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Integrated Methodology for Mineral Scale Inhibitor Squeeze Treatments

B. Bazin, N. Kohler and A. Zaitoun[*]

طريقة متكاملة لمعالجة تكوّن قشور معدنية بضخ مواد كيميائية

ب. بازين ون. كوهلر وأ. زيتون

إن ترسب القشور المعدنية لا يقتصر في العادة على المعدات السطحية وأنابيب البئر، ولكنه يتعداها ليشمل المنطقة القريبة من المكمن، ويأتي تكوّن قشور من الكبريتات نتيجة عدم توافق بين مياه الحقن البحرية وبين الماء المصاحب للتكوين الصخري، وتحدث الرواسب القشرية من الكربونات نتيجة لتعرض السوائل المنتجة لاختلافات مفاجئة في الضغط ودرجة الحرارة بين المكمن وعند السطح وما يصاحب ذلك من هروب مفاجئ لغاز ثاني أكسيد الكربون. وقد يخلق ترسب هذه المعادن نقصا في النفاذية نتيجة لانسداد الفتحات وهو ما يسبب تبعا لذلك نقصا كبيرا في إنتاجية البئر. وفي أغلب الأحيان لا يمكن تفادي تكوّن الرواسب القشرية، ولكنه دائما ما ينصح بالمعالجات الوقائية. ومن أهم التقنيات الفعالة التي تمنع ترسب قشور المعدن هو ضخ التكوين بنوع معين من مانع التآكل الكيميائي.

تقدم هذه الورقة طريقة متكاملة يتم استخدامها من قبل المعهد الفرنسي للبترول من أجل تعريف أفضل صياغة لمانع التآكل الكيميائي لنوع معين من العلاج بالضخ ولزيادة قدرة أدائها في المكمن الموازي. وتستعمل كل من الطريقة المعملية والعددية لاختيار موانع التآكل ولتقييم أدائها بمقادير سائبة تحت ظروف لب البئر والتعرف على أفضل استراتيجية لطريقة الضخ. وتحوي الاختبارات الكيميائية طرق الاختيار التقليدية التي تعتمد اختبارات ساكنة ومتحركة مختلفة بهدف تحديد أقل تركيز من مانع التآكل الكيميائي الذي يمكن بواسطته كبح تكون الرواسب القشرية، ويتم اضافة إلى مقارنة خواص موانع التآكل المستخدمة حاليا كالفوسفونات والمنتجات الجديدة صديقة البيئة على سبيل المثال، إجراء تجارب غمر البئر لتقييم خواص امتزاز ومجّ مانع التآكل تحت ظروف المكمن ومخاطر ضعف الإنتاج، وتمت عن النهاية المحاكاة العددية للعلاج باستعمال محاكاة مكمن محدد بهدف زيادة عمر المعالجة الكيميائية من مستوى المعمل إلى منزلة المكمن.

Abstract: *Mineral scale deposition often occurs not only in surface facilities and well tubing but also in the near well bore reservoir area. Sulphate scale formation is usually the result of poor compatibility between injected seawater and formation brine. Carbonate scales are mainly generated by abrupt pressure and temperature variations to which production fluids are submitted between reservoir and surface and the simultaneous loss of CO_2. The precipitation of both mineral deposits may create significant permeability impairments due to plugging of pore throats and consequently induce large well productivity loss. In most cases, scale formation cannot be avoided and preventive treatments are recommended. One of the most efficient techniques to prevent mineral scale deposition is the squeeze into the formation of a specific scale inhibitor.*

This paper presents an integrated methodology applied by IFP in order to define the best chemical inhibitor formulation for a specific squeeze treatment and to optimize its implementation into the corresponding reservoir. Both experimental

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[*] Petroleum Research Centre, P.O. Box 6431, Tripoli, Libya.

and numerical approaches are used to select the inhibitors, to evaluate their performance in bulk and in core conditions, and to define the best strategy for the squeeze process. Laboratory tests include classical inhibitor selection methods based on static Jar Tests and dynamic Tube Blocking Tests in order to determine the Minimum Inhibitor Concentration (MIC) to prevent scale formation. The properties of current scale inhibitors, i.e. phosphonates, as well as those of new environmentally friendly products are compared. Core flooding experiments are performed to evaluate inhibitor adsorption / desorption properties at reservoir conditions and the risks of production impairments. Numerical simulations of the treatment are finally performed using a specific reservoir simulator to upscale the squeeze life time of the treatment from the laboratory to the reservoir level.

INTRODUCTION

Scale inhibitor squeeze treatments provide one of the most common and efficient methods to prevent the formation of mineral scales in producing wells. Scaling is an undesirable precipitation caused by either mixing of incompatible waters or rapid changes of the thermodynamic conditions during fluid production. The nucleation and growth of salt crystals can occur both in the production system or in the near wellbore formation. One of the most valuable techniques to prevent or to fight the scale formation is to inject, *i.e.* squeeze, a scale inhibitor directly into the formation.

A typical squeeze treatment consists of injecting a slug of the chemical formulation into the reservoir followed by the shut-in of the well. During the shut-in period, the inhibitor is retained into the formation. When production is resumed, the inhibitor is released back into the produced water and prevents scale formation. The success of the treatment depends on how long the inhibitor concentration in the flowing water is efficient to prevent scale precipitation. This concentration has, in fact, to exceed the Minimum Inhibitor Concentration (MIC).

The focus of this paper is to review the methodology which contributes to a successful squeeze treatment, starting with the scale identification, followed by a laboratory study in reservoir conditions for the selection of the best inhibitor to prevent scale formation and ending with the design of the well treatment. Laboratory tests include the classical inhibitor selection methods based on Jar Tests and Tube Blocking tests. The purpose of these tests is to select the inhibitor on the basis of its MIC in the critical formation water/injection water mixture. Core floods are then carried out in order to obtain the inhibitor dynamic adsorption isotherms. Numerical simulations of the treatment are performed using a specific reservoir simulator to design the squeeze life time of the treatment, based on laboratory determinations of the inhibitor MIC and adsorption values. This integrated methodology extending from the laboratory testing to the treatment design is illustrated on a case study where the scale consists essentially of calcium carbonate deposition at the producing well.

The paper is organized as follows. The first section is a presentation of the scaling problem. The second part describes the different experimental methods used for the MIC determination and the core flood tests. In the third section, we focus on the numerical simulations for the design of the treatment.

PRESENTATION OF THE SCALING PROBLEM

In the case study presented here, scaling is due to the change in the thermodynamic conditions when well fluids are produced, the actual formation water being unstable in surface conditions. A particular procedure must then be applied to prepare the critical formation water/injection water mixture. We reconstruct this water by mixing two simplified waters containing respectively twice the precipitating cation concentration or the precipitating anion concentration. The 50/50 mixture of both cation-rich and anion-rich waters will then have the same composition as the produced water (Tables 1 and 2).

The identification of the precipitating salts is performed with the PHREEQ[1] software. Two types of calculations are performed:

Table 1. Reconstruction of both cation-rich and anion-rich waters.

Salt	Cation-rich Water (ppm)	Anion-rich water (ppm)
$CaCl_2.2\,H_2O$	59 134	0
$MgCl_2.6H_2O$	17 131	0
KCl	1 484	1 484
NaCl	70 000	70 000
$NaHCO_3$	0	3 162
Final pH (25°C)	6.83	8.6

Table 2. Ionic compositions of the different waters (ppm).

Salt	Cation-rich water (ppm)	Anion-rich water (ppm)	50/50 mixture
Na^+	27251	28387	27954
K^+	777	777	777
Mg^{2+}	2048	0	1024
Ca^{2+}	16090	0	8045
Cl^-	77037	42620	59828
HCO_3^-	0	2296	1148
TDS	123473	74080	98776

- Evaluation of the risk of precipitation for the 50/50 mixture of cation-rich/anion-rich waters at the reservoir temperature and saturated with CO_2;
- Evaluation of the risk of precipitation for the same 50/50 water mixture but at the atmospheric CO_2.

The saturation index is defined as:

$$SI = \log IP/SP$$

where, IP is the ionic product, *i.e.* the product of the anion and cation concentrations, and SP is the thermodynamic solubility product at the desired temperature. If SI is positive the salt is likely to precipitate, if SI is negative or nil, the mineral is soluble and the solution is expected to be stable.

The results of the computer calculations are given in Table 3. Carbonate salts (aragonite, calcite and dolomite) are likely to form during formation water degassing in the well.

Table 3. Calculated saturation indexes at 65°C.

Salt	Cation-rich water (ppm)	Anion-rich water (ppm)	50/50 mixture
Na^+	27251	28387	27954
K^+	777	777	777
Mg^{2+}	2048	0	1024
Ca^{2+}	16090	0	8045
Cl^-	77037	42620	59828
HCO_3^-	0	2296	1148
TDS	123473	74080	98776

EXPERIMENTAL STUDIES

Laboratory work consists mainly of the determination of MIC by both Jar Tests and dynamic Tube-Blocking Tests (TBT) and of the adsorption/desorption of the tested inhibitor during core flood experiments. Several products are usually comparatively evaluated. Results presented below in some detail will concern principally a commercial organo-phosphonate, but data obtained with other potential inhibitors such as another phosphonate, a polyacrylate and representatives of two families of new inhibitors[2] claimed as being environmentally friendly, are also given for comparison purposes (Table 4).

Determination of the MIC

The Minimum Inhibitor Concentration (MIC) is determined by two different methods: the static Jar Test or Becher Tests and the dynamic Tube Blocking Test (TBT).

The Jar Tests are conducted following the NACE[3] Standard Test Method 0374-20013. According to this Test Method cation-rich and anion-rich waters are prepared with the inhibitor incorporated in the anion-rich water at twice its testing concentration. Final 50/50 water mixtures are stored in an oven at reservoir temperature and saturated with CO_2. They contain 0, 5, 10 and 15 ppm active matter of the inhibitor. For the commercial organic phosphonate no precipitation is observed for the 3 inhibitor concentrations, meaning that even a 5 ppm concentration of this inhibitor is sufficient for preventing the scale formation. Thus MIC for this inhibitor is less than 5 ppm in the 50/50 water mixture at reservoir temperature.

For the TBT measurements, the 50/50 water mixture is injected at constant flow rate (3 ml/min) by using two pumps, (one for the anion-rich water, the other one for the cation-rich brine) into an 8 meter long stainless steel capillary tube (internal diameter 0.5 mm) (Fig. 1). The pressure drop across the capillary is continuously measured as a function of time since the start of injection. A blank test is first run with the 50/50 water mixture. Then, the inhibitor is dissolved in the anion-rich brine at twice the desired testing concentration. The results show that for the blank test, the capillary is blocked in ~ 25 minutes. In presence of the commercial organo-phosphonate, the blocking time increases above the blank time with increasing inhibitor concentration (Fig. 2). A long term inhibition in tube blocking is observed for less than 5 ppm of this inhibitor. A concentration of about 2.5 ppm (active matter) is taken as the MIC for the inhibitor in these testing conditions (about 5 times the blank time is reached before blocking). It is concluded that a very good agreement exists in the determination of the MIC value by either the Jar Test or the Tube Blocking Test.

The inhibitors of Table 4 were comparatively tested in the same experimental conditions. Figure 3

Table 4. Experimentally tested inhibitors.

Commercial name	Chemical formula	Tested formulation		Characteristics		
		L, S	AM %	M_n	M_w	IP
Phosphonate (HEDP) Dequest 2010	1-Hydroxyethylidene (1-1 diphosphonic acid): HEDP	L	60		206	
Polyacrylate (PAA) Romax 7200	Carboxylate copolymer	L	53	2000	3000	1.5
Green Products Baypure DS 100 (PASP)	Polyaspartate	L/S	40/90	1740	4810	2.8
MS 10 ter (lab IFP)	Polyaspartate	S	90	3200	7400	2.3
Dequest PB (CMPS)	Carboxymethylated Polysaccharides CMPS 14625 SD : 2.5 PD: 10	L/S	20/90	1730	5300	3
	SD : 2.5 PD : 24	S	90	4900	7300	1.5
	CMPS 14620 SD : 2.0 PD : 10	L/S	20/90	2160	6130	2.8
	SD : 2.0 PD : 24	S	90	3400	6000	1.8
	CMPS 14615 SD : 1.5 PD : 10	L/S	20/90	1760	4810	2.7

L = Liquid; S = Solid; AM = Active matter (weight %); SD= Substitution degree; PD = Polymerization degree; M_n = Average molecular weight (Size exclusion chromatography); M_w = Average molecular weight (Light scattering).

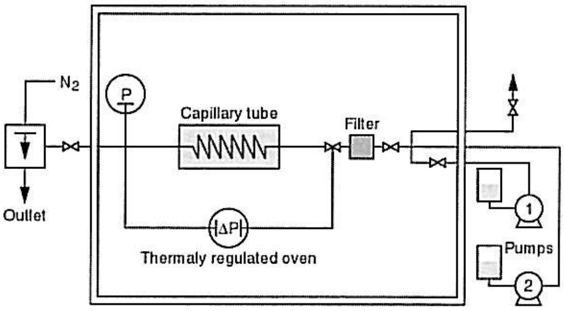

Fig. 1. Experimental device for the tube blocking test (TBT).

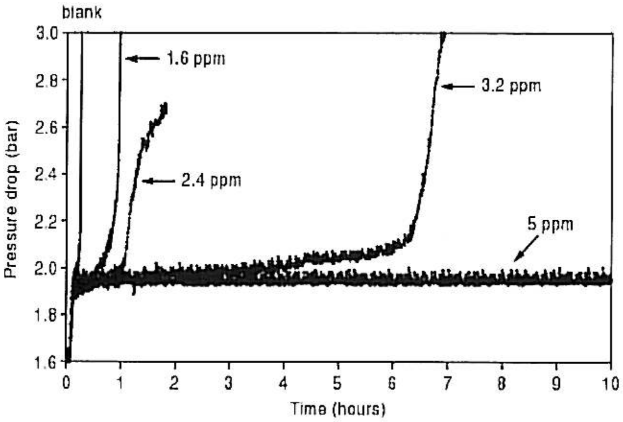

Fig. 2. MIC determination by the TBT method.

and Table 5 show the results obtained with these inhibitors. It can be seen that based on TBT results the inhibiting efficiency of green inhibitors is usually lower than that of phosphonates or polyacrylates.

Determination of Squeeze Lifetimes

Core flood experiments aim at defining the retention of the inhibitor during the injection of the inhibitor slug

Table 5. Comparative MIC of tested inhibitors.

Inhibitors	MIC $CaCO_3$ (ppm)
Phosphonate Dequest 2010 (HEDP)	< 4
Polyacrylate Romax 7200	2 < MIC < 5
Polyaspartates Baypure DS 100 MS 10 ter (lab IFP)	 5 2,5
Polysaccharides Dequest PB CMPS 2.5 DP 10 " DP 24 CMPS 2.0 DP 10 DP 24 CMPS 1.5 DP 10	5 < MIC < 10 7.5 < MIC < 10 < 10 7.5 10

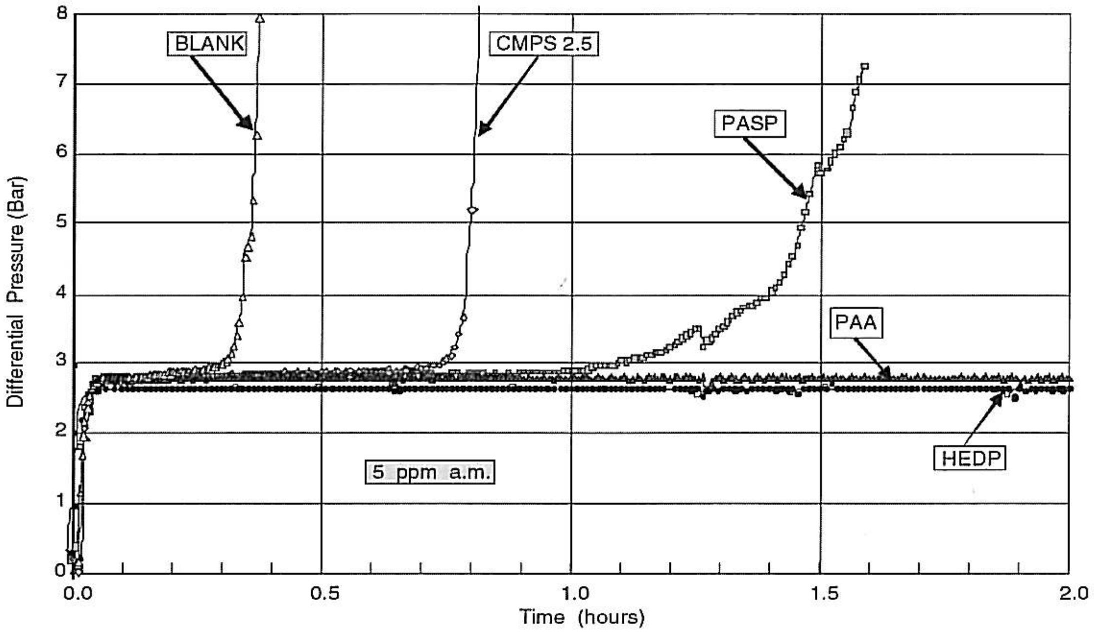

Fig. 3. Comparison of inhibitors by TBT, (C_{inh} = 5 ppm, 50/50 water mixture, 60° C).

and then the release of the product when the produced water is flushed into the core. The squeeze lifetime is determined from the released concentration and is defined as the number of pore volumes (PV) of water that can be flooded while keeping the inhibitor concentration higher than the MIC.

The squeeze lifetime measured in the experiment will be scaled to the well situation by numerical simulation (see below). To run the near wellbore simulations the inhibitor adsorption isotherm is required. The adsorption isotherm is calculated from the results of the core flood experiment performed at 100% water saturation.

The core flood involves mounting a reservoir core in a Hassler type flow cell placed in an oven at reservoir temperature (Fig. 4). The core is saturated with synthetic brine whose composition is representative of the produced brine. However, to avoid the precipitation of calcium carbonate and possible sulphates in the core, bicarbonate and sulphate ions are replaced by chloride ions. The sequence of injection involves the following steps: (1) injection of several pore volumes of the produced water for core conditioning and permeability measurement; (2) injection of three pore volumes of the inhibitor solution, at 10 g/l (active matter) dissolved in the injection water followed by overnight shut–in for inhibitor adsorption; (3) formation water back-production until the inhibitor concentration drops below the MIC (2.5 ppm active content). During the flood the differential pressure across the core and the pH are continuously recorded. The inhibitor concentration in the effluents is measured with the Hach method for the organo-phosphonate and the ferrocyanide method for the polyacrylate[4].

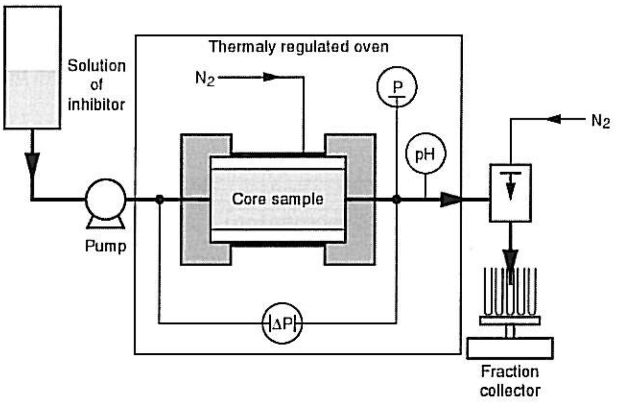

Fig. 4. Experimental device for core flood tests.

Figures 5 and 6 show the inhibitor return with the produced water for the organo-phosphonate and the polyacrylate respectively. For the organo-phosphonate, the concentration in the effluents rapidly declines to 10 ppm active after ~ 80 pore volumes of brine injected, followed by a long tail region. The concentration drops to the MIC after ~ 300 PVs are injected but remains higher than 1 ppm active after 800 PVs of production. For the polyacrylate, the laboratory squeeze life time is much shorter than for the organo-phosphonate. The MIC is reached after the injection of only 40-110 PV of produced water.

Evaluation of Formation Damage

The formation damage is evaluated from the pressure difference across the core. Strong formation

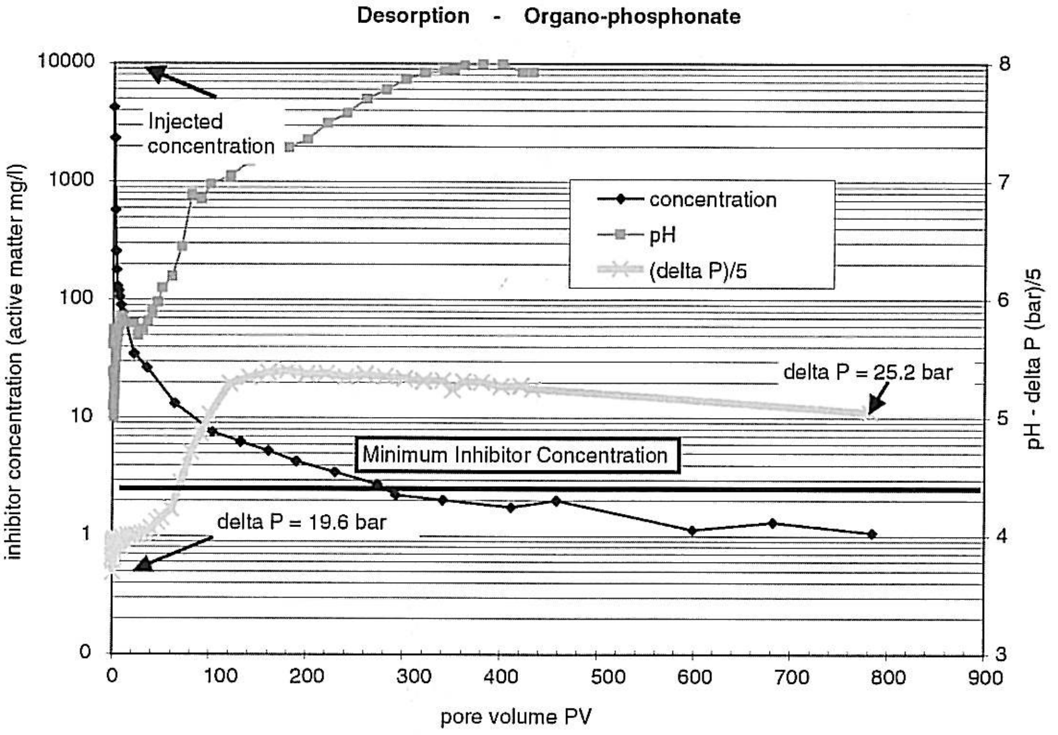

Fig. 5. Results of the core flood experiment: Inhibitor concentration in the effluent during water back-production, pH and ΔP as function of PVs injected. The inhibitor is an organo-phosphonate.

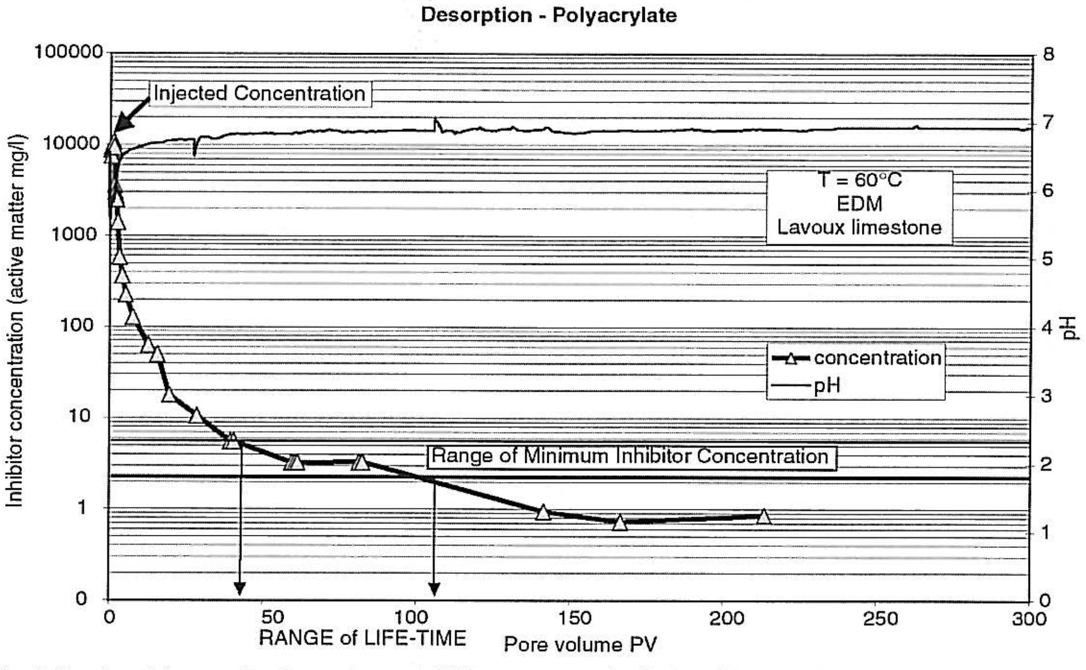

Fig. 6. Results of the core flood experiment: Inhibitor concentration in the effluent during water back-production, pH and ΔP as function of PVs injected. The inhibitor is a polyacrylate.

damage is observed with the organo-phosphonate whereas no damage at all occurs with the polyacrylate inhibitor. These differences are supposed to be due to the precipitation of the organo-phosphonate as explained below[5-7]. During the desorption stage of the organo-phosphonate (Fig. 5), the differential pressure rises significantly after 100 PV and then slowly declines. The increase of the differential pressure corresponds to the increase of the pH at values higher than neutrality. This feature is probably due to an unexpected precipitation of the phosphonate inhibitor during the early stage of back production. The precipitation behaviour is suspected to be due to the low solubility of the organo-phosphonate at neutral pH and/or to the formation of an inhibitor/calcium complex with calcium cations released by carbonate dissolution. Note that this precipitation behaviour occurs at low inhibitor concentrations, which is consistent with the limited solubility of this type of product in the low concentration range. The precipitate partly re-dissolves during the flood, and the permeability after ~ 800 PV of back production is two thirds of the permeability at the end of the inhibitor injection stage.

Summary of Laboratory Tests and Choice of the Best Inhibitor Product

At this stage, the laboratory tests show that the organo-phosphonate is the best inhibitor in terms of squeeze lifetime: the low MIC and the high retention capacity of the core makes the desorption profile favourable with a slow release of the inhibitor concentration. On the other hand, the polyacrylate has a low retention capacity, although its MIC is of the same order of magnitude. The only drawback for the organo-phosphonate is the precipitation behaviour which causes permeability reduction and formation damage. Remedial treatment against formation damage is absolutely necessary before re-squeeze of this product.

MODELLING OF THE TREATMENT

The organo-phosphonate is the inhibitor selected from the laboratory tests. The procedure used for the calculation of squeeze life time in the well is based on core flood experiments. The current procedure consists of the calculation of a dynamic adsorption isotherm[8]. Even if precipitation is observed, it is supposed that the process almost certainly goes through an adsorption stage. The level of inhibitor in the return curve is then thought to be due to the desorption either by a chemical or a physical mechanism.

The adsorption isotherm, $\Gamma(C)$, is calculated from the propagation velocity V_C at a given concentration:

$$V_c = V_{fluide}/(1 + (\rho/\phi)(\partial\Gamma/\partial c)_c))$$

The adsorption isotherm follows the Langmuir form:

$$\Gamma = \Gamma_{max}\, bc/(1 + bc)$$

The calculated isotherm shows the classical low concentration steeply-rising curve (Fig. 7). Once the isotherm has been derived, it can be validated by modelling the core flood (Fig. 8). The reasonable agreement between the calculated and the experimental results shows the validity of the modelling. The interpretation of the results shows that in the threshold concentration region corresponding to the MIC (2.5 ppm active content), the amount adsorbed represents only 62 % of the inhibitor quantity retained in the porous medium. This means that 38% of the product remains available for a subsequent treatment when the MIC is reached.

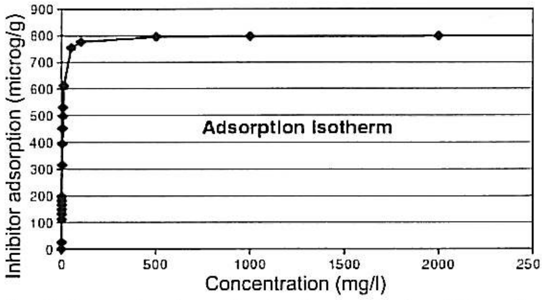

Fig. 7. Dynamic adsorption isotherm calculated from the results of the core flood experiment.

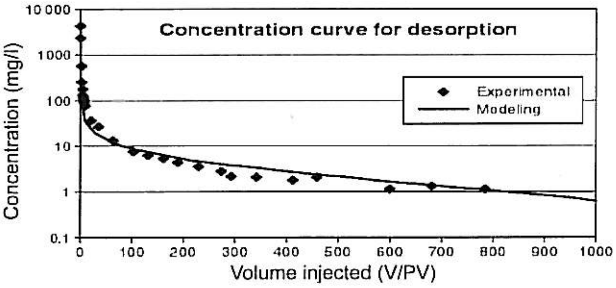

Fig. 8. Validation of the adsorption isotherm.

The wellbore scale modelling is done with an in-house reservoir simulator SARIP^{CH} [9]. The treatment consists in the injection of the following sequences: (1) a pre flush to condition the near wellbore with the make-up brine for the inhibitor solution; (2) the inhibitor slug; (3) a post flush to allow a deeper penetration of the chemical into the formation; (4) a shut-in period for inhibitor adsorption[10]. The simulator does not calculate stage (4) since adsorption is modelled as an equilibrium, i.e. instantaneous, process.

A homogeneous radial 3-D model is used to simulate fluid behaviour around the wellbore. Inputs of the simulation are: (1) well geometry and petrophysics data, (2) water and oil properties, (3) inhibitor properties, i.e. MIC and adsorption isotherm, (4) rock type and permeability data, (5) conditions at the beginning of the treatment. During the well treatment, the fluid properties are assumed to be constant. The treatment design is optimised to reach a one-year lifetime given the MIC of 2.5 ppm active content. The duration of each of the treatment sequence (pre-flush, slug, and post-flush) is optimized given injection constraints.

The injection of 1000 bbl of inhibitor at 4000 ppm active matter fulfils the MIC requirement (Fig. 9). The inhibitor concentration in the well effluents stays above the MIC limit. The concentration profiles (Fig. 10) are computed during the well production period. After a sharp drop in inhibitor concentration right at the start of the production (between 0.2 and 0.5 days), the concentration profiles are stabilised and smoothly decrease with time. The concentration profiles in the reservoir around the wellbore show that the treatment protects about 1.5 m around the well over the required one-year period.

In this paper, the simulation results presented are based upon homogenous reservoir properties. However, we recognise, in a complementary study, the influence of permeability heterogenities on squeeze inhibitor treatment.

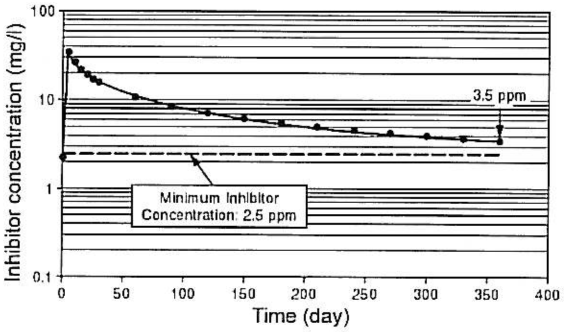

Fig. 9. Returned inhibitor concentration calculated at the producing well.

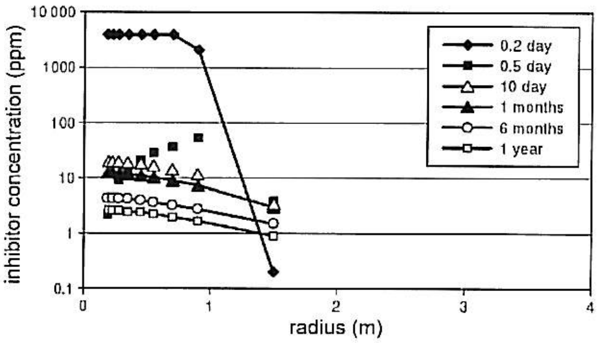

Fig. 10. Inhibitor concentration calculated by SARIP^{CH} in the near well-bore region.

CONCLUSIONS

An integrated methodology including laboratory experiments and numerical simulations is presented for the design of an inhibitor squeeze treatment. The inhibitor efficiency is evaluated by Jar Tests and Tube-Blocking Tests. The two methods give a good agreement for the value of the MIC. The core flood test shows that the inhibitor is retained by an adsorption/precipitation mechanism for the organo-phosphonate. Transient formation damage is observed during the water back-production. Formation damage is not observed with the polyacrylate. However, the squeeze lifetime is very short. The laboratory data are integrated in a reservoir simulator for the modelling of the squeeze treatment on the well. A one-year lifetime treatment is obtained by the injection of a reasonable quantity of inhibitor.

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