State and Biochemical Transformations of Stored Waste Wood. Analysis and Forecast

S. A. MEDVEDEVA[1], I. V. VOLCHATOVA[1], G. P. ALEKSANDROVA[1], I. A. ANTIPOVA[1], L. I. ANTONOVA[1], O. G. KUZMINA[2] and V. A. VEBER[2]

[1]*Favorsky Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, Ul. Favorskogo 1, Irkutsk 664033 (Russia)*

E-mail: irina@irioch.irk.ru

[2]*Sibgiprobum JSC, Ul. Stepana Razina 6, Irkutsk 664033 (Russia)*

(Received November 10, 2005; revised January 27, 2006)

Abstract

Physical and chemical composition of the stored waste wood taken from the pits of the Ust-Ilimsk Timber Industrial Complex (TIC) was investigated. The microbiological and sanitary-hygienic status of the waste wood was examined. The experimental data obtained provide evidence that the mass in the pits is friable because of large-size wastes, so oxygen access is provided even to the deep layers in the pit. Aerobic microorganisms (fungi and bacteria) that had occupied the lowest old layers have already created a united community that carries out biochemical destruction of waste wood forming ecologically dangerous lignin-like substances, neutral compounds, phenols and acids. Intense microbiological activity can lead to spontaneous ignition of waste wood, which belongs to the class of fire dangerous substances.

INTRODUCTION

Utilization of wastes comprises one of the substantial aspects of the programme of environmental protection from anthropogenic impact. This problem is extremely urgent for the Irkutsk Region because this territory is an industrially developed area. The resource potential of the Irkutsk Region provides the leading role of five special complexes, including lumber industry, in the structure of regional industry.

According to the data of State Statistics [1], more than 60 lumbering and wood processing plants are situated in the Irkutsk Region. These plants are the sources of a substantial amount (about 300 thousand m^3) of dense waste wood (bark, sawdust, wood chips). The amount of their utilization is 79.9 %, the rest mass is transported to proving grounds and dumps. Lignin tailings are also formed in the pulp and paper facilities. The annual yield of this waste product at the Baikal Pulp and Paper Mill (BPPM) alone is about 10 thousand tons. Lignin tailings remain almost unused; it is stored in accumulating charts.

One of the most widespread industrial wood wastes is hydrolysis lignin (HL); its annual amount at the two hydrolysis plants of the Irkutsk Region (Tulun, Biryusa) accounts for about 70 thousand tons [1]. Hydrolysis lignin is transported to dumps almost completely and thus occupies large ground areas acidifying soil (pH_{HL} ~ 2.5), surface and underground water. This brings about the danger of large-scale pollution of the territories adjacent to the plants. Fine HL fractions are easily swept away by wind polluting the air. In the recent years, auto-oxidation of a large mass of HL has become the reason of systematic fires in the Zima district. The dumps of hydrolysis plants contain more than 2 mln tons of HL.

Under the natural conditions, the aerobic microbiological decomposition of plant residues (wood, forest litter) occurs very slowly. The decomposition process takes place as a result of complicated multistep activities of a complex of microorganisms with a characteristic change in physiological groups. The main factors determining the microflora population and predominance of one group of microorganisms or another and therefore the intensity and direction of biological destruction include the chemical composition of structural components of wood residues, the degree of their humidity, temperature and aeration. So, depending on the conditions, the rate of wood material decomposition may vary. Small fallen or felled trees or branches turn into dust within 10–15 years. Smaller sized raw material, such as leaf litter, dry grass, would decompose much more rapidly under the same conditions [2].

The waste products of wood-processing and wood-chemical plants accumulated in dumps will transform with time, similarly to other accumulated wastes of organic origin; they will undergo microbiological degradation, as microflora inhabits them. In the case of HL, population with microflora becomes possible only after sulphuric acid that impregnates the substance is removed with atmospheric precipitation (rain, snow). That is why lignin dumps stay for more than 50 years.

Extractives and the products of biodestruction of the lignin from wood or bark are phenolic compounds and can exhibit toxic and carcinogenic properties when their concentrations are high. Their arrival into underground water in large amounts may be dangerous from the viewpoint of ecology. In addition, while time goes on, the dump mass may be populated with potentially dangerous microorganisms (pathogens and toxicogens) that are able to cause enteric infection in humans, epidemic in fauna, toxicosis in plants. Because of this, it is necessary to monitor not only biochemical but also sanitary-hygienic status of dumps, pits, and accumulation charts.

The goal of the present work was to analyse chemical and microbiological processes that take part in the stored waste wood, and prediction of the sanitary-hygienic state and temporal changes in these repositories.

EXPERIMENTAL

The objects of investigation were pits (dumps of waste wood) of the Ust-Ilimsk Timber Industrial Complex (TIC). Burying of wood wastes in the pit No. 83 was carried out since 1986; the wastes are stored over the area of 29 ha. The depth of the repository is 31 m. Filling of the pit No. 8 was carried out since 1983, the storage area is 1.6 ha, dump depth is 5–6 m.

Samples were taken from the central part of pits at different horizons with intervals (by the core) each 2 m at a depth of 30 m for the case of pit No. 83 (samples 1–9) and 7 m for pit No. 8 (samples 10–12). The samples were transported in polyethylene bags.*

The fractional and granulometric composition of the samples was determined. After removing mechanical impurities (stones, glass, *etc.*), humidity and pH of the medium were measured. Then the samples were dried to the air-dry state and ground in a mill. After thorough mixing, samples were taken by quartering; subsequent analyses (elemental analysis, group composition) were made with the resulting averaged samples. The humidity of air-dry samples was taken into account in calculations. The content of cellulose and lignin was calculated for the organic part of samples.

For biological analyses, the initial samples without preliminary treatment were used. The samples were kept before analyses at a temperature of 0 °C. Quantitative determinations of the microorganisms were carried out using a two-layer agar method according to GF XI (issue 2). To estimate the toxicity, we studied the germinating capacity of wheat seeds in the presence of samples to be analysed, in comparison with the reference [3].

RESULTS AND DISCUSSION

Analysis of the physical and chemical composition of the samples of stored waste wood in the pits of the Ust-Ilimsk TIC

It was established that the physical composition of the samples under investigation in both

*Sampling was carried out by the Geological and Geodesy Centre (Bratsk city).

TABLE 1

Granulometric composition of samples from the pits of Ust-Ilimsk TIC

Sample No.	Depth, m	Sample description	Content of a fraction, mass %		
			Coarse, >6.5 cm	Medium, >3.0 cm	Fine, <3.0 cm
		Pit No. 83			
1	1–2	Dust; chips and bark are not numerous	28.1	18.4	53.5
2	3–5	Clay lumps, ground, bark pieces; a small amount of chips and dust	67.2	14.1	18.8
3	6–8	Dust, chips, bark; ground	51.4	18.8	29.8
4	10–12	Dust, chips and bark; ground; crushed stone	52.2	17.2	30.7
5	14–16	Dust, bark; small amount of chips; ground	49.3	19.4	31.3
6	18–20	Dust, bark; small amount of chips; crushed stone	40.3	21.2	38.5
7	22–24	Dust, chips, bark; ground	56.6	18.9	24.5
8	26–28	Dust, chips; crushed stone	37.8	21.7	40.5
9	30–31	Dust, chips, bark, crushed stone	55.1	19.7	25.2
		Pit No. 8			
10	1–2	Dust	10.0	14.6	75.4
11	4–6	Dust, chips; stones	38.2	17.9	44.0
12	6–7	Ground with glass; small amount of dust and chips	48.9	23.2	27.9

pits is not uniform, because it is determined by the quality of waste material and includes chips, bark and dust. Since the wastes to be stored were interspersed with ground, a large number of mechanical impurities were present in the samples: sand, ground, clay, stones, glass, and crushed stone. These foreign bodies were especially noticeable in the samples from pit No. 8.

Granulometric composition showed (Table 1) that the coarse fraction with particle size above 6.5 cm dominates in the samples; the major part of this fraction is represented by the particles with a size of 6.5–8.5 cm. The content of this fraction was 40–60 % in the majority of samples, while the fine fraction accounted for 30–40 % (except for surface samples in which its content reached 50–70 %).

The maximal humidity (Table 2) was established in the samples from the upper horizon of the pits (61–62 and 53–58 % for samples from pits No. 83 and 8, respectively), because this horizon is most of all prone to the action of atmospheric precipitation. At the mid-level of pit No. 83, humidity varied from 48 to 54 % and increased to 57 % in the lowest horizon, perhaps due to the fact that water partially entered the bottom of the pit. No dependence of such a type was observed for pit No. 8.

The samples were mainly weakly alkaline (pH 7.6–8.0) (see Table 2). Only some samples with high bark content were acidic (pH 4.6–4.8) or neutral (pH 6.3–7.2). The acidic medium is characteristic of wood in general and especially of bark (pH 4.5–5.5), so high pH values (8.0–8.6) are due to the arrival of alkaline-containing materials – crushed stone or lime – into the wastes. An optimal pH level is individual for each microbe culture; however, many bacteria are relatively insensitive to pH variations within the range 6–9, so the formed environment in the dump is quite suitable for bacteria reproduction.

The content of ash, organogenic elements (carbon, nitrogen, sulphur) and chlorine was determined in the samples. The quantitative content of the residual inorganic part was estimated on the basis of sample ash content (Table 3). This value reached 50 % in separate samples, while it reached 73 % in sample 12.

The results obtained provide evidence that all the samples contain mainly carbon and a small amount of nitrogen, sulphur and chlo-

TABLE 2

Characteristics of samples from the pits of Ust-Ilimsk TIC

Sample No.	Humidity, %	pH	Content, mass %	
			Cellulose	Lignin
		Pit No. 83		
1	61.06	8.1	42.12	36.82
2	62.53	8.0	44.35	38.30
3	48.94	6.3	47.19	32.85
4	54.63	8.6	48.47	34.16
5	49.63	7.9	47.68	32.59
6	54.22	8.0	45.13	31.48
7	48.27	4.6	48.33	30.80
8	55.23	7.2	48.99	31.21
9	57.17	7.5	43.78	30.07
		Pit No. 8		
10	53.22	4.8	48.76	32.07
11	58.50	6.7	47.55	30.40
12	46.06	7.6	43.13	28.68

rine. Since wood itself contains only nitrogen (0.03–0.20 %) among heteroatoms [4], the arrival of sulphur, chlorine and a part of nitrogen in the samples occurs not through waste wood. The presence of these elements may be connected with acid atmospheric precipitation followed by sorption of the anions of sulphuric and nitric acids by wood dust. According to the data of the Research Institute of the Atmosphere, acid rains in East Siberia contain more nitrogen oxides that sulphur oxides, so the nitrogen content of the majority of samples exceeds that of sulphur. No clear dynamics of the distribution of these elements with waste burying depth was revealed, only relatively increased sulphur and nitrogen content was observed in the upper samples at the depth of 1–5 m in both cores.

Carbon and hydrogen content, depicting the status of the organic constituent of samples under analysis, also exhibits no regular distribution depending on the horizon. However, two zones can be distinguished for the core from pit No. 83: at the depth of 3–16 m (samples 2–5) where carbon content is 20–37 %, and 18–31 m (samples 6–9) with carbon content of 40–43 %. Such a character of distribution is likely to be due to the fact that mainly wood wastes were stored at the initial stages of pit operation. The content of the added mineral part is only 15–25 %. Only at the depth of 16 m waste wood was interspersed with ground at a ratio of approximately 1 : 1 (the ash content of samples is equal to 30–50 %).

In order to reveal the status of the organic part, we determined the content of its main macrocomponents peculiar to wood and bark: lignin and cellulose [4]. One can see in Table 2 that this value varies within the limits 28–38 and 42–48 %, respectively. In the case of samples from pit No. 8, the dynamics of a decrease

TABLE 3

Elemental composition of samples from the Ust-Ilimsk TIC

Sample No.	Concentration, mass %						
	Ash	C	H	N	S	Cl	C^{daf}
				Pit No. 83			
1	16.38	43.10	5.54	1.16	0.75	0.30	51.54
2	53.87	20.27	3.50	1.69	Нет	0.47	43.94
3	37.36	30.95	6.49	0.13	0.69	0.34	49.41
4	26.69	37.19	4.77	0.21	0.31	0.62	50.73
5	39.07	31.53	4.09	0.42	Нет	0.13	51.75
6	15.75	43.83	5.80	0.67	0.35	0.85	52.02
7	18.82	42.65	5.20	0.36	0.13	0.62	52.54
8	17.24	43.49	5.58	0.43	0.23	0.28	52.55
9	25.28	39.73	5.64	0.35	0.23	0.36	53.17
				Pit No. 8			
10	4.45	48.04	9.68	0.12	1.25	0.40	50.28
11	46.78	25.41	4.71	0.39	Нет	0.12	47.75
12	73.45	13.30	4.72	0.13	0.50	0.32	50.09

in cellulose and lignin content with an increase in depth was observed, while for samples from pit No. 83 we observed only a slight decrease in lignin content. Since it is impossible to establish unambiguously whether this is a consequence of the decomposition of organic matter or of sample heterogeneity, we investigated the composition and amount of organic compounds, which can be extracted from waste wood (Table 4).

Isolation of lignin-like substances (low-molecular polymers of phenolic nature), neutral compounds, phenols and acids was carried out according to the scheme accepted in chemistry of wood [5]. Extraction was carried out in an alkaline medium (pH 11). These conditions are more rigid than those existing in the pit depth (pH 7–8).

It was established that organic matter in the amount of 13 to 55 g/kg of sample can be extracted from the samples under analysis from pit No. 83. The maximal content of the extractives (up to 9 %) was discovered at a depth of 6–16 m (samples No. 3, 5), that is, in the middle of the pit. Then the total amount of extractables varies from 3 to 6 % depending on core depth (samples 6–9). The amount of lignin-like substances increased from sample 6 to sample 9 by a factor of 1.8, neutral substances by a factor of 2–3.3, phenols 1.8–2.5, acids 2–3.7.

It follows from the data obtained that biochemical destruction of lignocelluloses wastes and the formation of water-soluble high-molecular lignin-like and low-molecular substances (phenol compounds, acids and neutral substances) occurs in both pits. The amount of these substances increased with an increase in the horizon depth.

Analysis of the microbiological and sanitary-hygienic status of samples from the pits of the Ust-Ilimsk TIC

Substantial fungi content was observed in all the samples. The amount of fungi is much more than that at the corresponding depth in soil [6]. First of all, this is connected with an increase in the content of organic matter in these horizons of the pits in comparison with soil.

No clear dynamics of changes in the amount of microorganisms *versus* core depth was observed in the upper layers of the pit (down to 16 m, samples 1–5). For instance, some samples exhibited an increase in the amount of ei-

TABLE 4

Qualitative composition and quantitative content of water-extractable compounds in waste wood from the pits of the Ust-Ilimsk TIC

Sample No.	Concentration, mass %				
	Extractables	Lignin-like compounds	Low-molecular compounds		
			Neutral	Phenols	Acids
		Pit No. 83			
1	3.37	2.95	0.03	0.01	0.39
2	2.90	2.64	0.03	0.05	0.18
3	8.83	8.31	0.10	0.09	0.33
4	4.21	3.64	0.06	0.04	0.47
5	7.43	7.12	0.11	0.03	0.17
6	3.24	2.96	0.13	0.02	0.12
7	3.89	2.95	0.44	0.05	0.45
8	4.59	4.01	0.28	0.04	0.27
9	5.91	5.46	0.16	0.03	0.27
		Pit No. 8			
10	2.75	2.45	0.04	0.04	0.23
11	4.46	3.99	0.05	0.05	0.37
12	4.59	4.00	0.16	0.32	0.12

ther fungi (sample 2) or bacteria (sample 4), which is an evidence of localized (focal) occupancy of the dump depth by microorganisms at this depth (Table 5). Microbe sowing is likely to depend not only on the age of waste material but also on its chemical composition in this case.

Starting from sample 6 from pit No. 83, and all over pit No. 8, we observed an increase in the amount of fungi and bacteria with depth, which is not typical for soil horizons. The presence of a large number of aerobic microorganisms in deep layers is an indirect confirmation of the sufficient aeration of stored wastes, which is due to the high content of coarse fraction and not very high humidity. (The latter is inversely connected with aeration: the higher humidity, the lower aeration.)

The data of the sanitary-bacteriological examination showed that the pathogenic intestinal microflora, including bacteria of *Salmonella* genus, and anaerobic wound infection pathogens (*Clostridium perfringens*) are absent from the samples. At the same time, analyses revealed the presence of the bacteria of colibacillus group in the lower layers of pits Nos. 8 and 83 (samples 8 and 12). These microorganisms are detected in 0.001 g of samples and serve as an index of moderate contamination according to the sanitary-bacteriological evaluation for soil [7].

TABLE 5

Microbial semination and phytotoxicity of samples from the pits of the Ust-Ilimsk TIC

Sample No.	Amount per 1 g of sample, 10^5		Germination of test seeds, %
	Fungi	Bacteria	
	Pit No. 83		
1	2.95	3.27	96.7
2	22.47	0.50	96.7
3	0.76	1.07	80.0
4	7.93	15.81	93.3
5	1.09	0.27	83.3
6	25.83	15.45	96.7
7	29.60	23.17	96.7
8	30.88	77.21	93.3
9	33.38	66.89	96.7
	Pit No. 8		
10	15.93	12.99	100
11	31.25	25.84	96.7
12	53.18	241.40	100

To access the toxicity, we investigated the germinating capacity of the seeds of test plants (wheat) in the presence of samples under analysis (see Table 5). A small decrease in germination of wheat seeds, that is, weak phytotoxic properties were observed with two samples (3 and 5) which were distinguished by an increased content of extractives. Other samples had no toxic effect on the germination of wheat seeds.

CONCLUSIONS

The analysis of the state of waste wood stored for 17–29 years in the pits of the Ust-Ilimsk TIC allows us to make the following conclusions.

The presence of a large amount (40–60 %) of coarse fraction in the samples provided sufficient oxygen access into the dump depth and excluded the possibility of anaerobic processes. As a rule, the latter processes are undesirable because they are connected with the evolution of gases, first of all hydrogen sulphide and methane. Relatively low humidity of samples (48–60 %) also favoured the development and progress of biochemical degradation of wood material, promoted conservation of oxygen in the lower layers of pits and turned out to be sufficient for the development of aerobic microorganisms.

At the lower part of pits, at a depth of 18 m and more, a definite association of aerobic microorganisms has already formed during 17–20 years of dump existence. These mciroorganisms included bacteria and fungi that inhabited waste wood and started its destruction. It is the microbiologically active zone that exhibited changes in the chemical composition of samples and a rise in the content of water-soluble extractives, including lignin-like compounds, neutral compounds, phenols and acids. The amount of these compounds is not high yet, but it will increase with time because the microbiological settling in the dump depth and microbiological destruction of waste wood will progressively increase. Water-soluble substances will be accumulated at the pit bottom and/or enter the underground water. With their slow filtration and carrying away with underground water, they may have no essential negative effect on the chemical composition of underground water. However, in the case of high concentrations they may be ecologically dangerous, so it is necessary to monitor the chemical composition of underground water and first of all chemical oxygen demand, biological oxygen demand and phenol content.

At present, the pits of Ust-Ilimsk have no negative effect on the environment. However, analysis of the outlooks of waste wood storage suggests their latent ecological danger because the intensive microbiological activities may become the reason of self-ignition of waste wood, as it belongs to inflammable substance [8]. Examples are fires that occur at the pits of hydrolysis lignin in Zima city (Irkutsk Region). Precautions taken to eliminate fires are yet unable to change the situation crucially. Therefore, it is necessary to start within a short time the strategy of elimination of waste wood, that is, to introduce waste recycling. One of the approaches allowing the wide-scale use of waste wood was proposed in the technology of accelerated waste composting developed by the researchers from the Irkutsk Institute of Chemistry, SB RAS. This technology allows one to obtain high-quality organomineral fertilizer [[9] which is necessary to increase the fertility of agricultural land and perform revegetation of disturbed land.

REFERENCES

1 O sostoyanii i okhrane okruzhayushchey sredy Irkutskoy oblasti v 2003 g. (State Report), Irkutsk, 2004.

2 V. G. Storozhenko, M. A. Bondartseva, V. A. Solovyev, V. I. Krutov, Nauchnye osnovy ustoychivosti lesov k derevorazrushayushchim gribam, Nauka, Moscow, 1992.

3 Ten Hak Mun, Fermrntatsiya organicheskikh ostatkov s tsel′yu polucheniya udobreniy (metodicheskiye rekomendatsii), Khabarovsk, 1988.

4 A. V. Obolenskaya, Z. P. Elnitskaya, A. A. Leonovich, Laboratornye raboty po khimii drevesiny i tsellyulozy, Ekologiya, Moscow, 1991.

5 L. N. Petrushenko, S. A. Medvedeva, V. A. Babkin *et al., Khim Drevesiny*, 1 (1980) 71.

6 T. G. Mirchink, Pochvennaya mikologiya, Izd-vo MGU, Moscow, 1976.

7 N. P. Elinov, N. A. Zaikina, I. P. Sokolova, Rukovodstvo k laboratornym zanyatiyam po mikrobiologii, Meditsina, Moscow, 1988.

8 I. M. Abduragimov, A. S. Androsov, L. K. Isaeva, E. V. Krylov, Protsessy goreniya, Moscow, 1983.

9 Pat. 2192403 RF, 2000.