Treatment of Barium Sulphate Deposits

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Key-Words— water; reservoir; injection; barium sulfate; deposits; damage

I. INTRODUCTION

The natural exploitation of oil deposits, called natural spontaneous recovery (primary) mainly due to the initial pressure of the deposit, with the lowering of the pressure of the deposit during production, comes the intervention of producers to assist the recovery of hydrocarbons, with the use of several methods to follow, the injection of water, gas lift......

Even with recovery assistance but it is still mediocre, and the life of a deposit is poor over time, this time depends on recovery rate.

The aim of this paper is to study the method of recovery by water injection in the hydrocarbon fields of the Algerian Sahara, and the undesirable effects of this method, especially the barium sulphate deposits that they are created by the incompatibility between the reservoir water and the injection water.

Deposits formed during production and shipping represent a real calamity against which oil producers have been struggling for several decades, causing irreversible damage that is particularly dangerous for bottom production facilities such as surface and sometimes for the rock itself.

II. WATER IN OIL FIELDS

A. Injection water

Injection water used in secondary oil recovery, the injection of water is one of the means of maintaining the tank pressure as well as for the washing of salt wells.

The injection may be either of the type distributed in the oil zone or of the peripheral type in an existing aquifer

- *Washing salted wells*

Some formation waters may contain 350 g / l of sodium chloride and thus be so close to supersaturation that a very small temperature variation or a low water evaporation due to the fall causing a significant precipitation of NaCl on the walls of the tubing until capping and reduction of the section of the tubing which leads to the fall of production.

In order to put the wells back into production, we intervene on NaC1 by simply sending a quantity of fresh water. Irrespective of its use, water injection poses serious problems of incompatibility with reservoir water. In fact, the reservoir waters may contain ions of barium, calcium, and strontium, and be brought into contact with the washing water which contains sulphate ions. This results in the formation of deposits in the facilities.

- *Pressure maintaining water*

It is used as a means of production when the absolute static pressure at the wellhead decreases rapidly during the exploitation of a deposit and the recovery of oil in place will only reach a very small percentage of the estimated reserves.

B. *The reservoir water*

The reservoir water accompanies the crude oil in the producing deposit, this reservoir or formation water can come either from the aquifer which is at the base of the oilfields, or from the store rock itself. This water is generally very rich in salts until saturation; the predominant salt is sodium chloride, but it is always accompanied by varying amounts of calcium salt, potassium, magnesium, carbonates, bicarbonates, chlorides, etc.

Indeed, the reservoir water sometimes contains a considerable amount of barium strontium and calcium.

Table 1. Average analyzes of Albian water and Cambrian water

	ALBIN	CAMBRIAN
	(mg/l)	(mg/l)
(HCO3)-	170	0
CO32-	0	0
Cl-	420	210 000
(SO4)2-	600	0
Ca2+	210	36 000
Mg2+	70	6 500
Ba2+	0	800
Sr2+	0	970.00
Na+	250	80 000
K+	40	6 000
Fer total	0	5 500
pH	7.0	3.5
Density at 25°C	1.00	1.230
Profounder (m)	1050-1350	3300-3400

III. DEFINITION, COMPOSITION AND STRUCTURE OF BARIUM SULFATE (BASO4)

A. *Definition of barium sulphate (BaSO4)*

This is the most troublesome salt deposit because the solubility limits are very low and the deposits are hard and compact. In general, the problems of barium sulphate deposits arise from the incompatibility of two waters. The reservoir waters may contain barium (Ba + 2) ions and may come into contact with waters containing sulphate ions (SO4-2). The solubility of barium sulphate (for example) is one hundred percent. Less than that of calcium sulphate. However, the solubility of BaSO4 increases with the ionic strength of the water. An excess of sulfate ions tends to coagulate the precipitate while an excess of barium ions tends to disperse it. The level of saturation is an important element that regulates the rate of crystallization for barium sulphate. The higher the level of supersaturation, the faster the precipitation.


Fig.1. Barium sulphate (BaSO4).

B. *Conditions of formation of deposits*

An ion exchange in the rock can, among other things, be the cause of the state of saturation of the water. Whatever the case may be, the pressure drop between the deposit and the bottom of the well produces evaporation. Partial of this water, which oversaturates and precipitates crystals. Some have proposed an explanation based on electrical charges. The water droplets containing the seed crystals must carry a positive electric charge, and have a larger dielectric constant than that of the crude in which they swim. The rock is negatively charged due to the presence of clays; likewise, the flow currents in the pipes carry it to a negative potential. Hence attraction and fixation on the asperities. Crystals that have their own

polarity are electrically and mechanically retained. Their growth is, subsequently, easy to conceive.

Precipitation of barium sulphate is however not limited to oil reservoirs. Deposits can occur on wells, tubings, surface facilities, or in refinery equipment used for crude oil processing.

C. *The chemical reaction*

$$BaCl_2 + SO_4^{-2} \longrightarrow BaSO_4 + 2Cl^-$$
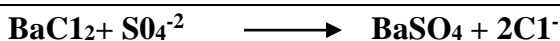
IV. COMPARISON BETWEEN THE THREE DEPOSITS

By way of comparison, the solubility of BaSO4 in fresh water is 2 mg / l, that is to say 10 times lower than that of CaCO3, 100 times lower than that of SrSO4 and a thousand times less than CaSO4, but its solubility increases with the ionic strength of water and can be found in a reservoir water up to 50 mg / l of dissolved sulphates.

On the other hand, the size of the crystals increases as the super saturation of the solution is small.

The table below gives a comparison of the solubility of barium sulphate and Calcium sulphate, so this table shows that the first one that is formed is BaSO4

Table 2. Solubility and solubility product of three sulfate deposits.

Element	BaSO4	SrSO4	CaSO4
Solubility product Ksp	1 ,1.10-10	2,8.10-7	6,1.10-5
Solubility 'S' (mol/l)	1,05.10-5	5,3.10-4	7 ,8.10-

Table 3. Solubility products of some frequent HMD deposits

Name of the deposit	Ionic product	Solubilit
FeS	[Fe2+]. [S-] 2	3.2 .10-1
BaSO4.	[Ba2+]. [SO24-]	1, 1.10-
CaSO4 .2H2O.	[Ca2+]]. [O24-]	6,1.10-5
SrSO4	[Sr2+]. [SO24-]	2,8.10-7
Ba CO3	[Ba2+]. [CO23-]	8,10-9
CaCO3	[Ca2+]. [CO23-]	4,8.10-9
Mg CO3	[Mg2+]. [CO23-]	1,0.10-5

V. DEPOSITION AND TREATMENT OF BARIUM SULPHATES

A. *The origin of barium sulphates*

As a result of the interaction of the water contained in the HMD reservoir (Cambrian-deposit water which is loaded with Ba2+ barium), and the injected water (injection water-Albian-which is loaded with sulfate element SO42-), it forms the deposition of barium sulfate and gives adverse results on the equipment used during desalting: clogging of wells and corrosion of facilities. These two phenomena have a great influence on the oil extraction process and consequently a decrease in oil production.

VI. CHARACTERISTICS OF BARIUM SULPHATES

A. *Physico-chemical properties of barium sulphate*

Barium sulphate has its chemical formula BaSO4. These are colorless or white orthorhombic crystals with a relative molecular weight of 233.4, a relative density of 4.5 (15 ℃), a melting point of 1580 ℃ and a refractive index of 1.637. It is almost insoluble in water with a solubility of 0.00022 to 18 ℃ and 0.0041 to 100 ℃. It is slightly soluble in concentrated sulfuric acid and soluble in an alkali metal carbonate solution in which it is converted into barium is insoluble in other types of acids or bases. In nature, it exists in the mineral form of barite.

Fig.2. white powder of barium sulphate

B. Crystal structure of barium sulphate

The crystals of BaSO4 as those of SrSO4 are, on the one hand, orthorhombic with very similar mesh, on the other hand, they are porous in nature with a tendency to absorb foreign ions that can co-precipitate. On the other hand, CaSO4 is orthorhombic, monoclinic with very different meshs from those of BaSO4 and SrSO4.

Barium sulfate crystallizes in the orthorhombic system (Pmma group). Its mesh parameters vary according to the authors. Miyake (Miyake et al., 1978) obtains:

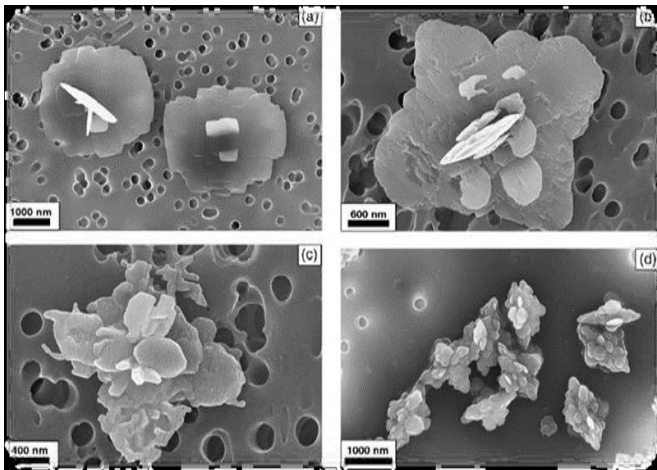$$a = 8.88 \,\text{Å} ; \quad b = 5{,}46 \,\text{Å} ; \quad c = 7{,}16 \,\text{Å}$$

Fig.3. Crystal structure of barium sulphate

C. Solubility of BaSO4

Solubility is the ability of a substance, called a solute, to dissolve in another substance, called a solvent, to form a homogeneous mixture called a solution.

In thermodynamics, solubility is a physical quantity denoted S denoting the maximum mass concentration of the solute in the solvent, at a given temperature. The solution thus obtained is then saturated. The solubility is expressed in g / L or in mol / L.BaSO4 is indeed the sulphate salt which has the lowest solubility. At 25 ° C, Rosseinsky 1958 measured by conductimetry a solubility equal to 1.04 × 10-5 mol / l or 2.5 mg / l.

The solubility product of BaSO 4 at 25 ° C. is 1.10×10 -10.

The solubility of BaSO4 in concentrated sulfuric acid (density 1.853) is 15.89 g in 100 g of saturated solution at 25 ° C. The solubility drops rapidly when the sulfuric acid solution is diluted (0.05 g per 100 g of dilute solution containing 83% concentrated acid).

The solubility was measured by Kohlrausch, here the results expressed in mg of salt per 100 cm3 of water.

VII. TREATMENT OF BARIUM SULPHATE DEPOSITION

A. The subtractive process

By elimination of the deposit-forming ions; example removal of the sulfate ions S4-2 contained in the injection water, precipitating them with BaCl 2 according to the following reaction:

$$SO_4{}^{2-} + BaCl_2 \rightarrow BaSO_4 + 2Cl^-$$
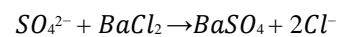
B. Inhibitor AD32

Inhibitor AD32 is a deposition inhibitor used for the treatment of water circuits in order to avoid the precipitation of calcium, strontium, barium, iron and other cations in combination with sulphates, carbonates and oxides. The AD32 inhibitor is particularly recommended for crude oil lines and for water injection circuits to control the trimming of tubing, pumps, pipes, etc.

Fig.4. the deposit inhibitor AD32

C. AD32 Inhibitor Instructions for Use

Injected directly into the system to be inhibited, pure or diluted in water, preferably by continuous injection using a metering pump.

Table 4.The physical-chemical properties of AD32 inhibitor.

1. Nature	2. Phosphonate
3. appearance	4. Liquid
5. Solidification temperature	6. -5 °C
7. PH	8. 6 – 8
9. Active matter	10. 25%
11. Flash point	12. 100°C (NF T 60-103)
13. Density	14. 1230-1280 Kg/m3
15. Viscosity	16. 10 m Pa/s

$$E = (Q\ after - Q\ before) / (Q\ before)$$

E: treatment efficiency.

Q after: flow after treatment.

Q before: flow before treatment.

The calculation of the treatment efficiency is:

$$E = (0.63 - 0.16) / 0.16 = 3.9375$$

Therefor the treatment efficiency is:

$$E = 393.75\%$$

REFERENCES

[1] Asa LAMBARKI A., L'impact des dépôts sur la production, mémoire de fin de formation IAP.

[2] KIEFFER R., Contribution contacteurs à membrane pour la précipitation du sulfate de baryum; simulation numérique ET résultats expérimentaux, thèse de doctorat, Université Claude Bernard- Lyon, 2006.

[3] KACI Y., ScaleBlaster and Tube Clean Reformat treatment through 2"7/8 CCE OMM32 (zone 1A- Complexe), stimulation program, September 2016, EP HASSI MESSAOUD.

[4] ALIA K., CHENGUEL R., Optimisation des paramètres d'inhibition des sels insolubles au niveau des installations industriels ET des puits pétroliers de la région Ourhoud, mémoire master, université d'El Oued, 2014

VIII. CONCLUSION

The increase in production flow from 26/08 / 2017and and stabilization at a good flow rate for a month, this increase is justified by the elimination of the damage caused by barium sulfate, so our well is stimulated.

The determination of the treatment efficiency is done by the following relation: