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FOREWORD

When someone has a look at the map of Hungary, a ring formed by the cities of Miskolc, Pécs, Sopron, and Szeged is clearly visible. This idea, namely "the alliance of the ring" was the initial spark behind the project, which now is approaching its completion. The EFOP-3.6.2-16-2017-00010 *Sustainable Raw Material Management Thematic Network – RING 2017* Project – in numbers – in brief: 4 cities, 4 partner universities, 5 research cells, more than 160 university lecturers–researchers, 200 students and young researchers and 140 other contributors did research and built this network together. In the 38 months so far more than 500 publications have been issued, of which more than 340 were in a language other than Hungarian (mainly in English), more than 330 people took part in research management and research skills improvement trainings, almost 100 potential Horizon 2020 partners contacted, almost 60 guest researchers–lecturers invited from EU/EGT or Carpathian Basin countries and more than 100 conference presentations held by our students during the 4 Sustainable Raw Materials International Project Weeks (IPWs) organized within the project.

The four networking universities – the University of Miskolc, the University of Sopron, the University of Pécs and the University of Szeged – joined their human and physical resources and carried out common scientific work in the following research cells:

- Innovative utilization of large-scale industrial and mining waste and by-products (SILICATE)
- Recovery of valuable materials from waste electronic and electrical equipment (WEEE)
- Municipal solid waste as a secondary source of raw materials (MSW)
- Utilization of lignocelluloses (LIGNOCELLULOSE)
- Utilization of wastewater and sewage sludge, low CO^2 emission technologies (CO2)

SILICATE Research Cell. 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. This results in the formation of large amounts of solid by-products, 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 joined by other mineral-derived materials, such as natural pozzolanic materials (pumicite, trass) or glass waste, the recovery of which has not been resolved. Recognizing the need for raw materials, 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.

Based on the above problems, the following thematic research directions were created in the project related to the Innovative Silicate Bearing Waste Recycling Research Group: 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 the recycling of silicate bearing waste and of selective mining.

The basic goal of the research cell is to develop the preparation processes of primary and secondary raw materials of mineral origin in order for them to appear on the market as higher value-added products. One of the utilization possibilities is the production of geopolymers suitable for various applications (thermal insulation systems, micro-cement, concrete, heat-resistant materials). 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 or classification); thus, the characteristics suitable for the purpose can be planned in advance.

As a result of our research we found that grinding had a key role 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. Geopolymer composites with appropriate mechanical stability could be obtained with various raw materials such as 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. 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. Furthermore, selective mining sites were investigated in the Borsod coal basin in north-eastern Hungary, with the Dubicsány deposit found to be the most promising.

WEEE Research Cell. The European Commission has adopted a new Circular Economy Action Plan – one of the main blocks of the European Green Deal, Europe's new agenda for sustainable growth. The new Action Plan announces initiatives along the entire life cycle of products, targeting for example their design, promoting circular economy processes, fostering sustainable consumption, and aiming to ensure that the resources used are kept in the EU economy for as long as possible. Waste electrical and electronic equipment (WEEE) or e-waste is electrical and electronic equipment (EEE) that becomes waste. High added value products usually require special materials, and without them production is not possible (e.g.: indium in LCDs). Nowadays some important raw materials mainly come from non-European countries, for example Rare Earth Elements (REE) from China. The E-waste generation was 44.7 million metric tons globally (in 2016), and only 20% of this amount is collected and recycled. The amount of WEEE is increasing because of the intensification of technological developments, increasing population, rapid societal and economic development (developing countries' access to modern technologies), changes in consumer habits (mobile phones, decreasing product lifetimes). On the one hand, untreated WEEE is hazardous to the environment and human health; on the other hand WEEE is a resource which should be used. WEEE processing faces many challenges, e.g. extreme small concentrations of valuable elements, composite materials, thin layers, covering materials, rapid changes in EEE technologies, substitution of elements, and market price variation of elements.

Various types of lithium-ion batteries were investigated, such as mobile phone batteries, notebook batteries and hybrid vehicle batteries. Structural and material compositions were determined (mobile, laptop, and car) and processing possibilities were investigated to avoid explosion during recycling. Mechanical and chemical treatment processes were developed in the case of the first two battery types. The most valuable materials recycled from the anode and cathode were cobalt and lithium.

In the case of LCD and LED, mechanical treatment processes were investigated. In addition to that, chemical and biological solubilisation experiments were carried out in order to solubilize the indium from waste LCD panels, and in a preliminary experiment, the potential of bioleaching of LEDs (light emitting diode) was examined as well. The newest types of displays (OLED) were also procured and analysed. These are used nowadays in mobile phones as well as in TVs, and shipment of them is increasing.

The solid-state drive (SSD) was introduced in the late 2000s as a new technology for storing data. Fundamental data for searching for appropriate treatment options of SSDs were analysed, such as the mass balance of the components of SSDs, material composition of the parts in SSDs, and size reduction of SSDs. The increasing demand for SSDs worldwide also fosters the research regarding SSDs recycling to ensure high effectivity and efficiency in handling "end of life" SSDs in the future.

To understand the structure of WEEEs and WEEE parts, CT measurements were performed in the 3D Lab of the University of Miskolc with a XYLON FF35 dual tube computer tomography equipment. For the measurements additional sample preparation was not necessary, because whole sample pieces could be placed inside the instrument. The sorting of WEEE parts was investigated by a camera with shape recognition software with one- and two dimensional code on the examined image. Market price tendencies were also examined from the economist's point of view, especially for EU critical raw materials.

MSW Research Cell. On the one hand quality and quantity enhancement of residue derived fuel (RDF) was one of the main topics of this research cell. The factors that affect fuel quality during the mechanical treatment process and the enhancement options after treatment were identified. Fuel particle size distribution, as well as heat value, moisture, ash, heavy metal and chlorine content of each size fraction were measured for an entire year. The results showed close correlation between particle size and both physical and chemical characteristics of the fuel. Components that make the combustion challenging, e.g. chlorine, heavy metal, ash and moisture, are concentrated in the <10 and 10–20 mm size fractions of the RDF, while their low heat values were only half of those measured in case of the >30 mm fractions. Another working group of the MSW research cell carried out intensive research work on the development of mechanical processing technologies for residual municipal solid wastes (RMSW). The KLME (combined air flow, electric and magnetic) separator was patented and built into the new RMSW processing plant in Zalaegerszeg-Búslakpuszta. Industrial scale processing tests were performed.

Our research ambitions also covered the enhancement of secondary raw material production during manual sorting processes (in material recovery facilities), by means of near infrared (NIR) optical separators that required preliminary data collection and assessment. Time series analyses were performed within one year to show the variation of the composition of the waste issuing from separate collection, the changes in particle size distribution of those fractions that promise optimum operation for near infrared (NIR) optical separators, as well as the correlation between the sorting position, the waste type and the picking number. Based on these analyses, only 61 wt% of the incoming material can go through the optical separators, after diversion of the oversize (>350 mm; 18 wt%) and the small (<70 mm; 21 wt%) fractions. The measurements showed that the >350 mm fraction contains 60 wt% cardboard and 9.4 wt% LDPE film, while the 70–350 mm fraction contains 34.5 wt% paper, 18.5 wt% PET bottle and 9.5% cardboard.

The third main axis addresses non-destructive measurement methods, aiming at characterizing heterogeneous waste deposits, potentially suitable for secondary raw material extraction. Our research cell developed models with a completely new approach to electrical impedance spectroscopy and tomography measurement evaluations. In the case of spectroscopy, besides producing high-quality data, it is important to use appropriate models, since the models used in today's practice grant primarily mathematical interpretations of the measurement data. In our case (mainly by modifying existing models), we have produced models that, in addition to being mathematically aligned with the data, produce information (material characteristics) that can be used physically, taking into account the dielectric properties of the investigated material. With regard to tomography, we have developed a new image reconstruction process based on a completely new numerical process, also developed by the University of Pécs. During modelling, the test substance, as a continuum, is converted into a concentrated parameter linear network. The matrix of the resulting linear equation system contains the concentrated parameter equivalents of the material characteristics. With this method, we were able to achieve a higher resolution and sensitivity than that documented in the literature at simulation level. As a consequence of the proprietary numerical process, a universal analytical solution scheme was found for second-order ordinary differentials in the one-dimensional case. We are currently working on its two-dimensional extension.

LIGNOCELLULOSE Research Cell. There are three research groups established within the research cell: BIOMASS, BARK, and MUSHROOM. The aim of the work of the BIOMASS research group was to investigate the new directions of dendromass production, harvesting mechanisation and utilization. The task was very complex, because the increased demand for woody raw material puts a lot of pressure on forests, and in order to achieve a sustainable raw material supply other additional options need to be considered. Thus, the potential of base materials with high lignocellulose content was analysed going beyond forested areas, also on agricultural land, such as in agroforestry or short rotation woody energy plantation systems. In the future, these may play an increasingly important role in the local raw material supply.

The important part of the project was to examine the right choice of forest management method, which plays an important role in the efficient development of the useable amount of dendromass. Forestry research begins with the mechanization of planting the seeds or seedlings. The group also examined highly mechanized logging technologies, because the use of the modern mechanization systems is expected to occur more frequently in the future.

It was also essential to analyse the factors that are influencing wood quality. To achieve a circular economy and carbon sequestration, efforts must be made to utilize wood first in the wood industry, while energy utilization should be the last option. Tree dimensions and wood quality (the presence or absence of wood defects, which can be related to origin or age) determine the composition of the forest assortment that can be produced during harvesting; these factors were also measured. The usability of woody materials is also affected by biotic and abiotic forest damage, which has been increasing worldwide in recent years.

In the third part of the research, attention was particularly focused on finding new ways of utilizing woody materials and industrial by-products, e.g. the production of lignocellulose biofuels and wood mixture pellets. Both have strict requirements for the raw material, which was examined from ecological, economical and sustainability points of view.

Cultivation of wood produces large quantities of renewable raw materials each year. 10% of produced round wood is bark, which in most cases has been dumped in landfills. However, tree bark can be a perfect raw material for production of thermal insulation panels. Some trees have high resin and wax content, which is beneficial because no glue is required when gluing boards together. Boards are heat treated mainly to reduce water uptake and thickness swelling. There are several factors influencing the thermal conductivity values of wood-based materials, of which temperature, moisture, and density are the most crucial parameters. The results show that 0.06W/mK insulation value can be achieved, which is very close to the values of consumable materials. Thermal insulation panels were produced with different density and different treatments, and the results show the potential of a successful bio-product from bark, which could be competitive on the market. The use of bark as a formaldehyde absorber is another possibility.

To characterize the properties and condition of the biomass, we chose FT-IR spectrometry as an analytical technique providing chemical information. A chemometric data analysis strategy (Spectrum Preparation + PCA-LDA) was used to evaluate FT-IR spectra. The spectra of plant foliage and wood, as well as that of fungi decomposing woods, are characteristic. The effect of genetic origin (species type) and environmental condition is reflected in the spectra. Different plant foliage, wood samples, and fungal cultures can also be distinguished by group analysis of their spectra. Degradation of wood by fungi can be monitored by PCA-LDA evaluation of indicative spectra.

As part of the project in interinstitutional cooperation, we applied our developed spectrometry-based evaluation strategy to both plastic and wastewater samples. FT-IR spectrometry also proved to be suitable for the identification and separation of plastics and for the monitoring of wastewater purity. Using various pre-treatments can promote the hydrolysis and increase the total biogas yield in case of the lignocelluloses. Application of mechanical, thermal and chemical pre-treatment have many advantageous effects but these are expensive and their toxic by-products can cause many problems. In contrast, biological pre-treatments have benefits such as cost-effectiveness and environmental friendliness. Two different fungi species; oyster mushroom (*Pleurotus sp.*) and chicken of the woods (La*etiporus sulphureus*) were applied for the pre-treatment of poplar and willow samples. The moisturised and chopped wood samples were inoculated with fungi strains and incubated in room temperature for 28–180 days. The alteration of cellulose and lignin content of samples were measured during the treatment. The biogas yields of pre-treated lignocelluloses in anaerobe digestion were tested under thermophilic (55 ºC) conditions in semi-continuous feeding lab fermentors. Correlations between the rate of fungal decomposition of wood sample and specific methane yield in anaerobe trials were revealed.

CO2 Research Cell. Water is a strategically essential material, and therefore the significance of water recycling and wastewater treatment technologies is of primary importance. Membrane separation, biotechnological approaches, advanced oxidation processes and agricultural fertilization alone or in combination are currently proven technologies in many areas, including wastewater treatments and utilization. The main limitation of the various filtration processes is the accumulation of matter at the membrane surface or in the pores, leading to two phenomena: concentration polarization and membrane fouling. Several combined approaches, including sonication, Fenton-oxidation and ozonation-coupled ultrafiltration have been successfully applied to increase the efficacy and decrease the costs of ultra- and nanofiltration techniques. Membrane fouling was substantially reduced by Vibratory Shear Enhance Processing. Novel self-cleaning nanocomposite membranes were also developed for better reusability of the filters. Oily wastewaters were also successfully treated with a combined microbiological/filtration method. A novel dielectric measurement technique was introduced for monitoring the sludge utilization process filtration.

Oily wastewater can be treated by biotechnological methods using “oil-eating” microbes. Moreover, natural waters are frequently contaminated by toxic hydrophobic materials. Annually, a huge amount of hazardous compounds is released into the environment, including xenobiotics, oils, oil derivatives, drugs. etc.; majority of them reaches and contaminates the groundwater zones and gets involved in water recycling. Various biotechnological approaches were successfully applied for treatment of contaminated groundwater and of wastewater containing fat/drugs both at aerobic and anaerobic zones. A unique strain capable of degrading drug intermediates was isolated, characterized and applied for treatment of industrial wastewater. Lubricant oils are widespread pollutants, therefore their degradation is extremely important. Culture dependent and culture independent, biostimulation, bioaugmentation strategies were designed and applied for intensified/accelerated removal of such contaminants for industrial interest. Together with industrial partners, the elimination of diesel oil contaminations in the groundwater of an abandoned military base was studied and an anaerobic microbial-enhanced energy recovery process was suggested to convert pollutants into biomethane. Methane/biogas, an important alternative energy carrier, can be produced from various sources, including wastewater, organic materials and energy plants. A variety of biomass sources, such as tomato and wood wastes, willow, microalgal biomass, algae-treated wastewater, could be efficiently converted into biogas and thus CO_2 emissions can be reduced. The processes were followed by numerous standard analytical and high-throughput biological methods. Various treatments including enzymatic or microwave pretreatments, and bioaugmentation were applied for intensification of biogas production and to increase the final yields. Microalgae can capture CO_2 and produce clean gaseous energy carriers, such as hydrogen. In collaboration, a carbon-free sustainable process was developed for continuous but cyclic production of photobiohydrogen from water.

Heterogeneous photocatalysis is one of the most investigated advanced oxidation processes which can be applied in wastewater purification technologies. This technology is quite advantageous: it is highly flexible, needs low energy input, and has low or no toxicity impact. Usually, nanostructured materials are used as photocatalysts, which are obtained after complicated synthesis procedures; however, natural minerals can also be applied. In the project, the applicability of natural minerals as photocatalysts was demonstrated in wastewater treatment technologies. Natural rutile nanoparticles in the size range of 20–100 nm could be successfully used for degradation of drug pollutants and xenobiotics, including ibuprofen and phenol in wastewater. Natural ilmenite showed significant photocatalytic activity towards the degradation methylene blue dye, suggesting its applicability in the decolorization process in dye, textile and paper industrial wastes/wastewaters. Natural cuprite nanomaterial obtained by nanogrinding was demonstrated to be an efficient degrader of a model drug pollutant, salicylic acid.

Sewage sludge utilization has three main directions: a) energetic utilizations, such as biogas/biohydrogen production, incineration, thermochemical conversions into solid, liquid and gaseous fuels; b) direct usage as fertilizer; c) composting as an indirect fertilizer. In the project, the agricultural applicability of wastewater sludge was tested. Our study focused on examining the changes in the extractable components of a Chernozem soil and the soil's biological activity as a consequence of low-dose municipal sewage sludge compost applications. The results clearly showed significantly increased soil-bound K2O, P2O5 and NO2− + NO3− contents linked to the sewage sludge treatments, but the toxic element content did not increase significantly. Microbiological analysis revealed that the sewage sludge treatments increased the number of the aerobic microbes and the biochemical activities in the samples. Consequently, low doses of municipal sewage sludge compost can be a sustainable fertilizing practice, taking advantage of their high N, P and K contents that are slowly converted to their soluble/bioavailable forms, thus preventing their excessive leaching into the groundwater. The measurements of CO_2 emissions on arable lands treated with sewage sludge confirm that the daily rhythm of soil moisture and temperature changes have much stronger effects on the CO_2 respiration than the low-dose sewage sludge treatments.

Dear Reader, accept this publication as a little taste of the work and results of the project!

Miskolc, 25 November 2020

Best regards,

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