Investigation of physicochemical properties of sludge lignin from Baikalsk Pulp and Paper Mill for assessing the possibility of its use for energy purposes

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Abstract. The paper is focused on the investigations into the properties of sludge lignin accumulated in large quantities in sludge storage pits as a result of the operation of Baikalsk Pulp and Paper Mill. Sludge lignin is a serious environmental hazard for Lake Baikal and therefore the development of effective and environmentally friendly methods for its utilization is an urgent issue. The physicochemical studies of sludge lignin involved the methods of thermal analysis, mass spectrometry and energy dispersive microanalysis, and aimed to assess the possibility of its use for energy purposes.

1. Introduction
During its operation, Baikalsk Pulp and Paper Mill produced about 6.5 million tons of sludge lignin, which is accumulated in storage pits. This poses a serious environmental hazard for the water area of Lake Baikal. The known ways of processing sludge lignin are ineffective, and their development is constrained by RF Government Resolution No. 643 of August 30, 2001, which restricts production activities within the boundaries of the Baikal ecological zone. In this regard, the issue of the development of an environmentally safe technology for sludge lignin utilization is a pressing scientific and applied task. The effective, environmentally safe technology however can only be created when the entire process cycle is considered: starting with the physicochemical properties of sludge lignin and ending with the feasibility study of the proposed technology.

High moisture makes it economically inefficient to transport sludge lignin from the Baikal ecological zone to other areas of the Irkutsk region for processing. It is advisable to have lignin dewatered in the immediate vicinity of the burial site to obtain a dry product, which will significantly reduce its volume and transportation costs. The capacities of the treatment facilities existing in the town of Baikalsk are unable to treat such a volume of slurry water. A possible solution in this situation may be the use of mobile treatment systems. However, sludge lignin contains sulfur and chlorine compounds, which makes the use of mobile treatment systems very difficult. Moreover, there is no available information on the content of sulfur, chlorine, organic matter and other components of sludge lignin. It is also worth noting that the content of the indicated compounds can vary from pit to pit.

Literature presents a small number of studies devoted to the disposal of sludge lignin from Baikalsk Pulp and Paper Mill [1-7]. The mentioned references focus mainly on the issues related to the disposal of the mineral component of sludge lignin, i.e. ash. Consideration is also given to various sludge dewatering methods (freezing, centrifugation). At the same time, there are practically no data on the
physicochemical properties of sludge lignin in the literature, and without them and it is impossible to develop an effective utilization technology.

2. Experimental

2.1. Lignin

Sludge lignin is a colloidal solution of hydrophilic particles of lignin and water, which is characterized by high viscosity and high moisture content (up to 85-90%). The composition of sludge lignin sediment (for storage pits No. 2, 3, 8, 9, 10) includes: lignin substances (50-55%), waste activated sludge (15-25%), cellulose fiber (5-10%), alumina (5-10%), polyacrylamide (5%), other mineral and organic impurities (5%) [6].

Lignin samples were taken from the storage pit No. 3 of the Baikalsk Pulp and Paper Mill landfill. The study of the physicochemical properties employed sludge lignin in the initial state (with a moisture content of 83-87%), air-dry lignin and lignin dried at a temperature of 105°C (Fig. 1).

![Image](image1.png)

**Figure 1.** View of the initial sludge lignin (with a moisture content of 85%) and lignin dried at 105°C.

2.2. Characteristics

Instrumental studies were carried out using a simultaneous thermal analyzer (NETZSCH). The device includes a thermal analysis unit STA 449 F1, a quadrupole mass spectrometer QMS 403 C and a pulsed thermal analysis unit PulseTA. The initial sludge lignin in the amount of 40-50 mg was placed in a corundum crucible and heated from room temperature to 1000°C at a rate of 10°C / min in the air stream. The air flow rate was 70 ml/min. The dried sludge lignin was also burned under the temperature program described above and subjected to pyrolysis. The char produced by pyrolysis was burned under the conditions of the thermal analyzer. In all cases of thermolysis, the resulting gaseous products were recorded with the mass spectrometer (mass 18, 44, 64 for H$_2$O, CO$_2$, SO$_2$, respectively, and 35 ($^{35}$Cl$^-$) or 36 ($^{35}$Cl) for Cl$_2$). The mass spectrometer signal was calibrated by pulsed injection of corresponding calibration gases. The elemental composition of the investigated samples was calculated using the data of simultaneous thermal analysis by the method [8], the chlorine content was not calculated by this method.

The microanalysis was performed using a scanning electron microscope TM 3000 (Hitachi, Japan) equipped with an attachment of energy-dispersive X-ray microanalysis system. This method allows determining both the morphology of the studied sample surface, and the content of all elements in the sample, except H, He, Li and Be. This method was used to study only the samples dried at 105°C.
3. Results and discussion

Figures 2a and 2b show the process of thermal decomposition of the initial sludge lignin in an oxidizing environment. In a temperature range of 35 - 200°C, lignin is dried and a large amount of water (about 85% by mass) is removed, as evidenced by the signal of the mass spectrometer for the corresponding substance. Immediately after drying, the organic matter of the sample begins to decompose to form predominantly CO\(_2\), H\(_2\)O, SO\(_2\) and Cl\(_2\). This process takes place in a temperature range of 200-600 °C. The mass of the organic matter is about 10%. The weight of the residue after the sludge lignin combustion is 3.5%, which characterizes ash content of the studied sample, without converting it to a dry-matter basis.

![Figure 2a. Thermogram of the initial sludge lignin combustion (TG – a curve of sample mass loss, lgA logarithmic curves of variation in ion current of the analyzed compounds).](image1)

![Figure 2b. Thermogram of the initial sludge lignin combustion (TG – a curve of sample mass loss, Ion current – curves of variation in ion current of the analyzed compounds).](image2)

Based on the results of the studies, we determined the elemental composition of sludge lignin, its ash content and moisture content. The content of carbon (54%), hydrogen (4.5%), oxygen (39%) and nitrogen (about 1%) is typical of lignin. The sulfur content is about 0.1%, which, however, is found only in the organic matter of the considered sample, since inorganic compounds start to decompose at higher
temperatures. Sulfur-containing organic compounds are formed under the conditions of sulfate cooking when oxygen atoms are replaced under the action of the nucleophile HS\(^-\) (Scheme 1).

**Scheme 1**

Thermal analysis of air-dry lignin when heated in an oxidizing environment up to 1000°C shows that the main combustion process occurs in a temperature range of 350-750°C, which is accompanied by Cl\(_2\) and SO\(_2\) production. The chlorine production occurs in two stages (Fig.3).

![Mass spectra and thermogram of combustion of dried sludge lignin (TG – curve of sample mass loss, Ion current – curves of variation in ion current of analyzed compounds).](image)

**Figure 3.** Mass spectra and thermogram of combustion of dried sludge lignin (TG – curve of sample mass loss, Ion current – curves of variation in ion current of analyzed compounds).

The moisture content of air-dry lignin was about 7\%, the ash content compared to the initial sludge lignin increased to 32\%. It is known that ash content in commercially produced sulphate lignin is 1.0-2.5\%, and the higher value for the sample at issue is due to the ash admixture.

The elemental analysis of dry lignin with EDXMA is also indicative of the presence of sulfur and chlorine in it (Table 1). In addition, this lignin contains such elements as aluminum, phosphorus and silicon, which is also explained by the admixture of ash and slag waste.

|          | C, %  | S, %  | Cl, % | Al, % | Si, %  | P, %  | O, %  |
|----------|-------|-------|-------|-------|--------|-------|-------|
| Sample 1 | 48.63 | 0.88  | 0.32  | 3.25  | 0.05   | 0.21  | 40.53 |
| Sample 2 | 53.51 | 0.65  | 0.30  | 3.50  | 0.05   | 0.37  | 41.53 |
| Sample 3 | 48.86 | 0.99  | 0.42  | 4.17  | 0.38   | 0.46  | 39.69 |

Compared to the data obtained by the thermal analysis method (0.1\%), the higher values of sulfur content (0.88-0.99\%) based on EDXMA data are due to sulfur distribution in the organic and inorganic
matter of the sludge lignin. The EDXMA method shows the total sulfur content. Accordingly, the sulfur content in the organic matter is 0.1%.

4. Conclusion
The results of the studies indicate that the process of sludge lignin drying does not produce chlorine and sulfur oxides. Thus, the drying can be considered an environmentally safe stage in the overall technology of sludge lignin utilization. For dry lignin, the total sulfur content (organic and inorganic) is about 1%, while for coal this value can reach several percent. As for chlorine, the chlorine content in coal in accordance with the standards of quality indices characterizing the safety of coal products (GOST (State Standard) P 51591-2000), should not be more than 0.60%, and the values for the investigated lignin do not exceed this index.

Thus, the effective drying technology will firstly lead to a significant reduction in the volume and mass of sludge lignin, and secondly, it will allow sludge lignin to be used for energy purposes as a component of mixed fuels with either coal or biomass.

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