



MINIMIZATION OF ATMOSPHERE POLLUTION BY UTILIZING CELLULOSE WASTE

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Abstract. The greenhouse effect is our planet's ability to pass the Sun's incoming radiation and to reflect the re-radiated long wavelengths from the Earth's surface, so increasing our planet's surface and atmosphere lower-layer temperature. As a result, the melting of glaciers and snow cover intensifies, and the water level of seas and oceans increases, flooding islands and coast lines. Increase in temperature intensifies water evaporation, increases the possibility of down-pour and cyclone formation in seaside regions, while on continents – droughts, heat-waves and forest fires.

So lowering of the greenhouse effect is one of the main global problems today.

The main greenhouse effect „agents“ are carbon dioxide CO₂ (53 %), freon, ozone, methane CH₄ and other substances. CO₂ is formed during breathing of live organisms, activity of microbes in the soil, also during the combustion of various organic substances. CH₄ and CO₂ are formed when cellulosic matter – wood, peat moss, agricultural production waste, vegetation – decay at treatment places, by tillage also in landfills processes take place. From all the mentioned processes mankind controls only the cellulose mater combustion and decay processes which it should decrease as much as possible to weaken the green-house effect. However, at present it is unrealistic to lower the amount of CO₂ formed by burning fossil fuel in industrial enterprises and heating systems.

Cellulose-containing waste can be reprocessed without emitting CO₂ or CH₄ by manufacturing building materials, thermal as well as acoustic insulating composites. Wooden waste has been used for these purposes for a long time. At present it is recommended to use other cellulose raw materials – straw, reeds, boon, peat moss and other materials. The utilization of straws given composites, containing straws, Portland cement (in some cases – construction gypsum and sand and polymeric additives – vinyl acetate (e.g. polyvinyl acetate PVA) or cellulosic materials (e.g. carboxymethylcellulose CMC) dispersions. The utilization of reeds gives composites containing reeds, Portland cement and PVA or CMC. The utilization of boon or chaff gives composites containing boons or chaffs, anhydrite or aluminat cements and PVA or CMC. Optimal composition composites distinguish themselves by good physico-mechanical as well as thermal and acoustic properties and can find applications as building materials as well as thermal and acoustic insulating materials.

Keywords: greenhouse effect, thermal and acoustic insulating materials, lowering of CO₂ emissions into the atmosphere.

1. Introduction

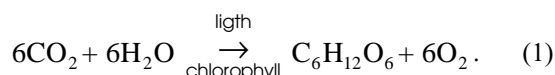
There are many interconnected environmental processes going on at the Earth's surface from the global point of view, and at the same time, they are contradictory. One of these processes is photosynthesis, when with the help of it oxygen (O₂) is formed from water and carbon dioxide as are hydrocarbons from wooden products. The second process is the combustion of wood and other sorts of fuel which gives CO₂ (accompanied in part by charcoal fumes), also decay process products – methane. CO₂ and CH₄ are well known “greenhouse”

effect intensifying “agents”. Now, let us take a look at the origin of photosynthesis and greenhouse effect processes, its properties and influence on mankind.

1.1. Photosynthesis

Besides CO₂ and H₂O, other mineral nitrogen, phosphorus and other element salts also light take part in the *photosynthesis* process; other photosynthesis process products are hydrocarbons e.g. glucose, also proteins and even fats.

The photosynthesis scheme can be illustrated as follows:



Polysaccharides are formed gradually in plants from glucose, the most important one being cellulose – a constituent of wood.

Chlorophyll (from greek *chloros* – green and *phyllon* – leave) is the green plant pigment – photosynthesis process sensibilizator, i e the “motor” of the photosynthesis process. Here light energy absorbed by chlorophylls, thanks to redox reactions in a complex photosynthesis mechanism, is transformed into chemical energy.

Chlorophyll has several modifications (a, b, c, d), however, all of them contain magnesium, e g a – $\text{C}_{55}\text{H}_{72}\text{O}_5\text{N}_4 \text{ Mg}$; b – $\text{C}_{55}\text{H}_{70}\text{O}_6\text{N}_4 \text{ Mg}$, etc. Chlorophyll is present in the vegetation green leaves, needles special cellular tissues – organelose (plastids) called chloroplasts. In spite of the fact that chlorophylls make up only (0,7–1,3) % of the plant dry mass, its role in the vegetation development process is very important, as we can see.

Also, as it can be seen from various chlorophyll species, if there were no magnesium on the Earth, there would be no vegetation (maybe), only fungus would grow.

Thanks to the photosynthesis reaction, vegetation assimilates 4×10^{10} t of carbon every year from the Earth's surface and oceans, also $1,2 \times 10^{11}$ t of water are decomposed, 1×10^{11} t of oxygen is liberated, and 4×10^{20} cal of solar energy is accumulated in photosynthesis products as chemical energy. The latter energy amount is 10 times higher than the amount of energy needed by mankind. The amount of vegetation used to feed animals in agriculture makes up only 2 % of the whole photosynthesis production.

So, it depends on mankind, if deforestation is to continue, and as a result less oxygen is released, or it is going to be done according to scientific recommendations accompanied by replanting of the cut forests.

1.2. Greenhouse effect

The greenhouse effect (in other words, the orangery effect) is the Earth's atmosphere ability to let through the incoming shortwave radiation from the Sun and trap the reradiated long-wave radiation from the surface, thus increasing our planet's surface and lower the atmosphere temperature.

The greenhouse phenomena is our planet's characteristic feature. The main causes are: 1 – the Earth's atmosphere is pervious to visible Sun rays, 2 – the incoming rays are absorbed by the Earth's surface, and only their part is reradiated, 3 – the warmed Earth's surface radiates only infrared rays, (80–90) % of which are absorbed by the atmosphere. Due to all this, the Earth's air temperature increases.

The greenhouse effect, although it causes global warming, has an adverse effect on further climatic changes on the Earth.

The Red Cross organisation in its report of 1999 about natural calamities has warned that due to gradual world climate changes there will be more and more extreme atmospheric occurrences which will endanger millions of lives.

From this standpoint, we can find many unfavorable prognoses in the press.

Due to air warming and expansion of the upper ocean layer as well as the melting of glaciers and snow, the sea water level will rise by 44 cm by 2080. As a result, densely populated coast areas will be in danger of floods more than 10 times. Cities like Tokyo, Shanghs, Lagos, Djakarta will be in danger. Analysis of the published data in the press conducted by the authors shows that the seaside of Lithuania will approach Kartena from Palanga.

Intensification of the evaporation process and climate warming will increase the probability of storms and cyclones in seaside regions. Intensive rains in deforested areas (e g Brazil) can cause landslides. At the same time increased heat and water evaporation will cause droughts in the middle of continents.

The water level will drop and water resources will diminish, rivers will sink (the Nile, the Nigers, the Inda). All this will cause infertility, famine and conflicts related to water resources. Exhaustive heat waves, forest fires will become more frequent.

So, decreasing of the greenhouse effect is one of the main modern time global problems.

Taking all this into account, Lithuania with other 154 countries signed the Rio de Janeiro United Nations General Climate Change Convention in 1992. Seimas (Parliament) of the Republic of Lithuania ratified this convention in 1995, and it came into force in our country. In 1996 Lithuania prepared a strategy for implementing the Convention and inventorized gaseous emissions increasing the greenhouse effect.

One of the greenhouse effect intensification causes is concentration increase in the air of one of the gases – especially, carbon dioxide CO_2 , methane (natural gas) CH_4 , ozone O_3 , nitrous oxide N_2O , freon (fluorochlorobrom hydrocarbons, e. g. CFCl_3 , CF_2Cl_2 , CF_2HCl , CF_3Br , etc.). According to the influence on the greenhouse effect intensification, the mentioned gases can be arranged as follows: carbon dioxide (53 %), freon (20 %), ozone (7 %), methane (6 %), nitrous oxide (4 %) [1].

As we can see from the given numbers, the main cause of the greenhouse effect is increase in the amount of CO_2 present in the air at the Earth's surface.

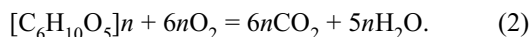
2. CO_2 and CH_4 paths into the atmosphere

The main CO_2 formation and emission paths are the following processes (in %):

- rotting, fermentation, breathing of land and water organisms 56,09;

• soil microorganism activity	38,00;
• combustion of crude oil, carbon and peat mass	3,08;
• breathing of animals	1,28;
• forest and steppe fires	0,38;
• breathing of humans	0,32;
• volcanoes and other CO ₂ sources	0,09;
• limestone burning	0,04;
• other sources	0,72.

The vegetation cellulose combustion process takes place as follows:



As follows from the reaction equation, if we want to burn 1 kg of cellulose we use up to 4 m³ of air and evolve 0,83 m³ of CO₂. Forest fires give off enormous amounts of CO₂ and H₂O vapour. Besides, CO and CH₄ various hydrocarbons, methanol acetic acid as well as resins and coke are formed during fires.

About 22,3 billion t of CO₂ are emitted into the Earth's atmosphere every year. CO₂ emission levels into the environment, possible consequences and CO₂ emission lowering means were first examined by the Kyoto Protocol, where the requirements for CO₂ emissions into the environment were determined. The European Union also joined the Protocol. At the conference of 2001 the participants of the Kyoto Protocol decided to determine a common emission level of pollutants in the EU. The European Commission decided that beginning with 2005 pollutant emission abatement mechanism would affect enterprises which emit especially large amounts of CO₂. The European Union has to decrease CO₂ emissions by 956×10⁶ t by 2005.

Forests cover about 30 % of the Earth's land area and about (27–28) % of Lithuania's territory which is almost equal to 2 million ha. The main vegetation present in Lithuania's forests are pines and spruce making up about 56 % of the whole forest area, i.e. about 1 million ha. Approximate calculations show that Lithuania's forests have about 4,5 billion m³ of pine and spruce timber.

If we assume that trees grow about (5–10 a) apart from one another, we get that one tree occupies about (0,5–1,0) a. Then we get that 1 ha "contains" 100–200 trees, while 1 million ha has (100–200) million trees. Taking into account that an average tree has 1 m³, we obtain a mean timber volume of (100–200) million m³. Since approximately 50 % of timber is made of cellulose, its mass in timber would be (60–120) billion m³ (taking into account a mean timber density of 1200 kg/m³). The burning of this amount of cellulose would emit (100–200) billion m³ of CO₂. This amount of CO₂ would greatly affect the greenhouse effect in the atmosphere, if emitted into it.

If this is not burnt, but cut, then the amount of O₂ emitted into the environment would decrease. Similar calculations give us the following: if Lithuania's pine and fir trees were cut, the amount of O₂ emitted into the

environment would decrease by (30–50) billion m³.

Of course, full destruction of forests is an extreme process limit which, we hope, will never be reached. However, if even 10 % of Lithuania's forests were destroyed, about (10–20) billion m³ of CO₂ would be emitted into the atmosphere above the territory of our republic, besides, there would be a decrease in O₂ amount by (3–5) billion m³.

The following amounts of CO₂ and CH₄ (thousand t) were emitted into the atmosphere in Lithuania in 1990:

CO₂: energetics – 37332; agricultural usage and forest changes – 2803; industry – 2203,

CH₄: agriculture – 180,7; waste – 165,7; energetics – 31,4; industry – 0,2.

It is foreseen that in 2010 from 36 to 53 million t of CO₂ and 330 thousand t of CH₄ will be emitted into the atmosphere in Lithuania.

3. Cellulose and its decay products in nature

In our opinion, the decay of cellulose and its decay products can take place according to two mechanisms in nature:

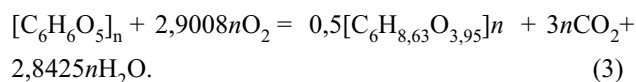
- 1) transformations in the air – by taking up O₂ and emitting CO₂ as well as H₂O,
- 2) transformations in a media containing water (soil, silt, water) – by taking up H₂O and emitting CH₄ as well as CO₂.

On the basis of various references we obtained formulae for wood, peat moss and other cellulose decay products according to transformation equations given below.

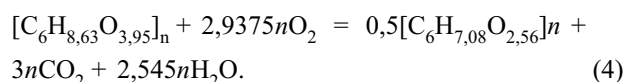
3.1. The first transformation complex – conversion formations by the action of O₂ (equations were derived by the authors)

In this case the reactive agent is O₂. The following processes are possible:

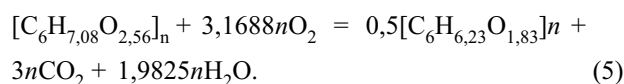
- 1st transformation „cellulose → wood“ –



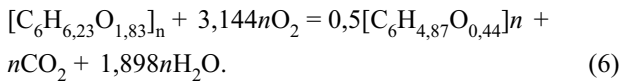
- 2nd transformation „wood → peat moss“ –



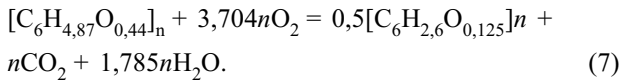
- 3rd transformation „peat moss → lignite“ –



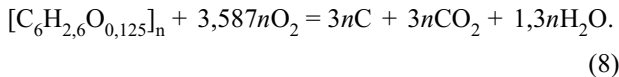
- 4th transformation „lignite → coal“ –



• 5th transformation „coal → anthracite“ –



• 6th transformation „anthracite → pure carbon“ –



Analysis of the reaction equations shows that in the sequence „cellulose → wood → peat moss → lignite → coal → anthracite → pure carbon“ the necessary oxygen molecule amount nO_2 for the formation of materials is directly connected with the amount of O_2 atoms present in the adjacent materials of the sequence.

The oxygen difference ΔO linear regressive equation in which number 5 represents the number of oxygen atoms in the cellulose formula:

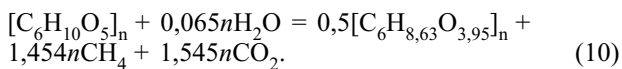
$$nO_2 = 0,775 (5 - \Delta O) \pm 0,2. \quad (9)$$

So, in such a way the amount of oxygen used up during the first transformation complex reactions is correlatively directly proportional to differences in the amount of oxygen in the initial and final transformation stages.

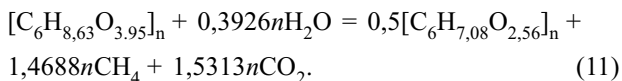
3.2. Second transformation complex – transformations in water-containing media (equations were derived by the authors)

In this case an aggressive factor is H_2O . The following process cases are possible.

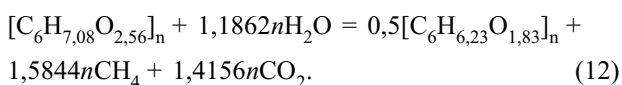
• 1st transformation „cellulose → wood“ –



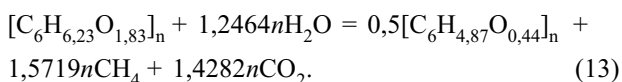
• 2nd transformation „wood → peat moss“ –



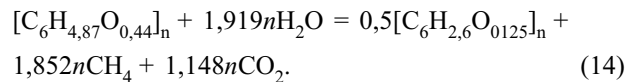
• 3rd transformation „peat moss → lignite“ –



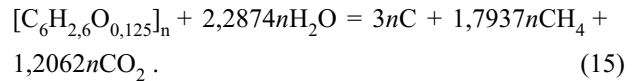
• 4th transformation „lignite → coal“ –



• 5th transformation „coal → anthracite“ –



• 6th transformation „anthracite → pure carbon“ –



The analysis of the equations shows that the amount of H and O atoms in the materials are almost linearly proportional to each other. This fact can be expressed by the following approximate equation:

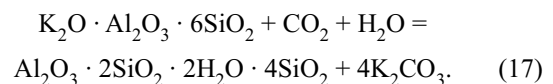
$$H \approx 4,5 + 1,1 O. \quad (16)$$

3.3. Reduction of CO_2 and CH_4 emissions into the air

How can we weaken increase of CO_2 emissions into the atmosphere?

At present reduction of CO_2 released into the atmosphere during combustion of fuel is an unsolved global problem. Besides, we cannot change the material metabolism process which is made of a whole complex of chemical reactions going on in living organisms – a process during which, among other things, CO_2 is also emitted.

A part of CO_2 emitted into the atmosphere is bound by land and sea vegetation. During the weathering of granite constituents feldspars, orthoclase, sand and clay are formed:



However, this process proceeds very slowly and does not weaken the greenhouse effect.

After a review of all the facts we came to a conclusion that if we want to stop some of the increase in CO_2 and CH_4 concentrations in the Earth's atmosphere, it is expedient and economically feasible not to burn or decay cellulose-containing waste but to reprocess it into building materials or heat-insulating as well as acoustic composites.

4. Investigation object

At present wood is the most widely used cellulose-containing raw material mainly for building material production. This material can be divided into three parts as follows:

I. Articles wooden parts of which are connected by inorganic binders. These are articles made from chopped wood, shavings, crumbles, bark binding the raw material with cements (including lime, gypsum, etc). Wood concrete or arbolite, cement-wood and cement-shaving

boards, Fibrolite fiberboards, veloks, diurasol bark concrete, cork agglomerates, sawdust concrete, wood concrete, thermoporite, thermooxisol, thermizine belong to this class of articles.

II. Articles wooden parts of which are connected by synthetic resins. These are articles made from wooden slabs, layers, prefabs, cuttings, shavings, sawdust impregnating them with synthetic resins during hot pressing. Plywood, wooden layer plastics, delta-wood (laminated birchwood), lignostone (laminated wood), chip boards belong to this class of articles.

III. Articles made from wood or cotton fibers. Fiberboard wool, paper and cardboard belong to this class.

Straws, reeds, chaffs, peat moss, sapropels and waste papers are used in small amounts for similar purposes.

On the basis of these fact investigation of using straws, reeds, chaffs and husks for the production of building composites, heat-insulating and acoustic materials was conducted at Vilnius Gediminas Technical University.

5. Materials

The following materials were used for the production of building composites.

Cellulosic fibrous fillers

Straws, chaffs and husks were from various agricultural enterprises in Vilnius and Ukmergė districts; reeds from the Vokė riverside, in Juodoji Vokė country side district.

Inorganic binders

- AB „Akmenės cementas“ 42,5 R class Portland cement CEM I 42,5 R.

- Constructional gypsum from Saulriešė Plant (Latvija), sand – from Pagiriai quarry.

- Anhydrite cement was manufactured by the „Palemonas ceramics“, Co, composition (vol.) (25,6–33,5) % CaO and (27,4–41,0) % SO₃; initial setting time (0,5–2,5) h, final setting time (2–4) h, max strength gained after 28 days: flexural strength (2,6–3,0) MPa. XDP analysis showed that CaSO₄ prevails in the material.

- Aluminate cements Gorkal 40 (G-40) and Gorkal 70 (G-70) were obtained from the Gorkal Co (Trzebinia, Poland) contained (69–72) % Al₂O₃ and (28–29) % CaO; initial setting time ≥ 40 min, final setting time ≤ 8 h; strength gained after 24 h; flexural – (6–8) MPa, compressive – (30–40) MPa. XDP analysis showed that the material consists mainly of CaO × Al₂O₃, CaO × 2Al₂O₃, 12CaO × 7Al₂O₃ and α-Al₂O₃.

Polymer binders

- Polyvinyl acetate (PVA)–HW 1 trademark commercial dispersion (Finland) containing 50 % dry solids; it is an aqueous dispersion.

- PVA powder–Vinnap RS55Z trademark commercial product; 4 % dispersion.

- Carboxymethylcellulose (CMC) powder–commercial product (Finland); 4 % dispersion.

- Walocell–commercial CMC product grade MK–3000 supplied in the form of powder; 4 % dispersion.

- Methylcellulose (MC) – „Methylan normal“ (Germany); 2 % dispersion.

6. Investigation methods

The work was carried out according to the following scheme: product composition design – manufacture of specimens – determination of specimen properties: durability – density – strength, specific thermal conductivity – thermal resistance – economic calculation – conclusions, recommendations.

The density, flexural and compression strength, specific thermal conductivity and pH of specimens were found by standard procedures. Using a derivatograph Q-1500 for analysis 5 specimens at a time performed thermographic testing. X-ray photographs were obtained by a diffractometer DRON-2 (Russia) (Co anode, Fe filter, slits – 1:2:0,5 mm); diffractometer tube's operating mode: $U = 3 \text{ kV}$, $I = 10 \text{ mA}$.

- The production of composites containing straw is described below.

The components were mixed in a spheric metallic disk in the following sequence: Portland cement, constructional gypsum, sand-straw-PVA, CMC or MC dispersion – a special additive.

Straw was dried for 1 day at (100–105) °C with the purpose to: a) remove the whole moisture because humid straw is hard to pulverizer; b) break up a natural waxy layer which covers the straw stem surface which worsens the adhesion of straw particles with binders. After that straw was treated in a hammer-mill and sieved. A (0,5–5,0) mm fraction with an average density of 90 kg/m³ was then introduced into the composition. Straw can also be treated by the thermal method. Then it should be chopped and steamed by boiling water or steam vapour. Treatment of straw by a (1–2) % sodium hydroxide solution for (5–6) h weakens H-bonds in cellulose and lignin. Caustic soda can be replaced by a cheaper (4–5) % soda solution or by lime “milk”.

Portland cement and constructional gypsum were sieved through a metallic sieve having 4900 holes/cm². Sand was dried for 1 day at (100–105) °C temperature and then sieved through sieves with (5; 2,5; 1,25) mm openings.

Polymeric additives were used in a dispersion form. To achieve that the commercial PVA was diluted with water at a ratio of 1:1 because at this ratio we obtained an optimal binder concentration and viscosity value. The other optimal polymer binder dispersion concentrations were the following: Vinnap – 4 %; CMC – 4 %; MC – 2 %.

In most cases we used special additives antipyrene – 1 % solution of borax; antiseptic – a saturated (0,65 % concentration) sodium hexafluorosilicate solution; hydrophobizator – hydraulic liquid GTZ–22.

The prepared raw material mixture was put into a metal or wooden form of required dimensions smeared with nigrol and compacted with a wooden paddle. The prefabricate was covered with a wooden board and pressed with a 2 kg weight (it is also possible to use a press) and held at room temperature for 7 days – first over water, later in the air. After 7 days the slabs were removed from the forms and allowed to dry (best at 60 °C temperature): small articles in a drying oven, large ones in drying chambers. At higher ambient temperatures it is possible to dry the specimens in the air.

(0,3–1,2) MPa force is used when specimens are prepared by the pressing method.

- The production of composites containing reeds is described below.

Reed stems were dried at room temperature and chopped in a hammer-mill to particles up to 10 mm in length. The preparation of other raw materials and specimen formation was the same as in the case of straw composites.

- The production of composites containing chaff or husks was conducted just in the same way as in other cases.

7. Results and discussion

The composition and properties of composites containing cellulosic fibrous raw materials are given below.

7.1. Composites containing straw [2–6]

- It was determined that the production of composites containing PVA should be as follows, mass %: straw – (6–17); cement – (12–32); constructional gypsum – (5–33); sand – (9–18); PVA (50 %) – (15–30); special additives – (0,2–2,0); cement-gypsum ratio – 1 : (0,25–1,50); pressing force – (0,3–1,2) MPa.

The main composite physico-mechanical and thermal characteristics are as follows:

1. *Density.* Articles dried at 80 °C temperature $\rho = (660–1180) \text{ kg/m}^3$. This index depends on the amount of straw in the material, also on its compactation degree.

2. *Strength.* $R_g = (6–11) \text{ MPa}$, $R_l = (4–7) \text{ MPa}$. The specimen does not crumble up to a certain limit during compression, i.e. it possesses a high deformation plasticity.

3. *Thermal properties.* $\lambda = (0,28–0,30) \text{ W/(m} \cdot \text{K)}$. The heating of one side of a 60 mm thick specimen with air of 500 °C increased the side surface temperature of the other specimens from 20 °C only to (35–40) °C after 3 h. The heated side did not get scorched charred. The material is frost-resistant and withstands 15 freezing-thawing cycles.

4. *Acoustical properties.* The sound absorption of specimens made from the investigated material gave sound absorption of 35 dB.

5. *Water-resistance.* The specimen water absorption

was (8–14) % (based on dry solids). The whole absorbed water in a specimen evaporated gradually by drying at 80 °C temperature.

6. *Resistance to microorganisms.* Specimens containing antiseptics showed no growth of microorganisms after 16 months.

- Composites containing CMC had the following composition, mass %: straw – (8–35); Portland cement, constructional gypsum and sand – 64–86; CMC (dry solids) – 1,2–3,7.

The main CMC-bound composite physico-mechanical and thermal characteristics are as follows:

1. *Density.* Composite density dried at 80 °C temperature was $\rho = (605–885) \text{ kg/m}^3$.

2. *Mechanical strength.* Composite $R_g = (1,2–2,8) \text{ MPa}$, $R_l = (1,1–1,7) \text{ MPa}$.

3. *Acoustical properties.* The sound absorption coefficient was: 1) low frequency ((100–500) Hz) range – (0,05–0,10); 2) medium frequency ((500–2000) Hz) range – (0,10–0,30); 3) high frequency ((2000–4000) Hz) range – (0,10–0,25).

4. *Thermal properties.* λ , W/(m · K), was: 0,08 – at $\rho = 605 \text{ kg/m}^3$ and 0,18 – when $\rho = 885 \text{ kg/m}^3$.

5. *Thermal resistance.* The specimens did not show any changes when heated in the (100–200) °C temperature range. At 250 °C it became brown in color, at 300 °C carbonised, and at 400 °C smoke was emitted.

- Composite performance properties.

1. *Mechanical treatment possibilities.* All the well-dried articles made from the investigated materials were easily mechanically treated by all the methods – it could be sawed, drilled, shaved, nails could be hammered and screws screwed. Several articles could be glued together or with other materials. Cement or polymer-cement mortars, polymeric adhesives (like PVA or perchlorvinyl glues), various mastics (KN–3, etc) could be used.

2. *Article surface decorative finishing.* A natural article's surface is of a grey-brownish colour. If we want to change an architectural appearance or other specific properties (increase noise absorption, water resistance, high-temperature resistance, improve hygienic properties), we need to apply special materials to its surface. This could be done by the above mentioned methods. Also, the surface could be painted by all sorts of paints, covered by wallpaper, etc.

3. *Usage.* The composites could be used for low-storey building exterior wall elements as well as for partitions, etc. A very effective construction is obtained when an exterior side is made of a high-density composite, a middle one – of porous, while an interior thin layer – again from a thin dense layer. A middle layer should be made of a very efficient heat-insulating material, leaving between an exterior and interior (thermo-insulating) layers a (20–30) mm air space.

7.2. Composites containing reeds [7, 8]

- The composition of this type of composites containing PVA is as follows, mass %: reeds – 20–22; Port-

land cement – 42–45; constructional gypsum – 21–22; PVA – 13–14.

Composite properties:

Density: (790–830) kg/m³.

Mechanical strength: $R_l = (1,9–2,4)$ MPa, $R_g = (5,6–8,0)$ MPa.

Thermal properties: λ , at $\rho = (790–830)$ kg/m³, is (0,134–0,148) W/(m·K). According to these indices, articles could belong to the third class of heat-insulating materials.

Acoustical properties. The normal sound absorption coefficient values for various frequency ranges are as follows:

1) low frequency range ((125–500) Hz) – (0,10–0,80); 2) medium frequency range ((500–2000) Hz) – (0,15–0,42); α maximum is equal to 0,80 and corresponds to 315 Hz frequency.

• The composition of composites containing CMC is as follows, mass %: reeds – 24–25; Portland cement – 55–56; construction gypsum – 19–20; CMC – 2–3.

Composite properties:

Density: (714–766) kg/m³.

Mechanical strength: $R_l = (1,4–1,8)$ MPa, $R_g = (1,5–2,7)$ MPa.

Thermal properties: λ , at $\rho = (714–766)$ kg/m³, is equal to (0,110–0,117) W/(m·K). According to these indices, articles could belong to the third class of heat-insulating materials.

Acoustical properties. The normal sound absorption coefficient values for various ranges are as follows:

1) low frequency range ((125–500) Hz) – (0,05–0,70); 2) medium frequency range ((500–2000) Hz) – (0,37–0,84). α maximum is equal to 0,84 which corresponds to 630 Hz frequency.

7.3. Composites containing boon [9–11]

• The composition of this type composites containing *anhydrite cement* is as follows, mass %:

1) PVA case: boon – 47–55; cement – 45–55; PVA – 1–5. Composite density is (112–831) kg/m³;

2) CMC case: boon – 40–55; cement – 42–60. Composite density is (107–1006) kg/m³. The thermal conductivity coefficient for specimens with a density of 225 kg/m³ is equal to 0,063 W/(w·K); specimens with 384 kg/m³ density have a flexural strength of 0,57 MPa.

• The composition of this type of composites containing *aliuminate cement* – 40 are as follows, mass %:

1) PVA case: boon – 11–45; cement – 50–78; PVA – 5–11. Composite density is (165–1108) kg/m³;

2) CMC case: boon – 40–45; cement – 50–60; CMC – 5. Composite density is (128–613) kg/m³. Specimens with a density of 593 kg/m³ have a flexural strength of 0,63 MPa.

• The composition of this type of composites containing *aliuminate cement* – 70 are as follows, mass %:

1) PVA case: boon – 45–60; cement – 35–60; PVA – 5. Composite density is (129–684) kg/m³. Specimens with a density of 119 kg/m³ have the heat conductivity coef-

ficient of 0,12 W/(m·K);

2) CMC case: boon – 45–65; cement – 35–55; CMC – 1–5. Composite density is (119–723) kg/m³. Specimens with a density of 723 kg/m³ have a flexural strength of 1,31 MPa.

7.4. Composites containing chaff [9–11]

The composition of this type of composites containing *anhydrite cement* is as follows, mass %:

• 1) PVA case: chaff – 45–60; cement – 35–55; PVA – 2–8. Composite density is (286–685) kg/m³;

2) CMC case: chaff – 45–65; cement – 30–55; CMC – 0,2–0,5. Composite density is (203–774) kg/m³.

• The composition of composites containing *aliuminate cement* – 40 are as follows, mass %:

1) PVA case: chaff – 40–60; cement – 45–55; PVA – 5. Composite density is (335–493) kg/m³;

2) CMC case: chaff – 40–50; cement – 45–55; CMC – 5. Composite density is (303–1103) kg/m³. Specimens with a density of 1103 kg/m³ have a flexural strength of 1,08 MPa.

• The composition of composites containing *aliuminate cement* – 70 are as follows, mass %:

1) PVA case: chaff – 45–60; cement – 30–50; PVA – 5–8. Composite density is (335–493) kg/m³;

2) CMC case: chaff – 45–70; cement – 30–55; CMC – 0,5–1. Composite density is (128–1105) kg/m³. Specimens with a density of 1105 kg/m³ have a flexural strength of 0,95 MPa.

In the Table summary of strength and thermal-insulating properties is given for dry and form-maintaining cellulosic composites.

According to heat conductivity coefficient values, one of the composites belong to class II of heat-insulating materials (some of the B–An–CMC system composites) others – to II and III class (some of the S–Pc–CMC system composites) and to class III (some of the R–Pc–PVA, R–Pc–CMC as well as boon-containing composites).

Composites made from straw, Portland cement and PVA exhibit a good sound absorption – 35 dB (slab thickness of 40 mm). Straw and reed composites also possess a high sound-absorption coefficient: 1) S – Pc – CMC system composites – 0,05–0,30; 2) R – Pc – PVA as well as R–Pc–CMC system composites – 0,05–0,84.

Such types of composites could be used to build noise-absorbing walls along highways in villages and near noisy streets.

The use of heat-insulating composites for insulation of buildings could give an appreciable economic benefit. The maintenance of a typical one-storey building (overall wall length of 70 m, ceiling height of 2,4 m and a general wall area without doors and windows of 150 m²), wall masonry of silica bricks (wall thickness of 2 bricks), interior plaster of 2 cm had the following heat losses during October–April, when the mean outdoor temperature was +0,7 °C, and indoor temperature was +20 °C: no insulation – 18 152 kWh; insulated with

Cellulosic composite strength and thermal-insulating properties. Abbreviations: A40 – aliuminate cement – 40; A70 – aliuminate cement – 70; An – anhydrite cement; R – reeds; C – chaff; Pc – Portland cement; B – boon; Sr – straw

Composite type	Density ρ , kg/m ³	Flexural strength, MPa	Heat conductivity coefficient, W/(m·K)
S – Pc – PVA	660–1180	4–7	0,28–0,30
S – Pc – CMC	605–885	1,1–1,7	0,08–0,18
R – Pc – PVA	790–830	1,9–2,4	0,134–0,148
R – Pc – CMC	714–766	1,4–1,8	0,110–0,117
B – An – PVA (CMC)	133–1006	0,57 (KMC; $\rho = 384$)	0,063 (KMC; $\rho = 225$)
B – A40 – PVA (CMC)	128–1008	0,63 (KMC; $\rho = 593$)	–
B – A70 – PVA (CMC)	129–723	1,31 (KMC; $\rho = 723$)	0,12 (PVA; $\rho = 119$)
C – An – PVA (CMC)	203–774	–	–
C – A40 – PVA (CMC)	303–1103	1,08 (KMC; $\rho = 1103$)	–
C – A70 – PVA	214–1105	0,95 (KMC; $\rho = 1105$)	–

8 cm boon composite ($\lambda = 0,08$ W/(m·K) layer covered with gypsum boards – 14 135 kWh; the difference in energy losses was 4017 kWh. An approximate redeemable heat insulation period is 3,23 years.

8. Influence of cellulosic composite usage on reducing CO₂ emission into the atmosphere

Taking into account the above described general building wall area and the used composite slab thickness of 0,1 m, the composite volume would be 15 m³. Assuming that an average composite density is 500 kg/m³, the composite mass would be equal to 7,5 t. Assuming that the amount of cellulosic materials present in it is 45 %, we get that there are 3,4 t. Cellulose contains 4 % of carbons, so there is 1,5 t which is equal to 3,7 t of CO₂. So the thermal insulation of a typical house by using the described composites could accumulate 3,7 t or 1880 m³ of CO₂ which otherwise would be emitted into the atmosphere. Implementation of building heat insulation on a global scale in cold and medium climate zones for only 100 thousand of buildings could „bind up“ 370 thousand t or about 200 million m³ of CO₂.

9. Conclusions

1. Increase in the amount of carbon dioxide (CO₂) and methane (CH₄) in the air has a negative effect on nature and human beings. CO₂ enters the atmosphere when fuel, forests and cellulose-containing waste are burnt, while in the case of CH₄ – when organic matter, including tilled-cellulose-containing waste, decays. So reuse of cellulose-containing wood processing and agricultural production waste, non-cultural vegetation and other cellulose-containing products for the production of constructional cellulose-containing composite products can contribute to a decrease in a local greenhouse effect.

2. There are lots of cellulose fiber-containing raw materials, such as wood waste, wood-processing enterprise waste, wooden article waste, used wooden articles,

wood-felling area waste, bark, agricultural production waste – grain, flax, hemp-reprocessing waste, non-cultural vegetation – reeds, rushes, cattails, non-valuable hay, coniferous cones, also needles; excavated vegetation raw materials – peat moss and sapropel; household waste – paper waste, cotton textile waste.

3. The following agricultural production grain waste (straw, chaff) and flax or hemp (boon, tow) could be used for manufacturing constructional composites.

* Straw constructional materials are obtained: 1) by steaming them for decomposing a natural waxy layer without pressing, so that the evolved resinous materials could bind the straw into a solid article; 2) by binding with inorganic binders (cement, clay); 3) by binding with inorganic binders containing polymeric additives.

Wall and heat-insulating articles, which belong to the straw class, are: steamed and hot-pressed “Stramit” slabs; Portland cement and clay-bound straw-bricks; pressed Portland cement with constructional gypsum and polymeric PVA and CMC-type additives.

* When boon and chaff are used for wall and heat-insulating constructional materials, they are bound with anhydrite or aluminat cements containing polymeric PVA as well as CMC-type additives. This type of articles belong to II and III class heat-insulating materials.

4. The production of constructional composites from non-cultural vegetation uses reeds, rushes, cattails and other similar vegetation. These types of composites could be made by binding dried and chopped plants with Portland cement with addition of PVA and CMC-type polymeric additives. These articles belong to II and III class heat-insulating materials.

5. The composite production cost price is made up of raw material and equipment costs, material mixture preparation costs, electric energy costs and lebow costs. The most economic composites are wood concretes, sawdust concretes as well as articles from straw, chaff and reeds. Their production is simple, does not require intricate equipment and is economic, besides, composites could be manufactured at a place of usage, what is es-

pecially important for rural areas.

6. Composites, containing agricultural production waste (e.g. straw) as well as non-cultural vegetation (e.g. reeds) distinguish themselves by fairly good sound absorption properties. Boards made from such composites can be used to build walls near highways, especially where they intersect city outskirts.

References

1. Sörensen, Ch. Wärmedämmstoffe im Vergleich. München: Umweltinstitut München, 1994.
2. Kazragis, A.; Nickus, I.; Gailius, A. Construction Material Production Technology Using Organic Fillers. In: Proceedings of the 4th International Conference „Modern Building Materials, Structures and Techniques“. Vilnius: Technika, 1995, p 234–238 (in Lithuanian).
3. Kazragis, A.; Gailius, A.; Nickus, I. Heat-Insulating Materials Made from Local Raw Materials. *Construction and Architecture (Statyba ir architektūra)*, No 4, 1996, p 15–16 (in Lithuanian).
4. Kazragis, A.; Milčiūnienė, V.; Kulinič, H.; Gailius, A.; Nickus, I. Investigation of Use of Organic Production Waste for Manufacturing Constructional Materials. *Environmental Engineering (Aplinkos inžinerija)*, No 2(6), 1996, p 18–24 (in Lithuanian).
5. Kazragis, A.; Kulinič, H.; Gailius, A.; Nickus, I. Straw Bricks Containing Carboxymethylcellulose in its Compositions. In: Proceedings of International Conference on Lithuanian Science and Industry „Silicate technology“. Kaunas: Technologija, 1999, p 142–147 (in Lithuanian).
6. Kazragis, A.; Gailius, A.; Kulinič, H. Influence of composition structure on the properties of building products with agricultural elements. Investigation. *Environmental Engineering (Aplinkos inžinerija)*, Vol 8, No 4, 2000, p 223–227 (in Lithuanian).
7. Kazragis, A.; Gailius, A.; Tamulaitienė, B.; Kulinič, H. Utilization of straw and reed in building product fabrication. Investigation. *Environmental Engineering (Aplinkos inžinerija)*, Vol 10, No 2, 1996, p 77–83 (in Lithuanian).
8. Gailius, A.; Kazragis, A.; Kulinič, H. Investigation into the Properties of Composite Materials Containing Agricultural Residues. In: Proceedings of International Conference on Lithuanian Science and Industry „Silicate technology“. Kaunas: Technologija, 2004, p 107–112.
9. Kazragis, A.; Gailius, A.; Juknevičiūtė, A. Thermal and Acoustical Insulating Materials Containing Mineral and Polymeric Binders with Cellulose Fillers. *Materials Science (Medžiagotyra)*, Vol 8, No 2, Kaunas: Technologija, 2002, p 193–195 (in Lithuanian).
10. Kazragis, A.; Juknevičiūtė, A.; Gailius, A. The Lightweight Building Materials Containing Agricultural Residues. In: Proceedings of International Conference on Lithuanian Science and Industry „Silicate technology“. Kaunas: Technologija, 2003, p 75–80.
11. Kazragis, A.; Juknevičiūtė, A.; Gailius, A.; Zalieckienė, E. The Use of Boon and Chaff for Manufacturing Lightweight Walling Materials. *Journal of Environmental Engineering and Landscape Management*, Vol 12, No 1, 2004, p 12–21.

ATMOSFEROS UŽTERŠTUMO MAŽINIMAS UTILIZUOJANT CELIULIOZĖS TURINČIAS ATLIEKAS

A. Kazragis

S a n t r a u k a

Gamtą ir žmogų neigiamai veikiančių šiltnamio efektą skatina anglies dioksido (CO₂) bei metano (CH₄) kiekių ore didėjimas. CO₂ patenka į orą naudojant kurą, degant miškams, pastatams, deginant celiuliozės turinčias atliekas, o CH₄ – pūvant organinėms, taip pat apartoms celiuliozės turinčioms atliekoms. Todėl celiuliozės turinčių medienos perdirbimo bei žemės ūkio gamybos atliekų, nekultūrinės augmenijos ir kitų celiuliozės turinčių produktų panaudojimas statybinių celiuliozinių užpildų turintiems kompozitams gaminti (nedeiginant bei nepūdant) lokaliai prisidėtų mažinant šiltnamio efektą.

Gaminant statybinius (termoizoliacinius bei konstrukcinius) kompozitus gali būti panaudotos celiuliozės plaušų turinčios žaliavos: medienos atliekos – medienos perdirbimo įmonių atliekos, medienos dirbinių atliekos, nereikalingi medienos dirbiniai, kirtaviečių atliekos, žievės; žemės ūkio gamybos – javų, linų, kanapių perdirbimo atliekos; nekultūrinė augmenija – nendrės, meldai, švendrai, menkavertis šienas, spygliuočių medžių kankorėžiai bei skujos; iškastinės augmenijos žaliavos – durpės ir sapropelis; buitinės atliekos – makulatūra, medvilnės tekstilės atliekos.

Statybiniams kompozitams iš žemės ūkio gamybos atliekų gaminti naudojamos javų (šiaudai, pelai) ir linų arba kanapių perdirbimo atliekos (spalvai, pakulos).

* Naudojant šiaudus statybinės medžiagos gaunamos: 1) juos šutinant, kad suirtų natūralus vaško sluoksnelis, ir karštai presuojant, kad to proceso metu išsiskyrusios sakingosios medžiagos surišų šiaudus į vientisą dirbinį, 2) surišant neorganiniais rišikliais (cementu, moliu), 3) surišant neorganiniais rišikliais, dedant polimerinių priedų. Dirbinių iš šiaudų pavyzdys – šutinimo bei karštojo presavimo būdu gaunamos „Stramit“ plokštės; portlandcemenčiu surištos plokštės bei moliu surištos šiaudaplytės; presuojant portlandcemenčių su statybinio gipso priedu ir polimeriniais PVA bei KMC tipo priedais gautos šilumos izoliacinės bei sieninės plokštės.

* Naudojant spalvius ir pelus, statybinės medžiagos gaunamos surišant juos anhidritiniu arba aluminatiniu cementais su PVA bei KMC tipo polimeriniais priedais. Šio tipo dirbiniai priklauso II bei III šilumos izoliacinių medžiagų klasėms.

Statybinių kompozitų iš nekultūrinės augmenijos gamybai naudojamos nendrės, tačiau šiam tikslui taip pat gali būti naudojami meldai, švendrai ir kita panašaus tipo augmenija. Šio tipo kompozitai gali būti gaunami surišant išdžiovintus ir susmulkintus augalus portlandcemenčiu bei pridedant PVA bei KMC tipo polimerinių priedų. Dirbiniai priklauso II bei III šilumos izoliacinių medžiagų klasėms.

Kompozitų gamybos savikainą sudaro žaliavų ir įrangos kaina, žaliavų mišinio paruošimo išlaidos, elektros energijos ir darbo jėgos kainos. Ekonomiškiausi iš kompozitų yra medbetonai, pjuvenų betonai bei dirbiniai, gaunami naudojant šiaudus, pelus, spalius ir nendres. Pastarųjų medžiagų gamyba yra paprasta, nereikalaujanti sudėtingos įrangos ir ekonomiška, o patys kompozitai gali būti gaminami tiesiog panaudojimo vietose. Tai ypač aktualu gaminant minėtuosius kompozitus kaimo vietovėse.

Kompozitams, kurių sudėtinė dalis – žemės ūkio gamybos atliekos (pvz., šiaudai) bei nekultūrinė augmenija (pvz., nendrės), būdinga pakankamos garso sugerties savybės. Plokštės, pagamintos iš tokių kompozitų, galėtų būti naudojamos statant triukšmą slopinančias sienes prie autostradų, ypač ten, kur autostrados kerta miestų pakraščius.

Raktažodžiai: šiltnamio efektas, šilumos bei garso izoliacinės medžiagos, į atmosferą išmetamo CO₂ kiekio mažinimas.

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