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Use of nanomaterials in fluids, proppants, and downhole tools for hydraulic fracturing of unconventional hydrocarbon reservoirs

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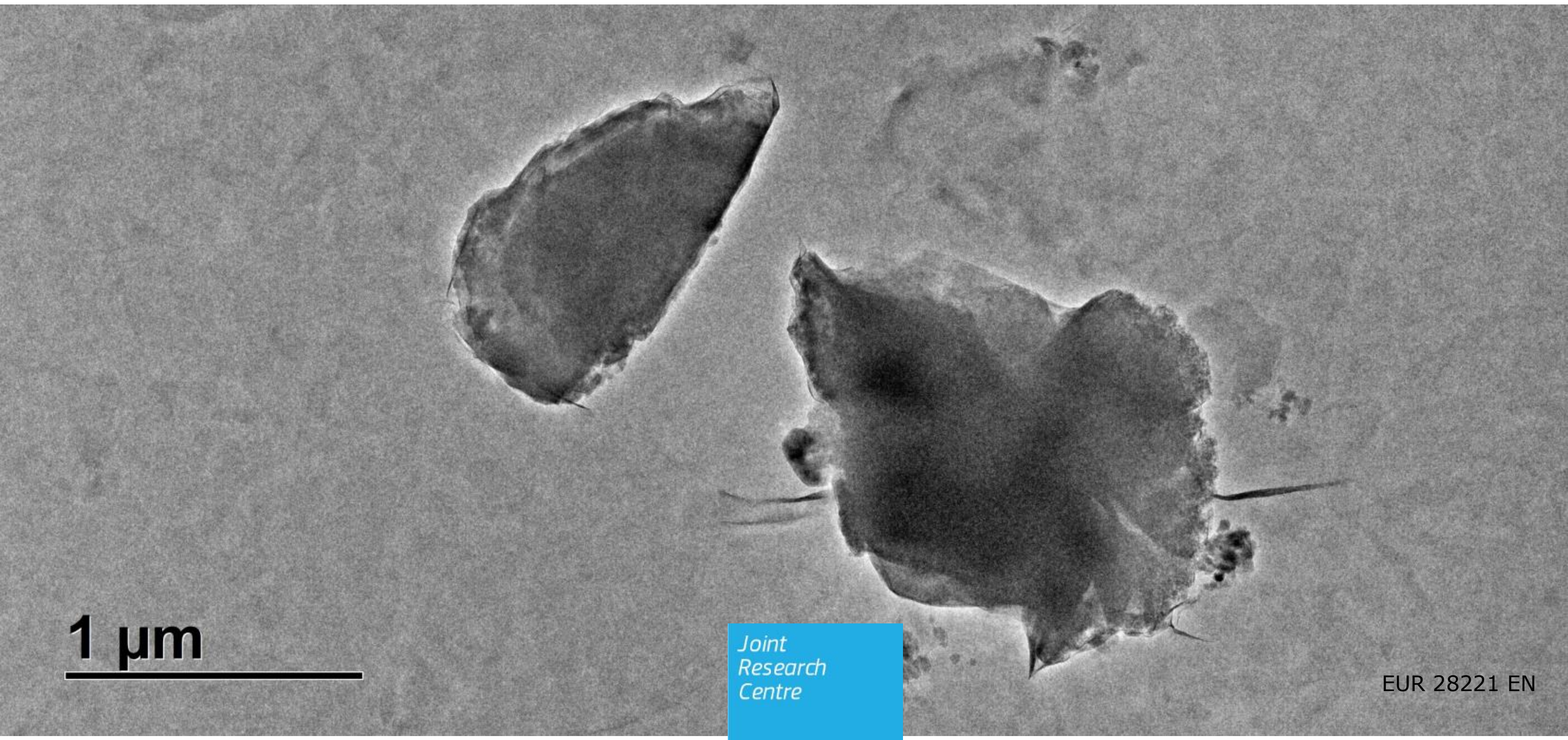

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Table of contents

Foreword

This report has been drafted by the European Commission's Joint Research Centre (JRC) in the context of a project on 'Unconventional Hydrocarbons'. The project started in January 2016 and had, among its objectives, the collection and review of published information on the use of chemicals and nanomaterials in downhole tools, proppants, and fluids for hydraulic fracturing of unconventional reservoirs.

The JRC project on 'Unconventional Hydrocarbons' is linked to the European Commission's Recommendation 2014/70/EU on minimum principles to be followed concerning the use of high volume hydraulic fracturing in Europe. The European Commission is currently reviewing the effectiveness of the Recommendation.

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Abstract

The present report illustrates the results of a literature and Internet search aimed to collect and review information on the use of nanotechnology in fluids, proppants, and downhole tools for hydraulic fracturing of unconventional hydrocarbon reservoirs.

Different sources were consulted to cover both potential nanotechnology applications, as proposed in peer reviewed scientific literature and patents, and commercially available applications, which are already used in products and advertised on company websites.

In summary, 25 different types of nanotechnology applications have been identified and a large variety of different nanomaterials has been encountered, ranging from inorganic and organic nanoparticles to more complex core-shells and nanocomposites. Most of the nanomaterials used in applications for hydraulic fracturing are of inorganic nature. About half of the application types are specific for unconventional reservoirs including tight and ultra-tight gas, shale gas, and coal-bed methane. Although more than two thirds of the application types are still at the research and development stage, 31 commercial products claiming to use nanotechnology have been identified. Only few of them are available in the European market, according to producers' claims.

The consulted sources consider the use of nanotechnology in fluids, proppants, and downhole tools for hydraulic fracturing of unconventional hydrocarbon reservoirs as successful. No disadvantage or additional cost from application of nanomaterials in hydraulic fracturing is mentioned.

1. INTRODUCTION

1.1. Aim of the document

The present report illustrates the results of a literature and Internet search aimed to collect and review information on the use of nanotechnology in fluids, proppants and downhole tools for hydraulic fracturing of unconventional hydrocarbon reservoirs. The search was specifically intended to:

- Identify what types of nanomaterials (i.e. chemical composition, size distribution, physicochemical properties) may be used in hydraulic fracturing and for what purpose or technical function;
- Distinguish between nanotechnology applications that are proposed in the scientific literature and are therefore still at the research and development stage and those applications that are already used in commercial products and marketed;
- Understand what are the advantages and disadvantages of using nanomaterials in those applications;
- Clarify how the nanomaterials exert their function when added to the fracturing fluids and what is the mode of action, if known.

Section 1 provides a brief introduction to the subject as well as the context and the scope of the document. Section 2 of the report illustrates the method used to perform the literature and Internet search and the sources that have been considered. Section 3 summarises the general results in terms of types of nanomaterials used in the retrieved applications, technical functions covered, target rock formations and market prospects. Section 4 reports and discusses in more detail the results by technical function.

The present report does not produce new knowledge on the use of nanotechnology for hydraulic fracturing of unconventional reservoirs but relies on publicly available knowledge and attempts to integrate information that can be found in peer-reviewed scientific literature with what is claimed by companies on their websites and other sources.

1.2. The project on 'Unconventional Hydrocarbons'

This work has been carried out by the European Commission's Joint Research Centre (JRC) in the context of a project on 'Unconventional Hydrocarbons'. The project started in January 2016 and had, among its objectives, the collection and review of published information on the use of chemicals and nanomaterials in downhole tools, proppants, and fluids for hydraulic fracturing of unconventional reservoirs.

The JRC has previously released several reports addressing issues concerning hydraulic fracturing, including economic and environmental aspects of hydrocarbons production from unconventional reservoirs [1]. In one of these reports, the JRC specifically assessed how the use of substances in fracturing fluids and their exposure scenarios may be registered in REACH dossiers [2].

The JRC project on 'Unconventional Hydrocarbons' is linked to the European Commission's Recommendation 2014/70/EU on minimum principles to be followed concerning the use of high volume hydraulic fracturing in Europe [3]. The term 'high volume hydraulic fracturing' indicates the use of a larger amount of water than in traditional hydraulic fracturing and is defined in the European Commission's Recommendation as follows: *"injecting 1000 m^3 or more of water per fracturing stage or 10000 m^3 or more of water during the entire fracturing process into a well".*

The European Commission is currently reviewing the effectiveness of the Recommendation [4]. Based on the results of a questionnaire to the Member States, exploratory drilling operations have been undertaken in shale gas plays in some countries, e.g. Poland, United Kingdom, and Germany, to evaluate the capacity of the reservoirs and to test the production rate. However, none of the explored shale gas reservoirs have been commercially exploited until now and there are no plans to grant authorisation for production in the near future [4].

1.3. Definition of a 'nanomaterial'

The term 'nanomaterial' is defined in the European Commission's Recommendation 2011/696/EU [5] as: *"A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm - 100 nm.".*

Nanomaterials are considered, in principle, to be covered by the definition of the term 'substance' under the REACH Regulation [6] and therefore REACH regulatory requirements apply to nanomaterials in a similar manner to other industrial chemicals. ECHA in its guidance on the implementation of REACH explicitly refers to the European Commission's definition of the term 'nanomaterial' [7].

1.4. Hydraulic fracturing and types of fluids

Unconventional oil and/or gas reservoirs consist of very low permeability and porosity rock formations that need to be stimulated before extraction and commercial exploitation can start. Hydraulic fracturing stimulates the rock formation by pumping a fluid into the wellbore at a high pressure, which exceeds the strength of the rock and generates a large network of fractures.

Fracturing fluids usually consist of a base fluid, a proppant and one or more chemical additives exerting different functions. The fractures created by the base fluid need to be kept open to allow hydrocarbons to flow more freely from the reservoir to the wellbore, i.e. to increase conductivity. This is achieved by adding a propping agent, which is solid, particulate material usually made of quartz sand, resin-coated sand, bauxite or ceramic granules, to the base fluid. To suspend and transport proppant beads into the fractures the viscosity of the base fluid may need to be increased by using a gelling agent that commonly consists of guar gum and guar derivatives or a viscoelastic surfactant. Fluid viscosity, however, decreases as temperature increases in deep rock formations and a cross-linker is added to maintain stability. Other chemical additives can be found in fracturing fluids such as: friction reducers, surfactants, breakers, fluid loss control agents, clays stabilizers, biocides, etc. (see Appendix I, adapted from Gottardo et al. [2]).

Fracturing fluids have been recently reviewed in the scientific literature [8] [9]. The most commonly used fracturing fluids in shale gas plays in the USA have water as base fluid and can be organised into four groups [8] according to the type of chemical additives they contain:

- Slick-water fluids mainly consist of water and proppant, and do not contain gelling agent.
- Linear polymeric fluids mainly consist of water, proppant, and gelling agent.
- Cross-linked polymeric fluids mainly consist of water, proppant, gelling agent, and cross-linker.
- Viscoelastic Surfactant (VES) fluids mainly consist of water, proppant, and surfactant(s).

Slick-water hydraulic fracturing is suited for complex reservoirs that are brittle and naturally fractured and are tolerant of large volumes of water [8]. It is mainly applied to shale gas wells where high fracture conductivity is not necessarily required [9]. It creates longer but less wide fractures that generate a higher network complexity; however, due to low viscosity, the slick-water fluid is a poor proppant carrier and does not have fluid loss control properties. Other base fluids, such as linear and cross-linked polymeric fluids, have higher viscosity and several benefits, including better proppant transport and reduced fluid loss into the surrounding rock matrix due to formation of a filter-cake on the fracture surface. Cross-linked polymeric fluids contain a lower concentration of gelling agent, which is an advantage from an environmental point of view, and are more stable at high temperature. Moreover, cross-linking is reversible and this facilitates clean-up of the fluid after fracturing. Cross-linked fluids are widely applied to shale oil wells due to higher conductivity requirements [9]. VES fluids represent a more environmentally friendly alternative to polymeric fluids as they use surfactants to create a micellar network and increase viscosity and elasticity. However, they can suspend a lower amount of proppant and do not have filter cake properties [8] [9].

Other fluids instead of water can be used for hydraulic fracturing. For example, liquid CO_2 has been successfully used for tight gas production in Canada and the USA [8]. In low permeability reservoirs, water-based fluids may get trapped in rock pores or contribute to clays swelling and may therefore cause damage in the area near the wellbore. Liquid CO_2-based fluids do not cause damage and can transport proppant without adding any viscosifier or other chemical [8]. CO_2 also has an adsorption capacity with shale that is higher than that of CH_4 and can therefore replace it, thus enhancing gas recovery [8].

2. SOURCES OF INFORMATION

Different sources were consulted to cover both potential nanotechnology applications, as proposed in peer reviewed literature and patents, and commercially available applications that are already used in products placed onto the market.

The sources are:

1. An extensive literature search through keywords in bibliographic databases and on line search engines, to collect relevant peer reviewed scientific articles, book chapters, conference/workshop proceedings, patents, thesis, etc.
2. Additional *ad hoc* literature searches in online search engines and webpages of international/national organizations driven by specific needs during the project, to identify other relevant peer reviewed and non-peer reviewed literature (including reports from public authorities, news from digital magazines).
3. Company websites, e.g. service companies that are known to produce fracturing fluids, to obtain information on commercially available products using nanotechnology.
4. Online platforms to obtain information on nanomaterials that are claimed to be used in hydraulic fracturing of specific oil and/or gas reservoirs and related wells.

The following sections describe in more details each information source.

2.1. Bibliographic databases and on line search engines

An extensive literature search was performed on specific bibliographic databases and online search engines to identify and collect peer reviewed scientific articles and reviews, book chapters, conference/workshop proceedings, patents, thesis, etc. proposing nanotechnology applications for hydraulic fracturing of both conventional and unconventional oil and/or gas reservoirs.

Two bibliographic databases and one search engine were initially selected:

- Scopus, which is the largest abstract and citation database of research literature. Peer-reviewed journals, conference proceedings, conference papers, and scientific books are equally covered under 'primary documents'. Scopus also provide results for 'secondary documents', i.e. those references that are not available in Scopus database but are records extracted from references in Scopus (e.g. quotations), and for patents.

- OnePetro[1], which is the major online library of technical documents and journal articles for the oil and gas exploration and production industry.
- Google Scholar[2], which is an online search engine providing an emerging new model for giving users access to journal articles over the web. Google Scholar gives prominence to articles and abstracts available through open access publishing and institutional repositories.

2.1.1 Search terms

The search strategy in Scopus, OnePetro and Google Scholar consisted of several combinations of search terms. In any combination, the first search term was aimed to perform a broad screening in the field of nanotechnology and retrieve all articles containing the word 'nano' as standalone or part of a longer word (e.g. nanotechnology, nanomaterial(s), nanoparticle(s), nanopolymer(s), nanoemulsion(s)) in the article title, abstract and/or keywords. The search term was aimed to restrict the search and focus it on the use of these materials for hydraulic fracturing of conventional and/or unconventional oil and/or gas reservoirs.

For the Scopus engine the combinations of search terms were as follows:

- The first keyword was 'nano*' in all combinations (the symbol * was used to retrieve all articles containing 'nano' as part of a longer word); and
- The second keyword was different in each combination i.e. 'hydraulic fractur*', 'fracking', 'fracturing fluid*', 'shale gas', 'shale oil', 'oil industry', 'gas industry', 'well* stimulation', 'unconventional hydrocarbon*' and 'well* productivity' (the symbol '*' was used to retrieve all articles containing 'fractur', 'fluid', 'well' and 'hydrocarbon' as part of a longer word e.g. fracturing, fluids, wellbore, hydrocarbons).

The results of the literature search by combination of keywords as used in Scopus are illustrated in Table 2.1 and discussed in section 2.1.4.

The same search strategy was initially applied to OnePetro but a large number of results were found and several documents were considered as not relevant (e.g. containing terms such as "nano-darcy", "nano-porous", etc. in the title or abstract, which are referred to the nanoscale of the porous media and not to the use of nanotechnology). In order to overcome this problem some changes to the first search term were made and the final search strategy was as follows:

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[1] https://www.onepetro.org/
[2] https://scholar.google.it/

- The first search term was modified and made more specific: 'nanotech*' and 'nanomat*' were used separately in combination with the second search term (the symbol * was used to retrieve all articles containing 'nanotech' or 'nanomat' as part of a longer word e.g. nanotechnology/ies, nanomaterial(s)); and
- The second search term was the same as in Scopus search.

The results of the literature search by combination of keywords as used in OnePetro are illustrated in Table 2.1 and discussed in section 2.1.4.

The same search strategy used for OnePetro was applied to Google Scholar. However, after trying few combinations of keywords the search was interrupted because of the impractical large number of results (see Table 1). As a consequence, it was decided to use Google Scholar only for *ad hoc* searches driven by project needs (see section 2.2).

2.1.2 Search period

The initial search on Scopus engine was carried out on 20-08-2015, followed by further search on 31-08-2014. In the case of OnePetro library the initial search was carried out on 02-09-2015, followed by further search on 04-09-2015.

2.1.3 Export to EndNote

The results from Scopus and OnePetro (including article title, abstract, keywords, publication year, journal, and author(s)) were exported as Research Information Systems (RIS) files and imported to EndNote. In the case of Scopus, the RIS files included both primary and secondary documents but excluded patents.

In EndNote, the search results from both databases were merged to find and remove duplicate records of the same reference. The results after removal of duplicates are reported in Table 2.1.

2.1.4 Search results

The results from the search are illustrated in Table 2.1.

Table 2.1 Number of references retrieved from bibliographic databases and online search engines for each combination of search terms before and after removal of duplicates. Double documents were identified and removed in EndNote. Search on Google Scholar was not accomplished due to an impractical large amount of results (n.a. = not applied).

SOURCE	Scopus			OnePetro		Google Scholar	
DOCUMENT TYPE	**Primary documents**	**Secondary documents**	**Patents**	**Primary documents**		**Primary documents**	
SEARCH TERMS	Nano*			Nanomat*	Nanotech*	Nanomat*	Nanotech*
Hydraulic fractur*	188	9	25	4	7	2250	4750
Fracking	11	-	2	3	3	195	626
Fracturing fluid*	84	3	48	22	40	10600	17300
Shale oil	214	2	-	11	18	n.a.	
Shale gas	341	45	-	21	59		
Oil industry	119	17	2	45	105		
Gas industry	253	38	8	69	117		
Well* stimulation	112	-	2	10	19		
Unconventional hydrocarbon*	13	-	-	-	14		
Well* productivity	28	-	-	23	49		
TOTAL BY SOURCE	1477		87	639		n.a.	
TOTAL ALL SOURCES	2116 documents + 87 patents					n.a.	
TOTAL ALL SOURCES (NO DUPLICATES)	1378 documents + 87 patents					n.a.	

The search on Scopus resulted in 1477 records in EndNote (295 from first search, 1182 from second search). The search on OnePetro resulted in a total number of 639 records (79 from first search, followed 560 from second search). As explained in 2.1.3, the results from both databases were merged in order to remove double records of the same reference and at the end the total number of files in EndNote decreased from 2116 to 1378 (i.e. 738 duplicates were found). Out of them, about 56% are journal articles, 28% conference proceedings, 12% conference papers, 1% book chapters, thesis and magazine articles and 3% generic or not reported sources.

The search on Scopus also retrieved 87 patents that could not be imported to EndNote.

2.1.5 Criteria for selection of relevant references

The relevance of references was assessed based on the title and to which extent it answered the objective of the project, which was to review existing nanotechnology applications for hydraulic fracturing of unconventional oil and gas reservoirs. Based on this criterion, 179 documents and 13 patents were considered as relevant and fully read (except for 6 documents written in a foreign language that could not be processed).

Those references that were considered as not relevant based on title but still could be linked to the objective of the project were organised into three groups based on the subject, i.e. nanotechnology applications for: 1) reservoir characterisation and monitoring (e.g. nanosensors); 2) drilling and wellbore stability; and 3) waste water/recovery fluids treatment. Those references were not consulted for the preparation of the present report. However, they could be considered at a later stage if an interest in extending the scope of the project is expressed.

2.2. Additional *ad hoc* searches

In addition to the extensive literature search described in section 2.1, *ad hoc* literature searches were performed via Google and Google Scholar to identify additional relevant peer and non-peer reviewed literature (e.g. reports, news in digital magazines). Moreover, webpages of international and national authorities (e.g. Polish government) were searched. These additional literature searches were triggered by specific needs arisen during the project while reading the relevant references identified in section 2.1 and should therefore be considered as complementary to the extensive literature search and as a refinement of the information initially retrieved. These additional searches resulted in 11 relevant peer-reviewed documents (journal articles and conference proceedings), 26 patents, 1 thesis, and 12 magazine articles, which were fully read.

2.3. Company websites

A targeted search also involved a number of company websites, including major fracturing fluids producers, to retrieve complementary information on nanotechnology applications that have been already placed onto the market and applied in unconventional oil and/or gas fields. This targeted search involved 27 websites including 9 companies producing nanomaterials used in applications for fracturing fluids, 9 companies producing different types of additives for fracturing fluids, and 9 service companies involved in oil and gas production and performing fracturing operations.

2.4. Online platforms

Existing online platforms used by industry to voluntarily disclose the chemicals applied in their fracturing operations were also considered as relevant sources to retrieve information on nanomaterials that have been already applied in oil and/or gas fields.

The International Association of Oil and Gas Producers Natural Shale Gas (IOGP NSG) facts[3] is a platform providing factual information concerning hydraulic fracturing of natural gas from shale wells and other related issues, including voluntary disclosure of chemical additives on a well-by-well basis in the European Economic Area (EEA). The IOGP NSG facts platform allows search of chemicals by well; however, the content is currently limited to 10 wells in Poland. For those wells, the disclosure sheets have been consulted (see section 3.2 for details).

Another important platform is the Fracfocus Chemical Disclosure Registry[4], which provides public access to voluntarily reported chemicals used for hydraulic fracturing in specific wells in the USA territory, where companies can also specify the purposes the chemicals serve and the means by which groundwater is protected. Fracfocus presently contains information on chemicals used in 112839 wells. The authors originally planned to consult this platform too; however, due the large number of wells in the USA territory, the time frame for the preparation of this document as well as its intent of focusing on the European context, the search was considered as impractical and the original plan was abandoned.

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[3] http://www.ngsfacts.org/

[4] http://fracfocus.org/

3. GENERAL RESULTS

3.1 Nanotechnology applications

The analysis of the retrieved information in the relevant sources (see section 2) resulted in 25 different types of nanotechnology applications in fluids, proppants, and downhole tools developed for hydraulic fracturing of unconventional hydrocarbons reservoirs.

For each application type, one or more nanomaterials have been used or proposed as candidates for use in the consulted sources. More specifically, a nanomaterial can be applied as: a material or component of a downhole tool for completion; a material for manufacturing of proppant or enhancing proppant's properties; or an additive to fracturing fluids with the aim of exerting a certain function e.g. cross-linking, formation fines control, surfactant (see Appendix I of this document for description of terms).

A total number of 11 technical functions (see Appendix I of this document for description of terms) have been identified to describe the use of nanomaterials in the retrieved applications, namely:

- Downhole tools for completion in multi-stage fracturing;
- Proppant;
- Formation fines control additive and clay stabilizer;
- Cross-linker and fluid loss control additive in Viscoelastic Surfactant (VES) fluids;
- Breaker system;
- Biocide;
- Fluid loss control additive in polymeric fluids;
- Cross-linker in polymeric fluids;
- Surfactant system;
- Fracturing additive in CO_2-based fluids;
- Any function;
- Other.

The full list of nanomaterials used in the retrieved applications is reported in Appendix II of this document along with the available information on their chemical composition, size and other physicochemical properties, target rock formation and market prospect. General results are presented in the following paragraphs (i.e. in 3.1 and 3.2). Detailed results are discussed for each technical function in section 4 of this document.

Figure 3.1 efficiently visualises the relationship between the encountered nanomaterial types and the technical functions they exert as components of downhole tools, proppants, or additives to fracturing fluids. A large variety of nanomaterials has been encountered ranging from inorganic and organic nanoparticles to more complex core-shells and nanocomposites. However, it is clearly visible from Figure 3.1 that most of the nanomaterials proposed and/or used in applications for hydraulic fracturing are of inorganic nature, mainly metals and metal(oids) (hydr)oxides, and cover a large variety of technical functions from fluid loss and migration fines control additive to proppant and material component of downhole tools for completion and multi-stage fracturing. The technical function that shows the largest variety of nanomaterial types is proppant.

As presented in detail in Appendix II of this document, the nanomaterial name and its chemical composition is usually reported in the considered sources; the nanomaterial name is indeed unknown in 10 cases (i.e. sources) only. In some papers, the authors specified the manufacturer of the nanomaterial that is proposed and/or used for that specific application and/or tested in laboratory/field experiments and this helped to identify additional information on chemical identifiers, size or other physicochemical properties from the manufacturer's webpage (see text in green, red or blue colour in Appendix II of this document). In most of the cases, the chemical composition is clearly indicated (e.g. SiO_2 nanoparticles) or described (e.g. metal composite including a substantially-continuous, cellular nanomatrix with a plurality of dispersed particles, each comprising a particle core material (Mg, Al, Zn or Mn) and a metallic coating). In other cases, a long list of chemical names or categories of nanomaterials that are possible candidates for application is reported (e.g. alkaline earth metal oxides, alkaline earth metal hydroxides, transitional metals, etc.). The latter situation often occurs in patents.

Information about size is usually provided in the sources; however, in most if the cases, the particle size range or particle average size is reported, and this does not allow understanding whether the material is compliant with the definition of the term 'nanomaterial' as provided by the European Commission's Recommendation 2011/696/EU [5], which is referred to in ECHA guidance for implementation of REACH [7]. There are also cases where the particles are claimed to be in the nano scale but the reported size range is above 100 nm (e.g. > 200 nm) or cover both nano and micro scale (e.g. 1-1000 nm) or the reported average size is in the micron range (e.g. 545.43 nm).

Other physicochemical properties are rarely mentioned: for example, in few cases information on specific surface area, zeta potential, and shape of nanoparticles could be retrieved.

About half (i.e. 12) of the applications types are claimed to be specific for hydraulic fracturing of unconventional reservoirs in the sources. In detail: 1 for unconventional oil, 2 for unconventional gas (including shale gas), 1 for tight gas, 3 for tight and ultra-tight gas, 2 for tight, ultra-tight and shale gas, 2 for shale gas, and 1 for coal-bed methane. The remaining types of nanotechnology applications are not specific for hydraulic fracturing of unconventional reservoirs but applicable to hydraulic fracturing of any type of oil and/or gas reservoirs including unconventional ones.

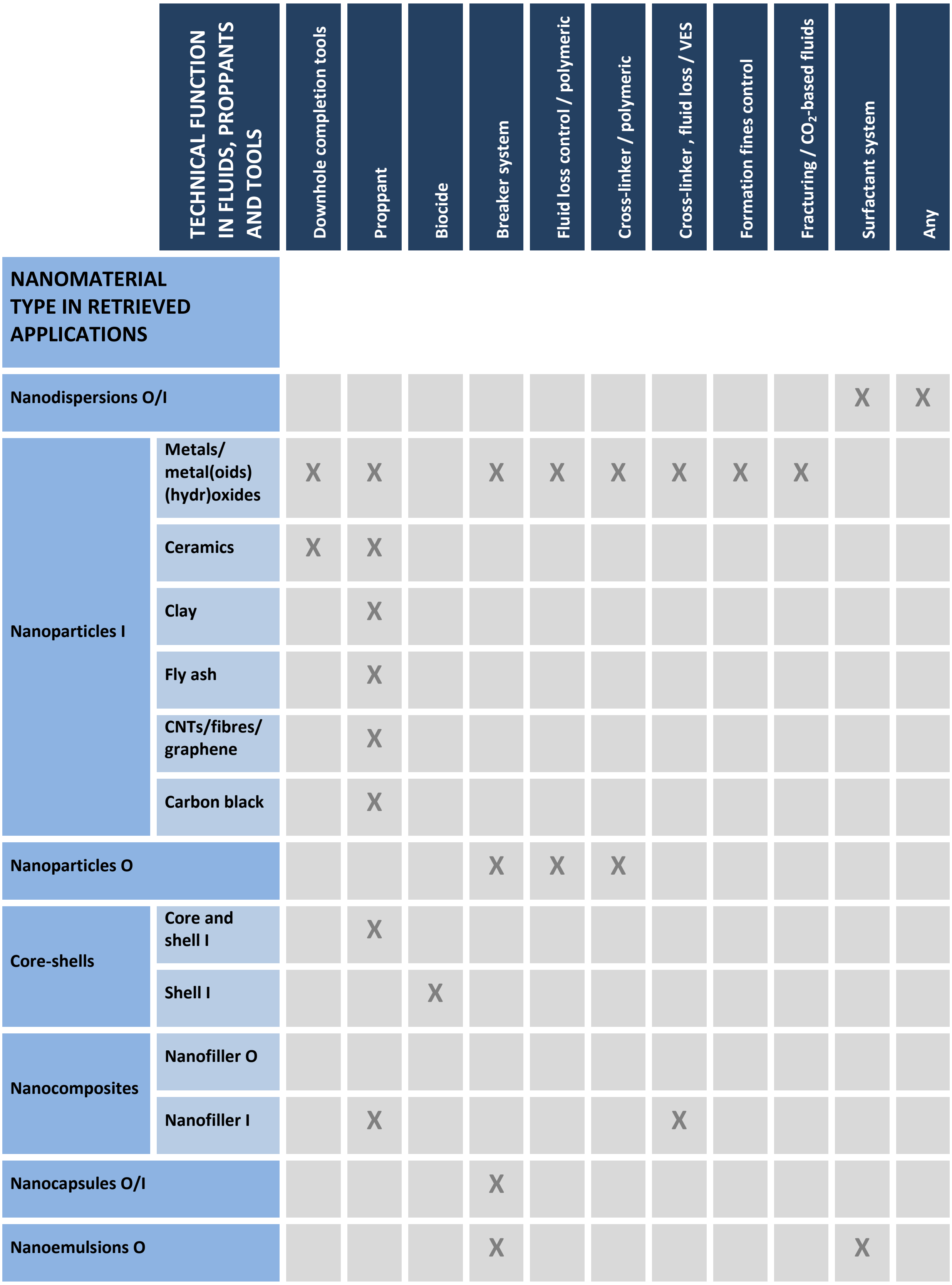
More than two thirds (i.e. 18) of the applications types are still at research and development stage. They are described in journal articles, conference proceedings and patents, and no commercially available products containing those applications have been identified. Generally, no field trial has been reported for those applications, except from 3 cases that have been already tested *in situ* based on the retrieved information.

In total, 7 applications types are already marketed and 31 commercial products could be identified. The product names along with the manufacturer names are listed in Table 3.1. For more than half of the products (i.e. 23) the chemical composition of the nanomaterial is not declared by the manufacturer; however, in several cases, some information on the chemical composition could be deduced from patents, peer-reviewed articles and/or magazine articles published by authors that are affiliated to the manufacturer.

For some products, information on the fracturing operations that have been already performed is reported in the sources. In all the cases, such operations occurred in the USA territory. Three products are claimed being applied in Europe in both shale and coal bed methane projects (i.e. FrackBlack™, FrackBlack HP™, FrackBlack HT™ by Sun Drilling Corporation, proppant, see section 4.2). Five products are claimed to be sold in Europe in addition to USA and Middle East (i.e. MA-844W, MA-845, Stim® GPHT, StimOil® FBA M, and StimOil® FD by Flotek Industries, surfactant system, see section 4.9).

The consulted relevant references consider the use of nanotechnology for hydraulic fracturing of unconventional hydrocarbons reservoirs as successful. Manufacturers of products exploiting nanotechnology as well as scientists who developed those applications and presented their results in patents or peer-reviewed publications tend to underline the advantages of using nanomaterials in fracturing treatments (e.g. addition of nanoparticles to VES fluids) and, in some cases, the advantages of using nanomaterials over the bulk counterparts (e.g. using nanobentonite over bentonite). A summary of the benefits from using nanotechnology applications, which have been claimed in the sources, is reported by technical function in Table 3.2. Accordingly, the use of nanomaterials always significantly increases the performance of a certain additive, fluid, proppant, or tool, thereby improving the production of hydrocarbons from unconventional rock formations (e.g. higher production rates). The resulting applications also seem to be more cost-effective and environmentally friendly than the traditional counterparts. No disadvantage or additional cost from the use of nanotechnology in hydraulic fracturing is reported in the considered sources.

Figure 3.1 Relationship between the types of nanomaterials used in the retrieved applications and the technical functions they are able to exert. O = Organic; I = Inorganic; VES = Viscoelastic Surfactant; CNTs = carbon nanotubes



	TECHNICAL FUNCTION IN FLUIDS, PROPPANTS AND TOOLS	Downhole completion tools	Proppant	Biocide	Breaker system	Fluid loss control / polymeric	Cross-linker / polymeric	Cross-linker , fluid loss / VES	Formation fines control	Fracturing / CO_2-based fluids	Surfactant system	Any
NANOMATERIAL TYPE IN RETRIEVED APPLICATIONS												
Nanodispersions O/I											X	X
Nanoparticles I	Metals/ metal(oids) (hydr)oxides	X	X		X	X	X	X	X	X		
	Ceramics	X	X									
	Clay		X									
	Fly ash		X									
	CNTs/fibres/ graphene		X									
	Carbon black		X									
Nanoparticles O					X	X	X					
Core-shells	Core and shell I		X									
	Shell I			X								
Nanocomposites	Nanofiller O											
	Nanofiller I		X					X				
Nanocapsules O/I					X							
Nanoemulsions O					X						X	

Table 3.1 Commercial products for hydraulic fracturing claimed to contain nanotechnology applications by manufacturer. VES = Viscoelastic Surfactant; n.r. = not reported.

TECHNICAL FUNCTION	PRODUCT NAME	COMPANY NAME	NANOMATERIAL TYPE	SOLD/USED IN EUROPE?
DOWNHOLE COMPLETION TOOLS	IN-Tallic Disintegrating Frac Balls	Baker Hughes Incorporated	Nanoparticles – Metallic/ceramic particles with metallic coating sintered in a nanomatrix (e.g. Mg, Al, Zn, Mn)	n.r.
PROPPANTS	FrackBlack^{TM} FrackBlack HP^{TM} FrackBlack HT^{TM}	Sun Drilling Corporation	Nanocomposites – Polymer with inorganic nanofiller (e.g. carbon black, CNTs, fibres, fumed silica, alumina, nanoclays, fly ash)	Claimed it has been applied in Europe in both shale and coal bed methane projects
	LiteProp108	Baker Hughes Incorporated	Nanocomposites – Composition not declared	n.r.
	OxFrac^{TM} OxBall^{TM} OxThor^{TM} OxSteel^{TM}	Oxane Materials	Core-shells – Hollow ceramic core and inorganic shell (e.g. fly ash)	n.r.
FORMATION FINES CONTROL	ConFINE Fines Fixing Agent	Baker Hughes Incorporated	Nanoparticles – Composition not declared. Most probably, metal oxides nanoparticles (e.g. MgO)	n.r.
CROSS-LINKER, FLUID LOSS / VES	DiamondFraq	Baker Hughes Incorporated	Nanoparticles – Composition not declared. Most probably, metal(oids) oxides (e.g. ZnO, MgO, SiO_2)	n.r.
SURFACTANT SYSTEM	NanoSurf 696	Oil Chem Technologies	Nanoemulsion – Composition not declared	n.r.
	Complex nano-Fluid® (CnF®) MA-844W, MA-845, Stim GPHT, Stimoil® EC, Stimoil® ENX, Stimoil® FBA M, Stimoil® FBA Plus Enviro, Stimoil® FD, Stimoil® AHS, Stimoil® E50, MA-844W, MA-845, Stim GPHT, StimOil® FBA M, StimOil® FD	Flotek Industries	Nanoemulsion – Composition not declared. Most probably, mixture of alcohol ethoxylates (surfactants), citrus terpene (solvent), and water	MA-844W, MA-845, Stim® GPHT, StimOil® FBA M, and StimOil® FD are claimed to be sold in Europe

Table 3.1 (cont.)

TECHNICAL FUNCTION	PRODUCT NAME	COMPANY NAME	NANOMATERIAL TYPE	SOLD/USED IN EUROPE?
	NPD® Solutions	FTS International	Nanodispersion – Composition not declared. Most probably, metal(oids) oxides (e.g. SiO_2)	n.r.
	G-Clean Well Wake-Up	Green Earth Technologies	Nanoemulsion – Composition not declared, Most probably, mixture of fatty acids, emulsifier and ionic surfactants.	n.r.
OTHER	OilPerm FMMs	Halliburton	Composition not declared	n.r.

Table 3.2 Summary of claimed advantages of using nanotechnology in applications for hydraulic fracturing based on the reported information in the sources. VES = Viscoelastic Surfactant.

TECHNICAL FUNCTION	CLAIMED ADVANTAGES OF NANOTECHNOLOGY APPLICATIONS
DOWNHOLE COMPLETION TOOLS	Higher strength, lighter weight, increased corrosion rate compared to reference material (downhole tools can flow back to surface without restricting the tubing or completely disintegrate)
	Time savings, cost reduction
ULTRA-LIGHT PROPPANTS	Lower density, less settling, better penetration into rock formation
	Greater resistance to heat distortion, stiffness and stability in the environment (can be used at higher temperature and closure stress than previous formulations)
	Smaller volumes and concentrations of proppant are required to generate sufficient fracture width and conductivity
	Higher conductivity than in the reference sample (e.g. up to 50%)
	Greater hydrocarbon production over a long time period (e.g. 25% more)
	If case of porous proppants, additives can be carried to be released directly inside a fracture or in response to environmental conditions
	In case of hollow proppants, the manufacturing process can be controlled at molecular scale to create proppant particles that are specifically tailored for the need of any rock formation
STRENGTHENED PROPPANTS	In case of fibre-coated proppants, improved mechanical properties (e.g. compressive strength about 32.5% higher) and greater suspension capability
	In case of hydraulic cement, presence of nanobentonite gives superior mechanical properties and a significant decrease in permeability (from about 29% to about 80%) as compared with conventional bentonite
PROPPANT FOR TIGHT AND ULTRA-TIGHT FORMATIONS	Deeper percolation, increased propped fracture network and flow area, reduced fluid loss, increased well productivity

Table 3.2 (cont.)

TECHNICAL FUNCTION	CLAIMED ADVANTAGES OF NANOTECHNOLOGY APPLICATIONS
FORMATION FINES CONTROL	Help fines associate, group or flocculate together, prevent them from moving close to the wellbore and cause formation damage
CROSS-LINKER, FLUID LOSS / VES	Enhanced fluid viscosity at high temperature due to "pseudo-crosslinking" effect (e.g. 10-fold increase of fluid viscosity and stability at temperature up to 250 °F)
	Reduced fluid loss and increased VES fluid efficiency to generate fractures due to generation of "pseudo-filter cake"
	Reduced amount of surfactant used in the VES fluid (e.g. from 2.5 to 1%), easier breaking of the gel in VES fluid at low temperature
BREAKER SYSTEM	Delayed and controlled release of internal breakers thank to nanoencapsulation
	More stable and longer shelf life when compared to liquid breakers for VES fluids
FLUID LOSS CONTROL / POLYMERIC	Reduced fluid loss, improved fracture propagation
	Weaker filter cake, easier to clean-up compared to the filter cake formed exclusively by the polymer gel
CROSS-LINKER / POLYMERIC	More environmentally friendly and efficient alternative to borate cross-linked polymeric fluids
	Amount of boron used with nanoparticles is less than with standard borate ions
	Increased viscosity (e.g. by a factor of 25)
	Cross-linking process can be delayed
BIOCIDE	Remain suspended and, consequently, not settle in the mud pit, or settle relatively slowly, so to retain their biocidal properties
	May maintain concentration and efficacy longer than other conventional biocides
SURFACTANT SYSTEM	Improved surfactant's ability of lowering interfacial tension and enhancing rock wettability
	Proppant permeability 2 times higher than with conventional surfactants
	Increased production and effective fracture length
	Fluids friction pressures dropped (e.g. of 10-15%), restored productivity of wells damaged by fracturing, and enhanced oil/gas production
	Environmentally compatible (biodegradable, plant-derived) and chemically safe (non-carcinogenic, non-toxic, non-hazardous, and non-containing Volatile Organic Compounds)
	Vastly improve asphaltene and paraffin removal efficiency over traditional microemulsions
	Much less treatment fluid is required during well remediation as compared to traditional methods
	Pressure to initiate clean-up lowered (e.g.) by 50%
FRACTURING / CO_2-BASED FLUIDS	Generate more fractures in the rock matrix
ANY	Surprisingly stability, can be easily transported to the subterranean location without the need of a thickened carrier fluid, dispersed additive becomes available when required, in response to conditions encountered underground
OTHER	Enhanced mobilization of liquid hydrocarbons resulting in improved oil production rate and recovery
	Rapid recovery of the aqueous flow-back fluids resulting in reduced time for fracturing clean-up with reduced time before production
	Stability, penetration into the fracture network and reduced adsorption losses

3.2 Disclosed nanomaterials

Table 3.3 summarises the information on substance names and related CAS numbers as retrieved from IOGP NGS facts online platform (see section 2.4).

No nanomaterial could be clearly identified in the available disclosure sheets. Certain types of substances e.g. non-crystalline silica, corundum or mullite, were reported in the disclosure sheets. It is known that these substances can exist as nanoforms, i.e. amorphous silica, nanocorundum and nanomullite, respectively, and both bulk and nanoforms are commercialised under the same CAS number. However, no additional information could be retrieved from the platform and thus no conclusion could be drawn.

In addition, some disclosure sheets specify that a "delayed borate cross-linker" and an "encapsulated breaker" were used as additives to fracturing fluids. It is known that nanoencapsulation can be used e.g. to carry breakers and delay their activation downhole (see section 3.1). However, no commercial product exploiting this specific nanotechnology application could be identified in the considered sources.

Based on the little information available on the IOGP NGS facts platform, no conclusion on the use of nanotechnology for hydraulic fracturing in Europe could be drawn.

Table 3.3 Substance names and related CAS numbers as reported in the disclosure sheets from IOGP NGS facts online platform.

CAS NUMBER	SUBSTANCE NAME
66402-68-4	Ceramic materials and wares chemicals Silica substrate Calcinated bauxite (proppant) Silica substrate (sand proppant) Silica crystalline-cristobalite
14808-60-7	Crystalline silica Silica, crystalline (quartz)
14808-60-7	Element is bentone 150 (quartz and 1,6 hexanediol)
7631-86-9	Non crystalline silica
1302-74-5	Corundum
1302-93-8	Mullite
71011-24-0	Alkyl quaternary ammonium bentonite
14464-46-1	Silica crystalline, cristobalite
14807-96-6	Magnesium silicate hydrate (talc)

4. DETAILED RESULTS BY TECHNICAL FUNCTION

In the sub-sections below the results are discussed in more detail by technical function.

4.1. Downhole tools for completion in multi-stage fracturing

One type of nanotechnology application as downhole tool for completion in multi-stage hydraulic fracturing has been found. Information on this application has been retrieved from 4 conference proceedings, 4 conference papers, 1 patent, and 2 company websites.

Flow control devices such as setting balls or plugs are used downhole for sleeve actuation or stimulation diversion during multi-stage fracturing. After fracturing, these devices must be removed to open the pathway for gas and/or oil production [10]. Disposal has conventionally been accomplished by milling or drilling the component out of the wellbore [11]. Such operations are generally time consuming and expensive [11].

To facilitate disposal light-weight, low-strength materials or degradable materials have traditionally been used for these devices. However, both solutions have drawbacks: light-weight, low-strength materials are prone to deformations that may hamper flow back and therefore require costly intervention; degradable materials such as biodegradable polymers lack the necessary strength to withstand high pressure during hydraulic fracturing and may have unreliable degradation rates [10] [11].

Baker Hughes Incorporated has developed a nanostructured metallic powder composite that combines high-strength, light-weight and is completely corrodible in typical downhole environments at a predictable and controllable rate in response to a change of a fluid property or environmental condition [10]. This material is called Controlled Electrolytic Metallics (CEM) material and is patented [12]. It is described as a substantially-continuous, cellular nanomatrix including a plurality of dispersed particles or grains in it; each particle comprises a metallic (Mg, Al, Zn, Mn or a combination thereof) or carbon-based core material and a metallic coating layer (Al, Zn, Mn, Mg, Mo, W, Cu, Fe, Si, Ca, Co, Ta, Re or Ni); the nanomatrix is formed by sintering metallic coating layers of adjacent particles to one another by interdiffusion and creation of a bond layer [12]. Particle cores have variable dimensions at the micron scale (from 5 to 300 um) while both metallic coating layers and nanomatrix thickness are at the nanoscale (e.g. 25 to 2500 nm and about 50 to 5000 nm, respectively) [12].

High strength and toughness of CEM material can be achieved by controlling the distribution of micro and nanoparticles in the matrix [13]. Carbon-based particles can be added to the matrix as strengthening agents and to reduce the density [12]. Moreover, metallic particles are electrochemically-active [12] and become the activation points for dissolution that could be triggered on demand [10]. Based on laboratory results reported by Xu et al. [10] [11], compressive strength of CEM material increased 3 to 6 times and corrosion rate by several hundred times compared to reference material.

According to Zhang et al. [13], CEM material is a promising candidate for a variety of well completion tools. One example is the IN-Tallic Disintegrating Frac Balls produced by Baker Hughes Incorporated [14] and used in the ball-activated sleeve system for multi-stage fracturing of shale gas reservoirs [13]. Based on the available information in the Internet [14], this product is onto the market since 2011 at least. The balls can be flowed back to surface or completely disintegrated in the well without blocking or restricting the tubing [10]. Consequent time savings associated to the elimination of trips greatly impact the cost of completion [15]. In one of the most recent publications it is stated that over 30000 IN-Tallic Disintegrating Frac Balls have been successfully ran for numerous operators across major USA tight formations including Bakken, Niobrara, Marcellus, Utica, Haynesville, Granite Wash, Woodford, Wolfberry, Bone Springs, and Eagle Ford [16].

4.2. Proppants

As explained in section 1.4, fractures created in shale deposits by means of high fluid pressure (i.e. hydraulic fracturing) have to be propped allowing unconventional gas migration to a borehole.

Proppant particles (beads, preferably spherical), which can be placed in the fracture in a form of a pack or a monolayer, must generally be made from materials that have excellent mechanical properties. The mechanical properties of greatest interest in most such applications are stiffness (resistance to deformation) and strength under compressive loads (resistance to crush), combined with sufficient "toughness" to avoid the brittle fracture of the particles into small pieces commonly known as "fines". In addition, the particles must have excellent heat resistance to be able to withstand the combination of high compressive load and high temperature that normally becomes increasingly more severe as one drills deeper. The good transport and low settling ability of proppants is another feature that has to be considered when choosing the propping agent. Commonly applied proppants consist of quartz sand and resin-coated sand that are used in the USA for fracturing of shale reservoirs since the early 50s of the 20th century. On the other hand bauxites and ceramic granules are more suitable for deeply deposited unconventional gas extraction at hard geomechanical conditions, such as in Europe, to increase output of gas even by 30-50% [17].

It has been demonstrated in the scientific literature [18] that nanoparticles may improve the above mentioned mechanical properties of proppants. Certain inventions propose the addition of nanoparticles into the material from which proppant particles are made and some others exploit the advantages that nanostructured materials offer.

Information on nanotechnology applications as proppant has been retrieved from 1 peer reviewed scientific article, 1 conference proceedings, 8 patents, 3 magazine articles, 6 company websites, and 1 thesis. Nanotechnology is applied to proppants to achieve the following goals:

- Development of ultra-light proppants (section 4.2.1);
- Improvement of strength of proppants (section 4.2.2);
- Development of proppants for tight and ultra-tight formations (section 4.2.3).

It has to be noted that in many cases the improvement of one mechanical property triggers changes of other properties like e.g. lowering the density improves strength and toughness; nonetheless each nanotechnology application is assigned to the group according to the main driver of the invention.

4.2.1 Ultra-light proppants (ULP)

Three different types of nanotechnology applications aimed to produce ultra-light proppants (ULP) for hydraulic fracturing have been identified. The information has been retrieved from 7 patents, 6 company websites, 3 magazine articles and 1 thesis.

The first application concerns a new type of nanocomposite material suitable for ULP production. Bicerano [19] [20] [21] proposed a new class of thermoset polymer nanocomposites that consists of a light thermoset polymer matrix with incorporated nanoparticles from an inorganic filler. Some examples of materials that may be suitable as nanofillers and consist of particles in the size range 1-500 nm are given in the sources: carbon black, carbon nanotubes and nanofibers, fumed silica and alumina as well as cellulosic nanofibers, nanoclays and finely divided grades of fly ash (Class C and F) among others.

The author claims that these new ultralight proppants, thanks to both polymer and nanofiller constituents, have much lower density than density of typical sand or ceramic-based proppants. This allows their transport without settling much further into the rock formation than traditional proppants. The outcome is a more effective fracture length, especially when using fracturing fluids of low viscosity like slick-water or VES fluids. Moreover, addition of nanoparticles results in greater resistance to heat distortion, stiffness and stability in the environment. Furthermore, such proppants can be placed in the fracture as a "partial monolayer". Smaller volumes and concentrations of proppant are required to generate sufficient fracture width and conductivity when a partial monolayer can be employed instead of a conventional proppant pack. Combined with greater effective fracture length, the ability to place the proppant as a partial monolayer would result in the exposure of more rock formation to the conductive path and thus would lead to greater hydrocarbon production over a long time period. A conductive test was performed [20] on proppant particles of 1.19-1.41 mm size (14/16 US Mesh) made of 84.365% styrene, 5.635% ethyl vinyl benzene, 10% divinylbenzene and 0.5% by weight of Monarch 280 (carbon black from Cabot Corporation, 310 nm) as nanofiller against a reference sample of same size proppant particles without nanofiller. The results demonstrated the advantage of using the nanocomposite particles in terms of enhanced retention of liquid conductivity under compressive stress of 4000 psi at temperature of 190 °F. After 260 hours the conductivity of nanocomposites proppant was 50% higher than in the reference sample.

A specific modification of this class of nanocomposites that contains an impact-modified thermoset polymer to improve the crush resistance and prevent embrittlement and fines formation of the proppant particles was also reported by the same author [21].

Three commercial products were identified that exploit the described nanotechnology and are protected under above cited patents [19] [20] [21] among others. FracBlack™, FracBlack HP™ and FracBlack HT™ from Sun Drilling Technologies [22] [23] are ultralight thermoset nanocomposite proppants that consist of a polymer (CAS: 9052-95-3) and a not specified nanofiller designed for use in partial monolayer fracture stimulation applications. FracBlack HT™ is the newest product of the series that can be used at closure stress approaching 8000 psi and temperatures approaching 275 °F, much greater than earlier formulations (FracBlack™ up to 5000 psi and FracBlack HP™ up to 7000 psi, respectively). The low specific gravity of FracBlack™ series approaches that of water (specific gravity: 1.06 g/cc), allowing for excellent proppant distribution throughout the fracture network and exceptional results in horizontal gravel pack applications. Currently, only FracBlack HT™ is commercially available on the company website [24]. The company claims that FracBlack HT™ was successfully applied in China in both traditional and coal bed methane projects, in South America as gravel pack material and in Europe for recovery of hydrocarbons in both shale and coal bed methane projects [22].

Another product, called LiteProp108, was mentioned in a magazine article [25] and a patent [26] by Baker Hughes Incorporated to be an ultralight proppant consisting of thermoset nanocomposite; however, this information could not be verified as the product is not mentioned on the official company website [27]. LiteProp 108 is a low density proppant with specific gravity of 1.06 g/cc with maximum closer stress up to 6000 psi, which can be applied in the partial monolayer hydraulic fracturing as well as frac-pack[5] and gravel-pack[6] operations. Furthermore, this product is claimed to be specifically designed for unconventional reservoirs such as coal-bed methane, tight gas and shale reservoirs.

A similar use of thermoset nanocomposites for ultralight proppants production, which besides polymer and nanofiller consist of a micron size filler (e.g. nutshell, silicon dioxide) that serves as cost lowering factor, was also reported under a patent [28] from Halliburton but no commercial product could be found. The authors mentioned the same type of nanofiller (in size range 1-500 nm) as the one proposed by Bicerano [19] and underline that the most suitable nanofillers are: carbon black, fumed silica and fumed alumina products from Cabot Corporation, ASTM fly ashes class F from Halliburton and fly ashes class C from Powder River Basin near Gillette (Wyoming, USA).

The second nanotechnology application for production of ULP exploits the porous materials properties. Porous materials are solid materials that contain pores of dimension up to 1000 nm. The presence of voids lowers significantly the density of the material resulting in major reduction of weight.

In the patent by Statoil porous $MgAl_2O_4$ (spinel) material was reported for production of ULP [29] but no commercial product could be found. The particles of the proposed material have pore diameter of about 19 nm and a specific surface area of 29 m^2/g (by BET). Results of a comparison test revealed that the reduced mass settling velocity of spinel-based proppant was 22.5% of traditional alumina-based proppant (corundym-crystalline form of α-Al_2O_3). All tested materials obtained by means of slightly different manufacturing processes were claimed to be very strong as measured by the attrition test described in ASTM D5757 and to give less than 2% fines after 5 hours. Further testing showed that their shape is close to spherical with a sphericity factor (by Camsizer XT) between 0.92 and 0.99.

Ottestad [30] explicitly discussed the applicability of porous $MgAl_2O_4$ (spinel) based materials for production of ULP in the Master dissertation. A series of samples was prepared and tested for stiffness, hardness, and tensile strength as well as crush resistance. The results showed that the most resistant proppant consists of spinel and

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[5] Frac-packing operations combine gravel packing with fracturing, creating wide, highly conductive fractures connecting the reservoir to the wellbore: http://www.glossary.oilfield.slb.com/

[6] Gravel pack is a sand-control method used to prevent production of formation sand. In such operation, a steel screen is placed in the wellbore and the surrounding annulus is packed with prepared gravel of a specific size designed to prevent the migration of formation sand: http://www.glossary.oilfield.slb.com/

15% wg of MgO (30000 psi); however, during the synthesis it lost its porosity hence its weight increased. On the other hand, the most porous sample and thus the lightest consist of spinel and 12% of MgO, which demonstrated resistance to 13000 psi. This proppant is 30% more resistant than the traditional corundum (α-Al_2O_3) and its bulk density is almost 50% lower than the corundum's one, which makes it a very good candidate for practical field use.

Another type of porous material discussed in the patent by Statoil [29] consists of carbon nanofibers (CNF) synthesized on the surface of a core (any traditional proppant). Carbon fibers provide a low density and high porosity surface that reduces the overall density of the proppant particles. Moreover, the authors claimed that CNF coated proppants may have a potential to link together in the fractures through the surface fibers and thereby prevent the proppant from leaving the fractures as the fracking fluid is removed.

Both Ottestad [30] and Rytter [29] reported potential additional advantages of such porous proppants: due to the presence of voids in the structure they could be used as a carrier of e.g. catalyst, surfactant or any other additive that may be then released directly inside a fracture or in response to environmental conditions.

The third nanotechnology application for fabrication of ULP utilizes hollow materials.

In a patent by Oxane Materials Incorporated [31] a new type of hollow sphere materials that consist of a hollow bohemite-like core and a ceramic shell made from sintered nanomaterials was presented. The template (hollow sphere) may consist of inorganic material such as a ceramic, glass, polymer or a naturally occurring material (nuts, coffee grinds, perlite, pumice, volcanic ashes) among others. The coating (shell) can be made of polymer reinforced by a nanoparticle material such as an alumoxane containing functional groups that react with the polymer or can be a ceramic made from a nanoparticle precursor such as alumoxane, nanoclays, carbon nanofibers, silica, carbon nanotubes, nanoparticle minerals, mica, graphite, carbon black, fumed carbon, fly ash, glass nanospheres, ceramic nanospheres, or any combination thereof. The patent is devoted to the synthesis pathways of a new proppant and no laboratory testing of such obtained propping agent under hydraulic fracturing conditions was performed. Nonetheless the authors claimed that such hollow materials possess optimal shape, size, size distribution, pore size distribution, and/or surface smoothness properties and suggested that flow resistance through the proppant pack could be reduced, such as by more than 50%. Additionally, the neutral buoyancy enhances proppant transport deep into the formation increasing the amount of fractured area propped thereby increasing the mechanical strength of the reservoir. Furthermore, the authors specified that such obtained proppants can achieve substantially increased flow rates and/or enhanced hydrocarbon recovery.

Four commercial products exploiting this nanotechnology have been identified. OxBall^{TM}, OxFrac^{TM}, OxTor^{TM} and OxSteel^{TM} are proppants produced by Oxane Materials Incorporated, a spin-off company of Rice University [32] [33]. These propping agents are highly conductive, ultra-light nanostructured hollow ceramic (made from waste material of coal-powered plants and various different nano-crystalline minerals (fly ashes is one of the coating ingredients [32])). The producer claimed that the manufacturing process can be controlled at molecular scale to create perfectly spherical, same size, mono-dispersed and hollow proppant particles. Consequently they may be specifically tailored for the need of any formation and be produced in any size (from nanometer to micrometer scale), with strength that resists closure stress up to 20000 psi [34]. OxFrac™, lighter and smaller, is designed to meet the conditions encountered in fracturing of shale reservoirs of intermediate depth, such as the North Texas Barnett Shale, coal bed methane and tight gas [35]. OxBall™, heavier and slightly larger, is focused on deeper shale reservoirs, such as the Haynesville and Eagle Ford. The OxSteel^{TM} is produced specifically to meet the needs of Delaware Basin (deep Delaware, Wolfcamp and third zone Bone Spring interval). Finally, the strongest and lightest proppant OxThor^{TM} is focused on technically demanding deep-water applications [34] (e.g. deep-water operations in the Gulf of Mexico [36]).

Furthermore the producer specified that these lighter and more buoyant proppants are capable of migrating deeper into the formation than conventional proppant materials (55 vs 40 m), yet strong enough to withstand high closure stresses without being crushed or settling out to improve recovery rates, particularly in unconventional shale and tight gas sand formations (flow rates claimed 100% higher). A test performed on OxBall^{TM} showed 25% increase in production [37].

4.2.2 Strengthened proppants

Two types of nanotechnology applications aimed to increase the strength of the proppant have been found. The related information has been retrieved from 1 journal article and 1 patent.

The first nanotechnology application as proppant strengthening exploits the properties of nanocomposite fibers.

It is well established in the literature that the applications of fibers in hydraulic fracturing can prevent proppant from flowing back, reduce proppant settling velocity and used polymer concentration, decrease fracture damage or improve proppant placement profile to form a better fracture morphology among others. However, commonly used fibers for proppant coating suffers major drawbacks: not suitable for use at high temperature, low strength, low salt and corrosion resistance, no good flexibility and dispersibility in treatment fluid. Therefore, sand carrying capability, effect of anti-flow back of proppant and sand control capacity cannot be guaranteed. It was therefore proposed that addition of nanoparticles to the fibers composition may improve their mechanical properties and final performance [38] [39].

Guo et al. [40] proposed the addition of SiO_2 nanoparticles to improve the properties of PP/PET fibers used as coating on traditional proppant. Series of carbolite based proppants coated in different mass ratio (0 to 2%) with nanocomposite fibers consisting of PP/PET and SiO_2 nanoparticles was prepared and tested in a fluid made of borate-crosslinked guar polymer. The laboratory tests showed that new nanocomposite fibers were both chemically (corrosion resistance) and thermally stable below 200°C. Compared with traditional proppant, the compressive strength of the coated (1%) proppant has increased by ~ 32.5%. The authors claimed that nanoparticles improved: i) fiber performance in increasing apparent viscosity of the fracturing fluid; ii) adsorptive power of fiber on rock particles and proppant, which stabilize proppant pack and reduce fluid loss; and iii) flexibility and impact toughness of the fiber. The density of such nanofiber is slightly smaller than water, so the fiber suspends steadily in fracturing fluid showing greater proppant suspension capability. Nanoparticles also make the fiber diameter larger than that of commonly used fibers, thus improving performance in fixing proppant pack and controlling sand invasion. Furthermore, the authors specified that such obtained nanofiber coated proppants showed good dispersibility in water-based fracturing fluid thank to its hydrophilic-lipophobic property, and thus it is expected to enhance oil recovery. They also concluded that with concentration > 0.7%, nanocomposite fibers can greatly improve proppant suspension capability in fiber-laden fracturing fluid. The use of nanocomposite fibers can effectively reduce the contribution of the particle size of a proppant by changing settling velocity (to avoid the fast settling of large-sized proppant). The authors claimed that the nanocomposite fibers stabilize proppant physically rather than chemically avoiding being degraded by formation fluid and allows slurry to flow back immediately after the treatment, which benefits the flow-back efficiency and formation permeability recovery. For weakly consolidated formation, the fiber can control sand production effectively (with increasing of fiber concentration, sand production rates decreases greatly, thus the conductivity increases).

In another nanotechnology application, nano-hydraulic cement was proposed for production of stronger proppants (see the patent by Halliburton Energy Services Incorporated [41]).

In the retrieved source, many types of nanomaterials are mentioned such as SiO_2, MgO, Al_2O_3, nano-clays, fly ashes or zeolites among others; however, the laboratory experiments were performed on nano-clay and nano-silica. The 24-hour and 14-day compressive strengths test, tensile strength and water permeability test were performed on series of samples (proppant particles) consisting of Class A Portland cement, water and different concentrations (0.5 - 8% bwoc[7]) of nano-bentonite (nano-clay by NanoCor Incorporated) and micron size bentonite (for comparison) and one sample where nano-clay was exchanged with nano-silica. The results showed that cement compositions comprising nano-bentonite have superior mechanical properties as compared with regular bentonite. Accordingly, cement compositions with nano-bentonite may be less susceptible to break down under load, suggesting that a cement sheath containing nano-clay may be less susceptible to failure. Additionally, a significant decrease in permeability was observed for cement compositions that comprised the nano-bentonite as compared with regular bentonite. The observed reduction ranged from about 29% to about 80%. The authors further specified that this indicates, for example, that cement compositions comprising the nano-bentonite should be less susceptible to gas migration or the penetration of corrosive fluids such as those containing CO_2.

4.2.3 Proppants for tight and ultra-tight formations

One specific type of nanotechnology application as proppant for unconventional tight and ultra-tight formations has been found. Information on this application has been retrieved from 1 conference proceeding.

Tight shale plays have lower permeability and higher brittleness than conventional plays, therefore "linear gels", "waterfracs", "slick-water" and "hybrid" jobs have been typically applied [42]. These fracturing fluids are less viscous and create fractures with smaller width and longer length. This helps in interconnecting a network of created and natural fractures. Thus, fracturing jobs in tight shale plays tend to generate or extend a network of fractures while a bi-wing fracture is typically generated in conventional reservoirs [42].

It has been found in the literature that the use of nano-proppants prior to the placement of conventionally used larger proppants can increase the total extended length of the fracture network by propagating longer micro-fractures and the conductivity of those fissures and micro-sizes fractures. This would help to sequentially fill the widened natural fractures, allowing deeper percolation of nano-proppants and consequent propping of more fracture length. This increases the flow area and reduces fluid loss, thereby enhancing well productivity [43].

Bose et al. [43] proposed to exploit fly ash as potential proppant for tight gas formation. In the laboratory test the particles of fly ash - Class F (SiO_2 (40-60%), Al_2O_3 (18-31%), Fe_2O_3 (5-25%), CaO (1-6%), MgO (1-2%), TiO_2 (1-2%), Inorganic As (16-210 ppm))

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[7] bwoc: weight percent by the weight of cement

were added to the fluid (hydroxypropyl guar (HPG) borate crosslinked gel) to form a final 1% concentration (wt) slurry. Fly ash nanoparticles were found to have the following properties: a) high sphericity as observed from the TEM images, which makes them ideal candidates to be used as proppants (better conductivity of the fracture); b) high mechanical strength and reduced elastic modulus which, as observed from the nano-indentation experiments, would enable them to withstand the stresses (and deformations) that proppants are likely to be subject to in most shale formations; c) effective fluid loss additives when tested with static fluid loss tests (reducing the fluid loss coefficient and the total fluid loss volume when added to the HPG gel solution); and d) forming a conductive proppant pack when used as proppants in the long term fracture conductivity tests. These particles could prevent fluid loss during the propagation of hydraulic fractures while they pack the system of micro-fractures induced by propagation of hydraulic fractures in tight and ultra-tight formations.

It has to be mentioned that OxFrac^{TM}, OxBall^{TM}, and OxThor^{TM} can be engineered in the appropriate size (down to 1 nm) and thus, as claimed by the producer, can be successfully applied as nano-proppants in tight formations too [34].

4.3. Formation fines control additives and clay stabilizers

One of the well-recognized problems encountered during many oil and gas recovery operations, such as acidizing, fracturing, gravel packing, and secondary and tertiary recovery operations is formation and migration of fines formation [44]. The migration of fines involves the movement of fine clay and/or non-clay particles (e.g. quartz, amorphous silica, feldspars, zeolites, carbonates, salts and micas) or similar materials within a subterranean reservoir formation due to drag and other forces during production of hydrocarbons or water. Fines migration may result from an unconsolidated or inherently unstable formation, improper choice of proppant that crushed under harsh conditions of well or from the use of an incompatible treatment fluid that liberates fine particles. Fines migration may cause the very small particles suspended in the produced fluid to bridge the pore throats near the wellbore, thereby reducing well productivity. Damage created by fines is typically located within a radius of about 3 to 5 feet (about 1 to 2 meters) of the wellbore, and may occur in hydraulic fracturing, gravel-pack completions and other operations.

It has been demonstrated in the scientific literature [45] [46] [47] that nanoparticles have potential to fixate dispersed fines, such as clay and non-clay particles, including charged and non-charged particles from migration during hydrocarbon recovery operations. Due to at least in part their small size, the surface forces (like van der Waals and electrostatic forces) of nanoparticles help them associate, group or flocculate the fines together in larger collections, associations or agglomerations. This physical attraction keeps the fines from moving close to the wellbore region and causing the formation damage [48]. In many cases, fines fixing ability of the fluids may be improved by use of nano-sized particulate additives that may be much smaller than the pores and pore-throat passages within a hydrocarbon reservoir, thereby being non-pore plugging particles that are less damaging to the reservoir permeability than the fines themselves [45]. This smaller size permits the nanoparticles to readily enter the formation, and then bind up or fix the fines in place so that both the fines and the nanoparticles remain in the formation and do not travel as far or at least are restrained to the point that damage to the near-wellbore region of the reservoir is minimized. There are two proposed possible methods to use nanoparticles for fines remediation: i) nanoparticles are coated on the proppant pack in hydraulic fracturing treatments; and ii) nanoparticles act as stimulating agents and are injected into the wellbore region along with the fracturing fluid to fix the fines at their source [46].

Two types of nanotechnology application as fines fixation agent used in hydraulic fracturing treatments for hydrocarbons reservoirs have been found. Information on these applications has been retrieved from 1 journal article, 4 conference proceedings, 4 patents, and 1 company website.

The first application type concerns addition of inorganic nanoparticles to the fracturing fluid. Patents addressing such an application are available from Baker Hugues Incorporated [49], and one commercial product was found on the company website [50].

In the retrieved sources, different metal oxides (e.g. alkaline matal oxides such as MgO, transition metal oxides such as TiO_2, post transition metal oxides such as Al_2O_3 or piezoelectric metal oxides such as ZnO) are mentioned as possible candidates but most of the laboratory experiments have been performed on MgO. The patents claimed that the most suitable nanocrystals to be exploited are in size range 1-500 nm and their concentration in the fluid (aqueous containing brine or non-aqueous) varies from 2 to 1000 pptg (i.e. 0.24-120 Kg/1000L). The laboratory test performed on MgO (provided by Inframat Advanced Materials, 35 nm nanoparticles (SSA > 50 m^2/g) dispersed in water containing colloidal silica and natural bentonite particles) showed that MgO nanoparticles efficiently fix both clay and non-clay types of fines.

Habibi et al. [46] reported the results of a series of fines fixation tests performed on MgO (63 nm, SSA = 160 m^2/g), Al_2O_3 (43 nm, SSA = 40 m^2/g) and SiO_2 (48 nm, SSA > 600 m^2/g) nanoparticles. The study verified that MgO nanoparticles were the best adsorbent for fines fixation.

A commercial product under trade mark ConFine Fines Fixing Agent from Baker Hughes Incorporated was found to implement the above described nanotechnology [50]. The producer does not reveal the chemical composition of the product nanoparticle on the company website. ConFine seems to take advantage of nanometer-size particles that create surface charges on proppant to fixate formation fines. The company claims that ConFine was successfully used to control sand and fines migration in deep-water Gulf of Mexico [50]. The well was shut down due to sand control problems. In this application, unique, inorganic nanocrystals with very high surface force interactions readily attached to the surface of ceramic and silica proppant particles efficiently fixed formed fines to the proppant and consequently allowed to bring back online the well with no sand control problems further reported [50].

According to Huang et al. [45] [51] [52] inorganic nanocrystals such as alkaline earth metal oxides, transitions metal oxides or piezoelectric crystals among others may not only be useful for fines fixation but also for clays stabilization in a subterranean formation, by inhibiting or preventing them from swelling and/or migrating. The authors reported that the addition of a small amount of e.g. 0.4 % by weight of 8 nm MgO particles (SSA > 230 m^2/g) to the mixture of 20/40 mesh (850/425 micron) sand proppant pack with 1 % by weight of (clays) bentonite and 1 % by weight of illite in water can successfully inhibit the clay particles from expanding and remaining dispersed in the fluid [51].

The second application type concerns the use of nanoparticles as a coating on proppant for formation fines fixation.

Belcher et al. [48] discussed the use of inorganic nanocrystals to treat proppant beds for fines fixation and clay stabilisation; however, the authors did not disclose the chemical composition of the proposed nanocrystals. The authors reported the results of one case study where this nanotechnology was applied to a well located in deep-water Gulf of Mexico for completion, an oil condensate producing zone. After 12 months the well showed production decline due to fines migration. The nanoparticles were introduced to the fracture at a concentration of 1 gal per 1000 lb[8] of proppant. The well was brought back on line and zero fines migration has been reported until now.

The applicability of 3 metals oxides namely MgO, Al_2O_3, and SiO_2 as coatings on proppants for reduction of fines migration was explicitly discussed by Ahmadi et al. [53]. Based on the results of the performed experimental study, the authors concluded that MgO nanoparticles are the most efficient while Al_2O_3 nanoparticles have the least effect on fines migration with respect to its zeta potential value (repulsion forces always stronger than attraction forces).

The performance as fines fixation agent of MgO nanoparticles with average 35 nm size crystals was more deeply investigated in the available scientific literature. MgO

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[8] Approximately 8.344 L/ 1000 Kg

nanoparticles were added to the mineral oil for coating 20/40 mesh sand proppant. The results of addition of such coated proppant into the solution of 5% KCl brine and colloidal silica as fine simulator showed that MgO nanoparticles successfully fix the fines [47].

In another test described in the patent by Baker Hughes Incorporated [45] and performed on a series of proppants (20/40 mesh gravel pack sand, 20/40 mesh light weight/high strength ceramic packs, 20/40 mesh procured resin coated sand) coated with 35 nm MgO nanoparticles, a clear formation fines slurry effluent was obtained from the nanoparticle treated proppant pack, thus indicating that the formation fines were retained in the treated column pack. The proppant pack conductivity test also revealed that the nanoparticles do not negatively affect the fracture proppant bed conductivity.

It was also found in the reviewed literature that the nanoparticles coated proppants may be multifunctional and not only inhibit fines formation and migration but also help more uniformly distribute the fines inside of the fracture in order to keep sufficient fracture conductivity for maintaining a particular production rate for longer periods. Furthermore, when added to a micellar fluid for fracturing, the nanoparticles coated proppants can increase fluid thermal stability and fluid loss control properties [45].

4.4. Cross-linkers and fluid loss control additives in VES fluids

According to several authors [54] [55] [56], Viscoelastic Surfactants (VES)-based fluids have two main disadvantages compared to cross-linked polymeric fluids: i) they are unable to form a filter cake, thus causing a large amount of fluid loss into the porous matrix and consequent formation damage; and ii) they have low thermal stability. This has limited the use of VES fluids e.g. for well stimulation in tight gas reservoirs [56].

It has been demonstrated in the scientific literature that nanoparticles can enhance and stabilise viscosity when added to VES fluids. Nanoparticles promote the formation of a three-dimensional network in the micellar solution through two mechanisms: the entanglement of the micelles and the formation of micelle-nanoparticle junctions [57] [58] [59]. Micelles physically attach themselves to nanoparticles' surfaces and causes formation of micelle-nanoparticle junctions [57]. The nanoparticles therefore act as physical cross-linkers and increase both effective length of micelles and number of entanglements per micelle [57]. This phenomenon is also called "pseudo-crosslinking" [56] [60] and is possible thank to nanoparticles' small size, high surface area and surface forces (including van der Waals's and electrostatic forces), which are responsible for their suspension stability in surfactant solutions and strong absorption ability [55]. In this way, viscosity of VES fluids is enhanced and maintained at high temperatures. Moreover, a pseudo-filter cake is generated, which significantly reduces the fluid loss into the formation matrix and increases VES fluid efficiency to generate fractures [60]. Another advantage is that internal breakers are located inside the micelles and do not leak-off but remain inside the micelles during the pseudo-filter cake development, thus facilitating its removal during flow-back operations [60].

Two types of nanotechnology applications as viscosity enhancers and stabilisers in VES fluids used in hydraulic fracturing treatments have been found. Information on these applications has been retrieved from 4 journal articles, 7 conference proceedings, 4 patents, and 2 websites.

The first application type concerns addition of inorganic crystals nanoparticles to VES fluids. Patents addressing such an application are available from Baker Hugues Incorporated [61] [62] [63]. In the retrieved sources, several types of metal oxides are mentioned as possible candidates but most of the laboratory experiments have been performed with ZnO, MgO and SiO_2 nanoparticles.

The performance of ZnO nanoparticles with average size of 35 nm and surface area up to 500 m^2/g when added to a VES fluid containing brine and a breaker was investigated in a fluid loss test with ceramic filter discs [60] [64]. The experiment demonstrated that: i) less than 0.1% loading of ZnO nanoparticles generates up to a 10-fold increase of fluid viscosity and stabilize it at high temperature (200 cP at 250 °F); ii) the pseudo-filter cake is built; iii) nanoparticles are small and can flow easily with VES fluid in and out of pore throats without generating formation damage; iv) nanoparticles improve VES fluid's proppant transport and placement in the fractures; and v) when internal breakers are used the VES fluid loses its viscosity dramatically and the pseudo-filter cake breaks into brine with nano-sized particles, which are small enough to pass through the pore throats of the formation matrix and therefore can be easily removed during flow back operations [60] [61] [62] [63] [64].

In another test described in a patent from Baker Hugues Incorporated [61], VES fluids containing 6 pounds per thousand gallons (pptg) (i.e. 0.7 Kg/m^3) of ZnO nanoparticles with an average size of 30 nm demonstrated enhanced viscosity over the case where no additive was used. The VES fluid containing the same amount of MgO nanoparticles also showed viscosity improvement over the base fluid alone but not as great an improvement as the VES fluid containing ZnO nanoparticles. In the case of ZnO nanoparticles, the leak off of the VES fluid was also significantly reduced. Opposite conclusions have been more recently reported by Gurluk et al. [65], when comparing the performance of VES fluids containing 6 pptg of either ZnO or MgO nanoparticles with average size of 30 nm. Their experiments showed a two-fold increase of viscosity in both cases with MgO nanoparticles performing better than ZnO nanoparticles. In addition, the apparent viscosity of VES fluid with MgO nanoparticles reduces rapidly with the loading of internal breaker, which turns wormlike VES micelles into spherical micelles. The authors also concluded that viscosity of VES micelles is independent of nanoparticles' concentration.

Huang and Clark [56] explicitly discussed the applicability of metal oxide nanoparticles in VES fluids that are specifically designed for hydraulic fracturing of unconventional tight gas reservoirs. The authors reported the result of a rheological test on a VES fluid containing 10 pptg (about 0.08% by weight) of metal oxide (not specified) nanoparticles with an average size of 35 nm and confirmed that nanoparticles are able to associate elongated surfactant micelles together into strong micellar networks that significantly increase the fluid capacity for proppant suspension and carrying. Specifically, the authors stated that addition of nanoparticles increased the surfactant micellar fluid's zero shear rate viscosity more than 100 times. Moreover, the VES fluid with nanoparticles maintained its initial viscosity at T = 250 °F for at least 100 minutes during the experiment. The authors also reported that a fluid loss test was performed and the VES fluid containing nanoparticles developed a filter cake. After the spurt, the fluid loss was noticeably lower, showing good fluid loss control like cross-linked polymeric fluids.

The addition of a small amount, such as 0.25% bw, of SiO_2 nanoparticles with average size of 15 nm was proven to be effective in increasing the viscosity of VES fluids of about 20% in a temperature range from 35 to 90 °C [55]. In other experiments, the addition of 500 ppm of 15 nm SiO_2 nanoparticles ensured high viscosity under high shear and a temperature up to 60 °C [58] and 70 °C [54]. In another paper, it was concluded that SiO_2 nanoparticles treated with average size of 20 nm are beneficial in terms of rheological properties of VES fluids if their concentration is carefully selected, i.e. up to 0.24% wt [57].

No available commercial product using nanoparticles as cross-linkers and fluid loss control additives in VES fluids could be found from company websites. However, Diamond Fraq by Baker Oil Tools is mentioned in two websites [66] [67] and described as a VES fluid using nanotechnology to associate (pseudo-crosslink) VES micelles together, stabilize VES micelle structures to 300 °F (148.8 °C) and form a pseudo filter cake composed of highly viscous VES micelles and nanoparticles [66]. The product is also mentioned in several patents as base fluid. On the 'trademarkia' website, this product is filed as 'abandoned' because applicant did not submit any proof of use [67].

The second type of nanotechnology application is specific for VES fluids when used in hydraulic fracturing of coal-bed methane formations and is claimed to overcome a series of field issues: i) loss of fracturing fluid (e.g. through micro-fractures in coal rock); ii) difficult clean-up via breaking due to low temperature of coal seam; and iii) low conductivity due to coal powder from the crush of coal rock, which can aggregate easily to block the front end of fractures and the pore throats of proppant [68]. The addition to

VES fluids of a nanocomposite fibre made of 90% wt polypropyle and 10% wt polyester with addition of inorganic nanoparticles belonging to the family of silicates/phyllosilicates (not specified) was proposed [68]. Tests were performed using several types of proppants mixed with an amount of nanocomposite fibre ranging from 0.4 to 2% wt. The authors concluded that the appropriate fibre concentration is 0.4-0.7% wt. The nanocomposite fibres reduced the velocity of the proppant settling in the VES fluid. It also allowed the reduction of the surfactant used in the VES fluid from 2.5 to 1% thus facilitating the breaking of the gel in VES fluid at low temperature. Addition of nanocomposite fibre generated an inhibition effect on the coal powder aggregation. After adding 0.5% wt nanocomposite fibre the leak-off coefficient and the leak-off velocity of fracturing fluid can be reduced by 13.4% and 30.1%, respectively. The nanoparticles of the nanocomposite fibre have large specific surface area with a lot of active groups and specific charges, which can adhere to the micelles to form a self-assembly filter cake structure, which results in reducing leak-off volume.

4.5. Breaker system

Breaker is used to reduce the viscosity of fracturing fluid by breaking long-chain polymeric molecules into shorter segments. Currently two different types of breakers are commonly applied in fracturing fluids: i) internal breakers that can be added directly to the fracturing fluid for downhole activation; however, this may lead to the early breakdown of the fluid hence preventing it from fracturing the rock formation properly; and ii) external breakers that are added directly to the flow back fluid for immediate effect at surface[9].

The delayed release of internal breakers is an important factor for proper fracturing of the hydrocarbon bearing formation. Encapsulation techniques have been used to inactivate internal breakers during injection and control their release downhole. However, the relatively large size of the capsules, which are usually designed to break open when the fracture recloses at the end of the injection, may result in incomplete degradation of the filter cake. In particular, VES fluids suffer from the lack of efficient and stable internal breakers. Breaker systems should indeed use products that are incorporated and solubilized within the VES fluid and activated by downhole conditions at a controlled rate over a rather short time (1-24 hours), similar to gel break periods in conventional cross-linked polymeric fluids.

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[9] http://www.glossary.oilfield.slb.com/Terms/b/breaker.aspx

It has been found in the literature that nanotechnology may improve performance of traditional breakers by using specific nanoencapsulation and provide solutions to the challenging issue of internal breakers for VES fluids [69].

Two types of nanotechnology applications for the delayed release of nanoencapsulated breakers have been found. Information on these applications has been retrieved from 2 journal articles, 1 conference proceeding and 2 patents.

Barati et al. [69] [70] and Bose et al. [71] proposed the encapsulation of a traditional breaker, i.e. pectinase enzyme, in a polyelectrolyte (PEC) nanoparticles. PEC nanoparticles are positively charged particles in the size range from 235 nm [69] to 851 nm [71], which consist of polyethylenimine branched (polycation) (PEI) and dextran sulfate sodium salt (polyanion) (DS). A set of nanoparticles with different PEI:DS ratio was synthesised and tested for breaking properties on the fluid that consist of a hydroxypropyl guar (HPG) solution (5000 ppm) containing 2% KCL and 1.35 g/L sodium thiosulfate and a 1000 or 2000 ppm borax aqueous solution (7.5 mL). The test results revealed that PEC nanoparticles made with a PEI:DS ratio of 2:1 (408-435 nm) showed good Entrapment Efficiency (EE) for pectinase breaker. They were stable over time and did not degrade with shear in the range studied. They showed the best controlled release of enzyme over time. Nanoparticle-entrapped pectinase was able to completely break borate-crosslinked guar and HPG gels, with the breaking being delayed significantly compared to un-entrapped enzymes at the same concentration. The delayed release of the enzyme allowed the loaded particles to be mixed with the gelant before gelation occurred. This, along with the small size of the particles, indicated that the enzyme was distributed homogeneously through the gel, which may have resulted in a more complete breakage of the gel and, hence, a higher post-treatment hydraulic fracture conductivity [69]. 547 nm PEC nanoparticles with entrapped pectinase as breaker were further studied by Bose et al. [70] and the resulted confirmed very efficient performance of such encapsulated breaker showing potential for improving the performance of hydraulic fracturing treatments in conventional oil and gas reservoirs [71].

In the joined patent of Rice University and Halliburton Incorporated the use of Nanoparticle-Assembled Capsule (NAC) made of self-arranged positively charged nanoparticles and negatively charged polyelectrolyte molecules for breaker encapsulation was proposed [72]. Different types of nanoparticles were mentioned as suitable such as: metals, metal oxides, metal-non-oxides (quantum dots), organic particles, linear polymers, biomolecules, fullerenols and SWCNT/MWCNT, among others. The method involved both encapsulation and release of viscosity breakers by using microcapsules assembled from charged nanoparticles and polyelectrolytes. During the microcapsule assembly process, breakers are encapsulated into the shell. The encapsulated species are released during the disassembly or deformation of the microcapsules induced by addition of salt. The method is designed in such a way that the reduction of viscosity is initiated by contacting fracturing fluids with brine solution (i.e. the capsule is permeable to brine). In the methods both enzymatic and oxidative viscosity breakers can be encapsulated. In the patent [72], an example of NAS sub-micron/micron-sized organic-inorganic spheres, in which the thick shell consists of negatively charged 12 nm silica nanoparticles and the poly-L-lysine (PLL) for entrapment of β-Mannanase (Megazyme) enzymatic breaker was made. The authors claimed that stability tests of enzyme-containing NACs and tests for triggered-release (at 50°C with 4 ml of 5 mL NaCl) of the enzyme from NACs showed significant changes in the fluid (0.5% of guar solution) viscosity.

Another patent described the use of nanohybride materials that are designed to stabilise emulsions but may also be used to entrap the breaker [73]. These nanohybrids are made from a hydrophobic carbon nanotube and hydrophilic inorganic second component (e.g., silica, alumina, magnesium oxide, titanium oxide, etc.) attached to each other. The inorganic component may have different shape: particles, nanowires or thin films [73]. The authors further specified that such nanohybrides can also be used to encapsulate a chemical (e.g. breaker) in an internal phase of an emulsion. As such nanohybrids can be modified or easily completely destroyed this can be used as a "switch" to selectively break the emulsion in a controlled manner.

The second type of nanotechnology application exploits nanoparticles as internal breakers of VES fluids. The information was retrieved form 1 patent.

Nanoparticles that act a breaker for VES fluids were proposed in a patent by Baker Hughes [74]. The breaker can be made of semiconductor nanomaterials of diameter between 1 and 1000 nm. The used nanomaterials may be of inorganic nature such as: CuO, Cu_2O, Si, SiC, Ge, GaAs, InSb, GaN, and combination thereof (cupric oxide, cuprous oxide, silicon, silicon carbide, germanium, gallium arsenide, indium antimonite, gallium nitride) or organic nature e.g. pentacene, anthracene, rubrene, poly(3-hexylthiophene), poly(p-phenylene vinylene), polypyrrole or polyaniline [74]. The authors claimed that the laboratory tests showed that nano-sized CuO acted as a breaker for the base fluid in contrast to other types of metal oxide nanoparticles (ZnO, MgO, TiO_2, and Al_2O_3) used as comparative samples, which actually stabilized the fluid. The effective amount of the breaker nanoparticles added to the gelled aqueous fluid ranges from about 0.1 pptg to about 100 pptg. The breaker nanoparticles were stable and had a long shelf life when compared to liquid breakers for VES fluids. The stability of the breaker nanoparticles will allow for them to be used even in harsh downhole conditions.

The authors further specified that the alteration which occurs in breaking the gelled aqueous fluid upon addition of the breaker nanoparticles is believed to be transition metal mediated and/or transition metal-catalysed [74]. The alteration may occur as an effect of: a rearrangement of the bond on the VES fluid, an addition to VES (e.g. hydrogen), elimination (decomposition, degradation) of VES, or chemical reaction (redox).

In the last identified nanotechnology application, a breaker fluid in the form of a nanoemulsion is proposed. The patent by Baker Hughes Incorporated [75] described a microemulsion or nanoemulsion containing an aqueous external phase (e.g. water, brine), a surfactant and a non-aqueous internal phase with at least one organic peroxide as an oxidiser that can then perform as an internal breaker for reducing the viscosity of aqueous fluids gelled with a polymer, such as a cross-linked polysaccharide. The organic peroxides that were mentioned in the patent included: cumene hydroperoxide, t-butyl cumyl peroxide, di-t-butyl peroxide, di-(2-t-butylperoxyisopropyl)benzene, benzoyl peroxide, among others. The authors claimed that the breaking method gives more complete break for polymer based fluids, such as borate cross-linked guar and linear HEC (hydroxyethylcellulose), at elevated temperatures in comparison to traditional breaker systems. This is partially due to the fact that the oxidizers that are used as internal breakers are triggered to act at the rock formation temperature for which the fluid is specifically designed.

4.6. Fluid loss control additives in polymeric fluids

Filter cake, i.e. invasion of fracturing fluid into the rock formation, causes damages to the rock formation both physically (e.g. clays swelling, which is typical in shale formations that contain smectite and montmorillonite clays) and hydraulically (i.e. shifting of relative permeability and capillarity pressure curves) [76]. This damage reduces fractures conductivity and consequent flow of hydrocarbons during production operations.

It has been stated by several authors that damage due to filter cake is more significant in tight and ultra-tight formations [76]. In these reservoirs, nano to micro-sized fluid loss control additives are needed to plug nano-sized pores and micro-sized fractures to reduce the fluid loss, thereby improving fractures propagation [76].

The search in the scientific literature resulted in 1 journal article and 1 conference proceeding proposing two different nanotechnology applications as fluid loss control additives in polymeric fracturing fluids.

The first application concerns the addition to the fluid of polyelectrolytes (PEC) nanoparticles consisting of polyethylenimine branched (polycation, CAS Number = 9002-98-6) and dextran sulfate sodium salt (polyanion, CAS Number = 9011-18-1) [76]. The reported average size of PEC nanoparticles is 547 nm. The efficacy of PEC nanoparticles was tested in a cross-linked polymeric fluid made of a hydroxypropyl guar solution and a borax aqueous solution. Based on the results, the authors concluded that PEC nanoparticles could successfully reduce the fluid loss volume of core samples with permeability values of 0.1 mD and below [76]. It was observed that the usage of nanoparticles led to the formation of a relatively weaker filter cake, which gets more easily cleaned up as compared to the filter cake formed exclusively by the polymer gel [76].

The second application concerns the addition to the fluid of SiO_2 nanoparticles with an average size of 110.7 nm [77]. Their efficacy was tested in a cross-linked polymeric fluid made of a hydroxypropyl guar solution with sodium phosphate monoborate used as a source of borate ions to cross-link guar gum and generate guar gel. The results were compared to the ones obtained from testing PEC nanoparticles with an average size of 547 nm. The authors concluded that both SiO_2 and PEC nanoparticles were successfully applied to reduce the fluid loss volume of low permeability cores (0.1 mD and below). Fluid loss volume of the low permeability cores was controlled more successfully when PEC nanoparticles were used both with and without guar solution. In addition, PEC nanoparticles reduced the fluid loss to zero when applied mixed with 2% KCl on tight cores, while SiO_2 nanoparticles showed small fluid loss volumes. When guar solution was used, SiO_2 nanoparticles also showed zero fluid loss volumes.

4.7. Cross-linkers in polymeric fluids

Three nanotechnology applications as cross-linkers in polymeric fluids have been found in 2 journal articles and 1 conference proceeding.

The first application proposes a more environmentally friendly and efficient alternative to borate cross-linked polymeric fluids, which is the use of so-called 'boronic acid functionalised nanolatex particles'. These particles with an average size of 17 nm and specific surface higher than 300 m^2/g were found to be more efficient in comparison to a borate ion that can crosslink effectively only two molecules of guar [78]. Nanoparticles, thanks to their high surface area, can provide more cross-linking domains so that many molecules of guar can be cross-linked with a single nanoparticle [78]. The authors claimed that at the same viscosity point the amount of boron used with nanolatex particles is 30 times less than with standard borate ions [78].

In the second paper, the authors demonstrated that TiO_2 (anatase) nanoparticles induce the cross-linking of hydroxypropyl guar (HPG) into a viscoelastic gel through hydrogen bonds between the OH functionalities present in TiO_2 nanoparticles and HPG [79]. At sufficiently high concentrations, this interaction results in a 3D network of polysaccharide strains linked together via the inorganic nanoparticles. Surface area was expected to play a key role in TiO_2 nanoparticles cross-linking efficacy. Based on experimental results, the authors concluded that TiO_2 nanoparticles must exhibit diameters lower than 10 nm to cross-link HPG sufficiently as is required in oilfield applications as the smallest size produce the highest viscosity increase [79]. It was specifically found that 6 nm TiO_2 nanoparticles can increase the viscosity of a HPG solution by a factor of 25 [79]. In addition, the authors showed that the cross-linking process can be delayed by modifying the TiO_2 nanoparticles surface with chelating ligands such as citric acid or triethanolamine, which need to be gradually displaced by HPG [79]. This application was proposed for use in hydraulic fracturing of unconventional oil reservoirs [79].

The same authors proposed in another paper the use of ZrO_2 amorphous hydrous nanoparticles to crosslink guar guam or its derivatives and achieve highly viscous gels. It was observed that Zr complexes hydrolyse and condensate within the polysaccharide matrix, thus resulting in nanoparticles with size 2-6 nm, and proved that the nanoparticles are responsible for the cross-linking effect [80]. The efficacy of ZrO_2 amorphous hydrous nanoparticles stabilised by triethanolamine with average diameter of 3 nm and ZrO_2 nanoparticles modified with citric acid with an average diameter of 11 nm was compared in a laboratory test. The citric acid modified nanoparticles performed less and this was attributed to the larger size, and consequent lower surface area available for the cross-linking process, and the structure (hydrous zirconia vs zirconia) [80]. The authors also argued that other less expensive nanoparticles might be used e.g. magnetite nanoparticles [80]. This application was proposed for use in hydraulic fracturing of shale reservoirs [80].

No commercial products using nanoparticles as cross-linkers in polymeric fluids could be found.

4.8. Biocides

Conventional biocides have drawbacks. They can be toxic to workers and leach from wellbores into aquifers or other unintended locations, where they may cause detrimental effects on the surrounding ecosystem. Some biocides require relatively high concentrations to be effective, which make them expensive. Many biocides break down or dissipate quickly and, therefore, must regularly be replaced, which leads to increasing costs [81].

One nanotechnology application as biocide in fracturing fluids has been found in a patent [81]. It concerns the use of core-shell nanoparticles with a core of non-metallic material and a surface of silver and silver dioxide. Based on reported information, the shell covers at least 20-75% of the core and nanoparticles' diameter is in the range 2-100 nm. The metallic nanoparticle composition includes metallic silver nanoparticles that are permanently, essentially permanently, or semi-permanently bonded to structured water that utilize multiple modes of biocidal action to destroy bacteria (e.g., pathogens) catalytically or synergistically (i.e., using multiple modes of toxicity), without using up the embodied modes of action. In addition, the small size of the nanoparticles, in conjunction with the structure of the nanoparticles and various fundamental forces, may cause the nanoparticles to remain suspended and, consequently, not settle in the mud pit, or to settle relatively slowly, so to retain its biocidal properties. Efficacy may also be aided by relatively high levels of Brownian motion of nanoparticles. As a result, the authors claimed that a biocide including a silver nanoparticle composition or a solution which includes essentially only the silver nanoparticle material may maintain concentration and efficacy longer than other conventional biocides [81].

4.9. Surfactant systems

The primary purpose of using surfactants in fracturing fluids is to reduce interfacial tension between the fluid and the rock/fracture surface to reduce surface tension of the base fluid on the rock surface, minimize fluid invasion into the porous media, and therefore facilitate its recovery after fracturing (as flow back fluid). Surfactants hence ensure that the conductivity of proppant packs is recovered before starting producing hydrocarbons.

However, surfactants may be adsorbed on the surface of the rock matrix or proppant pack, thus reducing their concentration below the critical level that is necessary to sustain a micellar solution and lowering their effectiveness in preserving low surface tension of fluid [82]. Adsorption may e.g. be due to precipitation of surfactants at high temperature [83]. The formulation into a nanofluid allows the surfactant blend to penetrate further into the matrix due to the small size of its droplets/particles and remain with the leading edge of the penetrating fluid [82]. This is believed to improve the surfactant's ability of lowering interfacial tension and enhancing rock wettability [83].

Information on nanotechnology applications as surfactants to be added to fracturing fluids has been found in 7 conference proceedings, 6 patents, 6 company websites and 3 magazine articles. The search has identified three different types of applications: nanoemulsions, nanoadditives to emulsions for oil field operations, and nanodispersions.

A 'microemulsion' or 'nanoemulsion' or 'complex nanofluid' has been proposed as a surfactant system to be added to fracturing fluids in 6 conference proceedings. In all cases, the surfactant system is a nanoemulsion of a blend that consists of one or more surfactants, a solvent, a co-solvent and water. The search on company websites has retrieved information on 3 commercial products that seem to implement this type of nanotechnology.

In 2004, Pursley and Penny [84] reported the results of laboratory and field tests with an emulsion of unknown composition and low concentration ranging from 1 to 5% of the injected fracturing fluid. Despite the name suggests that the application is at the micron scale, the authors specified that the micelles' dimension is at the nanoscale, i.e. roughly 2-4 nm. The nanostructures are believed to maximise the surface energy interaction by expanding to 12 times their individual surface area and hence lead to the following benefits: reduced surface tension, maximum penetration into the rock formation, uniform fines suspension in wellbore breakdown treatments to aid in damage recovery, maximised heavy or complex hydrocarbons breakdown or dissolution, control of ideal reservoir wettability resulting in effective surface cleaning, retarded inorganic/organic acid reactions, enhanced fluid loss control mechanism in fracturing, and reduced friction when pumped through treating tubular goods [84]. Indeed, laboratory tests showed proppant permeability doubled and pressure to initiate clean-up lowered by 50% when the nanoemulsion was included in gelled fluids. These results were confirmed by field tests showing fluids friction pressures drop of 10-15%, restored productivity of wells damaged by fracturing, and enhanced oil/gas production. The authors reported that the nanoemulsion was successfully used in 9 different oil/gas basins (DJ of Colorado, San Juan of New Mexico and Colorado, Uintah of Utah, Raton of Colorado, Green River, Pinedale, Big Horm of Wyoming, Fort Worth of Texas and Williston of North Dakota) and 19 different rock formations in the USA up to 2004 [84]. It was observed that 30% of the treated wells achieved a 350% production improvement and over 68% had lower lifting costs. In treated wells, production rates were from 20 to 100% higher than offset wells without the nanoemulsion and the higher increases were noticed in wells treated with cross-linked polymeric fracturing fluids. The authors also claimed that the nanoemulsion was environmentally compatible (biodegradable, plant-derived) and chemically safe (non-carcinogenic, non-toxic, non-hazardous, and non-containing Volatile Organic Compounds) [84].

More recently, the use of two nanoemulsion surfactants to recover the fluid filtrate during flow back operations has been investigated [83]. The two nanoemulsion surfactants, i.e. NES-1 and NES-2, were described as a blend of anionic surfactant, non-ionic surfactant, short chain alcohol and water with NES-1 consisting of oil and isopropanol and NES-2 of citrus and isopropanol. The reported stabilized diameter size of droplets was 10-20 nm. In the test, both blends were dispersed in two different formation waters at a concentration ranging from 0.5 to 5 gpt. The two surfactants were effective in lowering both surface tension and interfacial tension of water-air and water-condensate systems at a temperature range of 77-325 °F. Both surfactants did not exhibit any adsorption tendency with rock formation.

Another nanoemulsion made of D-limonene (oil), isotridecanol ethoxylate (non-ionic surfactant), isopropyl alcohol (co-surfactant), and tap water was tested as flow back additive to enhance fracturing fluid recovery [85]. In this case, the reported droplet size varied from 10 to 100 nm with a pick at 42.76 nm. Results showed that the nanoemulsion had higher contact angle than conventional additives but moderate surface tension. According to the authors, the use of D-limonene as oil makes the nanoemulsion environmentally friendly [85].

The commercial product Nanosurf 969 by Oil Chem Technologies (Texas, USA) is advertised on the company website [86]. It is described as a biodegradable microemulsion surfactant that can be used at a concentration ranging from 0.1 to 3% in low permeability formations, especially shale gas reservoirs [86]. The company declares that the technology is "patent pending". From a search in the Internet two patents by Oil Chem Technologies could be retrieved: despite the patents do not report information on any nanofluid, they may be linked to the product [87] [88].

The patented commercial product G-CLEAN WELL WAKE UP!™ by Green Earth Technologies is an oil well stimulation solution with formulations specifically engineered to break down the paraffin or asphaltenes and remove the build up from the well [89]. In the patent that is believed to describe the application implemented in G-CLEAN WELL WAKE UP!™, the authors referred to a nanoemulsion consisting of a micellar solution of fatty acids, such as tall and coconut oil fatty acids, a polysorbate emulsifier, one or more ionic surfactants and mixtures thereof [90]. The reported droplets size was in the range of 5-50 nm [90]. The company also stated that the nanoemulsion vastly improves asphaltene and paraffin removal efficiency over traditional microemulsions, is chemically non-reactive with subterranean formations, and is environmentally friendly [89]. In a magazine article [91] the company explained that the nanoemulsion releases and removes paraffin and asphaltene deposits by enabling a mechanism of structural disjoining pressure from a thin film of nanoparticles, which literally spreads between the rock formation and the built-up deposits. Colloidal micelles then disperse, capture and remove the hydrocarbon deposits allowing the well to resume normal production. The increased deposit removal efficiency of the nanoemulsion also means that much less treatment fluid is required during well remediation as compared to traditional methods due to the high surface area to volume ratio [91].

In one paper [82], a complex nanofluid containing alcohol ethoxylates (surfactant), oxyalkyated amine (polymer, demulsifier), citrus terpene (solvent), and water was tested in the laboratory and results compared with other conventional surfactant blends. A graph showed how the droplet diameter range of the complex nanofluid changes with dilution, moving from about 100-500 nm in the non-diluted blend to about 10-70 nm and

5-30 nm in two diluted blends containing 20 and 2 gpt[10] of complex nanofluid, respectively. The adsorption test showed that surface tension of the complex nanofluid is lower than in conventional surfactant blends, i.e. 20 and 30 dynes/cm compared to 40 and 70 dynes/cm[11]. Based on these results, the authors concluded that adsorption can be mitigated by utilizing complex nanofluids instead of common surfactants.

In another paper [92], the performance of two surfactants, i.e. poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) and lauryl alcohol ethoxylate, formulated with citrus terpene (solvent) either in a conventional blend or into a complex nanofluid was investigated in a series of column flow tests with different proppant packs (Ottawa sand or light ceramic of 70/140, 30/50 or 20/40 mesh size). The relative permeability of proppant packs with complex nanofluids resulted is 2 times higher than with conventional surfactants. Based on these results, the authors implied that the gas flow in shale reservoirs could be 2 times higher with complex nanofluids when compared to conventional surfactants [92]. A 7-fold increase in production and effective fracture length with e.g. 20/40 mesh proppant vs 100 mesh proppant was reported with common surfactants at low concentrations. The reported increase was 30-fold when surfactants formulated into a complex nanofluid were employed at a concentration of 0.15% or greater. Laboratory results were compared against a statistically significant population of 240 wells with sufficiently descriptive information. In some wells, a complex nanofluid was used. The authors claimed that the range and conditions for the laboratory observations corresponded well with the field-based observations [92].

In addition, the effectiveness of complex nanofluids at improving flow back fluid recovery from different proppant packs and enhancing permeability of gas in unconventional tight reservoirs was investigated through a series of column flow tests with different proppant packs (Ottawa sand -30/+50 and -70/+140 mesh size or ceramic -30/+50 mesh size) [93]. The complex nanofluid blends mainly contained ethoxylated alcohol (surfactant) and a natural terpene (solvent) at different concentrations and were loaded at 2 gpt. Complex nanofluid blends with a near balanced composition (i.e. oil-to-water ratio close to 1.2) appeared to represent an optimum formulation suitable for use in all applications studied [93].

The authors of the last three papers, i.e. [82] [92] [93], have CESI Chemical as affiliation, which is a company of Flotek Industries. One patent from CESI Chemical concerning complex nanofluids for enhancement of simultaneous production of oil and gas from wells has been found [94]. It has therefore been assumed that these sources

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[10] Gallons per thousand (gpt)

[11] 1 dynes/cm = 0.001 N/m

report and discuss the properties of the patented nanotechnology Complex nano-Fluid® (CnF®), which is advertised on the Flotek Industries website [95]. The products based on the CnF® nanotechnology are claimed to aid stimulation and improve oil and gas condensate production by reducing breakdown pressures, reducing surface tension, aiding flow back of water-based fracturing fluids, and reducing formation damage created by phase trapping [95]. Products' commercial names are: MA-844W, MA-845, Stim® GPHT, StimOil® EC, StimOil® EN, StimOil® ENX, StimOil® FBA M, StimOil® FBA Plus Enviro, StimOil® FD, StimOil® AHS, and StimOil® E50 [95]. Each product has slightly different properties. They are all claimed to be sold in North America and Middle East while MA-844W, MA-845, Stim® GPHT, StimOil® FBA M, and StimOil® FD are also sold in Europe [95]. They are all developed from citrus fruit, i.e. from d-Limonene extracted from oranges and therefore are considered as bio-based and non-toxic [95]. The company claims that the CnF® products represent a more effective alternative to traditional surfactants [95] and have been utilized in nearly every shale basin to improve the productivity of unconventional resources [96]. They also stated in a magazine article that payback time seen from the use of CnF® products is less than 30 days and production rates improved from 5 to 200% when compared to neighbouring wells in the same reservoirs not treated with CnF® products [96].

The second type of application concerns a nanoadditive to emulsions for oil field applications. It was proposed in a patent by Halliburton [97]. The inventors described a nanohybrid comprising CNT (with high aspect ratio > 1000 and tubular geometry) and an inorganic nano-sized component (e.g. SiO_2, Al_2O_3, MgO, and TiO_2) for use in emulsions for oil field applications and, in particular, for fracturing operations. It was claimed that the nanohybrids help emulsify and maintain the stability of the emulsion (i.e. prevent droplets of the internal dispersed phase from flocculation or coalescing in the external phase) and may therefore be used as gelling agents to create emulsions that are capable of carrying proppants [97]. Moreover, the inherent hydrophilic and hydrophobic character gives the nanohybrids surface-active properties and makes them very stable over time and temperature due to the very high thermodynamic energy required to displace nanohybrid stabilized emulsion from the interface [97].

The use of nanoparticles dispersions as surfactant systems has also been reported in the literature. In one paper [98], dispersions of SiO_2 nanoparticles with an average size in the range 4-20 nm were proposed as wetting agents to remove organic matter such as oil, paraffin and polymer from the rock formation, thus leaving the substrate water-wet. SiO_2 nanoparticles with unmodified surface and partially (20%) modified with a silane surface (i.e. slightly hydrophobic) have been used in the laboratory tests. Results showed that the samples containing 10% by volume of colloidal SiO_2 nanoparticles dispersion removed approximatively 90% of the polymer, and the surface modified particles removed 100% of the polymer significantly faster than the test solution with the unmodified particles. The authors therefore concluded that surface modifications of the particles can increase the efficacy of the fluid as a surfactant system [98].

The authors of this paper [98] has Frac Tech Services International has affiliation. The company has implemented this technology in the commercial product NPD® Solutions [99], which is a nanoparticle dispersion claimed to improve hydrocarbons and stimulation fluids recovery from reservoirs and near wellbore regions more rapidly than previously possible. According to the company website, this high-tech solution replaces traditional surfactant systems using nanoparticles to create complete water wetness in a formation [99]. The nanoparticles in NPD® Solutions indeed assemble into a film when they encounter a discontinuous phase, forming a wedge. The wedge generates a force, which displaces fluids and solids, such as paraffin, from within the reservoir formation, proppant pack or downhole tubular and equipment [99]. The chemical composition and size of nanoparticles used in NPD® Solutions is not specified on the company website. From a search in the Internet one patent by Frac Tech Services International, which could be linked to this product, has been found [100]. The patent describes a nanofluid for hydrocarbons recovery consisting of SiO_2 nanoparticles with an average size of 19 nm in an aqueous solution [100].

4.10. Fracturing additive in CO_2-based fluids

One nanotechnology application as additive to CO_2-based fracturing for unconventional gas reservoirs has been found in 1 journal article.

The authors proposed the use of a dispersion of silicon nanoparticles coated with polyethylene glycol and with diameter size in the range 5-20 nm to reduce CO_2 fingering and improve fracturing effect [101]. In their experiment, the authors found out that nanoparticles coat the CO_2 droplets and form a kind of foam layer in the CO_2 displacement front, i.e. between CO_2 and brine. Moreover, during the pumping of liquid CO_2 into the formation, nanoparticles gather on the CO_2 front and are transported into the nano-pores of the shale formations, where the normal size proppants cannot arrive, thus contributing to generate more fractures in the rock matrix [101]. Based on these results, an optimised protocol of nanoparticles application as pad fluids before liquid CO_2 injection was suggested.

4.11. Any function

In 1 patent by Schlumberger Technology Corporation, the general use of nanodispersions to deliver underground chemical additives in a carrier fluid in which they are insoluble was proposed.

The authors claimed that a dispersion of nanoparticles has surprisingly stability and can be easily transport to the subterranean location without the need of a thickened carrier fluid. This stability also provides a way to delay the availability of the dispersed additive so that it becomes available when required, in response to conditions encountered underground [102].

According to the authors the nanoparticles should have a size not exceeding 800 nm and possibly in a range from 1 nm up to 500 nm. They also stated that any chemical that is insoluble in the carrier fluid can be used and envisaged that the concentration of the dispersed chemical in the carrier fluid often may be less than 5%, possibly less than 1% or even less than 0.1% by weight of that fluid [102].

4.12. Other

Halliburton Incorporated claims on two company websites [103] [104] that nanotechnology is used in formulating a commercial product named OILPerm^{TM} Fluid Mobility Modifiers (FMMs).

OILPerm^{TM} FMMs are described as blends of solvents, wetting agents and non-emulsifiers designed to promote quick recovery of fracturing fluids and provide enhanced reservoir hydrocarbon production following fracture stimulation treatment. These blends are developed for use in tight formations where they penetrate along with the fracturing fluid to provide: i) enhanced mobilization of liquid hydrocarbons resulting in improved oil production rate and recovery; ii) optimized relative permeability to oil; iii) reduced capillary pressure enabling rapid onset of gas production, enhanced production rates and maximized recovery; and iv) rapid recovery of the aqueous flow-back fluids resulting in reduced time for fracturing clean-up with reduced time before production. According to the manufacturer, nanotechnology greatly improves properties such as stability, penetration into the fracture network and reduced adsorption losses.

It is claimed that OILPerm^{TM} FMMs were tested in a field study where the average oil production increased by 35% and the average gas production increased by 290% after 12 months and over 9 wells in comparison to 12 not treated wells. It is also reported that OILPerm^{TM} FMMs were used in Woodford shale play in Oklahoma where an increase in initial fluid recovery ranging from 60% to 340% was registered. After 30 days from treatment, the oil production improved from 309% to 559%.

5. CONCLUSIONS

The present report has been developed based on publicly available knowledge with the aim of integrating information that can be found in the scientific literature with what is claimed by companies on their websites or other sources.

The literature search performed on bibliographic databases and online search engines resulted in more than 2000 peer-reviewed publications. However, not all of them were consulted for the preparation of this document. About half of the retrieved papers were not relevant as they did not fully answer the objective of the project, which was to investigate existing nanotechnology applications in fluids, proppants, and downhole tools for hydraulic fracturing of unconventional oil and gas reservoirs. For example, several papers reviewed nanotechnology applications for reservoir characterisation and monitoring (i.e. nanosensors), drilling and wellbore stability, or waste water/recovery fluids treatment. Those references were not consulted for the preparation of the present report. However, they could be considered at a later stage if an interest in extending the scope of the project is expressed. On the contrary, those references that addressed nanotechnology in fracturing fluids for conventional hydrocarbon reservoirs have been considered, as such applications may be used or adjusted for use in unconventional reservoirs in the near future. Several publications reviewed the current use of nanotechnology in the oil industry and generally discussed its future perspectives, thereby containing few details on the individual applications or the types of nanomaterials used. Moreover, some papers addressed the same applications and were considered as duplications. In total, 179 documents and 13 patents were considered as relevant and read. Additional *ad hoc* searches were performed during the project to obtain information on specific aspects of certain nanotechnology applications, and this led to the inclusion of 24 documents and 26 patents more.

The search of company websites (27) has been essential to retrieve information on commercial products using nanotechnology. In some cases, details about the chemical composition and properties of these products are provided in magazine articles (e.g. interviews with the inventors or heads of department).

In summary, 25 different types of nanotechnology applications have been identified and a large variety of nanomaterials has been encountered, ranging from inorganic and organic nanoparticles to more complex core-shells and nanocomposites. Most of the nanomaterials used in applications for hydraulic fracturing are of inorganic nature, mainly metals and metal(oids) (hydr)oxides. Information on chemical composition and size of the nanomaterials could usually be retrieved in the references; however, in most of the cases, only the size range or average size of the particles or droplets were reported, and this has not allowed understanding whether the nanomaterial is compliant with the definition as provided by the European Commission's Recommendation 2011/696/EU [5].

Almost half of the applications types described in the sources were specific for unconventional hydrocarbon reservoirs including tight and ultra-tight gas, shale gas, and coal-bed methane.

More than two thirds of the applications types are still at the research and development stage. Results from efficacy tests in the laboratory were usually reported but field trials were rarely mentioned. 31 commercial products using nanotechnology could be identified; half of them are proppants. Three products are claimed as being applied in Europe and five to be available in the European market.

The consulted sources consider the use of nanotechnology in fluids, proppants, and downhole tools for hydraulic fracturing of unconventional hydrocarbon reservoirs as successful. No disadvantage or additional cost from application of nanomaterials in hydraulic fracturing is mentioned.

6. APPENDIX I: TECHNICAL FUNCTIONS

Adapted from [2]

TECHNICAL FUNCTION	DESCRIPTION OF PURPOSE
Breaker system	Allows a delayed break down of the gel polymer chains to reduce the viscosity of the fluid after fracturing and enhance its recovery
Biocide	Eliminates bacteria in the water that degrade the gels and produce corrosive by-products (e.g. hydrogen sulphide) Prevents microbial growth from occurring downhole which could restrict flow from the created hydraulic fracture network
Clay stabiliser	Prevents swelling, shifting and migration of expandable clay minerals (water sensitive clay minerals) which could block pore spaces and therefore reduce permeability, shut off flow paths (e.g. creates a brine carrier fluid)
Cross-linker	Maintains fluid viscosity as temperature increases
Downhole completion tool for multi-stage fracturing	Device for flow control used downhole for sleeve actuation or stimulation diversion during multi-stage fracturing
Formation fines control additive	Prevents migration of formation fines such as: clay and/or non-clay particles (e.g. quartz, amorphous silica, feldspars, zeolites, carbonates, salts and micas) or similar materials within a subterranean reservoir formation
Fluid loss control additive	Reduces the loss (leakage) of fracturing fluid into the formation matrix
Friction reducer	Slicks the water to minimise friction (extra pressure, interfacial tension) between the fluid and the contact surface of the pipe, to maintain laminar flow while pumping and allow fracturing fluid to be injected at optimum rates and pressures (reduces the power required to inject the fluid into the well)
Gelling agent	Increases fluid viscosity allowing the fluid to suspend and carry more proppant into the fractures
Proppant	Particulate materials that keep fractures open to allow gas/fluid to flow more freely to the well bore. Proppant can be placed in the fracture in a form of a monolayer or a pack.
Solvent (non-emulsifier, carrier fluid)	Additive which is soluble in oil, water and acid-based treatment fluids, which is used to control the wettability of contact surfaces or to prevent/break emulsions or to facilitate delivery of gelling agents/friction reducers
Surfactant system	Reduces surface tension of the fluid on the fracture face thus aiding its recovery and eliminate emulsions of oil and water

7. APPENDIX II: FULL LIST OF NANOTECHNOLOGY APPLICATIONS

Appendix II contains the Excel table with the full list of nanotechnology applications that has been found through the literature and Internet search. For each application, the tables displays the retrieved information on nanomaterials' name, chemical composition, size distribution, other physicochemical properties, market prospect and target rock formations. The nanotechnology applications in the table are grouped according to the technical function they have been designed to exert in the fracturing fluids.

Each row contains information on one nanotechnology application and most of the times the information was retrieved from one individual source. In several cases, the same type of nanotechnology application was addressed in more than one source and the correspondent rows are therefore grouped together.

The information in the table is most of the time original text taken from the investigated sources; the authors have rarely modified the original text for practical reasons and never added subjective interpretations or assumptions.

The information on a specific application that was retrieved from the main source is always reported in black. Blank cells mean that no information was reported in the main source (i.e. the one specified in the last column). The text in red, blue or green is used to indicate that additional, complementary information on chemical identifiers, size or other physicochemical properties could be found in other sources, such as a website or a magazine article.

Appendix II: Full list of the retrieved nanotechnology applications and available information on nanomaterials' name and chemical composition, size distribution, other physicochemical properties, market prospect and target rock formations. Every line contains data and information on an individual application as reported in one source or a combination of sources. Blank cells mean that no information was reported in the source. The text in green, red or blue indicates additional information on chemical identifiers, size or other physicochemical properties obtained through *ad hoc* searches in the Internet (e.g. from the manufacturer's webpage). Physchem = Physicochemical. VES = Viscoelastic Surfactants.

Appendix II: (cont.)

NANOMATERIAL NAME AND COMPOSITION	OTHER IDENTIFIERS	SIZE	OTHER PHYSCHEM PROPERTIES	MARKET PROSPECT	TARGET FORMATION	SOURCE
ANY TECHNICAL FUNCTION						
No name		The very small dispersed particles are generally sufficiently small to class as nanoparticles, having a size not exceeding 800 nm, and possibly a size in a range from 1 nm up to 500 nm.		Research	Hydrocarbons	[99]
BIOCIDES						
Core-shell nanoparticles with interiors of non metallic material and a surface of silver and silver dioxide.		Maximum diameter less than 100 nm a minimum diameter greater than 2 nm	The shell covers at least 20-75% of the core	Research	Oil	[78]
BREAKER SYSTEMS						
Polyelectrolytes (PEC) nanoparticles: polyethylenimine branched (polycation) (PEI) and dextran sulfate sodium salt (polyanion) (DS)	PEI branched with Mw = 25 kDa and DS with Mw = 500 kDa by Fisher Scientific [From manufacturer webpage (Fisher Scientific): Dextran Sulfate Sodium Salt (White to Off-white Powder), Fisher BioReagents; CAS 1 = 9011-18-1; physical form = solid; Sulfur (S) = 17 to 20%] Nanoparticles were made with different ratios of PEI:DS (A/A'=2:1, B/B'=3:1, C/C'=4:1, D=2:1, E=3:1) via stirring and were loaded with pectinase (breaker) at a different final concentration in % (ww) (A/A'/B/B'/C/C'=0.1, D=0.07, E=0.06)	PEC Mean Particle Diameter (nm) after 8 h and after 32 h at pH = 8.7: A = 433 - 408 A' = 435 - 424 B = 370 - 362 B' = 313 - 292 C = 250 - 238 C' = 239 - 235	PEC Zeta Potential (mV) after 8 h and after 32 h at pH = 8.7: A = 29.4 - 35.0 A' = 36.3 - 34.9 B = 28.3 - 29.6 B' = 28.2 - 24.3 C = 27.4 - 17.5 C' = 18.7 - 10.4	Research	Conventional oil and gas reservoirs	[69]
		PEC Mean Size (nm) vs pH (graph): PEC A': about 525 at pH=6.3, 850 (max) at pH=7.2, decreased to 450 at pH=8.7. PEC H': about 850 at pH=6.75, decreased to 425 at pH=9.5	PEC Zeta Potential (mV) vs pH (graph): PEC A': about 45 at pH=6.3, decreased to 35 at pH=8.7. PEC H': about 35 at pH=6.75, decreased to 27 at pH=9.5	Research	Conventional oil and gas reservoirs	[70]
Inorganic semiconductors: e.g. CuO, Cu2O, Si, SiC, Ge, GaAs, InSb, GaN, and combination therof. Tested on CuO.		1 - 1000 nm	Used as an additive in the concentration 0.1 pptg to 100 pptg (pound per thousand gallon)	Research	Hydrocarbons	[73]

Appendix II: (cont.)

NANOMATERIAL NAME AND COMPOSITION	OTHER IDENTIFIERS	SIZE	OTHER PHYSCHEM PROPERTIES	MARKET PROSPECT	TARGET FORMATION	SOURCE
Organic semiconductors: e.g. pentacene, anthracene, rubrene, poly(3-hexylthiophene), poly(p-phenylene vinylene), polypyrrole, polyaniline, and combinations thereof. (can be used in combination to inorganic semicondactors)		1 - 1000 nm	Used as an additive in the concentration 0.1 pptg to 100 pptg (pound per thousand gallon)	Research	Hydrocarbons	[73]
Nanoparticle-Assembled Capsule (NAC) made of self-arranged nanoparticles and polyelectrolite molecules Nanoparticles can be metals, metal oxides, metal-non-oxides (quantum dots), organic particles, linear polymers, biomolecules, fullerenols and S/MWCNT. Example of cationic polyamine poly-L-lysine (PLL) and negatively-charged 12 nm silica nanoparticles		Sub-micron or micron-sized organic-inroganic spheres Nanoparticles may have diameters of 1-100 nm (example of 12 nm silica nanoparticles)	Spherical and non-spherical shapes (rods, triangles, hexagons)	Research	Oil	[74]
No name	Microemulsion or nanoemulsion Baker Hughes		Microemulsion or nanoemulsion containing: an aqueous external phase (e.g. water, brine), a non-aqueous internal phase comprising at least one organic peroxide (oxidizer) (72-100 weight% or 32-48 weight%) and one surfactant	Research	Hydrocarbons	[75]

Appendix II: (cont.)

NANOMATERIAL NAME AND COMPOSITION	OTHER IDENTIFIERS	SIZE	OTHER PHYSCHEM PROPERTIES	MARKET PROSPECT	TARGET FORMATION	SOURCE
DOWNHOLE COMPLETION TOOLS FOR MULTI-STAGE FRACTURING						
Powder metal composite including: a substantially-continuous, cellular nanomatrix comprising a nanomatrix material; a plurality of dispersed first particles each comprising a first particle core material (Mg, Al, Zn or Mn) or a combination thereof and a metallic coating layer (Al, Zn, Mn, Mg, Mo, W, Cu, Fe, Si, Ca, Co, Ta, re or Ni); a plurality of dispersed second particles intermixed with the dispersed first particles each comprising a second particle core material that is a carbon nanoparticle; and a solid state bond layer extending throughout the nanomatrix between the dispersed first and second particles. The nanomatrix is formed by sintering metallic coating layers of adjacent particles to one another by interdiffusion and creation of a bond layer	Controlled Eletrolytic Metallics (CEM) material by Baker Hughes. CEM frac balls (made of CEM material) [From Baker Hughes' leaflet (2011): IN-Tallic Disintegrating Frac Balls]		A substantially continuous, cellular nanomatrix and metallic grains dispersed in the nanomatrix. The nanomatrix consists of nanoscale metallic and/or ceramic layers/coatings.	Applied [Marketed]	Shale reservoirs	[10] [14]
	Disintegrable Nanostructured Composite (DNC) by Baker Hughes		A substantially continuous, cellular nanomatrix and metallic grains dispersed in the nanomatrix. The nanomatrix is primarily comprised of various mechanical strenghtening reinforcements and corrosion enhancers introduced into the composite system by matrix particle coatings Density of DNC materials range from 1.5 to 2.0 g/cm3	Applied	Shale reservoirs	[11]
	Baker Hughes Incorporated	Particle cores size: any suitable size range, e.g. 5-300, 80-120, 100 um Metallic coating layer size: nanoscale, e.g. 25 to 2500 nm Nanomatrix thickness: about two times the thickness of the first and second coating layers, e.g. about 50 to 5000 nm	Powder Particle core shape: any suitable shape from spheroidal to more irregular shape (e.g. ceramics), nanotubes, flat graphene		Hydrocarbons	[12]
	Controlled Eletrolytic Metallics (CEM) material by Baker Hughes. CEM frac balls (made of CEM material)	Grain size = 25-300 nm	Powder	Applied Marketed	Shale gas reservoirs	[13]
	High-Strenght Disintegrable Metallics High-Strenght Disintegrable frac balls IN-Tallic by Baker Hughes			Marketed	Unconventional tight gas reservoirs	[16]

Appendix II: (cont.)

NANOMATERIAL NAME AND COMPOSITION	OTHER IDENTIFIERS	SIZE	OTHER PHYSCHEM PROPERTIES	MARKET PROSPECT	TARGET FORMATION	SOURCE
CROSS-LINKERS AND FLUID LOSS CONTROL ADDITIVES IN VES FLUIDS						
Piezoelectric and/or pyroelectric crystal particles including ZnO, berlinite (AlPO4), lithium tantalate (LiTaO3), gallium ortophosphate (GaPO4), BaTiO3, SrTiO3, PbZrTiO3, KNbO3, LiNbO3, BiFeO3, soidum tungstate, Ba2NaNb5O5, Pb2KNb5O15, potassium sodium tartrate, tourmaline, topaz and mixtures thereof - Example with ZnO and MgO		ZnO nanoparticles' size = 30 nm		Research	Hydrocarbons	[61]
MgO, CaO, Mg(OH)2, Ca(OH)2, NaOH, ZnO, TiO2, Al2O3		Average size MgO = 30 + 35 nm		Research	Hydrocarbons	[63]
MgO, ZnO, TiO2, Al2O3	Baker Hughes Incorporated	1 - 1000 nm		Research	Hydrocarbons	[62]
MgO and ZnO nanoparticles		Size = 35 nm		Research	Unconventional tight gas reservoirs	[56]
		Size = approximately 30 nm		Research	Hydrocarbons	[65]
		Size = 35 nm		Research	Hydrocarbons	[59]
		Average size = 35 nm	Surface area = up to 500 m2/g No solubility in water, oil, or solvent Pyroelectric	Research	Hydrocarbons	[60]

Appendix II: (cont.)

NANOMATERIAL NAME AND COMPOSITION	OTHER IDENTIFIERS	SIZE	OTHER PHYSCHEM PROPERTIES	MARKET PROSPECT	TARGET FORMATION	SOURCE
SiO2 nanoparticles	Silica nanoparticles by Hangzhou Wanjing New Material Company	Average size = 15 nm In powder: big aggregates and chain structures are formed due to strong interactions between particles In surfactant solution: clusters have diameters ranging from 100 to 500 nm with dozens of particles inside, smaller diameter than in powder Size distribution by ultrasonic: two picks at 350 and 5500 nm (non-uniform, large aggregation) Size distribution by Microfluidizer: size range 90-450 nm and one pick at 190 nm	In powder: most of the particles are spherical In surfactant solution: clusters have smaller size, i.e. larger surface area for absorption	Research	Hydrocarbons	[55]
	Nanoparticles by SRL Pvt. Ltd. (Mumbai, India) [From manufacturer webpage (SRL Sisco Research Laboratories Pvt. Ltd.): Silicon Dioxide Nanopowder (Hydrophilic SiO2); CAS = 7631-86-9; Mw = 60.08]	Particles size: 15 nm [From manufacturer webpage (SRL Sisco Research Laboratories Pvt. Ltd.): APS = 15 nm]	Purity: > 99.5% [From manufacturer webpage (SRL Sisco Research Laboratories Pvt. Ltd.): Mw = 60.08; Purity: min. 99.5%; SSA = 650 m2/g]	Research	Oil	[54]
	Nanoparticles by SRL Pvt. Ltd. (Mumbai, India) [From manufacturer webpage (SRL Sisco Research Laboratories Pvt. Ltd.): Silicon Dioxide Nanopowder (Hydrophilic SiO2); CAS = 7631-86-9; Mw = 60.08]	Particles size: 15 nm [From manufacturer webpage (SRL Sisco Research Laboratories Pvt. Ltd.): APS = 15 nm]	Purity: > 99.5% [From manufacturer webpage (SRL Sisco Research Laboratories Pvt. Ltd.): Mw = 60.08; Purity: min. 99.5%; SSA = 650 m2/g]	Research	Oil	[58]
SiO2 nanoparticles (surface treated with oil)		Size = 20 nm		Research	Hydrocarbons	[57]
No name	Diamond Fraq by Baker Oil Tools			[Trademark]	Hydrocarbons	[66] [67]

Appendix II: (cont.)

NANOMATERIAL NAME AND COMPOSITION	OTHER IDENTIFIERS	SIZE	OTHER PHYSCHEM PROPERTIES	MARKET PROSPECT	TARGET FORMATION	SOURCE
Nano-composite fiber laden (90% wt polypropyle content & 10% wt polyester content) with addition of nanoparticles of inorganic nature belonging to the family of silicate/phyllosilicate	[**A silicate** is a compound containing an anionic silicon compound. The great majority of the silicates are oxides, but hexafluorosilicate ($[SiF_6]^{2-}$) and other anions are also included. **Phyllosilicates** are sheet Silicate minerals, formed by parallel sheets of silicate tetrahedra with Si_2O_5 or a 2:5 ratio. (group of minerals that includes the micas, chlorite, serpentine, talc, and the clay minerals)]	Fiber (optimal) length 6-12 mm, diameter 35 µm, no size for nanoparticles reported		Research	Coal-bed methane	[68]
CROSS-LINKERS IN POLYMERIC FLUIDS						
Nanolatexes (boronic acid functionalized nanoparticles)	[Nanolatex: product of copolymerisation of styren with vinylbenzichloride and divinylbenzene as a cross-linking agent] Nanoparticles functionalised with phenyl boronic acid orto, meta and para isomers; and (para) fluoro and (meta)nitro derivatives	Tested on 17 nm	Surface area = > 300m2/g	Research	Hydrocarbons	[78]
TiO_2 nanoparticles - unmodified, modified with citric acid, and modified with triethanolamine	TiO_2 nanoparticles synthesized from tetraisopropyl orthotitanate (97%) purchased from Alfa Aesar (Karlsruhe, Germany)	Size distribution (nm) at pH = 9: 6 ± 2 8 ± 2.3 10 ± 3.6 14 ± 6.1 Agglomerates with diameters of about 70 and 120 nm at pH value of 10 and 11 respectively.	Crystalline structure: anatase Shape: spheres	Research	Unconventional oil	[79]
ZrO_2 amorphous hydrous nanoparticles stabilised by triethanolamine and ZrO_2 nanoparticles modified with citric acid	ZrO_2 nanoparticles synthesized from zirconyl chloride octahydrate	Diameter (ZrO_2 amorphous hydrous nanoparticles stabilised by triethanolamine): 3 nm Diameter (ZrO_2 nanoparticles modified with citric acid): 11 nm		Research	Shale reservoirs	[80]

Appendix II: (cont.)

NANOMATERIAL NAME AND COMPOSITION	OTHER IDENTIFIERS	SIZE	OTHER PHYSCHEM PROPERTIES	MARKET PROSPECT	TARGET FORMATION	SOURCE
FLUID LOSS CONTROL ADDITIVES IN POLYMERIC FLUIDS						
Polyelectrolytes (PEC) nanoparticles: polyethylenimine branched (polycation) (PEI) and dextran sulfate sodium salt (polyanion) (DS)	PEI branched with Mw = 25 kDa, Lot N° MKBL7852V by SIGMA-ALDRICH [From manufacturer webpage (SIGMA-ALDRICH): Polyethylenimine, branched; average Mw ~ 25.000 by LS; average Mn ~ 10.000 by GPC; CAS Number = 9002-98-6; Linear Formula = H(NHCH2CH2)nNH2; MDL Number = MFCD00084427; PubChem Substance ID = 24865591; impurities ≤ 1% water] DS with Mw = 500 kDa, Lot N° 116614 by Fisher Scientific [From manufacturer webpage (Fisher Scientific): Dextran Sulfate Sodium Salt (White to Off-white Powder), Fisher BioReagents; CAS 1 = 9011-18-1; physical form = solid; Sulfur (S) = 17 to 20%]	PEC Mean Size = 547 nm		Research	Unconventional tight and ultra-tight reservoirs	[76]
		PEC Mean size: 545.43 nm	PEC Mean zeta potential = 37.16 mV PEC pH = 8.70	Research	Unconventional tight and ultra-tight reservoirs	[77]
SiO2 nanoparticles [From manufacturer webpage (Nissan Chemical): SiO2 = 40-42 %(wt) and Na2O = < 0.07 %(wt)]	SNOWTEX-ZL by Nissan Chemical	Mean size = 110.7 nm [From manufacturer webpage (Nissan Chemical): particle size = 70-100 nm]	Mean zeta potential = -41,17 mV pH = 9 [From manufacturer webpage (Nissan Chemical): colloidal silica made by growing mono-dispersed, negatively charged, amorphous silica particles in water; pH = 9-10; particle shape = spherical]	Research	Unconventional tight and ultra-tight reservoirs	[77]

Appendix II: (cont.)

NANOMATERIAL NAME AND COMPOSITION	OTHER IDENTIFIERS	SIZE	OTHER PHYSCHEM PROPERTIES	MARKET PROSPECT	TARGET FORMATION	SOURCE
FORMATION FINES CONTROL ADDITIVES AND CLAY STABILIZERS						
Al2O3, SiO2, MgO nanoparticles	Nanoparticles purchased by Nano Shell Company	Mean size grain (nm): MgO = 63 Al2O3 = 43 SiO2 = 48	Specific surface area (m2/g): MgO = >160 Al2O3 = ~40 SiO2 = >600	Research	Hydrocarbons	[53]
		Mean size grain (nm): MgO = 63 Al2O3 = 43 SiO2 = 48	Specific surface area (m2/g): MgO = >160 Al2O3 = ~40 SiO2 = >600	Research	Hydrocarbons	[46]
Alkaline earth metal oxides (MgO); alkaline earth metal hydroxides (CaOH2); transition metal oxides (TiO2, ZnO), transition metal hydroxides, post transition metal oxides (Al2O3), post transition metal hydroxides, piezoelectric crystals and/or pyroelectric crystals (ZnO, AlPO4) - Example with MgO nanoparticles (tested)	MgO nanoparticles tested (product no. 12N-0801, Inframat Advance Materials) [From the Inframat Advance Materials website: nano MgO Powder, 99.9%]	The particle size of the additives and agents ranges between about: 1-500 nm 4-100 nm about 100 nm or less about 90 nm or less about 50 nm or less about 40 nm or less Tested: MgO nanoparticles with crystalline size 35 nm [From the Inframat Advance Materials website: nano MgO Powder, 30-nm]	[From the Inframat Advance Materials website: nano MgO Powder, 99.9%, 30-nm, m.p. 2850 oC, b.p. 3600 oC, density 3.60 g/cm3, BET multi-point specific surface area (SSA) >50 m2/g]	Research	Hydrocarbons	[47]
		The particle size of the additives and agents ranges between about: 1-500 nm 4-100 nm about 100nm or less about 90 nm or less about 50 nm or less about 40 nm or less Tested: MgO nanoparticles with crystalline size < 8nm	Tested: MgO nanoparticles with SSA >230 or <300 m2/g, on natural bentonite (clay)	Research	Hydrocarbons	[51]

Appendix II: (cont.)

NANOMATERIAL NAME AND COMPOSITION	OTHER IDENTIFIERS	SIZE	OTHER PHYSCHEM PROPERTIES	MARKET PROSPECT	TARGET FORMATION	SOURCE
Alkaline earth metal oxides (MgO); alkaline earth metal hydroxides (CaOH2); transition metal oxides (TiO2, ZnO), transition metal hydroxides, post transition metal oxides (Al2O3), post transition metal hydroxides, piezoelectric crystals and/or pyroelectric crystals (ZnO, AlPO4) - Example with MgO nanoparticles (tested)	Tested: MgO nanoparticles: Product #12N-0801 from Inframat Advanced Materials [From Inframat Advanced Materials webpage: Magnesium Oxide nano powder]	Size ranges (nm): 1-500, 4-100 Mean particle size (nm): 100 or less, 90 or less, 50 or less, 40 or less Tested: MgO nanoparticles' size = 35 nm	[From Inframat Advanced Materials webpage: purity = 99.9%, SSA = > 50 m2/g, m.p. = 2850 °C, b.p. = 3600 °C, density = 3.60 g/cm3]	Research	Hydrocarbons	[49]
No name	Nanocrystals	Less than 100 nm in size, with the preferred product having an average size of 35 nm	Surface area = approximately 200 m2/g (extremely high) Not soluble in water, oil, solvent Easily slurried for field pumping applications	Research	Hydrocarbons	[45]
No name	Nanoparticles as a coating on proppant		Nanoparticles are injected into the bledder tub in a liquid slurry form Nanoparticles as a coating on proppant	Applied/tested	Hydrocarbons	[48]
Inorganic crystals	Commercial name: ConFINE Fines Fixing Agent			Marketed	Hydrocarbons	[50]
OTHER						
No name	OILPerm FMMs Halliburton Producer doesn't provide any information of nanomaterial used: "nanotechnology is used in formulating OILPerm FMM blends"			Marketed	Hydrocarbons	[103] [104]

Appendix II: (cont.)

NANOMATERIAL NAME AND COMPOSITION	OTHER IDENTIFIERS	SIZE	OTHER PHYSCHEM PROPERTIES	MARKET PROSPECT	TARGET FORMATION	SOURCE
PROPPANTS						
Ultra-light proppants (ULP)						
Impact modified thermoset polymer nanocomposite (polymer + nanofiller) Nanofiller: carbon black, fumed silica, fumed alumina, CNTs, carbon nanofibers, cellulosic nanofibers, natural clays, synthetic clays, fly ash, polyhedral oligomeric silsesquioxanes, metal clusters, metal alloy clusters, metal oxide clusters, or mixtures thereof Impact modified polymer: styrenic polymer modified with rubber e.g. HIPS high-impact polystyren, various block copolymers (e.g styrene-isoprene), etc	FracBlack from Sud Drilling Products Corporation	At least one external dimension in 1-500 nm range	% of nanofiller in the nanocoposite particle: 0.1-65% wg	Marketed	Hydrocarbons	[21]
Thermoset nanocomposite particles made of thermoset polymer and inorganic nanofiller. Inorganic nanofillers: carbon black, fumed silica, fumed alumina, CNTs, carbon nanofibres, cellulosic nanofibres, nanotubes of inoroganic materials (such as boron nitride). Natural and synthethic nanoclays [Montmorillonite], fly ash, the polyhedral oligomeric silsesquioxanes, and clusters of different types of metals, metal alloys, and metal oxides. Tested on: Carbon black nano grades	3 compositions: nanofiller = carbon black 310 nm (0.5% by vol.); polymer = copolymer: styren 51.55% (61.86%, 41.24%), ethylvinyl benzene 8.45% (10.14%, 6.76%), divinylbenzene 15% (18%, 12%), acrylated epoxidized soybean oil (AESO) 25% (10%, 40%). 4th composition: instead of AESO maleinized acrylated epoxidized soybean oil was used Examples of polymers: crosslinked epoxies, epoxy vinyl esters, polyesters, phenolics, melamine based resin, polyurethanes, various copolymers e.g. using vinylic monomers, vinylidene monomers etc, non cross-linking monomores: styrenic monomers, styrene, methylstyleres, chlorostyrene, methacrytlates etc	Proposed carbon black = 310 nm At least one external dimension in 1-500 nm range	Shape: spherical, ovoid, fibre, disc and polygonal shape or combination. % wg composition: nanocomposite comprises from about 0.001% to about 60% nanoparticle by weght of the nanocomposite particulate	Research	Hydrocarbons	[26]

Appendix II: (cont.)

NANOMATERIAL NAME AND COMPOSITION	OTHER IDENTIFIERS	SIZE	OTHER PHYSCHEM PROPERTIES	MARKET PROSPECT	TARGET FORMATION	SOURCE
Thermoset nanocomposite particles made of thermoset polymer and inorganic nanofiller. Inorganic nanofillers: carbon black, fumed silica, fumed alumina, CNTs, carbon nanofibres, cellulosic nanofibres, nanotubes of inoroganic materials (such as boron nitride). Natural and synthethic nanoclays [Montmorillonite], fly ash, the polyhedral oligomeric silsesquioxanes, and clusters of different types of metals, metal alloys, and metal oxides. Tested on: Carbon black nano grades	Nanoscale carbon black, fumed silica and fumed alumina e.g. by Cabot Corporation. Natural and synthetic nanoclays e.g. Nanocor and Southern Clay Products [Currently BYK Additives & Instruments-not possible to identify the product in question]. Tested on: Carbon black nano grades by Cabot Corporation used as nanofiller = Monarch 280. [Producer is not claiming nano size of the product neither on the website nor in SDS]	At least one external dimension in 1-500 nm range Tested on Monarch 280	Nanofiller: 0.1% to 15% vol. Monarch 280: relatively low SSA, high structure and fluffy form, easy to disperse. [Nanocor nanoclay NanoMer: natural montmorillonite mineral treated with compatabilizing agents, enabling the mineral aggregates to disperse to nanoscale size in plastic resins. Thickness of nanoplates around 1 nm, lenght up to 1.5 um. Very high aspect ratio 1: 200-500] Tested on proppant particles of 1.19-1.41 mm size (14/16 US Mesh) made of: 84.365% styren, 5.635% EVB, 10% DVB-divinylbenzene and 0.5% by weight of Monarch 280	Research	Hydrocarbons	[20] [22]
No name	FracBlack HT™ Thermoset nanocomposite particles including nanofiller (not specified on the website of producer) Polymer: CAS: 9052-95-3 [1,2-divinylbenzene, 1-ethyl-2-vinyl-benzene, styrene copolymer]		Specific gravity = 1.06	Marketed	Hydrocarbons	[22] [23]
No name	LiteProp108, Baker Hughes On company website: "nano" is not mentioned for this product. In article magazine (see ref): the author claims that proppant consist of nano-composite. In patent: ultralight proppants consists of thermoset nanocomposites LiteProp108 is given as an example, along with FracBlack, of a nanocomposite based proppant			Marketed	Hydrocarbons	[25] [26] [27]

Appendix II: (cont.)

NANOMATERIAL NAME AND COMPOSITION	OTHER IDENTIFIERS	SIZE	OTHER PHYSCHEM PROPERTIES	MARKET PROSPECT	TARGET FORMATION	SOURCE
Nanocomposite made of: inorganic nanomaterials (nanoclays, carbon nanofibers, polyhedral oligomeric silsesquioxanes (POSS), carbon nanotubes, nanoparticle minerals (such as silica, alumina, mica, graphite, carbon black, fumed carbon, and fly ash), glass nanospheres, ceramic nanospheres, and combinations thereof) a polymeric resin and a filler (not nano)	Carbon Black: BLACK PEARLS, ELFTEX, VULCAN, MOGUL, MONARCH, EMPORER, REGAL, UNITED, SPHERON and STERLING, Cabot Corp. [No nano size in technical data sheet and safety data sheet. From company website: Used for hydraulic fracturing as additive to proppant or guar gum to make them more compatible with Frac Fluid or hydrocarbons] ASTM, Fly ash - Class F: Pozmix by Halliburton. ASTM, Fly ash - Class C high-lime: produced from combustion of low-sulfur, sub-bituminous coal originated from powder River Basin near Gillette, Wyo. POSS: polyhedral oligomeric silsesquioxanes [POSS: the smallest reactive particles of silica]	Size range = 1-100 nm , 1-500 nm	Shape: spherical, ovoid, fibre and polygonal shape. % wg composition: nanocomposite comprises from about 0.1% to about 30% nanoparticle by weght of the nanocomposite particulate	Research	Hydrocarbons	[28]
Ceramic material from oxide and hydroxide of aluminum called alumoxanes i.e. aluminum-oxigen macromolacular species with a bohemite-like core. The template material can be a hollow sphere; the shell material comprises a ceramic material or oxide thereof or a metal oxide. The template may be an inorganic material such as a ceramic or glass, a polymer, a naturally occurring material (nuts, coffee grinds); the coating can be a polymer reinforced by a nanoparticle material such as an alumoxane containing functional groups that react with the polymer; or the coating can be a ceramic from a nanoparticle precursor such as alumoxane. Alumoxanes can have functionalised groups derived from carboxylic acids.		With nm and um size. Proppant can have any particle size. Proppant can have a particle diameter of from about 1 nm to 1 cm or in the range of from about 1 um to about 1 mm, or from about 10 um to about 10000 um, or from about 1000 um to about 2000 um. The nanoparticles in the shell can have primary particle size of 0.1 up to 150 nm or higher. The nanoparticle can comprise primary particles alone, agglomerates alone, or a combination of both. The shell can have an average grain size from 0.1 to 1 um max. At least 90% of all grain sizes can be within the range of 0.1 to 0.6 um	Uniform hollow spheres. Particle density (low desirable), crush strength and hardness, particle size (depends on rock type), particle size distribution (tight distribution desirable), particle shape (spherical desired), pore size distribution (tight distribution desirable), surface smoothness, corrosion resistance, T stability, hydrophilicity (hydro-neu tral to phobic desired) Aspect Ratio can be from 0.1 to 5 Nanoparticles in shell from 5% to 50% vol or more. Any Aspect Ratio ranging from 1 to 1000 or greater, any shape. Wall thickness of the shell from 5 to about 150 um	Research	Hydrocarbons	[31]

Appendix II: (cont.)

NANOMATERIAL NAME AND COMPOSITION	OTHER IDENTIFIERS	SIZE	OTHER PHYSCHEM PROPERTIES	MARKET PROSPECT	TARGET FORMATION	SOURCE
MgAl2O4 spinel nanoporous particles and α-Alumina (α-Al2O3)	Synthezised from α and γ - Alumina (SASOL GMBh (no info on nano) impragnete with solution of magnesium nitrate hexahydrate MgN2O6*6H2O (Sigma Aldrich, non nano) and calcinated at 115 °C	Pore diameter 10-12.5 nm, crystallite size in the range 21-129 nm for different samples in the series (also non porous one)	SSA (BET): 18.5 m2/g for an α alumina spinel with MgO at 12 wt%, pore volume 0.18-0.2 cm3/g, crush resistance PSI (MPa) 30000 (207) for or an α alumina spinel with MgO at 15 wt%, and 13000 for sample with 12% of MgO	Research	Shale reservoirs	[30]
MgAl2O4 spinel nanoporous particles	Synthezised from Alumina (SASOL GMBh - no info on nano) impragnete with solution of Mg(NO)3 and calcinated at 114 °C	Pore diameter = 19 nm	SSA (BET): 29m2/g, pore volume 0.18 cm3/g	Research	Oil	[29]
Carbon nanofibres	Carbon nanofibres are cylindrical graphitic nanostructures with graphene layers stacked on top of each other in a regular fashion (platelet, fishbone, cups or cones). If the fibres are hollow they are called CNTs (multi- walled and doped varieties)	Less than 100 nm in diameter and length of several hundred microns and beyond		Research	Oil	[29]
Ceramic (from waste material of coal-powered plants and various different nano-crystalline minerals)	OxFracTM Produced by Oxane Materials Inc	Hundreds of micron	Manufacturing process can be controlled at molecular scale to create perfectly spherical, same size, mono-dispersed and hollow proppant particles	Marketed	Unconventional gas reservoirs	[32] [37]
	OxBallTM Produced by Oxane Materials Inc	Hundreds of micron	Manufacturing process can be controlled at molecular scale to create perfectly spherical, same size, mono-dispersed and hollow proppant particles	Marketed	Shale reservoirs	[32] [37]
	OxThorTM Produced by Oxane Materials Inc	100 micron		Marketed	Unconventional gas reservoirs	[32] [37]
	OxSteelTM Produced by Oxane Materials Inc	Hundreds of micron	Manufacturing process can be controlled at molecular scale to create perfectly spherical, same size, mono-dispersed and hollow proppant particles	Marketed	Unconventional gas reservoirs	[32] [37]

Appendix II: (cont.)

NANOMATERIAL NAME AND COMPOSITION	OTHER IDENTIFIERS	SIZE	OTHER PHYSCHEM PROPERTIES	MARKET PROSPECT	TARGET FORMATION	SOURCE
Strenghten proppants						
Nanocomposite made of PP/PET fibers and SiO2 nanoparticles		Not specified. From the reported SEM image one could assume that nano-SiO2 particles are below (around) 100 nm		Research	Hydrocarbons	[40]
Nano silica, nano-alumina, nano-zinc oxide, nano-boron, nano iron oxide an combination thereor. Nano-clay (nano-monmorillonite) Fly ash class F and Class C (e.g Pozmix A from Halliburton) Zeolites ((nano)porous alumino-silicate minerals) e.g. products of C2C Zeolite Corporation of Calgary, Canada	Product name: Nanomer from Nanocor [Nanocor nanoclay NanoMer: consists of natural Montmorillonite mineral which have been treated with compatabilizing agents, enabling the mineral aggregates to disperse to nanoscale size in plastic resins. Thickness of the nanoplateless around 1 nm, lenght even to 1.5 micron. Very high aspect ratio 1: 200-500] [Generally mentioned cements as examples: Portland cements, pozzolanic cements, gypsum cements, soil cements, calcium phosphate cements, high-alumina content cements, silica cements, high-alkalinity cements, or mixtures thereof. many of them includes nanomaterials see for details]	Mean particle size below 310 nm, (particle size distribution: 20-310 nm or 20-150 nm or 20-100 nm) In general nano cement consists of: particles with less than 1 micron size	Concentration 0.01-100%	Research	Hydrocarbons	[41]
Proppants for tight and ultra-tight formations						
Fly ash - Class F: SiO2 (40-60%), Al2O3 (18-31%), Fe2O3 (5-25%), CaO (1-6%), MgO (1-2%), TiO2 (1-2%), Inorganic As (16-210 ppm)	Fly ash - Class F by Alliant Energy	Size range (Fly ash - Class F): 100-300 nm	Shape (Fly ash - Class F): round/spherical particles	Research	Unconventional tight and ultra-tight reservoirs	[43]

Appendix II: (cont.)

NANOMATERIAL NAME AND COMPOSITION	OTHER IDENTIFIERS	SIZE	OTHER PHYSCHEM PROPERTIES	MARKET PROSPECT	TARGET FORMATION	SOURCE
FRACTURING ADDITIVE IN CO2-BASED FLUIDS						
Silicon nanoparticles coated with polyethylene glycol (PEG)		Diameter size range: 5 - 20 nm 5 nm nanoparticles selected for the experiment (small enough to transport into micropores of shale stones thus contributing to generate more fractures in the matrix)	Nanoparticles dispersion diluted to 5 wt %	Research	Unconventional gas reservoirs	[101]
SURFACTANT SYSTEMS						
Complex nanofluid: nonionic EO+PO block copolymer such as Pluronic L-64 [i.e. poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)] or an ethoxylated alcohol such as Biosoft 690 [i.e. LAURYL ALCOHOL ETHOXYLATE, POE-7] as surfactant, alcohol cosolvent, and citrus terpene	[From producer's website: Pluronic L-64 by Sigma Aldrich is poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) or PEG-PPG-PEG]. [From producer's website: Bio-Soft EC 690 by Stephan Company is LAURYL ALCOHOL ETHOXYLATE]			Applied/tested	Shale reservoirs	[92]
Complex nanofluid containing alcohol ethoxylates, oxyalkyated amine, citrus terpene, and water		Droplet diameter (nm) [from graph]: In a complex nanofluid = 100-500 In a complex nanofluid diluted (20 gpt, 2% KCl) = 10-70 In a complex nanofluid diluted (2 gpt, 2% KCl) = 5-30		Research	Hydrocarbons	[82]
Complex nanofluid: nonionic ethoxylated alcohol surfactant, alcohol cosolvent, glycol based freeze point depressor, distilled water, natural terpene as solvent (last one in different amounts) [From manufacturer's website: developed from citrus fruit: d-Limonene extracted from oranges as solvent]	[From manufacturer's website: Complex nano-Fluid® (CnF®) by Flotek Industries]			Marketed	Unconventional tight gas reservoirs	[93]
No name	Nano-emulsions: NES-1, NES-2	Nanoemulsions stabilized diameter size = 10-20 nm	Nanoemulsion surfactant is a blend of anionic surfactant, nonionic surfactant, short chain alcohol, water. NES-1: light amber liquid, consists of oil and isopropanol with pH = 6.7. NES-2: colorless liquid, consists of citrus and isopropanol with pH = 8.7	Research	Gas	[83]

Appendix II: (cont.)

NANOMATERIAL NAME AND COMPOSITION	OTHER IDENTIFIERS	SIZE	OTHER PHYSCHEM PROPERTIES	MARKET PROSPECT	TARGET FORMATION	SOURCE
Nanoemulsion of D-limonene (oil), isotridecanol ethoxylate (nonionic surfactant), isopropyl alcohol (co-surfactant), tap water	D-limonene from Jiangsu Rich Native Animal Products CoO, LTD Isotridecanol ethoxylate (i-C13EOn, n=3, 6, 10) from Huntsman Corporation-Htc Labs Isopropyl alcohol from Beijing Shiying	Nanoemulsion particle size varies from 10 to 100 nm. Pick size = 42.76 nm	Nanoemulsion	Research	Gas	[85]
No name	Microemulsion (ME) Commercial name: Nanosurf 969 (patent pending) by Oil Chem Technologies (Texas, US)		Biodegradable microemulsion surfactant Appearance: clear to slightly hazy yellow liquid pH: 2-8 Viscosity at 25°C: < 50 cps Dispersible	Marketed	Shale gas reservoirs	[86] [87] [88]
No name	Microemulsion, ME	Micelles are extremely small, being roughly the lenght of the surfactant's tail (2-4 nm)	Microemulsion or micellar solution: blend of biodegradable solvent, surfactant, co-solvent and water.	Applied/tested	Hydrocarbons	[84]
No name	Nanoemulsion The nanoemulsions may be prepared by subjecting the fatty acids, surfactants, alcohol and optional components to high intensity mechanical shear at room temperature, followed by successive membranes filtrations G Clean WELL WAKE UP!™	Droplets of 5-50 nm		Marketed	Hydrocarbons	[89] [90]
Nanoemulsion: micellar solutions of fatty acids, such as tall and coconut oil fatty acids, a polysorbate emulsifier, a non-ionic surface active agent and a non-ionic detergent and mixtures thereof	Product name: G Clean WELL WAKE UP!™	Less than 100 nm in size		Marketed	Oil	[91]
Silica nanoparticles (surface modified with a silane and unmodified ones). For the modified ones, it is estimated that 20 % of the hydroxyl groups of the particle tested are bonded to the silane.		4-20 nm	Dispersion	Research	Hydrocarbons	[98]

Appendix II: (cont.)

NANOMATERIAL NAME AND COMPOSITION	OTHER IDENTIFIERS	SIZE	OTHER PHYSCHEM PROPERTIES	MARKET PROSPECT	TARGET FORMATION	SOURCE
No name	Nanoparticle dispersions NPD® Solutions by FTS International		Dispersion	Marketed	Hydrocarbons	[99]
Nanohybrid comprising CNT and inorganic nano component (e.g. SiO_2, Al_2O_3, MgO, TiO_2)		Inorganic nanocomponent may be of different shape: particles, nanowires or thin films	Hydrophobic CNTs and hydrophilic inorganic nanoparticles	Research	Hydrocarbons	[97]

8. APPENDIX III: REFERENCES

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List of abbreviations and definitions

BET	Brunauer–Emmett–Teller
CAS	Chemical Abstracts Service
CEM	Controlled Electrolytics Material
CNF	Carbon nanofibre
CnF	Complex nanofluid
CNT	Carbon nanotubes
DS	Dextran sulfate
ECHA	European Chemicals Agency
EE	Entrapment Efficiency
EEA	European Economic Area
EU	European Union
FMMs	Fluid Mobility Modifiers
HPG	Hydroxypropyl guar
I	Inorganic
IOGP NSG	International Oil and Gas Producers Natural Shale Gas
JRC	Joint Research Centre
MWCNT	Multi walled carbon nanotubes
NAC	Nanoparticle-Assembled Capsule
NES	Nanoemulsion Surfactant
NPD	Nanoparticle Dispersion
O	Organic
PEC	Polyelectrolyte
PEI	Polyethylenimine
PLL	poly-L-lysine
REACH	Registration, Evaluation, Authorisation of Chemicals
RIS	Research Information System
SSA	Specific Surface Area
SWCNT	Single walled carbon nanotubes
TEM	Transmission electron microscopy
ULP	Ultra-Light Proppants
USA	United States of America
VES	Viscoelastic Surfactants

List of figures

List of tables

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