LECTURE 5. Part 1.

LECTURE 5: Reasons of hole-bottom region degradation and its influence on well's productivity. Basic methods of oil and gas recovery.

Degraded zone of formation, which is characterized by worsen filtration properties, is considered as a skin. Its influence on well's productivity is called *skin effect*.

$$s = \left(\frac{k}{k_1 - 1}\right)\ln\frac{r_w}{R_d} \qquad s = \frac{\Delta p}{2i} - \frac{1}{2}\ln\frac{2{,}25\kappa t}{r_w^2} \qquad \textbf{(1)}$$

Skin effect represents loss of positive depression as a result of additional filtration resistances.

Hole-bottom region (HBR) degradation can be caused by:

- **presence of solids (sand);**
- **filter cake of mud;**
- **salting up, wax and asphaltene precipitation;**
- **mechanical additives in water and corrosion.**

***Ways of increasing well's performance*:**

a) creation of new or increased perforation channels, micro and macro cracks;

b) removing of organic and inorganic substances from natural pores of reservoir;

c) extending cross-sections of natural pores or (at the very list) increasing the diameter of the wellbore.

Based on this ways, such methods of increasing well's performance exist:

1. Chemical methods – this means acid treatment of HBR in order to decompose particles that clog pores and cracks and increasing of their diameters.

2. Physical methods – thermal treatment, treatment with surface active agents and hydrocarbon solutions.

3. Mechanical methods – hydraulic fracturing, hydrosand blast perforation, additional cumulative perforation, vibro-acoustic treatment.

4. Complex methods – hydraulic fracturing using acids, thermochemical treatment, methods that include several of previously mentioned (these methods are used in case of complex geological conditions and presence of several

factors that cause decreasing of filtration properties).

Choosing the method of increasing well's performance one should take into account: geological properties of production layer, reasons of HBR degradation, based on real study of HBR condition.

Hydrochloric acid treatment (HAT)

This method is commonly used because of simplicity, presence of favorable condition for its implementation and relatively high efficiency. Hydrochloric acid treatment is

used for carbonate rocks (limestones, dolomites) and sandstones with carbonaceous cement.

During HAT, carbonate rocks are decomposed into highly soluble products of reactions and carbon dioxide. Besides that HAT creates exothermic reaction, which fluxes wax and asphaltene deposits that are clogging reservoir pores.

$$CaCO_3+2HCl = CaCl_2+H_2O+CO_2$$

$$CaMg(CO_3)_2+4HCl = CaCl_2 + MgCl_2 + 2H_2O + 2CO_2$$

Components of HAT solutions

1. Water.

2. Hydro-chloric acid (*HCl*) – synthetic acid (concentration of *HCl* not less than 35 or 31.5 %), technical acid (concentration of *HCl* not less than 27.5 %), off-gas *HCl* (concentration not less than 22 or 20 %).

3. Hydrofluoric acid (*HF*).

4. Corrosion inhibitor – substance, which reduces corrosion damage of equipment: BA-6, catapin-A, catapin-K, catamine-A, marvelan-K(O), technical urotropin, formalin, I-1-A, B-2, PB-5 (are added in amount 0.05 – 0.8 % from volume of acid).

5. Intensifier – surface active agents used to increase HAT efficiency due to increased treatment area and better removal of reaction products from production layer: catapin-A, catamine-A, marvelan-K(O), carbosoline, OP-10, OP-7 (are added in amount 0.1 – 0.3 % from acid volume).

6. Stabilizer – substances, used to prevent precipitation of iron and aluminum oxide compounds (are added in amount 0.8 – 2 % from acid volume).

Depending on the quality and brand, acid may include additives, which, if exceeded, will lead to negative side effects in HBR.

Additives	Quality 1	Quality 2 (brand A)	Quality 2 (brand B)
Sulphates in terms of SO, %	0.03		-
Hydrogen fluoride, %	-	-	<1
Iron, %	< 0.015	<0.03	<0.03
Sulfuric acid, %	< 0.005	-	-

Sulphates content of more than 0.03 % in hydrochloric technical synthetic acid (quality 1) leads to the formation of gypsum or anhydrous calcium sulfate in HBR, when the working agent, prepared on the basis of this acid, is reacting with the carbonate components of the formation.

The presence of hydrogen fluoride in hydrochloric acid, made of off-gas (quality 2, brand B) leads to the formation of a slightly soluble precipitate of calcium fluoride in pores. Therefore, this type of commercial acid can only be used in two-solution treatments (HAT + MAT).

The content of iron in acid solution is limited, in order to exclude the possibility of formation and precipitation of colloidal sediments such as iron hydroxide $Fe(OH)_3$ or its basic salts in HBR.

Commercial hydrochloric acid has such properties:

- density of 1154 – 1188 kg/m^3;
- viscosity at 20 °C – 2 mPa·s;
- chilling point – 58 °C;
- corrosive activity of a 10 % solution of *HCl* at 20 °C on steel grade St.3 is 7 g/(m^2·hour).

Density of water-base hydrochloric acid solutions at 18 ° C

Mass content, %	4	8	12	16	20	24	28	32	38
Density, kg/m^3	1019	1039	1069	1079	1100	1121	1142	1163	1194

From the supplying plants to the storage bases, hydrochloric acid is transported in rubber-coated steel tanks.

For treatment of terrigenous reservoirs and to increase the efficiency of influence on silicate rocks and materials (clays, mudstones, quartz) solution of 12 % *HCl* and 3 – 5 % *HF* is used. This type of treatment is called mud-acid treatment.

Lecture 5. Part 1

Choosing of type and composition of acid depends on chemical composition of rocks, type of reservoir and temperature.

Chemical composition of rock	**Type of acid**
Anhydrite $CaSO_4$	**Hydrochloric acid + potassium nitrate in content 6 – 10 % from solution mass ($HCl+KNO_3$)**
Sulfate- and iron-containing carbonate rocks	**Solution of 10 – 15 % acetic acid (CH_3COOH) and sulphamic acid (NH_2SO_3H)**
Sulfate-containing carbonate rocks	**Hydrochloric acid + calcium chloride ($CaCl_2$) in content 5 – 10 % or sodium chloride ($NaCl_2$) in content 6 – 7 % and potassium or magnesium sulfates (K_2SO_4 or $MgSO_4$) in content 3 – 4 %**
Iron-containing carbonate rocks	**Hydrochloric acid + acetic acid in content 3 – 5 % from solution mass or citric acid in content 2 – 3 % from solution mass**

Increased formation temperatures (above 60 °C) causes faster reactions between acids and rocks or equipment and this requires bigger amounts of inhibitors and usage of mixtures with delayed neutralization. Reducing acid neutralization time and, as a result, increasing of treatment depth is reached by usage of stabilized hydrocarbon-acid emulsions, calcium chloride, dilute organic acids (acetic and citric), inhibitor B-2.

Type of reservoir determines the necessary penetration depth, which influences on the treatment area and depth in layer, acid entering pores and micro cracks.

Condition	Type of acid
Porous low-permeability rocks (or in case of HBR pollution)	Solutions with high penetrating ability: acids inhibited with hydrophyle surface active agents (for injection wells) and acid aerosols (with major gas phase – usually nitrogen). Also known – foam-acid treatment
Decreasing equipment corrosion and increasing treatment area	Technology of acid solution formation in the wellbore of inside the formation. Is based on reactions of aqueous solution of formaldehyde with ammonium salts: $6HCHO+4NH_4Cl=4HCl+C_6H_{12}N_4+6H_2O$ $6HCHO+4NH_4NO_3=4HNO_3+C_6H_{12}N_4+6H_2O$ Hydrohloric and nitric acids react with carbonates and urotropin ($C_6H_{12}N_4$) causes slower interaction

Corrosion inhibitors

Corrosion inhibitors are used to prevent premature corrosion of equipment and pipes, which are in contact with acid (during transportation, storage and injection): casing, tubing, downhole filters, storage tanks, pumping units, regulation valves.

Demands to inhibitors:

- **reducing corrosion speed up to 20 – 100 times for low acid concentrations;**
- **low cost;**
- **no effect on the mobility of the solution (viscosity);**
- **no salting effect, that is, no precipitation while reducing the acidity of the solution;**
- **should not precipitate with the reaction products of the basic process, that is, with $CaCl_2$, $MgCl_2$ and others.**