Preparation of highly selective sorbents from metallurgical wastes based on cavitation activation of sorption centers

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Abstract. Having analyzed the initial data of RUSAL Krasnoyarsk Aluminium Smelter, we classified 45 types of waste, determined the hazard classes and estimated annual waste accumulation to be stored and disposed of. It has been defined that 14 types of waste can be recycled and reused as constructional materials of various purposes and sorbents for industrial wastewater treatment. In this study, we subjected a lining scrap of various origin, to a complete physical and chemical analysis in order to specify the type of modification and treatment of waste, specifically lining brick scrap, in the Testing laboratory of structural materials and chemical analysis of water of the School of Engineering and Construction, Siberian Federal University, and determined the chemical composition of this waste by the X-ray fluorescence (XRF) method. We also identified the substances suitable for modification of the sorbent – the oxides of aluminium, iron, silicon, and titanium – in the optimal percentage ratio, which resulted in obtaining functional active sorbents with high technical and operational characteristics at low costs for mechanical grinding and activation.

1. Introduction
Taking into account a large amount of metallurgical solid waste, specifically lining brick waste, being more than 14 tons/year, recycling with further reuse as the secondary product in other satellite manufacturing processes is believed to be quite a reasonable technology. One of the promising solutions here is to obtain highly efficient sorbents and use them in industrial wastewater treatment. Both economically and environmentally, it is rational to condition this wastewater for further reuse and closed-loop wastewater management. Process water is essential for many production operations in metallurgical plants, including:
- heat transfer in heating systems, cooling of liquids and solid bodies;
- flushing of gas cleaning filters to remove solid particles;
- surface treatment of heat power equipment;
- washing operations and wet treatment of the territory.

The quality of process water varies depending on numerous production processes; therefore, different technological systems are used in each case of wastewater treatment.

Enhancing wastewater treatment from petroleum products after washing of heat-power equipment requires both upgrading the standard filtration system by implementing new design parameters of the filtering units and utilizing filtration media with high sorption performance.
The double-layer quartz-carbon filters abundantly used are currently unable to provide the required quality of petroleum-containing effluent cleaning neither in accordance with the Russian hygienic regulations 2015 nor with the process water quality requirements. Besides, these filters are very bulky, difficult in operation and are not cost-effective for regeneration.

The standard water treatment scheme can be upgraded with the following structural and technological elements: filtration unit with replaceable cartridges and filtering bed made of the experimentally obtained sorbent based on a modified lining brick.

2. Materials and methods

We propose to use the experimentally obtained sorption bed based on a clay component as a sorbent. The raw material for this sorbent is waste, namely, lining brick scrap, the composition of which is determined by the XRF method (figure 1).

![Figure 1. X-ray fluorescence analysis of the raw materials (lining brick waste)water with surfactants; IV – water for SPS](image)

The obtained granular sorbent has a highly-developed active surface with micro-, meso-, and macropores which provide a high selective-sorption capacity to remove petroleum products and heavy metals from wastewater. The laboratory sorbent was tested in the Research Laboratory of the School of Engineering and Construction of SibFU (Testing laboratory of structural materials and chemical analysis of water). The sorbent was exposed to modifications, such as thermo-acid treatment, alkaline treatment, cavitation activation at 5000 rpm for 90 sec.

We determined core physical and chemical parameters of granules of the sorption material for various types of activation and studied the efficiency of removal of petroleum products and a number of heavy metals from wastewater. The sorbent showed stable activity to Fe, Mn, Pb, Zn, and turned out to be less active with Cu and Ni. The sorption properties of this material are significantly reduced in acidic media, but when a pH value was in the range of 8-9.5, sorption occurred in the optimum zone. The qualitative and quantitative composition of pollutants in the untreated wastewater and in the filtrate was analysed with the use of the standard methods of chemical analysis, IR spectrometry and atomic emission spectral analysis.
3. Results and discussion
The prepared sorbent has a high sorption capacity and its degree of extraction of petroleum products and heavy metals is 25% higher than that of the counterpart. At the same time, microscopy of the laboratory sorbent revealed an aluminium-containing surface layer which allows accelerating sorption based on the electrostatic attraction of pollutants. The results of the preliminary study are given in Table 1.

The cavitation-treated modification of the sorbent appeared to be the most effective. The experimental data are given in Figure 2. But a special focus should be placed on the results of studying the sorption capacity of the activated modified sorbent under various temperature conditions. The experimental data showed that, regardless of the temperature of the water fed to treatment, the efficiency of the sorbent activated by hydrothermodynamic cavitation remains consistently high and equals 86.7%.

Table 1. Characteristics of the sorbent

| Indicator                                      | Modified sorbent – thermo-acid treatment | Modified sorbent – cavitation treatment at 5000 rpm |
|------------------------------------------------|------------------------------------------|---------------------------------------------------|
| Morpho-physical parameters                    | Granules of free form, with the size of 1.15-1.3 mm; colour varies from grey to brown | Granules of free form, with the size of 0.03-0.3 mm; colour varies from grey to brown |
| Sorption capacity (absorptive capacity) for copper, mg/g | 17.52 – 25.6                              | 15.79 – 26.7                                      |
| Temperature of application, °C                 | +4...+25                                  | +4...+25                                          |
| Heavy metal extraction degree                  | 81.2%                                     | 95.1%                                             |
| Cu                                             | 64%                                      | 86.9%                                             |
| Fe                                             | 86.6%                                    | 98.9%                                             |
| Pb                                             | 92.9%                                    | 99.7%                                             |
| Maximum portion of the sorbent                 | 5 – 12.8 g/l                              | 5 – 9.4 g/l                                       |
| Portion of the discharged sorbent              | 0.7 mg/l                                  | 0.68 mg/l                                         |
| The rated height of the sorption bed in the adsorber | Depending on the diameter (D) of sorption filter 0.80 – 1.50m | Depending on the diameter (D) of sorption filter 0.45 – 0.60m |

A comparative analysis of the sorption efficiency is illustrated in the diagram below (figure 2).
**Figure 2.** Industrial wastewater treatment efficiency

**Table 2.** Treatment efficiency

| Line | Initial concentration of petroleum products in the water | Filtering conditions | Final concentration (cavitationly modified sorbent) | Cleaning effect (cavitationly modified sorbent) |
|------|---------------------------------------------------------|---------------------|--------------------------------------------------|-----------------------------------------------|
| 1    | 40 mg/dm³                                               | Standard conditions (+20±2°C) | 1.37 mg/dm³                                      | 96.57%                                         |
| 2    | 40 mg/dm³                                               | Heating (+40±2°C)      | 1.02 mg/dm³                                      | 97.45%                                         |
| 3    | 40 mg/dm³                                               | Cooling up to +0,1…+0,4°C | 5.32 mg/dm³                                      | 86.7%                                          |

4. Conclusion
The advantages of the obtained and sorption bed being studies are its high sorption capacity, the efficiency of extraction of petroleum products and heavy metals, the simple design and easy operation of the sorption filter, the maximum use of the filter capacity, the cost-effectiveness, and which is even more important – the high quality of purified water. Thus, the type of sorbent activated in a cavitation unit based on the hydrothermodynamic effects is recommended to be used as a sorption bed. This type of activation allows developing micro-, meso- and macrocracks on the surface of the sorbent, which undoubtedly leads to an increase in the area of the developed surface and results in an increase in the sorption capacity. During the laboratory tests at a pilot filtering unit, the degree of purification from petroleum products was 86.7% (with the final concentration of petroleum products of up to 0.05 mg/l).

These technical solutions allow achieving the required quality of water for reuse. The main advantages of the proposed sorption materials are:
1. the coal industry waste recycling with set variable sorption parameters (thermo-acid, alkaline or cavitation treatment);
2. Various types of activation of burnt clay enable setting a selectivity of sorption with a simultaneous increase in sorption capacity—the degree of extraction of petroleum products is 95% at the maximum designated portion of the sorbent.

The introduction of a cluster of similar sorption filters for industrial wastewater treatment and conditioning of process water will make possible to form a closed-loop water use cycle and significantly reduce operating expenses of the enterprise.

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