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INVESTIGATION OF THE INFLUENCE OF PHYSICAL INHIBITION DEVICES ON $CaCO_3$ PRECIPITATION IN PIPE FLOWS

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Abstract. *Scale formation commonly occurs in hard water pipelines and it may result in severe flow assurance problems in the oil industry. The injection of chemical additives on the flow and the use of insulation on the pipe walls are typical methods used for scale control in industry. However, these high cost systems do not provide a consistent and long-term solution for the problem. As an alternative, some attention has been devoted to the influence that physical external fields, such as magnetic and ultrasonic, exert on the properties of precipitation and crystallization of calcium carbonate in saline solutions. In this context, the purpose of the present work is to experimentally investigate the effects of magnetic and ultrasonic water treatment device in preventing scale formation in long pipes. Data obtained indicate that ultrasonic devices actually influence the scale formation and precipitation more efficiently than magnetic. In particular, the irradiated energy induced by ultrasonic might reduce the size and adhesion of the resulting calcium carbonate deposited to the pipe walls.*

Keywords: *scale formation, calcium carbonate, pipe flows, physical inhibition devices.*

1. INTRODUCTION

The precipitation of inorganic compounds in pipes is a problem typically found in many industrial applications, ranging from biomedical to oil engineering applications. Indeed, domestic water supply pipelines may suffer scale formation in places where the hardness of water is high.

Most of the precipitation found in nature and in many industries is due to calcium carbonate. Irrespective of the application, the scale formation on pipe walls always exerts significant influence on the current process. The performance of heat exchangers can be significantly reduced since calcium carbonate deposits reduce the heat transfer coefficient and increases considerably the pressure drop of the equipment. Nasser and Salin (2012) comments that oil pipelines are also prone to similar problems, since valves and localized accidents impose a pressure drop that favors precipitation, which may result in complete blockage of the flow.

The injection of chemical additives on the flow and the use of insulation on the pipe walls are typical methods used for scale control in the oil industry. However, these high cost systems do not provide a consistent and long-term solution for the problem. As an alternative, some attention has been devoted to the influence that physical external field exert on the properties of precipitation and crystallization of calcium carbonate in saline solutions.

Recent studies, Kunanz and Wöfel (2014) and Chang and Tai (2010), observed that physical external fields, respectively magnetic induction and ultrasonic irradiation, were able to induce the precipitation of $CaCO_3$ of a specific polymorph known as vaterite.

Research on this subject dates back to the sixties and most of the work available in literature is restricted to small scale experiment, mostly conducted in capillaries or small mixing vessels (Farshad *et al.*, 2002; Donnet *et al.*, 2009; Nasser and Ruiwaie, 2010; Nishida, 2003). Despite the number of investigations, e.g. Nasser and Ruiwaie (2010), Alimi and Tlili (2006), Tai and Wu (2008) and Kojima *et al.* (2009), the literature still lacks an extensive and detailed database that allows the comprehension of the influence of external fields on calcium carbonate formation and precipitation. This is a crucial step for advancing knowledge, since a reliable dataset is the only basis to provide information for the correct understanding and modeling of the problem.

In this context, the purpose of the present work is to experimentally investigate the effects of magnetic and ultrasonic water treatment devices in preventing scale formation in long pipes. A dedicated flow loop with three different circuits, temperature and pressure controlled was specifically constructed for that purpose. Experiments can be performed for pressures up to 420 bar for the 1’ diameter pipe circuit, 310 bar and 240 bar for the, respectively, 2” and 3” diameter pipe circuits.

The present experimental investigation has been performed in a 50 meters long, 1 inch plexiglass pipe to allow visual inspection of the temporal evolution of the calcium carbonate precipitation. The effects of commercially available magnetic and ultrasonic treatment devices have been evaluated through careful measurements of global properties of the flow and chemical characterization of the saline solution and scale.

Although there is no theoretical framework applicable for the problem, nor an established experimental proof of performance, since the early seventies many industries commercialize these kind of devices for both domestic and industrial applications.

The design of those equipment is totally empirical, and its effective result is always an open question. The present research is conducted with a perspective to answer three main points: i) to quantify the effectiveness of the above mentioned devices in preventing or controlling scale formation, ii) to understand which effects are beneficial or detrimental for the water treatment, and iii) to develop a design and predictive tool for field application if the principle of operation is proved to be effective.

2. EXPERIMENTAL PROCEDURE

2.1 Experimental Apparatus

Once the knowledge available in literature is embrionary, the aim of the present work is to investigate the process of precipitation of calcium carbonate in a turbulent pipe flow coupled with each device, respectively, magnetic and ultrasonic. An extensive experimental campaign has been performed to produce scales that retain similarity condition to real scale problem.

Figure 1 presents an overview of the multipurpose flow loop located at the Laboratory of Well Technology (LTEP/NIDF/COPPE) and its main characteristics are summarized in Table 1.

Figure 1: Overview of the multipurpose flow loop (LTEP/NIDF/COPPE).

Table 1: General characteristics of the multipurpose flow loop.

Circuit	**Length (m)**	**Pressure (bar)**
1” plexiglass pipe	50	10
1” steel pipe	100	420
2” steel pipe	100	310
3” steel pipe	300	200
Tanks	**Quantity**	**Capacity (m^3)**
Supply/Discharge	3	8.0
Utility	1	4.0
Salt Injection	2	1.0

Present experiments have been conducted on the plexiglass circuit where calcium carbonate was formed by the mixture of two feeding lines with solutions of calcium chloride and sodium bicarbonate, respectively, a shown in Figure 2. The flow rate of each supply pipeline was measured by sonic flow meters (Endress Hauser®) and controlled by the rotation of two progressive cavity pumps. This initial experimental campaign was developed at the low pressure flow loop to furnish

visual inspection of the scale formation process and to develop optimized experimental procedure. In fact, the amount of salts required for each experiment, besides the acids necessary to clean the pipes, involve considerable cost and must be used according to optimized procedures.

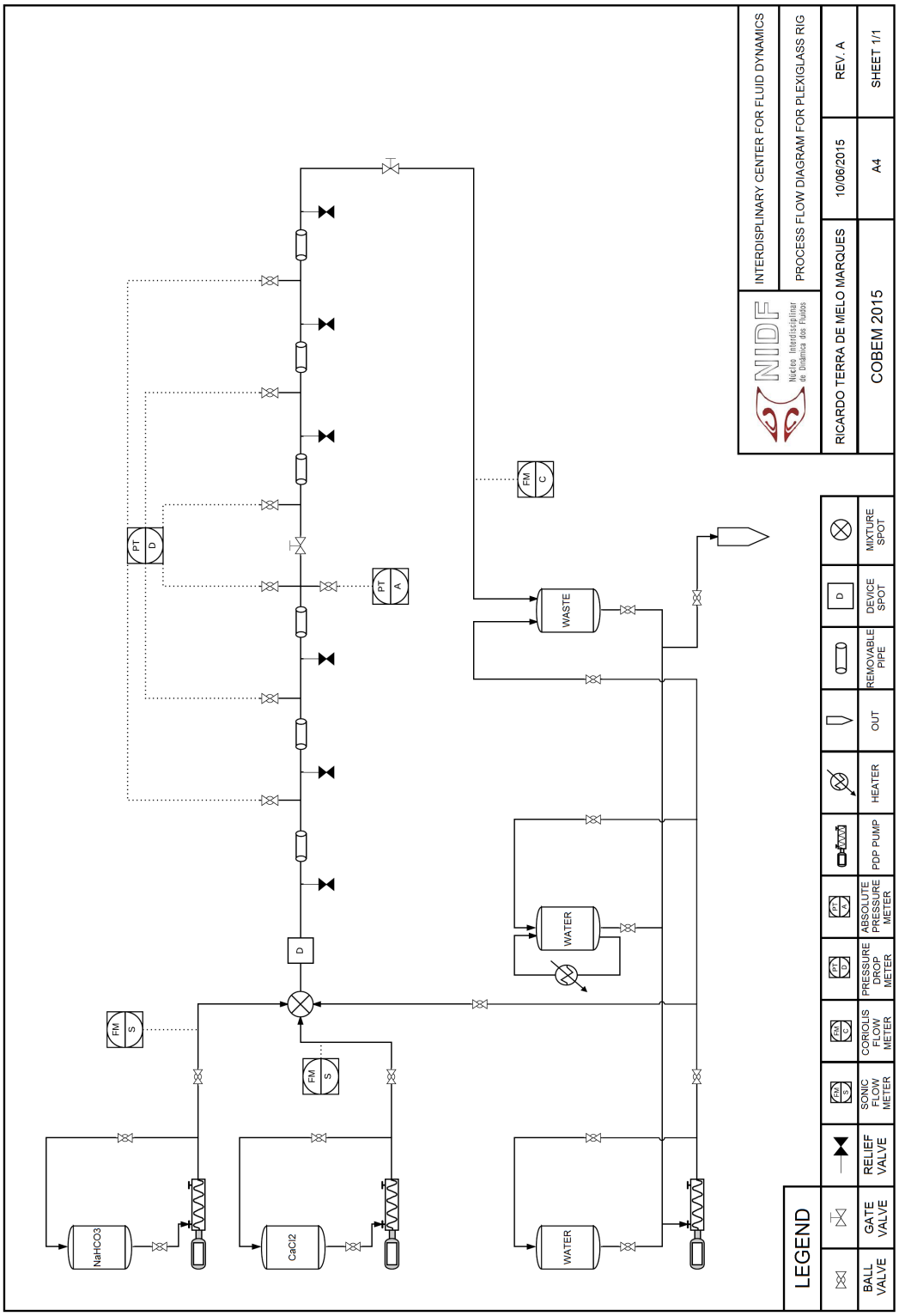


Figure 2: Process flow diagram of the flow loop.

Ambient temperature and humidity was monitored along every experiment and flow temperature was controlled by a 50kW heating system. Temperature measurement was made by a Pt-100 probe. Absolute and differential pressure transducers (Endress Hauser®) were used to monitor the scale formation along the time and length of the pipe.

The flow loop is equipped with six pressure taps for differential pressure reading and six removable test sections, which allow measurement of the weight of deposited mass at the end of each experiment. Fluid samples can also be extracted in six points along the pipe length, as illustrated in Figure 2, to provide temporal and spatial information about the evolution of the precipitation phenomenon inside the pipe. Chemical characterization of the water is performed by hardness, pH and conductivity measurements. Particles in suspension are analyzed in Malvern Mastersizer® that provides its diameter distribution by laser diffraction. Precipitated calcium carbonate are analyzed by X-ray diffraction (XRD) (Bruker®), by an electron scanning microscope (MEV) (TM3030 Hitachi®) to evaluate the crystal structure and its hardness.

The roughness of the pipe is also a relevant parameter for the experiment, since it may result in potential nucleation sites for crystal growth. As so, a crucial part of the experimental setup is to assure that the pipe is perfectly clean, i.e. with a smooth wall, prior to the next experiment. The cleaning procedure is performed by circulating concentrated acetic acid 1% v/v during one hour after each experiment.

2.2 Methodology

Three experimental tests were developed: i) flow of saline solution with no treatment, ii) saline solution with magnetic treatment and iii) saline solution with ultrasonic treatment. Given the time involved in preparing and performing each test, statistics are based only on a replication of each run.

Regarding the experimental procedure, questions are raised whether the experiment should be conducted in open or closed circuit. Many articles in the literature, Nielsen (1959), Wiecherst *et al.* (1974) and Dalas (2000), explored the formation of calcium carbonate in closed systems, i.e. systems where there is recirculation streams containing precursors of the salts besides calcium carbonate itself.

The main disadvantage of this approach is the loss of control over the concentration of species, once the recirculating system keeps concentrations of reactants and products simultaneously. Moreover, crystallization rates and particle growth are also affected. Bearing this fact in mind, the present experiment is operated in an open circuit, where the precursor salts of calcium carbonate were injected into a common mixture point in the circuit to generate a flow with chemical reaction. The saline solution flows through the test pipe and then follows to the discharge tank so there's no recirculation.

Equation 1 shows the chemical equilibrium of the reaction of $CaCl_2$ and $NaHCO_3$, used in the present work.

$$\mathrm{CaCl}_{2(aq)} + 2\mathrm{NaHCO}_{3(aq)} \rightarrow \mathrm{CaCO}_{3(s)} + 2\mathrm{NaCl}_{(aq)} + \mathrm{CO}_{2(g)} + \mathrm{H}_2\mathrm{O}_{(l)} \tag{1}$$

For each experimental run 700.0L of saline solution of calcium chloride (VETEC®) of concentration 7.350g/L plus 700.0L of saline solution of sodium bicarbonate (VETEC®) of concentration 12.60g/L were used. Each solution was stored in a $1.0\mathrm{m}^3$ tank and pumped at a flow rate of 150.0L/h, resulting in a global flow rate of 300.0L/h. Each experimental run lasted for four hours.

2.3 Magnetic Device

The magnetic device tested consists of a series of static magnets provided by Hidromag® company, shown in Figure 3a. The magnets were installed around the pipe and fastened with cable ties so that the field is formed in transverse position to the flow. Magnetic devices when aligned form a repulsive field, that is, unlike many other commercially available devices.

2.4 Ultrasonic Device

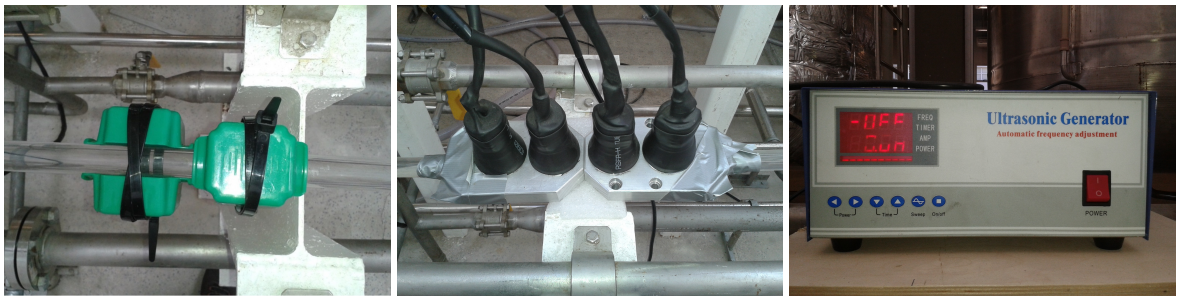
The ultrasonic device was housemade and consists of a controller, can be seen in Figure 3b, that allows the user to modulate frequency and potency of the ultrasonic waves. Pulses are conducted via cable to a transducer that is coupled with the plexiglass flow loop near mixture point (Fig. 3c). Some care was needed in order to tie the pipe firmly to prevent its excessive vibration.

3. RESULTS AND DISCUSSION

3.1 Scale Deposition and Temperature

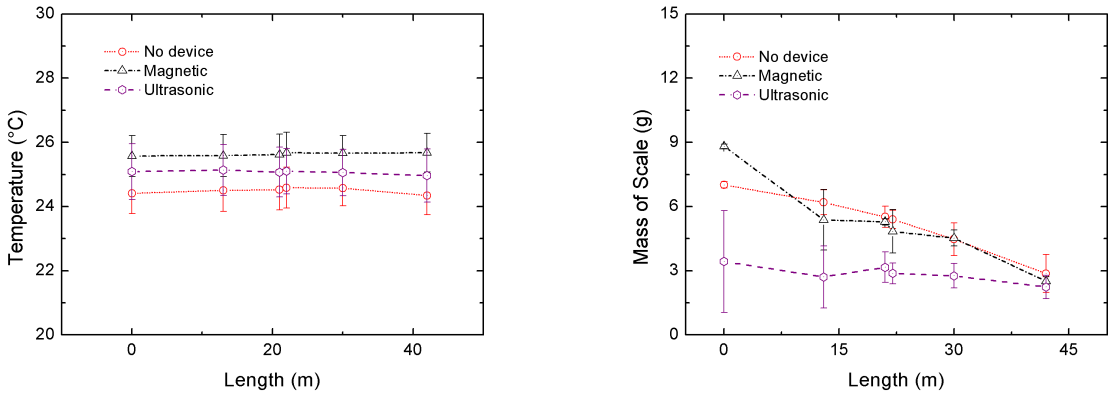
The temperature along the experiments remained between $24.0 - 26.0°\mathrm{C}$. Temperature control benefits from the fact that plexiglass is an insulating material and the chemical reaction that forms the calcium carbonate does not release or absorb significant heat, so as to influence the experiment. Figure 4a shows the temperature fluctuation along the apparatus length. These results indicate that the temperature fluctuations were of the same order of magnitude, so the solubility and

reaction rate of the species was also very close.



(a) Magnetic Device (b) Ultrasonic Device (c) Ultrasonic Controller

Figure 3: Physical inhibition devices used in this work.



(a) Temperature (b) Scale deposition

Figure 4: Temperature and mass deposition profile across the flow loop.

The deposited mass was analyzed once the experiment has finished and measured by weighting the removable test section after the drying process, i.e. one day to remove the residual humidity. Therefore, it was not possible to monitor the instantaneous deposition rate but only the initial and final variation of deposited mass. Figure 4b shows the scale values for the mass flow along the length of the flow loop.

It was observed that the deposited mass was higher in the upstream part of the circuit, slowing as it reached the downstream section. It can be concluded that in all systems this behavior is driven by the concentration gradient of the reactants along the pipe. The currents of calcium chloride and sodium bicarbonate reach the mixing point at maximum concentration, e.g. higher SI, so that near to this point of the circuit a more intense precipitation occurs.

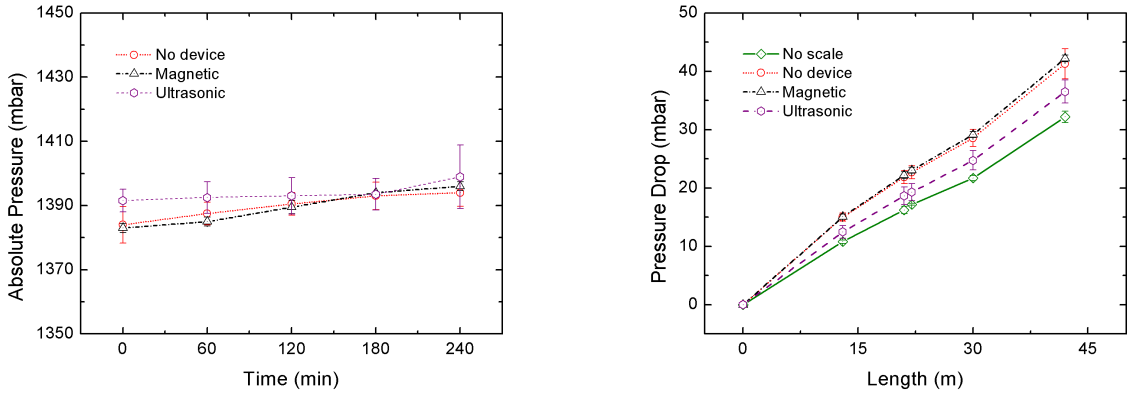
Moreover, as the saline currents mixes along the length of the apparatus, dilution of the species in solution and formation of aggregates occur. These aggregates are entrained by the flow, a fact that results in softer scale deposition on the surface. Regarding the effects of devices, it is clear that the embedded mass was slightly higher during magnetic device test than the condition without the device, but still very close. This shows that the devices do not work in the prevention of deposits, but perhaps in the crystal structure and in its adhesion to the surface.

Otherwise, the ultrasonic device resulted in a lower scale mass along the flow loop, being more effective than the system without device and with magnetic device. It was observed that ultrasonic device may operate not to prevent scale formation, but to accelerate nucleation process bypassing the crystal growth, by this way resulting in a global lower mass of scale deposits.

3.2 Absolute Pressure and Pressure Drop

Absolute pressure is a local measure, therefore, has only variation in time as shown in Figure 5a. The results show that the absolute pressure increased in all tests in a slight way, mostly caused by the scale deposition rate along the experiment time.

The results for the differential pressure measurements were made over space and time, revealing a pressure drop profile quite linear, as can be seen in Figure 5b. This behavior is confident with the results of scale deposits, showing that a more intense precipitation process causes a higher pressure drop.



(a) Absolute Pressure Drop (b) Relative Pressure Drop

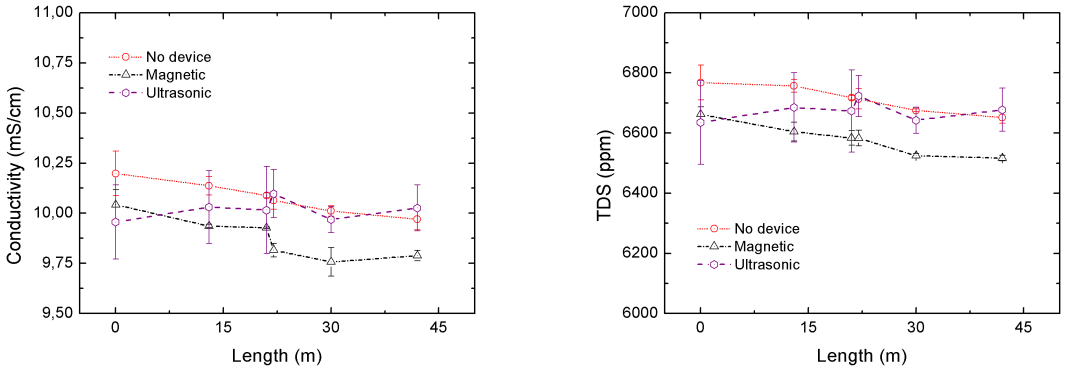
Figure 5: Pressure profile across the flow loop.

The pressure drop is related to two key factors: modified roughness and reduction of the useful diameter. These effects occur simultaneously because the deposition alters the pipe surface, i.e. the roughness, and the continuous deposition process tends to reduce the useful diameter of the pipe. The experiment with no device and magnetic device showed more mass of scale than the ultrasonic device, this way its diameter were more reduced, so pressure drop got higher.

3.3 Conductivity and TDS

The conductivity and TDS showed an almost constant behavior in each of the experiments, although in distinct ranges. An interesting pattern can be observed for the experiment with no device and magnetic device as a decrease in conductivity and TDS along the flow loop, as it shown in Figure 6a. This behavior is mainly caused by the dynamic of particle growth that is characterized by particle aggregation and formation of wider diameter distribution range.

However, results for ultrasonic device showed an increase in both conductivity and TDS, this is due to the nucleation rate boosting promoted by the ultrasonic irradiation. This phenomenon seems to either ceases or bypasses crystal growth, so there's an augmentation in quantity of smaller particles in bulk solution along the flow loop.



(a) Conductivity (b) TDS

Figure 6: Conductivity and TDS profile across the flow loop.

3.4 XRD and MEV

The results of XRD showed that the crystalline structure of the deposited calcium carbonate was slight modified by the exposure to magnetic device, such as occurred in previous experiments. Note that many of XRD results presented a blend of solids structures for all analyzed samples, this is due to the presence of other ions like iron (Fe^{2+}) and magnesium (Mg^{2+}) that can be included in calcium carbonate polymorph structure for its similarity with calcium (Ca^{2+}).

Therefore, the calcite has been the most common form found when analyzing solid samples withdrawn from all experiments, being easily recognized for its cubic structure. However traces of vaterite was found using MEV in most of the samples from experiment using the ultrasonic device, noticed by its needle or spherical wireframe shape. Table 2

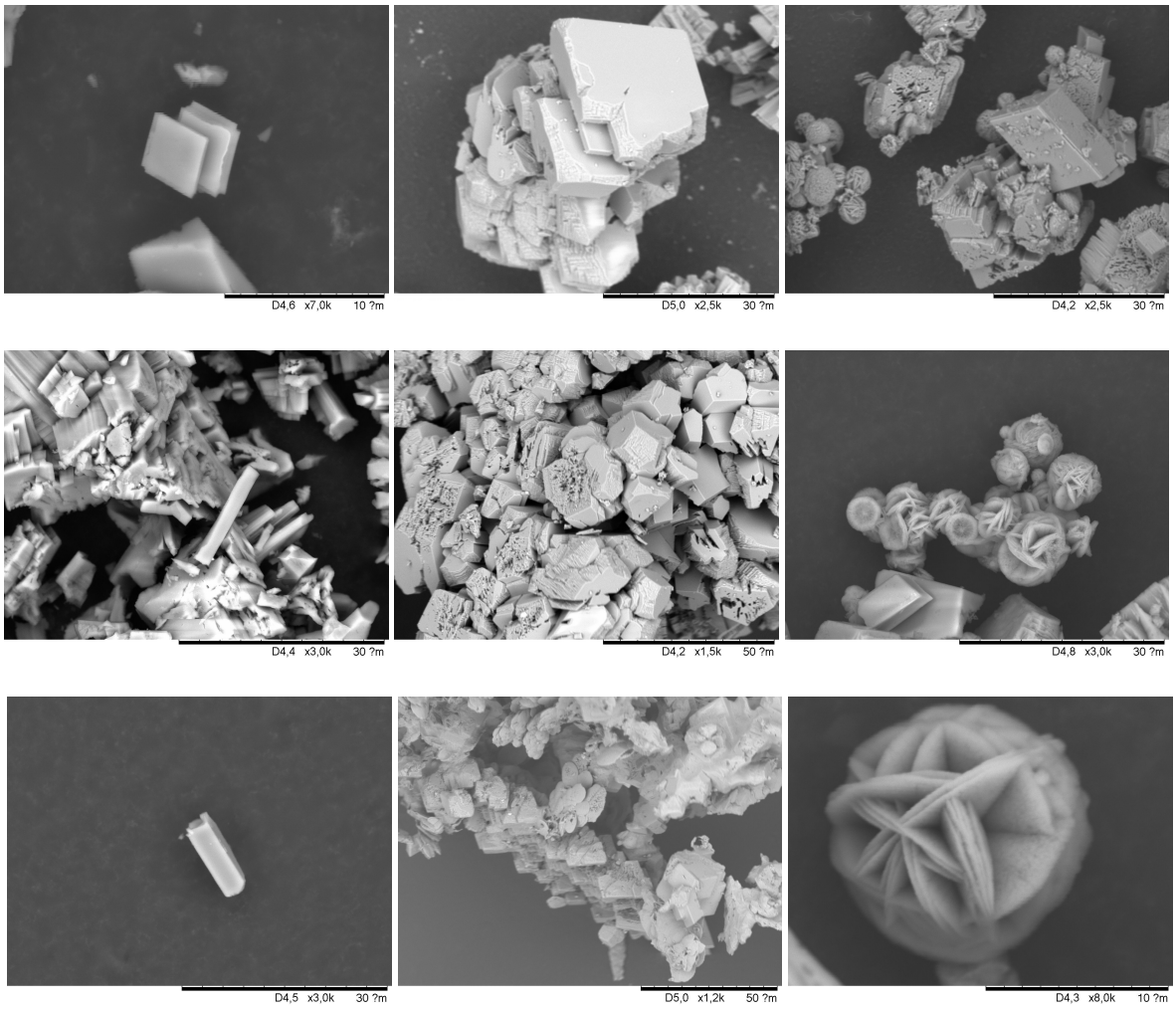
summarizes the results of XRD and MEV.

Table 2: Summary of results from XRD and MEV.

No device						
Test section	1	2	3	4	5	6
XRD	C	C	C	C	C	C
MEV	C	C	C	C	C	C
Magnetic						
Test section	1	2	3	4	5	6
XRD	C	C	C	c/v	c/v	c/v
MEV	C	C	c/v	c/v	c/v	c/v
Ultrasonic						
Test section	1	2	3	4	5	6
XRD	C	C	C	c/v	c/v	c/v
MEV	C	V	V	V	V	V

C – most calcite, V – most vaterite and c/v – calcite with traces of vaterite.

Figures 7 shows the MEV images obtained from the analysis of samples from three different runs: without devices, magnetic device and ultrasonic device.



(a) No device (b) Magnetic (c) Ultrasonic

Figure 7: MEV images of deposited scales.

First, this result was important because it proved that the conversion between calcite and vaterite crystal structures occurs under certain operating conditions, depending on the extent and intensity of the external field applied, respectively,

magnetic induction or ultrasonic irradiation.

Besides, it may be useful to manipulate the crystal structure of the calcium carbonate as a means to assure a lower fouling rate, whether due to a gain of solubility or even forming a layer that is soft and can easily be removed.

At this point, it's not possible to determine which method is ideal for scale prevention, but the results were able to show a positive role of physical inhibition devices and its effects on scale formation.

4. FINAL REMARKS

This work was successful in its objectives, so that the findings support an important study that may ultimately contribute to the flow assurance area and preventing fouling.

The experimental apparatus is successfully constructed in the form of a plexiglass circuit on a pilot scale, in order to ensure a greater likelihood with the industrial flows.

At this stage, it is not possible to assure the effectiveness of prevention devices, but the study provides evidence that rather than inhibit precipitation such devices act by modifying the structure and quantity of deposits, resulting in a scale with less intensity of adhesion and easier removal.

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