Electromagnetic field influence on the calcium carbonate crystallization in the iron ions Fe\(^{2+}\) presence in mineralized aqueous media

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Abstract. The influence of electromagnetic field (EMF), created in the frequency range from 100 to 200 kHz, on the calcium carbonate crystallization from supersaturated aqueous solutions on the model system CaCl\(_2\) – NaHCO\(_3\) - FeSO\(_4\) at 80°C at a molar ratio of CaCl\(_2\):FeSO\(_4\) (100:1), on the steel surface and in bulk was studied. It was found out that iron ions reduce the poorly soluble scales formed total mass (mainly CaCO\(_3\)) by ~12%, both adhered to the steel surface and in the solution volume. Under the EMF influence, the adhered crystals amount on the steel surface in the Fe\(^{2+}\) ions presence decreases by 40% and in the absence by 14%. In volume, under the EMF influence, on the contrary, the crystals' number increased by 15% in the iron ions' presence, in the iron ions absence it decreased by ~ 6%. In the Fe\(^{2+}\) ions presence and under the EMF influence, a decrease in the aragonite formation was noted while the calcite and vaterite content increased.

1. Introduction
The scale deposits formation problem in the developed oil fields most in recent years is particularly relevant. Scale deposition in the reservoir and wells leads to a decrease in the oil-bearing reservoir permeability, well production rates, an increase in operating costs and equipment failure [1, 2]. One of the most deposits main scale components is CaCO\(_3\) [1]. Laboratory research and practice have shown the using magnetic and electromagnetic fields (MF, EMF) promise to control the alkaline earth metal salts crystallization to prevent their deposition on the oilfield equipment surface [3-9]. When considering the MF impact on complex composition water media, mechanisms number are assumed, in particular, the emerging Lorentz forces importance on the crystallization processes is considered, interaction external MF and the intrinsic MF of the particles is assumed, the MF effect on the hydrogen bonds strength [10-12]. The electromagnetic field (frequency: 2 ± 0.2 kHz, amplitude: 10 V ± 0.3 V) Influence on the CaCO\(_3\) crystals nucleation and growth rate under dynamic conditions is considered in [13]. It is shown that the electromagnetic fields influence degree on calcium carbonate crystallization depends on the ratio Ca\(^{2+}/\)CO\(_3\)^{2-}. Exposure to an electromagnetic field significantly reduces the crystals' number formed at low values of the ratio Ca\(^{2+}/\)CO\(_3\)^{2-}, while simultaneously increasing the crystals formed size. In an electromagnetic field presence, the crystal agglomeration rate decreases and a precipitate formation time increases [12-14].
The Fe²⁺/Fe³⁺ ions influence on the crystallization of CaCO₃ in an external magnetic field absence is examined in [15-18]. It was noted that Fe²⁺ ions increase the nucleation time and slow down the crystal growth rate [17, 18]. Calcite formation inhibition and aragonite formation have been shown by X-ray diffraction analysis. In the oxygen presence, Fe²⁺ is oxidized to Fe³⁺, simultaneously at pH > 6.5 Fe³⁺ hydroxide is formed, and it plays a seed role: in its presence the nucleation of CaCO₃ crystals is initiated [16].

An early paper [19] investigated the iron hydroxide various forms effect on the heterogeneous nucleation of CaCO₃. It was found that trace concentrations of Fe²⁺/Fe³⁺ significantly inhibit the formation of calcite, but not aragonite. It is noted that a magnetic field use is effective precisely for the scale formation prevention, i.e. to inhibit the formation of CaCO₃ deposits on the heated metal surface [19]. Along with factors that determine the efficiency of CaCO₃ crystallization, such as the partial pressure of CO₂, temperature and the solution supersaturation degree, the cations Na⁺, Mg²⁺, anions Cl⁻, SO₄²⁻, the solution ionic strength can have a significant effect on the crystals formed morphology [20]. During the magnetic treatment of water, the effect of Na⁺, Mg²⁺ ions was expressed in a decrease in the crystallization induction time at an ionic strength of less than 0.02 and in a sediment amount general inhibition [20].

An implementation of a resonant wave complex (RWC), generating EMF in the frequency range from 100 to 200 kHz, on a complicated well stock characterized by deposits, mainly CaCO₃, on the surface, allowed to increase the trouble-free operation by more than 2 times [3, 6, 7]. Even though RWC shows fairly high efficiency in protecting wells from scale deposition, the mechanism of RWC influence on CaCO₃ crystallization requires substantiation. It is obvious that the EMF generated by the RWC does not affect the supersaturation of solutions, i.e. does not change the crystallization driving force. Presumably, the RWC EMF affects the process probability and changes the crystallization kinetics. In this regard we attempted to assess its operation effect on the crystallization of CaCO₃ from a model solution CaCl₂ - NaHCO₃ without and in the presence of FeSO₄ on a full-scale test bench that simulates flow conditions and temperature in the well. Since in the presence of CO₂ carbon steel corrosive dissolution is possible, we investigated the EMF effect on corrosion in NaCl solutions and the presence of Ca²⁺ ions.

2. Research materials and methods

Studies of the EMF effect on the calcium carbonate crystallization were carried out on the following ionic composition mineral water models: Ca²⁺ - 134.0, Fe²⁺ - 1.9, Na⁺ - 268.0, Cl⁻ - 237.0, HCO₃⁻ - 712.0, SO₄²⁻ - 3.2 mg/l and Ca²⁺ - 134.0, Na⁺ - 268.0, Cl⁻ - 237.0, HCO₃⁻ - 712.0 mg/l prepared from salts CaCl₂, FeSO₄·7H₂O and NaHCO₃ of analytical grade. RWC produced by the Pilot, ltd., was used. It was generating EMF in the frequency range from 100 to 200 kHz, in which the electromotive and magneuto motive forces resulting vectors are directed along the supersaturated aqueous solution motion axis.

The sizes of the formed CaCO₃ crystals were recorded on an Analysette 22 NanoTec Plus laser diffraction particle size analyzer. The morphology of CaCO₃ particles formed under an electromagnetic field influence was studied on a Rigaku Ultima IV X-ray diffractometer. The analysis was carried out in Cu-Kα radiation at a voltage of 20 kV and a current of 2 mA with a wavelength of λ = 1.5405 Å. The survey was carried out in the range of angles 2θ = 15-115° with a scanning step of 0.02°. Diffraction patterns and phase analysis were performed using the Match! software. The microstructure of the CaCO₃ samples was studied according to field emission scanning electron microscopy method (FE-SEM) on a Hitachi SU8000 electron microscope. The images were taken in the secondary electrons registration mode at an accelerating voltage of 10 kV and a working distance of 8-10 mm.

The experiments were carried out on a laboratory bench developed by the Pilot Research Institute, a diagram of which is shown in figure 1.

Heated to 80°C solutions of 22.21 g (0.2 mol) CaCl₂ and 0.55 g (0.002 mol) FeSO₄·7H₂O in 30 litres of water and 58.8 g (0.7 mol) NaHCO₃ in 30 litres of water were filed on the input using pumps at a rate of 12 l/min into the mixer and the resulting model of mineral water CaCl₂ - NaHCO₃ - FeSO₄ was
pumped through pipe 1 along the RWC placed in it, and then along a steel rod (steel 08) with a surface area of 350 cm$^2$, used to determine the resulting salts adhesion degree. The total experiment time was 4 h in all experiments. All experiments were carried out at atmospheric pressure.

After the experiment completion, the formed precipitate was filtered off, and the mass, the precipitate particle size and composition were determined. The calcium carbonate crystals amount adsorbed on the reference samples was determined by comparing the steel bar weight before and after the experiment.

To assess the EMF effect and iron ions, the experiments were carried out under similar conditions, but in the absence of FeSO$_4$·7H$_2$O and field. To determine the potential for scale deposition, the saturation index $SI$, calculated by the Oddo-Thomson method [21], and the formed scales absolute values, calculated from the ionic and heterogeneous equilibria equations were used.

To simplify the results' analysis, the following designations for scale-forming systems with and without exposure to EMF were introduced:

1. CaCl$_2$ - NaHCO$_3$ - FeSO$_4$
2. CaCl$_2$ - NaHCO$_3$ - FeSO$_4$ + EMF
3. CaCl$_2$ - NaHCO$_3$
4. CaCl$_2$ - NaHCO$_3$ + EMF

The magnetic field influence effect and Fe$^{2+}$ ions were estimated according to the equation, which was the action absolute effect ratio $\Delta g$ (EMF, EMF + Fe$^{2+}$, Fe$^{2+}$), i.e. changes in the formed scales specific amount on the surface and in volume to the scales specific amount, which was selected for comparison:

$$E = \frac{\Delta g_e}{g} \cdot 100\%$$  \hspace{1cm} (1)

where $E$ is the effect of EMF, EMF + Fe$^{2+}$, Fe$^{2+}$ on the steel surface or in volume, %;
$\Delta g_e$ - the exposure absolute effect, mg/cm$^2$ (mg/cm$^3$);
$g$ - scales specific amount selected for comparison, mg/cm$^2$ (mg/cm$^3$).

3. Results discussion

3.1. EMF effect on the calcium carbonate formation in the presence of Fe$^{2+}$ ions during crystallization from solution CaCl$_2$ + NaHCO$_3$

Obviously, the physical fields implementation effectiveness to prevent scale deposition on oilfield equipment is determined by their influence on the nucleation (nucleation) time and the crystal growth rate, as well as on the crystals' formation with low adhesion properties. Earlier it was found that under the EMF influence on saline water, in which the calcium carbonate crystallization proceeds [5, 6], there is a decrease in the average particle size of CaCO$_3$ and the aragonite crystals predominant formation, which has lower adhesion to the steel oilfield equipment steel surface.

The crystalline form of CaCO$_3$ in scale deposits is mainly represented by calcite, aragonite and, to a lesser extent, vaterite [19, 20], and the formation of one or another crystal structure strongly depends on
the water ionic composition and the conditions under which crystallization occurs. The effect, for example, of the concentration of Fe$^{2+}$ ions on the crystal structure of CaCO$_3$ is determined by both the pH value and the duration of the crystallization process [17, 21]. At 25°С in the presence of Fe$^{2+}$ ions, the main polymorphic calcium carbonate modification is aragonite, together with which siderite and ankerite are formed, and the aragonite content increases with the crystallization process duration.

The EMF influence results and Fe$^{2+}$ ions on the formed CaCO$_3$ crystals are presented in tables 1 and 2.

**Table 1.** Number, composition and size of CaCO$_3$ crystals formed without and in the presence of EMF and Fe$^{2+}$ ion.

| Crystallization in systems | Influence effectiveness on steel surfaces, % | Influence effectiveness in volume, % | Integral efficiency, % |
|---------------------------|---------------------------------------------|--------------------------------------|------------------------|
| The EMF and Fe$^{2+}$ influence on crystallization in the system CaCl$_2$ - NaHCO$_3$ - FeSO$_4$ + EMF relative to CaCl$_2$ - NaHCO$_3$ | 40.0 | -15.1 | 1.4 |
| The EMF and Fe$^{2+}$ influence on crystallization in the system CaCl$_2$ - NaHCO$_3$ - FeSO$_4$ + EMF relative to CaCl$_2$ - NaHCO$_3$ | 30.4 | 5.9 | 11.6 |
| The EMF and Fe$^{2+}$ influence on crystallization in the system CaCl$_2$ - NaHCO$_3$ + EMF relative to CaCl$_2$ - NaHCO$_3$ | 14.3 | -1.3 | 2.8 |
| The EMF and Fe$^{2+}$ influence on crystallization in the system CaCl$_2$ - NaHCO$_3$ - FeSO$_4$ relative to CaCl$_2$ - NaHCO$_3$ | 0.0 | 0.2 | 0.13 |
It was found that when exposed to EMF in the iron ions (CaCl₂ – NaHCO₃ - FeSO₄ + EMF) presence, scale deposition decreases by 40% (CaCO₃, CaSO₄, FeCO₃) relative to deposits from the CaCl₂ – NaHCO₃ (table 2). On the contrary, in the volume in this system, scales are formed in a larger amount by 15.1% (table 2), although the total amount is still less by 1.4%.

The EMF effect on crystallization in solutions with Fe²⁺ is quite effective. On the steel surface, reducing the crystals formed efficiency was 30.4%, in volume 5.9%, and the total efficiency was 11.6%.

If we consider the EMF effect on crystallization without Fe²⁺ ions, then it can be seen that reducing the crystals formed number efficiency is much less. However, it is obvious that the EMF effect is expressed in a change in the amount and ratio of polymorphs CaCO₃, so in the CaCl₂ - NaHCO₃ system, the aragonite content increases from 70.5% to 84.1%, while the vaterite formation was not detected.

In the EMF absence, the effect of Fe²⁺ ions under experimental conditions on the crystals formed number is insignificant. The EMF influence effectiveness integral assessment is less than 1%.

The precipitated scales actual amount may differ from the theoretically calculated amount (table 1). This is primarily due to the crystallization kinetics from a supersaturated solution, which, was not achieved in experiments. The formed scales calculated amount reflects their amount when an equilibrium state is reached, i.e. when saturation index SI = 0.

3.2. The EMF and Fe²⁺ influence on the CaCO₃ crystal sizes and polymorphs

The results of the formed crystals sizes distribution on the model of mineral water CaCl₂ - NaHCO₃ - FeSO₄ showed that an increase in the average crystal size (by ~ 4.2 μm) is observed under an electromagnetic field action in the time interval 15 - 55 min. and also the formation of a wider particle size distribution of CaCO₃ (by ~ 10.3 microns) (table 1). In the absence of iron ions (CaCl₂ – NaHCO₃ solution) in a supersaturated aqueous solution, both an increase in the average crystal size (by ~ 9.7 μm) and a wider CaCO₃ particle size distribution formation (by ~ 23.6 μm) (table 1). The crystals nucleation and growth processes occur simultaneously in the solution, as well as the formed crystalline particles' interaction with each other, which determines the polydispersity and size of the formed CaCO₃ crystals.

Under experimental conditions, under the EMF influence from a supersaturated aqueous solution in the model systems CaCl₂–NaHCO₃-FeSO₄ and CaCl₂ – NaHCO₃, the predominant formation (more than 70%) of CaCO₃ in the aragonite form (table 1). When crystallizing calcium carbonate from a CaCl₂ - NaHCO₃ - FeSO₄ solution, its cocrystallization with FeCO₃ and CaSO₄ is observed. When the content of ions Fe²⁺ and SO₄²⁻ in the initial solution is less than 1% concerning scale-forming ions Ca²⁺ and HCO₃⁻, as well as according to calculations in scale deposits should observed approximately 1%. FeCO₃ In fact, more than 2.1% is observed, and CaSO₄ should not be observed at all, however, 1.9% calcium sulfate was found in the sediments. It is assumed that this is due to the adsorption of Fe²⁺ and SO₄²⁻ ions on growing CaCO₃ crystals. It should be noted the aragonite (84%) high content in the sediment formed under the EMF influence on an aqueous solution of CaCl₂ - NaHCO₃ (table 1). In general, under the EMF influence, the predominant formation of aragonite is observed, which has lower adhesion to the steel surface.

Electron micrographs of CaCO₃ crystals obtained under the action of an electromagnetic field generated by the RWC indicate their polymorphism (figure 2). In the sample CaCO₃, there are aragonite elongated crystals, which is a fairly stable phase. During calcium carbonate crystallization in the EMF presence, a change in the formed crystals’ size and shape is observed on the metal surface, with crystal structure distortion clear signs.
4. Conclusions
It is shown that the EMF generated by the RWC, in the frequency range from 100 to 200 kHz, significantly reduces the crystallization efficiency on the steel surface from supersaturated water in the presence of Fe$^{2+}$ ions. During the calcium carbonate crystallization from a CaCl$_2$-NaHCO$_3$-FeSO$_4$ solution, its cocrystallization with FeCO$_3$ and CaSO$_4$ scales is observed, and their amount in the resulting CaCO$_3$ is more than it can be predicted from theoretical calculations. It is shown that under the EMF influence, the aragonite crystals predominant formation is observed.

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