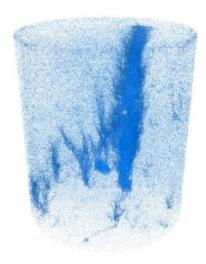
# Colloids and Surfaces A: Physicochemical and Engineering Aspects Development and application of a double action acidic emulsion for improved oil well performance: laboratory tests and field trials --Manuscript Draft--

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Graphical Abstract (for review)





# Development and application of a double action acidic

# emulsion for improved oil well performance: laboratory tests

### and field trials

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### **ABSTRACT**

Emulsified acid has attracted considerable attention of the oil and gas industry due to its delayed action that allows deeper penetration of acid into the formation which essentially facilitates improved well productivity, and at the same time minimizes corrosion of the downhole equipment. In this paper, for the first time, we report a new acidic emulsion suitable for acidizing carbonate reservoirs. The novel emulsion is of a double action type so that it is capable of simultaneously dissolving paraffin deposits and acidizing rocks thus increasing reservoir permeability and porosity. Results of the laboratory experiments and field tests indicate that the new emulsion reacts with carbonate rocks at reduced rate thus enabling the emulsion to penetrate deeper into the reservoir when injected for acidizing. At the same time the emulsion has lower corrosive effect towards steel, thus indicating better compatibility with downhole pumping equipment. Coreflooding experiments confirm the ability of the emulsion to acidize rocks forming highly permeable channels to the flow of hydrocarbons thus stimulating carbonate formations. The initial increase in oil recovery obtained after the acidizing operation suggests that the new emulsion provides better and faster return on investment thus making its use more economically viable. In addition, the developed and tested in this study emulsion requires fewer operations during its field implementation thus significantly reducing the operational costs. The developed novel emulsion, therefore, has characteristics comparable or exceeding those of solutions investigated or used thus far, combining all advantages in a single fluid thus allowing a highly efficient stimulation of production wells that can be achieved in a single operation. Hence, the presented results suggest that the double action emulsion presents a major advancement in acidizing science and technology.

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*Keywords:* carbonate reservoir, acidic inversed emulsion, corrosion retention, paraffin deposit washing, rock dissolution, cost effective formation acidizing

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### 1. Introduction

Oil field development efficiency depends on well productivity over the entire life of the field. During the operation of production wells, the reservoir properties such as porosity and permeability in the vicinity of the well gradually deteriorate thus resulting in an increase of the skin factor [1,2]. Clogging of the formation near a production well is caused mainly by the formation of paraffin deposits. Moreover, when reservoir fluid moves to the production well, the particles of the rock tend to clog pores and pore throats [3,4]. Improving productivity and reducing the skin factor is achieved by acid treatment or acidizing. The basic principle of acidizing is to dissolve rock by injection of acidic solution to form a network of microchannels or wormholes in the formation. This technology allows to increase and maintain oil production at the required level [5].

The effectiveness of acidizing depends primarily on the depth of penetration of acid into the formation and on the completeness of dissolution of reservoir rock in the acidic solution [6,7]. During the treatment of the formation with hydrochloric acid of concentration of 12-16 wt%, its maximum impact on the rock occurs in the near-wellbore zone. In the remote zone of the formation, the reaction of acid with the rock is less intense due to the loss of part of its activity after chemical interaction with rock in the vicinity of the well [8-10]. It is essential that the reaction between the acidic composition and the formation takes place at a slower rate so that the acid penetrates the rock as far as possible from the well. For this purpose, in practice, the so-called "inhibitor" of acid such as the "Neftenol", "Atsironiks", and "Soling" is used [11].

Paraffin deposits are also a typical complication during oil recovery. Paraffin deposits that correspond to specific pressure and temperature conditions clog the pore space thus reducing both the rock permeability and the efficiency of acidizing [12,13].

Efficient stimulation of production wells is still a challenging task thus development of effective acidic emulsions has been a focus of scientific research over the past five decades. Specific challenges associated with implementation of acidic emulsions include: i) achieving high efficiency of emulsions to dissolve reservoir rocks thus creating improved pathways to flows (microchannels or wormholes); ii) increasing depth of penetration of injected emulsion that requires an extended duration of acidic activity, which is normally achieved via use of inhibitors; iii) reducing corrosive effect of emulsion to minimize corrosion of well tubing and cements; iv) achieving efficient dissolution of paraffin deposits by the injected solution that leads to further improvement of reservoir petrophysical properties (porosity and permeability); v) keeping viscosity of the injected solution relatively low thus maintaining high mobility of the solution in order to not hindering the flow; and finally vi) developing such solution that allows removal of paraffin deposits and dissolution of rocks at the same time (so-called double action emulsion) thus reducing operational costs and time.

Today, many acidic compositions are known in oil and gas industry, but in most cases, they have a single effect of dissolving the rock in order to increase its permeability [12,14,15].

Other known technologies aim at dissolving reservoir rocks and removing paraffin deposits in the formation zone thus increasing formation permeability. However, these technologies are implemented in two stages. The first stage is associated with injection of a solvent to clean the bottom-hole zone from paraffin deposits while during the subsequent second stage acidic composition is injected in order to increase the permeability of the rock [5,16,17]. Although the obtained efficiency of rock dissolution and paraffin deposits removal is high in these conventional acidizing jobs, a well workover team is required. For example, although efficiency of paraffin removal was reported to be 33% in [16] and the rock dissolution

was 9256.1 mD [12], the use of two-stage acidizing technology and the involvement of a workover team significantly increases the cost of the procedure by \$25,000 [18].

Development and effective use of new acid compositions that can provide deep penetration into the reservoir and, at the same time, allow cleaning the pore space from paraffin deposits, is an important scientific and technological task. This task is of a paramount importance for oil reserves in the Perm Krai where a significant (about 45-50%) share of hydrocarbon reserves is found in carbonate reservoir, similar to the situation with oil reserves in carbonate reservoirs around the world [19,20]. To solve this problem, the authors have developed and tested a new proprietary double-action acidic emulsion termed Emulsion A. The developed Emulsion A is efficient in removing paraffin deposits, dissolving reservoir rocks, it has relatively low viscosity and therefore is mobile, it has extended duration of strong acidic action thus making it possible for the emulsion to penetrate deeper in the reservoir, and it has low corrosion rate making the acidizing less damaging to well equipment. All these properties make the developed emulsion novel, highy efficient and cost effective, thus significantly advancing the current state of acidizing science and technology.

Emulsion A is an acidic solution dispersed in a hydrocarbon fluid. The continuous phase of Emulsion A is a mixture of liquid hydrocarbons, and the dispersed phase is the hydrochloric acid. At present, the composition of Emulsion A is uniquely designed for oil fields of Perm Krai, Russia. One of the main advantages of the developed composition is that paraffin removal and acidizing is carried out in a single-stage procedure and without setting up a special team for workover thus reducing the costs of carrying out the task. When carrying out the conventional acidizing, the pumping equipment is removed from the wells. Which is done by the well overhaul service. The pumping equipment is removed since the acidic compounds are highly corrosive. The developed Emulsion A has low corrosive activity and therefore it can be injected without lifting the pumping equipment from the well and without involving the workover.

Another advantage of Emulsion A over the conventional acid is that when it is used in a carbonate reservoir, emulsified acid can enhance the acid delivery to formation and improve wellbore coverage across the target thickness of the reservoir [21,22]. Moreover, conventional acidic solutions have viscosity similar to that of water. Therefore, they will tend to flow into the formation intervals with higher permeability, leaving the tighter reservoir zones with higher formation damage untreated [23]. This non-uniform coverage of acid in the reservoir could lead to the overall unsuccessful acidizing. Therefore, the Emulsion A, which has viscosity of approximately 50 cp could enhance the zonal coverage, sweep efficiency and acid distribution in heterogeneous reservoirs [24-26].

The developed Emulsion A has passed industrial tests at 42 production wells in the Perm Krai and 12 wells in Udmurtia (Russia). In comparison with other solutions used today in different regions of the Perm Krai and elsewhere in Russia, as well as with some acidic compounds that are used in oil fields of China, USA and Canada, the use of Emulsion A results in increase of an average 20-30% [19] in oil recovery. Economic benefits achieved using Emulsion A account for about \$150.000 for treatments carried out in the Perm Krai and Udmurtia over the period of use of the emulsion.

### 2. Materials and Methods

2.1 Fluids

2.1.1 Emulsion A

153 Oil and gas operators and service companies at the Perm Krai carry out acidizing 154 operation of a well without workover. This has become possible due to the use of Emulsion A at the well with a significantly reduced corrosion rate compared to 155 156 standard acidic compositions. The main properties of Emulsion A are shown in Table 157 1. This type of emulsion allows aggressive hydrochloric acid to be dispersed in a 158 neutral hydrocarbon medium thus reducing the rate of formation and well corrosion 159 caused by the acid. Also, due to the inverse nature of the emulsion it does not dissolve 160 in water, while when mixed with formation water the viscosity of the mixture 161 increases thus reducing its mobility. Moreover, upon contact with crude oil the 162 emulsion becomes unstable and decomposes into separate hydrocarbon and acid phases. The hydrocarbon phase cleans the formation of paraffin deposits thus 163 increasing well productivity. On the other hand, the acid phase reacts with the 164 165 carbonate mineral of the reservoir causing its dissolution, which increases the 166 permeability of the reservoir. In addition, leaving the formation, the acid and the 167 hydrocarbon phases are no longer able to form emulsions thus adversely affecting the 168 operation of submersible equipment. The hydrocarbon phase also makes the formation 169 in the vicinity of the well more hydrophobic and removes paraffin deposits thus 170 increasing well productivity.

**Table 1**The properties of Emulsion A.

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Property	Value
Density at 20°C, g/cm <sup>3</sup>	1.03 - 1.13
Concentration of HCl, % (v/v)	8 – 13
Mass fraction of iron in the emulsion, %	< 0.025
The dissolution rate of steel, $\theta$ at 20°C g/(m <sup>2</sup> ×hour)	< 0.08 - 0.10
Viscosity prior to acidizing procedure, cP (mPa·s)	40 - 50
Viscosity after acidizing procedure, cP (mPa·s)	50 - 65

#### 2.1.2 Formation water

The characteristics of the formation water used in this study are presented in Table 2. Produced water was taken directly from the reservoir. To determine the content of ions in the formation water we used ion chromatography method (ion chromatography 940 Professional IC Vario, Metrohm).

 Table 2

 Characterization of formation water properties

Range of change
1.032 - 1.192
21000 - 363000
6.085 - 7.985
1.22 - 1.50
69211 – 85231
16434 - 21861
3550 – 5618
153601 – 168850
158 - 455
49.4 - 720
137 - 418

Br <sup>-</sup>	467 – 899
J-	11.4 - 23.0
$B^{3+}$	7 – 211
Li <sup>+</sup>	14 - 32

### 2.1.3 Crude oil

The crude oil used in this study is classified as light, low-viscosity, resinous, highly paraffinic, sulphurous with a high yield of light fractions during distillation. The characteristics of the crude oil are presented in Table 3.

**Table 3** Characterization of the properties of crude oil.

Parameter	Range of change
Density, g/cm <sup>3</sup>	0.710 - 0.877
Viscosity, cp	1.16 – 17.5
Gas content, m <sup>3</sup> /m <sup>3</sup>	21.3 – 251.3
Melting point of paraffin, °C	51.2 – 54.5
Boiling point, °C	44 – 57
Heavy oil fra	actions, vol%
Paraffins	2.71 - 5.4
Resins	6.54 – 18.95
Asphaltenes	0.86 - 7.3
Sulfur	0.32 - 1.53

Gas dissolved in the oil is characterized by low methane content of 28.28 mol%, high fat content of 50.04 mol% of methane homologues, and medium nitrogen concentration of 21.28 mol%). The hydrogen sulfide in the gas is found to be below the detection limit.

### 2.2 Rock samples

This study used over 300 rock samples from Perm Krai and Udmurtia Republic. A 30 mm diameter, 5-7 mm thick rock samples were used. Rock samples were taken directly from the producing oil reservoir (average depth of rock sampling was 2100 - 2200 m). The rock samples are carbonates that consist of mostly calcite and dolomite grains at different ratios. The mineralogy and basic petrophysical properties of rock samples is given in Table 4. Select rock samples were analyzed using thin sections and a microscope, which allowed to identify minerals comprising the samples. The analyses showed no presence of organic matter such as kerogen. Therefore, we are confident that observed dissolution of the samples, discussed later, cannot be attributed to chemical interaction between Emulsion A and organic matter. The samples investigated in this study have significant ranges for each of the mineralogical components as well as in their petrophysical properties as can be seen from Table 4. Despite the variability in porosity and permeability, the weighted average values of 11.7% and 41 mD were evaluated. There are inclined and sub-vertical cracks, short and long, hollow and partially filled with calcite.

**Table 4**The mineralogy and petrophysical properties of rock samples used in this study.

Property	Value
Mineralogy	
Calcite	42.5 – 95.7%

Dolomite	0 – 55.7%
Other (quartz, mudstones, siltstones)	1.2 - 34.5%
Cements	5 – 10%
Pore size	0.02 – 0.9 mm
Porosity	7.0 - 20.7%
Absolute permeability	0.52 – 641 mD

### 2.3 Methods

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### 2.3.1 Laboratory, free volume

The following parameters of Emulsion A were investigated in 5 different free volume experiments: 1) the rock dissolution rate experiment expanded towards the effectiveness of the reaction inhibitors used in the composition and duration of the neutralization of the emulsion; 2) compatibility with reservoir fluids; 3) oil-emulsion interfacial tension (IFT); 4) corrosion rate; and 5) dissolving (washing) ability of paraffin deposits [6,12,19]. These experiments are described in more detail below.

1) To evaluate the effectiveness of the inhibitors used in the emulsion studies were carried out both for the Emulsion A and for vol12% HCl solution and for three acidic compositions (Solution 1 Solution 2 and Solution 3), all of which are commonly used in Russia. First, the initial mass of rock samples is measured. Further the clean dried samples were heated in an oven to a temperature of 35°C that corresponds to the reservoir conditions. Then Emulsion A was poured into special containers (50 ml) and heated to reservoir temperature and the investigated rock sample was placed into a container with Emulsion A. Rock samples was allowed to react with the emulsion over the period of one minute, after which the sample was removed from the container, dried and its mass was measured again.

The rate of dissolution of the rock  $(\vartheta_{dissolution})$  was determined by the rate of change in rock mass relative to the initial surface area of the sample:

$$\vartheta_{dissolution} = \frac{(m_1 - m_2)}{S \cdot t} \tag{1}$$

where  $m_1$  is the initial mass of the rock sample in [g];  $m_2$  is the mass of the rock sample after reacting with Emulsion A in [g]; S is the initial surface area of the rock sample in  $[m^2]$ ; t is the reaction time in [min];

To evaluate the time of neutralization of the emulsion, a 30 mm diameter, 5-7 mm thick rock samples were used. The experimental protocol is similar to that described in 1) with the only difference being in the duration of the reaction. In this experiment, the rock sample was allowed to react with the emulsion until no further rock dissolution was observed. The termination of the reaction between the rock and the emulsion was evaluated in two ways: visually and by measuring pH of the emulsion. Visual determination of the termination of the reaction was confirmed by cessation carbon dioxide emission (bubbling) that accompanied the reaction between acidic solution and carbonates. We used the S47 Seven Multi instrument for regular pH measurements, so that stabilization of pH reading indicated the end of the reaction of the rock with the emulsion. This experiment was carried out in order to determine the reaction time of Emulsion A with the rock under reservoir conditions.

- 2) The following approaches were used to evaluate and characterize the interaction between the emulsion and formation fluids:
- Characterization of the interaction of the emulsion with formation water was conducted by mixing the two in a volumetric ratio of 1:1 with a paddle mixer with the speed of 500-600 rpm. Then the mixture was placed in a heating cabinet, where it was

kept for one hour at reservoir temperature of  $35^{\circ}$ C. After that, the condition of the mixture was visually assessed for presence of deposits. It was passed through a filter paper (pore size 1-2  $\mu$ m), which, after drying, was examined under a microscope to investigate the composition of the deposits. The emulsion was considered to be stable and compatible with formation water in the absence of any precipitation or deposited flakes.

- The investigation of the interaction between the emulsion and reservoir oil was the most important step in a series of laboratory experiments that aimed at designing effective technique and emulsion formulation for acidizing. Investigation of the interaction between the reservoir oil and Emulsion A was carried out using three different fluids:
- ✓ Pure Emulsion A. The reservoir oil and the emulsion were mixed in volumetric ratios of 25:75, 50:50, 75:25 with a paddle mixer with a speed of 500-600 rpm, and placed in a heating cabinet, where they were kept for one hour at reservoir temperature. Then, the state of the mixture was evaluated visually for the presence of deposits and/or phase separation. The mixture was filtered through a sieve with a 100-mesh cell while recording the absence or presence of any residue on the sieve.
- ✓ Emulsion A mixed with 2000 ppm or 5000 ppm of Fe<sup>3+</sup>, which served as an inhibitor. The mixture of Emulsion A and target concentration of Fe<sup>3+</sup> was prepared by adding 0.5 mg or 2 mg of FeCl₃ into 50 mL (equal to 50g) of Emulsion A. Thus, the emulsion with Fe<sup>3+</sup> content of 2000ppm and 5000 ppm was then mixed with reservoir oil in volumetric ratios of 25:75, 50:50, 75:25 using the paddle mixer and held for one hour at reservoir temperature. Then the mixture was filtered through a sieve with a 100-mesh cell while recording the absence or presence of any residue on the sieve.
- ✓ Emulsion A mixed with 2000 ppm or 5000 ppm of Fe<sup>3+</sup> and equilibrated with marble. The emulsion with Fe<sup>3+</sup> content of 2000 ppm and 5000 ppm was equilibrated with marble cube until stable pH of approximately 4.5 (pH was measured every 3-4 minutes using an S47 Seven Multi) was established. Stable pH values were considered to indicate the end of reaction and some degree of neutralization of the acidic component of the solution. Note that initial pH of 0.5 was measured prior to the equilibration process and the marble cube was allowed to equilibrate with Emulsion A for 7 hours until stabilization at 4.5 pH units. The equilibrated emulsion was then mixed with the test oil in volumetric ratios of 25:75, 50:50, 75:25 and held for one hour at reservoir temperature. Then the mixture was filtered through a sieve with a 100-mesh cell while recording the absence or presence of any residue on the sieve.
- 3) The emulsion-oil IFT was determined using an automatic tensiometer. We used the DataPhysics DCAT tensiometer (measuring range -1-2000 mN/m; resolution  $-\pm 0.001$  mN/m) and two measurements methods: i) the Wilhelmy plate, and ii) Du Noüy method. Each measurement was repeated 3 times to yield inaccuracies associated with repeatability of the measurement.
- 4) The corrosion rate caused by the emulsion was evaluated by the gravimetric method according to GOST 9.502-82 "Unified system of protection against corrosion and aging. Corrosion Test Methods" [27]. In this experiment, flat rectangular steel plates with dimensions of 5.0 cm width, 1.2 cm height and 0.025 cm thickness were used. The plates were weighed, then dipped into a container with the emulsion and placed in a heated cabinet with a pre-set reservoir temperature. Samples of metal plates were aged for 24 hours, after which the steel plates were removed, washed, and dried, and their mass was measured. The corrosion rate ( $\theta_{corrosion}$ ) g/(m<sup>2</sup>×hour) is defined as:

$$\vartheta_{corrosion} = \frac{m_1 - m_2}{S \cdot t},\tag{2}$$

where  $m_1$  is the mass of the metal plate before the test, [g];  $m_2$  is the mass of the metal plate after the test, [g]; S is the initial surface area of the metal plate,  $[m^2]$ ; t is test duration, [hrs].

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According to the guideline outlined in GOST 9.502-82 "Unified system of protection against corrosion and aging. Corrosion Test Methods" [27] the maximum corrosion rate for acid compositions should not exceed 0.2 g/(m<sup>2</sup>×hour) [Technical conditions 2458-264-05765670-99 "Inhibited hydrochloric acid"].

5) To determine the ability of the emulsion to dissolve (wash) paraffin deposits in static and dynamic modes, experiments were carried out using the Coldfinger Test Method, which are shown schematically in Fig. 1 [28-32]. The experimental setup consists of a glass container with a lid into which a so-called cold rod is mounted. The cold rod is a stainless-steel hollow cylinder equipped with a cap with embedded system to supply and discharge the coolant (water). Glass container is sealed with a cold rod lid and placed on a magnetic stirrer with heating element at the bottom. As a result of heating the container, a temperature difference develops between the glass container and the cold rod. Typically, the temperature in the glass container was kept 5°C above the temperature at which crystallization of paraffins begins. As a result of established temperature difference between the glass container and the cold rod, the temperature of the latter was 5°C below the temperature at which crystallization of paraffins begins. Therefore, paraffins begin to deposit on the surface of the cold rod. After the paraffins crystallized on a cold rod, the crude oil in the container was replaced with Emulsion A. Experiments to determine the washing ability of the Emulsion A continued for 8 hours (exposure of the Emulsion A for more than 8 hours did not lead to increased washing ability). Every hour, the weight loss of the paraffin wax was measured on the cold rod. The studies were carried out in two modes: static (the stir bar was not moving) and dynamic (the stir bar was moving). The washing ability of the emulsion to dissolve paraffin deposits is estimated using:

$$K = ((C_2 - C_1)/C_2) \cdot 100 \tag{3}$$

where K is the coefficient of washing ability, [%];  $C_1$  is the amount of paraffin in grams on the cold rod after entering Emulsion A;  $C_2$  is the amount of paraffin on the rod before entering Emulsion A.

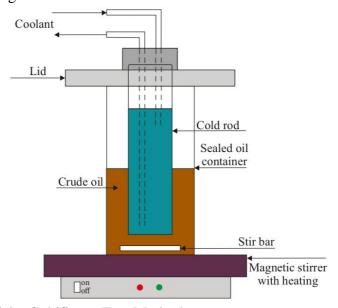


Fig. 1. Sketch of the Coldfinger Test Method apparatus.

2.3.2 Filtration (permeability) tests

Filtration tests on cylindrical rock samples (about 300 samples with 30 mm diameter from oil fields of the Perm Krai and Udmurtia Republic were used) were carried out using an AFS-300 (TEMCO Inc., USA) core holder at reservoir conditions in the following order. Initially, clean and dry core samples were saturated with kerosene in a vacuum chamber for 24 hrs to assure 100% kerosene saturation. The samples were then placed in the core holder, pressured to 22 MPa of confining pressure and heated to reservoir temperature of 30°C. Then, 3 pore volumes (PV) of kerosene were pumped through the rock sample in one direction at a constant rate of 1 cm³/min to determine the absolute rock permeability. The samples were subsequently cleaned in a Soxhlet extractor using methanol and toluene and following the procedure described by AlRoudhan at el. [33].

The clean and dry samples were saturated with water in the vacuum chamber for further 24 hrs to assure 100% water saturation. The samples were placed in the core holder and drained with crude oil at a constant rate of 1 cm<sup>3</sup>/min, confining pressure of 22 MPa and temperature of 30°C. The injection of oil continued until no more water was produced, thus reaching the irreducible water saturation. At the end of the drainage experiment the effective end-point permeability to oil at irreducible water saturation ( $K_1$ ) was measured. After drainage Emulsion A was pumped in the opposite direction at a flow rate of 1 cm<sup>3</sup>/min until no more oil was produced. Finally oil was pumped again in the same direction as during the drainage until cessation of emulsion production. At the end of this stage, the new effective permeability to oil ( $K_2$ ) that corresponds to the value post-acidizing was determined after. Note, that Emulsion A is immiscible in water and there was no water production at any stage after the completion of drainage. Therefore, the irreducible water saturation was assumed constant throughout the emulsion and oil reinjection stages. The coefficient of restoration of permeability,  $\beta$ , was evaluated as:

$$\beta = K_2/K_1 \tag{4}$$

### 2.3.3 X-ray Compute Tomography

The development of modern porous rock imaging methods relies on the acquisition of three-dimensional reconstructions from a series of two-dimensional projections taken at different angles: the sample is rotated and the absorption of X-rays in different directions is recorded and used to produce a three-dimensional (3D) representation of the rock. We imaged rock samples at the resolution of 3.43  $\mu$ m voxel size, and image size of  $8\times10^9$  voxels using X-ray micro-computer tomography XT H 225 (Nikon Metrology, Japan). Computer reconstruction of rock samples using the produces 2D images was carried out using the Avizo Fire software package. The software Avizo Fire was also used to calculate the pore volume and porosity of the rock samples before and after acidizing following the methodology outlined in [34-36].

### 2.3.4 Fields tests

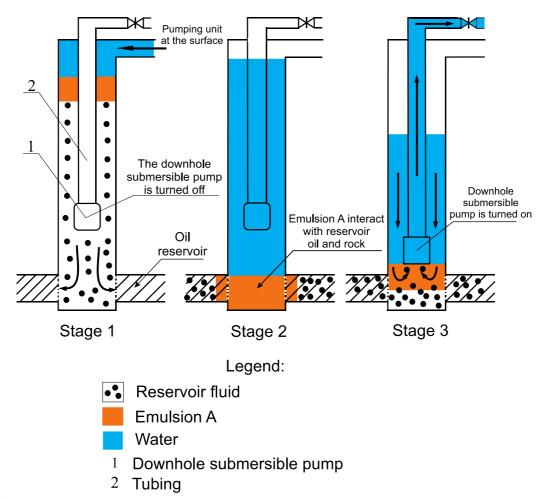
Upon completion of all laboratory tests, Emulsion A has undergone field trials in 42 production wells in the Perm Krai fields and 12 production wells in Udmurtia Republic. The geological and petrophysical features of the trial oil fields in which industrial tests of Emulsion A were carried out are provided in Table 5.

**Table 2**Geological descriptions of the oil fields Perm Krai and Udmurtia Republic. The ranges of the reported parameters correspond to variability across 2800 tested rock samples from Perm Krai and 1600 samples from Udmurtia Republic.

	Oil fields Perm	Oil fields Udmurtia	
Parameter	Krai	Republic	
Top of the reservoir depth	2000 - 2264.8 m	1855 - 2487 m	
Initial reservoir pressure, Pi	18.0 - 22.3 MPa	19.8 - 30.2 MPa	
Formation temperature	27 - 33°C	30 - 45°C	
Initial solution gas-oil ratio R <sub>s</sub> (or GOR)	$18 - 293.8 \text{ m}^3/\text{m}^3$	$50.5 - 184 \text{ m}^3/\text{m}^3$	
Bubble-point pressure, P <sub>b</sub>	10.5 - 14.5 MPa	12.4 - 20.6 MPa	
Reservoir oil viscosity	1.76 - 85.5 cp	35.8 - 112.8 cp	
Initial oil formation volume factor, FVF	1.01 - 1.21	1.05 - 1.41	
Reservoir thickness	3.2 - 26.7 m	1.8 - 18.4 m	
Effective permeability	20 - 641 mD	5 - 411 mD	
Average porosity	5.4 - 18.9 %	3.1 - 22.8 %	

Well acidizing operation using Emulsion A was carried out without well workover crew. Prepared Emulsion A is delivered to the wellhead in special containers and a pumping unit is used to pump the emulsion into the well with subsequent injection of formation water, which is used as a spacer fluid.

The emulsion injection standard operating procedure is shown schematically in Figure 2. The downhole submersible pump is turned off during injection of Emulsion A. A certain volume of emulsion, calculated based on the reservoir thickness, is pumped into the well using a pumping unit at the surface (Stage 1 in Fig.2). Emulsion A is pushed to the production interval by the injected water. The emulsion then penetrates into the reservoir and stays there for 8 hours to interact with reservoir oil and rock (Stage 2). When inside the reservoir, Emulsion A breaks into separate hydrocarbon and acidic phases so that the hydrocarbon phase cleans the formation from paraffin deposits, while the acid phase dissolves the rock. After 8 hours of this acidizing operation the downhole submersible pump is turned on to initiate production of water from the well (Stage 3). Once the pump produces the volume of water and emulsion equal to that of injected into the well, it starts producing formation fluids to the surface.



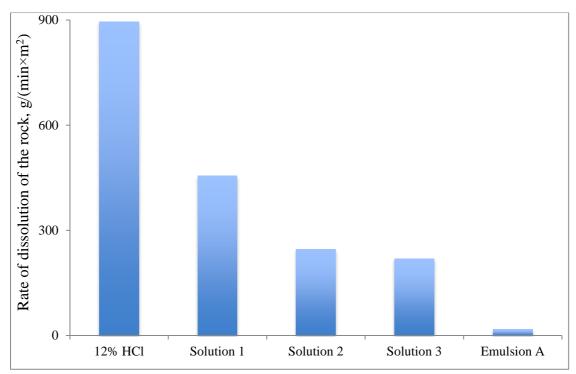
**Fig. 2.** Schematic representation of the standard operating procedure of injection of Emulsion A into the well. Stage 1 - injection of the Emulsion A into the well using a surface pumping unit. Stage 2 - displacement Emulsion A inside the formation. Stage 3 - pumping out Emulsion A and water from a well using the downhole submersible pump.

### 3. Results and discussion

The results of the laboratory tests (free volume, filtration and X-ray CT scanning) will be discussed prior to the analyses of the field test and the correlation between the two.

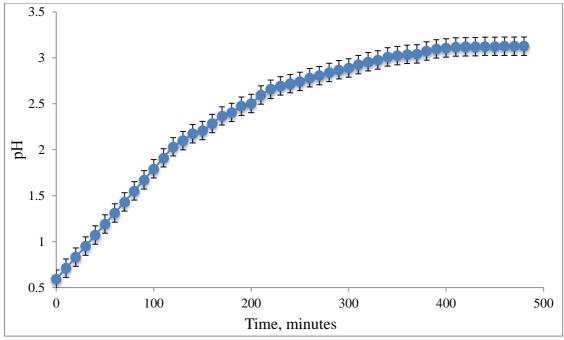
### 3.1 Analysis of the laboratory experiments

Figure 3 shows the results from rock dissolution tests. Rock dissolution rate of 17.37 [g/(min×m²)] was obtained with Emulsion A in comparison with an average rate of 894.37 [g/(min×m²)] obtained with 12%v/v HCl, which is routinely used in Russia [37,38]. Moreover, rock dissolution rate reported in [39,40] is greater by a factor of 2-3 relative to the rate obtained with Emulsion A. This suggests a slower reaction between Emulsion A and the reservoir rock thus providing evidence to a deeper penetration of Emulsion A into the reservoir. Results from dissolution tests carried out on carbonate rock samples using three other acidic solutions, also commonly used in Russia are shown in Figure 3 for comparison. Solution 1 Solution 2 and Solution 3, all of which are commonly used in Russia [37,38]. The composition of the three standard solutions 1, 2 and 3 used in Russia are: 11.5% HCl (Fluxocor-210), 10% HCl (NPS-K) and 8% HCl (KSPEO-2), respectively.



**Figure 3.** Comparison of carbonate rock dissolution rates obtained with Emulsion A relative to other conventionally used solutions.

Figure 4 shows the neutralization time of Emulsion A when in contact with rock samples. The figure shows that after approximately 7 hours of interaction between carbonate rock sample with Emulsion A, the pH readings stabilize at 3.12 units. This suggests that Emulsion A actively interacts with the rock during the first 7 hours, after which no further reaction between Emulsion A and the rock takes place. Based on this observation, the residence time of Emulsion A in the formation of 8 hours was used in the field tests as described in Section 2.3.4.



**Figure 4.** Temporal variation of pH of Emulsion A during interaction with rock samples. The error bars represent the accuracy and repeatability of the measurements.

The neutralization time of approximately 6 hrs and stabilization of pH at 3 shown in Fig.4 suggests that the developed Emulsion A has comparable or improved

neutralization time and similar or lower stabilized pH compared with previous studies, where stabilization time varied between 5-10 hrs and pH between 2.5 and 5.5 [37,38,39]. Therefore, Emulsion A remains highly efficient in dissolving reservoir rocks for a longer period of time thus improving the penetration depth for acidizing action. Moreover, previous studies that reported long neutralization time and low pH only investigated emulsions that were only capable of dissolving rock but were ineffective in removing paraffin deposits [38]. In a different study [41], the neutralization time was reported to be 2-3 hrs, while at the same time, the resulting permeability to oil after acidizing was only 78-203.5 mD, which is much lower that the permeability obtained with Emulsion A suggesting that rock dissolution efficiency is significantly higher for the emulsion presented in this study.

Figure 5 shows visual changes in rock samples after 8 hours of interaction with Emulsion A. After 8 hours of neutralization of Emulsion A, the mass of the rock samples decreases by 50-55%, which is greater than the emulsions presented in the works [38,42,43] where the reported weight change is 35-40%. Besides the measured change in sample mass, its shape and permeability also change significantly as can be seen from the figure and will be discussed in detail later.

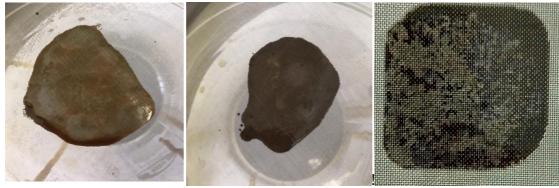


**Figure 5.** The figure shows rock samples before (left) and after (right) 8 hours of neutralization with Emulsion A.

Ability of Emulsion A to efficiently interact with reservoir fluids was also studied in the laboratory. Figure 6 shows the results of stability tests carried out with Emulsion A mixed with crude oil. The mixture was filtered through a 100-mesh sieve and it was found that it completely passes through the sieve. No lumps remain on the sieve as can be seen from the right sub-picture of Fig.6. Thus, if the mixture of crude oil and Emulsion A is capable of passing through the 100-mesh screen without being hindered or leaving residues, its viscosity is assumed to be similar to that of water. If Emulsion A mixed with crude oil formed highly viscous stable emulsions, clots would be deposited on the sieve. As a result, most of the mixture between Emulsion A and crude oil would remain on the sieve, rather than seeping through it, as shown in Fig. 6. This result suggests that Emulsion A is stable with crude oil and no deposits are expected in the reservoir.

Previous studies [16,44] reported acidic solutions forming high viscosity emulsions with crude oil. The viscosity of these emulsions was found to be in the range 100-850 cP, so that when filtered through a 100-mesh sieve 50-80% of the emulsion remained on the sieve. Such high values of emulsion viscosity would inevitably result in decreased mobility of reservoir fluids and therefore in reduced well efficiency [e.g. 45]. Therefore, Emulsion A performs significantly better than

previously used solutions with no significant increase in viscosity (Table 1) and no residues on the sieve after filtration.



**Figure 6.** The results of filtration of Emulsion A mixed with crude oil through a 100-mesh sieve that corresponds to approximately 150 μm diameter pores. The left picture shows that the mixture of crude oil with Emulsion A retains properties of a single-phase fluid capable of flowing through 150 μm pores of the reservoir. The middle and right picture show no residues on the filter after flowing the mixture of Emulsion A and crude oil.

Interactions between Emulsion A and reservoir fluids were further investigated via IFT measurements. The results of measured IFT between Emulsion A and reservoir oil are shown in Table 6. The use of Emulsion A results in significant reduction of IFT from 18 mN/m to less than 1.5 mN/m, which is lower compared with the values of 3 mN/m, 7 mN/m and 10 mN/m which were measured with the same crude oil and conventional Solutions 1, 2 and 3, respectively [37,38]. Therefore, the low interfacial tension between Emulsion A and crude oil allows the emulsion to penetrate into low-permeability (smaller pores and pore throats) oil-saturated layers by lowering the capillary entry pressure.

**Table 6**The results of measured IFT between Emulsion A and reservoir oil. The initial (without Emulsion A) measurements were carried out on a kerosene-crude oil system.

The value of IFT obtained with 12% HCl is taken from [38].

	Initial (without Emulsion A)	Final (with Emulsion A)	12%HCl
IFT, mN/m	18	1.5	15

To make sure Emulsion A is also compatible with the well pumping equipment, corrosion tests were performed using steel 316 to evaluate how corrosive the emulsion is. The tests were carried out with steel billets made of the same grade steel as the one used for downhole pumps. The results of these tests indicate a low corrosiveness of Emulsion A to metal. The corrosion rate of steel in Emulsion A at 20°C is found to be 0.08 g/(m²×hour), well below the rate required by GOST 9.502-82 for conventional acid compositions is 0.2 g/(m²×hour). This finding indicates that the developed Emulsion A will not have a negative effect on the downhole pumping equipment.

The results of the washing tests that investigate the capability of Emulsion A to wash (dissolve) paraffins are shown in Table 7. The coefficient of washing ability of the emulsion is fond to be 42.6% in static tests while, the efficiency of 54.2% is obtained in dynamic tests. The obtained results of the washing ability of Emulsion A indicate that the coefficient of washing ability is approximately 20-30% higher compared with conventionally used emulsions [41,46,47]. Thus, Emulsion A allows a significantly better dissolution of paraffins while being significantly less corrosive to

the downhole pumping equipment and lower crude oil-Emulsion A IFT allowing the emulsion to penetrate smaller pores.

**Table 7**Results of washing ability Emulsion A.

	6							
Interaction time, hrs	1	2	3	4	5	6	7	8
		Static test						
Coefficient of washing ability, %	6.7	11.8	16.4	24.1	29.7	33.8	38.1	42.6
				Dynan	nic test			
Coefficient of washing ability, %	9.7	15.2	20.1	29.4	35.7	40.1	46.8	54.2

Coreflooding experiments were conducted in order to evaluate the effect of acidizing rock samples saturated with crude oil and irreducible water. The results of the filtration experiments are presented in Table 8 (presents the main results covering a significant range of relative permeability from 0.56 to 453.7 mD), allowed to establish the following: the use of Emulsion A leads to an increase in the relative permeability of core samples to oil.

**Table 8**The results of filtration test of the Emulsion A. The appearance of high permeability values (100s of D) provides an experimental evidence to formation of highly hydraulically conductive channels as a result of acidizing.

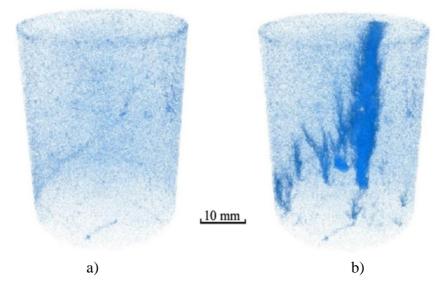
nydrauncany conductive chainless as a result of acidizing.						
Initial effective permeability to oil, mD	Effective permeability to oil after acidizing with Emulsion A, mD					
0.56	8.74					
1.1	79.20					
1.39	217.95					
2.74	437.58					
2.89	593.61					
2.97	993.47					
6.5	581.10					
8.51	132.76					
11.2	3865.12					
15.6	3110.64					
18.79	3780.55					
26.78	26844.27					
27.65	23615.87					
28.06	14063.67					
31.58	11510.91					
36.33	15298.56					
42.61	45013.20					
47.48	46744.06					
54.9	6708.78					
57.9	116442.69					
64.5	36410.25					
	Initial effective permeability to oil, mD  0.56 1.1 1.39 2.74 2.89 2.97 6.5 8.51 11.2 15.6 18.79 26.78 27.65 28.06 31.58 36.33 42.61 47.48 54.9 57.9					

22 (21.7)	114.5	22957.25
23 (11.9)	128.49	40538.60
24 (24.1)	141.8	30118.32
25 (18.8)	181.2	664170.48
26 (24.3)	194.6	1543.10
27 (21.4)	201.5	197248.35
28 (18.6)	272.5	147722.25
29 (42.5)	336.79	332613.80
30 (37.1)	453.7	614672.76

The increased permeability of reservoir rocks shown in Table 8 is comparable with results obtained with previously investigated acidic emulsions [37,38,39] which reported permeabilities between 155 mD and 864 D after the acidizing process. However, the reported high permeability values were achieved via a 2-stage injection, in which 15%-60% of paraffin deposits were first removed using surfactants, followed by injection of acidic emulsion to dissolve reservoir rocks. The achieved rock dissolution (final permeability) and paraffin deposits removal reported in [16,37,38] is comparable with the performance of Emulsion A. However, the implementation of this 2-stage process resulted in increased operational costs by \$70,000 - \$150,000 compared with a single-stage injection of Emulsion A.

In addition to filtration tests, X-ray computer tomography was carried out on selected rock samples and the results are presented in Figures 7 and 8. The images were taken before and after acidizing rock samples with Emulsion A, and Tables 9 and 10 show the corresponding changes in porosity of the rock samples after acidizing tests with Emulsion A.

Figure 7b shows that as a result of exposure to the Emulsion A, a highly conductive filtration channel, a "wormhole", is formed in the sample, which is clearly visible on the CT images of the rock sample. The permeability of the core sample shown in Fig.7 has increased from 114.5 mD to 22957.25 mD (increase in permeability by a factor of 200), while the porosity of the sample increased from 18.88% to 22.04% (Table 9).



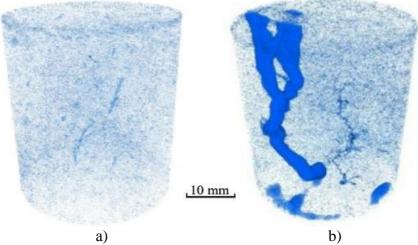
**Fig. 7.** CT images of a rock sample with initial permeability of order of 100 mD: a) before exposure to Emulsion A; b) after exposure to Emulsion A.

### **Table 9**

The change in pore volume and porosity of the rock sample shown in Figure 7 after exposure to Emulsion A.

Pore volume in [mm <sup>3</sup> ] and porosity in %				
before acid exposure		after acid exposure		
2283.20 mm <sup>3</sup>	18.88%	2652.71 mm <sup>3</sup>	22.04%	

Analysis of the X-ray tomography data obtained with another rock sample with different initial permeability also confirms the formation of a highly hydraulically conductive channels as a result of the acidizing effect of Emulsion A on the rock sample (Fig. 8b). The permeability of the tested core sample increased from 201.5 mD to 197248.35 mD (increase in permeability by a factor of 978), while porosity increased from 11.76% to 17.34% (Table 10).



**Fig. 8.** CT images of a rock sample with initial permeability of order of 200 mD: a) before exposure to Emulsion A; b) after exposure to Emulsion A.

Table 10

The change in pore volume and porosity of the rock sample shown in Figure 8 after exposure to Emulsion A.

Pore volume in [mm <sup>3</sup> ] and porosity in [%]				
before acid exposure		after acid exposure		
1404.15 mm <sup>3</sup>	11.76%	1842.17 mm <sup>3</sup>	17.34 %	

From the X-ray CT images of selected rock samples we establish that after acidizing with Emulsion A, porosity of the rock samples increases on average by 20% relative to the initial value, and the pore volume increases by 18%. This result suggests that Emulsion A performs significantly better compared with conventional emulsions used worldwide, with which the average increase in porosity is in the range between 10 to 15% [19,48-51].

It is well established that carbonate rocks are chemically reactive with acids in general and with HCl solutions in particular. Previous studies [e.g. 52-55] showed significant dissolution of tested carbonate rock samples exposed to HCl solutions with increased porosity and permeability, similar to and consistent with the results of this study. Thin section analyses of our rock samples did not show any noticeable inclusion of organic matter (e.g. kerogen) in the samples, thus the majority of minerals exposed to Emulsion A are those listed in Table 4, with calcite and dolomite being prone to dissolution in acidic solutions [52]. Therefore, we are confident that the increased porosity and permeability of the samples after acidizing result from dissolution of

carbonate material in acidic solution. The laboratory experiments with Emulsion A show that the emulsion:

- reacts with carbonate rocks with reduced rate, which implies that Emulsion A will be able to penetrate deeper into the reservoir when injected for acidizing;
- efficiently acidizes rock samples, thus resulting in significant increase of porosity and permeability, which is evident from the filtration tests and X-ray CT images showing formation of additional channels highly conductive for flow;
- has lower corrosive effect towards steel of the same grade as the downhole equipment, thus indicating better compatibility of Emulsion A with downhole pumping equipment;
- prevents formation of highly viscous stable emulsions when interacting with reservoir fluids thus staying hydraulically mobile in the reservoir after injection;
- is highly efficient in dissolving paraffin deposits thus further improving reservoir properties.

Based on a complex of the laboratory studies, recommendations were given for conducting industrial tests and the results of these tests are discussed below.

### 3.2 Results of fields implementation of Emulsion A

The results fields tests Emulsion A carried out on production wells in Perm Krai and Udmurtia are summarized in Tables 11 and 12, respectively.

**Table 11**Results of field implementation of Emulsion A in oil fields of the Perm Krai.

Indicator	Emulsion A	Standard solution
The average initial actual		
increase in oil production,	4.3	3.9
[tons/day]		
Ultimate incremental oil	1.68	1.0
recovery, [%OIIP]		
Number of operations	42	50
performed	42	50

Table 12
 Results of field tests of the Emulsion A in the oil fields of the Udmurtia.

Indicator	Emulsion A	Standard solution
The initial actual increase in oil production, [tons/day]	3.8	3.5
Ultimate incremental oil recovery, [%OIIP]	1.34	0.87
Number of operations performed	12	20

The results shown in Tables 11 and 12 indicate that Emulsion A leads to improved well productivity, which ultimately results in higher final oil recovery form acidized well compared with wells acidized with conventional solutions. The benefit of using the emulsion lies in its ability to dissolve carbonate rocks via acidizing with HCl, and at the same time via dissolving the paraffin deposits thus increasing rock permeability and improving reservoir's sweep efficiency. Moreover, the initial increase in oil recovery obtained after acidizing with Emulsion A suggests that the

emulsion also provides better and faster return on investment thus making the use of Emulsion A more economically viable. In addition, the developed and tested in this study Emulsion A requires fewer operations during its field implementation thus significantly reducing the operation costs.

### 4. Conclusions

In this paper we report laboratory experiments and field tests of a new acidic emulsion of hydrochloric acid in a continuous hydrocarbon phase. This emulsion, termed Emulsion A allows the aggressive hydrochloric acid to be enclosed in a neutral hydrocarbon shell, which significantly reduces the corrosive effect. Moreover, Emulsion A does not easily dissolve in water thus increasing the viscosity of high salinity formation water. On the other hand, upon contact with liquid hydrocarbons, the emulsion becomes unstable and decomposes into hydrocarbon and the acid phases, so that the former phase efficiently dissolved paraffin deposits in the formation while the acidic phase reacts with carbonate reservoir rocks which results in increased permeability and porosity of the reservoir.

The laboratory experiments and field tests have shown that Emulsion A has several advantages in comparison with acidic compositions that are routinely used in Russia and worldwide.

- The developed Emulsion A has low IFT at the interface with crude oil, which allows the emulsion to penetrate into low-permeability (smaller pores and pore throats) oil-saturated layers by lowering the capillary entry pressure;
- The acidic component of Emulsion A causes corrosion of steel at a lower rate compared with conventional solutions, which allows to implement the emulsion for acidizing in a single operation thus reducing the operational costs;
- Emulsion A breaks into acidic and hydrocarbon phases upon contact with reservoir oil, which delays the acidizing of reservoir rock thus increasing the penetration depth towards more remote areas of the formation;
- Emulsion A improves the acidizing coverage of the formation by flattening the acidizing front and increasing its penetration depth;
- Implementation of Emulsion A increases well productivity through both, the dissolution of the carbonate rock by the acidic component of the emulsion, and by dissolution of paraffin deposits that clog the pore space of the rock. Wettability alteration during injection of Emulsion A could also be responsible for improved oil recovery. However, to confirm or refute this hypothesis the wetting state of the intact samples used in this study could not be determined as the methods for such analyses (e.g. Amott Wettability Index) are based on the assumption that petrophysical properties of rock (porosity and absolute permeability) remain constant during the spontaneous and forced imbibition stages of the experiment, whereas these properties did significantly change during acidizing process reported in this paper.
- Emulsion A combines two main actions in a single fluid it is highly efficient i) in dissolving rocks and ii) in removing paraffin deposits. At the same time, the developed emulsion maintains relatively low viscosity thus making it mobile in the reservoir, it is not strongly corrosive towards well equipment, and it has a prolonged activity of the acidic component thus improving the depth of its penetration into reservoirs. These properties of Emulsion A make it a significant improvement and advancement of the currently available technologies. The developed novel emulsion also advances the scientific

research in the area and allows the acidizing to be carried out in a single-stage operation thus significantly reducing operational costs.

The abovementioned advantages of Emulsion A combined with its cost comparable with that of conventional solutions makes the use of Emulsion A also economically preferable.

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## ${\bf CRediT\ authorship\ contribution\ statement}$

**Dmitriy A. Martyushev:** conceptualization, data curation, methodology development, processing and analysis of results, writing the original draft. **Jan Vinogradov:** discussion and analysis of results, data curation, writing, revision and editing of the manuscript.

Declaration of Interest Statement

**Declaration of interests** 

☑ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.	
□The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:	
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