

Objects of Accumulated Environmental Damage as Raw-Material Base for Building Materials Manufacture

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Abstract—The article provides an overview of the problem of environmental damage caused by the economic activities of Open Joint-Stock Company (OJSC) Baikal Pulp and Paper Mill (BPPM). As a result of more than 40 years of operations, the BPPM has accumulated and stockpiled on the shores of Lake Baikal more than 6,2 million tons of production waste. The technologies analysis results proposed for waste disposal are presented. There are several technological solutions. However, none of them is definitively acceptable for implementation. A promising direction is the use of waste for the production of building materials. The solution of the problem of waste utilization is a priority task of the nature protection activity on Lake Baikal.

Keywords—waste; sludge-lignin; construction materials; ash-and-slag; colloidal precipitation; cement

I. INTRODUCTION

The Baikal’s Pulp and Paper Mill (BPPM) waste dumping grounds are aspects of the environmental damage caused by BPPM’s economic activities. During more than 40 years as the result of its operation the Baikal Pulp and Paper Mill has

accumulated and stockpiled on the shores of Lake Baikal more than 6.2 million tons of production waste. Two waste dumping grounds “Solzansky” (138.09 ha in area) and “Babkhinsky” (42.08 ha in area) were used to store the waste accumulated during the BPPM operation. The Baikal Pulp and Paper Plant is located in the high seismicity zone. Any man-made accident or natural catastrophe can lead to the storage maps destruction, the dams breakthrough and a discharge of a huge amount of toxic waste into Lake Baikal, which will lead to an ecological catastrophe. To eliminate threats to the unique Lake Baikal ecological system, it is necessary to liquidate (including processing) waste from the Baikal Pulp and Paper Mill production and to recultivate it. Around the problem of elimination of the BPPM’s accumulated waste, the debates between scientists, environmentalists and structures, to whom the Russian government commissioned dealing with issues, have been continuing for many years. However, the issue of liquidation of the accumulated damage has not been resolved to this day.

II. ANALYSIS OF THE RESEARCH OBJECT

The BPPM's waste dumping grounds are experiencing environmental damage from the Mill's economic activities. During more than 40 years, as the result of the factory's operation, the Baikal Pulp and Paper Mill has accumulated and stockpiled more than 6.2 million tons of production waste on the shores of Lake Baikal. Two waste dumping grounds "Solzansky" (138.09 ha in area) and "Babkhinsky" (42.08 ha in area), on which 13 cards are located, were used to store the waste accumulated during the BPPM operation. One more waste dumping ground is an intermediate ash-and-slag-pit located on the BPPM industrial site. It was sent to the slurry pipeline during the winter period, and in summer they were assigned by two dredgers on the maps of the Solzan waste dumping ground [1].

The Babkhinskiy waste dump of the BPPM is located between the rivers Babha and Utulik, at 1.35-2.0 km from the Lake Baikal. At the waste dump, ash and slag are being buried from the burning of coals at the Thermal Power Plant (TPP) of the BPPM and Solid Municipal Waste (SMW).

For many years, BPPM various production and consumption waste has been accumulated on the landfills. In addition to sludge-lignin, the following polygons were dumped: ash-and-slag from coal combustion, waste containing coal, solid household waste and construction waste.

Now, sludge-lignin, as the main waste component accumulated by BPPM, is a multicomponent colloidal system containing a small amount of toxic substances, both in the solid and in the dissolved states. The liquid and solid phases are poorly separated.

These types of practice of waste joint disposal are not typical of the pulp and paper industry and have not been used anywhere in the world on such a scale.

Waste analysis showed that in several accumulators, the sludge-lignin joint storage with industrial and domestic waste (garbage), ash resulted in the sludge-lignin self-transformation and increase in its toxicity. The sludge-lignin composition includes chlororganic, polyaromatic compounds and other toxicants. The greatest harmful impact of the Baikal Pulp and Paper Mill's waste is exerted on the groundwater state, as its pollutants enter Lake Baikal.

In the process of filling and storing sludge-lignin maps, regular leakage occurred due to imperfection of the loamy anti-filtration screen, which led to an increase in mineralization and a change in the chemical composition of the groundwater, which are discharged in Lake Baikal.

All drains also contain dissolved foul-smelling sulfur derivatives: hydrogen sulphide, methyl mercaptan, dimethyl sulfide and dimethyl disulphide. A considerable part of the inorganic salts, in particular sodium sulphate, also enters the drains [2, 3].

At the Baikal Pulp and Paper Plant, not only easily oxidizable substances but also difficult-oxidizing compounds were removed from wastewater [4, 5]. For this purpose, in addition to the biological treatment facilities at the plant, a chemical cleaning method was used. At the wastewater

treatment plants of the BPPM, waste water from sulphate-cellulose production passed through a complex single-stage multistage purification in the world, consisting of the following main stages: biological in aerotanks with activated sludge to remove easily oxidizable organic substances; chemical - for the purpose of discoloration of industrial wastewater; mechanical - for clarification of sewage from suspended solids; oxygen saturation - in the pond-aerator.

Biological treatment facilities have the form of aeration stations in aerotanks, where the removal of easily oxidizable organic compounds is carried out by microbial mass with intensive saturation of production waters with air.

The process of industrial effluents chemical purification consists of sequential treatment with a coagulant (solution of aluminum sulphate and flocculant (polyacrylamide)). Aluminum hydroxide promotes high-molecular compounds coagulation as sulphate lignin, chlorlignin and other colloidal impurities and their precipitation.

The action of Polyacrylamide (PAA) in the chemical purification is based on greater aggregation of small flakes through bridge bonds of active centers of precipitate and polyacrylamide. The dosage of aluminum sulfate is 30 mg/dm³, and polyacrylamide is 3 mg/dm³.

The discolored sewage water was sent to a filter station and a pond-aerator. In the sewage water of the BPPM in 1976-1977 and after biological treatment Chemical Oxygen Demand (COD) was 190-205 mg/dm³ O₂, and after the chemical purification decreased accordingly to 69-74 mg/dm³ O₂. Suspended substances concentration in the sewage water after biological treatment was 154-174 mg/dm³, and after chemical treatment they decreased to 6.6-9.1 mg/dm³.

The sediment from the settler was removed to the Solzan waste dump sludge accumulators. The total amount of sediment was 90 tons / day, with a moisture content of 99.7 %, its consumption was 34.6 thousand m³/day.

BPPM ash dumps, in addition to impact on groundwater, as a result of dusting, have a harmful effect on atmospheric air, soil cover, adjacent areas vegetation [6, 7].

The existing position on the factor of atmospheric air pollution is considered on the basis of full-scale studies.

The studies were carried out for the following components of the gas-air mixture: sulfur dioxide, nitrogen dioxide and oxide, carbon oxide, hydrogen sulphide, methyl mercaptan, and Polycyclic Aromatic Hydrocarbons (PAHs) (including benzopyrene).

In the places where the gases emanated on landfills, the content of hydrogen sulphide and methyl mercaptan sulfur was determined below the Maximum Allowable Concentration (MAC) for the work area.

Concentrations of sulfur, nitrogen and carbon oxides are below the MAC for human settlements. The concentration of benzopyrene is found at the sensitivity level of the method used without exceeding the MAC.

Table 1 shows the concentrations of the main pollutants that enter the air from the sludge accumulators. In the existing

situation, atmospheric air pollution sources are tanks №. A, B, C, D of the Solzansky waste dump. The tanks of the Babkhino waste dump are not sources of atmospheric air pollution.

TABLE I. CONCENTRATIONS OF THE MAIN POLLUTANTS THAT ENTER THE ATMOSPHERE FROM SLUDGE ACCUMULATORS

Sampling Point	Gaseous Phase Concentration, $\mu\text{g}/\text{m}^3$			
	<i>SO</i> ₂	<i>NO</i> ₂	<i>NO</i>	<i>CO</i>
tank A, west part	0-1	8-9	23-26	0.1
tank A, east part	0-1	8	16	0.1
tank B, west part	-	8	20-21	0.1
tank B, east part	0-1	6-8	17-22	0.1
tank C, west part	-	9-11	19	0.1
tank C, east part	-	11	21	0.2
tank D, west part	1	7-11	35-37	0.1
tank D, east part	2	18-21	16-21	-

The gas components concentration was significantly lower than the corresponding MAC: for sulfur dioxide - $50 \mu\text{g}/\text{m}^3$, for nitrogen dioxide - $40 \mu\text{g}/\text{m}^3$, for nitrogen oxide - $60 \mu\text{g}/\text{m}^3$ and $1 \text{ mg}/\text{m}^3$ for carbon monoxide - $3 \text{ mg}/\text{m}^3$.

The calculated levels of atmospheric air pollution at the border of the Solzansky village and on the border of horticulture for hydrogen sulphide were 1.16 MAC and 0.26 MAC, respectively, for methantioi - 1.05 MAC and 0.24 MAC respectively [8, 9].

The Baikal Pulp and Paper Plant is located in the high seismicity zone, any man-made accident or natural catastrophe can lead to destruction of the storage maps, the dams breakthrough and a discharge of the huge amount of toxic waste into Lake Baikal, which will lead to an ecological catastrophe [10].

The main ecological risks for the ecosystem of Lake Baikal in the area of the BPPM landfills are determined by:

- pollution of groundwater in the area of the Solzan waste dump tanks;
- overflow of water through the dams of tanks and its entry into the Big Osinovka river with the discharge of ash pulp;
- overflow of the tanks with water after prolonged downpours and discharge of liquid sludge-lignin masses from the upper tanks to the lower ones and so on to the bottom one by the "domino" principle, and then by the flow into Lake Baikal;
- a disastrous mudflow, which capable of removing all organic waste into the lake, destroying railway and automobile routes.

The determining problem is the presence in the region of the danger of disastrous mudflows.

The Baikal spurs of Khamar-Daban and the rivers flowing from them to Lake Baikal were among the 3 regions, dangerous because of the disastrous mudflows. This is the area of Alma-Ata in Kazakhstan, the Black Sea coast of the Caucasus and the coast of the Baikal from the river Pokhabicha (Slyudyanka town) to the river Snowy: the

disastrous mudflows pass here every 40 years. In 1934 a considerable quantity of houses in Slyudyanka was demolished by a mudflow. In 1971, the mudflow destroyed a number of houses in the gardening of the Baikalsk city, demolished several houses and structures in the city itself, destroyed a road and a railway in 20 places. It demolished 7 bridges; part of the railroad track was dropped into the lake Baikal, the movement for the Moscow route and the East Siberian Railway has been stopped for a week. Mudflows along the Small Osinovka River partially violated the dam of one tank.

All the factors of mudflow in the region of the river Babha, Harlath, Solzan, B. and S. Osinovki are known. A great shower can be a trigger.

Especially dangerous ones are the mudflows for the Solzan range of tanks - sludge storage tanks. Probable village on the B. Osinovka River can, after hitting the middle part of seven tanks, take out the sludge-lignin accumulated in them in the lake. Such quantity of BPPM's lignin could be dumped in the lake for 700 years.

To prevent a natural disaster related to the mudflow in the territory of Baikalsk, it is necessary to conduct engineering and geological surveys with an inventory of existing and planned mud protection facilities, expeditionary and GIS technical works to assess mudflow risk of rivers with pre-design studies and proposals for an effective mudflow protection system. The next stage is the design of mud protection facilities on the coastline of the Babhi River to the S. Osinovka River. For urgent protection of the sludge storage tanks of the Solzan range from the village, it is necessary to clear the Osinovka river bed, deepen the upland ditch of the upper map and free it from the sludge - lignin, turning it into a pool for receiving loose masses of mud [11].

These works can be included in the number of emergency measures to eliminate damage from the BPPM's waste and will require additional financing. Part of the work is already underway.

III. DISCUSSION

Around the eliminating the problem of BPPM's accumulated waste, debates between scientists, environmentalists and structures, which the Russian government commissioned to deal with issues of the BPPM, have been continuing for many years, but the issue of liquidating the accumulated damage has not been resolved to this day.

To eliminate threats to the unique Lake Baikal ecological system, it is necessary to liquidate (including processing) waste from the Baikal Pulp and Paper Mill production and to recultivate them.

To date, special attention has been paid to the physical-and-chemical characteristics of sludge-lignin from the tanks, its composition, and the degree of dehydration.

The main characteristics of sludge that prevent their export outside the Baikal Natural Territory (BPT) incineration, use in building materials, etc. are high humidity, the presence of

hydrogen sulphide and methyl mercaptan. For the dehydration of sludge lignin, alumina is used in industry, for deodorization - trichloro iron.

The mixing of coal ash with lignin sludge leads to the following effects: due to the action of alumina particles of ash on liquid sludge-lignin, the water connected to it enters the free aqueous phase. From sources and experimental-industrial data, up to 75 % of the bound water is released. Iron particles, mixed with lignin, simultaneously bind hydrogen sulphide and other foul-smelling gases.

The first task of the research was to study the composition of the promo events on all tanks. Wells were drilled, samples were taken. The humidity for tanks 1, 2, 3, 4, 6, 7, 9, 10 ranges from 92 to 98 %. After mixing with the bound water ash, 10-17 % remains. The rest of the water is discharged through the wells to the treatment facilities. Work on the dehydration of sludge lignin and its mixing with ash was carried out in large volumes at the Selenga pulp and paper mill in 1985-1995.

According to research data, the water mirror over all the tanks is about 620 thousand of cubic meters. In spring, after the melting of snow, the volume of water can increase to 1 million of cubic meters of water. The composition of over-slice water in the tanks is different. The chlorphenol content in these waters is lower than in the ponds of the aerators and the water area of the lake near the discharge of sewage [8, 9].

Sludge-lignin belongs to the IV category of hazardous waste.

Over the period of the plant's activity, more than a dozen ways to eliminate this large-tonnage waste and subsequent recultivation were proposed, and attempts were made to implement some of them [11, 12]:

- technology of dehydration, deodorization and burial of sludge lignin with ash of coal, providing complete remediation of the Solzansky and Babkhinskiy ranges;
- technologies for obtaining composite building materials from the BPMC's prompropels for road construction and equipping sports grounds with a wide range of products from paving slabs to roofing, construction of mud-resistant structures, etc.;
- technologies for creating organomineral composts for reclamation of territories;
- method of drying and burning, which is used in the modern technological scheme (did not justify itself because of the modified accumulated sludge-lignin toxicity);
- sludge lignin processing by Californian worms (unfavorable physical and chemical environment and other features);
- dehydration with dry bark, permanent surface water drainage from storage maps, etc. The expected result could not be achieved due to either large and constant costs, or overdelivery.

In recent years, two main directions for neutralizing slime lignin have been discussed:

- joint grouting technology, represented by Limited Liability Company (LLC) "VEB Engineering";
- Limnological Institute Siberian Branch of the Russian Academy of Sciences specializes in burial sludge-lignin technology with the help of ash coals.

Both technologies are aimed at neutralizing hazardous wastes with the hazard class lowering, and not for their processing with the marketable products obtaining possibility.

Hopes to correct the situation were assigned to the sludge-lignin "joint grouting" waste recycling project. It was assumed that the waste would be concreted, which would prevent them from entering Lake Baikal, but the "joint grouting" did not justify itself, and the project turned out to be unrealizable.

In 2017, measures were proposed to neutralize the BPPM waste using two technologies [13, 14].

The first technology involves the sludge-lignin transfer to a solid aggregate state with the safe non-toxic material production by binding to inert and bonding substances and the reclamation fertile soil preparation, the supernumerary water cleaning from phenolic and bacteriological contamination in mobile treatment facilities. Sludge-lignin will be processed to obtain a mineral solid. The mixture for neutralizing the sludge-lignin components and associated water is based on mineral components and strength enhancers in the form of microdisperse silica. The reference mineral solid strength is sufficient for the land further return to economic circulation.

The second technology involves the disposal of sludge-lignin in thermolysis reactors in a closed loop to produce a product of processing in the synthetic oil and carbon form; gaseous emissions are absent. At the same time, the resulting synthetic oil is used as fuel for the sludge-lignin subsequent volume utilization. The low-temperature thermolysis is applicable for neutralizing slime-lignin, bark and wood waste utilization (the content of which is about 500 thousand tons) and solid waste with the use of an installation developed by LLC "RPE Termolysis". This method has advantages in that the recycling products are not available and allows one to dispose solid household waste present in the maps.

But these two technologies were never adopted.

In accordance with Federal Law № 89-FL of June 24, 1998 "On Production and Consumption Wastes", the waste contained in sludge depository should be considered as technogenic raw materials to be processed with the aim of obtaining valuable components from them [15-17].

One of such research trends can be the publicly held corporation "BPPM" sludge depository colloidal sludge-lignin possible recovery study with the aim to produce α -alumina, as one of the components for producing corrosion-resistant hydraulic cement [18]. The colloidal sludge-lignin sediments recovery possibility with obtaining α -alumina is due to the fact that a large amount of aluminum hydroxide is included in the sludge-lignin composition. With an increase in the sediment depth, the aluminum content increases to 25 – 28 % (Fig. 1) [17, 18].

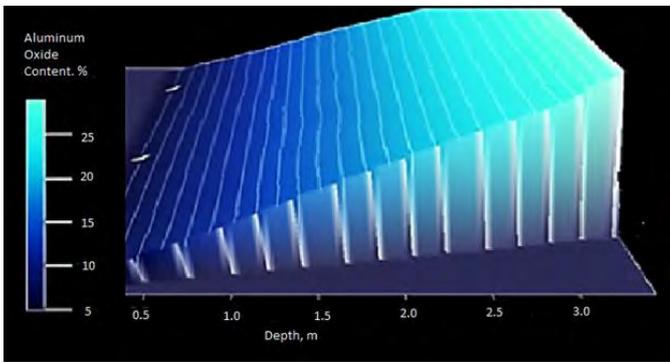


Fig. 1. Aluminum content in terms of oxide (%) in sludge-lignin precipitatio

According to the technology at the Open Joint-Stock Company (OJSC) “BPPM”, the sludge-lignin was burnt at a temperature of 1100 ° C with the Sludge-Lignin Ash (SLA) formation in the amount of 3 tons / day (in absolutely dry substance). Sludge-Lignin Ash (SLA) analysis showed the presence of such compounds as aluminum oxides (65–75 %), silicon (12–25 %), iron (1–3 %), calcium, and carbon. According to the existing technology, prior to the plant closure, SLA were stored together with other enterprise waste in sludge depository.

To obtain cement clinker, in addition to aluminum oxide, which increases the hardening rate, lowers the sintering temperature, increases strength, it is also necessary to have components that increase the corrosion resistance and also possess astringent properties. For this purpose, studies were conducted on the following waste from the Baikal region: fluoroanhydrite — a hydrogen fluoride production waste generated at OJSC “Angarsk Electrolysis Chemical Plant” (Angarsk) and carbide sludge — calcium carbide waste upon acetylene receipt (second grade lime, bluish tint) formed on LLC “Usoliekhimprom” (Usolye-Sibirskoe) (table 2).

The starting content of components in the raw mix composition was calculated based on the following conditions:

- the clinker composition includes SiO₂, which is in the belite form (2CaO * SiO₂) and is designated as C2S;
- the clinker composition includes Al₂O₃, which is in the calcium sulfoaluminate form (3CaO * 3Al₂O₃ + CaSO₄), which is designated as C4A3 \hat{S} , and also in the tetracalcium aluminoferrite form 4CaO * Al₂O₃ * Fe₂O₃, designated as C4AF;
- which is designated as C4A3 \hat{S} , and also in the tetracalcium aluminoferrite form 4CaO * Al₂O₃ * Fe₂O₃, designated as C4AF;
- gypsum, introduced into the mixture in sufficient quantities, prevents the high alumina calcium alumina ferrites formation, causing the C4A3 \hat{S} and C4AF appearance in the product. Therefore, iron oxides in clinker are in the C4AF form (CA + C3F).

TABLE II. THE COMPOSITION OF THE WASTE IN THE RESULTING CLINKER

Wastes	Content, %					
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	SO ₃	Other
Sludge lignin ash, OJSC “BPPM”	22	71	3	2	1	1
Fluorhips, OJSC “Angarsk Electrolysis Chemical Plant”	2	0,6	0,4	32	43	22
Carbide silt, LLC “Usoliekhimprom”	2	0,7	0,4	70	0,2	27

According to the calculations, the clinker mixture following composition was obtained: for one part of carbide sludge, there are 0.73 parts of ASL and 1.4 parts of fluorogips. At the same time, ASL is 23% of the total mass.

To study the obtained material component composition, an analysis was carried out on the basis of the X-ray diffractometry method using a BRUKER D8 ADVANCE instrument at the “Vinogradov Institute of Geochemistry Siberian Branch of the Russian Academy of Sciences” (Fig. 2) [17, 18].

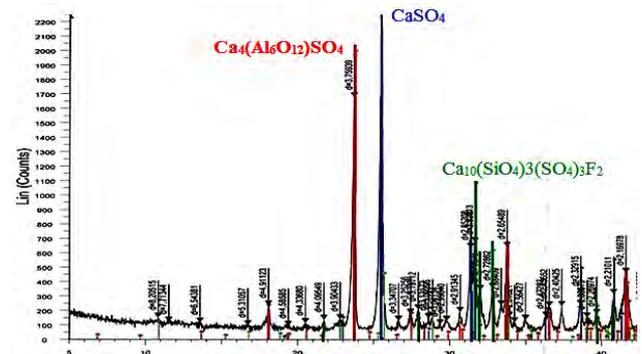


Fig. 2. X-ray diffractogram of the obtained sample clinker

According to Figure 2, calcium sulphate - CaSO₄ has the best substance effect, followed by calcium sulfoaluminate Ca₄(Al₆O₁₂) SO₄ (according to the hardening rate of cement and an expanding additive), the third in content is Ca₁₀ (SiO₄)₃(SO₄)₃F₂ (increases the strength of cement). The compressive strength after the twenty eight days of tempering was 83.2 MPa, the corrosion resistance coefficient was 1, which corresponds to the quality indicators of cement grade M-400. The material obtained from ash from sludge lignin sludge burning (cement M-400) is covered by RF patent № 2552288.

IV. CONCLUSION

Thus, in the case of the implementation of the sludge-lignin sludge recovery technology of the publicly held corporation “BPPM” with partial use of the existing equipment of the plant, α-Al₂O₃ can be obtained, which can later be used in the process of sediment eco-concrete for producing an entombment - an environmentally safe and reliable engineering structure. In parallel, issues of disposal of accumulated wastes of the Baikal region by the limited liability company Usoliekhimprom and the publicly held

corporation Angarsk Electrolysis Chemical Plant will also be resolved, which will put a premium on the proposed technology and will significantly reduce the technical and economic costs of its implementation.

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