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**SUMMARIZING RECENT ACHIEVEMENTS
OF THE SILICATE WASTE RESEARCH GROUP,
UNIVERSITY OF MISKOLC,
WITHIN THE RING 2017 PROJECT**

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Abstract: In the present paper the main research results are summarized that were carried out under the umbrella of the project entitled *Sustainable Raw Material Management Thematic Network – RING 2017* and that are related to the Innovative Silicate Bearing Waste Recycling Research Group. The following thematic research directions were created: nano grinding and the development of fine grinding for mechanical activation; geopolymer raw materials; geopolymer foam; mineralogical investigation of silicate bearing wastes and recycled products; utilization of construction and demolition waste and industrial by-products; and legal issues of silicate bearing waste recycling and selective mining. As a result of the research work it was found that geopolymer composites can be produced from various waste streams. Shortcomings of the current regulation and the soft-law regulating tools are addressed, which are meant to shape the future development of the field.

Keywords: waste utilization, grinding, geopolymer, hydraulic binder, selective mining

1. INTRODUCTION

The population of our earth is growing significantly, which means a continuous, drastic increase in both the demand for raw materials and the demand for energy for the future. In terms of energy, the BP Statistical Review of World Energy (2013) stated that coal-based energy production is one of the most prominent in the world in terms of energy production, due to its economical extraction and favourable price. This results in the formation of large amounts of solid by-products (fly ash and slag),

the utilization of which is one of the most important tasks today. This amounts to nearly 800 million tonnes per year. Also, a significant amount of by-products are metallurgical slags, which represent around 500 million tonnes per year worldwide. Furthermore, approximately 120 million tonnes of red mud are generated annually during alumina production. These by-products and wastes, predominantly containing silicates, are well complemented by other mineral-derived materials, such as natural pozzolanic materials (pumicite, trass) or glass waste, the recovery of which has not been resolved. The steady decline in the volume of primary raw materials and the rise in their prices worldwide encourages professionals to research the large-scale availability of secondary raw materials. Examples include industrial and mining by-products and wastes such as fly ash and slag from coal-fired power stations, glass waste of various origins, red mud from alumina production, waste from the production and preparation of mining, or metallurgical slag. Due to their good physical and chemical properties, these materials are excellent for use in the construction or building materials industries, among others.

Most industrial by-products and waste are currently deposited in landfills, which is disadvantageous in several respects. First, the landfills reduce valuable agricultural and industrial land and pose an environmental risk (water and air pollution) in the event of improper disposal. Furthermore, the utilization of the by-product in question as a raw material would mean the rational and sustainable management of the primary mineral resources and raw materials. Last but not least, it also contributes to the reduction of CO₂ emissions, as a significant amount of CO₂ is produced during the production of the cement to be replaced. The right quantity and quality of raw materials are essential for the European economy as well as for the Hungarian economy. Recognizing these needs, the European Union's raw materials strategy was developed, the importance of which is reflected in the Horizon 2020 calls for 'industrial leadership' and 'societal challenges' pillars.

Therefore, the basic goal of our research group is to develop the preparation processes of primary and secondary raw materials of mineral origin in order for it to appear on the market as a higher value-added product. One of the utilization possibilities is the production of geopolymers suitable for various applications (thermal insulation systems, microcement, concrete, heat-resistant materials). These are inorganic polymers which can be prepared by reacting aluminosilicate oxides and aluminosilicates in an alkaline medium. The thermal insulation properties of the fly ash-based geopolymer can be enhanced by creating a foam structure. These materials are characterized by excellent fire and chemical resistance, which makes it possible to use them as a refractory or – with low thermal conductivity – thermal insulation material. The subject of the present research is the development of technologies and products whose properties can be controlled by mechanical process engineering operations (mainly by grinding, classification); thus, the characteristics suitable for the purpose can be planned in advance. Our primary goal is to develop a thermal insulation material that is air permeable, non-combustible and priced lower than other mineral-derived thermal insulation materials. This is made possible by a thermal insulation material with a foam structure obtained from the utilization of a secondary raw

material. Another utilization solution for secondary raw material-based foam products is the development of special functional materials whose high specific surface area is provided by the open-pore foam structure: for example, the production of ion exchange materials that can be used for either remediation, environmental or energy purposes.

Last but not least, supplementary cementitious materials (SCMs) are of great importance. They can be obtained at significantly lower prices than products currently on the market (e.g. microsilica, metakaolin), while also producing high-strength, acid-resistant, heat-resistant products. These materials can be manufactured from waste materials, therefore one of our focus is SCM development from secondary materials sources.

Based on the above-mentioned research areas, an additional goal of the project is to investigate the legal circumstances of waste processing and utilization in the European Union as well as on the Hungarian level.

2. THEMATIC RESEARCH RESULTS

2.1. Application of nano-grinding and the development of fine grinding for mechanical activation

Within the framework of the project developments in various fine grinding areas were carried out. In the first topic the differences and similarities of the wet and dry grinding in a stirred media mill were investigated from energetic and mechanochemical point of view. Grinding experiments in batch stirred media mill were carried out with zeolite and kaolin. The grinding experiments were carried out at different stress energy and stress number values and the grinding was measured during milling. After grinding, X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), and particle size analysis by laser scattering were carried out on the ground materials. It was found that wet stirred media milling was much more effective than dry stirred media milling from the size reduction point of view. However, more significant changes were observed in the structure during dry grinding, based on FTIR measurements. Dry grinding is more effective in amorphisation than wet grinding, as observed from the evolution of amorphous fraction based on XRD. More progressive crystallite size decrease and amorphous fraction increase is observed with the higher energy dry grinding. Based on the above, it can be stated that dry stirred media milling is much more effective for the mechanochemical activation, while the wet process is more suitable for particle size reduction [1]. The same milling experiments were carried out in with limestone and with quartz. The aim of the measurements was to understand the main differences in the method of wet and dry stirred media milling. Based on the results, in the case of the non-cohesive quartz dry grinding was more effective than wet in the comparison of the product median at a certain specific grinding energy. For limestone, which is a cohesive material, the wet process was much more efficient. Connecting to the development of the mechanical activation in a stirred media mill, a continuous dry grinding stirred media milling system was developed within in the project, where mainly the effect of the

operational parameters on the product particle size was investigated [2] and also the system itself was modified and developed in numerous steps [3]. As a final step the system received a self-developed airflow control that ensures an even amount of air inside the mill during operation.

The second main topic was carried out in cooperation with the University of Szeged, where wet stirred media milling and nano-grinding of different Ti, Fe and Cu-oxide and phosphate minerals were performed. During the experimental work nano-grinding of ilmenite, vivianite, hematite and cuprite was carried out in a continuous operation wet stirred media mill. During the experiments the particle size distribution and specific surface area of the ground materials were determined after certain grinding times and the specific grinding energy was measured, thus determining the grinding kinetics of the different minerals. After the milling, scanning electron microscopy (SEM) and FTIR measurements were carried out on the samples to characterize the nanoparticles. The nano rutile, ilmenite, vivianite and cuprite particles produced were later applied as photocatalysts for the development of novel wastewater treatment technologies by the colleagues from Szeged.

2.2. Investigations concerning possible geopolymer raw materials

Nowadays several studies are being conducted on the use of waste materials in order to eliminate the increasing toxic threat to the environment. The solution is an economically viable utilization of waste materials in new products for other applications rather than disposal in landfills. The new product can be formed by alkali activation of alumina-silicate materials containing highly reactive phases. The possible raw materials can be power plant fly ash, ground granulated blast furnace slag, red mud, silica fume, or rice husk ash, but other mine tailing waste can also be successfully utilized in geopolymer production. In most studies fly ash is used as a source material [4, 5, 6, 7], as millions of tonnes of fly ash are generated each year by coal-fired power stations.

Fly ash (*Figure 1*) is the fine solid particulate residue separated from the flue gas of a power station burning pulverized coal, where the particle size, amorphous content, loss on ignition, morphology and origin influence the stability of fly ash used in a geopolymer. Fly ash also possess pozzolanic properties, which allows it to serve as a reagent for the synthesis of geopolymers, which is an inorganic amorphous polymeric Si-O-Al framework formed by alkali activation with alkali hydroxide and alkali silicate solution [8]. The result is a cement-like product with better mechanical properties (compressive strength, flexural, splitting tensile strength), better physical properties and higher durability (resistance to chloride, sulfuric acid, thermal, freeze-thaw cycles). Besides these advantages, geopolymerization can trap and fix toxic metal elements from fly ash. The process and the final properties depend on the Si/Al ratios, the type and the amount of the alkali solution and the curing conditions.

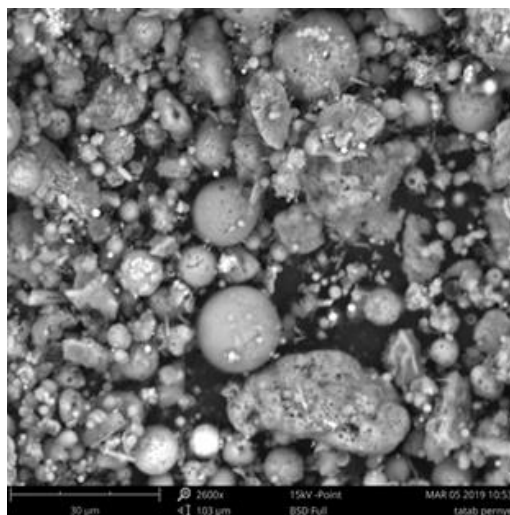


Figure 1
SEM image of brown coal fly ash from Tatabánya

The mechanical properties and durability can be improved by the mechanical activation of fly ash, by slightly changing the Si/Al ratios, alkali solutions, curing conditions, or by adding other types of wastes, such as slag or red mud [9] and/or fibers to reach the optimal chemical composition for geopolymerization with better mechanical properties. Experiments with mechanical activation of brown coal fly ash from Tatabánya revealed that with an optimized liquid/solid ratio (0.82) and appropriate activator solution composition (25 wt.% 8 M NaOH solution and 75 wt.% water glass), the uniaxial compressive strength of the specimens can be increased. As seen in *Figure 2*, the highest average compressive strength values could be achieved with 5–10 minutes grinding; however, further grinding time resulted in decreasing strength values [10].

The addition of fly ash can also improve the mechanical properties of raw materials with high crystallinity and low reactivity, by bounding the undissolved inert particles together to achieve enhanced compressive strength. The best results can be obtained by mixing in half proportions the binding reactive fly ash and the highly crystalline rhyolite tuff with alkaline solution consist of 75 wt.% waterglass and 25 wt.% 6 M NaOH, which reaches 22.5 MPa compressive strength. This result is better than the compressive strength of a geopolymer made of only fly ash (9.44 MPa).

Along with fly ash, the application of red mud as a possible supplementary geopolymer raw material has also been an area of investigation during the past decade. Due to its availability and high alkalinity, it has proven to be an appropriate material for geopolymerisation [11, 12]. With the use of red mud sample from Almásfüzitő, the preparation of fly ash–red mud-based geopolymers exhibited 5.5 MPa maximum compressive strength with the addition of 15% red mud. Furthermore, a linear correlation was observed between the compressive strength and the specimen density

of the specimens. Overall, the experiments proved that the red mud could substitute some of the alkali activators for geopolymer production [9].

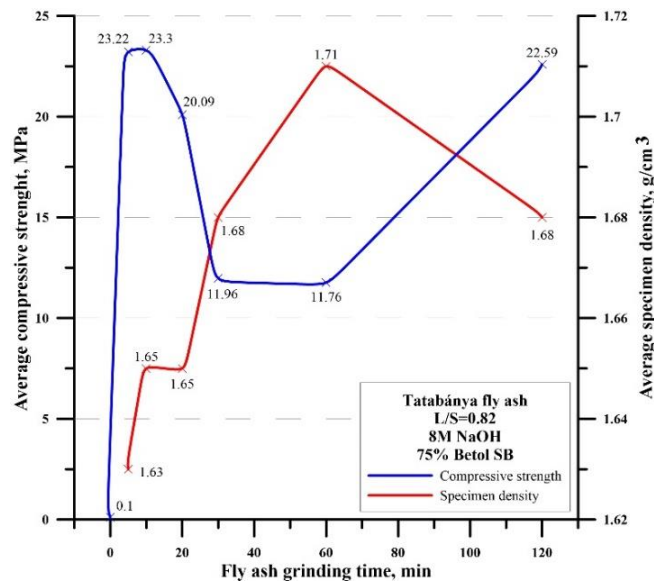


Figure 2
 Average compressive strength and specimen density of ground fly ash geopolymers [10]

As geopolymer exhibits brittle behavior due to its low tensile strength, several composites have been developed to increase flexural strength or heat resistance. The addition of natural or artificial fibers [13] can change brittle behavior to ductile or quasi- ductile with significant improvement in mechanical properties, depending on the type and length of the fiber, which can improve the strength, reinforce-matrix interaction by fiber-bridging behavior, heat resistance and resistance against chemical and physical corrosion [14].



Figure 3
 Biomass-geopolymer composites [15]

A joint research project with the University of Sopron included the investigation of biomass-geopolymer composites. Using woody biomass from the Botanical Garden of the University of Sopron, fly ash based geopolymer specimens were prepared using 30 wt.%, 50 wt.% and 70 wt.% biomass fibers (*Figure 3*). With increased biomass fiber content, decreased specimen density was experienced. Based on the microstructural analysis, the fibers were compatible with the geopolymer matrix, with the prepared composites applicable for sound or heat insulation or as a lightweight composite.

2.3. Effect of the amount of foaming agent and fly ash fineness on the properties of geopolymer foam

The rate of foaming of the geopolymer (and thus its properties) can be influenced by several parameters such as the foaming method, the amount of foaming agent and surfactant, or the rheological properties of the initial mixture (geopolymer paste) [16, 17, 18, 19, 20, 21].

The generation of gas into the geopolymer paste can be realized by adding foaming agents. Chemical foaming agents form gaseous products (such as O_2 and H_2) and other byproducts by thermal decomposition or chemical reactions. Metal powders (such as aluminum or silicon) and hydrogen peroxide are used most frequently for the fabrication of geopolymer foams [22]. Based on the experimental results it was found that the higher content of foaming agent (aluminum powder) resulted in lower compressive strength, specimen density and higher porosity of fly ash-based geopolymer foam. However, for a given foaming agent content, no change in the strength and density values of geopolymer foam is detected [23].

The rheology of the mixture can be easily changed by the amount of added liquid activator, i.e. by the liquid/solid ratio (L/S ratio) or by using a superplasticizer [20, 21, 24]. However, the rheology of geopolymer paste can also be controlled at a given L/S ratio by the size reduction of the solid component, by grinding. At the start of grinding, the particle size of the material becomes finer relatively quickly, and the work required for grinding (optionally grinding time) is approximately proportional to the new surface formed, i.e. the degree of dispersion of the resulting product. It was found that the geopolymer paste with a given fly ash content (55 w/w%), with originally non-Newtonian (Bingham-plastic) behavior, became a Newtonian fluid – regardless of the fly ash type (lignite or brown coal) – over a given specific surface area of fly ash (about $3,000 \text{ cm}^2/\text{g}$) due to increasing the fly ash fineness. Based on the experimental results it was found that the flow behavior of the geopolymer paste significantly influenced the porosity, the size and the amount of the pores, and thus the compressive strength of the brown coal fly ash-based geopolymer foam made using hydrogen peroxide foaming agent. Due to the high viscosity of the geopolymer paste the formation of pores was inhibited, so the pore size of geopolymer foam was too small. In case of very low viscosity the oxygen gas can easily escape from the geopolymer paste and as a result of this the geopolymer foam had a compact structure with few bigger pores [6, 25].

Overall, it can be stated that not only by changing of the amount of foaming agent but also by modifying the rheology of geopolymer paste, the pore structure of geopolymer foam can be changed, thereby altering its compressive strength and density.

2.4. Mineralogical investigation of silicate bearing wastes and recycled products

X-ray powder diffraction investigations were carried out on the Bruker D8 Discover instrument of the 3DLab (Institute of Mineralogy and Geology, University of Miskolc). The measurements were run in Bragg-Brentano geometry (θ - θ goniometer, reflection mode, top-loaded sample holders) with Cu K-alpha radiation (40 kV, 40 mA), using a LynxEye XE-T energy-dispersive position-sensitive detector with 2° detector window opening, in high resolution mode to cut fluorescence from Fe. Patterns were recorded in the $2-70^\circ(2\theta)$ range with $0.007^\circ(2\theta)/24$ sec counting time. Crystalline phases were identified from ICDD PDF4 (2018) database with the Search/Match module of the Bruker *Diffraction Plus* EVA.11 software. Quantitative composition was calculated by Rietveld refinement using fundamental parameters approach (FPA) from instrumental convolutions and crystal structure data from the Crystallography Open Database [26] and American Mineralogist Crystal Structure Database [27]. Amorphous content was calculated by the amorphous hump method. The chemical analysis was completed by a Rigaku Supermini 200 type WD-XRF, which has an air-cooled 200W X-ray tube with Pd target (50kV, 4.00mA). The measuring was done at 1.2–1.6 Pa pressure with ZSX driver and evaluation programme. The peak and the background(s) angle positions were measured by LiF crystal in the range of $^{22}\text{Ti} - ^{92}\text{U}$, PET crystal in the range of $^{13}\text{Al} - ^{21}\text{Sc}$ and RX25 crystal in the range of $^8\text{O} - ^{12}\text{Mg}$. For detection scintillation counter (SC) for heavy elements and P10 gas flow proportional counter (F-PC) for light elements was used. The grain size of the sample was crushed under $65\text{ }\mu\text{m}$, then it was dried at 120°C for 2 h. For powder pellet preparation 4,000 g of the dried powder was mixed and homogenized with 1,000 g of Cereox binder (ultra-pure and fine polyethylene powder), and the mixture was pelletized with $\varnothing 32\text{ mm}$ at 25 tonnes. As additional data, the L.O.I. (Loss on Ignition) was measured at 1050°C .

Statistical methods were applied in order to characterize the correlation between change of rare-earth element (REE) content along vertical profiles, cross-correlated as well with the change in mineral and major element composition.

The red mud samples investigated by XRD have the same major phases – hematite and cancrinite – while minor and accessory phases vary both in type and amount. Based on the Rietveld refinement data, cancrinite is present both as carbonate and an OH^- enriched species of the cancrinite group, although a reliable distinction requires vibrational spectroscopy analysis [28]. Hydrogarnets, the byproduct of the Bayer process, were identified as hibschite [29] and katoite [30]. Although in some samples grossular was observed, our results have now indicated the presence of almandine. Carbonates appear as calcite and dolomite, but in some of the samples aragonite is also detected. Kaolinite, illite, gibbsite, böhmite and diaspore are residual ore minerals,

while nordstrandite in traces, observed by Bolanz et al. [31], could be a residual phase or crystallized after red mud deposition. Quartz, zircon and anatase are also possible residual phases. Amorphous material content is in the range of 10–20 wt.%, different for each sample.

Goethite found in important amounts could be also a residual bauxite phase, but if it forms as a precipitated product of red mud, it could have an important role in fixing REEs existing in solution. Hematite is a potential carrier phase for Ce^{4+} , as shown by detailed investigations of Bolanz et al. [31]. None the less, REE bearing phases cannot be evidenced by XRD. An approximated limit of detection for REE minerals could be around 1–2 wt.% due to the severe peak overlapping of the >10 crystalline phases. However, chemical analysis suggests quantities < 1 wt.% for such phases.

The main chemical components are Fe_2O_3 (hematite and goethite, mainly), Al_2O_3 and SiO_2 . The Na_2O is contained in the cancrinite structure, while most of CaO is carbonate (calcite) form, also contributing to cancrinite, hydrogarnets (hibschite and katoite) and dolomite. The toxic heavy metal content is low, especially Pb, Cu and As < 100 ppm. The somewhat elevated Cr content (400–600 ppm) may be fixed in the crystal structure of hematite, thus immobilized with regard to leaching. These properties make the investigated red mud materials suitable for incorporation into silicate-based products, like geopolymers. The composition of amorphous phase observed by XRD is a mixed aluminum-silicate with Na, as a residue of silicate crystallization from the Bayer process. The anion exchange property of cancrinite – to remove $(\text{OH})^-$ and replace it by $(\text{CO}_3)^{2-}$ – makes the material suitable for CO_2 sequestration also.

Cross-correlation matrixes built up on component changes along the vertical profiles of red mud residue storage facilities show that there are only tiny differences between REE profiles. The cross-correlation calculations show that profiles of La-Pr-Nd(Sm) are very similar and these comprise one group. There is another group of heavy REEs (Dy-Ho-Er-Tb-Gd) where the profiles show close similarities. Cross-correlation values show similarities for TiO_2 - Al_2O_3 - Fe_2O_3 , which practically do not change along the profile. Among the more changeable components, stronger similarity is found among SiO_2 and Na_2O and Al_2O_3 . This is explained by the fact that after hematite the second most common mineral phase in the samples is the cancrinite. Mineral composition changes along the profile indicate that rare earth elements and Yttrium (REY) show good correlation with cancrinite. The best correlation values are with hematite concentration of which shows very little changes along the profile. Incorporated in mineral phases, REE are primarily associated with phosphates. This observation is supported by microprobe analysis of aggregated samples from cells VIII and IX, detecting primarily xenotime and monazite grains.

2.5. Utilization of construction and demolition waste and industrial by-products as potential raw materials for the building industry and road construction

Several by-products are issued during different production technologies. One serious issue is how to handle and utilize construction and demolition (C&D) waste in an

appropriate way. These materials are generated in significant quantities year by year, while storage of them as waste can be harmful to the environment in the long term. Therefore, our team focused on two main research directions: utilization of C&D waste and industrial by-products (fly ash and alumina dross) in building materials and as potential raw material for road construction. Reviews on these fields are made in [32, 33].

In an experimental series, the effects of different curing conditions on geopolymer foam were analyzed [34]. Foams were prepared using Class F type fly ash and sodium-hydroxide activator and were cured in a furnace or in autoclave for six hours. The temperature range was varied between 60–90 °C and the pressure of autoclave was changed between 2–7 bar. Results showed that autoclaving has less effect on the compressive strength than being cured in a furnace. Within the pressure and temperature ranges investigated, autoclaving produced no change in the properties of the samples.

C&B (concrete and brick waste) and industrial by-product (alumina dross) powders were used to prepare geopolymers [35]. As the performance of geopolymers is highly dependent on the properties of the initial powders, different methods (particle size distribution, density, elemental and chemical composition, microstructural analysis) were used to reveal the features of these powders. For preparing samples, an alkali activator (NaOH solution in different concentrations) and waterglass (Na_2SiO_3) were applied. After curing, compression strength was determined at the age of 7 and 28 days. The test results confirmed that not only the type and amount of waste materials affect the forming of a geopolymer structure, but the concentration of alkali activator is important as well. We found that samples with concrete powder had the highest compressive strength (>17 MPa) after 28 days. According to this result, concrete may be a potential raw material for preparing geopolymers. The brick powder may also be suitable as a raw material; however, in this case the use of a proper concentration of alkali activator is required. During the reaction of metallic Al of aluminum dross and liquid activator solution content a low density foamed geopolymer was prepared, which may be useful for thermal insulating applications.

Asphalt is a special composite material, which consists of bitumen as a binder and a high volume of mineral aggregates in a specific particle size distribution. Mining of these minerals will cause the depletion of natural sources and thus it is necessary to search for potential materials to substitute these minerals in part or in full. Aluminum dross, brick powder and concrete powder were investigated as potential asphalt filler ($d < 0.063$ mm) for road construction [36, 37]. Different tests (particle size distribution, elemental composition, electron microscopy) suitable to characterize the powder samples were made. Limestone filler, which is one of the best fillers in asphalt, was used as a reference material. The cohesion between the binder and fillers were also revealed. According to the hydrophilic coefficient, we found that aluminum dross has an advantageous property, because it is similar to limestone powder. Brick powder also shows good results. To sum up, aluminum dross and brick may be used in asphalt pavements as fillers.

2.6. Legal issues of silicate bearing waste recycling

In their article ‘The legal categorization of Fly ASH in EU and the Hungarian law’ [38] the authors examined the rules on utilization of fly ash in Hungarian and EU law and introduced the dilemmas that lawmakers have to face when it comes to its utilization¹. They also examined the sustainability of the coal combustion power plants – which are major sources of fly ash – from an economic and environmental aspect. Regarding the relevant EU law they came to the conclusion that it is rather divergent². The authors devoted a section to the case law of the European Court of Justice (CJEU), which has a paramount role in shaping EU law by elaborating definitions and clarifying the law.

In their article, called ‘A KKE országok hulladékgazdálkodási szabályozása és azok konformitása az uniós joggal – Az EuB vonatkozó joggyakorlatának elemzése / Waste management regulations in East-Central European countries and their conformity with EU law – Analysis of related CJEU case-law’ [39] the authors – building on Csilla Csák’s earlier writings [40, 41] – examined the rules on waste management in the EU law and in the legal systems of Central and Eastern European countries with special regard to industrial wastes like fly-ash and construction and demolition waste. In this article too, they examine the related case law of the CJEU.

In their forthcoming article ‘A hőszigetelő anyagokra vonatkozó uniós szabályozás, különös tekintettel a geopolimer alapú hőszigetelő anyagokra / The law of the European Union of heat insulating materials, with special regard to the geopolymer based insulating materials’ the authors provided an overview of the energy policy of the EU and its environmental protection objectives and examine how the law on the heat insulation of the buildings fits into this policy, which aims at reaching the highest possible energy efficiency by decreasing the demand of the consumer side. Considering the fact that in the EU the major part of the energy consumption is attributable to the energy demands of buildings, modern and efficient heat insulation of the buildings is a major step in reaching the energy-efficiency goal. In connection with this, the authors introduced the shortcomings of the current regulation and the soft-law regulating tools, which are meant to shape the future development of the area.

2.7. Opportunity for selective mining in the Borsod coal basin in northeastern Hungary

Numerous underground coal mines were in operation in the Borsod coal basin in the northeastern part of Hungary until the beginning of this century. The main areas of

¹ As an example: while the EU law prefers utilization of waste materials in order to create a circular economy, the principle of proximity – which shall be taken into consideration – does not facilitate the utilization of fly ash, since this principle – alongside economic considerations – excludes the transportation of material for greater distances.

² While the Waste Directive – which classifies fly ash as waste and thus determines its legal standing – provides the regulatory framework, other directives, regulations and decisions of the Commission provide for the detailed rules of utilizing fly ash.

utilization of the mined-out coal were power and heat generation and supplying households with fuel, mostly for heating. So almost the whole output of the mines was burned. Only a part of the by-products of this mining activity is available. Coal combustion products of household heating became scattered throughout the region over the past centuries; just the part – probably smaller – from industrial consumers is available on the sites of power stations and other plants. Mine waste that was disposed on the mine sites consists of mostly country rocks of the coal seams containing variable amounts of coal. The coal content of the waste was certainly burnt or slowly oxidized during this long time. The mine waste disposal sites were reclaimed during the past two decades. Consequently, new mine waste and coal processing by-products can be obtained only from the operation of new mining operations.

Several cases were examined to select the proper mine site throughout the northern part of Hungary. Finally, the Dubicsány deposit was found to be the best of them. Its mineable reserves are estimated at 50 million tonnes with a little bit more than 12 MJ/kg calorific value, enabling operation of more than three decades. The main difference between the classic and the future ways of utilization is that this time only coal chemistry can be taken into account to extract its carbon content, but burning it as fuel in power plants is practically excluded. The subjects of research were sustainability as well as technical, safety and economic aspects. The following main results of the research can be summarized as follows [42, 43]:

- Research confirmed the well-known facts of coal quality properties that calorific value can be estimated accurately as a function of ash and moisture content furthermore sulfur, volatile and carbon contents. A very fine analysis was made for all properties using data of over 5600 samples demonstrating linearity. Estimations proved to be accurate as coefficients of determination were fairly high ($0.7670 < R^2 < 0.9948$) and estimated errors of calorific value were low ($0.335 \text{ MJ}\cdot\text{kg}^{-1} < D(\Delta F) < 2.248 \text{ MJ}\cdot\text{kg}^{-1}$). A huge number of samples (5648) were analyzed and extremely good correlation (a 0.9845 coefficient of determination and $0.814 \text{ MJ}\cdot\text{kg}^{-1}$ mean residual square of estimation) was found for calorific value and carbon content. This proves that calorific value can be considered a basic parameter for coal chemistry, even instead of carbon content, for the given deposits.
- Water hazard and quantity of mine water was examined to assure safe mine operation and the least possible environmental impact. The mine dewatering method considered it a part of potable water supply for the inhabitants and industrial water for the mine.
- All of the coal properties were found to vary throughout the deposits, both horizontally and vertically. Therefore, a 3D numerical analysis is being developed to enable selective cutting and accurate quantity and quality design of the mine output. As coal quality changes (deteriorates) from the covering layer of Seam V downwards, determining the proper height of the coal face of the longwalls (*Figure 4*) is an extremely important question. This is also important for the correct selection of the longwall equipment, thus enabling selective

cutting. The aim of the numerical analysis was to find the distribution functions of the mass and the heat content, and furthermore the mean calorific value of the coal as a function of coal face height for the four parts of the mine. Future owners will be able to use these results for proper decisions in mine valuation and mining engineering design.

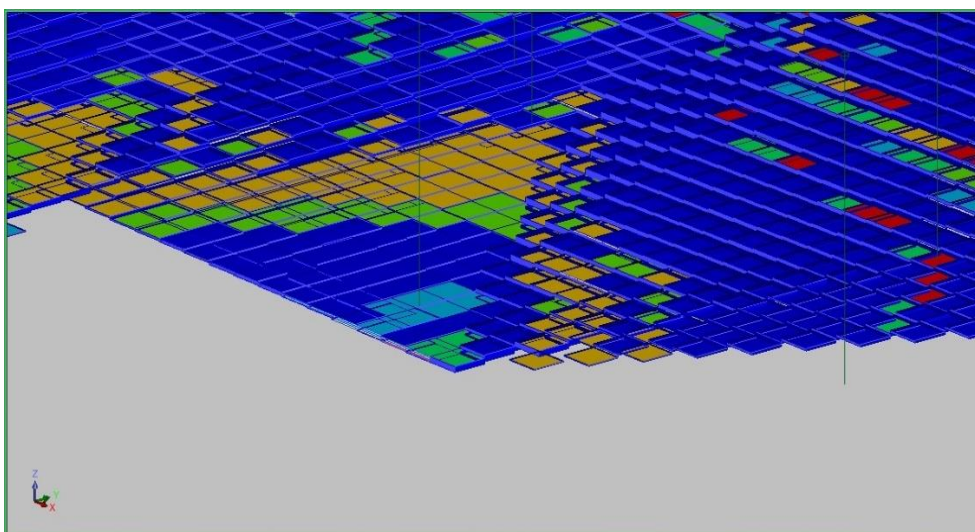


Figure 4

Orthographic view of a zoomed smaller part of the 3D block model of Seam V of the Dubicsány deposit highlighting its fine resolution

Drawn by Tompa R., 2018

3. SUMMARY

The following research results were achieved by the Silicate Bearing Waste Recycling Research Group in the RING 2017 project:

- grinding had a key role in the project in order to prepare a more reactive raw material for geopolymers by mechanical activation, as well as for nano-grinding of ilmenite, vivianite, hematite and cuprite;
- a geopolymer composite with appropriate mechanical stability could be obtained with various raw materials like fly ash, red mud and biomass;
- it was found that the cell structure of geopolymer foam, and thereby its compressive strength and density, can be controlled by grinding of the raw material;
- a mineralogical investigation of red mud was carried out in order to monitor the metal components, revealing that REE are primarily associated with phosphates;
- utilization of construction and demolition waste and industrial by-products (fly ash and alumina dross) is possible in building materials and as potential raw material for road construction, while concrete and brick waste may hold potential for preparing geopolymers;

- regarding the legal issues of recycling silicate bearing waste, researchers examined the rules on utilization of fly ash in Hungarian and EU law and introduced the dilemmas that lawmakers have to face when it comes to its utilization;
- selective mining sites were investigated in the Borsod coal basin in northeastern Hungary and the Dubicsány deposit was found to be the most promising.

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