Inorganic Pollutants in Recovered Wood from Slovenia and Boards Made of Disintegrated Wood

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Abstract: Due to increasing demands on wood, recovered wood is becoming more and more important. It is mainly used for energetic purposes and for particle board production. This material was polluted with various chemicals (surface coatings, biocides, concrete residues, etc.) during service life. These chemicals causes difficulties at the end of service life. In order to elucidate presence of inorganic pollutants in Slovenian recovered wood, 30 specimens were collected on city Ljubljana dump/sorting site, and analysed with x-ray fluorescence spectrometer (XRF). Those values were compared to the concentration of inorganic elements in boards made of disintegrated wood collected in Slovenian market. In recovered wood, as well as in imported particle boards increased concentrations of the following elements was confirmed: Cl, Cr, Fe, Cu, Zn and Pb. This indicates that at lest part of contaminated recovered wood is used for production of some particle boards.

Keywords: Pollutants, biocides, XRF, particle boards, recovered wood.

INTRODUCTION

Each product has limited service life, including wooden products. At the end of this service life there is an issue what to do with recovered wood, for example. This material is becoming more and more important, due to limited and more expensive fuel, oil predominately [1]. In Europe, recovered wood is used for various purposes, but energetic and for particle board production are the most important end uses [2]. Disposal of recovered wood to land-fields is not desired according to the EU regulations and it is expected that it will be banned in the near future. The main reason for this decision is fact, that there are considerable amounts of methane (green house gas) emitted during anaerobic degradation of wood in land-fields [3]. In spite of this directive, considerable amounts of wood are still land-fielded, and part of it is used for energetic purposes under non-controlled conditions (Fig. **1**).

All problems related to recovered wood, originates from contamination during production process or within service life. It is rather difficult to find wooden products that were not either glued, surface coated or treated with biocides. Wood from construction and demolition sites is frequently contaminated with concrete residues, oxidized iron, etc. as well. All this chemicals can cause difficulties at the end of service life (Table **1**) [4].

Arsenic compounds are one of the most problematic compounds in recovered wood. Arsenic was used for wood preservation for almost half of the 20th century. Common abbreviation for this preservative based on Cu, Cr and As is CCA. It is foreseen, that there will be approximately 8 % of the recovered wood in 2020 contaminated with CCA preservatives in the UK [5]. If arsenic treated wood is burned up at temperatures above 275°C, solid arsenic compounds are transformed into volatile arsenic oxides. There are numerous reports on cancer and other types of diseases at people in UK and US, that utilised CCA treated wood as energy source for heating and cooking in the past [6]. Fortunately, arsenic compounds were removed from the market almost 20 years ago within most of the continental Europe [7]. However, there are considerable amounts of wood treated with chlorine containing wood preservatives, glues, or surface coatings. In case of uncontrolled incineration of chlorine containing wood, there is a possibility that extremely toxic dioxins are formed. Furthermore, considerable amounts of wood is treated with biocides or surface coatings based on heavy metals like; copper, chromium, zinc, lead, tin… Those compounds remained in the ash after incineration, and such ash must be deposited in approved lad-field sites.

Considerable amounts of recovered wood (3 million t year^{-1} in EU) are used for particle board production, particularly in Belgium, Spain, Germany, Italy, UK and Denmark [1]. European panel federation (EPF) prepared voluntary standards for raw material for panel boards production, where maximal concentrations for selected, most frequent, pollutants are defined (Table **1**). Despite of this recommendations, there are several particle board producers that do not respect those limits and uses non-suitable raw-material as well, predominately due to increasing prices of wood on the market [2]. In general, inorganic compounds does not present considerable threat for the users, but it is believed, that customers should be informed whether purchased furniture

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Fig. (1). Copper treated old electricity poles prepared for uncontrolled burning.

Table 1. Origin of the Pollutants in the Recovered Wood, Threshold Values for Particle Board Production and for Fuel Applications Compared to Average Values in Non-Contaminated Wood

Pollutant	Explanation, Origin of Respective Pollutant in Recovered Wood*	Threshold Values for Particle Board Production** (ppm)	Threshold Values for Fuel Wood***	Average Value In Non-Contaminated Wood *(ppm)
Cl	Biocides in wood preservatives Contamination during transport and storage with sodium chloride during winter Chlorinated water PVC residues	1000	150	100
Ca	Construction debris	/	/	900
Cr	Fixative in wood preservatives Antioxidant in surface coatings Waste motor oil residues Wear metal	25	/	1
Fe	Corrosion of steel Wear metal	/	/	25
Ni	Waste motor oil residues Wear metal	/	/	0,5
Cu	Biocides in wood preservatives	40	20	2
Zn	Additives- siccatives in surface coatings	/	/	10
As	Biocides in wood preservatives	25	3	<0.1
Br	Residues of fire repellent coatings, additives	/	/	<0.1
Mo	Waste motor oil residues	/	/	<0.1
Sn	Biocides in wood preservatives	/	/	<0.1
Cd	Additive in plastics, laminates, surface coatings	/	50	0.1
Hg	Old biocides in wood preservatives Residues of the thermometers..	2,5	0,4	<0.1
Ti	Antioxidant in surface coatings	/	/	<20
Pb	Additives- siccatives in surface coatings Additive in the plastics	90	/	2

* [9]** [11] *** [7]

Fig. (2). Variety of recovered wood on the temporary dump site.

contains residues of biocides or not. Secondly, this material will have limited service life as well. Threshold values, for hazard fuels are in some countries lower than EPF recommendations [8]. Therefore, it might happen that consumers will have to pay to get rid of their "toxic furniture" in the future. Thirdly, it should not be forgotten, that in famous action of WWF, 76 different chemicals (biocides, phthalates, fire or flame retardants…) was proved in the blood of European parliament members [9]. It has to be considered, that average parliament member did not work in the industry, and they do not live in the extremely polluted environment. At least part of those chemicals was introduced to the body in the working and living environment. Therefore, it is believed that non-necessary contact with potentially dangerous chemicals should be avoided in all stages.

The objective of this paper is to elucidate the presence of contaminants in recovered wood. In the second part concentrations of selected contaminants in particleboards was determined, as recovered wood is becoming more and more important source in particleboard industry. Measured concentrations are evaluated from legislation point of view.

MATERIAL AND METHODS

In Slovenian wood manufacturing companies fifteen specimens of boards made of disintegrated wood, from five different producers were collected. Three groups of boards were produced in Slovenia (particle board III, MDF (medium density fibreboard) and HDF (high density fibreboard). Particle board I and II were produced in well known European companies. Boards were collected in September 2007. In parallel, 30 specimens of recovered wood from waste sorting site were collected (Fig. **2**). There was a lot of wood from various applications. The majority of the wood came from the demolition sites, windows, fences, poles, decking, etc. Most of the collected wooden specimens were surface treated with various treatments. Collected specimens were documented, oven dried (24 h; 103°C) milled with laboratory mill (IKA) and pressed into tablets (r = 16 mm; d = 5 mm) with Chemplex press for further analysis.

For analysis x-ray fluorescence spectroscopy was applied (XRF, TwinX, Oxford instruments). In the first step qualitative analysis was performed. The most frequent pollutants were identified. For those elements calibration curves were prepared and in the second step quantitative analysis was carried out. Most of the measurements were performed on PIN detector (U = 26 kV, I = 115 μA, t = 300 s). However, chlorine concentration was determined with proportional detector in helium atmosphere.

RESULTS AND DISCUSSION

Qualitative analysis of the recovered wood specimens confirmed the presence of the following elements: chlorine, chromium, iron, copper, zinc, bromine, titan, lead and strontium (Fig. **3**). Concentration of those elements in control, fresh wood (mixture of beech and Norway spruce wood) was below detection limits (Table **3**). Fortunately, there was no arsenic, tin or mercury determined in any of the analysed specimens.

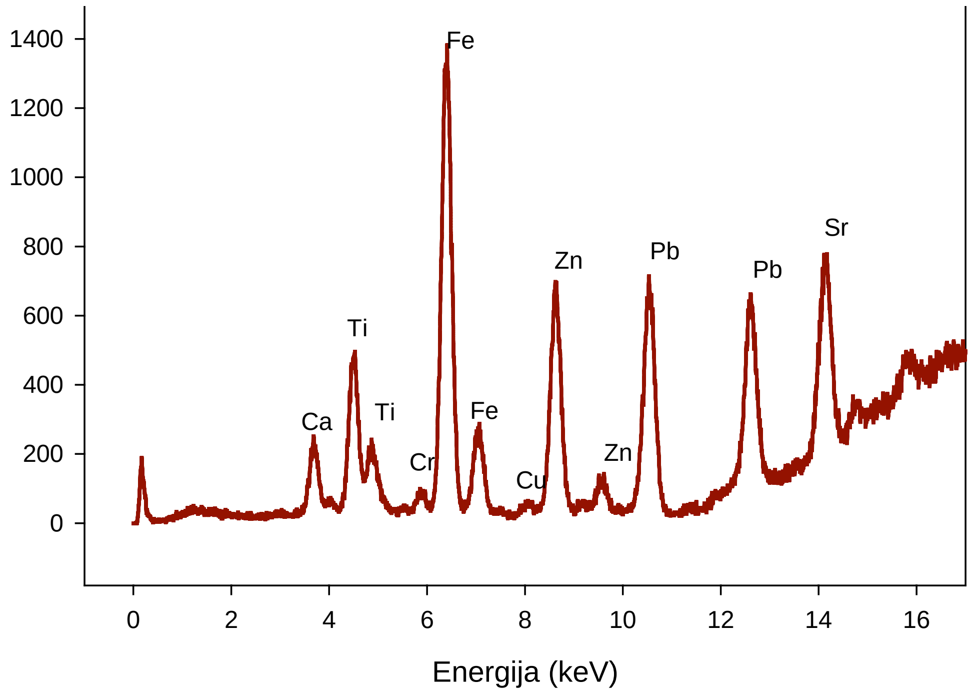

Fig. (3). XRF spectra of contaminated recovered wood sample.

On the basis of the literature data [10,11], visual estimation of the samples and data in the table 1 it is presumed, that the reason for increased concentration of inorganic pollutants originates in surface coatings (Zn,Ti, Pb), biocide treatments (Cr, Cu and partially Cl), gluing (partially Cl), steel corrosion (Fe and Cr), fire retardant additives (Br). In one of the specimens even strontium was determined (Fig. **2**). According to the available data [12], strontium is not used in the field of wood technology. Therefore, it is presumed, that wood was polluted with strontium on the collection site. The most important strontium application is (was) production of classical CRT screens for TV or monitors. It can be presumed, that one of those screens was demolished near analysed specimen, what consequently resulted in polluted wood.

Zinc, was the chemical element that was present in the highest number of the analysed specimens of recovered wood. In average, there was 910 ppm of zinc determined in collected recovered wood. The highest concentration was determined in specimen no 10, where 7545 ppm of Zn was measured. This sample used to belong to the window frame, and was surface treated with white alkyd surface coating. It was evident, that this window was brushed for several times, as there were several layers visible. Besides zinc, chlorine (716 ppm) and iron (553 ppm) were the second most frequent pollutants determined. The main reason for high iron content is corrosion of steel elements in contact with wood (fasteners, metal parts…) as at least the smallest steel parts were not separated from the recovered wood. Among all pollutants determined, iron is one of the least problematical elements in recovered wood. In contrary to iron, chlorine causes more problems. Among 30 analysed specimens, 7 of them exceed limit (1000 ppm) for raw material for particle board production [8], and almost all of the analysed specimens contains too much chlorine (150 ppm) to be used for energetic purposes according to the Slovenian legislation [13] (Table **2**). Even the specimens that contains more than 1000 ppm of Cl, does not have common properties, with exception that all of them were surface coated. There is several possible explanations for high chlorine content; biocides in surface coatings (quaternary ammonium compounds, isothiazolones…), transport (use of sodium chloride during winter), chlorinated water… [10,11].

There was considerably higher concentration of lead determined in recovered wood as well. Analysed specimens in average contain 79 ppm of lead. More than 25 % of the collected specimens contained more than 90 ppm of the lead, what is limit for the raw material in particle board industry. The highest concentration of lead (451 ppm) was determined in specimen 24, treated with dark surface coating (Table **2**). However, there was considerably less copper (67 ppm) and chromium (10 ppm) determined in average. It was expected that concentration of chromium and copper will correlate, as those two compounds were usually used in the same preservative solution. However, visual analysis of the specimens resolved that high copper concentrations were measured in specimens with thick surface coatings, where copper was added predominately as pigment, biocide or siccative [11]. The only specimen that was impregnated with copper based wood preservative was specimen no 26 (958 ppm). This specimen was probably treated with novel generation of copper-amine wood preservatives, as there was no chromium determined in this specimen.

However, it was of the significant interest, if the inorganic pollutants determined in the recovered wood from sorting facilities will occur in the panels in the Slovenian market as well. According to the data obtained, panels can be di-

Table 2. Concentration of Selected Elements in the Recovered Wood Samples

Sample	Pollutant Concentration (ppm)						
	Cl	Cr	Fe	Cu	Zn	Br	Pb
Control	0	0	0	0	0	0	0
1	354	0	581	6	37	0	0
2	306	0	44	0	22	0	5
3	3697	0	690	51	1583	0	53
4	0	0	10	0	9	0	6
5	201	0	165	0	21	0	18
6	175	0	49	0	15	0	0
7	296	0	44	5	80	0	53
8	781	0	176	110	3006	0	83
9	227	0	58	114	3755	0	115
10	1037	0	226	252	7545	0	122
11	619	0	461	34	1106	0	245
12	651	0	107	185	6082	5	77
13	304	0	86	0	15	0	17
14	1226	0	1841	19	426	6	254
15	466	260	1601	146	28	0	7
16	290	0	64	0	9	0	5
17	177	0	541	0	35	0	8
18	611	0	72	8	48	0	0
19	394	0	419	0	19	0	8
20	1463	0	149	0	23	0	7
21	406	0	474	0	16	0	81
22	877	0	551	9	235	0	57
23	1257	0	532	74	2548	0	98
24	605	0	2366	11	101	13	451
25	1627	25	2928	11	302	0	347
26	1108	0	326	958	61	0	24
27	451	15	644	6	65	0	25
28	633	0	240	0	17	0	12
29	644	0	509	5	94	6	161
30	601	0	639	5	9	0	19
average	716	10	553	67	910	1	79

Remark: Value 0 indicates, that the concentration of analysed element was below detection limit.

vided into two groups (Table **3**). In the first group (particle board III, MDF and HDF), there was no increased concentrations of possible contaminants observed, with exception of slightly increased iron concentrations. It is presumed that the reason for this increase originates from the wear of metals during milling, cutting grinding of the particles during production process. There was slightly increased chlorine concentrations observed as well. The reason for chlorine might be additives and catalyst in glue, sodium chloride, and chlorinated industrial water… In the second group (particle board I and II), particle board contained considerably higher concentrations of pollutants. The highest concentration was determined in particle board I, which contained 70 ppm of zinc, 4 ppm bromine, 29 ppm of lead, 8 ppm of copper and 981

Table 3. Concentration of Selected Elements in Boards Made of Disintegrated Wood

Sample	Pollutant Concentration (ppm)						
	Cl	Cr	Fe	Cu	Zn	Br	Pb
Particle board I	981	0	676	8	79	4	29
Particle board II	634	0	250	0	43	0	16
Particle board III	335	0	183	0	11	0	0
MDF	180	0	151	0	8	0	0
HDF	153	0	52	0	6	0	0

ppm of chlorine. Those values are rather high, and indicate that there was non suitable raw material used for production of particle boards as well. In one board even bromine was determined, that is used for fire retardant applications.

CONCLUSIONS

Half of the wood specimens collected from sorting site, is too polluted to be used for particle boards production or to be used for energetic purposes according to the Slovenian legislation. The most important pollutant found in recovered wood was Cl, Zn and Pb. Chemical analysis of the particle boards from Slovenian market revealed, that some of the imported boards contains significant concentrations of pollutants, what indicates that they are produced from non-suitable raw material. There should be more control performed on the use of contaminated wood for particle board production.

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