METĀLPĀRSTRĀDES ATKRITUMU IZMANTOŠANAS IESPĒJAS TERMISKI APSTRĀDĀTU BŪVMATERIĀLU RAŽOŠANĀ

POTENTIALITIES OF USING THE METAL-WORKING WASTE IN PRODUCTION OF THE HEAT TREATED BUILDING MATERIALS

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1. Introduction

Manufacturing of building materials by using industrial waste is becoming increasingly popular at present [1-2], as it is related to attempts of improving quality of environment in the industrial estate. As with every coming year the global pollution problem is becoming more pressing, due to industrial development, utilization of industrial waste and its recycling is put forward as a priority in the environmental sector of each state [3-4]. In many states, reutilization and recycling of raw materials is subsidized. In this way, natural resources are saved, external environment pollution is considerably decreased, and the means required for safe storage and management of waste are used more economically. Building materials produced by using the untreated or specially treated industrial waste and by-products, with or without special state subsidies, are competitive materials at the market of building materials of any state, due to their functional properties and corrosion resistance [5-7, 8].

Metallic aluminium, aluminium and other metal oxide compounds in the aluminium recycling process are one of the main types of waste that, depending on chemical composition of the compound, can be successfully used in production of different building materials [7, 8]. If earlier aluminium, alumina and other metal oxide compounds were considered to be the waste, which storage was economically inefficient, harmful to the environment and health of people (in accordance with the Basel Convention, Annex III, marking of this waste is H 4.3 (reaction with water results in highly inflammable substances) and H 10 (reaction with water results in increased concentration of toxic gases, for instance, ammonia) [9]), at present, the largest aluminium metal scrap recycling companies more or less have found the way of successfully using this industrial waste by creating additional profit to the company [9-14].

Non ferrous metal-working scrap waste has complicate composition from the ecological point of view. In the aluminium recycling process, a mixture of the soluble in water salts is used to limit the metallic aluminium oxidation during the metal scrap melt. According to the literature data [10], to obtain 1 t of the recycled metallic aluminium, about 0.5 t of chlorides containing salts are used in the recycling process. The primary waste, appearing in this production process, contains a considerable amount of the soluble in water compounds and is classified as toxic and harmful. Storage of such waste or deposition without recycling is prohibited.

Primary industrial waste is a mixture of the soluble in water salts and various metal oxides, which, in addition, contain also a considerable amount of metallic aluminium. Recycling and utilization of the primary waste or slag can be divided into three stages [10, 11]:

1. separation of the remaining metallic aluminium (if economically beneficial);
2. separation of the soluble in water salts (if their concentration is sufficiently high) and their repeated utilization in production;
3. useful utilization of the metal oxide compound or the secondary waste.

Cost efficiency of each company is considerably reduced by the waste storage costs related to usage of large land areas and the increased natural resource tax tailored to the waste producing industrial companies. Although the aluminium scrap recycling companies, available in Latvia, process the primary industrial waste by performing the first or the first two of the aforesaid recycling stages, according to data of the aluminium scrap recycling companies, volumes of the accumulated secondary waste or the metal oxide compound are increasing yearly by 12000-15000 tons [8].

This work investigates various technological processes for the secondary waste, when used as one of the raw materials in manufacturing the heat treated building materials. Primarily, the most appropriate method of forming the raw material mass is clarified. Its choice is undoubtedly related both to chemical and mineralogical composition of the secondary waste and its responsiveness or stability when coming into contact with other raw materials, including water. Another direction of the research is changes in chemical and mineralogical composition of the secondary waste during heat treatment. These investigations are especially significant to forecast the processes for the building materials during heat treatment and to forecast their properties after melting, on condition one of raw materials of the building materials is the metal industry secondary waste.

2. Chemical and Mineralogical Composition of the Secondary Waste of the Aluminium Metal Scrap Recycling

To evaluate the most rational way of utilizing the secondary waste for the aluminium metal scrap recycling companies, multiple research of the chemical and mineralogical composition of the secondary waste has been performed, in order to check on homogeneity of the accumulated waste.

According to the chemical analysis results, the secondary waste contains: metallic aluminium - Al (on average 7%), alumina - Al_2O_3 (on average 25%), silica - SiO_2 (on average 6%), aluminium nitride - AlN on average 5%), ferric oxide - Fe_2O_3 (on average 4%), aluminium chloride - $AlCl_3$ (on average 3%), potassium and sodium chlorides - KCl and NaCl (in total 5%), as well as: MgO, MnO, CaO, CuO, ZnO, TiO_2 and other compounds, which average amount does not exceed 1%.

Simultaneously with the chemical tests, analysis of elements with the help of the X-ray fluorescent spectrometry method (XRF) has been performed for the secondary waste (Table 1).

The XRF results (Table 1) well correlate with the chemical analysis data and show that the aluminium metal scrap recycling waste contains Al (on average 22%), Fe (on average 3%), Si (on average 3,5%), K (on average 1.5%), Cl (on average 2%) and Ca (on average 1%), as well as other elements, which amount is below 1%.

Table .1. Chemical Composition of the Metal Scrap Recycling Waste Containing Aluminium (XRF)

NO.	ELEMENT	MASS %
1.	ALUMINIUM, AL	18.0-26.0
2.	SILICON, SI	2.6-4.4
3.	FERRUM, FE	2.4-3.6
4.	CALCIUM, CA	1.0-1.3
5.	COPPER, CU	0.4-1.4
6.	POTASSIUM, K	0.8-2.1
7.	ZINC, ZN	0.1-1.1
8.	TITANIUM, TI	0.2-0.3
9.	SULPHUR, S	0.1-0.2
10.	MANGANESE, MN	0.1-0.2
13.	BARIUM, BA	0.1-0.3
16.	CHLORINE, CL	0.1-4.0

By using the XRD analysis, the mineralogical composition is determined for the grinded secondary waste. According to the analysis data, this waste contains corundum (Al_2O_3), silica (SiO_2), ferric sulphide ($FeSO_3$), aluminium chloride ($AlCl_3$), calcium ferric oxide ($Ca(FeO_3)$), calcium, magnium or ferric carbonate ($Ca(Mg,Fe)(CO_3)_2$), gibbsite ($Al(OH)_3$), spinel ($FeAl_2O_4$) or ($MgAl_2O_4$) and aluminium nitride (AlN) (Figure 1).

Metallic aluminium (Al) is not convincingly shown during the XRD analysis. This might be explained by the fact that during the secondary waste storage in the humid environment metallic aluminium is covered with the oxide layer and can not be clearly identified.

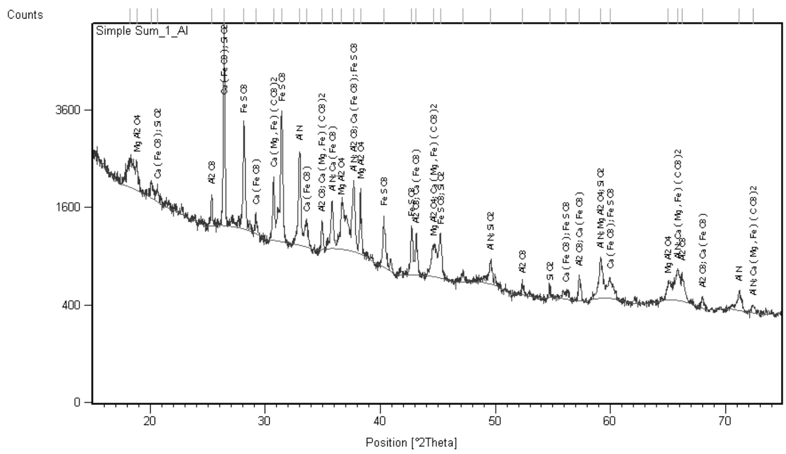

Fig.1. The mineralogical composition of the grinded secondary waste without heat treatment

3. Grading Composition and Mineralogical Composition of the Fractions

The secondary waste is separated into fractions and, for each of them, the mineralogical composition is determined, to establish homogeneity of the mineralogical composition depending on the size of the particles.

The grading composition of the secondary waste is reflected in Table 2. The size of the dominating particles of the secondary waste is from 1 mm to 63 μm. The amount of particles, which are larger than 1 mm, is 0.7%, and that of the powdery particles (less than 63 μm) is 3.5%.

There are no significant differences in the mineralogical composition of separate secondary waste fractions determined by using the XRD analysis. With the help of this analysis, the amount of different minerals cannot be established in the specific sample.

Table 2. Grading Composition of the Metallic Aluminium and the Metal Oxide Compound

SIZES OF FRACTIONS	PERCENTAGE, %
>1 MM	0.7
1 MM - 500μM	15.5
500 – 250 μM	25.1
250 – 125 μM	26.5
125 – 63 μM	28.7
< 63 μM	3.5

4. Factors Limiting Selection of the Method of Forming Building Materials

When separating metallic aluminium and the soluble in water compounds, the secondary waste, which is an object of this research, has been obtained from the primary waste. The soluble in water compounds are separated from the primary waste by using the dissolution – crystallization method, which has been successfully implemented in national economy of some states [10]. Hence, the production expenses are reduced and the risk of environmental pollution is considerably limited, as well as utilization of waste is made easier.

However, the soluble in water compounds have been found even in the investigated secondary waste, and their concentration is still sufficiently high, in order to considerably impact selection of the formation method for such building materials, where the secondary industrial waste is used in production.

As the secondary waste is not sufficiently stable in the humid environment, it is necessary to quantitatively and qualitatively establish the compounds that can react with water by forming soluble compounds and toxic gases. Formation of such potential compounds can significantly limit safe utilization of the secondary waste in the field of manufacturing building materials, as they might not only cause harm to environment and health of people but might also complicate the process of recycling the waste into environmentally harmless products.

In accordance with the earlier made investigations, the secondary waste still contains the compounds that, as a result of reacting with water (especially in the hoarfrost environment), form gaseous substances [10, 14]:

$$AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3 \uparrow \quad (1)$$

$$FeSO_3 + H_2O \longrightarrow Fe(OH)_2 + SO_2 \uparrow \quad (2)$$

To establish volatile substances evolved in the hoarfrost humid environment, 10 g of the secondary waste have been mixed with 5 g of the Portland cement and poured with 10 ml of distilled water. The obtained composition has been kept for 2 hours in a desiccator's at room temperature. Gas samples for identifying the volatile substances have been taken after the two hours exposition, by using the Gilair air pumps.

317 mg/m^3 ammonia (NH_3) have been discovered in the investigated air samples. According to the performed estimations, one gram of the recycled metal scrap secondary waste emits over 0.25 mg of ammonia during two hours. It is possible that a part of the nitrogenous compounds, which as a result of reaction with water create ammonia, has not entered into reaction.

Similarly, sulphur dioxide (SO_2), with the average concentration of 0.41 mg/m^3, which corresponds to 0.00031 mg SO_2 per one gram of the secondary waste, has been found in the investigated air samples. A part of SO_2 could have reacted with the magnesium or calcium oxides contained in cement.

In addition, tests are made to determine composition of hydrogen sulphide and mercaptans in the volatile substances. Concentration of these substances is below the sensitivity method, i.e. for hydrogen sulphide (H_2S) <0.28 mg/m^3 and for mercaptans <0.5 mg/m^3. The boundary of feeling smell of hydrogen sulphide and mercaptans is much lower than the method determination sensitivity. Hence, according to the odorimetric evaluation, presence of such compounds in the composition of volatile substances cannot be excluded.

With the help of the gas chromatographic method, by using the flame ionization detector, it has been established that concentration of methane, propane, butane and other volatile substances is below the method sensitivity boundary (<0.5m g/m^3).

According to the chemical and mineralogical analyses data, the secondary waste contains on average 5% of aluminium nitride (AlN), which in the water environment is unstable and decomposes by creating gaseous compounds with a smell characteristic of ammonia, and this is also confirmed by the performed analyses of air. In the same way, this waste contains aluminium chloride - $AlCl_3$ (on average 3%), potassium and sodium chlorides - KCl and NaCl (in total, up to 5%) and ferric sulphide - $FeSO_3$ (up to 0.5%). All these compounds are unstable in the water environment and significantly limit selection of such formation method of building materials that is related to creation of plastic mass and lasting presence of water.

Hence, the dry powder pressing method can be used as one of the methods of forming building materials. Another offered formation method is the one, where the minimal amount of water is used for preparing the mass, and samples are delivered to the heat treatment furnaces within a short time since being formed, where the mechanically tied water is separated fast. In this case, the reaction between active constituent parts of the secondary waste and water cannot take place, due to the short interaction time.

5. Changes in the Secondary Waste Composition during the Heat Treatment Process

The secondary waste is heat treated to establish the processes taking place as a result of impact of the higher temperature. For the heat treated samples, changes in the mineralogical composition are identified and the ignition loss is determined.

5.1. Changes in the Mineralogical Composition (XRD Analysis)

To determine the mineralogical composition changes for the secondary waste during heat treatment, the RXD analysis is performed also for the waste treated at temperatures of 1200°C and 1500°C.

The waste treated at temperature higher than 1150°C does not contain aluminium nitride (AlN), ferric sulphide ($FeSO_3$) and metallic aluminium (Al) any more, and the amount of ferric oxide (Fe_2O_3) is considerably reduced. Whereas, the amount of corundum (Al_2O_3) and spinel ($FeAl_2O_4$) is considerably increased (Figure 2).

Intensity of formation of new minerals is growing with the temperature increase. In the waste treated at the temperature of 1500°C, apart from the aforesaid compounds that have already decomposed at the temperature of 1200°C, ferric oxide (Fe_2O_3) is not established any more, and the amount of spinel ($FeAl_2O_4$) is considerably increased (Figure 3). The obtained data well correlate with the ones received when investigating the waste ignition loss during heat treatment.

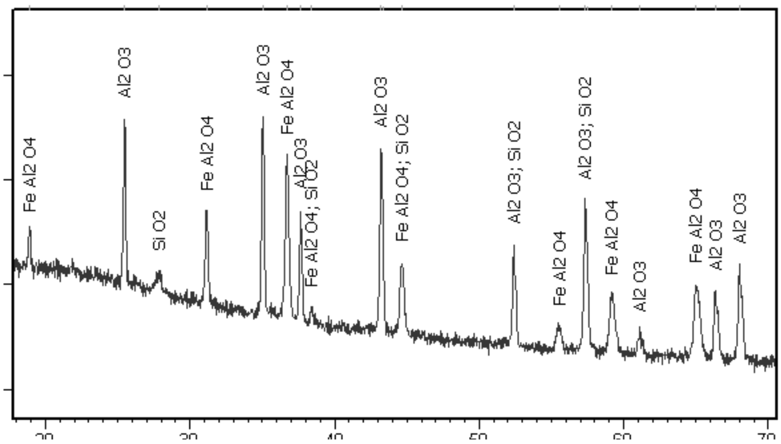

Fig.2. The mineralogical composition of the grinded secondary waste treated at the temperature of 1200°C

5.2. Weight Loss

The weight loss is quantitatively characterized by the compounds, which at the higher temperatures decompose or transform by forming gaseous substances. In this case, the sample weight is reducing during the heat treatment process. Simultaneously, the process of oxidation or formation of new substances can take place at high temperature, and that is often related to increase of the treated sample mass. Hence, the ignition loss is determined by the comparison method - with its help it is possible to establish the temperature when each process is going more intensively.

The secondary waste is processed at temperatures of 1000°C, 1100°C, 1200°C, 1300°C, 1400°C and 1500°C at the rate of 5°C/min and kept at the maximal temperature for 1 hour. When increasing the treatment temperature up to 1200°C, the weight loss increases to 11.61% (Figure 3). At this temperature, the theoretically enhanced decomposition of AlN, $FeSO_3$ and other compounds take place by forming gaseous substances, which contain nitrogen or sulphur (this is confirmed by XRD performed for the heat treated waste). The weight loss intensity reduces when the temperature increases over 1200°C. This is explained by the fact that intensity of formation of new phases is higher than that of gaseous substances.

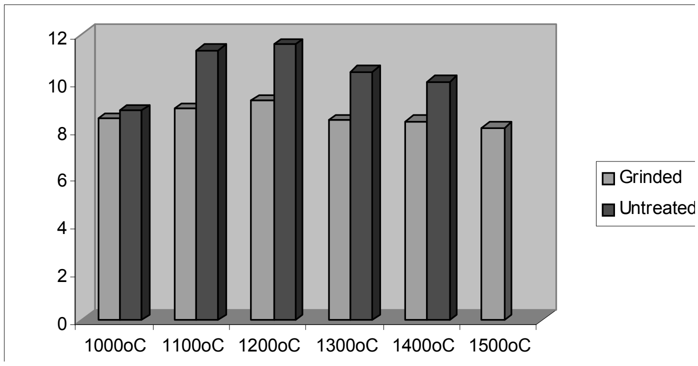

Fig. 3. Weight loses determined after heat treatment of grinded and real (untreated) secondary waste on the different temperatures.

Prior to heat treatment, the weight loss is less expressed for the grinded secondary waste (maximally 9.4% at the temperature of 1200°C) than for the real (untreated) waste. Changes of the weight loss intensity, depending on the heat treatment temperature, are similar both for the previously grinded secondary waste and for the real (untreated) one (Figure 3). Hence, it can be concluded that more intensive formation of new phases take place for the grinded waste, and this also limits the weight loss intensity during heat treatment.

According to the literature data for such type of waste, when it is treated at the temperature exceeding 1450°C, mass loss is not observed, and even on the contrary – the mass is increasing [1]. In the opinion of the authors, it is mainly related to AlN and metallic Al oxidation and Al_2O_3 formation. If the sufficiently efficient oxidising environment is not formed during the heat treatment process, formation of alumina and other new compounds is limited and the ignition loss increases.

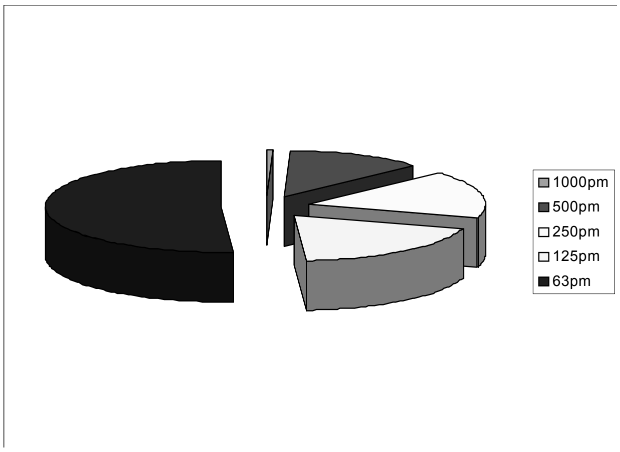

Fig 4. Weight loss at the temperature of 1200°C, proportionally attributed to different waste fractions

When investigating the weight loss of the fractioned waste during heat treatment, it can be established that proportionally the largest weight loss is for the fraction, having the size of 0 to 63 µm. The weight loss of this fraction, irrespective of the heat treatment temperature, on average constitutes 50% of the total ignition loss (Figure 4).

Hence, it can be concluded that the refined fraction proportionally contains the largest amount of compounds that decompose during heat treatment. By separating this fraction from the secondary industrial waste, it is possible to reduce the amount of the compounds that create gaseous substances, when decomposing at high temperature.

6. Conclusions

1. According to the chemical and mineralogical analyses data, the secondary waste contains on average 5% of AlN that in the water environment decomposes by forming ammonia and the soluble in water compounds: $AlCl_3$ (on average 3%), KCl and NaCl (in total up to 5%) and $FeSO_3$ (up to 0.5%). These compounds are soluble in water or actively reacting with water, and, thus, usage of waste in manufacturing building materials can be significantly limited by applying traditional industrial technologies.

2. The dry powder pressing method or the formation method with the limited amount of water are the appropriate methods of forming heat treated building materials, if the mass of their raw materials contains the untreated secondary non ferrous metal-working waste.

3. The waste treated at temperature higher than 1150^{o}C does not contain the compounds any more that can react with water or are unstable in the water environment. Hence, the secondary waste becomes stable in the humid environment and does not limit selection of the method of forming building materials.

4. The previously untreated and unprocessed secondary waste should be appropriate for production of the building materials that are treated at high temperature, as they do not contain harmful compounds after heat treatment.

5. Usage of the secondary waste in production of the specific heat treated building materials can be perspective and, hence, urgency of their further research is undoubted.

7. Literature

1. Samuel M., A new technique for recycling aluminium scrap // Journal of Materials processing Technology, Volume 135, Issue 1, April 2003 - p. 117-124
2. Yoshimure H.N., Abreu A.P., Molisani A.L., A.C. de Camargo, J. C.S. Portela, N.E. Narita. Evaluation of aluminium dross waste as raw material from refractories // In press Ceramic International, 2007
3. Rozenštrauha I., Drille M., Višs R. Rūpniecisko neorganisko atkritumu izmantošanas iespējas // In: International conference” EcoBalt 2004”, Proceedings – Riga, 2004 – p. 58.
4. Rozenštrauha I., Drille M., Rūpniecisko neorganisko atkritumu reciklēšanas iespējas // LJA 7. Zinātniski – praktiskās konferences materiāli, Proceeding – Riga, 2005 – p. 98 – 101.
5. Rozenstrauha I., Bajare D., The influence of various additions on the glass-ceramic based on industrial waste //In: International Conference Silicate Technology, Proceedings - Kaunas, 2003 - p. 100 – 104.
6. Rozenstrauha I., Bajāre D., Fizikāli- ķīmisko īpašību pētījumi stiklkeramikai no Latvijas silikātu rūpnieciskiem atkritumiem // In: International conference” EcoBalt 2003”, Proceedings – Riga, 2003 - p. 29.
7. Rozenstrauha I., Bajare D., Cimdins R., Berzina L., Bossert J., Boccaccini A.R. The influence of various additions on a glass-ceramic matrix composition based on industrial waste // In: Ceramic International, Vol.32, 2 – issue, 2006 - p. 115-119.
8. Bajare D., Rozenštrauha I., Saliņš G., Korjakins A. Karstumizturīgu javu sauso maisījumu ieguve, izmantojot metāla pārstrādes atkritumus //In: International conference” EcoBalt 2006”, Proceedings – Riga, 2006 - p. 143.-144.
9. Proposal to regulate salt slag under the Hazardous waste (Regulation of Exports and Imports) Regulations 1996, Australian Government, Department of the Environment and Water Resources.
10. Shen H., Forssberg E., An overview of recovery of metals from slags // In. Waste Management, 23, 2003 - p. 933-949.

11. Lucheva B., Tsonev Ts., Petkov R., Non-waste Aluminium Dross Recycling // Journal of the University of Chemical Technology and Metallurgy, 40, 4, 2005 – p. 335-338.
12. Hwang J.Y., Huang X., Xu Z., Recovery of Metals from Aluminium Dross and Saltcake // Journal of Minerals & Materials Characterization & Engineering, Vol. 5, No. 1, 2006 – p. 47-62.
13. Shinzato M.C., Hypolito R., Solid Waste from Aluminium Resycling Process: Characterization and reuse of its Economically valuable Constituents // Waste Management, 25., 2005 – p. 37-46.
14. Garcia-Valles M., Avials G., Martinez S., Terradas R., Nogues J.M., Acoustic Barriers Obtained from industrial Waste // Chemosphere, 72, 2008 – p.1098-1102.

Bajāre D., Korjakins A., Rozenštrauha I., Krāģe L. Metālpārstrādes atkritumu izmantošanas iespējas termiski apstrādātu būvmateriālu ražošanā.

Metālpārstrādes sekundāro atkritumu izmantošana augstās temperatūrās termiski apstrādātu būvmateriālu ražošanā ir aktuāla un perspektīva. Pēc termiskās apstrādes augstās temperatūrās sekundārie atkritumi vairs nesatur kaitīgus savienojumus, kuri var ietekmēt cilvēku veselību un apkārtējās vides kvalitāti. Tie ir kļuvuši apkārtējai videi nekaitīgi, droši uzglabājami un viegli utilizējami. Tas saistīts ar to, ka termiskās apstrādes procesa laikā augstā temperatūrā sadalās tādi atkritumu sastāvā esoši savienojumi kā alumīnija nitrīds (AlN), dzelzs sulfīds (Fe_2SO_3) un alumīnija hidroksīds ($Al(OH)_3$), kā arī ievērojami samazinās metāliskā alumīnija (Al) un dzelzs oksīda (Fe_2O_3) daudzums. Paralēli tam veidojas jauni savienojumi, kuri ir raksturīgi apdedzinātai keramikai., piem., korunds (Al_2O_3), spinelis ($FeAl_2O_4$) un citi minerāli. Iepriekš neapstrādātus vai speciāli apstrādātus sekundāros atkritumus ir iespējams veiksmīgi izmantot kā vienu no komponentēm, kas būtiski izmaina augstās temperatūrās apdedzinātu būvmateriālu funkcionālās īpašības un pielietojumu.

Bajare D., Korjakins A,. Rozenstrauha I., Krage L. Potentialities of using the metal-working waste in production of the heat treated building materials.

Usage of the secondary metal-working waste in production of the building materials, which are heat treated at high temperature, is urgent and perspective. After heat treatment at high temperature, the secondary waste does not contain harmful compounds any more that can affect health of people and quality of the environment. The waste becomes environmentally friendly, safe for storage and easy in utilization. The waste treated at high temperature does not contain aluminium nitride (AlN), ferric sulphide ($FeSO_3$) and metallic aluminium (Al) any more, and the amount of ferric oxide (Fe_2O_3) is considerably reduced. Whereas, the amount of corundum (Al_2O_3) and spinel ($FeAl_2O_4$) is considerably increased. The earlier untreated or the specially treated secondary waste can be successfully used as one of the components, which significantly changes functional properties and application of the building materials heat treated at high temperature.

Баяре Д., Корякин А., Розенштрауха И., Краге Л. Возможности использования отходов металлообработки в производстве термически обработанных строительных материалов.

Идея использования вторичных продуктов металопереработки для производства строительных материалов после высокотемпературной термической обработки является актуальной и перспективной. После проведения высокотемпературной обработк, вторичные отходы не содержат вредных примесей, которые могут оказывать влияние на здоровье человека и качество окружающей среды. Эти отходы становятся безвредными, легко утилизируемы и безопасны в хранении. Это связано с тем, что в процессе термической обработки при высокой температуре разлагаются такие соединения как нитрид аллюминия (AlN), сульфид железа (Fe_2SO_3) и гидороксид аллюминия ($Al(OH)_3$), а так же значительно снижается содержание аллюминия (Al) и оксида железа (Fe_2O_3). Параллельно образуются новые соединения, которые встречаются в обожженной керамике, например корунд (Al_2O_3), спинель ($FeAl_2O_4$) и другие минералы. Предварительно обработанные или необработанные вторичные отходы могут быть успешно применены как один из компонентов, который существенно изменяет функциональные свойства и расширяет сферу ицльзования обожигаемых при высокой температуре строительных материалов.