LECTURE 5. Part 2.

We continue this chapter .

1. Inhibitor BA-6 is the condensation product of benzylamine with urotropin.

Properties:

- **high-viscous light brown substance**
- **has a poor amine odor**
- **density 1058 kg/m^3**
- **viscosity at 20 °C about 65 mPa·s**
- **molecular mass 250 – 260.**
- **well soluble in inorganic acids (hydrochloric, sulfuric, phosphoric) and in organic solvents (ether, acetone, ethyl alcohol, ethyl acetate and dioxane).**
- **insoluble in water.**
- **degree of inhibitory action at concentrations of inhibitor 1 g/l at a temperature of 100 °C is 98 %.**
- **stable in time and does not coagulate in the presence of ferric iron. Non-toxic.**

2. Inhibitor B-2.

Properties:

- high level of protection: for 0.25 % concentration it reduces corrosion speed of steel grade St.3 or grade 20 in technical hydrochloric acid up to 0.15 g/(m^2·hour)

- **coefficient of corrosion reduce for 20 °C is 260**
- **dosage 2 – 8 g/l**
- **is used for temperatures less than 100 °C and content of *HCl* up to 36 %.**

3. Inhibitor I-1-A is complex composition of polyalkylpyridines, obtained by condensation of paraldehyde with ammonia on the basis of synthetic rubber production wastes.

Properties:

- **viscous dark brown liquid with a characteristic odor of pyridines**
- **density 1010 – 1030 kg/m^3**
- **viscosity at 20 °C about 560 mPa·s**
- **chilling temperature – 5 °C, flash point 114 °C, self-ignition temperature 375 °C**
- **well soluble in organic solvents (alcohols, acetone, ketones), in strong mineral acids (hydrochloric, sulfuric, etc.), partly in oil, poor in gasoline and insoluble in water**
- **low-toxicity product without carcinogenic action.**

- **protection effect against carbon steel when added to a 15 % solution of *HCl* at a temperature of 50 °C is 99 % and in conditions of hydrogen sulfide corrosion – 97 – 100 %.**
- **corrosion rate in the inhibited 20 % *HCl* solution does not exceed 0.1 g/(m^2·hour).**
- **is effective at elevated temperatures (about 80 – 90 °C). Usage at higher temperatures (up to 130 °C) requires adding of potassium iodide to it.**
- **recommended content at normal and elevated temperatures is 0.1 and 0.4 %, respectively. At temperatures up to 130 °C – 0.4 % with the addition of 0.01 % of potassium iodide.**

4. Catamine-A – average recommended content 0.2 % for temperatures 20 – 40 °C.

5. Catapin-A is cationic surface active agent. One of the best hydrochloric acid corrosion inhibitors for steel.

Properties:

- **corrosive activity of the solution with the 0.1 % inhibitor content is reduced by 55 – 56 times**
- **precipitate is not formed**
- **recommended content: 0.05 % under normal conditions, 0.1 – 0.2 % under intense conditions (at 80 °C and long acting period on steel)**
- **at temperatures above 80 – 100 °C is ineffective.**

6. Catapin-K is the inhibitor that has properties close to catapin-A.

Recommended content for temperature 20 – 40 °C is in average 0.1 %. Is used for temperatures up to 110 °C and content of *HCl* below 25 %. When the content is less than 8 % and more than 18 % decomposes within 24 hours.

7. Marvelan-K(O) is less effective than catapin and catamin but is recommended for usage as a basic inhibitor as soon as under normal reservoir conditions hard-to-remove precipitates practically do not form. Recommended content in working hydrochloric acid solution is 0.05 – 0.1 %.

Stabilizers of acid solutions

Sources of iron compounds:

- steel tanks, where acid solutions are stored;
- tubing, which is used for acid supplying;
- iron-containing components of rocks (hematite, magnetite, siderite, chlorite);
- corrosion products after water injection.

In the process of acid solution neutralization with the formation rock is iron compounds hydrolysis takes place with the formation of iron hydroxides:

$$Fe^{+3} + 3H_2O = Fe(OH)_3\downarrow + 3H^+$$

$$Fe^{+2} + 2H_2O = Fe(OH)_2\downarrow + 2H^+$$

The precipitation of Fe^{+3} ions – from 1.5 to 4.1 *pH*.

The precipitation of Fe^{+2} ions – from 6.5 to 7.5 *pH*.

Formation of insoluble iron hydroxides results in blocking of the pore channels and reducing the permeability of the formation.

After injection of 25 m^3 of hydrochloric acid solution containing 1 % iron chloride, after neutralization under formation conditions, about 200 kg of iron hydroxides can fall out. Pumping of acid solution without iron compounds through a 1700-m-long tubing results in approximately 50 kg of insoluble precipitates due to washing of the iron oxide film from the metal surface and its neutralization in the formation.

The stabilizer’s action is based on forming complex compounds with iron ions. Several organic acids (acetic, tartaric, lactic, gluconic) and organic compounds (containing ions of oxygen, nitrogen, sulfur, phosphorus) are capable of producing such compounds.

Stabilizing properties of citric acid depend on iron concentration in acid solution, acid concentration, temperature, time of reaction between acid and formation.

When expected concentration of iron is 0.3 – 0.6 %, than citric acid concentration should be 0.6 – 1.2 %. In this case iron ions will be stabilized for 5 days of formation treatment and for temperatures 20 – 80 °C. Increasing of reservoir temperatures negatively effects on stabilizing properties of citric acid: for temperatures 90 – 110 °C citric acid concentration should be 0.8 % for stabilization of 0.3 % concentration of iron ions; for temperatures 110 – 130 °C citric acid is not effective.

Besides citric acid, acetic acid is also used as stabilizer. Concentration of acetic acid in acid solution should be from 1 to 3 % depending on the content of Fe in acid solution.

Properties of acetic acid:

- **density at 20 °C is 1049.2 kg/m^3**
- **dynamic viscosity**

  at 25 °C 1.155 mPa·s ;

  at 50 °C 0.79 mPa·s
- **molecular mass 60.05.**
- **temperature of melting 16.75 °C**
- **temperature of boiling 118.1 °C**
- **corrosive activity of a 10 % solution of acetic acid at 20 °C on steel grade St.3 is 2.97 g/(m^2·hour).**

Acetic acid is a liquid without colour with specific (special) odor. It is soluble in water and in alcohol.

Besides water, hydro-chloric acid (*HCl*), hydrofluoric acid (*HF*), corrosion inhibitor, intensifier (surface active agent) and stabilizer (acetic acid, citric acid), barium chloride is also added to acid solution. Barium chloride is added to acid solution to neutralize (for neutralization) of sulfuric acid. Because there is small content of sulfuric acid in acid solution.

HAT can be performed in 4 ways:

1. **Acid bath – acidizing of wellbore without injection of acid inside the formation.**
2. **Usual HAT.**
3. **HAT under pressure – with intense injection of acid inside the formation, usually requires usage of packer.**
4. **Interval or serial HAT – with regulation of treatment areas and periods of acidizing.**

Acid baths **are used in wells with opened wellbore directly after drilling during development. Hydrochloric solution is injected inside the tubing while annular space is opened. Its volume depends on treatment area, remaining mud and cementation solutions, expected amounts of corrosion, but not less than 3·V of wellbore in HAT area.**

As soon as hydrochloric solution is polluted with reaction products it is necessary to minimize its consumption by formation. That is why liquid level inside the well should be as low as possible during reaction time.

Acid baths are using hydrochloric solutions with 15 – 20 % of *HCl*.

Component	Concentration, %			
	1	2	3	4
Hydrochloric acid	20	20	15	15
Catapin	0.3	-	-	-
Acetic acid	-	-	3	3
B-2	-	-	0.2	-
Marvelan-K(O)	-	0.5	0.5	0.5
I-1-A	-	-	-	0.4

Treatment time is 2 hours – for temperatures 15 – 30 °C ;

1 – 1.5 hour – for temperatures 30 – 60 °C;

30 min. – for temperatures more than 60 °C.

Treatment time for wells without casing is 2 – 4 hours.

Acid bath can be also used for intensification of hydrocarbon's recovery. Multiplex acid baths can be used to create caverns in carbonate low-permeability layers. Volume of acid solution for first bath – 2.5 – 3 m^3 and for next ones is increased by 15 – 20 %.

As a result of acid bathes productivity of well can be increased 3 – 20 times, coefficient of well productivity increases 27 – 40 times and permeability of HBR increases from 0.005 – 0.008 to 0.142 – 0.182 D.

***Usual HAT* is a treatment of pore space of the productive layer at the HBR. Hydrochloric solution is also injected inside the tubing while annular space is opened. After solution reaches the tubing's end annular space is closed and acid is injected inside the rock. Injection of solution inside the layer is performed for the maximum possible pressure to increase the treated area and depth.**

Acid solution with 8 – 16 % of *HCl* is taken in the amount 0.4 – 1.5 m^3 for 1 m of effective depth. For next treatments volume of solution is increased by 20 – 50 %. After acid injection inside the layer, development procedures are started immediately to prevent precipitation (up to 1 – 2 hours).

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HAT under pressure assumes creation of high wellhead pressures (20 – 30 MPa). This allows injection of *HCl* solution in greater depth and distances. Usually this requires packer installation.

Mud-acid treatment (MAT)

Hydrogen fluoride (*HF*) is a colorless, mobile and low-viscosity liquid with a pungent odor. Its boiling point corresponds to temperature of +19.5 °C, that is why for higher temperatures *HF* is in gas state.

Only hydrofluoric acid and its complex derivatives (hydrofluoboric and silicon-hydrofluoric) can interact with silicon-containing materials. The reaction of the acid with silicon dioxide and glass occurs with the formation of silicon fluoride:

$$SiO_2\ (\text{quartz}) + 4HF\ =\ SiF_4 \uparrow + 2H_2O$$

$$CaSiO_3\ (\text{glass}) + 6HF\ =\ CaF_2 \downarrow + SiF_4 \uparrow + 3\ H_2O$$

The interaction speed of hydrofluoric acid with silicon dioxide increases with temperature. When it is raised from 25 to 50 ºC and from 50 to 80 ºC, it approximately doubles.

Hydrofluoric acid reacts with clays in following way:

$$H_4Al_2Si_2O_9 + 14HF = 2AlF_3 + 2SiF_4 \uparrow + 9H_2O$$

$$Na_4SiO_4 + 8HF = SiF_4 \uparrow + 4NaF + 4H_2O$$

$$SiF_4 + 2HF = H_2SiF_6$$

Hydrofluoric acid is significantly more active in reaction with $CaCO_3$ than with clay, and less active with SiO_2 (sand, quartz). Contact of HF with carbonate rock leads to the formation of insoluble calcium fluoride - CaF_2 :

$$CaCO_3 + 2HF = CaF_2\downarrow + H_2O + CO_2\uparrow$$