As a result of the science and technology development, more advanced tools are now being developed to apply the technique of hydraulic flow units, as a consequence of which there is a necessity of research in this direction. In addition, the method will allow determination of correlation dependences for water saturation and clay volume.

As a further work, it is planned to produce a complete cycle of log data interpretation, modelling and simulation using the described technique and consideration of possible risks using real field data.

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DEACTIVATION PATTERNS OF ZEOLITE-CONTAINING CATALYSTS OF CATALYTIC CRACKING

Nazarova G.Y., Shafran T.A., Kislinskaya A.A.
Scientific supervisor – professor E.N. Ivashkina
National Research Tomsk Polytechnic University, Tomsk, Russia

The various feedstock types are processed during a catalytic cracking: vacuum and atmospheric gasoils, residues of secondary refining processes, fuel oil, etc. With increasing the boiling point of fractions, the content of resinous compounds and metals rises. It has a significant effect on the catalysts deactivation which is lead to loss of the catalyst operational properties.

The reason of the activity chemical loss of the zeolite catalysts is the coke adsorption at acid sites. The catalyst deactivation by coke is a reversible process, the catalyst activity is generally recovered during regeneration. The catalysts deactivation, the accumulation and the amorphicity degree of coke (C/H ratio) undoubtedly depend not only on the feedstock characteristics, process conditions, but also the type and chemical composition of the catalyst (acidity, pore size and porous structure of the zeolite) [3].

Deactivation by heavy metals, including nickel and vanadium, lead to an irreversible activity loss and a change in the catalyst selectivity due to their deposition on the active surface, the pore space blocking and the catalyst structure destroying. It has a significant problem for refineries at increasing the consumption of the expensive catalyst.

Forecasting of the activity and the deactivation degree of the catalyst using mathematical models that are sensitive to the concentration of decontamination factors and take into account not only the feedstock nature, but also the structure-selective properties of the catalysts is an important step at the existing industrial catalytic cracking units optimization.

The aim of the work is to predict the activity of the regenerated catalysts depending on the nickel and vanadium concentrations in the feedstock taking into account its composition using the mathematical model. Reversible deactivation of the catalyst is taken into account by introducing into the model a function ψ= f(Ccoke) which is depend on the coke concentration formed on the catalyst in the reactor in accordance with the formalized scheme of hydrocarbons conversions [4]. Thus, the calculation of the relative activity of the coked catalyst concerning ZSM-5 (AZSM-5) and Y (AY) type reactions is described by an exponential dependence determined from experimental data, taking into account the acid and structural properties of the catalyst zeolites:

$$A_Y = A_0 \cdot e^{-0{,}077 \cdot C_к} \qquad A_{\text{ZSM}} = A_0 \cdot e^{-0{,}113 \cdot C_к}$$

here AY, AZSM – the relative activity of the coked catalyst concerning Y and ZSM-5 type reactions, respectively; A0 – the relative activity of the regenerated catalyst, depended on the concentration of the residual coke on the catalyst and the heavy metals in the feedstock, –0.077 и 0.113 – deactivation constants determined experimentally on the basis of the zeolites acidity data, Cк – coke content on catalyst, wt%.

The rate and degree of the coke formation increase with rising the zeolite acidity, the coke yield decreases with decreasing the pore size at equal acidity of the zeolite. However, deactivation is faster for the zeolite with the small pores (ZSM-5), because a relatively small amount of coke results in a significant catalyst activity loss [6]. Thus, the deactivation degree of ZSM-5 is higher in comparison with Y zeolite due to the stronger acidity of ZSM-5 zeolite [1] and a smaller pore size (0.2 nm less than for Y zeolite).

The catalyst deactivation degree depends on the regenerated catalyst activity (A0), which largely depends by heavy metals. The joint effect of heavy metals in the cracking feedstock is taken into account at prediction of the regenerated catalyst activity. Thus, deactivated effect of vanadium (dealumination) is reduced with increasing the nickel content, but dehydrogenation capacity of the catalyst and the content of coke on the catalyst increase.

To account for the nickel deactivation effect on the catalyst, the dependence of the dehydrogenation capacity of the catalyst (ϒ) on the metal content is revealed, characterizing the intensity of hydrogen formation during the dehydrogenation, aromatization, condensation and coke formation reactions of catalytic cracking:

$$\text{ϒ} = 0{,}142 \cdot e^{1{,}1554 \cdot \text{CNi}}$$

here CNi – the nickel content in the feedstock, ppm.

The combined effect of heavy metals on the regenerated catalyst activity is determined in accordance with [2]:

1. Formation of metal oxides at the contact of the metalorganic compound adsorbed on the catalyst surface with air stream of regenerator

$$2Ni+O_2=2NiO$$
$$4V+5O_2=2V_2O_5$$

2. Formation of vanadic acid at the contact of metal oxide with water stream

$$V2O_5+3H_2O=2H_3VO_4$$

3. Calculation of the vanadium acid amount required to react with nickel oxide

$$2NiO+2H_3VO_4=Ni_2V2O_7+3H_2O$$

4. Vanadium deactivation effect accounting Calculation of the aluminum oxide amount required to react with the vanadic acid residue

$$2H_3VO_4+Al2O_3=2AlVO_4+3H_2O$$

The influence of the nickel and vanadium content on the regenerated catalyst activity taking into account the volume of the processed feedstock (annual volume is 2.4 million tons) and the activity of the coked catalyst is possible to be estimated using the mathematical model under the equal process conditions (table 1). The range of the heavy metals concentration in a vacuum distillate was chosen in accordance with [5]: nickel content – 0 ÷0,6 ppm, vanadium content – 0 ÷1,9 ppm.

The predicted calculations showed that the catalyst activity decreases from 79.1 to 75.62 due to its dealumination (Figure 1)with increasing the vanadium concentration in the feedstock at 1.9 ppm,. At the same time, the deactivation effect of vanadium is reduced by 0.95% with increasing the nickel content in the feedstock at 0.6 ppm. The deactivation effect of vanadium connected with formation of vanadium acid which leads to destroy the structure of the zeolite at the contact with skeleton aluminum of the catalyst, reduce of the pore volume, the amount of acid site and catalyst activity. The nickel inhibitory effect is connected with the interaction of nickel with a part of vanadium acid. Thus, the catalyst activity is higher (79.1-76.57%) at the nickel and vanadium feedstock processed than vanadium feedstock (79.1-75.6%).

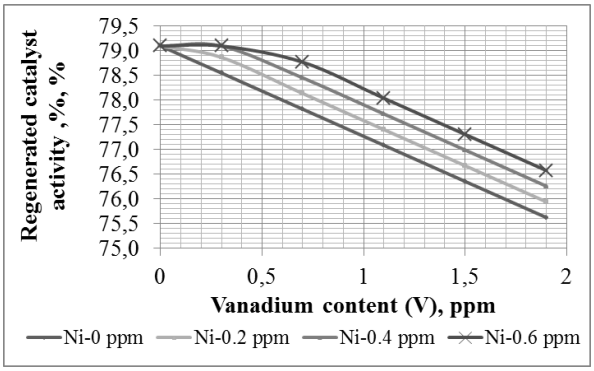

Fig. 1 – Dependence of the regenerated catalyst activity on the content of nickel and vanadium

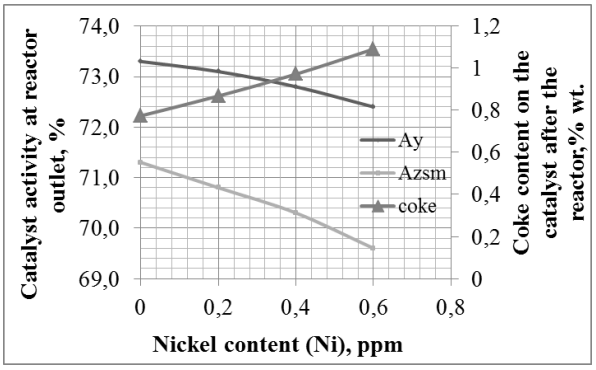

Fig. 2 – Dependence of the catalyst activity and coke content on the nickel content in the feedstock

The catalyst activity at the reactor outlet is determined by the content of coke on its surface, which in turn depends on the feedstock composition, the regenerated catalyst activity, the process condition of the catalyst operation, the structural-selective properties of the catalyst, and the heavy metal content in the feedstock. Thus the nickel leads to increase in the dehydrogenating capacity of the catalyst. Calculations showed that the coke content on the catalyst increases from 0.774 to 1.091wt% (Fig. 2) with increasing the nickel content in the cracking feedstock from 0 to 0.6 ppm, and equal vanadium content (0.7 ppm). The current catalyst activity decreases from 71.3 to 69.6% and from 73.3 to 72.4% concerning ZSM-5 and Y type reactions.

The proposed scheme of the catalysts deactivation of catalytic cracking allows to predict the cracking efficiency taking into account the catalyst activity loss, depending on the heavy metals concentration in the feedstock and the intensity of coke formation taking into account the structural and selective properties of the catalyst. Prediction of the catalyst activity in the cycle "operation-regeneration", taking into account the composition and properties of the feedstock and the catalysts, ensures the optimization of the operating modes to increase the yield of the target products at reducing the coke formation on the catalyst and prolonging its service life.

The work was supported by a grant from the President of the Russian Federation for young Russian scientists and doctors MD-4620.2018.8

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THE ASSESSMENT OF CATAGENETIC SOURCE ROCK ZONING IN THE KYNDAL GRABEN OF THE BUREYA BASIN USING PALEOTECTONIC AND PALEOTEMPERATURE MODELING SOFTWARE (THE FAR EAST OF RUSSIA)

P.N. Prokhorova

Scientific supervisors: professor V.I. Isaev, associate professor I.A. Matveenko

National Research Tomsk Polytechnic University, Tomsk, Russia

Modeling of sedimentary basins makes it possible to trace the evolution of a sedimentary basin over time as it is filled by sediments which may ultimately form or contain hydrocarbons. Today, several computer programs for basin modeling are used, such as MatOil, Genex, Temis, PetroMod, GALO, etc.

In the Far East of Russia, computer modeling has been used in the study of the Sakhalin and Sea of Okhotsk sedimentary basins. The basins in the continental Far East are less thoroughly studied, and computer technologies are occasionally used to study the thermal history only one of the areas in the Pereyaslavsky Graben [2].

The main aim of the study is the oil-gas potential evaluation of Jurassic-Cretaceous deposits within Kindal Graben by tectonic and thermal history modeling of 1C, 1A and 1PR wells.

There are two stages of modeling. The first stage involves obtaining the basic geological, geophysical, and geochemical data on the basin structure and development, and also preparation of the initial parameters for the basin modeling. The input data set includes the following information: data on the current basin structure, absolute dates of geological boundaries, sedimentation washout/no sedimentation periods, climatic secular temperature variation on the Earth's surface, measured vitrinite reflectivity values. The second stage is the modeling process of subsidence history, rifting parameters, thermal history and HC generation in the basin.

The Bureya basin (BB) is the best-preserved part of the Bureya marginal trough in the boundary between the Bureya Massif and the Sikhote-Alin orogenic belt (Fig. 1) [4]. The sedimentary cover of the BB consists of the lower molasse composed of Upper Triassic–Jurassic marine sediments and the upper molasses composed of Middle Jurassic–Cretaceous continental coal-bearing deposits. In the central part of the BB, the continental coal-bearing deposits make up a large syncline structure such as the Kyndal graben–syncline, complicated in its center by the Kyndal graben (KG).

The sedimentary section of the KG consists of (bottom–up) the Talynzhan (tl), Urgal (ur), Chagdamyn (cg), Chemchuko (cm), Iorek (jr), and Kyndal (kn) suites; and Sandstone (ps) suite [1].

Having conducted the one-dimensional modeling the following conclusions are formulated. The BB bottom within the KG was subsided to a maximum depth 98 Ma ago, at the beginning of the Late Cretaceous. The greatest subsidence to the depth of 4089 m has been recorded for well 1C. The total subsidence reached 3338 m and 3437 m in wells 1A and 1PR, respectively.

The Kyndal graben–syncline was formed under thermal flow of 49–51 mW/m2 at the bottom. In the extension period, the thermal flow gradually increased to 51–52 mW/m2. In our model, the high sedimentation velocity obtained for the Kyndal suite caused a corresponding decrease in the thermal flow values during the deposition. After completion of the riftogenesis stage, the thermal flow gradually declined to 48–49 mW/m2.

In accordance with the vertical zoning of katagenesis and the location of oil and gas deposits based on the Ro diagrams, the oil-and-gas formation zones were identified as follows: ($0.1 < Ro < 0.55$) is a zone of intensive formation of HC gases; ($0.55 < Ro < 1.3$; 50–150°C) is a major oil-formation zone; ($Ro > 1.3$; 150–200°C) is a zone of intensive formation of wet condensate gas and, deeper, of dry HC gas. According to the proposed classification, the HC maturation history obtained in the three simulated wells is as follows (Fig. 2). In the period of 165–150Ma ago, the time of the Talynzhan deposition and the subsequent break in the subsidence, the regional heating was insufficient to generate hydrocarbons. In the following period of deposition of the Urgal–Chemchuko suites 150–118 Ma ago, the thickness of the sedimentary cover in the most subsided zones reached 2.5 km. Talynzhan suite was heated to 100–120°C, while the vitrinite reflectance values exceeded the level of 0.55%; in other words, all of the rocks achieved the main oil-formation phase (MOF). The Urgal, Chagdamyn, Chemchuko and partially Iorek suites entered the oil window 116–98 Ma ago, in the period of deposition of the Iorek–Kyndal suites. Approximately 95 Ma ago, the Ro parameter exceeded 1.3% at the bottom of the Talynzhan suite and the sedimentary deposits of the formation moved to the lower phase of gas generation.

Currently, the major part of the Talynzhan suite; the Urgal, Chagdamyn, and Chemchuko suites; and the Iorek suite bottom are still at MOF; the tops of the Iorek and Kyndal suites are in the upper phase of gas formation, while the Talynzhan