Greening Uranium-Containing Solid Fuels

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Abstract—The results of thermodynamic and experimental investigation of plasma processing of uranium-containing Nizhneilli brown coal (NBC) and Estonian dictyonema shale (EDS) are presented. The essence of plasma processing of the uranium-containing solid fuels (SF) is in the conversion of the organic mass of SF into synthesis gas, with the simultaneous release of uranium-containing compounds into the gas phase, followed by the production of uranium-free ash. Thermodynamic analysis showed that the gaseous phase of the SF plasma steam gasification products consists, basically, of synthesis gas with a concentration of up to 95.2 vol.% at 1,800 K. At this temperature, uranium-containing compounds completely pass into the gas phase in the form of uranium oxides. Experiments on plasma steam gasification of EDS were performed in entrained-flow plasma reactor. The results of the research testify to the insensitivity of the plasma processing technology to the quality of the SF used.

Index Terms—Chemical reactor, Gasification, Plasma chemistry, Plasma materials processing, Uranium.

I. INTRODUCTION

Since solid fuel (coal, shale, lignites) is one of the main energy sources of the 21st century, the problem of its efficient and environmentally friendly combustion is given great attention around the world. The share of solid fuel (SF) in fossil fuel reserves is 66.1% [1], and in the generation of electricity that is 39.3%, which significantly exceeds the contribution of other energy sources.

Conventional technologies of solid fuels burning for power generation lead to a higher level of harmful pollutants emissions than when burning liquid and gaseous fuels. Increasing the share of SF in the world energy balance, while reducing their quality [2], requires the development of new more efficient and environmentally friendly technologies for their use.

By coking and steam coal reserves Kazakhstan is among the top ten leading countries, behind only China, the USA, Russia, Australia, India, South Africa and Ukraine [3]. The state balance accounted for reserves of 49 deposits; they are 33.6 billion tons, including bituminous coal - 21.5 billion tons, brown coal - 12.1 billion tons. However, because of the uranium content in the coals, huge coal reserves, for example, Nizhneilli basin (10 billion tons) are not included in the State Fuel Balance of Kazakhstan [4]. To involve in the fuel and energy balance of uranium-containing coals, it is necessary to develop a technology for their processing.

On the other hand, Kazakhstan is the world leader in uranium reserves, having, according to current estimates, 12% of the world uranium reserves [5]. The explored reserves of uranium in Kazakhstan are at least 1.1 million tons with world consumption of 50-60 thousand tons per year. Note that the Nizhneilli brown coal (NBC) contains more than 5 million tons of uranium which by its world price ($ 45,000 per 1 ton) is of serious economic interest for expanding the resource base of the uranium industry in Kazakhstan. More than 15,000 tons of uranium is also found in the dictyonema shale of Estonia, which are also off-balance fuel of the Baltic [6]. Table I presents the composition and thermal characteristics of the above-mentioned uranium-containing SF. It can be seen from the table that the uranium content in the NBC is 2.5 times higher than that in the Estonian dictyonema shale (EDS). The ash content of the EDS is more than 7 times higher than the ash content of the NBC, as a result of which the higher heating value (HHV) of these fuels vary greatly: 6,275 and 20,400 kJ/kg, respectively. Nevertheless, these SFs could be an energy fuel if they did not contain uranium, which poses a danger of radioactive contamination of the environment when they are used on pulverized coal-fired power plants.

It is known that the amount of individual trace elements (U, Mo, Pb, V, etc.) entering the environment when burning solid fuels exceeds their total industrial production [7]. Most of the trace elements of the coals, when incinerated, pass into fly ash or slags, while the other part is taken out with flue gases and the thinnest fraction of the ash that is not captured by the electrostatic precipitators. A particular danger to the environment and, at the same time, special value as a target product is, among other microelements, uranium compounds. Various methods have been developed for extracting trace elements from coals. All of them are multistage and capital intensive, with a low degree of extraction of target products (30-40%) [8].
A promising solution to the problem of the use of uranium-containing SF is the use of technologies for their plasma gasification. Plasma technologies for SF processing have proved efficiency in obtaining synthesis gas from the organic mass of coal and valuable components from the mineral mass of coal [9, 10]. The use of electric arc plasma for the processing of uranium-containing SF makes it possible to eliminate the above disadvantages and to obtain from the SF a clean energy gas, a mineral residue suitable for use in the construction industry and uranium-containing concentrate.

TABLE I. COMPOSITION OF URANIUM-CONTAINING SF

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<thead>
<tr>
<th></th>
<th>NBC</th>
<th>EDS</th>
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<tr>
<td>Moisture (Total), wt.%</td>
<td>38.3</td>
<td>11.5</td>
</tr>
<tr>
<td>Volatile Matter, wt.%</td>
<td>33.72</td>
<td>6.0</td>
</tr>
<tr>
<td>Fixed Carbon (By Difference), wt.%</td>
<td>53.68</td>
<td>6.0</td>
</tr>
<tr>
<td>Ash, wt.%</td>
<td>12.0</td>
<td>88.0</td>
</tr>
<tr>
<td>HHV (Dry Mass Basis), kJ/kg</td>
<td>20,400</td>
<td>6,275</td>
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</table>

The most complete information necessary for the development of plasma technology for SF processing, along with experiment can be obtained with the help of numerical methods that determine the optimum characteristics of the process and the design parameters of the device for its implementation. Thermodynamic calculations give the parameters of the working medium (yield of target products, the specific power inputs, by-products content, degree of SF conversion) in the limiting state, which may not be realized, since in many cases the indicators of real processes of thermochemical transformations of fuels deviate from thermodynamically equilibrium values and to a certain extent, are corrected by kinetic calculations taking into account heat transfer and mass transfer in the systems under consideration.

This paper is devoted to the development and research of plasma processing technology for uranium-containing SF using the example of NBC and EDS. It consists of two stages: the thermodynamic analysis of plasma pyrolysis and plasma-steam gasification of uranium-containing SF using the universal program for thermodynamic calculations TERRA [11, 12] and the experimental study of plasma complex processing of uranium-containing SF in a specialized installation for gasification of SF with a plasma reactor of 100 kW power [9, 10].

II. THERMODYNAMIC CALCULATIONS

To carry out the thermodynamic analysis of coal plasma processing, the TERRA software is used. It is intended for numerical calculations of high-temperature processes and possesses its own extensive database of thermodynamic properties of 3,000 individual substances [11]. The database includes thermodynamic properties of organic and mineral components of SF.

For the calculation of the SF gasification, the following steam-coal mixtures were selected, weight percent: 100% of NBC + 85% of steam and 100% of EMF + 10% of steam. The calculations were carried out in the temperature range 300-4,000 K at atmospheric pressure in the system. The criteria for choosing the mass ratio of SF: the oxidizer was to achieve 100% gasification of carbon and the complete conversion of uranium and uranium-containing compounds to the gas phase.

Figure 1 shows the results of calculations of the NBC plasma gasification. The gas phase basically consists of synthesis gas. Its concentration reaches 95.2 vol.% in the temperature range 1,300-1,700 K. With an increase in temperature, molecular hydrogen dissociates into atomic hydrogen, which concentration reaches 28.8 vol.% at 4,000 K. In the temperature range 1,300-1,700 K, the concentration of carbon dioxide is about 0.1 vol.%. In the entire temperature range, there is molecular nitrogen with a concentration of 1 to 0.15 vol.%. The concentration of nitrogen oxides even at this temperature does not exceed 79.7 ppm, which is below the permissible level of harmful emissions of nitrogen oxides for environmentally friendly coal-fired TPPs [13]. Sulfur in the gas phase is mainly in the form of hydrogen sulphide with a concentration not exceeding 3.4 vol.% in the temperature range 1,300-1,700 K, and that of sulfur oxides is less than 139.9 ppm even at 4,000 K, which is also below the permissible level of harmful emissions of sulfur oxides for environmentally friendly coal-fired TPPs [13]. The most interesting is the behavior of uranium and uranium-containing compounds in the gasification of SF in the temperature range of 3,000-4,000 K, at which their concentrations become significant. At a temperature of 4,000 K, the uranium concentration in the gas phase does not exceed 1x10^-4 ppm, uranium dioxide – 0.24 ppm, uranium monoxide – 0.015 ppm, and uranium trioxide concentration does not exceed 0.15 ppm.

![Figure 1. Temperature dependence of the concentration of components in the gas phase at the NBC plasma-steam gasification.](image-url)
Figure 2 shows the results of calculations of the EDS plasma gasification. The gas phase basically consists of synthesis gas. Its concentration reaches 95.2 vol.% in the temperature range 1,300-1,700 K. With an increase in temperature, molecular hydrogen dissociates into atomic hydrogen, which concentration reaches 28.8 vol.% at 4000 K. In the temperature range 1,300-1,700 K, the concentration of carbon dioxide does not exceed 0.15 vol.%. In the entire temperature range, there is molecular nitrogen with a concentration of 1 to 0.15 vol.%. Oxides of nitrogen in the gas phase are observed at temperatures above 1,800 K. At a temperature of 2,500 K, their concentration is 7.3 ppm, increasing with a temperature of up to 1,286 ppm at 4,000 K. Sulfur in the gas phase is presented in the form of hydrogen sulfide with a concentration not exceeding 3.4 vol.% in the temperature range 1,300-1,700 K, sulfur oxides (SO + SO2) at a concentration of 1 ppm at 1,700 K and atomic sulfur with a concentration of 10.8 ppm at 1,700 K. At a temperature of 4,000 K, the uranium concentration in the gas phase does not exceed 1-10-5 ppm, uranium dioxide – 0.24 ppm, uranium monoxide – 0.015 ppm, and uranium trioxide concentration does not exceed 0.15 ppm.

One of the main characteristics of the gasification process is the temperature dependence of the degree of gasification of carbon (Fig. 3). It was calculated according to the following formula: \[ X_c = \frac{C_{in} - C_{fin}}{C_{in}} \cdot 100\% \], where Cin and Cfin are the values of the carbon concentration in the SF at 298 K and the current temperature of the process, respectively.

Figure 3 shows that the degree of gasification increases with temperature in all the cases considered. The degree of gasification of the carbon reaches 100% at close and relatively low temperatures 1,150 and 1,250 K in the gasification of the NBC and EDS, respectively. Thus, for both SF at a temperature exceeding 1,250 K, all the carbon passes into the gas phase mainly in the form of CO (Figs. 1 and 2). Note that in the process of plasma-steam gasification, the degree of gasification of NBC exceeds that of EDS. This is due to the much higher ash content of the EDS. In the case of plasma pyrolysis, the degree of complete gasification of the EDS is achieved at a much lower temperature (2,000 K) than for the NBC (3,500 K). This is due to the higher content of gasifying agent - oxygen in the EDS composition (Table 1).
consumption for the process of steam gasification of NBC and EDS at the temperature of complete transition of uranium-containing compounds to the gas phase (1,750 K) is 2.0 and 0.92 kWh/kg, respectively.

Thermodynamic calculations have shown that the gas phase of the products of plasma-steam gasification of strongly different by composition SFs consists of synthesis gas with a yield of more than 95% achieved in the temperature range 1,300-1,700 K for both types of SF. Uranium oxides, also regardless of SF, go into the gas phase at a temperature above 1,750 K in the form UO, UO2 and UO3. Carbon of the SFs completely passes into the gas phase in the form of CO at a temperature above 1,250 K, which ensures complete gasification of the both fuels.

Specific energy consumption for the process at complete gasification of the SF and the conversion of uranium-containing compounds into the gas phase is relatively low and does not exceed 2 kWh/kg. The specific energy consumption for gasification of high-ash EDS is more than twice lower than those of low-ash NBC.

The results testify to the insensitivity of the plasma technology of SF gasification to the fuels quality.

III. EXPERIMENTAL

Figure 5 shows schematic view of the plasma installation.

![Figure 5. Schematic of the experimental unit for plasma comprehensive processing of solid fuel: 1 – plasma reactor; 2 – gas and slag separation chamber and orifice; 3 – slag catcher; 4 – heat exchanger; 5 – the system of gas flow measure; 6 – water quench chamber; 7 – pulverized coke feeder; 8 – the cooling system; 9, 10 – electric power supply system; 11, 12 – gear for rod electrode supply; 13 – water steam generator; 14 – safety valve; 15 – stand for slag catcher.](image)

The essence of the plasma technology for the production of uranium oxides from SF is in the processing of its mixture with steam in the plasma reactor 1 (Fig. 5). The process of extracting uranium from coal (shale) using plasma heating is carried out as follows.

Coal dust from the hopper 7 enters the plasma reactor 1, where it is mixed with steam. To intensify the interaction of the plasma with the SF, the electric arc rotates by means of an electromagnetic coil and heats uniformly the reaction zone (Fig. 6). Graphite electrodes, rod cathode 5 and ring anode 3, are used in the DC plasma reactor. In the plasma reactor, the steam plasma heats the coal dust to the temperature of the SF gasification and transfer of uranium oxides to the gas phase. As the SF is heated, gasification of its organic mass and sublimation of uranium compounds contained in the mineral part into the gas phase takes place. Then, the two-phase plasma flow (gas phase + molten slag) through the orifice 8 enters the gas and slag separation chamber 9, from where the slag through the outlet pipe enters the slag collector and the gas phase is directed through the exhaust gas outlet to the heat exchanger for cooling and condensation of the targeted products. In the heat exchanger 4 (Fig. 5), the gas phase is cooled to the temperature of uranium oxides (UnOm) condensation. From the heat exchanger 4, the synthesis gas enters the water quench chamber 6.

![Figure 6. Scheme of electric arc reactor with rod and ring graphite electrodes: 1 – vertical reaction chamber; 2 – the bottom of the reactor; 3 – internal ring graphite electrode; 4 - cover; 5 - rod electrode; 6 - the input device of solid fuel and gaseous oxidant; 7 - electromagnetic coil; 8 - the discharge aperture; 9 – an intermediate section for separating the gaseous and condensed phases; 10 - connection of an additional electrode for ignition of an electric arc; 11 - device for moving the electrode; 12 - transformer with isolated neutral (isolating transformer); 13 – controlled thyristor DC power supply; 14 - mixer of pulverized solid fuel and oxidant gas (air or steam); 15 - external thermal insulation of the reaction chamber; 16 - water jets of drop cooling; 17 - superheater; 18 - collection header; 19 – outlet pipe of cooling water; 20 - magnetic field ring capacitor; 21 - retraction of a part of turns of the electromagnetic coil; 22 - short-circuiting key; 23 - annular molten bath of refractory material; 24 – melt release hole.](image)

The main objective of the experiments was to determine the efficiency of the plasma processing of SF for the purpose of extracting uranium into the gas phase and producing synthesis gas. The efficiency of this process is determined primarily by the integral indices of processing: the degree of conversion of uranium to the gas phase (XU), the total degree of gasification of solid fuel (XC), the specific energy consumption (QSP) and the mass average temperature of the process (TAV). These indices can only be obtained on the basis of the material and heat balances, chemical and spectral analysis of the condensed phase of SF processed products.

Chromatograph SRI 8610C implemented gas analysis. Carrier gas is helium or argon, detectors are thermal conductivity sensors. Analysis of light gases H2, CO, O2, N2,
CH4 was provided in columns filled with molecular sieve CaX and analysis of CO2 in silica gel column. Method of absolute calibration was used for experimental data handling. A sampling was implemented in off-gas cooling section 6 (Fig. 5). Composition of the solid residue was investigated using chemical analysis.

Table II presents the experimental results of the plasma processing of EDS, containing 0.02% of uranium (Table I), and comparison with thermodynamic calculations.

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<th>Г1</th>
<th>Г2</th>
<th>Г3</th>
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<tbody>
<tr>
<td>6.60</td>
<td>0.66</td>
<td>0.1</td>
<td>2.700</td>
<td>3.17</td>
<td>78.6</td>
<td>66.4</td>
<td>2.41</td>
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<td>100</td>
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<tr>
<td>4.33</td>
<td>0.43</td>
<td>0.1</td>
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<td>4.41</td>
<td>83.6</td>
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<td>3.41</td>
<td>100</td>
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At plasma-steam gasification of EDS, the degree of conversion to the gas phase of uranium reached 83.6% at average temperature in the reactor of 3,150 K, and the degree of gasification of the shale carbon was 70.4%. The obtained experimental data are in qualitative agreement with the thermodynamic calculations. The calculated integral indices of the processes of plasma gasification of SF, as might be expected, significantly exceed those obtained in the experiment. This is due to the fact that the plasma reactor is not a completely isolated thermodynamic system for which thermodynamic calculations were performed.

IV. CONCLUSIONS

Thermodynamic calculations have shown that the gas phase of the products of plasma gasification of highly different SFs consists of synthesis gas with a yield of more than 95%. Uranium, regardless of the type of SF, enters the gas phase in the form of oxides at temperatures above 1,750 K.

Complete gasification of carbon is achieved at 1,250 K at the steam gasification of both SFs.

Specific energy consumption for the process of plasma processing of fuels is relatively low and does not exceed 2 kWh/kg with complete extraction of uranium into the gas phase.

In plasma-steam gasification of EDS, the degree of conversion to the gas phase of uranium reached 83.6% at a mean mass temperature in the reactor of 3,150 K, and the degree of gasification of the shale carbon - 70.4%.

The experimental data obtained agree satisfactorily with the thermodynamic calculations. Integral indices of plasma processing of uranium-containing SF can be improved by increasing the residence time of reagents in a plasma reactor and reducing its heat loss. To increase the conversion rate of uranium-containing solid fuels the SF: oxidant ratio has to be varied.

The obtained results testify to the insensitivity of the plasma technology of SF gasification to the quality of the initial fuels.

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REFERENCES


