

ENVIRONMENTALLY CLEAN INCINERATION OF ORGANIC SLUDGES CONTAMINATED WITH CHROMIUM IN A FLUIDIZED BED

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The Republic of Belarus has a large-scale leather industry. The production is accompanied by accumulation of a large amount of leather waste per annum. Only one big factory in Gatovo near the city of Minsk produces more than 20 000 tons of waste. It has a calorific value of 21,9 MJ/kg on dry basis and ash content 38,8 %. Up to the present time, this leather waste has been considered as rubbish. Its disposal has become a very pressing environmental problem. As a result, incineration is seen as a future alternative for sludge disposal. But incineration itself is faced with the problem of emission limits that requires further creative efforts to lower the ejection of poisonous gases and satisfy requirements on solids waste.

The purpose of the present communication is to suggest the results of research on burning the leather processing sludge in relation to its environmental impact and to benefit from leather waste as a fuel. Since little knowledge has been accumulated to date on remedial acting technologies for burning such sludge contaminated with chromium, various methods were subjected to laboratory-scale tests.

It was advisable to co-fire leather waste with a coal. Under such conditions Cr(III) is not transformed into Cr(VI) and ash obtained can be used in production of refractory materials.

The determination of the temperature and time limits of the main stages of physicochemical conversions of the sludge was performed by the method of derivative thermogravimetry (DTG). A thermal analysis was performed for specimens of the original sludge (1), and the sludge with the addition of 25% of hydrolyzed lignin (2) and of brown coal (3).

Common to all the three specimens is the presence of two thermal effects: endothermal and exothermal. The transition of the former into the latter is associated with oxidation of the organic part of the specimens by air oxygen. It is specific for each specimen and is most vigorous in specimen 1, virtually terminating at 440° C. A small amount of pyrocarbon is formed in this case the removal of which continues up to 740°C. Oxidation of the organic part of specimens 2 and 3 occurs gradually and involves a wide temperature region. While its beginning is fixed equally at a temperature of about 300°C, the termination is observed at temperatures 660 and 760°C, respectively, not only indicating the difference in the amount of the pyrocarbon formed, but also its different proclivity to chemical interaction. The optimum temperature of burning sludge from perspective of the presence of pyrocarbon in the system is about 750°C in the case of the addition of brown coal and about 650°C on addition of lignin. When the system is heated above 440°C without a carbon-containing admixture, an insignificant amount of pyrocarbon is formed leading to the oxidation of chromium (III) into chromium (VI).

These assumptions about the conversions occurring in the system confirm the results of experimental investigations on a laboratory fluidized bed rig. Different specimens of leather waste were burnt whose main characteristics are presented in Table

1.

Table 1. Physicochemical Characteristics of Chromium-containing Sludge (I,II,III)

Parameter	I	II	III
W ^p , %	50.2	75.0	25.0
A ^p , %	4.5	8.8	26.5
V ^p , %	43.0	12.0	36.1
C ^p , %	35.2	12.5	37.5
H ^p , %	3.6	1.4	4.2
N ^p , %	0.7	0.5	1.5
S ^p , %	0.9	0.2	0.4
O ^p , %	4.9	1.6	4.9
Q ^p , MJ/kg	13.2	3.7	16.4

We carried out the analysis of the specimens of ash calorimetrically using diphenylcarbazide. The ecological effectiveness of the process is characterized by the quantity E:

$$E = \left(1 - \frac{\text{Chromium VI}}{\text{Chromium general}} \right) \cdot 100\%$$

The results obtained are presented in Table 2.

Table 2. Chromium YI-related Ecological Effectiveness in Fluidized-bed Burning of Sludge

($\alpha=1.0-1.2$)

Ordinal N	Specimen	Temperature, °C	In a reactor			In a cyclone		
			Chromium YI	Chromium general	E	Chromium YI	Chromium general	E
1	11	750	1.4	7.2	80.55	1.3	7.5	82.7
2	II	800	1.25	7.3	82.9	1.6	8.5	81.2
3	11	850	2.3	8.1	71.6	1.8	8.4	78.6
4	II	900	2.8	7.2	61.1	1.6	7.1	71.5
5	in	800	0.9	8.2	89.0	0.9	7.25	87.6
6	I	800	0.2	3.6	94.5	0.1	3.2	96.9
7	I+25 wt.% brown coal	800	0.1	3.3	97.0	0.05	3.2	98.5
8	II+25 wt.% brown coal	750	0.3	7.8	96.1	0.25	8.2	97.0
9	II+25 wt.% brown coal	800	0.25	5.4	95.35	0.5	9.2	94.6
10	II+25 wt.% brown coal	850	0.6	6.8	90.9	0.5	6.0	91.7

11	II+25 wt.% brown coal	900	0.75	7.2	89.6	0.8	7.5	89.3
12	II+25 wt.% brown coal	800	0.9	7.5	88.0	1.1	7.85	87.0
13	II+25 wt.% hydrolyzed lignin 800	1.35	6.9	80.4	1.5	7.7	80.5	
14	II+25 wt.% coke	800	1.4	7.6	81.6	1.25	7.4	83.1

As is seen the addition of 25 % of brown coal to the leather processing sludge substantially, up to 0.7-0.8% (0.5 % chromium YI and 8.7 % chromium III) preserves chromium III, available in the system, from oxidation. Comparison with the data on the composition of ash formed in an industrial rotary furnace reveals that in this case the chromium YI-related ecological efficiency does not exceed 75-79 % (2.3 % chromium YI and 7.0-8.5 % chromium III).

It is interesting that preliminary temporary heating of the sludge decreases the content of chromium YI in ash through not to such an extent as in the case of adding brown coal. Some increase in the content of chromium YI in ash taken from the reactor, as compared with that taken from a cyclone, is associated with a partial oxidation of chromium III contained in ash particles that remain in the fluidized bed. Obviously, the developed design of a facility for fluidized-bed combustion of the sludge foresees the maximum entrapment of ash from the bed to decrease the possible oxidation of chromium III.

Thus, when burning the sludge in a fluidized bed with addition of 25 % brown coal a chromium-containing ash of the IYth group of toxicity (low-hazard) is formed allowing one to run the equipment and utilize waste adhering to usual sanitary norms.

Analysis of the products of burning specimens the sludge shows that the degree of desulfurization attains 97 % due to an elevated content of calcium oxide CaO in ash: S=10.5-12.5. The degree of the conversion of fuel nitrogen into NO_x does not exceed 8 % and depends little on temperature, since nitrogen oxides are formed predominantly due to the oxidation of nitrogen-containing compounds.

Visual observations of fluidized-bed combustion of the leather waste particle show that the skeleton of the mineral portion (ash) does not disintegrate, whereas the core of the combustible components burns out. Burning follows the scheme of a "unreacted core" and it is this scheme which is used for processing kinetic data [3]. In this case it is assumed that the fixed portion of combustible coke particles that remained after the efflux of volatiles consists mainly of carbon that in the process of burning is oxidized to carbon dioxide. The mean efficient rate of the diffusional-kinetic regime of burning of leather waste particles is 0.04-0.07 m/sec when the bed temperature changes from 700 to 800°C and the size of particles changes from 6 to 25 mm, however, as the temperature increases, the rate of burning of the sludge increases more slowly than the rate of burning of coal under similar conditions (0.18—0.40 m/sec) being explained by the effect of the intradiffusional retardation of burning by a bed of coal residual.

In view of the standardization of the content of chromium and other metals that enter into the composition of ash, the proposed ways of its subsequent treatment should take into account the possibility of the minimum transition of these metals from the articles produced into the surrounding natural medium. Preliminary investigations showed that the chromium-containing ash formed may serve as one of the components for the production of refractory materials.

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