

Modeling of cobalt-based catalyst use during CSS for low-temperature heavy oil upgrading

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Abstract. One of the methods, which is actively used on deposits of heavy oils of the Upper Kungurian (Ufimian) sandstones of the Republic of Tatarstan, is cyclic steam simulation (CSS). This method consists of 3 stages: injection, soaking, and production. Steam is injected into a well at a temperature of 300 to 340° C for a period of weeks to months. Then, the well is allowed to sit for days to weeks to allow heat to soak into the formation. Finally, the hot oil is pumped out of the well for a period of weeks or months. Once the production rate falls off, the well is put through another cycle. The injection of the catalyst solution before the injection of steam opens the possibility for upgrading the heavy oil in the process of aquathermolysis directly in the reservoir.

In this paper, the possibility of using a catalyst precursor based on cobalt for upgrading the hydrocarbons of this field in the process of their extraction is represented. SARA analysis on oil saturated sandstones shows an increase in the proportion of saturated hydrocarbons by 11.1% due to the hydrogenation of aromatic hydrocarbons and their derivatives, the content of resins and asphaltenes are remained practically unchanged. A new method for estimating the adsorption of a catalyst based on taking into account the change in the concentration of the base metal before and after simulation of catalyst injection in the thermobaric conditions of the reservoir is proposed. During the study of catalyst adsorption in the rock, when simulating the CSS process, it is found that almost 28% of the cobalt, which is the main element of the catalyst precursor, is retained in the rock.

Keywords: ThEOR, CSS, catalyst, cobalt, SARA, adsorption, heavy oil.

1. Introduction

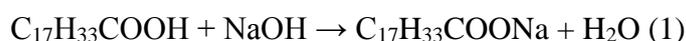
With the depletion of light and medium oil reserves, heavy oils and natural bitumen become an important source to meet the growing demand for fuel and petrochemicals. Today we know a lot of extraction technology for heavy oil and natural bitumen, which are practically



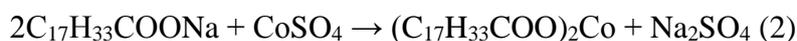
proved to be effective. One of them is the Cyclic Steam Simulation (CSS), that is accidentally discovered by Shell in Venezuela, and which is actively developed in the oil fields of the Republic of Tatarstan. Including catalytic nanoscale systems in this technology, it leads to refinement of heavy oils due to the aquathermolysis process [1-4].

Field testing (5-7 days) in the Liaohe deposit (China) a water-soluble catalyst salt VO^{2+} , Ni^{2+} , Fe^{3+} , sequential injection of 400 m^3 of water vapor, the catalyst solution and re-injection of 1600 m^3 of steam, oil production increases (in one cycle) by 30-60%, reduction in the viscosity of oil, which is important for oil production and pumping [5]. In another variant, an oil-soluble catalyst using molybdenum as the active metal is used in the same field. The catalyst solution along the steam is introduced into the tank, after which the deposit is closed for 7-10 days. After the action of the catalyst, the viscosity decreases by 78.2%, the content of oxygen, sulfur and nitrogen in the oil decreases. The authors of these studies note slight differences between laboratory tests and field tests in the oil field [6].

In this work Co^{2+} based catalyst precursor, which is synthesized at the Kazan Federal University, is researched. It refers to a class of oil soluble metal compounds, namely the salts of organic acids -naphthenates, tallates [7, 8]. Cobalt carboxylate produces an exchange reaction of the inorganic metal salt with the sodium salt of DTM:



Carboxylate of sodium interacts with the cobalt salt when heated:



It is assumed that the catalyst solution will be pumped in one of the cycles of the CSS. Initially, the layer will be heated, after that the catalyst will be introduced into the reservoir and will spread under the influence of vapor pressure. Then, the catalyst must be adsorbed and hydrocracking must begin at the temperature $178 \text{ }^\circ\text{C}$.

The effectiveness of a catalyst based on cobalt in the aspect of reducing the proportion of asphalt-resinous oil compounds in the Ashalchinskoye field extracted using SAGD technology was shown in [2]; as a result of catalytic aquathermolysis ($180 \text{ }^\circ\text{C}$), the viscosity of the converted oil decreased by 31.1%.

Object of the research is native bitumen in oil saturated sandstone from the Upper Kungurian (Ufimian) stage, that is sampled from the well no. 160 (Nijne-Karamalskoye oil field, the depth interval is 165-169 m).

2. Methodology

Laboratory modeling of the aquathermolysis process is carried out by using a high-pressure reactor (300 ml volume) manufactured by Par Instruments, USA. The model system is a

compressed sample of a bituminous sandstone of cylindrical shape with a diameter and length of 30 mm with the addition of 10 g water. This system is subjected to a temperature effect (180 °C) under catalytic conditions. The precursor of the cobalt-based catalyst is introduced in an amount of 2.2% by weight as a solution in a hydrogen donor, based on the mass content of bitumen in the native rock, which is 5.42 wt%. The operating pressure is maintained at 0.22 MPa. The experiment duration is 6 hours after the process has entered the regime.

Separation by the SARA method is carried out by taking into account the methodical recommendations of ASTM D4124-09 and GOST 32269-2013 in several stages. This method is based on the separation of bitumen into four groups of compounds: saturated hydrocarbons, aromatic compounds, resins and asphaltenes (SARA) according to their solubility and polarity [9].

Initially, asphaltenes precipitation is carried out according to the Golde cold method [10], with appropriate preparation of maltenes, including the remaining three groups (saturated hydrocarbons, aromatics and resins) that are separated by using a glass chromatography column by successively eluting with aliphatic and aromatic hydrocarbons from the adsorbent dehydrated neutral aluminum.

To research the adsorption features of the Co^{2+} based catalyst laboratory testing under the conditions, which are close to the production field that is made. The core of natural bituminous sandstone of $d=30$ mm and $h=30$ mm from Nijne-Karamalskoye heavy oil field of Tatarstan is saturated under the vacuum by solution of the catalyst. After that the core is heated with water up to 180 °C. Then the core is installed to the filtration camera and 200 ml of water is filtered through the sample at temperature 50 °C, cell pressure 7 MPa and pressure difference 1 kPa (reservoir conditions in oil field) (fig 1). After that the core is heated with water up to 180 °C. Then the core is installed to the filtration camera and 200 ml of water is filtered through the sample at temperature 50 °C, cell pressure 7 MPa and pressure difference 1 kPa (reservoir conditions in oil field). The cobalt concentration in tested sandstone is analyzed by using Neptune Plus high resolution multicollector ICP-MS system.

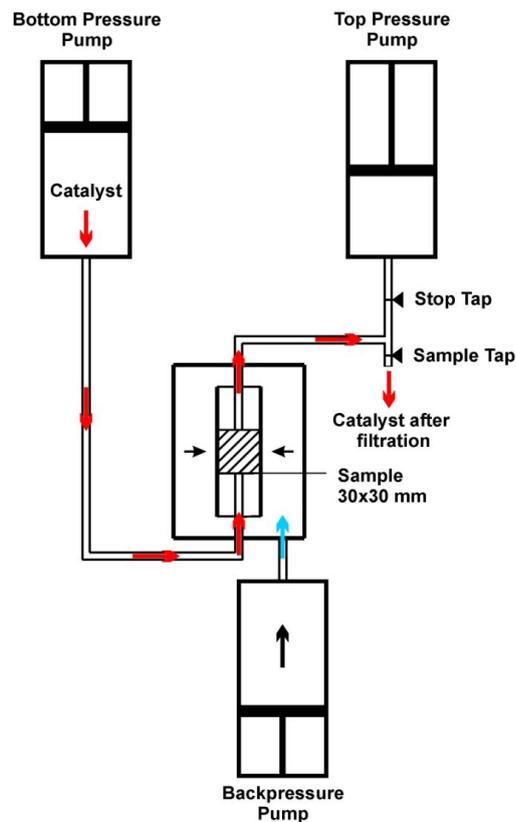


Figure 1. Scheme of the filtration experiment. A sample is installed to the holder and it is pressed up by the water from backpressure pump. Then the filtration of catalyst solution starts because of the pressure difference in the bottom and top pumps.

3. Results and Discussions

3.1. SARA group composition

The results of the determination of the composition group of the test samples by the SARA method are given in Figure 2.

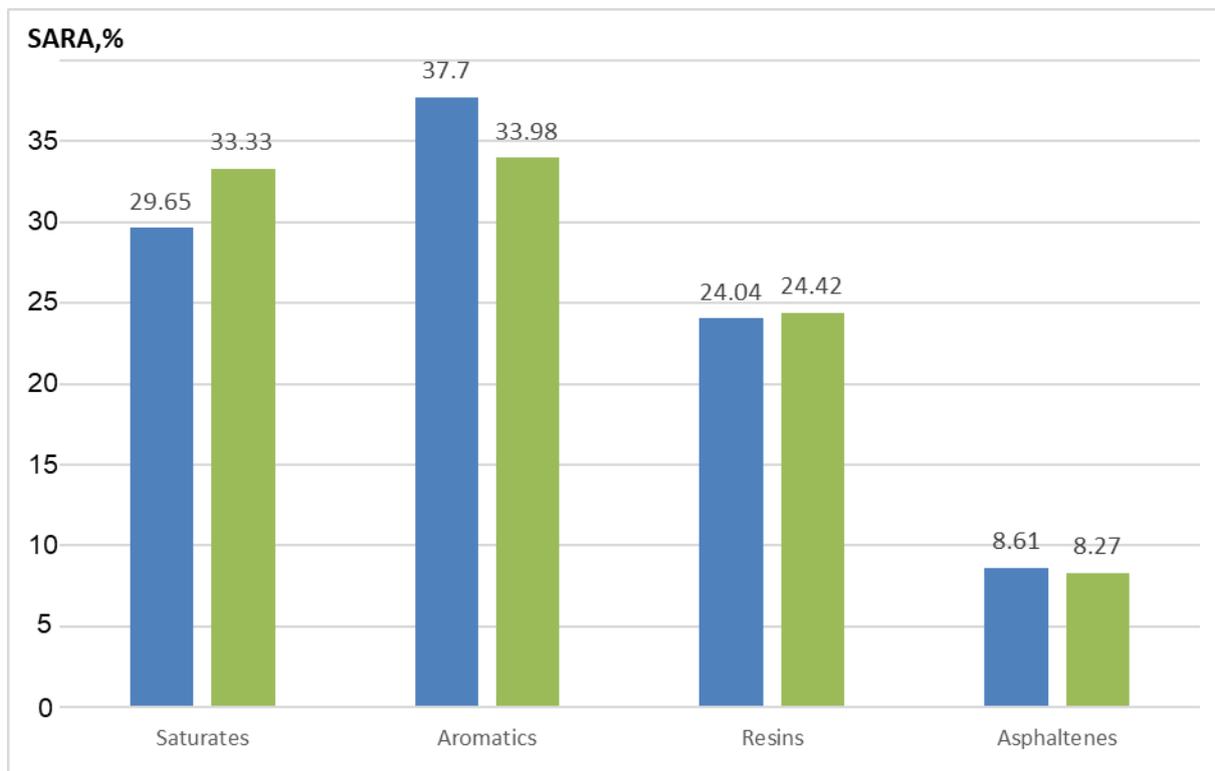


Figure 2. Distribution of SARA composition group in the initial bitumen (white) and after catalytic aquathermolysis (black).

As a result of studies, an increase in the proportion of saturated hydrocarbons is observed, which may occur due to the hydrogenation of aromatic hydrocarbons and their derivatives at the expense of elevated temperature and the presence of a catalyst in a hydrogen donor solution. However, the content of high-molecular components of oil (resins and asphaltenes) does not practically change as a result of catalytic aquathermolysis, apparently because of the short time of exposure to the sample under study.

3.2. Catalyst adsorption

The received data from this testing by this moment show that the biggest part of heavy oil saturated in solvent. The filtration of water through the bitumen sample, after removing catalyst solvent, does not give a big inflow of hydrocarbons. About 28% of catalyst is adsorbed in the sandstone sample, predominantly by clay minerals [11].

Table 1. Cobalt concentrations in the sample

No.	Sample	Cobalt concentration, ppm	Cobalt concentration, %
1	Natural heavy oil saturated sandstone	11.2318	2.5
2	Original catalyst solution	431.9742	97.5
3	Sandstone sample after filtration experiment	123.6636	27.9

4. Conclusions

Thus, the effect of the catalyst precursor on the basis of cobalt (II) is tested for the sandstones of the Nijne-Karamalskoye heavy oil deposits of the Republic of Tatarstan. SARA analysis shows an increase in the proportion of saturated hydrocarbons by 11.1 % due to the hydrogenation of aromatic hydrocarbons and their derivatives. At the same time, the content of resins and asphaltens remains practically unchanged, which may be due to a short exposure time to the sample under study. During the study of catalyst adsorption in the rock, when simulating the CSS process, it is found that almost 28% of the cobalt, which is the main element of the catalyst, is retained in the rock.

Acknowledgements

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