Book of Abstract

Training School

Al-rich

Industrial Residues for Inorganic Materials

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Technische Universität Wien, Faculty of Civil Engineering Institute of Material Technology, Building Physics, and Building Ecology, Austria

PROGRAMME AND THE BOOK OF ABSTRACTS

Students online Training School - Al-rich Industrial Residues for Inorganic Materials
May 24-28, 2021
Belgrade, Serbia

Edited by:
dr Miloš Nenadović
dr Ljiljana Kljajević
dr Snežana Nenadović
dr Miljana Mirković

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dipl. ing. geol. Katarina Šter, Slovenian National Building and Civil Engineering Institute, Slovenia

WELCOME MESSAGE

Dear Colleagues,

As the RIS-ALiCE project coordinator I take great pride in welcoming all attendees to our training school regarding Al-rich Industrial Residues for Inorganic Materials. Maximising material recycling and recovering industrial waste and by-products are some of the most important tasks currently faced by our society. Many interesting lectures, provided by experts from the project consortium, as well as by prominent researchers from outside the consortium, will tackle topics related to the sustainable use of natural resources, and the characterization of secondary raw materials, along with their recovery potential and use in environmentally friendly materials. I am glad to see that so many of our young colleagues from various academic disciplines were curious to be involved in the training school project tasks, with a great deal of enthusiasm leading to their successful realization. A one week gathering represents an exciting opportunity to meet people with different competencies and establish contacts, which will no doubt help in the development of future research collaborations. I also wish to acknowledge all those who have made this event possible.

Assist. Prof. Dr. Sabina Dolenec

PROGRAMME OF STUDENTS ON LINE TRAINING SCHOOL

Al-rich industrial residues for inorganic materials

May 24th-28th, 2021

Day 1 Monday May 24th 2021

9:00-9:30 Registration

9:30-9:45 Opening ceremony- Director of *VINČA Institute of Nuclear Sciences, National Institute of the Republic of Serbia, University of Belgrade*

9:45-10:00 Presentation of RIS-ALiCE project, *dr Sabina Dolenec*, Slovenian National Building and Civil Engineering Institute, Slovenia

Session 1:

Chair: dr Miloš Nenadović, Vinča Institute of Nuclear Sciences-National Institute of the Republic of Serbia, University of Belgrade

10:00-10:30 Plenary lecture, PL

Low CO_2 and low energy cements, *dr Sabina Dolenec*, Slovenian National Building and Civil Engineering Institute, Slovenia

10:30-11:00 Invited lecture, I-1

Alumimium rich primary resources, *dr Klemen Teran*, Geological Survey of Slovenia (GeozS)

11:05-11:35 Virtual presentation of Belgrade, Serbia

11:35-12:00 Students Q and A discussion Quiz

Session 2:

Chair: dr Ivana Vukanac, Vinča Institute of Nuclear Sciences-National Institute of the Republic of Serbia, University of Belgrade

12:00-12:30 Invited lecture, I-2

Radiological and mechanical properties of cements with different fly ash granulation, *prof dr Emilija Fidanchevski*, Ss. Cyril and Methodius University in Skopje, Faculty of Technology and Metallurgy, Republic of North Macedonia

12:30:12:50 USJE virtual presentation

13:00 Assignment of project tasks to students

Day 2 Tuesday May 25th 2021

Session 3:

Chair: Jelena Krneta Nikolić- Vinča Institute of Nuclear Sciences-National Institute of the Republic of Serbia, University of Belgrade

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Potential valorization of red mud tailings in construction industry, prof dr Mira Vukčević, Faculty of Metallurgy and Technology, University of Montenegro, Montenegro

9:30-10:00 Invited lecture, I-3

Major and minor elemental analysis of Al-rich industrial residues, *dr Bence Kószó*, Bay Zoltan Ltd., Szeged, Hungary

10:00-10:30 Invited lecture, I-4

Critical Metals Recovery from Waste: illustrations from Research Projects, *dr Richard Laucournet*, Université Grenoble Alpes, CEA, LITEN, DTNM, Grenoble, France

Session 4:

Chair: dr Sabina Dolonec, Slovenian National Building and Civil Engineering Institute, Slovenia

10:30-11:00 Invited lecture, I-5

Recycling of industrial Al-rich residues, *dr Ljiljana Kljajević*, Vinča Institute of Nuclear Sciences-National Institute of the Republic of Serbia, University of Belgrade

11:00-11:30 Invited lecture, I-6

Radiological analysis of environmental samples, *dr Ivana Vukanac*, Vinča Institute of Nuclear Sciences-National Institute of the Republic of Serbia, University of Belgrade

11:30-12:00 Lunch break

12:00-12:20 Virtual presentation of company and short presentation (BZN), Hungary

12:20 Work on the project task

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Session 5:

Chair: prof. dr Emilija Fidanchevski, Ss. Cyril and Methodius University in Skopje, Faculty of Technology and Metallurgy, Republic of North Macedonia

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Fly ash as raw materials for synthesis of ultra-light cements, *prof dr Claudio Ferone,* University Parthenope of Naples, Italy Materials Sciences and Enginee6ring Research group MASERG

10:00-10:30 Invited lecture, I-7

Construction and demolition waste as potential secondary raw material, *dr Biljana Angjusheva*, Ss. Cyril and Methodius University in Skopje, Faculty of Technology and Metallurgy, Republic of North Macedonia

10:30-11:00 Invited lecture, I-8

Properties of cementitius building materials containing secondary raw materials, *Doc.dr Ildiko Merta*, Technische Universität Wien, Faculty of Civil Engineering, Institute of Material Technology, Building Physics, and Building Ecology, Austria

Session 6:

Chair: dipl.ing.geol. Katarina Šter, Slovenian National Building and Civil Engineering Institute, Slovenia

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Institute of Nuclear Sciences-National Institute of the Republic of Serbia, University of Belgrade

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Sustanable Utilization of Ferrous Slag, *dr Mojca Loncar,* SIJ Acroni d.o.o, Slovenia

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Chair: dr Ljiljana Kljajević, Vinča Institute of Nuclear Sciences-National Institute of the Republic of Serbia, University of Belgrade

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NORM materials *dr Jelena Krneta Nikolić*, Vinča Institute of Nuclear Sciences-National Institute of the Republic of Serbia, University of Belgrade

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Chair: dr Miljana Mirković, Vinča Institute of Nuclear Sciences-National Institute of the Republic of Serbia, University of Belgrade

9:00- Students virtual poster presentations and discussion

Closing ceremony and best poster presentation award

PLENARY LECTURES

Low-carbon and low-energy cements

Dolenec Sabina[1], Maruša Borštnar[1], Katarina Šter[1]

Slovenian National Building and Civil Engineering Institute, Dimičeva ulica 12, 1000 Ljubljana, Slovenia

Ordinary Portland cement (OPC) is one of the most important construction products, as it is a main component of concrete, which is one of the most heavily consumed materials in the world. As such, despite its embodied energy and CO_2 being low compared to other construction materials, it is considered the third-largest source of CO_2 emissions, accounting for 5 to 8 % of CO_2 emissions globally [1]. Furthermore, its production is energy-intensive and consumes large amounts of mineral resources. The European Union's strategic directions, however, tend towards the recycling of industrial waste.

The cement industry is continuously reducing the carbon footprint and energy consumption of the cement production process. The reduction of CO_2 emissions can be achieved through the use of alternative fuels, increased energy efficiency in the cement production process, the use of clinker substitutes, and carbon capture and storage [2, 3]. Many research groups have been intensively involved in the development of various alternative binders, which are based on either the partial or full replacement of OPC clinker.

One of the most promising routesarises from the substitution of various components of cement with alternative materials, i.e. replacing a substantial proportion of clinker with supplementary cementitious materials (SCMs), such as fly ash or ground granulated blast furnace slag, many of which are waste or by-products from other industries [2]. Recently, studies have focused on the substitution of clinker with a combination of calcined clay and fine limestone -a cement known as limestone calcined clay cement or “LC3” [4]. Furthermore, belite-rich Portland clinkers are processed with less limestone in the raw meal, meaning that CO_2 generation is reduced.

As a potential alternative to OPC, magnesium-based cements, cements consisting of special calcium silicate clinkers (CCSC),and alkali-activated cements have also been discussed [2].

One solution that allows the simultaneous reduction of CO_2 emissions and a lowering of energy consumption in clinker production, as well as enabling the recycling and recovery of secondary raw materials, is belite-sulfoaluminate cements (BCSA) [5]. The lower embodied energy and CO_2 emissions required compared to OPC clinker production (leading to a 20-30 % reduction) result from a lower limestone requirement, lower grinding energy, and lower clinkering temperatures (100-200 °C lower). Moreover, BCSA clinkers can be manufactured using existing technology currently used for the production of OPC, and the mechanical properties of BCSA cements are comparable to OPC. A lack of high-alumina raw materials such as bauxite, however, still limits its implementation.

Within the framework of BCSA clinkers a wide range of compositions are possible. Nowadays, the research stream is strongly focused on iron-rich BCSA clinkers, which are also referred to in the literature as belite-calciumsulfoaluminate-ferrite clinkers or belite-ye‘elimite-ferrite clinkers. Iron-rich BCSA clinkers are described to have a targeted phase composition of 40–70 wt.% belite; calcium sulfoaluminate is usually in the range 20 to 40 wt.%, and brownmillerite-type ferrite varies from 10 to 25 wt.%.

The main phases in BCSA clinker are belite and calcium sulfoaluminate, and it may also contain other minor phases, such as mayenite, gehlenite, perovskite, periclase and excess anhydrite, while the main hydration products of the cement are ettringite, monosulfateand aluminium hydroxide, as well assträtlingite, portlandite and C–S–Hat later ages [6].

Last, but not least, this contribution will present the use of various secondary raw materials in BCSA clinkers and discuss their influence on the clinker phase formation, reactivity and properties of cements (Figure 1).

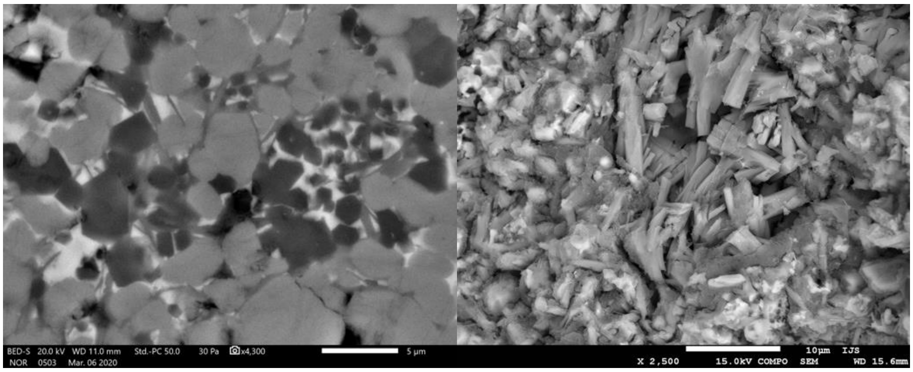

Figure 1. BCSA cement clinker (left) and cement hydration products (right) (SEM/BSE).

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Potential valorization of red mud tailings in construction industry

Mira Vukčević[1], Ivana Bošković[1]

Faculty of Metallurgy and Technology, University of Montenegro, Montenegro[1]

Recently, considerable scientific effort has been expended in the finding of the solution of potential application of bauxite residue (red mud). Still there are some influencing factors that affect the feasibility and economical side of the solution. One of the key factors is the question of the nature of this residue and its classification as hazardous or non-hazardous. In addition to the chemical composition, other parameters that affect the utilization in various applications are the residual of sodium species and the moisture content. A lot of scientific argue has also been vivid concerning the radioactivity of red mud.

Commercial application continues to be a major challenge. In many cases the possible use involves replacing another low cost raw material so whilst the concept may be technically feasible, the risks are still not justified. The questions like maintaining the site, transport, storage issues must be taken into economical analysis.

Number of technological lines can be applied like extraction of iron or rare earths, using it as a source of a particular component (iron and alumina in cement), materials for specific use (colours), construction material (brick, tiles, aggregates , blocks, cements, concrete clinker, foams, filters). The majority of research has involved bauxite residue being used in construction sector. This overview will focus on the geopolymerization process which so far enables the use in the production of light forms in construction sector with the significantly lower radioactivity risk.

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Fly ash as raw materials for synthesis of ultra-light cements

Claudio Ferone, Giuseppina Roviello, Raffaele Cioffi

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Over the past decades, considerable progress has been made in the field of energy efficiency by reducing energy consumption through rational use of energy and the development of new thermal insulating materials. These materials are able to limit heat exchange between the interior and exterior of buildings, thus improving the quality of life of their occupants and offering both environmental and economic advantages.

Commercially available systems for thermal insulation can be roughly classified as: i) lightweight polymeric materials, such as expanded polyurethane and polystyrene; ii) lightweight natural materials, such as wood, wool and cork and iii) lightweight inorganic materials such as cellular cement or autoclaved aerated concrete (AAC). AAC shows interesting mechanical properties as well high thermal resistance and no flammability. For these properties, AAC is often considered the first choice for a safe building insulation. Unfortunately, AAC is a cement-based system requiring the consumption of significant amounts of energy and natural resources for its production. Much attention is being currently devoted to the development of alternative lightweight materials, characterized by a lower cost and a lower environmental impact as compared to cement and concrete-based materials.

Compared to ordinary Portland cement (OPC)—geopolymers could possibly reduce CO_2 emissions thanks to the low carbon footprint of some of the raw materials from which they can be prepared (such as industrial waste, fly ash or mud) [1]. However, geopolymers suffer of brittle mechanical behaviour that limits their application in buildings.

In order to overcome this limitation, a great effort has been done in developing composites of organic–inorganic hybrid geopolymeric materials with improved mechanical properties with respect to unmodified ones [2,3]. In this presentation, the possibility of preparing lightweight hybrid materials from industrial waste such as fly ash (instead of the more expensive metakaolin) is discussed. In this way, lightweight insulating systems with lower cost and limited environmental impact have been prepared, thus providing a possible contribute towards the circular economy.

Foaming was realized in situ using Si^0 as a blowing agent. Samples with density ranging from 0.3 to 0.7 g/cm^3 that show good mechanical properties (with compressive strength up to ≈5 MPa for a density of 0.7 g/cm^3) along with thermal performances ($\lambda = 0.145 \pm 0.001 W/m \cdot K$ for the foamed sample with density 0.330 g/cm^3) comparable to commercial lightweight materials used in the field of thermal insulation were prepared. Upon completion of the work, an environmental evaluation of the industrial production of aerated systems based on geopolymer hybrid foams (GHF) was carried out by comparing the environmental impacts of GHF derived from fly ash (GHF-FA) with the ones derived from metakaolin (GHF-MK) and commercial AAC systems, by performing a Life Cycle Assessment (LCA) study. In particular, the valorisation of waste raw materials in the production of GHF-FA, allows to extended commercial application of geopolymer-based products thanks to the use of a low-cost raw material and a low consumption energy process, that makes the final products competitive both from an environmental and economic point of view, if compared to the AAC systems.

This environmentally friendly approach could contribute to create, develop and optimize technologies to close the loop for wastes and turning them into resources, with a circular economy actuation.

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Secondary raw materials in the geopolymer research and the advantages of mechanical activation

Gábor Mucsi

University of Miskolc, Hungary

Geopolymers are inorganic alumina-silicate materials with excellent physical and chemical properties. Despite being a rather recent research topic, many papers and books have been published focusing on various aspects of geopolymerisation: the history, properties, production, raw materials, applications and development of geopolymers. A brief overview of geopolymer technology is presented in this work, emphasizing the great variety of raw materials that can be used for geopolymer production. Considering the variety of the origin of these materials, three categories are distinguished: primary raw materials which consist of natural minerals, secondary raw materials which are industrial wastes and by-products, and wastes and by-products of natural origin. In general, these waste materials have low reactivity which can be improved by mechanical activation in various mills.

The goal of this paper is to present the most important waste types which can be possible raw materials of geopolymers and to introduce the effect of mechanical activation on the reactivity of secondary raw materials as well as on the geopolymer properties.

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INVITED LECTURES

Aluminium rich primary resources

Klemen Teran[1], Emil Pučko[1], Gorazd Žibret[1]

[1]Geological Survey of Slovenia, Dimičeva 14, 1000 Ljubljana, Slovenia

Aluminium (Al) is the third most abundant element in the Earth's crust, just after oxygen and silicon, accounting for 8.2% of its mass. Aluminium forms oxides, hydroxides, chlorides, phosphates, sulphates, alumino-silicates, arsenates, carbonates, and other compounds which are occurring as minerals.

The highest concentrations of alumina (up to 60% Al_2O_3) can be found in bauxites, which are the main source of alumina and Al worldwide. Bauxites are white to grey to reddish-brown soft residual sediments. They have earthy lustre, a low specific gravity, between 2.0 and 2.5, and often a pisolitic structure.

Bauxites are formed by lateritic weathering of parent rocks, which contain aluminosilicates. While the soluble elements are leached out with time, the Al mineral phases remain in the insoluble residual sediment causing Al enrichment in this material with time.
Bauxite ores are a mixture of different minerals, mainly of Al hydroxides such as gibbsite, boehmite and diaspore, as well as accompanying minerals, such as hematite, goethite, quartz, rutile/anatase and kaolinite.

Based on the conditions under which bauxite deposits are formed, they can be divided into two main categories:

(I). Lateritic bauxite deposits that overly aluminosilicate rocks were formed by lateritic weathering of various silicate rocks such as granites, gneisses, basalts, syenites, and shales in hot and humid tropical regions.
(II). Karstic bauxite depositsthat overly carbonate rocks and were formed by lateritic weathering of limestone, intercalated clastic

layers, material eroded from nearby lithologies and material deposited by aeolian transport.

Lateritic bauxites are the main source for global bauxite production. They cover large areas of equatorial regions such as, Guinea, India, Australia, Brazil, and Guyana(European Commission, 2020).

In contrast, karstic bauxites can be found as smaller lenticular ore bodies containing residual sediments that have accumulated in larger limestone cavities and paleorelief depressions. Karstic bauxites predominantly occur in the Caribbean, Mediterranean, Middle East, China, Central Urals, and Kazakhstan (European Commission, 2020).

Global bauxite ore reserves are estimated at 30,000 Mt (USGS, 2021). However, regions with unfavourable geological conditions for discovering bauxite deposits are highly dependent on its import or have been forced to seek alternative raw materials for alumina production.

The most widely used alternative source of alumina is nepheline syenite, a coarse-grained alkaline intrusive igneous rock composed mostly of feldspars and nepheline. It is mined mainlyto produce ceramics and fertilisers, but since it contains up to 30% Al_2O_3, it can also be used for the production of Al metal and in the cement industry. Russia is the only country that viably exploits nepheline syenite as a source of alumina (Lepezin et al., 2010).

Another globally abundant Al-rich commodity is anorthosite, an intrusive igneous rock composed of calcium-rich plagioclase feldspars. It is believed that future Al resources will consist mainly of anorthosites. Although alumina has been successfully extracted from anorthosites, no commercial production is yet known (Patterson, 1977; European Commission, 2020).

Minerals of the sillimanite group (andalusite, sillimanite and kyanite) also represent a promising Al source. The content of Al_2O_3 in their concentrates can exceed 60 % (Lepezin et. al., 2010).

An important industrial source of Al compounds is also alunite. This sulphate mineral forms pockets, seams, and alteration zones in volcanic rocks such as rhyolites, trachytes, and andesites. The content of Al_2O_3 in exploited alunite can be as high as 15% (Patterson, 1977).

Alumina can also be obtained from other aluminous materials, such as kaolinite clays, dawsonites from oil shales, aluminous phosphate rocks, as well as fromillite and kaolinite clays from coal washings, clays overlying coal seams and aluminous shales. Considerable amounts of Al can also be contained within different secondary resources, such as mining wastes, steel slags, red muds, and fly ashes (Žibret et al., 2021).

At present, the extraction of Al from alternative sources is potentially profitable only when combined with other industrial uses of the exploited material, e.g., in the production of ceramics, fertilisers, fillers and cement (Lepezin et al., 2010).

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Radiological aspect and mechanical properties of cements with different fly ash granulation

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Cements present an excellent target for recycling and valorization of wastes or by-products from different industries. Development of cements based on reuse of mineral wastes or by-products is priority line of research and technological innovation in the pursuit of sustainable industry. High thermal and electrical energy demand, need to query large quantities of lime-stone and clay and emission of greenhouse gasses, especially CO_2 present the environmental challenges for cement manufacture. Different types of mineral wastes or by-products can be used in cement production, representing an environmentally friendly and clinker-saving way of production.

European Standard EN 197-1:2011 lists 27 types of cements, 26 contain some manner of mineral additions which can include industrial residues like siliceous or calcareous fly ash, blast furnace slag or silica fume. The additions are industrial by-products and dependent on the content of natural radionuclides some of them are listed as naturally occurring radioactive materials (NORM). The trend of mineral by-products recycling is expect to continue and new potential cement constituents are being explored, such as construction and demolition waste, paper sludge ash, bauxite residue (red mud) from aluminium production, bottom ash, cooper slag, etc.

Industrial wastes and by-products can be used not only in blends with Portland cement, but also can be added in clinkers, partially or totally replacing the virgin raw material in the raw mill or contributing as secondary fuel. Different types of mineral wastes or by-products can be used as partial raw meal replacement, including blast-furnace slag, waste from clay-based manufacture, aluminium recycling etc. To be appropriate for the purpose, the mineral wastes or by-products must exhibit certain chemical, physical and microstructural characteristics that favour their reactivity and behaviour. Also, radiological aspect has to be considered. Council Directive 2013/59/Euroatom arranged control measures with regard to the emitting gamma radiation. For screening and evaluation of building materials the Council directive 2013/59/Euroatom uses an activity concentration index (I):

$$I = C_{226Ra}/300 + C_{232Th}/200 + C_{40K}/3000 \qquad (1)$$

where C_{226Ra}, C_{232Th} and C_{40K} are the measured activity concentrations (*Bq/kg)*for, respectively^{226}Ra, ^{232}Th and ^{40}K.

The activity concentration index (I) is only a screening parameter. In the case the value of I>1 is found for a given building material, than it needs to be verified that, upon use in building, the exposure to gamma radiation is less than the reference level of 1mSv y^{-1} (the real criteria for building materials).

Fly ash is well-known cement constituent and in recent years its recycling has become increasingly important due to increasing landfill costs and current interest in sustainable development. According to the chemical composition fly ash is classified in two main groups: class F and class C fly ash. In both cases fly ash consists of fine particles that could contain some heavy metals and natural occurring radionuclides. There are two main applications for fly ash in cement production, (1) first as a raw material to produce Portland clinker and (2) second as a mineral or pozzolana addition. Fly ash can be added to the Portland cement clinker as a pozzolanic constituent in the production of CEM II (Portland–composite cement), CEN IV (pozzolanic cement) or CEM V (Composite cement). The amount of fly ash in the cement goes from 6% to 55%. High amount of fly ash incorporated in cement leads to a decrease in the early strength of cement due to the early low reactivity of fly ash, which could be approved by grinding. In this study cements fabricated with different fly ash granulometria (taken from different zones of electrofilter and mechanically activated) will be the subject of discussion. The investigation will be discussed from radiological aspect as well as the influence of fly ash granulometry on the mechanical properties of cement based products.

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Major and minor elemental analysis of Al-rich industrial residues

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Major and minor elemental analysis of Al-rich residues is done by specific, high performance analytical instruments, often requiring well-chosen, correct sample preparation. Such techniques are NAA (Neutron Activation Analysis, XRF (X-ray fluorescence), AAS (Atom Absorption Spectroscopy), ICP-OES (Inductively Coupled Optical Emission Spectroscopy), ICP- MS (Inductively Coupled Plasma Mass Spectrometry) [1]. Three of them are presented here.

ICP-OES, ICP-MS:

In the high temperature (6000-8000°C) of the argon plasma the components of the sample are broken to atoms and ions and get excited. In that excited state elements emit light with very specific wavelengths. The light can be analysed in a spectrometer at the ICP-OES measurements [1]. At ICP-MS the ions are extracted from the plasma and are measured in the mass spectrometer by atomic mass.

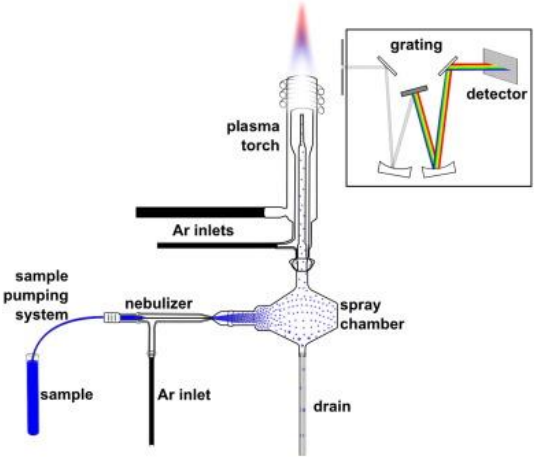


Figure 1. Typical configuration of an ICP-OES intrument

In the usual manner liquid sample is introduced to the plasma in the form of aerosol. That is why the solid samples need to be dissolved prior to analysis. In the case of aluminium rich residues all samples are solid. The commonly used aqua regia can't decompose the SiO_2 matrix and the materials which are incorporated in that phase even at elevated temperatures and pressures. Digestion of the silica matrix is possible with acid mixtures containing hydrofluoric acid, which is quite dangerous to work with. Other solution is to fuse the samples with an adequate reagent (lithium-metaborate, sodium-carbonate, boric acid etc.) at high temperature and get an acid soluble glass bead. In the RIS-ALICE project we employed lithium-metaborate in platinum crucibles at 1000°C for 1h. The silicate content of the sample is converted to soluble salts according to the following reaction:

$$2LiBO2 + MeSiO3 \rightarrow Li2SiO3 + Me(BO2)2$$

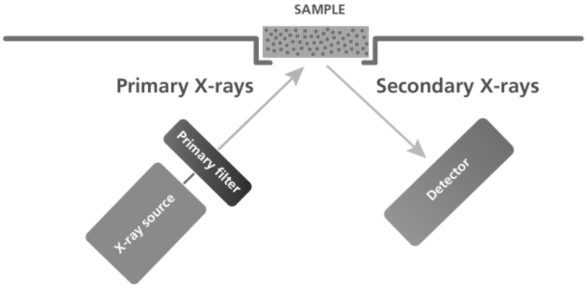
After wards we used dilute hydrochloric acid to dissolve the fused glass bead. The acid concentration can't be much greater in order to avoid the precipitation of the silica, but should be high enough to keep the constituents in solution. The optimum concentration is around 3% hydrochloric acid. The recipe is from a Hungarian standard for cement analysis (MSZ 525-17) [2].

In ICP-OES technique use of an internal standard (e.g. Y, Sc, Co, Pt, Au) is very common. Since we had samples with considerable amount of Y, Sc, Co and we used crucible made of platinum, we chose Lu as internal standard (which corrects the results very well for the Rare Earth Elements).

Typical lowest measurable concentration for ICP-OES lies around 1-10 mg/kg. ICP-MS technique can measure concentration at two or three magnitude lower, but is less tolerant to high matrix content.

XRF:

In the X-ray fluorescence method the sample is irradiated with short wavelength X-rays. These gamma photons hit electrons out of the inner orbital of the atoms creating an electron vacancy. As electrons from the outer orbitals fill the hole secondary gamma photons are emitted with wavelength specific for the elements and for the difference between the energy levels of the orbitals. We can measure the wavelength and the intensity of these secondary radiations to get qualitative and quantitative information about the sample.



1. figure Configuration of an XRF analysis

Solid samples can be introduced as loose powder, pressed pellets or fused beads. The cost, effort and the quality of the results increase in that order. XRF has higher detection limits than ICP techniques.

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Critical Metals Recovery from Waste: Illustrations from Research Projects

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Raw materials are crucial to Europe's economy. They form a strong industrial base, producing a broad range of goods and applications used in everyday life and modern technologies. Reliable and unhindered access to certain raw materials is a growing concern within the EU and across the globe. To address this challenge, the European Commission has created a list of critical raw materials (CRMs) [1] for the EU, which is subject to a regular review and update. CRMs combine raw materials of high importance to the EU economy and of high risk associated with their supply.

- Link to industry - non-energy raw materials are linked to all industries across all supply chain stages.
- Modern technology - technological progress and quality of life rely on access to a growing number of raw materials. For example, a smartphone might contain up to 50 different kinds of metals, all of which contribute to its small size, light weight and functionality.
- Environment – raw materials are closely linked to clean technologies. They are irreplaceable in solar panels, wind turbines, electric vehicles, and energy-efficient lighting.

The measures in the European Circular Economy Action Plan cover the whole life cycle of products from production and consumption to waste management as well as the market for CRMs. Innovation and investment in the field have been promoted through the H2020 programme.

The presentation will highlight several illustrations of scientific and technological approches regarding CRMs extraction from waste coming from new technologies for energy such as:

- Li-ion battery with the selective recovery of Co, Mn and Ni [2],
- Rare earth elements from used permanents magnets and recycling slags [3],
- Ag from used Photovoltaic panel [4].

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Recycling of industrial Al-rich residues

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Enormous amounts of various Al-rich residues (steel slags, red mud, ashes, and landfills of bauxite mines) present high secondary mineral resources potential. In order to preserve the environment, one of the ways of recycling these waste mineral materials is the synthesis of sustainable mineral binders with high Al content, which can be further used as environment-friendly construction material. According to the Law on Waste Management [1] ash and slag generated by burning coal from thermal power plants are classified as secondary raw materials. In Serbia, out of six million tons of ash, which is produced annually, only 2.7% is used by the cement industry. However, the problem of disposing these materials is reflected in soil pollution; entering the food chain by releasing heavy metals/substances that plants absorb; the spread of very small particles of fly ash through the air has a detrimental effect on all living beings, especially humans. Fly ash and slag are used as raw materials in different cases: construction industry, agriculture, in treatment of hazardous and radioactive waste, manufacturing aluminum, rare materials, and some heavy metals. Also, mixtures of fly ash of Class F and bentonite are used as water proof coating for lining the bottom of the landfill.

Red mud is a by-product of the alumina production process, which is produced by the processing of bauxite by Bayer method. Improper storage of bauxite residue can lead to harmful contamination of water, land and air in the surrounding area because of its high alkalinity. The global growth of bauxite residue highlights the urgency to develop and implement improved means of storage and remediation, and utilization options of its residue as an industrial by-product [2]. During the last two decades, extensive work has been done to develop various processes for utilization of RM by the researchers in the various areas: as a special cements [3], in the ceramic industry [4], in ceramic glazes [5], in the aluminum industries by producing glasses and glass-ceramics [6], as an additive for construction materials [7], as the raw meal for the production of Portland cement clinker [8] and in production of heavy clay ceramics [9]. In any case in a pioneering investigation the main characteristics of Al-rich residue were ranged in order to establish their potential to be alkali activated [9]. Alkali activated materials (geopolymers) (Fig. 1) are a new class of materials obtained by activation of inorganic precursors of alumosilicate origin. Activation occurs thanks to the use of strong alkaline solutions and unlike other industrial processes (e.g. sol-gel, clinkerization, sintering processes), alkali activation process does not require expensive chemical reagents, use of carbonate-based raw materials or high temperature thermal treatments. In the construction sector, geopolymers represent an eco-friendly, low cost and low power consumption alternative of traditional inorganic matrices and composites.

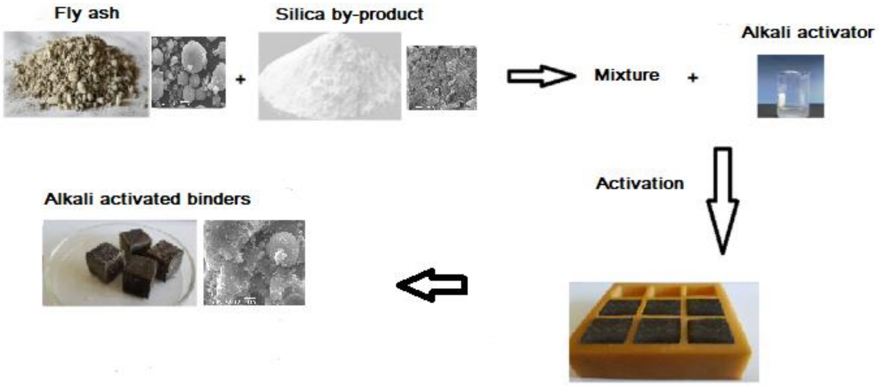

Fig. 1 Process of alkali activation of fly ash

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Radiological analysis of the environmental samples

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Our environment is radioactive because all nature, all that surrounding us is radioactive. Radioactivity is the immanent characteristic of matter. The most important natural radionuclides are members of natural radioactive chains (uranium, thorium and actinium series), ^{7}Be and ^{40}K. Exposure to radioactivity have been enhancing over the years due to different kind of human activities (artificial radioactivity, medical exposure, technological enhancement). In total human exposure, natural radioactivity participate with over 80% (more than half comes from radon). (UNSCEAR 1993, 2008, 2000)

In order to estimate the radiation exposure due to the materials present in our environment, radiological analysis, i.e. determination of radionuclide content has to be performed. The choice of method used strongly depends on the type of radionuclide emission (alpha, beta or gamma) whose content needs to be determined, the type of the sample (soil, water, plants, food, building material, etc.) and available time and resources.

The most common measurement methods that are used in different kind of environmental monitoring campaigns are:

- Gross alpha/beta counting,
- Determination of the tritium and strontium concentration,
- Gamma spectrometry.

Gross alpha/beta counting is the screening method which gives the information about the level of the total activity of all radionuclides, alpha and beta emitters present in the sample, while the other two give the radioactivity concentration of the specific radionuclide(s). All of these methods implies certain sample preparation procedure –

radiochemical preparation and/or separation of the radionuclide of interest or mechanical preparation.

Gamma ray spectrometry is the most common method used for radiological analysis of different kind of samples. It is a nondestructive method for determination of gamma emitting radionuclides which provides qualitative and quantitative information – identify the radionuclides present in the sample and their concentration.

The radiological analysis of different kind of environmental samples is most often performed by gamma ray spectrometry with a semiconductor high purity germanium (HPGe) detector. Method does not require chemical treatment of samples. Energy and efficiency calibration of spectrometer needs to be performed in accordance with international recommendations IAEA (1989).

Prepared samples should be measured in the same geometry as the calibration is done, otherwise some corrections need to be applied.

After mechanical preparation, samples needs to be placed in appropriate beakers, sealed with bee wax and left for six weeks in order to reach the radioactive equilibrium. After that time, samples are measured and spectra are recorded and analyzed. Analysis of recorded spectra includes identification of present radionuclides through characteristic full energy peaks, and calculation of its specific activity using the relevant nuclear data (DDEP, 2017) and equation $A=\frac{N(E)/t}{\varepsilon(E)mp}$, where N denotes net area, t is measurement time, $\varepsilon(E)$ denotes efficiency at energy E, p is probability of gamma emission and m is a mass of measured sample. The specific activities are expressed in Bq/kg and are given with associated combined standard uncertainties which include the efficiency calibration uncertainty and the statistical uncertainties of the recorded peaks.

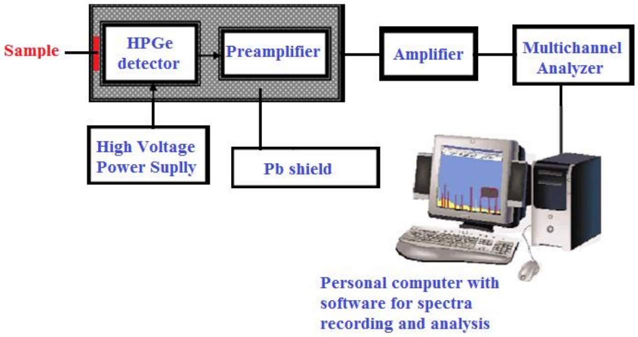

Diagram of high purity germanium detector system

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Construction and demolition waste as secondary raw material

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Major waste streams in urban areas are produced from the demolition of buildings. The sustainable usage of demolition wastes as construction materials has numerous environmental and economic advantages. New opportunities to recycle demolition wastes into alternative resource materials for construction industries would mitigate landfill issues and significantly reduce environmental problems.

Construction and demolition (CDW) waste is defined as the unnecessary and damaged products and materials that resulted from construction, renovation, demolition and other construction activities. According to Eurostat, around 30% of all waste generated in the EU 27 for 2018 can be associated with construction and demolition waste, and it consists of various materials such as concrete, bricks, wood, metals, plastic, glass, asbestos, gypsum etc. with recycling levels varying within member states from 10-90%. A more concerning problem is that in developing economic countries annual quantity is expected to rise with the development of the economy [1].

There are various reports dealing with information on the quantity of CDW generated, the quantity of CDW recovered, main obstacles and drivers to sustainable CDW management for 28 EU countries [2]. The main problems and obstacles in several Balkan countries noted (i, ii, iii) in terms of construction & demolition waste management are [2]:

(i) mentality in the construction sector, lack of treatment facilities and low territorial network, lack of incentives for recycling.

(ii)historic practices including illegal dumping, technical documentation for the quantities of construction waste, lack of benefits and levers to motivate recovery, lack of recycling capacities.

(iii) legislation and regulation, treatment facilities and their territorial network, collecting and tracking data about generated and treated CDW, public awareness, public procurement, market conditions.

Construction and Demolition Waste (CDW) management plays a crucial role when it comes to meeting recycling targets for two reasons. On the one hand, there is a huge difference in material composition between buildings (tiles, bricks, mortars, plaster board etc.) and civil infrastructure (e.g., pavements, roads, etc.), making potential recycling rates difficult. On the other hand, it is a large volume and heavy waste which might be difficult or expensive to transport.

Researchers have been reported for possible quantification and management of construction waste [3]. Sorting of waste materials is a crucial step in recycling. The materials included in the European List of Waste are: stony material, wood, metals, glass, paper, plastics, insulation material, asbestos containing material, mixed materials and sorting residue.

Stony materials, metals and wood are accountable for more than 80% of the total C&D waste generated. Examples of stony materials include concrete, bricks, gravel, sand-lime brick, roof tiles, gypsum based materials etc. The building sector is the most promising area for recycling and re-use of stony materials.

Concrete aggregates can be used for substituting grind in concrete production [4]. Use of up to 20% concrete aggregates as a substitute of grind has a low influence on concrete properties and workability. There are several technologies to prepare concrete for recycling: Crushing, sifting and washing; advanced dry recovery; thermal treatment; smart crushing. There has been substantial research carried out into the use of CDW and cements and lime as binding agents, mortars and aggregates [5-6]. The experiments conducted with three ceramic wastes in the quantity of 8, 24 and 40% by mass as supplementary cementitious materials in Portland Blended Cements showed that ceramic wastes from the construction demolition process have pozzolanic activity with indication that they must be classified as slow pozzolana. Baroso and Pala investigate the effect of incorporation of construction and demolition waste in the clay–based ceramic materials, showing that the mixture containing 20 % of C&DW owns the best chemical and mechanical properties, with conclusion that no significant changes to the industrial procedure is needed, making construction and demolition waste a potential raw material.

The recycling and re-use of C&DW is a huge and complex problem and education, research, discussions and dissemination might contribute to improvement of environmental, economic and social understanding of C&D waste management, and open the possibility for production of different products with properties comparable to the ones commercially produced.

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Properties of cementitious building materials containing secondary raw materials

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Concrete, as the most prominent representative of cementitious building materials, is the most used building material on Earth and is the second most consumed substance after water. With its main ingredients Portland cement, natural aggregate (gravel, crushed stone and sand) and water, concrete is a vast raw material consumer composite. The aggregates and cement constitute around 70% and 10% of its total volume, respectively. The manufacturing of Portland cement is a highly energy-intensive process, resulting in high pollution, carbon dioxide (CO_2) emissions and consequently in global warming and climate change. Producing a ton of cement generates nearly a ton of CO_2 and alarmingly the cement industry alone emits around 6% of the total CO_2 on Earth.

Recently, the construction industry is strongly focused on the improvement of the overall environmental performance of concretes by reducing the use of Portland cement and natural aggregates in concrete and their substitution with secondary raw materials (SRM). The amount of cement can be (partially or completely) replaced by supplementary cementitious materials (SCM) of industrial by-products such as metallurgical slags, coal combustion-based fly ashes, ground granulated blast furnace slag, silica fume, etc. Whereas natural aggregates could be increasingly supplemented with various recycled aggregates from demolition waste (DW).

The utilization of SRMs effectively improves the sustainability and footprint of concretes by simultaneously reducing the waste generation problem of the industrial sector, however, it could significantly influence the properties of the composite itself. In this lecture, an overview of the major physical, mechanical, fracture mechanical and durability properties of cementitious building materials containing SRMs will be given.

Mineralogical composition of fly ash as a secondary raw material for potential usage as construction materials

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Large amounts of fly ash and other secondary raw materials are currently still not used and disposed, in order to protect the environment the need to exploit them in construction sector is growing. In the area of building materials research, one of the potential comprehensive solutions to the problem is the synthesis of alternative mineral binders such as cement clinkers and also alcali activated materials e.a. geopolymers [1, 2]. Geopolymer based materials in nowdays are also called green construction materials, where at least one component is used for their production, which starts from waste material and thus directly affects the preservation of the environment [2]. Fly ash vary in mineral composition and depending on that their application is determined. In so far investigations of selected fly ashes originating from Serbian Thermal power plants turned out to be a good starting material for the production of cement clinkers, but also alcali-activated concretees [3,1]. Based on the composition of the initial component or coal used as the initial raw material and the mineral composition of the fly ash therefore differs phase and structural properties of synthesized products. Nowdays, organic components such as polyvinyl alcohol-PVA are adding to obtain composite with good chemical bonding [4]. Based on satisfactory chemical and mineralogical composition and also structural properties, it is possible to define and select a good starting fly ash material for the synthesis of environmentally friendly geopolymer materials. Besides good construction properties the satisfactory radiological properties is extremely important. The main aim of this work is defining chamical, mineralogical composition, morphological and radiological properties of fine fly ash (Nikola Tesla power plant, TENT B) and its geopolymer products with addition of $1\%_{wt}$ and $2\%_{wt}$ of PVA component. The phase evaluation study of aging period during 7, 14, 21 and 28 days are investigated by XRPD analysis. Results shows that with $2\%_{wt}$ of added PVA during 28 days of aged time leads to rearegement of the amorphousness geopolymer matrix better and interconnection of grains. Radiological results have shown that geopolymer products do not increase the effective dose of population exposure.

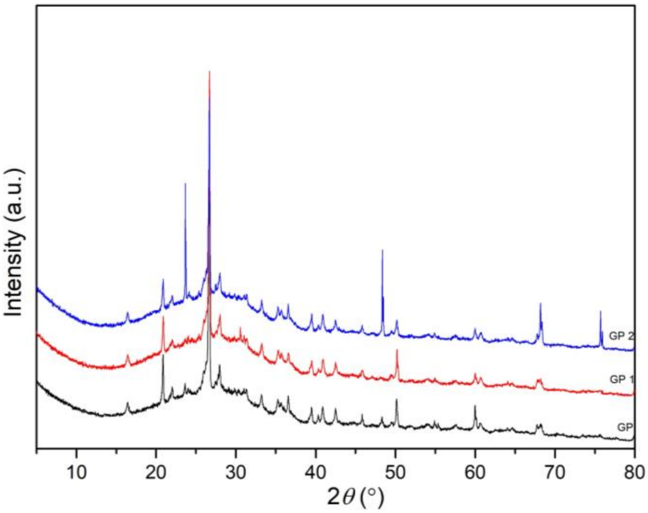

Figure 1. XRPD -patterns of geopolymer material-GP and with $1\%_{wt}$ PVA-GP1 and $2\%_{wt}$ PVA-GP2

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Applications of MALDI-TOF analysis in characterization of alkali-activated materials

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Matrix-assisted laser desorption and ionization time-of-flight mass spectrometry (MALDI TOG MS) is usually applied for the analysis of biomolecules and organic polymers. It is a soft ionization technique based on the illumination of a sample mixed with organic molecules, matrices followed by desorption and ionization. Ions are usually singly charged; therefore, MALDI spectra are easy to analyze. Modern MALDI techniques also enable fragmentation, thus making structural analysis possible.

There are numerous applications of MALDI methodology since the method is sensitive, fast and require only low amounts of a sample. However, there are only rare applications for the structural characterization of inorganic polymers. In this presentation, we will give examples and discuss the potential of using MALDI TOF mass spectrometry to monitor the process of ageing and polymerization of calcinated clay, i.e., metakaolin. As an alkali activator, various concentrations of NaOH were applied at various times. Two types of organic matrices were successfully applied for this purpose: 2,6-dihydroxyacetophenone (THAP) and 2,5-dihydroxybenzoic acid (DHB). The positive ion mode was applied for the detection of signals arising from polymers [1]. Most signals arise from the fully protonated unit $Al_2O_3(SiO_2)_2$, but some are also generated by the addition of a further SiO_2 unit. Singly positively charged ions are detected, and they are generated by protonation or sodiation since excess NaOH is used for activation. The signal at the lowest m/z position (m/z 310.88) has the identity $Al_2O_3(SiO_2)_3H_6Na$. At the same time, the signal at the highest m/z position (m/z 924.67) is also formed by clustering with DHB matrix and has the identity $Al_2O_3(SiO_2)_3(AlSiO_6H_4)_2H_3Na_7$(DHB-H+Na). No regularities in the signal intensity and appearance could be established with the treatment, but new signals at higher m/z ratios were detectable after treatment with increased concentrations of NaOH [2]. Therefore, MALDI analysis can be suitable to follow the structural changes in geopolymers, but since the method is not routine for this purpose, it requires still some validation.

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Sustainable utilization of ferrous slag

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Ferrous slags are valuable raw materials that are obtained during the pig iron and crude steel production processes. In total, 70% of the world steel is produces utilizing the first, based on the Blast Furnace (BF), where iron ore is reduced to pig iron, which is afterwards converted into steel in the Basic Oxygen Furnace (BOF). The second route, based on the Electric Arc Furnace (EAF) using scrap steel as the input as well as electricity as the energy source. Slag is the biggest by-product stream of the steel sector, accounting for 90 % by mass of by-product and waste generated. On average, the production of one tonne of steel via EAF route results in 168.6 kg of steel slags and via BF route results in 400.8 kg of slags[1]. Base on worldwide steel production in year 2018, the amount of slag generated was estimated to around 600 Mta of slags, of which 58 % are blast furnace slags and 42 % are steel slags[2].

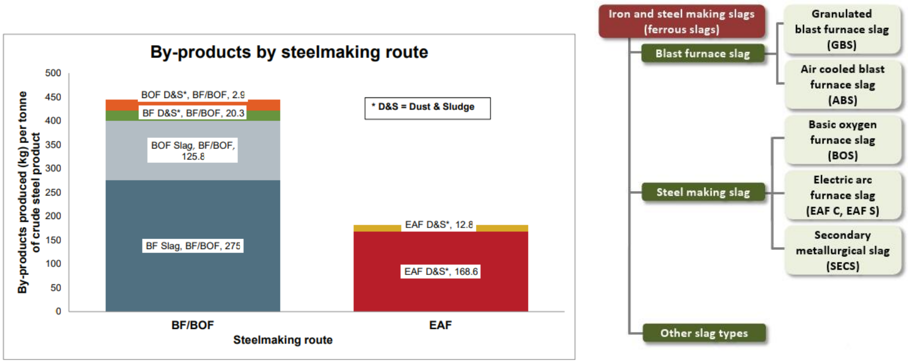

Figure 1: Main solid co-products per steelmaking route (left)[1] and different ferrous slag types[3]

At least 19.2 million tons of blast furnace slag and 15.7 million tons of steelmaking slag were produced in Europe in year 2018 (Figure 2)[3]. With the recovery rate almost 100 % blast furnace slag, either granulated or air cooled, significant contributes to the circular economy in numerous countries in Europe. It is widely used in the cement industry, as a main constituent of cement or as additive for concrete. According to the Slag cement association[4] replacing Portland cement with Portland slag cement in concrete can save up to 59% of the embodied CO_2 emissions. Use in road construction is also widespread, representing 17 % of use BFS in Europe.

The use of steel slags is more challenging, because due to the different steel production processes and produced steel quality, variation in slag chemical composition, physical and mechanical properties occurs. However, in most cases slag producers and processing plants have overcome this barrier. The widest use of steel slag is in construction sector. In year 2018 69.9% of the steelmaking slag in the EU was used in road construction, followed by recycling in metallurgical processes with 13.4 % and cement and concrete addition with 5.5 %[3].

In Europe most of the ferrous slag is registered according to the REACH regulation 1907/2006, which strengthens its position and its value in the market. However, the market is characterized by strong competition between slag producers and producer provide the natural materials. Transport cost may represent limitations for slag producer.

Although iron and steel slag is highly recyclable, with a worldwide average recovery rate from over 80% (steelmaking slag) to nearly 100% (iron making slag), the European steel industry has focused its efforts on the improvement of by-product recovery and quality, resulting in being closer to its “zero-waste” goal. In the way to achieve this goal, it is fundamental to increase the quality of the by-products recovered[5]. In addition, the concept of a Circular Economy has recently been strongly emphasized at the European level. Where waste cannot be avoided, its economics value must be recovered and its impact on the environment and on climate change avoided or minimised. In parallel, EU countries should benefit from a robust and integrated single market for secondary materials and by-products[6].

In the light of achieving the “zero waste goal”, it is important to invest in the research and development of new technologies to improve by-product quality, while also looking for other applications for by-products that are not yet in widespread use. In the cement industry, the possibility of producing low carbon and low-energy cements using secondary mineral raw materials rich in aluminium is a promising technology, which would save natural resources and reduce the environmental impact of the production processes.

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Protection of natural resources by utilization of industrial waste

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Amongst waste of metallurgical industry, especially slag from iron and steel production are of a significant importance. Since the total production of iron and steel is increasing globally, it is necessary to fallow world trends of processing slag. Things to its physical and chemical properties slag is classified. Therefore, it can be used primarily for the needs of construction industry, for production of insulation, fertilizers, etc. The use of slag as a raw material can contribute to preservation of natural aggregates, since slag has some properties similar to the natural aggregates properties.

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NORM materials

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NORM (Naturally Occurring Radioactive Material) is a term representing radioactive materials, which can be found in nature or produced and/or augmented via different human activities. Exposure to naturally occurring radiation is responsible for the majority of an average person's yearly radiation dose and is therefore not usually considered of any special health or safety significance. However, certain industries handle significant quantities of NORM and large scale production of these materials could elevate the exposure of the general population to the ionizing radiation. Over time, as potential NORM hazards have been identified, these industries have increasingly become subject to monitoring and regulation [1].

Also, in modern-day technology, utilisation of the waste materials and by products of processing, takes up ever more prominent place. In the light of this technology development, it becomes necessary to evaluate these new materials from the radiological protection point of view.

Coal industry (combustion, ash and mining): Most coals contain uranium (U) and thorium (Th) and their decay products, as well as 40-K. The total levels of individual radionuclides typically are not great and are about the same as in other rocks near the coal, which varies according to region and geology. Enhanced radionuclide concentration in coal is associated with the presence of other heavy metals and high sulfur content. During combustion the radionuclides are retained and concentrated in the flyash and bottom ash, with a greater concentration to be found in the flyash. The concentration of U and Th ash can be up to ten times greater than for the burnt coal, while other radionuclides such as Pb-210 and K-40 can concentrate to an even greater degree. Some 99% of flyash is typically retained in a modern power station and while much flyash is buried in an ash dam, a lot is used in building construction. Coal produces a significant amount of waste rock, and drainage water that can contain elevated levels of radioactivity. Underground coal mines are subject to increased radon levels, while elevated levels of radium and K-40 can be found in mining waste rocks and soil [1, 2].

Oil and gas industry: Analysis of oil and gas from many different wells has shown that the long-lived U and Th isotopes are not mobilized from the rock formations that contain them. However Ra-226, Ra-224, Ra-228 and Pb-210 are mobilized, and appear mainly in the water co-produced during oil and gas extraction. These isotopes and their radioactive progenies can then precipitate out of solution, along with sulphate and carbonate deposits as scale or sludge in pipes and related equipment. Radon-222 is the immediate decay product of radium-226 and preferentially follows gas lines. It decays (through several rapid steps) to Pb-210 which can therefore build up as a thin film in gas extraction equipment [1, 2].

Metal mining and smelting and industrial processing of ores: The mining and processing of metal ores, other than uranium, may also generate large quantities of NORM wastes. These wastes include ore tailings and smelter slag, some of which contain elevated concentrations of U, Th, 226-Ra and their decay products that were originally part of the process feed ore. Radon exposure is often an issue in metal mines. Mineral sands contain zircon, ilmenite, and rutile, with xenotime and monazite. The NORM aspect is due to monazite – a rare earth phosphate containing a variety of rare earth minerals (particularly cerium and lanthanum) and 5-12% Th, with traces of uranium and thorium. Zircons typically have activities of up to 10,000 Bg/kg of U-238 and Th-232 [1].

Phosphate fertilisers industry: Phosphate rock used for fertiliser is a major NORM due to U and Th. Phosphate is a common chemical constituent of fertilizer. It is principally mined from apatite and phosphate rocks (phosphorite) in which the concentration of phosphate has been enhanced by sedimentary, igneous, weathering and biological processes. Uranium can also be concentrated in these processes so that a high phosphate content generally coincide with high uranium content. Treatment with sulfuric acid leads to the production of gypsum (phosphogypsum) which retains about 80% of Ra-226 and 30% of Th-232 and 14% of U-238. This means that uranium and thorium are enhanced to about 150% of the value of the beneficiated ore, making it a significant NORM [1].

Building industry (next lecture): In 2015 the IAEA (NORM VII) says that there is still a lack of harmonization of national approaches to the management of NORM residues [3,4]. However, acceptance of the need to minimize NORM waste by recycling NORM residues or using them as by-products (with dilution if necessary) continues to grow. This includes use in building materials, subject to 1 mSv/yr reference level for exposure.

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NORM in Buildings Industry

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Natural radioactive nuclides in building materials originating from raw materials or residues from industries involving NORM. Materials derived from rock and soil contain mainly the natural radioactive isotope of K-40 and radionuclides of the U-238 and Th-232 series. In the uranium series, the decay chain segment starting from radium (Ra-226) is radiologically the most important, due to reference is often made to Ra-226 instead of U-238. The activity concentrations in common building materials and industrial by-products used for building materials will be presents in this presentation.

This radionuclides upon decay cause public exposures by external and internal radiation. The external exposure is caused by direct gamma radiation, while the internal exposure is caused by the inhalation of radon (Rn-222) and thoron (Rn-220), which are Ra-226 and Th-232 decay products.

Radon is an inert gas, so it can move rather freely through porous media such as building materials and in most cases the main part of indoor radon on the upper floors of a building originates from building materials. Thoron concentrations are usually rather low, while typical excess indoor radon concentration due to building materials is about 10–20 Bq/m^3, but in some zones and in rare cases it may rise up to greater than 3000 Bq/m^3. Due to, it is important to have an assessment of the radiological hazard associated with the exposure to the radiation.

European Commission [1] recommends that the reference level for building materials should be of the order of 1 mSv/y or less expressed as effective dose caused by external gamma radiation to members of the public. A common screening method the dose caused by building materials is the use of an Activity Concentration Index (ACI), the value of which is calculated on the basis of the concentrations of Ra-226, Th-232 and K-40. ACI is related to the gamma radiation dose in a building, in excess of the typical outdoor exposure and it given by the following formula:

$$ACI = \frac{Ac_{Ra-226}}{300} + \frac{Ac_{Th-232}}{200} + \frac{Ac_{K-40}}{3000}$$

where $A_{C,Ra\text{-}226}$, $A_{C,Th\text{-}232}$ and $A_{C,K\text{-}40}$ are the activity concentrations in Bq/kg.

For ACI > 1, the dose must be determined. The effective dose - E (Sv), corresponding to the gamma radiation of a building material was determined from the expression:

$$E(mSv) = D\left(\frac{nGy}{h}\right) * 8760(h) * 0.8 * 0.7\left(\frac{Sv}{Gy}\right) * 10^{-6}$$

D (nGy/h) represents the absorbed dose in the air:

$$D = q_{Ra-226} * Ac_{Ra-226} + q_{Th-232} * Ac_{Th-232} + q_{K-40} * Ac_{K-40} - 50$$

where q_i is specific dose rate for isotope "i" in nGy·kg/(h·Bq), $A_{C,i}$ is the activity concentration of isotope "i" in Bq/kg and 50 nGy/h is the average background originating from the earth's crust.

For assessing the specific dose rate, more elaborate methods need to be used in order to consider the actual concentrations and locations of a certain building material in a building. European Commission [1] recommends the model represents by Markkanen in reference [2].

A protection strategy should be established with the aim to promote building materials that do not exceed the reference level.

The strategy may encompass measures such as providing information on the levels of exposure caused by different building materials, labelling of materials, suggesting the use of materials with low radioactive concentration or limiting the use of certain materials causing significant exposures.

Dimensions of the model room	4 m x 5 m x 2.8 m		
Thickness and density of the structures	20 cm, 2350 kg m^{-3} (concrete)		
Annual exposure time	7000 hours		
Dose conversion	0.7 Sv Gy^{-1}		
Background	50 nGy h^{-1}		
	Specific dose rate, nGy h^{-1} per Bq kg^{-1}		
Structures in a building causing the irradiation	^{226}Ra	^{232}Th	^{40}K
Floor, ceiling and walls (all structures)	0.92	1.1	0.080
Floor and walls (wooden ceiling)	0.67	0.78	0.057
Floor only (wooden house with concrete floor)	0.24	0.28	0.020
Superficial material: tile or stone on all walls (thickness 3 cm, density 2600 kg m^{-3})	0.12	0.14	0.0096

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STUDENTS PRESENTATIONS

Thermodynamic parameters of alkaline activators and porous properties of high molar concentration geopolymers

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This paper describes the production of environmentally friendly, economical energy, clean technology for the preservation of the natural environment and resources using metakaolin as a precursor for the synthesis of inorganic polymer (geopolymer). The geopolymerization process, in addition to metakaolin, requires an alkaline activator consisting of a mixture of sodium silicate and sodium hydroxide.

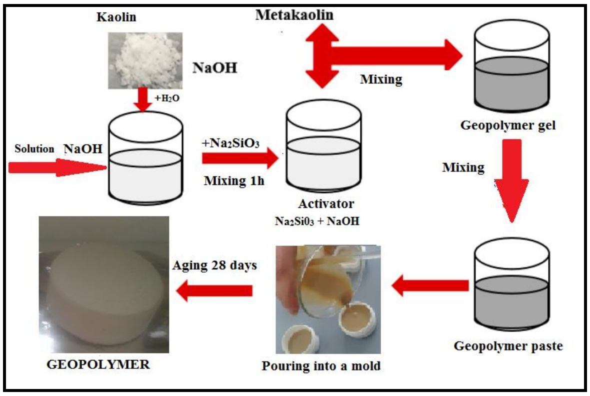
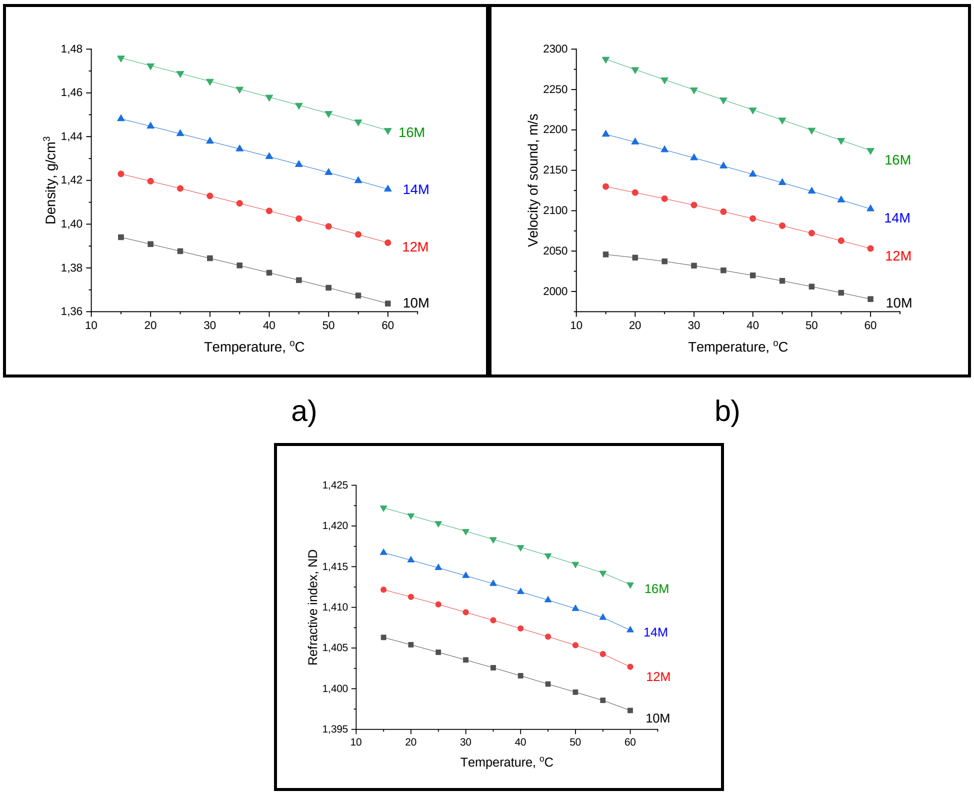


Figure 1.Geopolymerization process from raw material to geopolymer formation

Four different mixtures of alkaline activators of molar concentrations 10M-16M were made, with step 2. Figure 1 shows the geopolymerization process from the starting raw material to the geopolymer. The aim of this study was to investigate the influence of thermodynamic parameters (density, refractive index and speed of sound) of alkaline activators and to predict the properties of synthesized materials. Thermodynamic parameters were examined as a function of temperature in the temperature range 15-60°C corresponding to the geopolymerization process. As the concentration of NaOH increases, the dependences of density, refractive index and speed of sound as a function of temperature become more linear [1]. The results are shown in the figure 2.



a) b)

c)

Figure 2. Influence of temperature on a) density, b) velocity of sound and c) refractive index for different concentrations of NaOH (10M, 12M, 14M, 16M) respectively

Since there are no significant changes in thermodynamic parameters with temperature, we can conclude that the geopolymerization process is influenced by the concentration of alkaline activator. For that reason, a material with a high molar concentration of NaOH (16M) was synthesized (GP16M).

Specific surface area and porosity were additionally determined by BET method. The specific surface area of the sample GP16M was 40 m^2/g. Porosity is a percentage of the total volume occupied by the pores. The pore structure of the sample is characterized by the total porosity, the pore size distribution (PSD), the inner surface of the pores as well as the characteristic pore sizes.

Key words: Thermodynamic parameters, alkaline activators, concentration NaOH, BET.

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Physical-chemical characterization of fly-ash for utilization in building material industry

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Fly ash utilization, especially in blended cements and concrete [1], has significant environmental benefits such as: increasing the life of concrete roads and structures by improving concrete durability; reduction in energy use, greenhouse gas and other adverse air emissions due to fly ash utilization as a binder instead of cement; reduction in amount of coal combustion products that must be disposed in landfills [2].

Coal thermal power plants TENT A and TENT B from Obrenovac (TPP „Nikola Tesla A“ and „Nikola Tesla B“) are located about 30 km from the center of Belgrade (Serbia). Depending on the amount of burned coal, the annual amount of ash that is released in the electrostatic precipitators in TENT A and TENT B varies. There is a potential market for the use of fly ash, but for now it is used exclusively by cement plants. The radioactivity of fly ash can be one of the important reasons against its wider use in the construction industry of Serbia [3]. Suitability and radiologically safe use of materials in the construction industry is expressed through the gamma index [4]. In this work, influence of physical-chemical characteristics of fly ash on the gamma-index is investigated. Five samples of fly ash from TPP Nikola Tesla (FA1, FA2, FA3, FA4 and FA5) (Figure 1) were examined.

Mineral composition of the samples was determined. Samples consisted of amorphous phase (51.0-75.4%), followed by quartz, mullite, feldspars, hematite and sometimes calcite and anhydrite. Quartz amount is ranged from 10.0% for the FA1 sample up to 35.1% for the FA4 sample. Among chemical parameters which are analyzed by wet chemistry after SIST EN 196-2, SiO_2 amount is in the range from 56.40% for the FA5 sample up to 67.21% for the FA4 sample. The values for Al_2O_3 were the lowest for the FA4 - 14.65%, while the highest value was in the FA3 - 23.70%.
FA5 had higest BET specific surface area 17.9 m^2g^{-1} and the lowest value in the FA1 sample was 5.7 m^2g^{-1}.

Figure 1. Samples of fly ash from TPP Nikola Tesla a) FA1, b) FA2, c) FA3, d) FA4 and e) FA5

A detailed physical-chemical characterization of the samples included the determination of radionuclide content in fly ash samples. Based on measured specific activities of 226ram 232Th and 40K the gamma index was calculated, and obtained values ranged from 0.43 for the FA5 sample to 0.87 for the FA1 sample.

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The influence of the addition of brushite on the mechanical properties of geopolymer binder

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The growing need to protect the environment and reuse abandoned raw materials is increasingly used in the construction industry to make in addition to cementitious materials and geopolymer materials. Geopolymers are alkali-activated materials, in which the starting material is mainly some residual material such as: clay, fly ash, slag or red sludge [1,2]. There is growing need to create new binders which can replace portland cement and geopolymer materials are increasingly being used for this purpose. For geopolymerization reaction process high concentration basic solution with alkaline activators are adding and the process itself leads to modifications of the structures of the starting raw materials [1]. Due to growing needs to improve mechanical properties of geopolymer binders, different calcium sources can be added and one of them is brushite-dicalcium phosphate dihydrate [3]. The aim of this paper is synthesis and characterization of Brushite-metakaolin-based geopolymer material samples, with different percentages of pure Brushite material added. Brushite, was obtained by solution precipitation reaction from appropriate acetate salts solution, by green chemistry process. Raw kaolinite clay from the Rudovci deposit (Serbia) was used as Al and Si source for geopolymer binder production. Kaolinite was thermally treated at 750°C for three hours, to produce metakaolin and remove residual organic matter. In order to investigate the influence of calcium phosphate compound on mechanical and microstructural properties geopolymer material samples were synthesized using metakaolin mixed with activator solution prepared from sodium silicate and sodium hydroxide (6M) in relation 1,6 with addition of 2%, 4%, 6%, 8%, 10%, of pure brushite. Phase, structural, and microstructural characterisation were preformed in a mening of XRPD and SEM analysis. Difference between diffractograms of starting materials and Brushite-metakolin analogues indicates that geopolymerization process was successful in all samples. DRIFT technique was used to obtain characteristic vibrations of functional groups in obtained materials. The compressive strenghts of geopolymer binders containing brushite were in a range of 15-55 Mpa. The the highest hardness was achieved by a geopolymer with 10% of brushite.

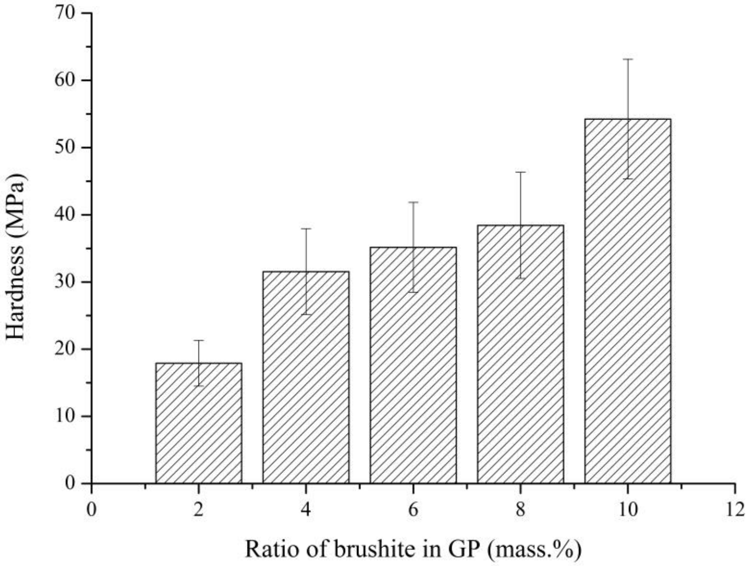

Figure 1. Hardness of geopolymer binders with 2%, 4%, 6%, 8% and 10% brushite

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Influence of alkaline activator concentration on geopolymerization process

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Based on the literature reviews of previous research, the need for the synthesis of silicate materials that would find application in the field of environmental protection has been identified. Such materials are very environmentally friendly due to their low energy consumption and limited emission of gases during synthesis, as they lead to a reduction of the greenhouse effect. Alkali-activated materials (AAM) are a newer group of binders that are obtained by alkaline activation of various silicate materials. Materials belonging to the AAM subgroup, which is characterized by a low calcium content in the binding phase, are called geopolymers. Geopolymers are formed by the reaction of aluminosilicate materials with an alkaline activator. Solutions of alkaline hydroxides and alkaline silicates are used as alkaline activators for the synthesis of geopolymers. The most common alkaline activator is a combination of NaOH or KOH with Na_2SiO_3 or $K_2Si_2O_5$. Na_2SiO_3 is most commonly used in combination with NaOH to achieve sufficient activation potential.

In this paper, the influence of different concentrations of NaOH as a component of an alkaline activator mixture in the geopolymerization process was investigated. Metakaolin was used as a starting material, and a solution of different molar concentrations of NaOH was prepared as an alkaline activator.

The characterization of the geopolymerization process and the geopolymers themselves was followed by different methods. Changes in the structure of the synthesized material as well as the morphology of the precursor powder particles and the microstructure of the synthesized samples were monitored by XRD methods (X-ray diffraction analysis), FTIR analysis (Fourier transformed infrared spectroscopy), Raman spectroscopy, SEM analysis (scanning electron microscopy). Phase identification and monitoring of crystallite sizes and amorphous phase fractions in the synthesized porous silicate material were performed by XRD analysis and Raman spectroscopy. The morphology of precursor powder particles, pore size and shape of synthesized porous materials was examined by SEM method, and the composition of powder particles and phases of both precursors and synthesized materials was determined by energy dispersion spectroscopy (EDS) method.

Key words: Alkaline activator, Geopolymerization, Metakaolin, XRD, FTIR, SEM

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Recycling and reuse of wood ash in geopolymer concrete to reduce environmental pollution

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Geopolymers as an inorganic, non-combustible, heat-resistant, three-dimensional network of alumino-silicate materials form polymeric Si-O-Al bonds and are obtained from a chemical reaction between alumino-silicate oxides in an alkaline solution. This reaction form amorphous to semi-crystalline three-dimensional silico-aluminate structures of the following types [1]: Poly(sialate)-(-Si-O-Al-O-); -Poly(sialate-siloxo)-(-Si-O-Al-O-Si-O-); Poly(sialate-disiloxo)-(-Si-O-Al-O-Si-O-Si-O-). Geopolymerization is a developing field of research for utilizing solid waste and by-products. It provides a mature and cost-effective solution to many problems relative to concrete production using Portland cement, such as great energetic consumption and high CO_2 emissions in atmosphere.

With increasing focus on energy production from renewable sources, incineration of wood material became increasingly popular over the last decades. Wood ash (WA) is the solid residue after the combustion of wood (chips, saw dust, bark, etc.) and its chemical composition depends on sort of the wood, and the operational conditions of the combustion. High content of ashes is produced, of which the majority is currently deposited on landfills, often at high costs. Low density and high bearing capacity would make ash suitable for various uses [2-5]. In this work geopolymer (GPWA) was formed from wood ash (WA) as a solid precursor. Alkaline activator was prepared by mixing of solution of NaOH (Sigma-Aldrich) and Na_2SiO_3 solutions (Galenika Magmasil d.o.o, technical grade). Structure and mineralogical composition of wood ash and geopolymer (GPWA) was evaluated using X-ray diffraction, SEM and FTIR techniques. Analyzing SEM images, there are amorphous and crystalline phases in both samples, in particular in GPWA sample there is geopolymer matrix amorphous phase and most of the crystals are calcite with different sizes, while in WA sample it's possible to see lamellar crystals typical of portlandite. XRD and FTIR analysis on GPWA sample also confirms that the geopolymerization reaction occurred, in fact in XRD diffraction pattern peak of illite disappears, while FTIR analysis shows functional groups typical of geopolymers, in particular peaks at about 1066 and 700 cm^{-1} due to Si-O-Al bond and there are also peaks at about 1400 and 800 cm^{-1} due to carbonates to indicate the formation of calcite crystals in the sample.

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Geopolymer coating and the impact of acid rain

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Acid rain is a term that refers to a precipitation with lower pH value than normal rain, due to the presence of sulfur dioxide as well as nitrogen compounds. It is also named as 'carbonated water' due to the presence of carbonic acid, formed by carbon dioxide and water. Normal rainwater pH varies from 5.5 to 5.6, while acid rain's water can have much lower values, even up to 3.0. This phenomenon has a negative impact on both flora and fauna. Also, it is known that it fastens the corrosion of many air-exposed materials and is one of the main 'culprits' for deterioration of marble and limestone objects.

Therefore, it is very important to get a quality and durable coating based on geopolymers, which will protect the base material from the effects of acid rain for a long time. These coatings can be applied to all types of materials such as: wood, metal and concrete. The function of the geopolymer coating is to prevent corrosion induced by the action of carbonic acid and at the same time its adhesion is very good. Adhesion properties depend on many factors among which are Si/Al ratio, Al/Na ratio, water content, precursor type, alkali cation type, curing conditions, etc. In order to obtain a geopolymer with the best properties, parameters that can affect its properties must be optimized.

Geopolymer coatings are obtained by the spin-coating method by carefully controlling the process parameters, such as speed, acceleration, spin coating duration, temperature and humidity. The rheology of the geopolymer paste applied to the desired substrate is also particularly important.

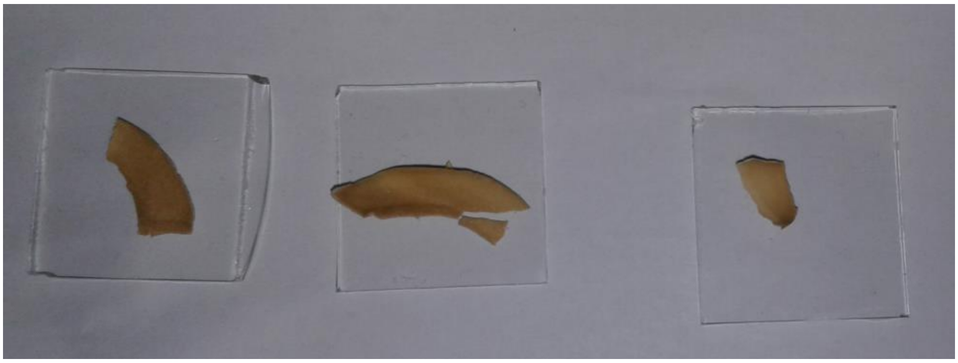

Figure 1. 20 μm geopolymer foil obtained by spin-coating

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The characterization of the geopolymer materials modified with Pb and Cu

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Geopolymer materials are a group of compounds formed by alkaline activation of natural materials which are rich in silicon and aluminum, as well as various industrial wastes rich in silicates. These materials, similar in structure to zeolites, have been shown to be potentially good sorbents of heavy metals from waste water. This research was done with the aim of potentially solving the problem of decontamination of metal ions from wastewater from the Aluminum Plant - Podgorica and fly ash from the Pljevlja [1].

In this work, geopolymers synthesized by alkaline activation of precursors based on industrial waste: red mud from the Aluminum Plant - Podgorica and electrofilter ash from Thermal Power Plant-Pljevlja were used to remove copper and lead ions from waste water. A combination of 10M NaOH and Na_2SiO_3 in the volume ratio Na_2SiO_3 / NaOH = 2.5 was used as the alkaline activator. Several geopolymers with different volume ratios of red sludge and electrofilter ash (20:80, 50:50 and 60:40) were synthesized with two different drying treatments, and the geopolymer with the highest value of compressive strength at the end of the synthesis process was selected for further research.

Compressive strength analysis revealed that geopolymer sample with a ratio of red sludge and electrofilter ash of 20:80, had the highest value of 29.54 MPa, so it was tested for further research. The sorption experiments were performed at room temperature at different operating parameters: pH value of the solution, adsorption time, initial metal concentration and mass of adsorbent in order to define the optimal values of the given parameters. After sorption, the solutions were filtered and the filtrate were analyzed. The characterization of the geopolymer material modified with Pb and Cu in terms of mineral composition and structure was performed using XRD, DRIFT and SEM analysis and the compressive strength of the obtained material was determined [2].

For sorption processes, the solution of copper ion was prepared by dissolving $CuCl_2$ x $2H_2O$ in deionized water, while the lead solution was prepared by dissolving $Pb(CH_3COO)_2$ x $3H_2O$ in deionized water, also. The concentrations of prepared metal solutions were 50 mg/l. The initial pH of the solutions was adjusted with HCl or NaOH to a desired value. The best adsorption efficiency for Cu was achieved at pH =4, while for Pb that was at pH=5.

XRD results shows that geopolymer samples are consist of three main mineral phases: quartz, hematite and calcite. Based on XRD results there is no significant difference between samples. The diffraction results showthat after adsorption small changes are noted on diffractogram in range from 5 to 40° 2θ. Adsorption process leads to better arrange of amorphous phase and background reduction,and it is related to the entry of copper and lead ions into the amorphous matrix of geopolymers, while the mineral composition remains unchanged.

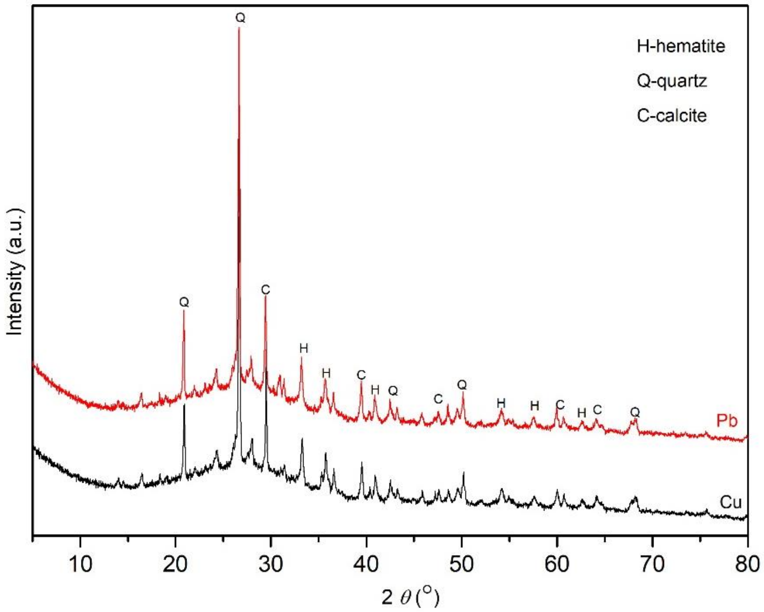

Figure 1: XRD patterns of geopolymers sorption precipitate with Cu and Pb

Key words**:** geopolymers, sorption, XRD, DRIFT, SEM.

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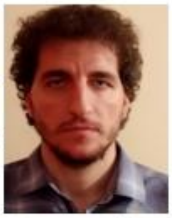

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