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DEVELOPMENT OF ECOLOGICALLY ACCEPTABLE TECHNOLOGY FOR PROCESSING LARGE PARTICLE KUKERSITE IN VERTICAL RETORTS

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The ecologically acceptable technology for processing large particle shale includes the retorting in a thin bed, the use of recycle heat carrier heated in heat exchangers, semicoke deep gasification in the lower part of the retort, separate take off of oil vapours and gasification gases, and also a cleaning process for desulfurization of the retort gas and flue gases coming from the burners of heat exchangers.

Vertical retorts of different capacity (throughput rates ranging from 50 to 1000 tonnes oil shale per day) are the only units now in operation in Estonia and in Russia for retorting large particle kukersite on a commercial scale. Although these retorts are widely used and have an over seventy-years-old history of development, from the point of view of environment protection against the pollution with harmful substances the technology used leaves much to be desired. For example, retort oils contain rather high amounts of benzo(a)pyren (BaP) - 80-120 mg/kg, and solid residues, in their turn, - water-soluble sulfide sulfur - up to 0.2-0.3 %, BaP - 50-800 μg/kg, volatile phenols - 50-100 mg/kg, and other compounds.

As established by our studies, the main amount of BaP (over 95 %) formed during thermal decomposition of kukersite passes into oil. Oil vapours and mist present in the gas recycled into retort and burnt in burners represent the main source of its formation. Improvement of the perfomance of the condensation system is the most effective way to decrease the BaP content of oil - the lower the concentration of light oil fractions in gas leaving the condensation system, the less benzo(a)pyren is formed during the preparation of heat carrier, and, consequently, the lower the BaP content of oil.

A very radical way to reduce the formation of BaP is complete refusal of preparing the heat carrier by burning recycle gas in burners. The preparation of recycle heat carrier in heat exchangers should be used instead. As a result of such a substitution the BaP content of oil could be reduced to 10-20 mg/kg [1, 2].

The main source of BaP in the kukersite retorting solid residue is the presence of uncompletely processed shale (kerogen) in the latter. Benzo(a)pyren is formed already at the early stage of thermal decomposition of kerogen at 300-350 °C. At 450 °C, BaP is vaporized and removed from the reaction space and condensed together with oil vapours. The process of kerogen decomposition ends at 520 °C, and by then the BaP content of the residue has decreased to the level of the natural background, which is very low - 1-5 μg/kg [3].

Only 1-2 % of the total quantity of BaP formed during thermal decomposition of kukersite in vertical retorts passes into the solid residue. The concentration of BaP in the retort solid residue disposed on ash dumps is not allowed to exceed 10-20 μg/kg, because on the latter it is subjected to the action of water and wind contributing to spreading of carcinogens in the natural surroundings. For that reason the problem of maintaining the BaP concentration at a very low level is highly important.

The results of our studies have demonstrated that uniform heating of the shale bed in the retorting shaft up to 520 °C is the solution of the above problem [5]. Both non-uniform distribution of the heat carrier across the shale bed and/or troubles with the uniform descent of the shale bed cause the passage of insufficiently retorted shale from the retorting shaft into the discharged shale residue, and, consequently, lead to elevated contents of BaP in it. Improving the uniformity of the heat carrier distribution within the shale bed in the retorting shaft is, therefore, an effective way to produce low carcinogenic solid retort residue.

It was shown by our tests in a pilot retort that the presence of toxic compounds in the solid retort residue can be avoided by the process of deep gasification of semicoke in the lower part of the retort. By bringing the content of residual carbon in the solid residue by gasification from 8-10 % down to 1-2 % the concentration of BaP in the residue would be as low as 5-10 μg/kg, that of volatile phenols 5-10 mg/kg with practically zero concentration of water soluble sulfide sulfur [1, 2].

Consequently, the technology of processing large particle oil shale in vertical retorts will be essentially improved from the point of view of environment protection provided the present practice of producing heat carrier by burning gas in burners will be changed for the use of recycle heat carrier heated in heat exchangers. Simultaneous deep gasification of the semicoke in the lower part of the retort would accomplish this novel technical solution. However, as known from the long experience of retorting shale in vertical retorts, the process of deep gasification of the semicoke may represent the source of oxygen which penetrates into the retorting shaft and affects the oil yield. Therefore, the process of gasification has to be realized avoiding the access of gasification gases into the retorting shaft. For this purpose the gasification gas has to be taken off from the gasifier separately and directed, for example, into heat exchangers for heating recycle heat carrier needed in the retorting shaft [6, 7].

The principal flow diagram of ecologically acceptable technology for processing large particle shale is presented in Fig. 1. As seen from this diagram, it includes besides the use of recycle heat carrier heated in heat exchangers, and the use of semicoke gasification in the lower part of the retort, also a cleaning process for desulfurisation of the retort gas and flue gases coming from the burners of heat exchangers.

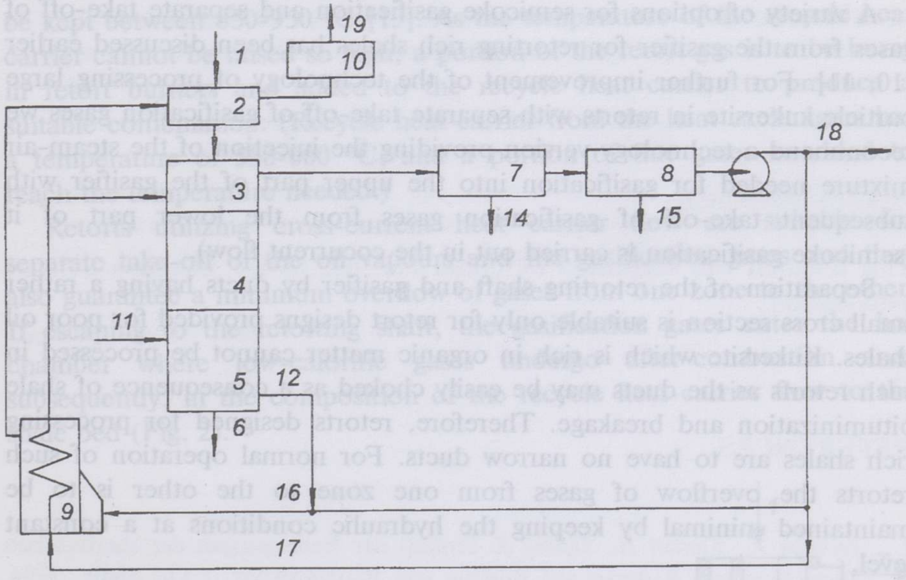

Fig. 1. Principal flow diagram of processing oil shale in retorts with separate take-off of the oil vapours and the gasification gases. *1* - oil shale, *2* - drying zone, *3* - semicoking zone, *4* - separation zone, *5* - gasification and cooling zone, *6* - spent shale, *7* - condensation and recovery system, *8* - desulfurization, *9* - gas heater, *10* - dust removal and desulfurization system, *11* - oxidizing agent, *12* - gasification gas to burner, *13* - oil vapours and gas, *14* - crude shale oil, *15* - sulfur, *16* - make-up recycle gas to burner, *17* - recycle gas, *18* - product gas, *19* - flue gas

The processing of large particle oil shale according to this flow diagram not only guarantees a practically clean from the ecological point of view realization of the retorting process but simultaneously brings about an essential rise in the process efficiency:

- oil yield of the Fischer assay oil may be increased from 70-75 up to 95-100 %;
- calorific value of the retort gas - from 3-4 up to 15-25 MJ/m^3;
- organic matter of the initial shale will be used more completely and the content of residual carbon in the discharged solid residue will be reduced from 8-10 down to 1-2 %.

Consequently, the proposed technology represents a good combination of ecologically clean and high-efficient production.

It is pertinent to add that Japanese specialists are also successfully searching for ecologically acceptable solutions for processing organically poor oil shales and work is under way to solve the problems of cleaning gas flows from sulfur compounds and nitrogen oxides [8, 9].

A variety of options for semicoke gasification and separate take-off of gases from the gasifier for retorting rich shales has been discussed earlier [10, 11]. For further improvement of the technology of processing large particle kukersite in retorts with separate take-off of gasification gases we recommend a technology version providing the injection of the steam-air mixture needed for gasification into the upper part of the gasifier with subsequent take-off of gasification gases from the lower part of it (semicoke gasification is carried out in the cocurrent flow).

Separation of the retorting shaft and gasifier by ducts having a rather small cross section is suitable only for retort designs provided for poor oil shales. Kukersite which is rich in organic matter cannot be processed in such retorts as the ducts may be easily choked as a consequence of shale bituminization and breakage. Therefore, retorts designed for processing rich shales are to have no narrow ducts. For normal operation of such retorts the overflow of gases from one zone to the other is to be maintained minimal by keeping the hydraulic conditions at a constant level.

The best conditions for the process are created when the steam-air mixture for semicoke gasification is directed into the upper part of the gasifier and the overflow of gases is reduced to a minimum by keeping the pressure of the steam-air mixture and that of the recycle heat carrier directed into the lower part of the retorting shaft as close as possible to each other.

Injection of the steam-air flow into the upper part of the gasifier is expedient also because it leads to a decrease in the oil content of gasification gases. The point is that in case of gasification in counter-current flow, as is widely used in the world-wide experience, gasification gases are characterized by elevated concentrations of oil due to the access of some portions of incompletely retorted shale to the upper part of the gasifier [12]. The retorting process will be finished there, and additional amounts of oil formed are taken off from the gasifier in the composition of gasification gases. The content of oil in the gasification gas is as high as 8 g/m^3 on an average, which was shown by our tests [1]. Oil droplets precipitate on the heat exchanger surfaces, and are polymerized there so impairing the efficiency of these units. The result is that heat exchangers (and, naturally, the retort, too) are often to be stopped for cleaning.

In case of the inverse process of gasification (i.e. oxidizing agent is fed into the upper part of the gasifier and it moves cocurrent with semicoke) oil vapours are pyrolized in the gasifier and the gasification gases contain only 1-2 g/m^3 of oil [10]. It is to be expected that the use of such technology increases the efficiency of the heat exchange unit, and, correspondingly, prolongs the run between overhauls of the retort.

Long-time experience of operating vertical retorts has shown the advantages of retorting kukersite in a thin bed, e.g. in retorts with the cross-current flow of the heat carrier. The temperature of the latter is to be kept between 850-950 °C [13]. As the temperature of the recycle heat carrier cannot be raised so high, a portion of the retort gas is to be burnt in retort burners and added to the recycle heat carrier to produce a suitable combination. (Recycle heat carrier from the heat exchangers has a temperature of 550-600 °C, and a portion of flue gases is added to reach the temperature needed.)

Retorts utilizing cross-current heat carrier flow are suitable for separate take-off of the oil vapours and the gasification gases and they also guarantee a minimum overflow of gases from one zone to the other. If escaping to the retorting shaft, the gasification gases enter the hot chamber where low-calorific gases undergo after-combustion and, subsequently, in the composition of the recycle heat carrier flow to the shale bed (Fig. 2).

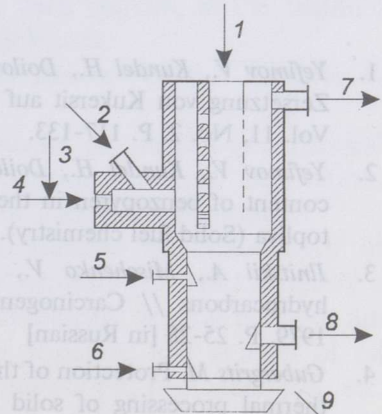

Fig. 2. Oil shale retort with separate take-off of the oil vapours and the gasification gas. *1* - oil shale, *2* - recycle gas, *3* - gas, *4* - air, *5* - oxidizing agent, *6* - air (gas), *7* - oil vapours and gas, *8* - gasification gas, *9* - spent shale

The overflow of gases in the opposite direction is represented mostly by a mixture of recycle heat carrier and flue gases from the hot chamber. However, since in both cases the gas flows contain practically no oil, they have no effect on the retort oil yield.

Conclusions

Analysis of results from research and operational experience of vertical retorts at home and abroad enabled to develop an ecologically acceptable technology for processing large particle oil shale rich in organic matter. The main features characterizing this technology are:

- retorting oil shale in a thin bed, e.g. in retorts with cross-current heat carrier flow;
- separate take-off of oil vapours (retort gas) and gasification gases;
- injection of the steam-air flow into the upper part of the gasifier and take-off of gasification gases from its lower part with subsequent use in heat exchangers designed for heating the recycle heat carrier used in the retorting process.

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