The article presents the results of a study of high-agglomeration unburned waste coal flotation with the development coal-mineral briquette. The technology is that the process of removing moisture is carried out without external supply of heat or coolant and heat generated due to stirring with a dehydrating component (lime dust - waste from the production of burnt lime CaO not less than 70%) due to the exothermic reaction, and heating binder, which is used as the prepared coal resin by heat generated by the implementation of the chemical dehydration. Combining chemical processes of dehydration hydration of lime materials, curing mixture molding processes allow to obtain chemically bonded agglomerated material strength, satisfying the requirements of metallurgical production. The optimum temperature and time parameters of the process and the equity ratio of lime dust, coal tar and dissected initial moisture content of waste coal flotation in achieving their high strength.

Keywords: waste flotation coal, coal-mineral briquette, dehydration, chemical dehydration, coal tar, a binder.

INTRODUCTION

Waste coal flotation is highly dispersed, soaking, swelling ability, etc. In general, flotation waste is represented by particles with a particle size <74 μm. Complex mineralogical and petrographic analyzes show that the main mineralizing component of flotation waste is a clay substance (up to 92%), in smaller quantities quartz and carbonates are contained. The content of combustible mass (carbon) in waste is 35-50%. The sulfur content is much lower than in the breed of large classes. The predominant amount of clay substance in flotation tailings, compared to other carbonaceous wastes, makes them a plastic material.

These properties of the waste make it difficult to separate the phases during the flotation process and then dehydrate the resulting products to a transportable state that allows them to be removed from the enterprise by belt conveyors, by road or rail. Therefore, dewatering of flotation residues at coal preparation plants, near which there are opportunities to seize unused or low-value agricultural lands, is carried out in tailing dumps. A small concentration of solids in the pulp and poor sedimentation require a long service life of these facilities to a full concentration of waste and the possibility of cleaning them for reuse.

All the complexity in the disposal of liquid wastes of metallurgical production, which include flotation waste, in wet coal enrichment processes lies in the fineness and their high humidity, which requires the use of expensive and complex systems of preliminary dehydration and preparation technologies. At present, a number of technological processes for the processing of dusts and sludges into the conditioning materials of ferrous metallurgy, often with simultaneous separation of non-ferrous metals, have been proposed, tested and introduced into industrial practice [1-7]. With the disposal of these technogenic products, non-firing agglomeration methods are increasingly used, the application of which increases the efficiency of waste processing. A number of such methods have been introduced into industrial practice [1-5].

At the same time, with regard to non-burning agglomeration, its cardinal advantages in comparison with high-temperature methods (agglomeration and roasting of pellets) in the main technical and economic (prime cost, capital and current costs, energy consumption, technological fuel numbers, etc.) and environmental indicators (3-5 fold decrease in the degree of environmental pollution) are shown repeatedly, for example in [4-7], and are not disputed by anyone. With a moisture content of 25-30%, the water separation in flotation waste is almost stopped, the waste acquires flowability. The studies were based on the conditions for obtaining in flotation waste or
their mixtures the moisture required for normal briquetting and utilization in metallurgical production.

1. Theory of dewatering of flotation waste coal

The hardening of the sludge-limestone mixture is a consequence of the physico-chemical processes taking place in the salt-water system, of which the components CaO, SiO2, Al2O3, Fe2O3, H2O, etc. are compounds contained in man-made production waste. According to the colloid-chemical theory of hardening of hydraulic binders AA. Baikova chemical transformations occurring when mixing lime with a slurry of high humidity can be expressed by the following reaction:

\[ 3\text{CaO}.\text{SiO}_2 + 4.5\text{H}_2\text{O} = \text{CaO}.\text{SiO}_2.2.5\text{H}_2\text{O} + 2\text{Ca(OH)}_2 \]  

(1)

However, calcium hydrosilicate in water is very slightly soluble and remains in the colloidal state for a long time, gradually recrystallized, and then compacted and hardened. Phenomena as a result of which the cement dough acquires coherence and strength and turns into a solid monolithic body, is, according to A.A. Baikov, a purely physico-mechanical character. Chemical processes are completed within a few hours (not more than a day) after the interaction of the binder, in our case of pulverized lime, with the water of the slurry with the formation of a fragile loose mass. Turning it into a stone-like body occurs mainly during the next few hours or days due to the formation of a crystalline splice of hydroxide and calcium hydro-silicates. The crystallization period is the longest and is characterized by a negligible release of heat.

When the binder interacts, in our case of pulverized lime, with slurry water, there is a so-called preparatory period in which a saturated solution forms. The heating of the mixture at this point is insignificant, since the dissolution process is endothermic. Only when saturation is achieved, the cement dough is quickly heated by the hydration reaction. Depending on the conditions (mineralogical and disperse composition, initial slurry moisture and mixing speed), the intensity and speed of hydration varies.

The process of chemical dewatering of flotation waste flows in the kinetic region and is characterized by exothermic reaction of the dehydrating component with water with formation of calcium hydroxide by reaction (1) and is accompanied by an increase in temperature and the rate of dehydration.

2. The experimental part

The heat released in the process of phase interaction goes to the evaporation of moisture. There is a removal of the bulk of moisture, accompanied by a rapid dehydration rate and ending when the maximum temperature of the mixture is reached. Similar results were established in the works conducted by the NGO "Tulachepeet" [6,7]. Experiments on dewatering were carried out in sequence with a change in the main parameter of the process-the initial moisture content of the flotation waste.

The maximum temperature was observed during the first 5 minutes after the mixing and reached 100-108 °C in mixtures with a volume ratio of 1: 1.5, 1: 2 (66.88%). The dynamics of temperature change in mixtures shows that the main part of moisture evaporates during the first 5-10 minutes and cooling to room temperature was fixed in the middle 1.5 - 2 hours after the mixing. This is due to the flow of the process in the diffusion region, the essence of which is as follows. The process of binding residual moisture is controlled by diffusion transfer of water molecules through a thin diffusion pore layer that forms on the surface of the dehydrating material particles at this time point. The fine surface, permeate layer consists of crystallized hydroxide and calcium carbonate...
formed as a result of the flow of the reaction of calcium hydroxide absorption of carbon dioxide from the surrounding atmosphere by reaction:

$$\text{Ca (OH)}_2 + \text{CO}_2 = \text{CaCO}_3 + \text{H}_2\text{O}$$ (2)

From the results of experiments it follows that the highest rates of dehydration were observed when preparing mixtures with a volume ratio of 1: 1.5, 1: 2, which is explained by the rapid flow of exothermic reaction between active CaO and water of the coal-dressing slurry. The intensity of the process of chemical dehydration depends on the type of dehydrating materials used, the activity of CaO, MgO, their fractional composition, and the degree of mixing of the main components determined by the maximum region of contact between the reacting phases.

The chemical compositions of some mixtures, which are presented in Table 1, have been selected selectively. The chemical composition data determine the possibility of using float-lime mixtures in the metallurgical range, in particular in agglomeration and steelmaking industries.

**Table 1. Chemical Composition of Flotation and Limestone Mixtures**

<table>
<thead>
<tr>
<th>Ratio of flotation and lime waste</th>
<th>The initial moisture content of the flotation waste</th>
<th>C&lt;sub&gt;общ&lt;/sub&gt;</th>
<th>CaO</th>
<th>SiO&lt;sub&gt;2&lt;/sub&gt;</th>
<th>FeO</th>
<th>MgO</th>
<th>AL&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
<th>P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</th>
<th>Losssonig nit</th>
<th>tion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:0.5</td>
<td>20</td>
<td>32.85</td>
<td>22.59</td>
<td>16.99</td>
<td>1.50</td>
<td>0.56</td>
<td>6.96</td>
<td>0.085</td>
<td>49.62</td>
<td></td>
</tr>
<tr>
<td>1:1.0</td>
<td>20</td>
<td>25.67</td>
<td>32.12</td>
<td>12.84</td>
<td>1.06</td>
<td>0.58</td>
<td>5.29</td>
<td>0.080</td>
<td>46.03</td>
<td></td>
</tr>
<tr>
<td>1:1.5</td>
<td>20</td>
<td>22.50</td>
<td>42.70</td>
<td>11.19</td>
<td>1.03</td>
<td>0.50</td>
<td>4.48</td>
<td>0.073</td>
<td>43.06</td>
<td></td>
</tr>
<tr>
<td>1:2.0</td>
<td>20</td>
<td>17.30</td>
<td>44.15</td>
<td>7.83</td>
<td>0.81</td>
<td>0.52</td>
<td>3.08</td>
<td>0.066</td>
<td>39.95</td>
<td></td>
</tr>
<tr>
<td>1:0.5</td>
<td>25</td>
<td>30.35</td>
<td>23.05</td>
<td>18.66</td>
<td>1.63</td>
<td>0.74</td>
<td>6.70</td>
<td>0.096</td>
<td>46.86</td>
<td></td>
</tr>
<tr>
<td>1:1.0</td>
<td>25</td>
<td>25.90</td>
<td>33.22</td>
<td>14.38</td>
<td>1.16</td>
<td>0.62</td>
<td>5.60</td>
<td>0.082</td>
<td>44.55</td>
<td></td>
</tr>
<tr>
<td>1:1.5</td>
<td>25</td>
<td>22.67</td>
<td>41.14</td>
<td>12.74</td>
<td>1.28</td>
<td>0.66</td>
<td>4.98</td>
<td>0.082</td>
<td>41.86</td>
<td></td>
</tr>
<tr>
<td>1:2.0</td>
<td>25</td>
<td>24.39</td>
<td>37.22</td>
<td>12.13</td>
<td>0.63</td>
<td>0.89</td>
<td>4.54</td>
<td>0.080</td>
<td>40.78</td>
<td></td>
</tr>
<tr>
<td>1:0.5</td>
<td>30</td>
<td>32.94</td>
<td>19.20</td>
<td>17.62</td>
<td>1.60</td>
<td>0.72</td>
<td>7.21</td>
<td>0.105</td>
<td>49.44</td>
<td></td>
</tr>
<tr>
<td>1:1.0</td>
<td>30</td>
<td>23.99</td>
<td>39.03</td>
<td>12.98</td>
<td>1.19</td>
<td>0.51</td>
<td>4.70</td>
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<tr>
<td>1:1.5</td>
<td>30</td>
<td>22.84</td>
<td>34.68</td>
<td>11.96</td>
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<td>0.61</td>
<td>4.89</td>
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<td>42.83</td>
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</tr>
<tr>
<td>1:2.0</td>
<td>30</td>
<td>21.25</td>
<td>46.37</td>
<td>10.52</td>
<td>1.02</td>
<td>0.43</td>
<td>4.14</td>
<td>0.071</td>
<td>42.17</td>
<td></td>
</tr>
</tbody>
</table>

The optimal ratio for mixing the original components were 1: 1.5; 1: 2, in which self-depositing pulverized mixtures of the "fine sand" type were obtained. According to the results of work at the Dnipro Metallurgical Combine, a mixture with such a ratio of carbon-bearing and lime-containing materials can be successfully applied in convection melting [8]. In a 1: 1 ratio, mixtures with more coarse particles, such as "fine sand", were obtained. In mixtures with a ratio of 1: 0.5, a large "lump" formed about 10 mm in size (especially in mixtures with an increased initial moisture content of the flotation waste), which were easily broken by mechanical action. All mixtures did not have a tendency to dust. This is due to the presence of clay components: Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, which form CaO and MgO silicates, aluminates and calcium and magnesium in calcareous dust, in addition to active oxides of CaO and MgO. These compounds, when in contact with water, are rapidly solidified in the air.

The heat released during the reaction of calcium and magnesium oxides with water is consumed by the evaporation of water, which accelerates the drying of the mass. The established
characteristics of the process of chemical dewatering of waste flotation by pulverized lime served as a basis for the technology of their preparation for disposal at JSC "ArceorMittal Temirtau", in particular, for the production of coal mineral beets from them.

3. Energy-saving way of processing of coal slimes

Analysis of the known methods of agglomeration of coal enrichment wastes [9, 10] showed that the production of a solid agglomerated material (briquettes) from high-moisture coal slimes is achieved when the sludge is pre-dried to a residual moisture of about 10%, binding binders mainly in the form of coal tar and their derivatives and preheating the batch to the melting temperature of the binder component. Therefore, we set the task of developing a method that has low energy consumption and a simplified technology for processing coal slurries of high humidity during the disposal of pulverized lime production waste.

As the results of the research have shown, the best results are achieved by using chemical dewatering (drying) of high-moisture coal flotation waste using pulverized calcined lime (pulverized lime) waste and as a binder of a small amount of coal tar (3-5%).

The essence of the proposed method consists in combining the processes of chemical dewatering of coal slurry with shaping, and as a chemical dewatering agent, dust-like lime, which is trapped from the waste gases during calcination of limestone in lime kilns by dry dust-gauging apparatus, is used as a binder pre-dispersed to 0-1 mm prepared coal tar at a rate of 3-6% and kept for 15 minutes at a temperature of 100 - 110 °C and then pressed with a or 250-350 kg / cm2. In the proposed method, the drying of coal slurry (flotation waste coal) of high humidity is carried out at the expense of the heat released during hydration of pulverized lime, and the heat released during chemical dehydration is also used to heat the coal tar at a temperature of 100-110 °C. To obtain strong, well-formed briquettes, a mixture of 3 components is mixed in the mixer for 5-6 minutes and held for 15-20 minutes and then without cooling the mass is pressed (molded) on a roller press at a pressure of 250-350 kg / cm2.

The essence of the method is based on the established new regularities of the process of moisture removal by chemical bonding it with the dewatering component (hydration) and hardening of the mixture that were established by our studies [6, 11,12]. In addition, lime performs the functions of the binder as it relates to air binding materials and facilitates the cementation of the crystallized particles of flotation waste into the conglomerate and the conditions for obtaining strong coal-mineral briquettes are improved.

To ensure better compressibility, the mass is held at these temperatures for 15-20 minutes. With these parameters, the resin passes into a plastic state, in which its astringent properties are improved. In addition, as the temperature increases, the plasticity of the coal enrichment waste increases, which increases the strength of the briquettes. On the other hand, as the temperature is raised, the viscosity of water decreases and it is easier to leave it from the capillaries to the surface of the particles. The increase in the strength of briquettes from heated materials is also explained by the fact that during pressing, stronger covalent bonds arise between the functional groups of the macromolecules of coal. At the same time, the optimal ratio between the mass fraction of calcareous dust and coal tar (mass, %) from the moisture content of flotation was established (Tabl.2).

The novelty of the proposed technical solution lies in combining the hardening processes of the slurry-limestone mixture with the shaping processes, which is achieved in accordance with the proposed method for mass pressing in molds. To obtain strong briquettes that are stable to atmospheric precipitation and transportation, a binder in the form of a prepared coal-tar mixture in an amount of 3-6% is introduced into the lime-mud mix with stirring, which is heated by the internal heat released during chemical dehydration by reaction (1) with pulverized lime with the content of CaO (more than 70%), i.e. without supply of heat from outside.
4. Discussion of results

The results of pilot studies at these optimal temperature and time parameters of the process and the proportional ratios of pulverized lime, prepared coal tar and the initial moisture content of flotation waste of coal have shown that high strength of coal-mineral briquettes is achieved in the absence of weight loss of the mass during pressing. Moreover, the content of calcium oxide in the dewatering component (pulverized lime) should be at least 70%.

When the duration of the temperature holding of the mixture is less than 15 and more than 20 minutes, with the remaining parameters within the optimal limits, a low strength of the briquettes, which tend to spill, is obtained. With a mass fraction of coal tar in a mixture of less than 3%, the required strength of the briquettes is also not ensured. With a mass lime dust content of less than 10%, and with a calcium oxide content in pulverized lime of less than 70%, the complete chemical dewatering and hardening of the mixture is not ensured, which also leads to insufficient strength of the coal-mineral briquettes produced and mass losses of the mixture during compression are observed. The mass fraction of calcareous dust in a mixture of more than 25% is undesirable, since this leads to a reduction in the heating value of the briquette.

Studies have shown that the strength of beets is affected by the granulometric composition of the initial components. In the presence of increased content of large particles in them, the number and dimensions of the voids in the mass to be massed increase, and the part of the processing energy is stopped for the dissolution of a certain fraction of large grains and the filling of voids. Therefore, the strength of the purchased beets will be lowered. On the basis of the experiments performed, it is possible to distinguish the most optimal ratios of components in the mixture to be processed at a temperature of 110 °C and a discharge time of 15 minutes.

The innovative method of the patent of the Republic of Kazakhstan No. 21583 for the invention "Method for processing coal slime" was obtained on the developed method [13]. Based on the study of the smolomagnesite shop of JSC "ArcelorMittal Temirtau", which has press equipment, an industrial technological scheme for production of coal-minerals briquettes for steelmaking production was developed (Fig. 1). Coal minerals can be used as deoxidizing, refining and fuel materials.

Conclusion

The proposed method is characterized by a new set of characteristics:
- the process of moisture removal is carried out without external supply of heat or coolant;
- The heat necessary to remove excess moisture from the coal slurry is released when it is mixed with the dewatering component as a result of the exothermic reaction;
- as a dewatering component, waste from the production of calcined lime in the form of pulverized lime, trapped from dusty process gases when calcining limestone in lime kilns in dust-gas-cleaning devices with a high content of calcium oxide (CaO at least 70%) is used;
Fig.1. Technological scheme of processing of coal slimes.

- the heating of the binder, in which quality the prepared resin is used, is produced with mixing due to the heat of chemical dehydration released during the process and its flow in the kinetic region; Fifth, the prepared coal tar is pre-dispersed to 0-1 mm.

The following optimal process parameters were established: the preheating temperature before pressing 100-110 °C, the holding time 15-20 min, as well as the ratio of the consumption of pulverized lime, prepared coal tar, depending on the initial moisture content of coal flotation waste.

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Article accepted for publication 11.06.2018