshop Revitalizing Reservoirs.

ROGALA, A., KRZYSIEK, J., BERNACIAK, M. AND HUPKA, J., 2012. Non-aqueous fracturing technologies for shale gas recovery. Physicochemical Problems of Mineral Processing, 49(1), pp. 313-322.

SALAZAR, A., ALMANZA, E., CHIRA, P. AND FOLSE, K., 2002. Application of propellant high-energy gas fracturing in gas-injector wells at EI Furrial Field in Northern Monagas State - Venezuela. Lafayette, The SPE international symposium and exhibition on formation damage control.

SASK TODAY, 2020. Horizontal, hydraulicly-stimulated geothermal well is "remarkable," says DEEP CEO. [Online] Available at: <u>https://www.sasktoday.ca/south/oil-gas/horizontal-hydraulicly-stimulated-geothermal-well-is-remarkable-says-deep-ceo-4159347</u> [Accessed 10 Dec 2020]. [Accessed 8 August 2022].

SCHLUMBERGER, 2021. Schlumberger online glossary. [Online] Available at: <u>https://glossary.oilfield.slb.com</u> [Accessed November 2021]. [Accessed 8 August 2022].

SHAFIQ, M. AND MAHMUD, H., 2017. Sandstone matrix acidising knowledge and future development. Journal of Exploration and Production Technology, Volume 7, pp. 1205-1216.

SKINNER, L., 2021. Workovers. In: Well integrity for workovers and recompletions. Houston: Gulf Professional Publishing, pp. 275-428.

SOLHAUG, K., 2017. Fishbones A/S. [Online] Available at:

https://www.norwep.com/content/download/32604/236929/version/1/file/Fishbones+-+Fishbones Stimulation Technology.pdf - page not available [Accessed 10 November 2021].

SOLHAUG, K., 2019. The Norwegian Petroleum Directorate. [Online] Available at: https://www.npd.no/globalassets/2-force/2019/events/2019/20190611fishbone/fishbone-solhaug.pdf

[Accessed 10 November 2021]. [Accessed 8 August 2022].

SONI, T., 2014. LPG-based fracturing: an alternate fracturing technique in shale reservoirs. Bangkok, Thailand, IADC / SPE.

SUN, Y. AND OTHERS, 2019. A critical review of risks, characteristics, and treatment strategies for potentially toxic elements in wastewater from shale gas extraction. Environment International, Volume 125, pp. 452-469.

TAMALMANI, K. AND HUSIN, H., 2020. Review on Corrosion Inhibitors for Oil and Gas. Applied Sciences, Volume 10, p. 10.

THE ROYAL SOCIETY, 2012. Shale gas extraction in the UK: a review of hydraulic fracturing, London: The Royal Society.

TORRES, L., YADAV, O.M. AND KHAN, E., 2016. A review on risk assessment techniques for hydraulic fracturing water and produced water management implemented in onshore unconventional oil and gas production. Science of the Total Environment, Volume 539, pp. 478-493.

TORVUND, S. AND OTHERS, 2016. First installation of multilateral drilling stimulation technology in tight sandstone formation. Anchorage, Society of Petroleum Engineers Western Regional Meeting.

TUDOR, E.H., NEVISON, G.W., ALLEN, S. AND PIKE, B., 2009. 100% Gelled LPG Fracturing Process: An Alternative to Conventional Water-Based Fracturing Techniques. Charleston, SPE.

US EPA, 2016. Hydraulic Fracturing for Oil and Gas: Impacts from the Hydraulic Fracturing Water Cycle on Drinking Water Resources in the United States (Final Report), Washington, DC: U.S. Environmental Protection Agency.

UGURSAL, A., ZHU, D. AND HILL, A., 2018. Development of acid fracturing model for naturally fractured reservoirs. The Woodlands, Texas, Society of Petroleum Engineers -SPE Hydraulic Fracturing Conference and Exhibition.

UMWELT BUNDES AMT, 2012. Environmental Impacts of Hydraulic Fracturing Related to Exploration and Exploitation of Unconventional Natural Gas Deposits, s.l.: Federal Ministry for the Environment, Nature Conservation and Nuclear Safety.

US ENVIRONMENTAL PROTECTION AGENCY, 2022. AP-42: Compilation of Air Emissions Factors. [Online]

Available at: <u>https://www.epa.gov/air-emissions-factors-and-quantification/ap-42-</u> <u>compilation-air-emissions-factors</u>

[Accessed 15 April 2022]. [Accessed 8 August 2022].

VAJPAYEE, M., GOGINENI, S. AND SHUKLA, Y., n.d. A novel way to reservoir stimulation: LPG gel based fracturing, s.l.: s.n.

VAN HONG, L. AND BEN MAHMUD, H., 2018. A preliminary screening and characterization of suitable acids for sandstone matrix acidizing technique: a comprehensive review. Journal of Petroleum Exploration and Production Technology, Volume 9, pp. 753-778.

VELDKAMP, J.G. AND BOXEM, T.A.P., 2015. Sector Outlook: Geothermal power increase in the Netherlands by enhancing the capacity, Utrecht: TNO.

WANG, H. AND OTHERS, 2020. Research status and prospects of supercritical CO₂ fracturing technology. Acta Petrolei Sinica, 41(1).

WANG, L. AND OTHERS, 2016. Waterless fracturing technologies for unconventional reservoirs - opportunities for liquid nitrogen. Journal of Natural Gas Science and Engineering, Issue 35, pp. 160-174.

WAN, J., 2017. Report on developing a US-China joint project on CO₂-based fracturing techniques, Berkeley: Lawrence Berkeley National Laboratory.

WAN, J., 2017. Report on Developing a US-China Joint Project on CO₂-Based Fracturing Techniques, Berkeley, CA, USA: Lawrence Berkeley National Laboratory.

WANNIARACHCHI, W. AND OTHERS, 2015. Current opinions on foam-based hydrofracturing in deep geological reservoirs. Geomechanics and Geophysics for Geo-Energy and Geo-Resources, Volume 1, pp. 121-134.

WARNOCK, W., HARRIS, P. AND KING, D., 1985. Successful field applications of CO2foam fracturing fluids in the Arkansas-Louisiana-Texas Region. Journal of Petroleum Technology, 37(01), pp. 80-88.

WEBB, E., SCHULTZ, R., HOWARD, R. AND TUCKER, J., 2006. Next-generation fluidic oscillator. The Woodlands, Texas, USA, Society of Petroleum Engineers - SPE/CoTA Coiled Tubing and Well Intervention Conference and Exhibition.

WEITAN, D., YUTING, H., SANDERS, M. AND FARAG, S., 2007. Reliable hydraulic fracture evaluation with a state of the art sonic tool. Abu Dhabi, Society of Petrophysicists and Well Log Analysts (SPWLA) Middle East Regional Symposium.

WILKINS, R., MENEFEE, A. AND CLARENS, A., 2016. Environmental life cycle analysis of water and CO-based fracturing fluids used in unconventional gas production. Environmental Science and Technology, 50(23), pp. 13134-13141.

WILSON, B., 2013. GasFrac: A Cost-Benefit Analysis of Hydraulic Fracturing with Liquefied Petroleum Gas Gel. Technology Law & Policy, Volume XIV, pp. 142-157.

XIE, W. AND OTHERS, 2021. Progress and prospects of supercritical CO₂ application in the exploitation of shale gas reservoirs. Energy Fuels, 35(22), pp. 18370-18384.

XU, T. AND OTHERS, 2003. Reactive transport modeling of injection well scaling and acidizing at Tiwi field, Philippines. Geothermics, Volume 33, pp. 477-491.

ZALUCKA, A., GOODENOUGH, A. AND SMYTHE, D., 2021. Acid stimulation: Fracking by stealth continues despite the moratorium in England. Energy Policy, Volume 153, p. 112244.

ZHANG (a), Z. AND OTHERS, 2019. Advances in waterless fracturing technologies for unconventional reservoirs. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, Volume 41.

ZHANG (b), Y. AND OTHERS, 2019. Characteristics of fracture propagation induced by supercritical CO₂ in inter-salt-shale reservoir. Geofluids, Volume 2019, p. 7132843.

ZHANG, R. AND OTHERS, 2018. Investigation on hydraulic fracture initiation and propagation with LPG fracturing in shale formation based on true tri-axial laboratory experiments. Bangkok, Thailand, IADC / SPE.

ZHANG, X. AND OTHERS, 2017. Experimental study on fracture initiation and propagation in shale using supercritical carbon dioxide fracturing. Fuel, Volume 190, pp. 370-378.

ZIMMERMANN, G., MOECK, I. AND BLOCHER, G., 2010. Cyclic waterfrac stimulation to develop an enhanced geothermal system (EGS) - conceptual design and experimental results. Geothermics, Volume 39, pp. 59-69.

ZORANOC, n.d. LPG Fracturing Technology and Its Application. [Online] Available at: <u>https://www.zoranoc.com/LPG-Fracturing-Technology-and-Its-Application_1203.html</u> [Accessed 14 April 2022]. [Accessed 8 August 2022].

Would you like to find out more about us or your environment?

Then call us on

03708 506 506 (Monday to Friday, 8am to 6pm)

Email: enquiries@environment-agency.gov.uk

Or visit our website

www.gov.uk/environment-agency

Incident hotline

0800 807060 (24 hours)

Floodline

0345 988 1188 (24 hours)

Find out about call charges (https://www.gov.uk/call-charges)

Environment first

Are you viewing this onscreen? Please consider the environment and only print if absolutely necessary. If you are reading a paper copy, please don't forget to reuse and recycle.