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APPLICATION OF PAPER MILL SLUDGE AND ADDITIONAL CHEMICAL SUBSTANCES IN THE PRODUCTION OF CONTAINER CARDBOARD

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The possibility to dispose of paper mill sludge as part of a composition of container cardboard from secondary raw materials has been investigated. The fractional composition of the sludge was studied and it was shown that the main part of the fibers is represented by small particles with a size of up to 1.2 mm. Studying the processes of formation of container cardboard when using paper mill sludge showed that an increase in the consumption of fibrous-inorganic waste leads to a deterioration in the physical and mechanical properties of cardboard. However, the increase in sludge consumption does not affect the surface absorption of water during one-sided wetting. The value of these indicators is within the normal range and is 25 and 70 g/m^2, respectively. In addition, an increase in sludge consumption from 10 to 50 % in the manufacture of cardboard leads to a decrease in the degree of fiber retention on the grid from 86.3 to 82.1 %. Regularities of using strengthening additives, namely industrial cationic and anionic flocculants, as well as native corn and modified starches for the strength of cardboard and the quality of sub-grid waters, have been established. Research results show that the effect of flocculants is quite ambiguous. On the one hand, there is a clearly observed positive impact on the quality of the sub-grid waters. This is due to the reduction of their turbidity due to smaller fiber washes. Nevertheless, the positive effect on physical and mechanical parameters is minimal, and in some cases, there is a decrease in strength indicators. The greater the efficiency of keeping fine fiber on the grid when using flocculants, the lower the values of physical and mechanical indicators. In general, when using sludge in the composition of cardboard in combination with flocculants and starch, the indicators were achieved that are considered standard for waste paper container cardboard of grade KT-1 according to TU U 17.1-41085075-002:2017

Keywords: fiber sludge, container cardboard, wastepaper processing, flocculant, Praestol, Percol, Polimin

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1. Introduction

The volume of production and use of cardboard and paper products in the world is growing annually. Although the introduction of multimedia and computer technologies has reduced global consumption, and therefore the production of certain types of paper, such as newsprint, the production of wrapping paper and cardboard is steadily growing. Moreover, the production of cardboard and paper articles from secondary fibers (wastepaper) is growing rapidly – about twice as fast as paper production from primary cellulose fibers due to both economic and environmental factors [1, 2].

The main feature of secondary cellulose fibers is the initially slightly lower physical and mechanical properties compared to the primary fibers. This is due to the influence of the technological stages of preparation of the fibrous mass, as well as the formation, pressing, and drying of paper or cardboard. In addition, further paper and cardboard recycling processes contribute to the fact that the fibers acquire new properties. All this is the cause of the low strength of individual secondary fibers. As noted by the authors of work [3], secondary fibers are characterized by low ability to swelling, fibrillation, a propensity to shorten, and the loss of ability to form hydrogen bonds.

The composition of wastepaper in terms of fiber is a heterogeneous raw material as it is characterized by a high content of short fibers and impurities of various nature. An increase in the volume of fibers in the paper pulp has a significant impact on the process of forming the canvas and, as a rule, it worsens it due to a decrease in the fiber retention on the grid, resulting in increased pollution of wastewater. Sludge, which is formed in the processes of wastewater treatment, is characterized by high humidity, which can reach 99 %; it is a multi-tonnage waste from the production of paper and cardboard of a fibrous-inorganic nature, which need to be disposed of [4].

Research aimed at ensuring the resource efficiency of technological processes in paper production by reducing the use of expensive fibrous raw materials and fresh water is extremely relevant.

2. Literature review and problem statement

Incineration and disposal are the two main ways to further handle the sludge. However, they are economically and environmentally unprofitable. The main problem related to the effective disposal of sludge is high humidity (93–98 %), which must be eliminated by dehydration. The authors of work [5] propose to use mechanical methods to dehydrate the sludge. However, characteristic of fibrous-inorganic waste from paper production is the poor ability to dehydrate because of the high content of colloidal substances. Scientists have developed many ways to dispose of sludge, including for the production of biofuels by gasification or the use of enzymes. In [6], it is noted that the paper mill sludge can be a substrate for the production of bioethanol using enzymes. However, the main disadvantage of the proposed technology is the high content of mineral components in the substrate, as a result of which the yield of biofuels is quite low. In the case of using enzymes, the inorganic component acts as an inhibitor of biochemical processes. The authors of work [7] propose to use sludge to produce biomass. However, the calorific value of the resulting fuel is quite low, which indicates its low caloric content.

It is possible to use sludge as part of building materials, organic and inorganic composites. Examples of the implementation of this approach in the disposal of sludge are described in work [8], the authors of which performed a thorough analysis of the methods of preparing the sludge, its activation and use in cement compositions. However, these techniques require preliminary dehydration of the material, the organization of which requires significant investments for the arrangement of drying plants and power boilers. Paper [9] reports the results of the use of fiber-inorganic waste in the composition of epoxycomposites. Samples of materials with increased resistance to aggressive media but with unsatisfactory physical and mechanical parameters, were obtained. In addition, the implementation of this technique requires the use of the dehydration and drying stage to ensure effective mixing of the hydrophobic components of the epoxycomposite. In [10], the possibility of using sludge in the production of wood-plastic materials for construction needs has been investigated. However, the effectiveness of this approach is in doubt since the introduction of sludge has led to a decrease in tensile strength, bending and impact of the resulting composite materials. None of these methods has found industrial implementation and the most common way to dispose of sludge is to bury it, which requires expansion of landfill areas.

Another example of the possible disposal of sludge is its use as fertilizer, as noted by the authors of work [11]. The results of their research also indicate that in terms of nutritional value, it is significantly inferior to synthetic fertilizers.

For enterprises in the paper industry, in order to reduce energy and resource costs for dehydration and transportation of sludges, it is necessary to establish its effective disposal directly at the sites of formation. It will also avoid the need to expand landfills of fiber-inorganic waste. Effective disposal of sludge can be realized by returning it to the technological process as a component of paper pulp in the manufacture of paper and cardboard. However, its use is effective and does not lead to a deterioration in the performance of finished articles subject to applying not more than 10 %. The results of work [12] indicate that exceeding this value has a negative impact on the strength indicators and on the composition of wastewater in the relevant industries.

Designing an effective composition of cardboard using sludge could enable resource-saving production by saving cellulose fibers.

3. The aim and objectives of the study

The aim of this work is to determine the effect of sludge consumption and flocculating and starchy substances on the efficiency of making container cardboard from wastepaper. This will make it possible to ensure resource savings in the technological processes of cardboard production, which will not only contribute to greening but also have a positive impact on the cost of production.

To accomplish the aim, the following tasks have been set:

– to investigate the fractional composition of industrial sludge and establish its impact on the quality indicators of the finished cardboard and on the quality of wastewater;

– to investigate the influence of industrial flocculants on the quality indicators of manufacturing container cardboard from wastepaper using sludge;

– to investigate the influence of starches on the quality indicators of manufacturing container cardboard from wastepaper using sludge;

– to investigate the feasibility of simultaneous use of starches and flocculants in the production of container cardboard from secondary fiber using sludge.

4. The study materials and methods

The object of this study was laboratory sheets of container cardboard and sub-grid water from the production of cardboard.

The hypothesis of the study assumed that the introduction of sludge in combination with chemical reagents could improve the physical and mechanical performance of cardboard while the selection of an effective flocculant would reduce the turbidity of sub-grid waters.

To perform the experiments, we used wastepaper of different brands as a raw material (secondary fiber), taken in the same ratio. The industrial sludge from PJSC "KCPM" (Obukhiv, Ukraine) with a dry matter content of 16.2 g/dm^3 and a content of ash substances of 30.5 % was used in the composition of cardboard with a consumption of 15–50 %. Bleached sulfate cellulose from coniferous wood and bleached sulfate cellulose from hardwood (primary fiber) were used for comparison.

The primary and secondary fibers were first soaked for 15–20 minutes. Then part of the suspension was dispersed to prepare a 0.1 % suspension to determine the fractional composition at the FS-100 apparatus of the company "Kajaani" (Finland). The fibrous suspension was also dissolved in a hydraulic breaker and then ground at a disc mill to obtain waste paper mass. The degree of waste paper pulp was 32 °SR. For the preparation of samples of container cardboard, compositions of wastepaper mass with different consumption of sludge from 5 to 50 % and with different consumption of auxiliary chemicals were used.

In the studies, we used flocculants from Stockhausen (Germany), the Praestol-650VS type; Shiba (Germany) the Percol-455 type, Zetag-7563, and Magnoflok-10 from BASF (Germany), the Polimin SK type. Praestol-650VS flocculants with a molecular weight of ~ 600×10^3, Percol-455, and Zetag-7563 with a molecular weight of ~ 5–20×10^6 are cationic polymerization products of acrylamide monomer. Flocculant Polymin SC is a linear polyethyleneimin with a molecular weight of ~300×103. Flocculant Magnoflok-10 refers to anionic flocculants with a molecular weight of ~ 2–15×10^6. As a firming additive, native cornstarch and modified starches were used at different consumption. Phosphorylated starch of the company "Modifier" (Ukraine) of the CMS type, cationic starch of the company "Ograna" (Austria) of the type Cationamyl-8425 based on corn starch, and highly catalytic starch of the company "Ceresan" (Germany) of the type Ceresan MK were used at a consumption of 0.7–1.3 %.

After making the cardboard composition, the mass was kept for 15 minutes with constant stirring to ensure the effective adsorption of auxiliary substances on cellulose fibers. The mass of 1 m^2 of container cardboard was 125 and 230 g. Studies of physical and mechanical indicators of cardboard samples were carried out in accordance with international procedures [13]. During the manufacture of cardboard samples, samples of wastewater were taken to determine its turbidity [14].

5. Results of studying the effect of sludge and auxiliary chemicals on the efficiency of the manufacture of container cardboard

5. 1. Results of studying the influence of sludge on the quality indicators of container cardboard and on the quality of wastewater

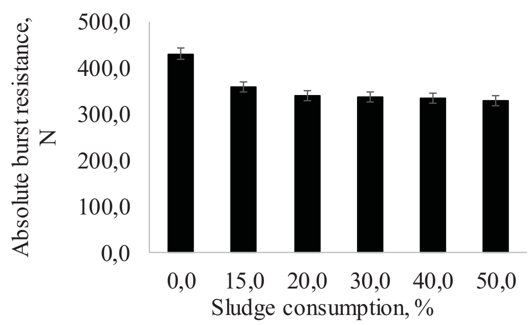
The main raw material for the manufacture of container paper and cardboard in Ukraine is waste paper, the use of which is associated with many problems. One of the issues is the formation of a large amount of contaminated wastewater, during the purification of which large volumes of fibrous-inorganic waste are formed – sludge. Disposal of such waste requires significant financial costs for its dehydration and transportation to disposal sites. As part of the research described in this paper, the possibility of disposing of sludge in the composition of cardboard was studied. The results of studying the fractional composition of the sludge in comparison with the primary and secondary fibers are given in Table 1.

Table 1

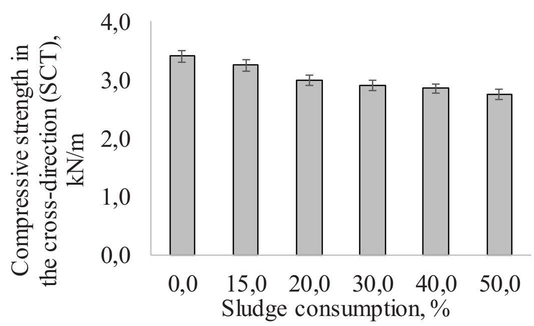
Fractional composition of sludge in comparison with cellulose fibers

Raw material	The content of the fibrous fraction, %				
	0.20–0.60 mm	0.61–1.20 mm	1.20–2.00 mm	2.00–3.00 mm	3.00–7.00 mm
Sludge from PJSC «KCPM»	73.1	24.7	2.14	0.1	0.0
Waste paper pulp	65.3	25.4	7.7	1.5	0.1
Sulfated bleached softwood pulp	23.1	22.5	22.0	20.5	11.9
Sulfated bleached leaf cellulose	21.8	62.4	15.5	0.3	0.0

When the cardboard composition contains a predominantly short-fiber fraction, both the quality of the finished product and the quality of circulating water deteriorate. First of all, this is due to the retention of mass on the grid when forming the canvas on a cardboard machine. Therefore, the effect of sludge consumption on the process of forming paper from a secondary fiber on its physical and mechanical parameters was studied. Shown in Fig. 1, *a, b*, the results indicate that the absolute burst resistance and compressive strength in the cross-direction for the resulting samples of waste paper cardboard are naturally reduced when using sludge. Especially so with an increase in its content to 50 %, compared to a purely waste paper sample.



a



b

Fig. 1. Physical and mechanical properties of sheets of wastepaper cardboard with different sludge content: *a* — absolute burst resistance; *b* — compressive strength in the cross-direction

It is obvious that the inclusion of the short-fiber fraction of the sludge in the composition of the wastepaper pulp leads to a deterioration in the content of the fiber on the grid during the formation of wastepaper cardboard, as evidenced by the graphic dependence in Fig. 2.

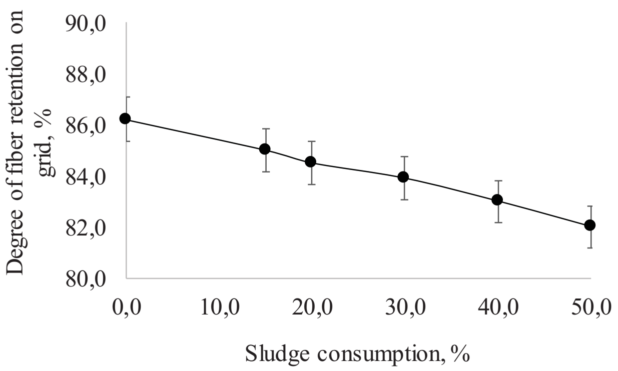


Fig. 2. The effect of sludge consumption on the content of fiber on the grid in the manufacture of wastepaper cardboard

With an increase in sludge consumption from 15 to 50 %, the degree of fiber retention on the grid changes linearly – it decreases from 86.3 to 82.1 %.

5. 2. Investigating the effect of flocculating additives on the quality indicators of container cardboard made from wastepaper using sludge

The results of studying the effect of auxiliary chemicals' consumption on the quality indicators of cardboard samples and the quality of the sub-grid waters are given in Tables 2, 3. These data indicate a positive effect of increasing the dose of flocculants on reducing the turbidity of the sub-grid water. The best results were obtained when using the Praestol-650VS cation flocculant. Sufficiently high efficiency was achieved with the use of flocculants Perkol-455 and Polimin SK. With a sludge content of 50 % at a dose of flocculants of 0.15 %, a significant reduction in wastewater turbidity was achieved. However, in the case of using these flocculants, the increase in sludge consumption has a significant impact on their consumption to achieve minimal turbidity of the sub-grid waters.

With the consumption of sludge in the composition of cardboard of 50 % at the consumption of Percol-455 and Polymin SK, the degree of fiber retention on the grid was increased to 98.0 % and 97.6 %, respectively. Less effective in terms of reducing the turbidity of the sub-grid waters and fiber washes was the use of Magnoflock-10.

The slightly lower flocculation capacity of Polimin SC is due to the fact that it is characterized by a molecular weight of ~ 300×10^3, which is significantly lower than that of other studied cationic flocculants (~ $5–20\times10^6$).

Further studies on the effect of the type of starch glue and its consumption on the efficiency of the formation of cardboard canvas were carried out using sludge at a consumption of 20 %.

Table 2

Influence of sludge (IS) and flocculants (IF) on the turbidity of sub-grid waters (TW) and on the degree of fiber retention on the grid of the cardboard-making machine (DR)

IS, %	IF, %	Praestol-650VS		Percol-455		Polimin SK		Zetag-7563		Magnoflok-10	
		TW	DR	TW	DR	TW	DR	TW	DR	TW	DR
15	0.05	90	97.8	90	98.0	180	96.5	109	98.3	170	96.3
	0.1	35	98.4	70	98.6	70	98.6	80	98.6	83	98.7
	0.15	33	99.0	53	98.8	39	99.1	60	98.5	56	98.4
	0.2	25	99.6	45	99.0	33	99.3	45	99.0	35	98.5
	0.25	23	99.8	38	99.1	29	99.8	40	99.1	33	99.3
	0.3	22	99.8	190	96.3	24	99.8	28	99.3	30	99.25
20	0.05	150	98.5	115	97.6	280	94.3	130	97.8	250	95.2
	0.1	45	99.0	95	98.0	185	96.4	110	98.3	185	96.5
	0.15	28	99.3	86	98.0	130	97.8	90	98.2	130	97.8
	0.2	23	99.8	80	98.3	120	98.0	67	98.6	117	97.6
	0.25	23	99.8	75	98.3	110	98.3	60	98.5	85	98.2
	0.3	22	99.8	205	95.9	100	98.4	40	99.1	90	98.4
50	0.05	70	98.6	125	97.0	395	91.3	163	97	290	93.6
	0.1	39	99.0	105	97.3	280	93.5	140	97.5	250	95.2
	0.15	33	99.3	98	97.4	180	96.5	115	97.6	180	96.5
	0.2	29	99.3	95	97.8	150	97.3	83	98.2	155	97.3
	0.25	24	99.8	90	97.8	140	97.4	70	98.2	150	97.2
	0.3	70	98.6	90	98.0	135	97.6	55	98.3	110	97.3

Table 3

Influence of sludge (IS) and flocculants (IF) on absolute burst resistance (ABR) and compressive strength in the cross-direction (CS) of wastepaper container cardboard

IS, %	IF, %	Praestol-650VS		Percol-455		Polimin SK		Zetag-7563		Magnoflok-10	
		ABR	CS	ABR	CS	ABR	CS	ABR	CS	ABR	CS
15	0.05	273.2	2.8	258.0	2.8	293.4	3.4	389.5	4.9	278.2	3.9
	0.1	217.5	2.6	252.9	2.4	283.3	3.5	339.6	4.6	265.8	3.2
	0.15	212.5	2.6	252.9	2.4	298.5	3.5	313.6	4.1	257.0	3.1
	0.2	211.0	2.6	227.3	2.5	278.6	2.8	278.2	3.9	220.5	3.0
	0.25	211.0	2.4	230.1	2.5	283.9	2.9	258.1	3.7	221.0	3.0
	0.3	166.9	2.4	227.6	2.4	278.8	2.8	258.2	3.1	220.2	2.7
20	0.05	289.3	2.9	249.1	2.8	264.7	3.1	419.9	5.6	303.6	3.0
	0.1	281.2	2.7	237.1	2.8	260.0	2.5	292.0	5.2	289.5	2.9
	0.15	277.4	2.6	229.6	2.8	260.3	2.6	356.0	5.0	288.9	2.6
	0.2	269.2	2.5	227.6	2.7	272.9	3.1	251.1	4.9	264.3	2.5
	0.25	250.0	2.5	202.3	2.6	290.6	2.8	218.9	4.9	243.0	2.6
	0.3	200.7	2.5	192.2	2.7	277.8	2.8	228.2	5.0	242.0	2.6
50	0.05	323.2	3.9	260.0	3.0	285.0	3.2	364.7	5.3	264.7	3.0
	0.1	318.7	3.7	258.8	2.9	271.1	3.2	360.0	5.3	260.0	2.7
	0.15	318.0	3.7	258.2	2.9	266.8	3.1	357.0	5.2	260.0	2.6
	0.2	263.6	3.6	245.9	2.9	277.8	2.9	322.9	5.0	247.8	2.4
	0.25	215.3	3.3	214.9	2.8	277.5	3.0	289.6	4.9	252.1	2.2
	0.3	199.5	3.4	198.3	2.8	283.5	3.0	275.8	5.0	250.7	2.0

5. 3. Investigating the influence of starches on the quality indicators of container cardboard made from wastepaper when using sludge

We investigated the influence of starch consumption of various types on the efficiency of making cardboard when manufacturing samples weighing 125 g/m^2. The results of laboratory tests are given in Table 4. The data indicate that in all cases there is no complete retention of fiber and starches on the grid.

Table 4

The influence of starch consumption on the efficiency of the formation of container cardboard

Type of starch	Starch consumption, %	The turbidity of sub-grid waters, mg/dm^3	Absolute burst resistance, N	Compressive strength in the cross-direction, kN/m
–	–	158.6	206.3	1.6
Corn	0.7	150.4	211.9	1.7
	1.0	98.1	218.3	1.7
	1.3	78.4	252.1	1.8
CMC	0.7	163.5	212.1	1.8
	1.0	150.2	244.1	2.0
	1.3	85.4	255.6	2.3
Cationamyl	0.7	150.4	228.6	2.0
	1.0	72.6	250.6	2.0
	1.3	65.4	267.0	2.7
Cerezan	0.7	142.5	226.1	2.0
	1.0	65.4	288.8	2.3
	1.3	32.7	293.2	2.9

In all cases, the use of starch substances makes it possible to improve the quality indicators of container cardboard. However, the issue of keeping the short-fiber fraction on the grid when forming a cardboard canvas remains unresolved.

5. 4. Investigation of the influence of starch adhesives and flocculants on the efficiency of making container cardboard

We investigated the influence of starch consumption on the quality indicators of samples of container cardboard and sub-grid waters while manufacturing laboratory samples weighing 125 g/m^2. Our results are given in Table 5.

The use in the composition of wastepaper container cardboard, together with native and modified starches of flocculants, made it possible in some cases to reduce the turbidity of the sub-grid waters. The studies used Percol-455, which showed the best effectiveness in reducing the turbidity of the sub-grid waters compared to others. Flocculant Zetag-7563 was chosen as the one that ensured the production of castings with the best physical and mechanical indicators. Anion flocculant Magnoflok-10 was used for comparison.

The use of flocculant Zetag-7563 in the composition of cardboard has a minimal positive effect on the strength indicators of cardboard, despite the lowest turbidity values of the sub-grid waters. It is obvious that in this case, the high coagulating capacity of this flocculant contributes to the formation of large fibrous globules, which are unevenly located in the cardboard canvas and cause anisotropy properties.

Table 5

Influence of the consumption of starches and flocculants Perkol-455 (I), Zetag-7563 (II), Magnoflok-10 (III) on the efficiency of manufacturing container cardboard

Starch	Consumption, %	The turbidity of sub-grid waters, mg/dm^3			Absolute burst resistance, N			Compressive strength in the cross-direction, kN/m		
		I	II	III	I	II	III	I	II	III
Corn	0.7	92.0	85.0	130	186.2	185.7	187.7	1.8	1.9	1.9
	1.0	89.7	69.7	115	190.9	204.9	188.7	1.9	2.0	2.2
	1.3	54.0	60.8	125	202.9	226.6	199.8	2.0	2.1	2.3
CMC	0.7	65.0	80.1	190.1	212.1	202.4	225.6	1.8	2.1	1.7
	1.0	50.0	60.2	145.0	244.1	214.5	231.7	2.0	2.2	1.9
	1.3	40.9	40.3	125.9	255.6	220.1	250.4	2.3	2.1	2.0
Cationamyl	0.7	62.0	58.0	140.1	178.6	203.5	184.2	1.7	1.6	1.8
	1.0	34.1	43.2	110.0	202.9	212.9	192.0	1.9	1.9	1.9
	1.3	28.0	25.1	80.0	208.5	244.1	202.3	2.1	2.0	2.0
Cerezan	0.7	80.0	128.0	115.0	211.1	200.3	226.7	1.8	1.9	1.8
	1.0	45.2	53.0	95.6	242.0	208.0	233.7	1.9	2.1	1.9
	1.3	28.1	64.0	89.9	268.0	212.5	237.2	2.1	2.2	2.1

The use of Magnoflok-10 anionic flocculant in composition with starches is rather ineffective since the turbidity value of the sub-grid waters is somewhat higher compared to other flocculants. Magnoflok-10 in combination with cationic starches CMS and Ceresan provides slightly greater strength of cardboard samples than with the use of corn starch and phosphorylated starch Cationamyl. Taking into consideration the electrokinetic properties of Magnoflok-10 macromolecules, cellulose fibers and starches, which are important only at the stage of preparation of the waste paper pulp, since they affect the efficiency of flocculation of the suspension components, the results obtained are quite natural. At the stage of making the composition and mixing the components, the flocculating effect of the low-anionic flocculant Magnoflok-10 is low, which causes poor retention of the short-fiber fraction with starch on the grid when forming a cardboard canvas. When using Magnoflok-10 in combination with weakly cationic starch Cationamyl and sludge, the results obtained are close to the values for corn starch but the quality of the sub-grid waters is slightly lower. It is obvious that the negative charge of the surface of the cellulose fiber and starch particles compensate for the electrostatic repulsion forces between the anionic flocculant and the fiber surface.

6. Discussion of results of studying the use of sludge and additional chemicals in the composition of cardboard

When we investigated the composition of the sludge, it was found that it is significantly different in the size of the fibrous fraction from the primary and secondary cellulose (Table 1). The main part of the fibers of the industrial sludge is represented by small particles with dimensions from 0.2 to 1.2 mm. In terms of the content of the short-fiber fraction, fiber-inorganic waste is ahead of not only coniferous and deciduous cellulose but also secondary fibers – wastepaper.

It is important that when using sludge in the production of cardboard, regardless of its consumption, the surface absorption of water during one-sided wetting ($Cobb_{60}$) corresponds to the normalized values. For the KT-1 cardboard brand, the surface water absorption values of the surface and bottom layers are 25 and 70 g/m^2, respectively. It should be noted that in all cases of using sludge, the physical and mechanical parameters of cardboard do not correspond to the cardboard of grade KT-1 with a mass of 230 g/m^2 +5/–12 % in accordance with TU U 17.1-41085075-002: 2017. According to the standard, the values of these strength indicators are normalized at the level of 430 N and 3.4 kN/m, respectively. Increasing the proportion of short fiber with an increase in sludge consumption from 15 to 50 % leads to a decrease in the degree of fiber retention on the grid from 86.3 to 82.1 %.

In all the cases studied, the influence of industrial flocculants is rather ambiguous. On the one hand, there is a clearly visible positive effect on the quality of sub-grid waters (Table 2) but the positive effect on physical and mechanical indicators is minimal (Table 3). In some cases, on the contrary, there is a decrease in the strength indicators of the obtained laboratory samples of cardboard. When using cationic flocculants, the degree of fiber retention increases from 86 % to 96–99 %. The maximum effectiveness of flocculant action is observed when the sludge content in the cardboard composition is 15 % per dose of 0.05 % and with a sludge content of 20 % and 50 % per dose of flocculant 0.2 %. Probably, in this case, favorable conditions are created for the flocculation of the wastepaper composition.

The high efficiency of cationic flocculants Perkol-455, Praestol-650VS, Zetag-7563, and Polimin SC in the formation of cardboard is due to the negative value of the electrokinetic potential of the surface of the fibrous component. When using Magnoflok-10, which by its nature is a high molecular weight low-charged anionic compound, the flocculation process occurs according to the principle of the "bridge" mechanism (fiber-flocculant-fiber). This is due to the formation of hydrogen bonds between the flocculant macromolecule and cellulose fiber. In this case, the energy of hydrogen bond formation is higher than the electrostatic repulsion energy between the negatively charged surfaces of the cellulose fiber and flocculant.

Analyzing the effect of Praestol-650VS, Perkol-455, and Polimin SK on the strength indicators of cardboard, we can clearly see that the greater the flocculating efficiency, the greater the efficiency of fine fiber retention. And the greater the content of fine fiber on the grid during the formation of cardboard, the less physical and mechanical properties of the finished cardboard samples. Probably, as in the case of flocculants Praestol-650V and Percol-455, fine fiber contributes to the formation of floccules with large fibers in the presence of cationic flocculants.

For almost all variants of the composition of container cardboard using flocculants, its physical and mechanical properties were lower than for compositions without flocculants and than in the case of pure waste paper mass (Table 3). Moreover, an increase in the dose of flocculant in the process of manufacturing samples to some extent helps reduce the absolute resistance to pushing and the compression force in the transverse direction. It is obvious that this is due to an increase in the content of the fraction of short fibers in the formed sheet, which leads to heterogeneity of the sheet.

The use of flocculants as auxiliary chemicals in the manufacture of cardboard from secondary fiber in combination with sludge is effective in terms of the quality of the sub-grid waters. The turbidity of the sub-grid waters decreases significantly, and the quality of the sub-grid waters corresponds to the clarified sub-grid waters of waste paper production [15]. However, the question of achieving the required indicators of the strength of cardboard remains unresolved.

When native corn starch is used in the composition of cardboard, the turbidity of the sub-grid water decreases with increasing starch consumption. This may indicate a coagulating effect of strengthening substances, which provides a significant improvement in the retention of short fibers of waste paper and sludge on the grid when forming a cardboard canvas. When using phosphorylated starch CMS, the content of suspended solids in sub-grids is the highest. When using Cationamyl starch, the content of suspended solids is slightly lower and the turbidity value is 150.4–65.4 mg/dm^3. These values are close to the use of natural corn starch. Lower content of suspended solids in the sub-grid waters is provided by the use of Cerezan strong cationic starch.

It is obvious that the use of starches in all series of experiments leads to an increase in the physical and mechanical parameters of cardboard samples. A significant impact on the strength of finished products and on the quality of sub-grid water is exerted by starch consumption. In all cases, the use of modified starches provides greater efficiency in the process of forming cardboard. In terms of achieving the required quality indicators of cardboard samples, corn starch and CMS provide strength values at about the same level. At the same time, the cationic starches Cationamyl and Ceresan can significantly increase the absolute pushing resistance and compression force in the transverse direction. However, the question of reducing wastewater pollution remains open.

It was possible to solve the issue of ensuring the necessary indicators of strength and low turbidity of the sub-grid waters when using sludge by using starch adhesives in combination with flocculating additives. The use of flocculant Zetag-7563 in the composition of cardboard has a minimal positive effect on the strength indicators of cardboard, despite the lowest turbidity values of the sub-grid waters. It is obvious that in this case, the high coagulating ability of this flocculant contributes to the formation of large fibrous globules, which are unevenly located in the cardboard canvas and cause anisotropy of properties.

The use of Magnoflok-10 anionic flocculant in composition with starches is rather ineffective since the turbidity value of the sub-grid waters is somewhat higher compared to other flocculants. Magnoflok-10 in combination with cationic starches CMS and Ceresan provides slightly greater strength of cardboard samples than with the use of corn starch and phosphorylated starch Cationamyl. The electrokinetic properties of Magnoflok-10 macromolecules, cellulose fibers and starches are important only at the stage of preparation of waste paper pulp. They affect the effectiveness of the flocculation of suspension components. At the stage of making the composition and mixing the components, the flocculating effect of the low-anionic flocculant Magnoflok-10 is low, which causes poor retention of the short-fiber fraction with starch on the grid when forming a cardboard canvas.

When using Magnoflok-10 in combination with weakly cationic starch Cationamyl and sludge, the results obtained are close to the values for corn starch but the quality of the subgrid waters is slightly lower. It is obvious that the negative charge of the surface of the cellulose fiber and starch particles compensate for the electrostatic repulsion forces between the anionic flocculant and the fiber surface. In the case of using Ceresan with a flow rate of 1.3 % in combination with flocculant Percol-455, samples were obtained that, in terms of strength, correspond to cardboard of the KT-1 brand with a mass of 125 g/m^2 +3/–10 % (TU U 17.1-41085075-002: 2017). According to the standard, the value of absolute burst resistance for KT-1 is 260 N, and the compressive strength in the cross-direction is 1.9 kN/m. In general, the combination of traditional flocculants with adhesives in the composition of waste paper pulp when using sludge is beneficial from the point of view of greening the process of making cardboard. And, in contrast to the use of multicomponent systems of auxiliary substances from cationic firmers, cationic starches and cationic or anionic polymers [16], provide less turbidity of wastewater.

The use of strengthening additives in the form of starch adhesives in the composition of container cardboard made from waste paper in combination with sludge and flocculating additives makes it possible to solve several issues simultaneously. The developed technological solution makes it possible to effectively dispose of the sludge and at the same time achieve the required values of physical and mechanical indicators of the finished product and the quality of the sub-grid waters. The proposed method of processing sludge is economically effective compared to recycling by obtaining biofuels. This approach does not require attracting financial investments for sludge dehydration [17] or the use of chemical reagents for its preparation [18] and, at the same time, reduces the cost of finished products.

It is also possible to organize effective disposal of the fiber-inorganic waste directly in production processes to obtain finished products with the necessary quality indicators. At the same time, the quality of the sub-grid waters will remain satisfactory, which will allow it to be used as reversible after the stage of local purification. The presented data indicate a high prospect of practical use of the research results in the form of mass compositions at the enterprises of the pulp and paper industry.

It should be noted that the limitations of the implementation of the study on an industrial scale are associated only with the need to use optimal doses of auxiliary chemicals. The main disadvantage of the research is the need for financial means to establish a storage system and supply additional chemicals to the composite pools.

The need for further research on the use of sludge as a component of paper pulp is due to the need to develop effective ways to modify native starch adhesives to increase the efficiency of sludge retention.

7. Conclusions

1. The fractional composition and influence of the sludge of paper production on the efficiency of manufacturing container cardboard from wastepaper were investigated. An increase in sludge consumption from 15 to 50 % naturally leads to a decrease in absolute burst resistance and compressive strength in the cross-direction, due to an increase in the content of the short-fiber fraction, the individual fibers of which are characterized by low strength. In addition, there is an increase in fiber washes during the formation of cardboard, as a result of which the degree of fiber retention on the grid decreases from 86.3 to 82.1 %.

2. The influence of flocculants on the formation of cardboard from wastepaper when using sludge is determined. The use of industrial cationic flocculants with a flow rate in the range of 0.025–0.100 % has a positive effect on the strength of cardboard with a sludge content of up to 20 %. In this case, the strength indicators of the finished product are higher than in the case of using a purely waste paper mass.

3. The influence of the consumption of native corn and modified starch on the efficiency of cardboard production is determined. The most effective for achieving the required strength indicators of container cardboard using sludge with minimal pollution of wastewater is the use of highly calcium starch Ceresan with a consumption of 0.7–1.3 %.

4. When using a composition containing 20 % sludge and 0.1 % flocculant Percol-455 and starch Ceresan, the physical and mechanical properties of container cardboard increase with an increase in the dose of starch while reducing the turbidity of the sub-grid water.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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