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APPLICATION OF MULTIFUNCTIONAL FLUIDS TO IMPROVE HYDROCARBON PRODUCTION

1. INTRODUCTION

A major problem of mature gas wells is liquid accumulation in the well bore. It provides to lower gas production and in some cases even kills the well [6, 7, 8]. Moreover, the presence of water favors the development of corrosion and the formation of emulsions. There are different techniques to solve this problem, i.e. mechanical or chemical methods. Cost effectiveness and ease of application due liquid foamers the simplest way to deliquifying gas wells. Surfactants reduce the effective density and surface tension of the produced brines so that they can be removed from the well with the gas flow. Foaming agents are often injected with corrosion inhibitors and hydrate inhibitors to address another exploitation problems. A single continuous chemical injection line for a mixture of different types of additives can reduce the cost of injection facilities (multiple tanks, multiple injection pumps etc.) [2, 3]. The current global trend is the application of liquid mixtures containing various chemicals allowing to use synergistic effect of additives. Such mixtures are called multifunctional fluids. Commercially available additives, the composition of which is usually a trade secret, require each time before using in the well to check their compatibility with reservoir fluids and other chemicals. Chemical additives have high requirements for thermal and chemical stability and physicochemical properties [2]. The parameters determining the suitability of the component include:

- Flash point min. 45°C,
- Dynamic viscosity at 4°C < 100 Cps,
- Stability at 4°C > 1 month,
- Compatibility with methanol, glycols, brines.

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This study examined the interactions between available on the Polish market corrosion inhibitors, inhibitors for gas hydrate formation and foaming agents. It was observed in formed mixtures both synergistic effect of tested additives as well as antagonistic [4, 5]. Proper selection of the type of additives and their concentrations in the mixture can improve its overall efficiency and reduce demand for chemicals. Multifunctional product injected via gas lift was described by Jackson [3], the application of such mixture quadrupled oil production. Pogessi *et al.* [2] described a methodology for the selection of components and testing their properties with an example of multifunctional fluids used on Girassol and Dalia fields. Statistical approach to compose mixtures and predicting their properties brought Huang *et al* [4]. There is no data in Polish literature regarding a domestic usage of chemical additives and their possible interactions hence this subject of research was undertaken.

2. EXPERIMENTAL AND METHODS

Pre-selection of applicable chemicals

The objective of this paper is to study interactions in multifunctional products that contain additives used in the Polish petroleum company, PGNiG. Antykor PP, CONQOR 303A and Dodigen 5594 were selected as corrosion inhibitors for further study. The simplest method to remove water from well is to drop a soap stick. The only one continuously injected foaming surfactant is Sicol L. Methanol and ethylene glycol are one of the most commonly used winterizing solvents and hydrate inhibitors. Synthetic brine was prepared by dissolving 10% NaCl and 2% $CaCl_2*2H_2O$ by weight in deionized water. The characteristics of the selected chemicals are presented in Table 1.

Table 1

Characteristics of pre-screening chemical additives

Type of chemicals	Trade name	Composition	Producer
Corrosion inhibitor	Antykor PP	mixture of quaternary ammonium salts, phosphate esters and triglyceride of ricinoleic acid	Polski Serwis Płynów Wiertniczych
	Dodigen 5594	quaternary ammonium compounds	Goldschmidt AG.
	CONQOR 303A	morpholine process residue (15–40% wt.) water (40–70% wt.)	M-I SWACO
Foaming agent	Sicol L	mixture of anionic and amphoteric surfactants	
Hydrate inhibitor	Methanol	pure for analysis	POCH S.A.
	Ethylene glycol	pure for analysis	Krakchemia S.A.

Study of mutual compatibility of chemical additives

Because of the completely different chemical composition of the additives, their mutual miscibility have to be tested. For this purpose, the selected corrosion inhibitor was mixed with foaming agent and solvent (volume ratio 1:1:1) and homogeneity of the mixture after shaking was obtained visually. Multifunctional product have to be stable under different storage conditions. Thermal stability of each mixture was investigated in a hot-cool stress cycle. The tested mixture was placed in refrigerator at 4^{o}C for 1 day, and then heated to 40^{o}C for 1 day. The cycle was repeated three times, each time checking visually the homogeneity of the mixture.

Corrosion inhibition measurement

Corrosion inhibition performance of the additives formulations was evaluated using electrochemical methods [1, 9]. In the applied cyclic voltammetry the potential of the working electrode was changed linearly up to a peak value and then returned at the same rate to the initial value. The surface of the platinum electrode is greater than the surface of the working electrode. The current between the working electrode and the platinum counter electrode depends only on the processes occurring at the working electrode. The measurements were carried out using a BAS 100/BW potentiostat. The conventional three electrode system with platinum counter electrode and a silver chloride (3 M NaCl) as reference was used. The working electrode has the form of a disc cut from steel N80 with diameter of 2.0 mm. All tests were performed in argon- deaerated solutions at room temperature. The NaCl and $CaCl_2$ corrosive solution was used as the basic analyte. Before each measurement, the working electrode was pre-treated by grinding with emery paper SiC, then rinsed with Milli-Q water and dried. Electrochemical polarization was started after the working electrode has been immersed in solution.

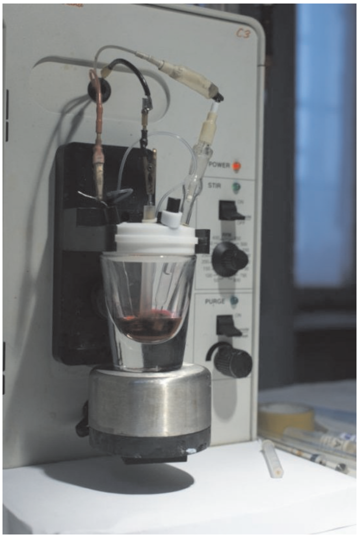

Fig. 1. A conventional three-electrode cell used in electrochemical measurements (fot. author)

Foam measurements

The liquid unloading efficiency of foamer formulations was measured using a dynamic foaming test apparatus (Fig. 2). An essential part of the apparatus is glass tube with an inner diameter of 32 mm and a total length of 1200 mm. Tube is provided with a volumetric scale and a condensing arm leading the foam or liquid from the glass column to a receiving container. Tube is closed with stoppers: upper and lower. The air is sparged through a medium porosity frit (10–20 μm) above the bottom stopper. The system is equipped with a rotameter for 0–100 l/min and is supplied with air from the cylinder through the pressure reducing valve. Set completes beaker of 5 liters for collecting unloaded liquid and a balance. Measurements of foamability consist in passing the air through the sample of the tested fluid and recording the unloaded liquid mass uplifted by gas flow.

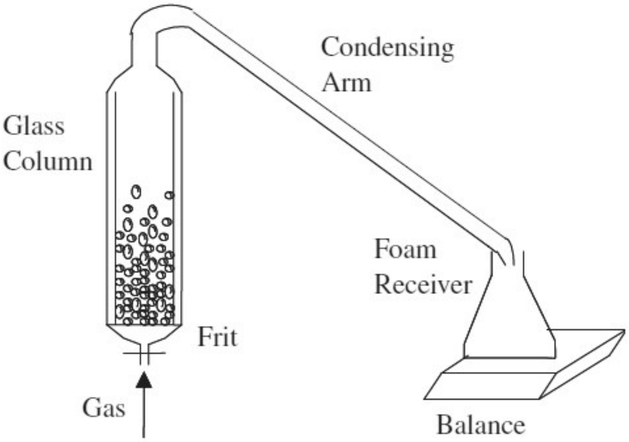

Fig. 2. A dynamic foaming test apparatus [4]

Pour point measurement

Pour point of the various chemical additives and their mixtures were determined on the basis of the literature or by the method according to PN-55/C-04016 standard.

3. RESULTS AND DISCUSSION

Study of mutual compatibility of chemical additives

Evaluation of mutual miscibility and stability of chemical additives in their mixtures was determined visually. All additives or mixtures of them are dissolved in ethylene glycol and brine and form stable formations. Methanol as a solvent is not useful because of the emulsion formation. For this reason methanol is not considered in further research as a component of multifunctional mixture.

Table 2

Compatibility tests of chemical additives

	Antykor PP	Dodigen 5594	CONQOR 303A
Sicol L	+	++	+
Metanol	-	+	-
Glikol etylenowy	+	+	+
Sicol L + Metanol	-	+	-
Sicol L + Glikol etylenowy	+	++	+

Compatibility:

++ very good, the mixture does not separate even when heating and cooling,
\+ good, light cloudiness observed without dissection,
– insufficient, the mixture separates under the influence of temperature.

Corrosion inhibition measurement

Corrosion of N80 steel occurs in brine relatively easily at the potential of about –0.51 V. The corrosion potential of the electrode shifts to more positive values and the anodic and cathodic Tafel slopes alter unremarkably as the concentration of Dodigen 559 increases. Dodigen 5594 is both an anodic and cathodic corrosion inhibitor. The greater coverage of the electrode surface provides to better corrosion protection. Concentration of approximately 1000 ppm of additive should be considered as the optimum value above that the corrosion rate is reduced only slightly. As shown in Figure 3a foaming agent Sicol L also has anticorrosion properties. Its effectiveness, however, is small, the desorption process occurs very easily, even spontaneously, during subsequent measurements.

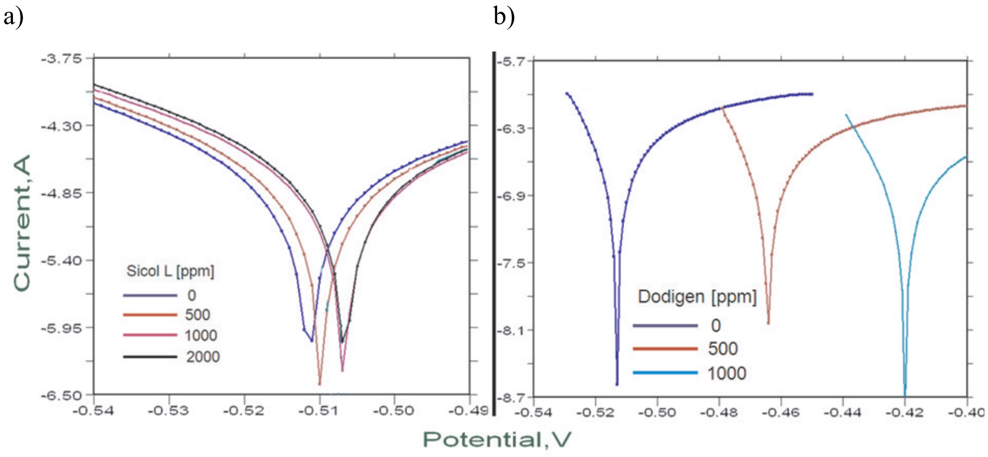

Fig. 3. Polarization curves for N80 steel in brine containing various concentrations of: a) foaming agent; b) corrosion inhibitor

The extrapolation of the Tafel regions of the cathodic and anodic polarization curves allows the calculation of the corrosion current density (i_{corr}) [9]. The corrosion mass rate is calculated employing the formula:

$$\Delta m = \frac{M}{zF} \cdot j_{corr} \tag{1}$$

where:

M – molar mass of metal (M_{Fe} = 55.85 [g/mol]),
F – Faraday's constant, F = 96 485 [C/mol],
z – number of electron moles transferred in the balanced equation, z = 2,
j_{corr} – corrosion current density in the absence and in the presence of the inhibitor [A·cm^{-2}].

Corrosion mass rate for selected additives and mixtures are summarized in Table 3.

Table 3

Corrosion mass rate of N80 steel in brine without and with corrosion inhibitors

Additive	**Concentration of additive in brine [ppm]**	**Corrosion current density [A/cm^2]10^{-6}**	**Corrosion mass rate $\left[\frac{g}{m^2 \cdot day}\right] 10^{-7}$**
Brine 10% wt. NaCl, 2% wt. $CaCl_2$	–	202.39	50.61
Sicol L	5000	191.19	47.81
Sicol L	10000	187.75	46.95
Sicol L	20000	184.47	46.13
Dodigen 5594	500	21.84	5.46
Dodigen 5594	1000	4.96	1.24
Antykor PP	1000	35.55	8.89
CONQOR 303A	1000	19.12	4.78
Ethylene glycol	1000	116.45	29.12
Sicol L + Dodigen 5594	10000+1000	3.64	0.91
Sicol L + Dodigen 5594	10000+500	4.56	1.14
Sicol L + Dodigen 5594 + Ethylene glycol	10000+500+500	4.16	1.04

Table 3 shows that the most effective corrosion inhibitor is Dodigen 5594. It reduces a value of corrosion mass rate almost 50 – fold compared to the uninhibited brine. Ethylene glycol reduces the corrosion rate about 40%, and Sicol L up to 10%. The mixtures of additives have slightly better performance than single corrosion inhibitor which shows the synergistic interaction of components in the mixture. The use of mixtures of additives Sicol L +Dodigen 5594 + ethylene glycol (10 000 + 500 + 500 ppm) can reduce the demand for inhibitor by half (1000 ppm for a single inhibitor and 500 ppm of additive in the mixture) maintaining the same level of corrosion protection.

Pour point measurement

The pour point of the individual additives and mixtures thereof are presented in Figure 4. Ethylene glycol has the lowest freezing point. Sicol L can not be used in cool conditions. Corrosion inhibitors include in their composition typical winterizing solvents (glycol, methanol) so that the pour temperature is in the range from –4 to –6°C. Ternary mixture has good low temperature properties, and there is no risk of freezing in the surface facilities of the injection system. The combination of the Sicol L and low freezing components allows to it year-round use without having to need to use another foaming agent suitable for winter conditions.

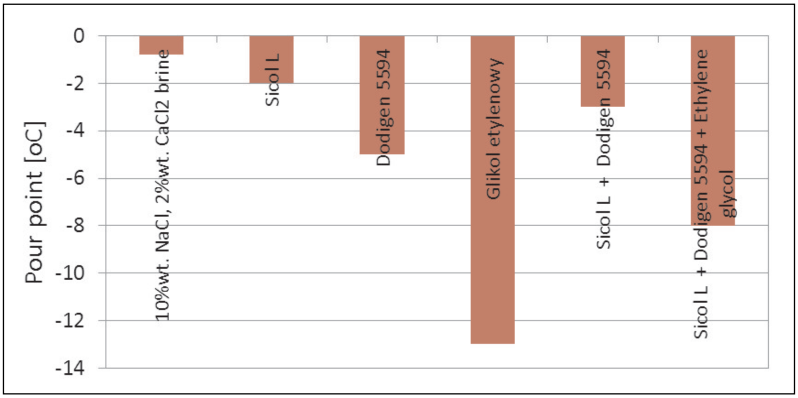

Fig. 4. The pour point of the individual additives and mixtures thereof (the volume ratio of individual components in a mixture is 1:1:1)

Foam measurements

Foaming agent is considered as effective if in a short time is able to reach 70 g of liquid inflow into the beaker [10]. The more convenient it is, the faster rupturing of foam films occurs. Equation (2) was used to calculate liquid unloading efficiency of the foamers:

$$S = \left(\frac{m_{ww}}{m_p} \cdot 100 \right) \% \tag{2}$$

where:

m_{ww} – the weight of the fluid collected in the foam receiver,
m_p – the initial fluid weight into the test column.

All measurements were done at temperature room with a linear air flow of 0.5 m/s. The higher the concentration of the surfactant, the better liquid unloading, for example: Sicol L at a concentration of 5000 ppm generates 65 g of a liquid, and at a concentration of 20 000 ppm to 75 g of liquid. Ethylene glycol does not exhibit foaming. The effectiveness of the water unloading by corrosion inhibitors is satisfactory, about 50% for higher concentrations. Ternary mixture (Sicol L + Dodigen 5594 + ethylene glycol) produces about 75 g of a liquid, which is slightly better than for Sicol L at a concentration of 10 000 ppm in the brine. The presence of corrosion inhibitor and glycol makes a foam heavier and easier to collapse, which is important for the separation process.

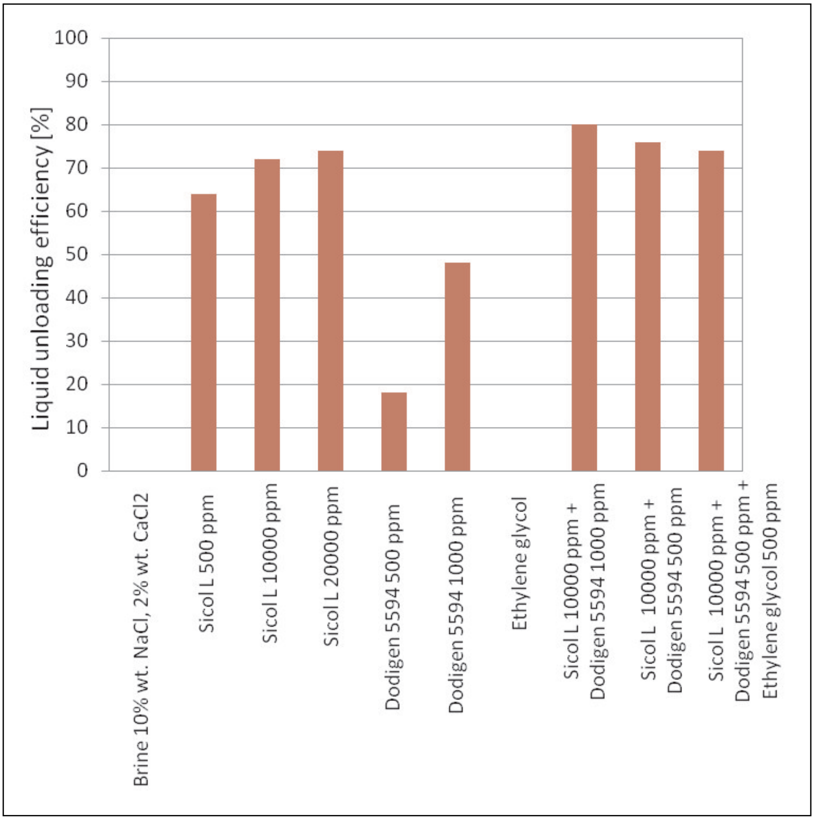

Fig. 5. Comparison of the effectiveness of selected additives and mixtures thereof

4. CONCLUSIONS

Chemical additives used to solve a variety of operational problems (corrosion, hydrate formation, water supply) can be injected into wells in a single multi-purpose mixture, which reduces the cost of the injection installation. A mixture of various additives requires testing its thermal and chemical stability and mutual compatibility of additives. Chemicals may exhibit both a synergistic effect and antagonist. Usage of multifunctional mixtures can reduce the consumption of individual components. Tests have shown that the combination of Sicol L, Dodigen 5594 and ethylene glycol has similar or better performance in fluid unloading and corrosion protection than a single additives dosed at optimal concentrations specified by the manufacturer.

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