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Special Issue Introduction

Introduction to the 10th Anniversary Issue of the Recycling & Sustainable Development Journal

With the opening of this issue, we mark the 10th anniversary of the journal of Recycling & Sustainable Development (RSD).

Ten years ago, the first issue was launched on the basis of the simple assumption that the authors of the articles published in the Conference proceeding "Recycling Technologies and Sustainable Development" would like to have their expanded and revised articles published in the journal within the same scientific field. In 2011, with the change of Editor-in-Chief, the editorial policies changed and the journal became a peer-reviewed journal where original research articles, expended conference articles and review articles have been published since. Figures which show the number of online accesses, downloads and citations have reached satisfied levels and they continue to increase. Today, as we look back over our first decade, we can see that the premise was correct. Ten years is a long time but a short period for a new journal and we thank all the dedicated researchers, reviewers and editors who have powered this trajectory.

This special issue is composed of invited review articles from a number of eminent authors, who have surveyed a broad range of topics, with a special emphasis on matters of current interest. We hope you will appreciate these contributions, and enjoy the next decade of the journal Recycling & Sustainable Development as well.

I would like to take the opportunity of the fact that this is our 10th anniversary issue to sincerely thank all those members of the Editorial team who actively supported RSD journal from its inception and contributed to the high quality of our journal, both online and in printed version.

Of course, all this is only achieved through hard work and dedication of our Editorial board members and reviewers who have unselfishly given their expertise and time to peer-review manuscripts.

On behalf of the editorial and publication teams, we wish a very happy 10th birthday to the RSD Journal and we wish all our readers and colleagues a very fruitful and happy New Year 2019 and hope that the journal will continue on its way and become the highest ranking journal in the scientific publication world.

Editor-in-Chief

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Functionalized geopolymers - a review

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ABSTRACT

The geopolymer technology provides an alternative good solution for the utilization of industrial waste and the preservation of primary minerals to produce an economically valuable product that can be used for several purposes. This review summarizes the preparation, the structure modifications and functionalization of geopolymers for adsorbing purposes. The mechanical performances of the geopolymers (compressive strength, flexural strength, durability such as resistance to sulfate, acid, thermal effect) are the primary concerns that depend on the chemical composition.

1. Introduction

Geopolymers are amorhpous aluminosilicate materials with three dimensional frameworks of SiO_4 and AlO_4 tetrahedra that can be produced by alkali activation even at ambient temperature and low pressure. It was first developed by Davidovits in 1978 (Davidovits, 1989). After the mechanical activation (Kumar et al., 2017; Mucsi et al., 2015; Temuujin et al., 2017) of the aluminosilicate powder with appropriate parameters (particle size distribution, specific surface area) it has to be mixed with alkali solution (NaOH, KOH, water glass) to produce amorphous gel-like substance that quickly solidifie into hard geopolymer (Barbsa et al., 1999). This alkali activated material possess excellent physical, chemical and mechanical attribution such as low density, micro and nanoporosity, high mechanical strength, heat stability, fire resistance and chemical resistance.

Geopolymers can be prepared from reactive industrial by-products: granulated blast furnace slag, iron ore tailing, power station fly ash, slag, red mud and agricultural waste (rice husk ash, palm fuel ash), from primary raw material such as kaolin. After the suitable geopolymer structure is balanced, geolopolymer foam can be produced by adding foaming agent to the geopolymeric gel (Kumar et al., 2017; Mucsi et al., 2015; Temuujin et al., 2017), that can be used for various purposes such as heat insulator material or adsorbing material. The produced highly porous gepolymer foam structure ensures active surfaces for adsorption of heavy metals from aqueous solution due to the high specific surface area and the surface bonded hydroxyl-groups due to the alkali activation. This high specific surface area can be chemically modified to produce more adsorption site.

2. Functionalization

2.1. Factors influencing the mechanical properties

The quality of the geopolymers is influenced by the amorphous nature of geopolymers (amount of geopolymer gel), the type and concentration of alkali activating solution, the ratio of the NaOH/ Na_2SiO_3, Si/Al

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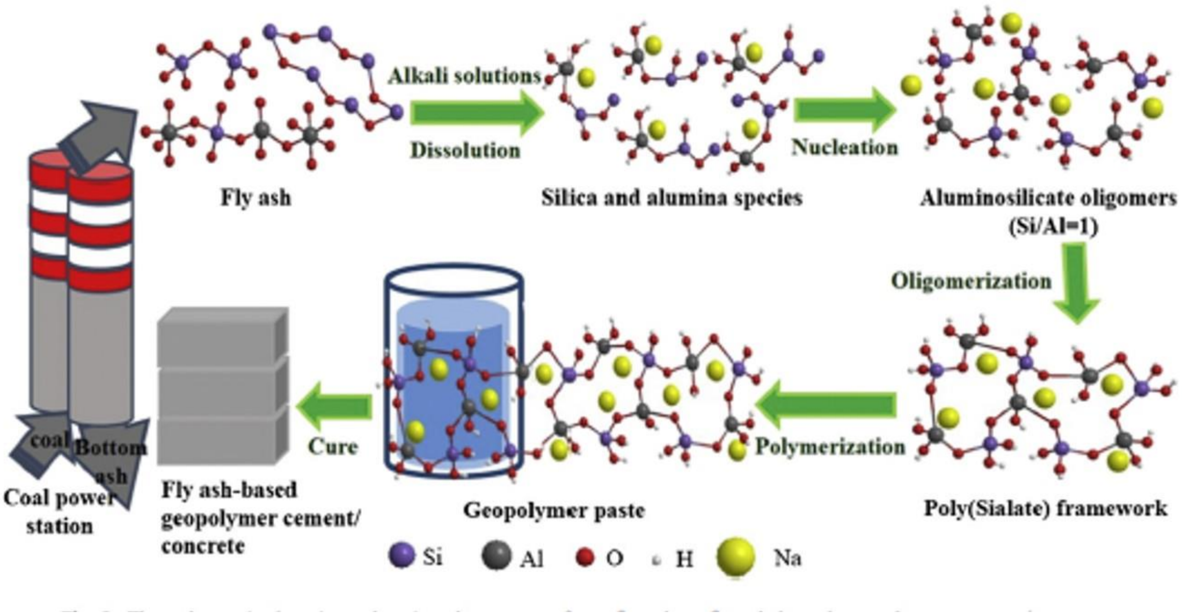

Figure 1. Geopolymer synthesis (Zhuang, 2016)

ratio, water content in the mixture, the curing time and temperature, the initial solid/liquid ratio, and the CaO content of the raw material (Barbsa et al., 1999).

The final structure of the geopolymer is influenced by the porosity depend on the composition of geopolymer. The high Si/Al ratio increases the compressive strength of the geopolymer that can be reached by adding Na_2SiO_3, slag, rice husk ash and red mud. The addition of water glass results in finer pore structure and lower porosity. The silica fume makes the geopolymerisation faster, decrease the porosity and increase the compressive strength.

After the formation of geopolymer structure (Xu and Van Deventer, 2000) having the appropriate mechanical properties and a stable structure, the use of a special chemical foaming agent can be used to produce a porous geopolymer foam suitable for further use, which have a high physical, chemical and mechanical properties to ensure low density, high strength, heat stability, depending on the parameters used in the production. To produce macroporous geopolymer aluminium powder, silicium powder (FeSi, SiC), sodium-perborat, sodium hypochlorit (NaOCl) or hydrogen-peroxid react with the alkali solution in which oxygen gas is formed.

The foam formation is based on the fact that H_2O_2 is thermodynamically unstable and easily separates into water and oxygen gas (Szabó et al., 2017). Increasing H_2O_2 concentration increases the amount of oxygen resulting in increased bubble formation, which is greatly influenced by the pH of the solution. The pore size distribution of the geopolymers depends on the hydrogen peroxide separation reaction and the geopolymerization reaction. Narrow pore size distribution improves insulating ability, while the wider pore size interval leads to complex air conduction channels and improves the acoustic resistance of the foams. Varying amount of foaming agent (1, 2, 4, 6 wt %) produces geopolymers with varying pore size. The addition of 6 % H_2O_2 seems to be an upper limit since H_2O_2 above this amount cause the very porous structure to collapse (Palmero et al., 2015). The created geopolymer foams can reach relatively high compressive strength values 5.5 to 10.9 MPa, which is highly dependent on the liquid/solid ratio and the added foaming agents, the increase of which reduces the strength values, with lower density (0.4-1.2 g/cm^3). Increasing H_2O_2 leads to decrease in density, thermal conductivity, increase in macroporosity, decrease in flexural and compressive strength values.

The porosity and specific surface of the geopolymer foams can be increased by using the combined method of saponification/peroxide/gelcasting (Cilla et al., 2014), which is nowadays increasingly used for the production and development of micro and mesoporous geopolymers with high specific surface. According to the saponification method sunflower oil react with the alkaline geopolymer and results in the formation of carboxylate surfactant (soap) molecules. This combined method produces high porosity with open pores and with regular morphology and spherical cells. Saponification leads to the formation of smaller cells with fewer open pores, while the use of peroxide leads to the formation of large but predominantly closed cells. The advantage of these method is that the open porosity can be increased by approximately 10 %. The open pore morphology play a significant role on the thermal conductivity and water absorption of geopolymers.

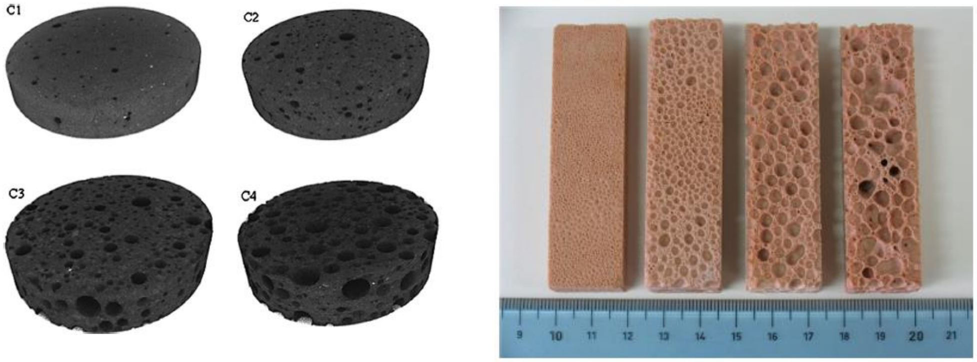

Figure 2. Geopolymer foams with different a) Al content c1-c4=5, 10, 15, 20 mg Al powder, 100 ml alkali solution, c4=70 % porosity (Zhang et al., 2014), b) H_2O_2 content, 1,2,4,6 wt %, H_2O/Na_2O=13 (Palmero et al., 2015)

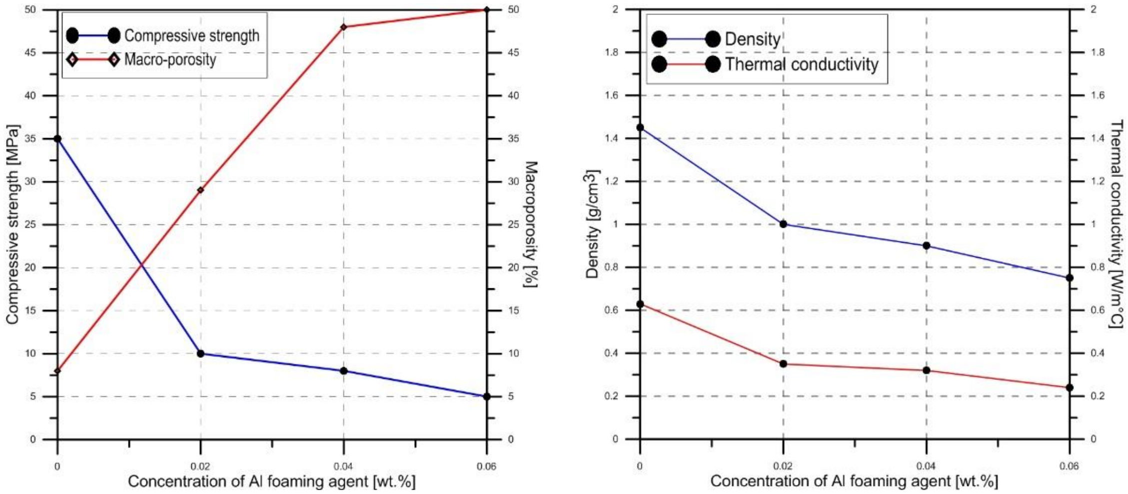

Figure 3. The relation of the compressive strength, density, heat conductivity, macroporosity and the added Al powder (based on Rickard, 2013)

After the formation of a stable foam structure, the surface of the pores can be modified with various chemical compounds, which gives the properties of the geopolymer matrix better. Previous studies have put great emphasis on modifying the geopolymer matrix with various organic compounds (Zhang et al., 2009; Ricciotti et al., 2013) such as polyvinyl acetate, polypropylene, polyvinyl alcohol or water soluble organic compounds. In the geopolymerization process, the added organic material interacts chemically with the geopolymer gel, during which hydroxyl groups develop.

2.2. Heavy metal ion adsorption of the functionalized geopolymer

Geopolymer preparation is a new technology for the removal of heavy metal ions from contaminated water. Different natural minerals normally have lower adsorption capability that can be increased by surface treatment due to the hydroxylation of the waste (for example fly ash) that transforms the non-porous hydrophobic material into mesoporous hydrophilic material with a large number of ion exchange sites. The heavy metal ion adsorption is performed on the functionalized material through ion exchange and physisorption processes due to the difference in chemical potential between the light and heavy metal ions. One of the most characteristic features of the inorganic polymers is the exchangeable K^+ and Ca^{2+} cations in the structure that can be subsituted with heavy metal ions and can migrate in the mesoporous structure of the aluminosilicate material.

2.3. Metakaolin based geopolymer

Svingala and Varela (2009) used a mixture of metakaolin and slag for geopolymer synthesis reaching 2.9-9.5 MPa compressive strength and 1.2 g/cm^3 specimen density. The mechanical properties of the geopolymers can be enhanced with chitosan and fibers, such ash polypropylene, which improves the dehydration resistance of the material at high temperature due to the formation of hydrogen bonds that connects the formed microcracks and delay the formation of them and fibers can increase the permeability of the material at high temperature. The foam structure was made from a geopolymer matrix having an average compressive strength of 54 MPa and a specimen density of 1.61 g/cm^3. The polypropylene fiber (1 wt %) was added to the geopolymer with these parameters reduces the compressive strength to 36 MPa. The addition of foam-forming aluminium powder (Rickard et al., 2013) (0.02, 0.04, and 0.06 wt. %) changed the compressive strength to 9.5 MPa, 7.9 MPa and 4.4 MPa with increasing porosity and decreasing densities between 0.7 and 1 g/cm^3. The higher amount of aluminium powder caused increased presence of large pores. Without fibres the pore structure was significantly unstable leading to pore collapse after foam formation.

In metakaolin based geopolymers the evaporation of large volumes of water added to the activating solution leads to the formation of micro cracks, that can be delayed by adding resin to the gel. The resin of 20 wt % can increase the compressive strength up to 60 MPa.

Autef et al., (2012) investigated the source of silicon and its effect on the formation of mechanical properties (quartz or amorphous silicon) in the geopolymerization process, according to which the growing amount of amorphous material increases the formation of well-consolidated geopolymer. The addition of amorphous nano grain sized (0.5-2 wt %) SiO_2 with 670 m^2/g specific surface area covered with hydroxyl surface (Autef et al., 2012) to the metakaolin increased the compressive strength from 58.9 MPa up to 71.1 MPa after 56 days.

Adsorbent material can be prepared from a mixture of organic and inorganic substances where the linkage between the organic sodium alginate and the inorganic metakolin was ensured by Ca^{2+} with soaking the sample into $CaCl_2$ solution. The beneficial physical and chemical properties of the organic material serve to improve the adsorption capacity while the inorganic phase increases the mechanical strength and heat stability. The adsorption capacity of the produced blended material is 60.8 mg/g (Yuanyuan et al., 2017).

Porous metakaolin (9.56 m^2/g specific surface area) based inorganic spheres can be formed by adding sodium dodecyl suplhate and (K12) foaming agent (1.5 wt %). According to the pore structure studies, BET indicates a high specific surface area with mesoporous property (53.95 m^2/g), low density (0.79 g/cm^3), 60 % porosity that serves as an active surface for binding Cu^{2+}, Pb^{2+}, Ca^{2+} and other ions. The adsorbed Cu(II) with the increase the contact time reached a maximum of 34.5 mg/g.

Metakaolin-based geopolymer is also effective in the removing of Ni^{2+} from aqueous solution (Yuanyuan et al., 2015). The BET specific surface area is the highest at $H_2O/Na_2O=19$ with 39.66 m^2/g adsorption capacity and 18.67 MPa compressive strength. López et al., (2014) produced metakaolin and rice husk based geopolymer foams with 50.8 mg/g adsorption capacity.

Yousef et al., (2009) prepared metakaolin based geopolymers with the addition of zeolitic tuff. The resulting geopolymer has good mechanical properties and adsorption capability for methylene-blue and Cu^{2+}. The affinity, the attractive force between the hydrated ion and the metal is affected by the size of the hydrated cation, the lower the hydrated radius, the greater the affinity. According to the heavy metal adsorption studies, the results are: Pb^{2+}=86.2 mg/g, Cu^{2+}=40.9 mg/g, Cr^{3+}=9.8 mg/g and Cd^{2+} =68.9 mg/g.

2.4. Fly ash based geopolymer

Yang et al., (2014) examined a mixture of fly ash and high magnesium nickel slag (HMNS) with the activation of Na_2SiO_3 (water glass), and stated that the HMNS was functionalized as micro aggregate making smaller the pores. Using 20 % HMNS results in 60 MPa compressive strength. The results indicate that the higher the amount of slag the higher the compressive strength that lead to the formation of cracks due to the shrinkage of the slag.

By activating the mixture of fly ash and iron ore tailing (30 wt % iron ore tailing) with multi-component alkali solution, higher compressive strength values can be achieved compared with the activation only in NaOH solution. The result after the addition of H_2O_2 foaming agent is a highly porous geopolymer foam showing 113.41 mg/g Cu^{2+} adsorption capacity at 40 °C and pH=6 (Duan et al., 2016).

According to recent researches, the geopolymer made from rice husk ash and fly ash mixture can be widely used as a functional material with compressive strength of 15-20 MPa after 7 days. Organic melamine resin given to the geopolymer shows a good incorporation in the inorganic geopolymer frame in nanometric scale, improving the mechanical properties and thermal stability. The organic phase provides physical reinforcement to the geopolymer, improving mechanical stability and reducing fracture. The silane-derived APTES also improves the interaction between organic and inorganic material, which in small amounts, also serves a significant structural improvement of the substance, because resin-containing panels are less rigid, thus reduce the chance of fracture.

Al-Zboon et al., (2011) investigated the Pb^{2+} adsorption capacity of the fly ash based geopolymer that produced 90.6 % removal efficiency compared to the raw fly ash with 39.87 %. Lee et al., (2017) used a fly ash/slag mixture with nano-crystalline zeolite to investigate the cezium-adsorption capacity that reach 15.24 mg/g. This material possess high compressive strength (16.57 MPa) and high specific surface area (114.16 m^2/g).

Fly ash based geopolymer (Javadian et al., 2015) can be applied for removing cadmium nitrate from water. For comparison, the adsorption capacity of Cd^{2+} by the raw fly ash at pH=5 was 7 mg/g, while the fly ash based geopolymer is 14.431 mg/g.

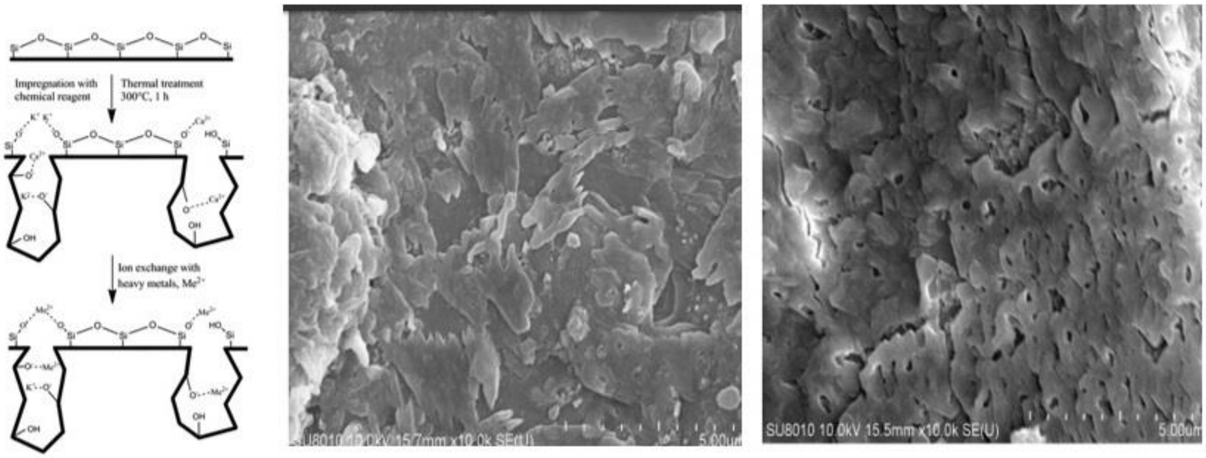

Figure 4. Surface functionalization (Hadi et al., 2016), fly ash and iron ore tailing without and with H_2O_2 (Duan et al., 2016)

2.5. Zeolite

For the construction of water storage facilities, functionalized geopolymer can be prepared from the mixture of zeolite tuff and kaolinite (Alshaaer et al., 2016). The kaolinite-based geopolymer mixed with zeolite tuff has high compressive strength, density and adsoption capacity for cadmium. Zeolite as reactive filler material may be involved in the geopolymerization process as functional reactive fillers, so it is important to properly investigate the geopolymers. The most important test is to determine the optimal amount of water to produce the geopolymer which provides adequate mechanical properties for water retention and high adsorption capacity for water purification. Zeolite tuff increased the adsorption capacity of metakaolin towards micro contaminants as a reactive filler. The optimal amount of water is close to the plasticity limit for high quality building materials.

After hydrothermal treatment, the geopolymer can be transformed into faujasite, which has a nano-sized pore structure and good heavy metal ion adsorption capability. Zeolite consists of pores of a given size that pass through certain metals, which allows for selective separation. The Pb^{2+} at pH=3-6 adsorbed is 74.83 mg/g. The adsorption capacity of faujasite (pH=3) is 143.3 mg/g, for geopolymer is 118.6 mg/g. The increase in pH increases the amount of adsorbed heavy metal ion. The best adsorption capability was reached at pH=6 is 45 °C 152 mg/g.

Zeolite has a good adsorption ability to remove metals, phosphates, ammonium and petroleum derivatives, which can be enhanced by various modifications. The adsorption nature of chitosan (Li et al., 2013) in removing heavy metals and dyes is that the amino and hydroxyl groups serve as active surfaces for heavy metal ions. In the presence of higher amounts of H^+ the surface of the adsorbent is covered with protons, the decrease in electrostatic attraction results in less adsorption.

Mesoporous silica modifies (Pizarro et al., 2015) the surface properties of raw fly ash that can be functionalized with 3-aminopropyl-triethoxysilane to achieve better adsorption capacity of Cu^{2+}. The specific surface area of mesoporous silica modified and APTS - functionalized fly ash is 415.25 m^2/g.

According to the results (Duan et al., 2016) the porous geopolymer Cu^{2+} removal efficiency is 90.7 %, while for the reference geopolymer is only 33.9 % depending on the pH. It ranges from pH=1 is 4.95 % to pH=5 is 93.5 %. Compared to the reference geopolymer and the porous geopolymer, the adsorption trend is similar, but the porous geopolymer exhibits higher values due to the increased number of active surfaces.

3. Summary

Geopolymers can be prepared from different aluminosilicate materials by alkali activation. The mechanical properties of the geopolymers depend on the chemical composition but it can be increased by mixing different materials with different nature. When compared with the initial raw material, the synthesized geopolymer foams showed a great number of active sites with large specific surface area due to the porous structure. The geopolyemer with appropriate attribution can be functionalized as a highly porous geopolymer foam structure for which its high specific surface area can be increased by adding nano-silica or after chemical modifications. The adsorption can be enhanced by modifications. The so-produced geopolymer foams with large specific surface area are suitable for the adsorption of heavy metals from aqueous solution. The produced geopolymer foams are not flammable and possess low thermal conductivity.

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Funkcionalizovani geopolimeri - pregled

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I Z V O D

Tehnologija geopolimera predstavlja alternativno dobro rešenje za proizvodnju ekonomsko isplativog i višenamenski primenljivog proizvoda korišćenjem industrijskog otpada, doprinoseći ujedno i očuvanju primarnih minerala. U radu su dati postupci pripreme, strukturne modifikacije i funkcionalizacije geopolimera u svrhu adsorbovanja. Mehaničke karakteristike geopolimera (dinamička čvrstoća - otpornost na savijanje, otpornost na pritisak, dinamička izdržljivost - otpornost na sulfate, kiseline, termalni efekat) zavise od hemijskog sastava i igraju veoma važnu ulogu u oceni kvaliteta geopolimera.

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Assessment of construction and demolition waste management in the city of Aveiro, Portugal

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ABSTRACT

Quantification is very important for construction and demolition waste management. Estimation of C&D can be reached by establishing waste quantification model for C&D waste that is applicable in urban areas. In this paper, it is presented model for quantification of C&D waste considering Aveiro. The analysis is done for single-family urban sector. In this paper, it is combined empirical data given from Portuguese Statistical Bureau (INE) considering construction activities and C&D waste. Estimations provide data and yearly estimation for C&D waste generation for a period 2015 until 2020 in Aveiro. LCA tool is applied in order to calculate environmental impact of certain C&D waste materials.

1. Introduction

Construction industry is the third-largest CO_2 emitting industrial sector, and representing 10 % of the total anthropogenic CO_2 emissions in the European Union (EU) (Habert et al., 2009). Waste stream from the construction and demolition processes was identified as a priority waste stream by the EU, as it constitutes one of the largest waste streams, since it represents approximately 49 % of the total waste generation in the EU. It is estimated that 887 million tons of construction and demolition waste is generated in the EU in the year 2008 (Eurostat, 2011).

Only small amount of construction and demolition (C&D) waste is recovered in EU (in general), despite the fact that C&D waste has a very high recovery potential (it is assumed that 80 % of waste can be recycled) (Ortiz et al., 2010).

The amount of waste at construction site is in extent. In Brasil, the amount of waste in the Brazilian construction materials on site (Pinto and Agopayan, 1994). In the Netherlands an average is 9 % of the construction materials ends up as site waste in the Netherlands (Bossink and Brouwers, 1996). Besides waste which is found on the construction sites, there is waste generated from the process of renovation and demolition (Table 1). Construction authorities have to implement new regulations in order to stimulate the use of low-waste building technology, to adopt better waste management (WM) practices, recording quantitative data, and make useful guidelines and measures in order to a more manageable and minimized construction waste generation (Jaillon et al., 2009).

2. Objective

The objective of this paper is to present a model for quantification of C&D waste yearly in urban areas for a period 2015-2020, particularly analyzing single-family residential areas in Aveiro, which also provides current

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Table 1
Percentage of waste generated per activity (Bossink and Brouwers, 1996; Vanderley, 2000; Statistics Norway, 2006)

Type of activity	**% of waste per activity**		
	Western Europe	Norway	USA
Construction	20	20	8
Renovation	80	44	44
Demolition		36	48

and comprehensive information concerning the characterization and management of C&D waste using tools such as material flow analysis (MFA) and life-cycle assessment (LCA). The aim of this paper is reflected in the following:

- Detailed elaboration of the basic theoretical postulates considering C&D waste,
- Development of a theoretical model for determining the amount of C&D waste in urban areas of Aveiro,
- Estimation of C&D waste in Aveiro,
- Development MFA approach,
- LCA approach concerning environmental impacts of C&D waste.

3. Available methods for C&D quantification

Recent research trend in this field signalize that surveys and case studies are the main methodologies for data collection (Yuan and Shen, 2011). By Associates (1998), sampling and weighing at landfills, would be the most appropriate method for this study if sufficient time and funds were available. However, even on the local level there may be significant barriers to this method. Early efforts to estimate C&D waste have employed the same methods used to estimate municipal solid waste, which is by using *per capita* multipliers (Yost and Halstead, 1996). *Per capita* multipliers, do not reflect C&D activity.

Characterization of C&D waste is the initial stage of data collection and it is crucial (Gheewala and Kofoworola, 2009). This process consists of identifying type of waste materials being generated. Most authors conducted detailed study for characterization of various types of C&D waste materials. Most studies (Associates, 1998; Fatta et al., 2003; Bergsdal et al., 2007; Cochran et al., 2007; Gheewala and Kofoworola, 2009; Martinez Lage et al., 2010) focus on the major type of C&D waste with significant amount, such as concrete, bricks, timber, steel and drywall. Data gathered from C&D sites are described as '*waste assessment data*'.

These data were utilized to produce the average C&D waste generation rate per area, which is usually expressed in unit of amount (weight or volume) per area of activity.

The outcome is the quantity of national C&D waste generation in particular year.

The methodology should be well prepared for updating or predicting (Associates, 1998).

Yost and Halstead (1996) and Associates (1998), used National Statistical data and C&D waste assessment data from different sites in the USA. Yost and Halstead (1996), carried out a case study concerning gypsum wallboard waste generation in the USA, in order to assess the feasibility of wallboard recycling program, while Associates (1998) carried out a study for national C&D waste generation rate.

Total waste generation of certain year (tons/year), presents the product of total area (m^2) multiplied by the average waste generation (kg/m^2), given from the waste sampling. Estimation accuracy is related to the data accuracy (Cochran et al., 2007).

Model of quantification for C&D waste, which is also presented by Cochran et al., (2007) and Bergsdal et al., (2007), is given below: Waste produced in a region = [Activity level of construction; demolition or renovation in a region] x [Waste produced per activity].

By Associates (1998), an average C&D waste rate of generation for residential construction, non-residential construction, residential demolition, non-residential demolition, and non-residential renovation are 21.38 kg/m^2, 18.99 kg/m^2, 561.47 kg/m^2, 844.66 kg/m^2, and 86.27 kg/m^2.

The surveys conducted at the sites present main source of data for waste assesment in this case. By Bergsdal et al., (2007), concrete, bricks and wood are the main waste materials for new construction projects in Norway with 67 % and 15 %, and for demolition projects, 85 % present concrete.

Gheewala and Kofoworola (2009), presented results for new residential and non-residential projects in Thailand. This model is not taking into account demolition and renovation process. Quantification model presented in this case was developed to evaluate the capacity of national C&D waste recycling program. Gheewala and Kofoworola (2009), found that waste generation rate for new residential and non-residential projects were 21.38 kg/m^2 and 18.99 kg/m^2.

The quantification model:

$$Qx = A \cdot Gav \cdot Px \qquad (1)$$

Qx = quantity in tons; A = area of activity in m^2; Gav = waste generation rate; Px = percentage of waste material. Fatta et al., (2003), presented the model with waste generation rate and density of C&D waste which shows the average value from Greek Statistical Bureau.

Quantification model is expressed as:

$$CW = [NC + EX] \cdot VD \cdot D \qquad (2)$$

CW = construction waste in tons; NC = new construction in m^2 (from NSSG); EX = extension infrastructure in m (from NSSG); VD = volume of generated waste per 100 m^2 = 6 m^3/1000 m^2 (national average); D = density of waste = 1.6 ton/m^3 (national average).

$$DW = ND \cdot NF \cdot SD \cdot WD \cdot D \qquad (3)$$

DW = demolition waste in tons; ND = No. of demolitions (from NSSG); NF = mean value of no. of floors that building has = 1.3; SD = surface of each building being demolished = 130 m^2 (national average); WD = generation rate of each demolition = 0.8 m^3/m^2 (national average); D = density of waste = 1.6 ton/m^3 (national average).

Martinez Lage et al., (2010), presented a model of the generation and composition of C&D waste in any region. Martinez Lage et al., (2010), used historical data concerning new constructions, renovation and demolitions. This model was applied in the case of Galicia. Several presumptions were considered in this case:

- The number of construction, renovation, and demolition works may be adjusted to a theoretical function (linear, parabolic, exponential) that varies over time (if data from a time series is known),
- Construction activities distribution in the whole region is assumed to be the same every year,
- Surface area of construction, renovation, or demolition project can also be adjusted for a variable function over time,
- Quantity of waste generated per area is assumed to be the same for each type of construction.

Quantification model is presented as:

$$R_{build} = \sum_{counties}(R_{Ci} + R_{Ri} + R_{Di}) = \sum_{counties}(C_C \cdot S_{Ci} + C_R \cdot S_{Ri} + C_D \cdot S_{Di}) \qquad (4)$$

R_{build} = C&D debris generated during a given year or horizon year (HY) distributed over counties; RC = waste from new construction; RR = waste from renovation; RD = waste from demolition; SC = total surface area for new construction; SR = surface area for renovation; SD = surface area for demolition; CC = waste quantity per surface area of new construction; CR = waste per area for renovation; CD = waste per area for demolition.

Minimum data needed includes the number of buildings constructed in the whole area over sufficient number of year to be able to establish correlation between year and number of building constructed, and an indicator on which to base the calculation of the mean area of existing construction. In this study, new construction work generates 80 kg of waste per m^2, which is equivalent to 0.11 m^3 of waste per m^2 (density = 700 kg/m^3). Demolition work generates 1350 kg of waste per m^2, while renovation process generates 90 kg/m^2.

Llatas (2011), is using method which involves: identifying building elements of the project and their construction processes, waste classification system (including remains, soil, and packaging) and modeling. Suggested model is presented as:

$$CW_B = \sum_j CW_{SBEj} = \sum_{ji} CW_{BEi} = \sum_{ji} CW_{Pi} + \sum CW_{Ri} + \sum_{ji} CW_{Si} \qquad (5)$$

CWB = volume of waste expected; $CWSBEj$ = volume of waste expected in the system building element 'j'; $CWBEi$ = volume of expected waste from building element 'i'; $CWPi$ = volume of expected packaging waste element 'i'; ΣCWRi = volume of remains expected from building element 'i'; $CWSi$ = volume of expected soil in building element 'i'.

$$CW_{Pi} = \sum_k (EWL)_{pk} \cdot Q_i \cdot F_P \cdot F_C \cdot F_I \qquad (6)$$

$$CW_{Ri} = \sum_k (EWL)_{Rk} \cdot Q_i \cdot F_R \cdot F_C \cdot F_I \qquad (7)$$

$$CW_{Si} = \sum_k (EWL)_{Sk} \cdot Q_i \cdot F_S \cdot F_C \cdot F_I \qquad (8)$$

$(EWL)pk$ = code of packaging; $(EWL)Rk$ = code of remains $(EWL)Sk$ = code of soil; Qi = amount of building element 'i'; FP = packaging waste factor; FC = conversion factor; FR = remains factor; FS = soil factor; FI = increased volume factor.

Waste generation rate (without soil) is assumed to be 0.1388 m^3/m^2 in this case.

Hsiao et al., (2002), consider dynamic model of materials flow (waste from concrete fraction) in Taiwan. This model quantifies concrete waste output as the major component of C&D waste from national C&D activities.

The data required for calculation were given by statistical bureau of Taiwan. Hsiao et al., (2002), established the model to estimate relevant values. Model by Hsiao et al., (2002) is presented as:

$$W_c = d_{cc} \cdot [\sum A_{ij} \, x \, F_{ci}] \cdot P_{cc} \qquad (9)$$

$$W_d = d_{cd} \cdot [\sum A_{ij} \cdot F_{ci}] \qquad (10)$$

WC/D = generation of waste concrete from construction/ demolition (tons); dcc/d = specific gravity of C&D waste concrete (1.8 tons/m^3 for construction, 2.2 tons/m^3 for demolition); Aij = total floor area on use permits built

(m^2); *Fci* = volume of waste per area (m^3/m^2); *Pcc* = percentage of waste concrete in construction waste (21.17 %).

Martinez Lage et al., (2010) model can be regarded as the most accurate and comprehensive. The model uses reasonable assumptions, taking account C&D waste from all activities, density of waste, detailed waste assessment data from all counties of the region, and supported by strong data for building permits from a number of governmental sources.

4. Methodology

Aveiro is located in the northwest of Portugal within the central region of the country which encompasses around 1/3 of the continental coastline (around 275 km). Aveiro is the main municipality of the Baixo Vouga sub-region (NUTS III) which is integrated within the Portuguese Central Region (NUTS II).

Aveiro city is the sub-regional centre as is also the most populated of all municipalities (72,919 inhabitants – INE, 2010). Other sub-regional major cities include Águeda, Ílhavo and Ovar. The sub-region covers an area of 1807 km² and has a total population of 394,393 inhabitants for an overall density of 218 inhabitants/km².

Minimum data needed includes the number of constructed buildings in the whole area over sufficient number of year to be able to establish correlation between year and number of building constructed.

The procedure involves the calculation for: number of buildings (construction, renovation, and demolition), distribution of activities in Aveiro, quantity per area of activities and total waste generated from 1994 to 2014.

Data considering new construction, renovation and demolition activities for Aveiro are obtained from Portuguese Statistical Bureau (INE).

Model for quantification of C&D waste in Aveiro is presented in this paper. Model presented, is focused on C&D waste quantities from construction, demolition, and renovation process which is focused on single-family housing sector.

According to the data and analysis of single-family house from Aveiro which is used as a sample, it is known that 1,155,140 kg of construction materials were used for construction. This single-family house is used as a reference in order to acquire values for C&D waste in Aveiro.

Considering construction waste, data from new construction activity are used in order to estimate quantities. In Table 1, percentages of generated C&D waste per activity are presented. It is estimated that 20 % of construction materials used for new constructions represent waste according to Table 1. Model for calculating the amount of generated construction waste is:

$$QCW_{(20\%)} = NRO \cdot RVO_{(20\%)} \tag{11}$$

QCW - Quantity of generated construction waste,
NRO – Number of residential objects,
RVO – Referent value for object (amount of construction materials).

Table 2
Construction activities in Aveiro concerning single-family housing sector in a period 1994-2014 (INE, 1994-2014)

Activity/Year	New construction	Renovation	Demolition
1994	39	39	23
1995	118	36	11
1996	183	35	10
1997	173	24	10
1998	260	36	22
1999	278	18	21
2000	226	20	29
2001	306	19	25
2002	347	55	25
2003	340	43	5
2004	375	31	2
2005	281	43	4
2006	233	35	12
2007	229	48	26
2008	172	47	10
2009	138	27	8
2010	116	25	5
2011	104	25	4
2012	89	24	4
2013	68	20	2
2014	39	14	3

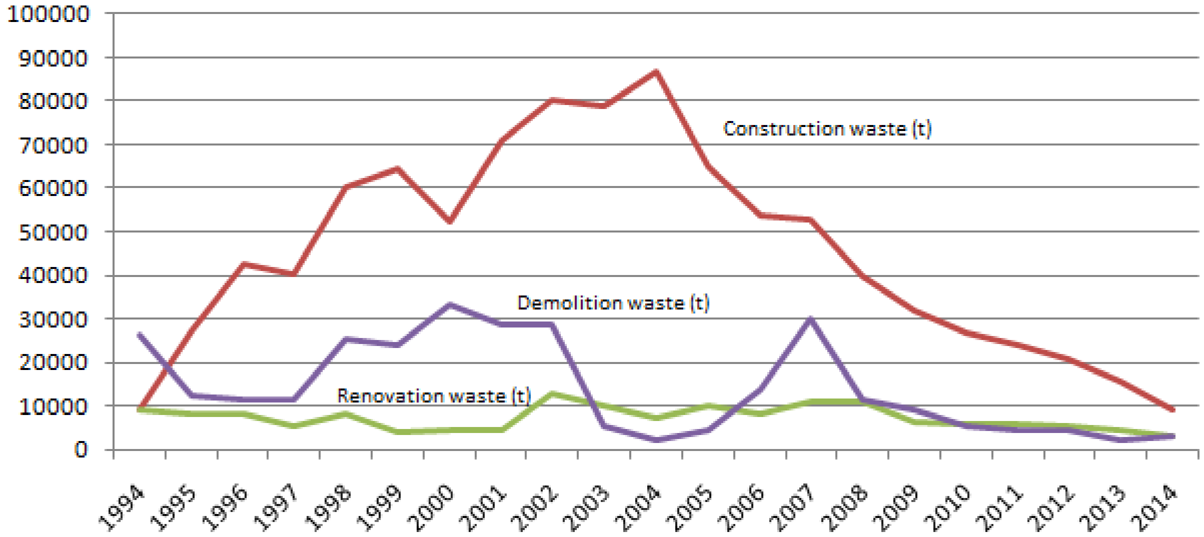

Figure 1. Amount of generated C&D waste (tonnes) in Aveiro considering single-family housing sector from 1994 until 2014 (excavation materials are not included)

It is estimated that waste derived from the process of renovation of residential objects represent equal amount as the amount of construction materials needed for reconstruction of residential objects (input=output) in this case. Analyzing current situation in Aveiro and data from Table 1, considering percentage of waste activity derived from renovation process, it is assumed that 20 % of waste is generated compared with the amount of used construction materials in the process of renovation.

Model for calculation of the amount of waste derived from the process of renovation:

$$QRW_{(20\%)} = NRO \cdot RVO_{(20\%)} \quad (12)$$

QRW – Quantity of generated waste derived from the process of renovation

Considering demolition waste in this case, it is assumed that the process of demolition is performed conventionally (with no extraction of recyclable materials), and all the waste from demolition process remains in situ.

Model for calculation of the amount of demolition waste:

$$QDW = NRO \cdot RVO \quad (13)$$

QDW – Quantity of generated demolition waste

According to the Figure 1, it is visible that construction waste has larger share in generation of C&D waste then the waste generated from the processes of renovation and demolition.

It is interrelated with the fact that in period processes of renovation or demolition in single-family sector.

5. Results

5.1. MFA Approach

Material flow analysis (MFA) is a systematic assessment of the flows and stocks of materials within a system defined in space and time (Brunner et al., 2004). MFA is applied in this study and it shows yearly estimation of groups of construction materials and C&D waste from a period 2015 until 2020 in Aveiro.

In Portugal, data considering generation and treatment of construction and demolition (C&D) waste are recorded every year, and those results are presented in the “Integrated Map for Waste Registration (MIRR)” of the “Integrated Registration System developed by Portuguese Environment Agency (SIRAPA)”. Considering this platform, data regarding quantities of C&D waste generation and treatment, are obtained from two sources: Portuguese statistical bureau (INE) and Portuguese Environment Agency (APA). In this case, Portuguese statistical bureau presented data between 2008 and 2013.

In the following table, results of C&D waste management in Portugal are presented. Also, in Table 2, data from two different sources in Portugal are collected (European Commission, 2016).

According to the data given by the Portuguese statistical bureau (INE) and Portuguese environmental agency (APA) concerning generated and treated C&D waste in Portugal from 2008-2013, MFA scenario for Aveiro is developed comparing the values from Table 2, representing the actual state of managing of C&D waste in this city.

This MFA scenario considers projection of generated and treated C&D waste of single-family residential sector

Table 3
C&D waste generation and treatment data 2008-2013 in Portugal (European Commission, 2016)

C&D waste (tonnes)	Source of data	Year					
		2008	**2009**	**2010**	**2011**	**2012**	**2013**
Generated	INE	2,096,475	2,146,524	2,195,128	2,522,541	1,224,861	1,746,652
	APA	-	1,647,795	-	-	-	-
Treated	INE	1,411,280	1,221,147	925,687	1,620,559	657,744	1,038,039
	APA	-	1,276,060	-	-	-	-
Recycled C&D waste	INE	250,657	299,312	362,721	851,608	429,746	845,930
Backfilled C&D waste	INE	-	-	-	-	-	-
Landfilled C&D waste	INE	1,160,102	918,843	556,310	762,068	227,288	190,158
Energy recovery	INE	522	2,993	6,656	6,883	711	1,951

Table 4
Quantities of treated C&D waste (single-family residential sector), current status of generated C&D waste in Aveiro

C&D waste fraction	Share (%)	Quantity (t)	Recycled (t)	Landfilled (t)
Minerals	92.2 %	21,140	incl.in minerals	incl. in minerals
Copper	0.35 %	80	35	45
Steel	1.5 %	343	150	193
Metal framework	0.15 %	35	incl.in minerals	incl. in minerals
Wood	3.5 %	802	353	449
Isolation materials (Foam)	0.1 %	23	incl.in minerals	incl. in minerals
Polymer material	0.1 %	23	incl.in minerals	incl. in minerals
Plastic materials	2.00 %	459	202	257
Glass	0.1 %	23	10	13
Minerals + Foam + MF + Polymer material	/	21,221	9,337	11,884

from 2015 until 2020 in Aveiro. Data given for a period 2008-2013, show that in average 44 % of C&D waste is recycled in Portugal, while 56 % is landfilled in the case of single-family residential sector.

Part of the C&D waste which is used for energy recovery represents share that is non-accountable in this case. In this MFA scenario, all fractions which are considered as C&D waste, as well as construction materials have equal share of recycling/landfilling treatment ratio in percentages, 44 % for recycling option, and 56 % for landfilling option.

Results calculated for treated C&D waste according to the data given for Portugal for a period 2008-2013 are presented in Table 3. Software STAN 2 is used as a tool in order to perform modeling for material flows of C&D waste in this case. Software STAN 2 is developed and published by the Institute for Water Quality, Resource and Waste Management of Vienna University of Technology.

5.2. LCA (Life Cycle Assesment) considering certain C&D waste materials in Aveiro

In this study, it is performed life cycle assessment (LCA), according to the international standards (ISO, 2006 a, b). One of the aims of this paper was to assess the environmental performance of C&D waste materials in Aveiro with the focus on C&D waste management where the results given from MFA are applied (Figure 2).

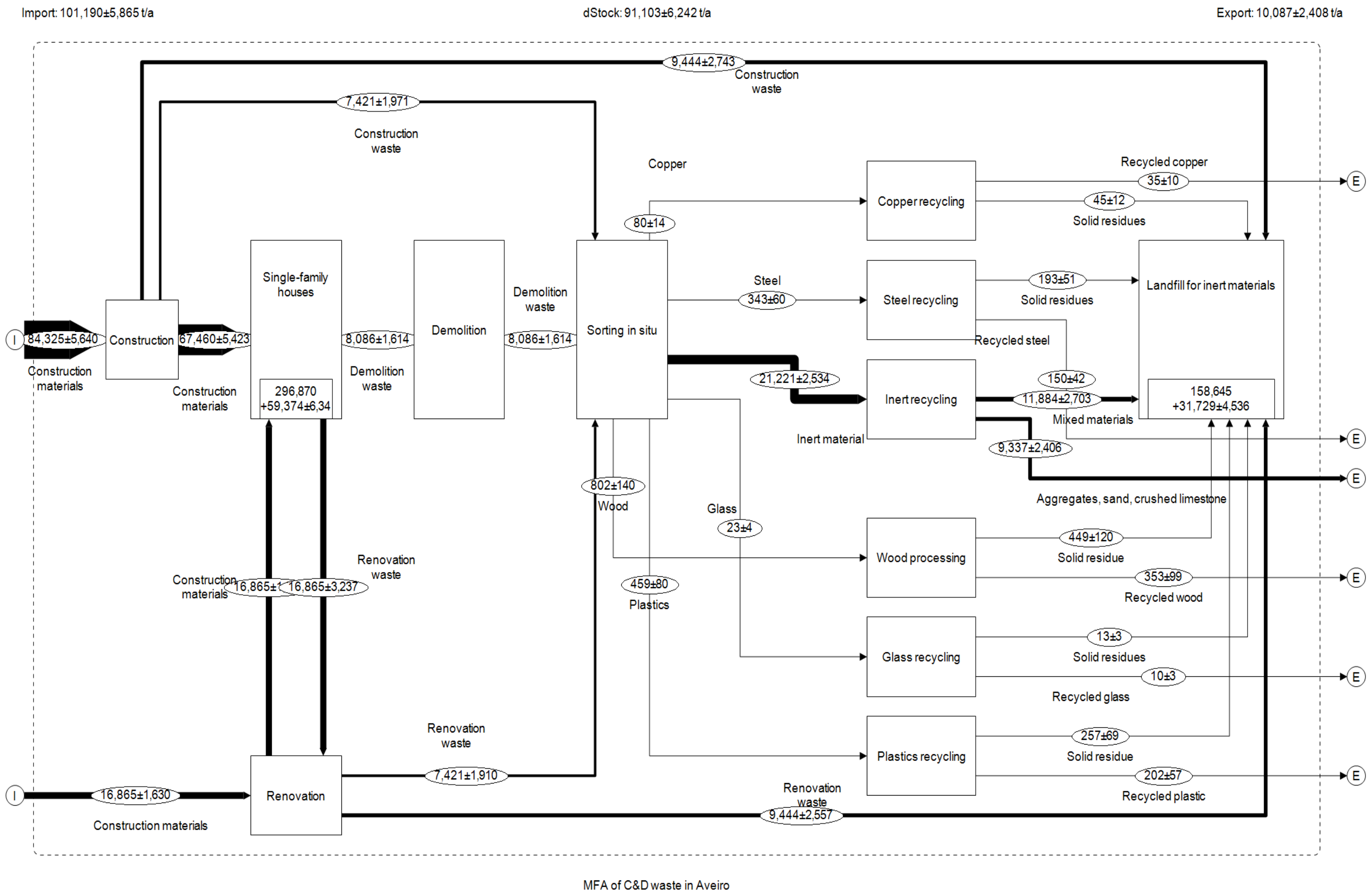

Figure 2. MFA of C&D waste management system in Aveiro (tonnes/year) from 2015 to 2020

Emissions of treatment and transport regarding different C&D waste materials are considered by applying LCA impact assessment IPPC 2013 and CML 2001. CO_2 emissions to the atmosphere and human toxicity are observed. Initial values regarding C&D waste materials were taken from the database Ecoinvent 3.2. Software openLCA is used in order to perform calculation considering environmental impact of certain C&D waste materials.

In this case, life cycle analysis is performed only for C&D waste in Aveiro, not including construction materials. In Table 5, there are presented calculated values concerning environmental impact of calculated values from MFA model in Figure 2 on a yearly level.

Table 5
Initial values of certain processes (values extracted from Ecoinvent 3.2) per 1 tonne of C&D waste treatment in Aveiro

Process	**Initial values**	
	IPCC 2013 (GWP 100a) (kg CO_2_eq)	CML 2001 (Human toxicity 100a) (kg 1.4 DCB-Eq)
Transport (Lorry 3.5-7.5 m^3)	0.525	0.127
Scrap copper (market)	0.018	0.318
Scrap steel (market)	0.015	0.08
Waste wood (market)	0.013	0.0049
Waste glass (market)	0.022	0.012
Waste plastic (market)	0.013	0.0064
Waste C&D inert fraction (market)	0.011	0.0057

Table 6
Calculated values of certain processes of C&D waste treatment in Aveiro

Process	**Calculated values**	
	IPCC 2013 (GWP 100a) (kg CO_2_eq)	CML 2001 (Human toxicity 100a) (kg 1.4 DCB-Eq)
Transport (Lorry 3.5-7.5 m^3)	3,210	776
Scrap copper (market)	6,300	11,130
Scrap steel (market)	2,250	12,000
Waste wood (market)	4,589	1,730
Waste glass (market)	220	120
Waste plastic (market)	2,626	1,293
Waste C&D inert fraction (market)	102,707	53,221

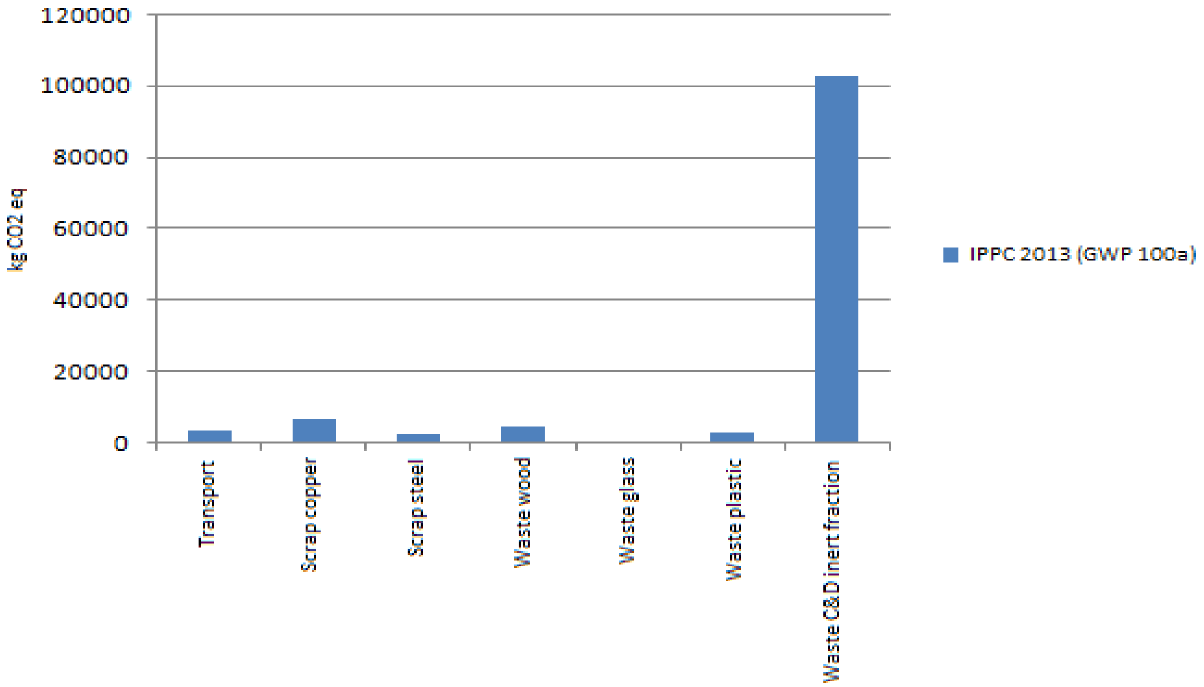

Figure 3. Impact assesment IPPC 2013 (GWP 100a) (kg CO_2 eq) according to the MFA model for C&D waste in Aveiro

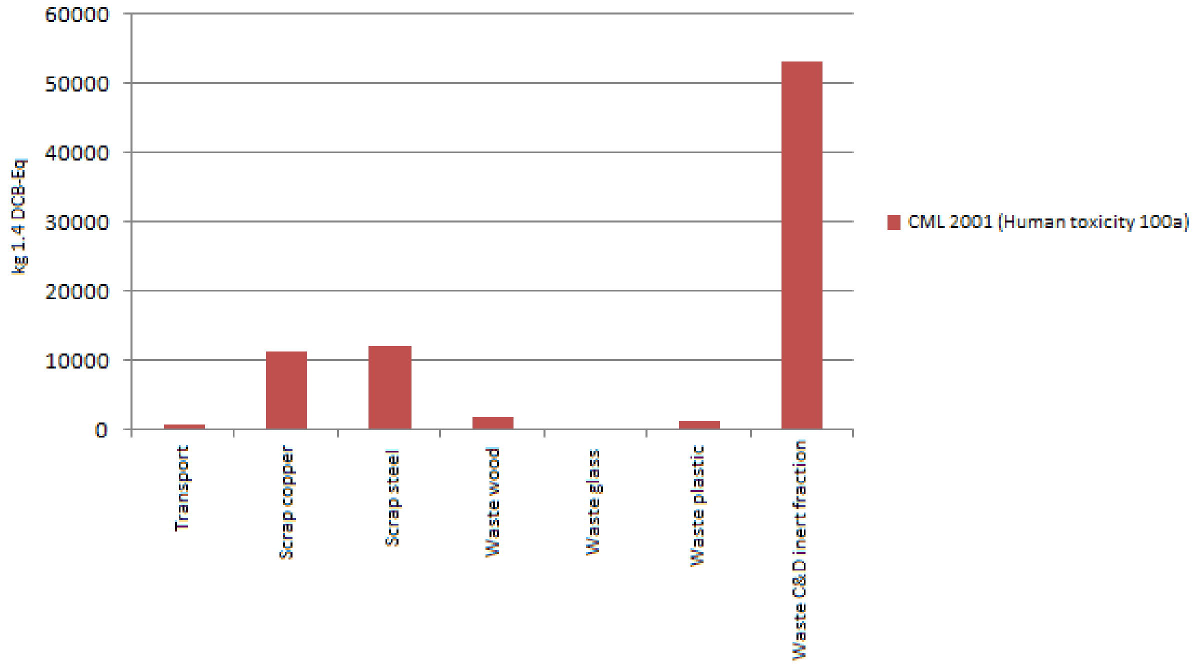

Figure 4. Impact assesment CML 2001 (Human toxicity 100a) (kg 1.4 DCB-Eq) according to the MFA model for C&D waste in Aveiro

6. Conclusion

In this paper, different methods of quantification of C&D waste are shown. It is very important to underline the fact that quantification of C&D waste is crucial in order to make proper waste management plan for a city such is Aveiro.

Life cycle assessment investigated and quantified the environmental impacts occur at the end-of-life phase of C&D waste materials in Aveiro.

The analysis included the waste from new construction, renovation and demolition process, defining and quantifying the material flows between the different processes. The estimated results to the overall environmental impact of the investigated C&D waste management in this case, show a crucial role of the recycling of different waste streams, in particular C&D inert fraction, copper and steel. The results show that C&D waste materials (inert fraction, copper, steel) with higher recycle potential could be better managed in order to reduce environmental impact in Aveiro.

In order to reduce environmental impact of different C&D waste materials, prevention, reuse, and recycling of C&D waste materials should be increased. Also, end-markets for recycled C&D waste materials are one of the crucial factors in order to increase recycling of C&D waste materials.

In order to increase recycling efficiency, state and local government should provide benefits to the recycling companies in order to correlate economical and environmental benefits.

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Analiza upravljanja građevinskim otpadom i otpadom od rušenja u gradu Aveiru, Portugalija

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I Z V O D

Kvantifikacija građevinskog otpada je veoma važna u kontekstu upravljanja građevinskim otpadom. Procena količina građevinskog otpada može se postići uspostavljanjem modela kvantifikacije građevinskog otpada koji se primenjuje u urbanim područjima. U ovom radu predstavljen je model kvantifikacije građevinskog otpada koji se primenjen u Aveiru. Analiza se odnosi na urbani sektor sa porodičnim tipom stanovanja. U radu su korišćeni empirijski podaci dobijeni od Portugalskog zavoda za statistiku (INE), u kojima su predstavljene sve građevinske aktivnosti i podaci koji se odnose na građevinski otpad. Procena koja se odnosi na količinu građevinskog otpada, doprinosi podacima o građevinskom otpadu, kao i podacima koji se odnose na procenu generisanja građevinskog otpada za period 2015 - 2020 u Aveiru. LCA softver se primenjuje kako bi se odredio uticaj određenih materijala iz građevinskog otpada na životnu sredinu.

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Precipitation of boron from waste water of Kirka borax plant

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ABSTRACT

Kirka Boron Inc., which is the largest boron processing plant in Turkey, produces tincal from the run of mine ore and sodium penta borax in the same complex. However, the deficiency of the tailings ponds causes significant problems, since approximately 75 % of the current pond volume is filled with waste water, which consists 3 g/L boron. The boron content of this water should be decreased for its usage in the plant again, meanwhile about concentration of 3 g/L boron creates an environmental risk. In this study, the boron in the effluents of the Kirka Boron Inc. was precipitated using $Ca(OH)_2$ and Al_2SO_4. The effects of several parameters such as $Ca(OH)_2$ dosage, initial pH, agitation duration, and settling duration were investigated. It was found that, the precipitation was strongly related to the Ca^{2+} concentration. Therefore, when the initial pH was proceeded towards acidic values, boron precipitation was increased. In conclusion, 97 % of the boron could be precipitated from the solution by two stages and a precipitate assaying 38 % B_2O_3 was obtained.

1. Introduction

Boron has an important role in manufacturing different types of products such as glass, ceramics, high quality steel, catalysts, cosmetics, and flame retardants (Yılmaz et al., 2008a). Boron is found in the crust of earth as salts (borates) or boro-silicate (Parks et al., 2005; Yılmaz et al., 2008a); acid can easily be dissolved in water (solubility of 55 g/L at 298 K) according to following reaction (Yılmaz et al., 2008a):

$$B(OH)_3 + H_2O \rightleftarrows [B(OH)_4]^- + H^+ \qquad (1)$$

In some cases, boron is desired to be removed from water. These cases can be classified as: a) environmental issues, b) technological issues, which maintain a recyclable water for the beneficiation plant and diminish some kind of precipitates in tailing ponds so it is provided new volumes for the tailings.

Today, there is not any specific boron removal technology, which leads to the utilization of the methods in conjunction with the other target parameters. These involve coagulation-electrocoagulation, adsorption (on oxides and activated carbon), chemical precipitation, ion exchange, solvent extraction, electro dialysis, membrane filtration, thermal treatment, and use of resins. When the boron concentration in the solution is relatively high, chemical precipitation is preferred, while milk of lime, oxides of manganese, copper, cobalt and magnesium are the precipitants used (Frütwirth et al., 1891; Boryta, 1995; Yamada and Eto, 1995; Kalafatoğlu, 1997; Hasenmuller and Criss, 2013). Large boron reserves in Turkey require tailings ponds with large volumes. However, the management of large volume tailings ponds imposes some difficulties. Kirka Boron Inc. encounters a number of problems and will probably

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encounters a number of problems and will probably face in the future, related to its capacity.

Kirka Borax Plant is located 70 km away from Eskisehir near the town of Kirka. It is the largest boron plant in Turkey with 1,000,000 tons of run-of-mine ore processing capacity producing borax ($Na_2B_4O_7 \cdot 5H_2O$). Tailings are pumped to 14,000,000 m^3 capacity tailing ponds that are mostly filled up. The shortage of waste ponds creates a serious problem in terms of environment. Currently, tailing ponds hold about 12,000,000 m^3 of material of which 11,500,000 m^3 is waste water containing about 3 g/L of boron.

There are 5 tailings ponds in Kirka, 4 of which are used for the tailings of the borax concentrator and the remaining one is used for the tailings of the sodium penta borax plant. Concentrator tailings contain 5-10 % solids by weight. The tailings are fed to the ponds in a cascading fashion, therefore, solids are primarily settle out in the first pond. The last tailings pond primarily contains boron rich solutions from the tailings of the concentrator and the penta borax plant. One of the most important problems faced in boron minerals processing plants is tailing ponds. Tailings of those plants have to be kept in well-constructed leakage free ponds. Although trace amounts of boron are needed for living organisms and the habitat, higher concentrations become environmentally hazardous (Adams, 1964; Wong, 1984; Börekçi, 1986; EPA, 1986). Therefore, concentrator tailings containing high amounts of boron must be strictly kept under control to prevent environmental pollution and urgent precautions must be taken. This investigation aims to remove boron from the liquid phase of the vast Tailings Ponds of Kirka for both economic and environmental reasons. Because of the boron concentration of 1 mg/L more in the water used for agricultural activities, it can cause problems (Ayers and Westcot, 1976; Uygan and Çetin, 2004). But water containing 3 mg/L boron can be used for dilution of durable plants (Uygan and Çetin, 2004). The drinking water in Turkey up to 1 mg/L B comprises is allowed (Official Gazette, 2013).

2. Materials and method

2.1. Material

Boron containing effluents used in the experimental studies were collected from the tailings pond of Kirka Borax plant. A homogenous solution was prepared by mixing 30 L lots. The chemical composition of the blended test solution is given in Table 1. According to the analysis, 3.93 g/L B, 6.38 g/L Na, and 675 mg/L SO_4 was determined, while the pH of the solution was 9.44. Boron analyzes were carried out using volumetric titration method and other analyzes were carried out using atomic absorption spectrometry.

Table 1
The chemical composition of the test solution

Component	Concentration	Component	Concentration
B	3.93 g/L	Ca	6.28 mg/L
Na	6.38 g/L	Fe	0.42 mg/L
K	102.8 mg/L	SO_4	675 mg/L
Al	0.52 mg/L	Cl	536 mg/L
Mg	19.1 mg/L	As	0.52 mg/L

2.2. Method

This study investigates the removal of boron from the waste solutions in order to obtain a solution, which contains below environmentally acceptable average level of 2 mg/L B (Uygan and Çetin, 2004). The boron removal tests were performed by utilizing the chemical precipitation method in two steps (preliminary and basic tests). With reference to the results obtained from the preliminary tests, basic tests were conducted in two stages. The parameters given below were examined in the first stage:

- The amount of $Ca(OH)_2$ – initial pH,
- Agitation duration,
- Settling duration.

Following the first stage basic precipitation, the solution was subjected to second stage precipitation, in which the effect of $Ca(OH)_2$ usage only and $Ca(OH)_2$ usage with $Al_2(SO)_4$ as precipitants were observed.

The precipitation tests were performed in a 400 mL beaker using 100 mL of solution. The solution was agitated with a magnetic stirrer. During the precipitation tests, $Ca(OH)_2$ and $Al_2(SO)_4$ were used, while HNO_3 was utilized to decrease the pH. The reason for the use of HNO_3 is that the damage and toxic effects of chlorine and sulfate anions on the water and the environment are more than nitrate ions.

After the agitation test, the solution was let to stand for the particles to settle out and then some amount of aliquot was taken. The boron analyses were performed with titration method. Besides, all of the reagents used in the experiments were analytical grade. The parameters and ranges of the precipitation tests are shown in Table 2.

Table 2
The parameters tested in precipitation experiments

Parameters	Ranges
$Ca(OH)_2$ dosage (g/L)	10, 20, 40, 60, 80
Initial pH	3, 6, 8, 9.44
Agitation duration (min)	5, 15, 30, 45, 60
Settling duration (min)	5, 10, 20 30, 60, 120, 240,480

3. Results and discussion

3.1. The Preliminary Precipitation Tests

The preliminary tests revealed that the maximum Ca^{2+} solubility in the waste solution at the original pH (9.44) was 300 mg/L. Above this pH, reaction between boron and calcium cannot develop. However, if the initial pH is decreased, then the Ca^{2+} concentration in the solution increases, which promotes the reaction between calcium and boron. At the first stage, preliminary tests were carried out in order to observe the effect of solution temperature on precipitation. As a result, it was found that an increase in solution temperature did not provide an enhancement in precipitation reaction. Therefore, following tests were decided to be performed at the temperature of 20 °C. Preliminary tests indicated that reaction kinetics of calcium-boron compound formation was found to be slow. Even after the agitation stopped, the formation of calcium-boron compound continued, which led to an enhancement in the efficiency of boron precipitation. Test results revealed that the discharge of one stage precipitation was inadequate in terms of environmental issues. Therefore, a second stage precipitation process was decided to be necessary.

3.2. The Basic Precipitation Tests

3.2.1. One Stage Precipitation

The Effects of $Ca(OH)_2$ Dosage and Initial pH

In the first part of the experiments, the effect of $Ca(OH)_2$ was examined at different dosages, where different initial pH values were tested under the following conditions:

- Agitation duration: 30 min,
- Solution temperature: 22 ± 2 °C,
- Settling duration: 60 min.

The results of the tests carried out at this conditions are given in Table 3. According to the results given in Table 3, the precipitation of boron increased almost linearly, when the initial pH value decreased, particularly at low $Ca(OH)_2$ additions. The increase in boron precipitation at decreasing initial pH values could be related to the increasing solubility of Ca^{2+} ions. Boron precipitation efficiencies showed similar values at $Ca(OH)_2$ dosages exceeding 20 g/L. About efficiency of 87 % boron precipitation could be reached at this group tests, but boron concentration at the solution discharged to the tailings pond was inadequate in terms of environmental issues. Therefore, a second stage precipitation process was needed. It was found that the solubility of Ca^{2+} ions strongly depended on the solution pH, which can be confirmed by Figure 1. These indications show that initial pH of the solution has a significant effect on calcium-boron interaction. Increasing the initial pH from 6 to 9 prevents the dissolution of $Ca(OH)_2$ in the solution and therefore calcium-boron interaction cannot develop because of insufficient Ca^{2+} ions concentration.

Table 3
The effects of $Ca(OH)_2$ dosage and initial pH on boron precipitation

$Ca(OH)_2$ Dosage (g/L)	**Initial pH**	**Final Boron Concentration (g/L)**	**Precipitation Efficiency (%)**
10	9.4	2.64	32.8
	8.0	2.50	36.5
	6.0	2.35	40.1
	2.6	2.20	44.0
20	9.4	1.17	70.3
	8.0	0.71	81.8
	6.0	0.59	84.9
	2.9	0.52	86.7
40	9.4	1.07	72.8
	8.0	0.69	82.5
	6.0	0.56	85.8
	2.8	0.50	87.3
60	9.4	1.04	73.5
	8.0	0.70	82.1
	6.0	0.55	86.2
	2.8	0.50	87.4
80	9.4	1.01	74.3
	8.0	0.74	81.2
	6.0	0.54	86.4
	2.8	0.49	87.5

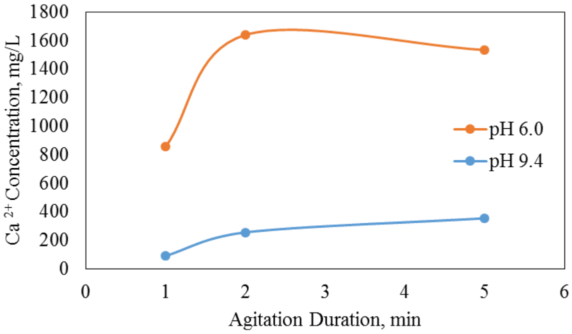

Figure 1. The variation in Ca^{2+} concentration with respect to pH and agitation duration

The Effect of Agitation Duration

In these tests, the effect of agitation duration on the precipitation was investigated by adding varying dosages of $Ca(OH)_2$ under following conditions:

- Initial pH: 6,
- Solution temperature: 22 ± 2 °C,
- Settling duration: 60 min.

The results in Figure 2 show that even 5 minutes agitation duration would be enough for more than 80 % precipitation. When the agitation duration was increased from 5 to 15 minutes, 5 % marginal increase in the precipitation efficiency was observed.

15 minutes agitation duration was found to be sufficient as an optimum the precipitation time. The reaction between boron ions and Ca ions takes place in two stages.

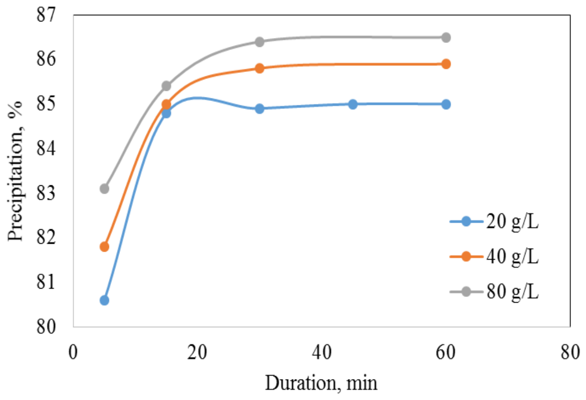

Figure 2. The effect of agitation duration on boron precipitation with different $Ca(OH)_2$ dosages

During the first 15 minutes of agitation, the reaction kinetics was very fast, but slows down suddenly at later times. However, the second phase also continued in the settling duration.

The Effect of Settling Duration

Precipitation tests were performed under the following conditions, in order to observe the effect of settling duration:

- $Ca(OH)_2$ dosage: 20 g/L,
- Agitation duration: 15 min,
- Initial pH: 6,
- Solution temperature: 22 ± 2 °C.

These tests are particularly important in terms of the solid-liquid separation, since this process requires particular space and equipment in industrial scale operations.

According to Figure 3, it is seen that the precipitates could readily settle out with 85 % efficiency even in 30 minutes. Thus, there is no need for prolonged durations.

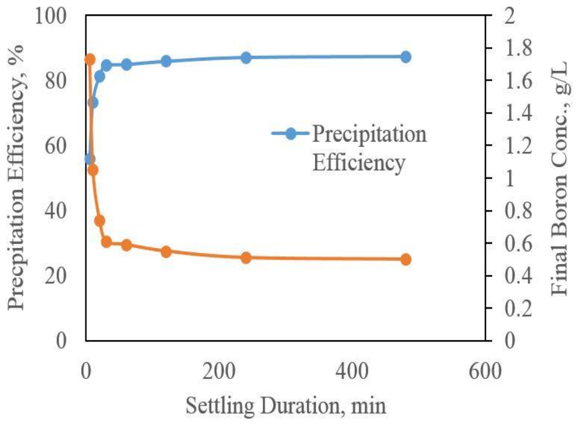

Figure 3. The effect of settling duration on boron precipitation

3.2.2. The Second Stage Precipitation Tests

As a result of one stage precipitation, 87 % of boron could be removed using 20 g/L $Ca(OH)_2$, agitation duration of 30 min, solution temperature of 22 ± 2 °C and settling duration of 60 min. However, the residual boron concentration obtained under optimum conditions was found to be 0.61 g/L, which was not close to the environmental limitations (2 mg/L).

While the initial pH was 6, agitation duration was determined to be 15 min. The final pH of the solution was measured as 12.4. On the other hand, in this group of tests, the effects of $Ca(OH)_2$ addition only and $Ca(OH)_2 + Al_2(SO_4)_3 \cdot 18H_2O$ were investigated.

The Effect of $Ca(OH)_2$ Addition Only

During the tests, $Ca(OH)_2$ dosage was changed from 2.5 to 20 g/L. HNO_3 was used to decrease the pH of the solution, under the experimental conditions:

- Initial pH: 6,
- Agitation duration: 15 min,
- Solution temperature: 22 ± 2 °C,
- Settling duration: 30 min.

It could be concluded from Figure 4 that the increase in $Ca(OH)_2$ dosage had a slightly positive effect on the precipitation. 0.44 g/L boron content was obtained by 20 g/L $Ca(OH)_2$ usage, which is unsatisfactory.

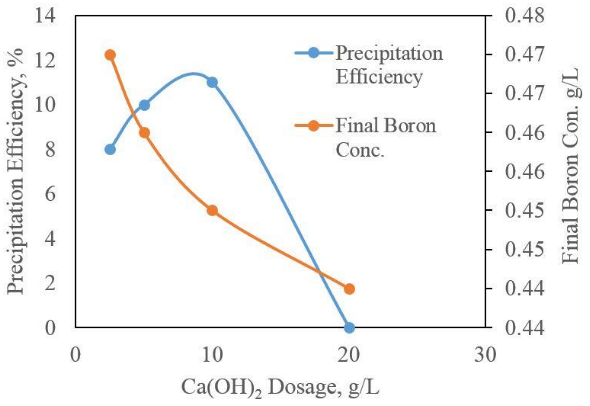

Figure 4. The effect of $Ca(OH)_2$ dosage on boron precipitation in the second stage

The Effect of $Ca(OH)_2 + Al_2(SO_4)_3 \cdot 18H_2O$

In these tests, varying dosages of $Al_2(SO_4)_3 \cdot 18H_2O$ from 40 to 120 g/L was added in the presence of 10 and 20 g/L of $Ca(OH)_2$. The reason for $Al_2(SO_4)_3 \cdot 18H_2O$ addition is to decrease pH to facilitate the reaction of Ca^{2+} ions (Yamada and Eto, 1995).

Table 4
The effect of $Al_2(SO_4)_3 \cdot 18H_2O$ addition on boron precipitation in the second stage

$Ca(OH)_2$ Dosage (g/L)	$Al_2(SO_4)_3 \cdot 18H_2O$ Dosage (g/L)	Initial pH	Final pH	Final Boron Concentration (g/L)	Precipitation Efficiency (%)	Total Precipitation Efficiency (%)
10	40	3.7	8.0	0.20	61.0	94.9
	60	3.5	3.7	0.14	71.8	96.3
	80	3.4	3.6	0.12	75.8	96.9
	100	3.3	3.5	0.12	76.2	96.9
	120	3.2	3.4	0.12	77.4	97.1
20	40	3.7	10.2	0.16	69.5	96.0
	60	3.5	7.4	0.13	74.5	96.7
	80	3.4	4.1	0.11	77.7	97.1
	100	3.3	3.8	0.11	78.5	97.2
	120	3.2	3.5	0.11	79.0	97.3

Following conditions were kept constant in the tests:

- Agitation duration: 15 min,
- Solution temperature: 22 ± 2 °C,
- Settling duration: 30 min.

During the tests, it was observed that pH decreased from 12.4 to lower levels. These can be seen in Table 4 as the initial pH values. However, the final pH values changed depending on the reagent addition.

According to the results given in Table 4, $Al_2(SO_4)_3 \cdot 18H_2O$ greatly affected the precipitation efficiency of boron. The precipitation efficiency in the second stage increased up to nearly 75 % with elevating $Al_2(SO_4)_3 \cdot 18H_2O$ dosages than the levels off. The ultimate boron precipitation efficiency obtained was 97 % as a result of two stages of treatment. The final boron concentration in the effluents was about 110 mg/L, which was still too high for safe environmental discharge.

4. Conclusion

The boron in the effluents of the Kirka Boron Inc. contained 3.93 mg/L B, 6.38 g/L Na, and 675 mg/L SO_4.

The effluents could be precipitated at its natural pH 9.44 up to 74.3 %. However, when initial pH was lowered by HNO_3, the precipitation efficiency increased up to 87 %.

It was found that the boron precipitation is strongly related to the Ca^{2+} concentration in the solution. As the pH proceeded towards acidic values, Ca^{2+} concentration in the solution increased to from 300 mg/L to around 1600 mg/L.

Second stage precipitation using $Al_2(SO_4)_3 \cdot 18H_2O$ in addition to $Ca(OH)_2$ increased the precipitation efficiency yet remained ineffective to reach the environmentally accepted values of around 2 mg/L discharge concentration.

In conclusion, when the pulp was agitated for 15 min with 20 g/L $Ca(OH)_2$ and let to settle 30 min, 84.8 % boron could be precipitated. After solid-liquid separation, the remaining solution was subjected to second stage precipitation, in which the solution was agitated for 15 min with 20 g/L $Ca(OH)_2$ and 80 g/L $Al_2(SO_4)_3 \cdot 18H_2O$ for 15 min and then settled for 30 min. As a result, 97 % boron precipitation was achieved. Yet, 0.11 g/L B remained in the solution.

After one stage precipitation, 38 % B_2O_3 was determined in the solid fraction. The XRD analysis on the precipitant showed the chemical composition is in the form of $2CaO \cdot 3B_2O_3 \cdot 13H_2O$, which is suitable for boric acid production.

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Izdvajanje bora iz otpadnih voda postrojenja Kirka boraks

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Proširena i recenzirana verzija rada - rad prezentovan na simpozijumu X IMPS

I Z V O D

Kirka Boron Inc. je najveće postrojenje za preradu i dobijanje bora u Turskoj, proizvodi “tincal” (borax) iz rudnika i natrijum penta boraksa u istom kompleksu. Međutim, jalovište predstavlja značajan problem, jer aproksimativno 75 % zapremine postojećih bazena je ispunjeno otpadnom vodom koja sadrži 3 g/L bora. Udeo bora u ovoj vodi mora da se smanji kako bi se ona ponovno koristila u postrojenju. Pri tome koncentracija od 3 g/L bora predstavlja i rizik za životno okruženje. U ovom radu, bor iz vode koja se izliva iz Kirka Boron Inc. postrojenja je istaložen pomoću $Ca(OH)_2$ i Al_2SO_4. Praćen je uticaj nekoliko parametara kao što su količina $Ca(OH)_2$, polazna pH, vreme mešanja i vreme taloženja. Može se reći da koncentracija Ca^{2+} jona ima veliki uticaj na proces precipitacije i da je stepen precipitacije veći ukoliko polazna pH teži kiselim vrednostima. Istraživanja su pokazala da 97 % bora se može istaložiti iz rastvora kroz dva stepena, i pri tome je utvrđeno da se pri taloženju dobije 38 % B_2O_3.

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Analysis of efficacy of the process of remediation of landfill site soil contaminated with leachate using material flow analysis

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ABSTRACT

There are two possible cases concerning non-sanitary municipal solid waste landfills due to failure to meet requirements with respect to impermeability and thickness of geological barrier as well as absence of implementation and use of a waste and leachate management system, and also depending on type and the mineral composition of the geological barrier. In the first case, impermeable clay, kaolinite, is prevailing in the composition of the geological barrier the final outcome of which is the spillage of leachate into the volume of the deposited waste, as well as its outbreak on the surface of the landfill site. In the second case, permeable clay, smectite, is prevailing in the composition of geological barrier with dominant leachate infiltration into the ground flow. In accordance with the first case, using STAN software the substance flow analysis (SFA) was carried out, of cadmium primarily, within three scenarios. Efficacy of remediation of the landfill site soil contaminated with leachate from the aspect of heavy metal reduction, focused primarily on cadmium, using *in-situ* and *ex-situ* systems, was presented within Scenario 1 and Scenario 2. Possibility and efficacy of direct treatment of leachate in a corresponding plant for its processing, in case of implementing and using the leachate management system, was presented within Scenario 3. Efficacy of cadmium flow reduction accomplished within Scenario 1, Scenario 2 and Scenario 3 amounts to 99.04 %, 55 % and 99.2 %, respectively. Prevention of landfill site contamination with leachate using the system of its management is an optimum option and a desirable practice, while in the case of the already existing contamination of the landfill site and its immediate environment, using *in-situ* system of landfill site soil remediation, based on achieved results, high efficacy was achieved contrary to use of the *ex-situ* system.

1. Introduction

Contamination of a landfill site is a condition influenced by a complex of factors, before all the absence of or inadequate implementation and use of a waste and leachate management system. Non-sanitary municipal solid waste landfills are an optimum example of absence of implementation and use of both systems mentioned. Requirements pertaining to impermeability and thickness of natural geological barrier in the event of non-sanitary landfills were not met, whereby the absence of a system for collection and removal of leachate from the landfill

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body are additional aggravating and risky circumstances (Ministry of Environment, Mining and Spatial Planning, 2010; Karanac et al., 2015).

In such circumstances, the role of protective liner between the landfill body and the unsaturated area is performed by impermeable layer consisting of a combination of a geological barrier and a bottom liner of the landfill and a base which, considering its geological composition, consists of clay. Depending on mineral composition of clay, of which the base is made, there are two possible situations. If impermeable clay - kaolinite is present on the landfill site, infiltration of leachate of the landfill into the groundwater flow is the slightest possible, whereby the increase in the volume of filtrates in water storage within the landfill site is prevailing. After exceeding the capacity of water storage, leachate goes through constitutive layers of landfill site cells, if any, or they are discharged into the volume of the deposited waste. Therefore, leachate comes up to the surface of the landfill site causing it to collapse. Due to complex qualitative and quantitative composition of leachate, landfill site and its immediate environment become contaminated. In the second case, if clay, of which the base is made, falls into a group of permeable smectite according to its mineral composition, the occurrence of leachate infiltration into the groundwater flow will be prevailing. Tendency towards outcome of the first case is beyond any doubt, however its realization will take a longer period of time. Groundwater is a primary contaminated medium in the said case. Leachate is an entity influenced by a complex of factors, both within the very landfill body (landfill age, morphological composition of waste, temperature and content of moisture, migration flow of liquid, technology of waste treatment before disposal, thickness of the landfill body, waste decomposition stages) and outside of it (meteorological parameters, with a focus on annual precipitation, the seasons). The process of forming landfill filtrate comprises decomposition of solid substances in water being filtrated through the landfill body and the separation of dissolved or suspended matter incurred through biological and chemical processes inevitably taking place within the landfill body (Antić, 2016). Basic physical features characterizing landfill leachate are dark-brown colour of filtrate and intensive odour, while high level of pollutant concentration and the values of biological consumption of oxygen over the course of five days in the amount of 5,000 mg/l, represent their exemplary chemical parameters.

Pollutants represented in the composition of leachate of municipal landfills can be divided into four groups: soluble organic components, inorganic macrocomponents, heavy metals and xenobiotic organic components (Kjeldsen et al., 2002; Renou et al., 2008; Abbas et al., 2009; Bušatlić et al., 2017). Except for the mentioned four groups of components, other compounds and elements such as borate, sulphide, selenate, barium, lithium, mercury and cobalt (Kjeldsen et al., 2002) can also be identified within chemical composition of leachate. Due to complex qualitative composition of leachate, as a potential contaminant, Assessment of condition of the environment of a contaminated site as well as the creation of a Plan of recultivation, sanitation and remediation are deemed as necessary activities. Selection of adequate remediation technologies for treatment of landfill site soil contaminated by leachate is among last stages in the creation of the Plan, whereby aspiration towards separation of targeted pollutants, efficiency and price of remediation technologies are considered as primary factors.

Mediums of the environment contaminated with toxic heavy metal cadmium are a basic cause of harmful effects on the environment and on people’s health as well due to its allocation in food chain. Harmful effects on people’s health are varying and depend on intensity of exposure to cadmium concentrations. Cadmium poisoning symptoms are diarrhea, pain in stomach, nausea, while the consequences are reflected in the immune system disorders, sterility, possible DNA damage (Crichton, 2012). Cadmium is characterized by high bioconcentration factor (BCF) and therefore it is predominantly deposited in liver, kidneys and bones, causing bones to become more fragile with the possibility of osteoporosis. Several epidemiological studies have confirmed that the intake of cadmium is related to lung and prostate cancer, and recently it has been classified according to IARC as Group 1 carcinogen (Nodberg et al., 2007). Acute poisoning with cadmium can have a fatal outcome. A case of mass poisoning of population after consuming rice grown in the fields irrigated with river water contaminated with cadmium from industrial waste water of the nearby factory was recorded in Toyama prefecture of Japan in early 1912. Poisoning with toxic heavy metal cadmium was manifested in a disease called “Itai-itai”. Basic pathophysiological mechanism explaining toxicity of cadmium is enzyme inactivation via sulfhydryl (SH) groups. This way synthesis of hem (a haemoglobin component) is reduced and enzymes of significance for bone metabolism are inhibited. All this leads to demineralization of bones and to cadmium excretion through urine and also to “bone softening”, the so-called osteomalacia. In addition to this mechanism, cadmium also replaces calcium in bones; however since it does not have the same properties as calcium, bones become soft and fragile. The mentioned poisoning is accompanied with heavy pain which is why the disease was named “Itai-itai”, which means “It hurts-It hurts disease” (Nodberg et al., 2007).

Three scenarios were created in the paper the goal of which is to establish efficacy of heavy metal reduction, of cadmium before all. Efficacy of remediation of the landfill site soil contaminated with leachate, from the aspect of heavy metal reduction, with a focus on cadmium, using *in-situ* and *ex-situ* systems, is presented within Scenario 1 and Scenario 2. Due to high efficacy of heavy metal reduction and financial feasibility, two remediation technologies have been selected within the *in-situ* system - chemical oxidation and phytoremediation, whereas within the *ex-situ* system, soil washing and vitrification have been applied.

Possibility and efficacy of direct treatment of the landfill filtrate in the leachate treatment plant is presented within Scenario 3. The formed system represents an integration of conventional and alternative treatment methods, namely physical and chemical methods of coagulation/flocculation, biological treatment using membrane bioreactor with side flow and alternative tertiary treatment, using phytoremediation methods, with a goal of enhancing efficiency of heavy metal flow reduction. After achieving these results it will be concluded whether the direct treatment of landfill filtrate within the leachate treatment plant represents an optimum prevention of landfill site soil contamination, namely whether it is necessary to implement and apply the leachate management system. Also, in case of the already contaminated landfill site soil, comparison of the efficacy of the reduction of cadmium flow will be carried out within Scenarios 1 and 2, namely within *in-situ* and *ex-situ* remediation system.

2. Methods

By analysing the flows of material using STAN software, the substance flow analysis (SFA) was carried out, of cadmium before all, within three scenarios (Brunner and Rechberger, 2004; Cencic and Rechberger, 2008; Stanisavljevic and Brunner, 2014).

2.1. Development of Scenario 1

In-situ treatment of landfill site soil contaminated with leachate is presented within Scenario 1. The selected technologies, chemical oxidation and phytoremediation, were selected due to high efficacy of the reduction of heavy metal flows and economic feasibility.

The use of a method of chemical oxidation presupposes construction works within the landfill body, with a goal of installing injection, extraction and observation well. Oxidation agent, most typically it is H_2O_2, is inserted in the contaminated soil through an injection well, while the remaining oxidation agent, with accumulated congeners of toxic pollutants from contaminated soil is extracted through an extraction well. Extracted oxidant is treated in the plant for recovery of oxidation agent with a goal to repeat the use within the mentioned process. Also, within the mentioned plant toxic congeners accumulated in the oxidation agent are being deposited within the *in-situ* process of chemical oxidation, after which the formed deposit is extracted from the system. The process of chemical oxidation is shown in Figure 1. By applying the mentioned process an efficient treatment of deep layers of contaminated soil is achieved and, if necessary, of contaminated groundwater as well.

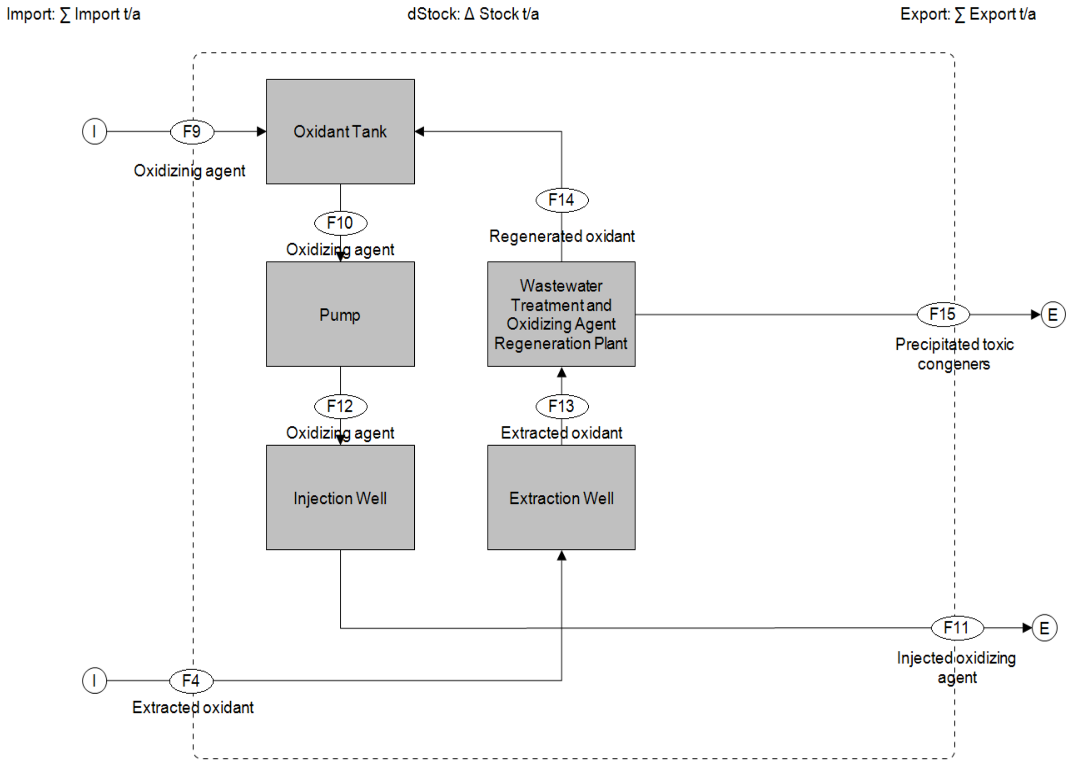

Figure 1. *In-situ* process of chemical oxidation implemented within contaminated landfill site

Phytoremediation method represents another selected technology for the treatment of contaminated landfill site soil. High efficacy in the reduction of heavy metal concentration in surface layers of contaminated soil is achieved by implementing hyperaccumulating biomass, such as *Typha domingensis*, *Brassica napus* and *Typha latifolia L*. After applying this method, heavy metals accumulated within waste biomass are extracted from the system, whereby they can be applied in cement plants in the form of alternative fuel or in the form of hazardous waste they can be forwarded to an operator for further handling and treatment. The benefit of applying the said method is in short-term enhancement of an aesthetic aspect of the treated landfill site.

Overview of the entire *in-situ* system for the treatment of landfill site soil contaminated with leachate is shown in Figure 2.

By applying the mentioned *in-situ* treatment of landfill site soil contaminated with leachate allows a full-scale treatment of both deep and surface layers of contaminated soil. Implementation of the said system is recommended primarily for municipal solid waste landfills within which a voluminous scattered contamination of soil with heavy metals and with xenobiotic organic compounds as well was identified through Assessment of the condition of the environment.

2.2. Development of Scenario 2

Ex-situ treatment of landfill site soil contaminated with leachate is presented within Scenario 2. Soil washing and *ex-situ* variation of the vitrification method were selected due to high efficacy of the reduction of heavy metal concentration and exceptional efficiency. Optimum efficient reduction of the concentration of heavy metals in surface layers of contaminated soil is performed by applying the method of soil washing. Soil allocated through the process of excavation is treated outside the landfill site whereby reducing potential risks to people's health and environment, while at the same time incurring substantial financial transportation costs, as well as negative aspects of applying the mentioned method. Final products of the said treatment are filtered water, which can be used within the treatment plant as a technical fluid or it can be drained into a water-receptor, and treated soil which is in practice normally returned to the landfill site.

Treatment of coarse fractions of treated soil as well as of heavy metal flows within produced vitrified soil is

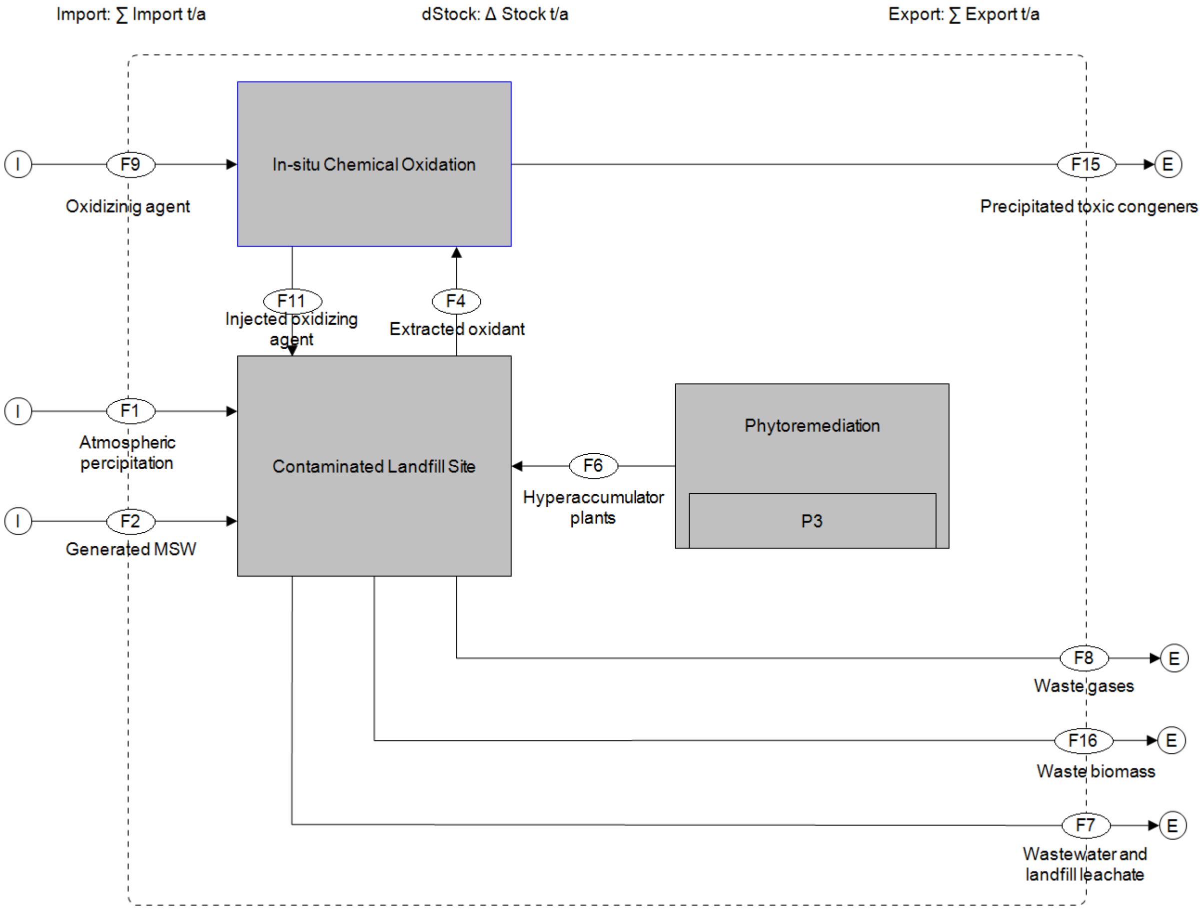

Figure 2. *In-situ* treatment of landfill site soil contaminated with leachate

carried out using vitrification method. Final products of the said method are vitrified soil and waste gases. The incurred vitrified mass is of great strength and it is resistant to the leaching of pollutants trapped in it which are therefore prevented from melting and migration into groundwater or any other possible impact on the environment. In practice, vitrified soil typically returns to the landfill site or, as a hazardous waste, it is further treated by operator. The system of *ex-situ* treatment of landfill site soil contaminated with leachate is shown in Figure 3 while *ex-situ* processes of soil washing and vitrification are shown in Figure 4 and Figure 5.

The application of the presented *ex-situ* system of treatment of landfill site soil contaminated with leachate is recommended primarily in case of concentrated pollution of surface layers of landfill site soil with heavy metals.

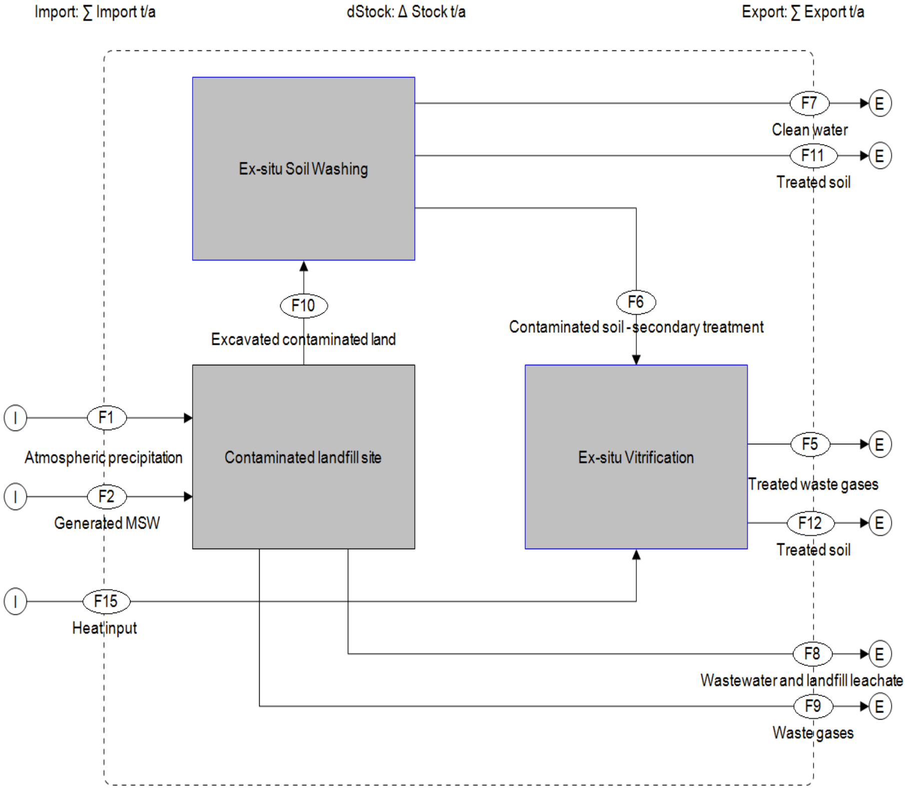

Figure 3. *Ex-situ* treatment of landfill site soil contaminated with leachate

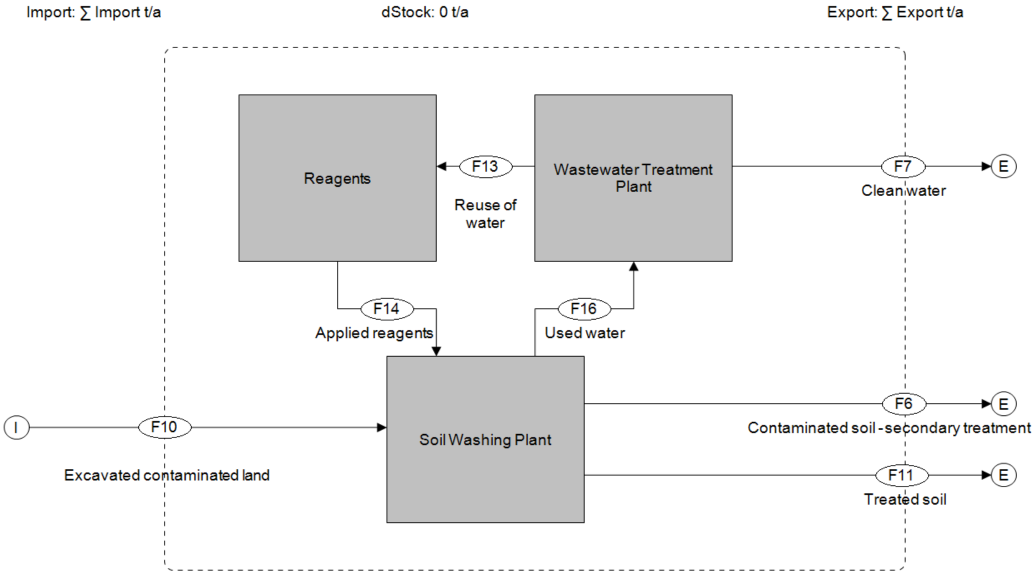

Figure 4. Overview of *ex-situ* process of washing soil of contaminated landfill site

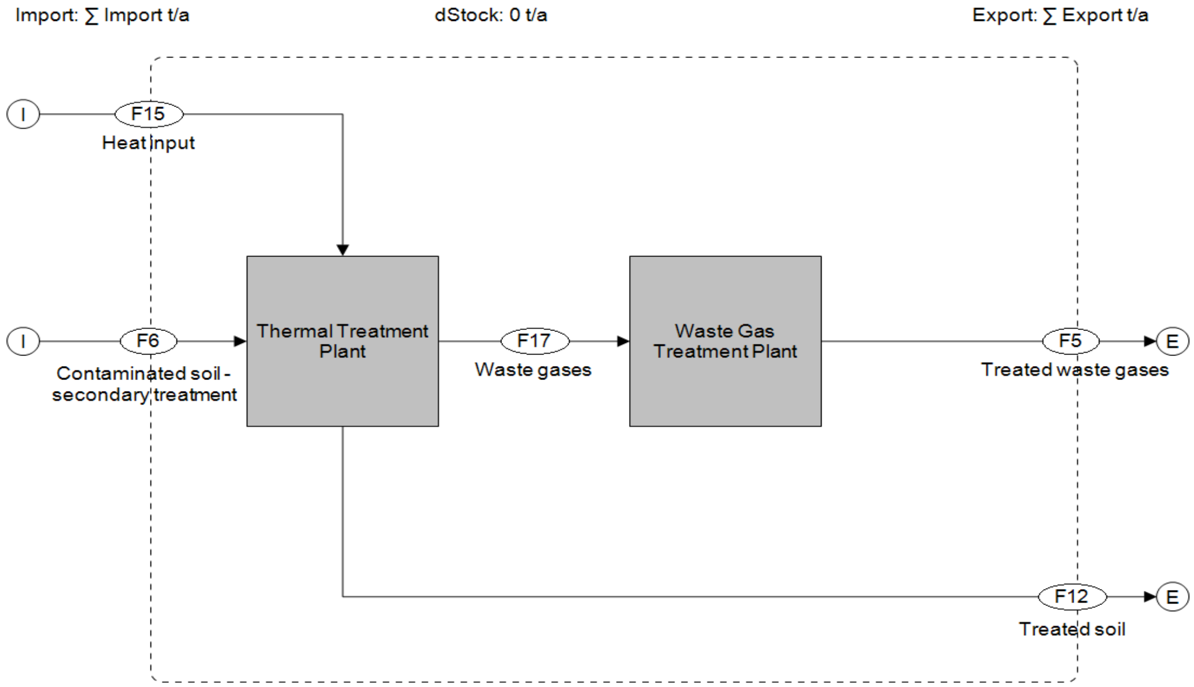

Figure 5. Overview of *ex-situ* process of vitrification as a secondary treatment of coarse fractions retained after the process of soil washing

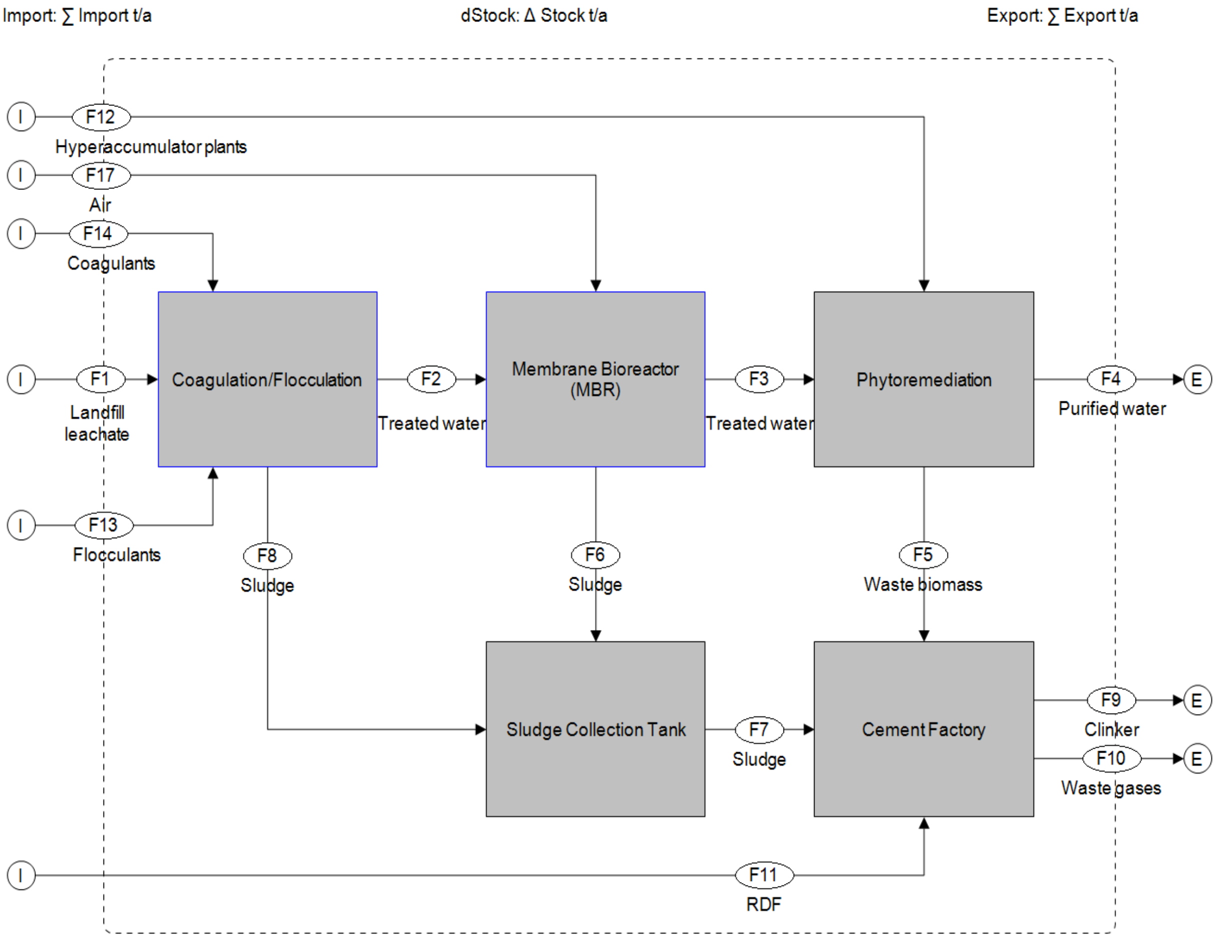

Figure 6. Model of a landfill leachate treatment plant

2.3. Development of Scenario 3

Figure 6 shows treatment of landfill filtrate within the leachate treatment plant. The shown system represents an integration of conventional and alternative treatment methods, namely physical and chemical methods of coagulation/flocculation, biological treatment by applying membrane bioreactor with side flow and alternative tertiary treatment by applying the method of phytoremediation, with aim to improve efficacy of the reduction of heavy metal concentration.

The process of applying coagulation/flocculation treatment is shown in Figure 7 whereas the implementation of the method of membrane bioreactors is shown in Figure 8.

The line of sludge incurred within physical and chemical process of coagulation/flocculation and of applying biological MBR process is collected in the sludge collecting tank. Collected sludge and waste biomass from the process of phytoremediation can be efficiently treated at cement plants if concentrations of heavy metals in waste products do not exceed prescribed limits in alternative fuels suitable for use in cement plants.

2.4. Applied data

Data applied for determining the input flow of cadmium within Scenarios 1 and 2 are represented as a generated volume of solid municipal waste in the municipality of Novi Sad, which amounts to 133,104 kg/year and a mass percentage of cadmium within the solid municipal waste stream, which amounts to 11 mg/kg (Korzun and Heck, 1990; Vujić et al., 2009a).

When calculating daily and annual volumes of generated leachate within Scenario 3, the following formula (1) applies (Miloradov, 2006):

$$Q_f = \frac{k \cdot (P + Q)}{365} \tag{1}$$

where:

- Q_f - daily volume of filtrate [m^3/day],
- k - coefficient characterized by ability to absorb moisture and evaporation of waste,
- P - total annual volume of precipitation on the surface of waste [m^3/year],
- Q - total annual volume of water distributed on the surface of waste [m^3/year],
- F - surface [ha].

Data applied when calculating daily and annual volumes of generated leachate come from real sources. The data referring to the surface of a hypothetical landfill site has been projected on the basis of real data of exploited surface of landfill site “City Landfill” Novi Sad and amounts to 35,381 m^2, while the annual volume of precipitation was measured on the level of synoptic station Novi Sad in the period between 1981 and 2010

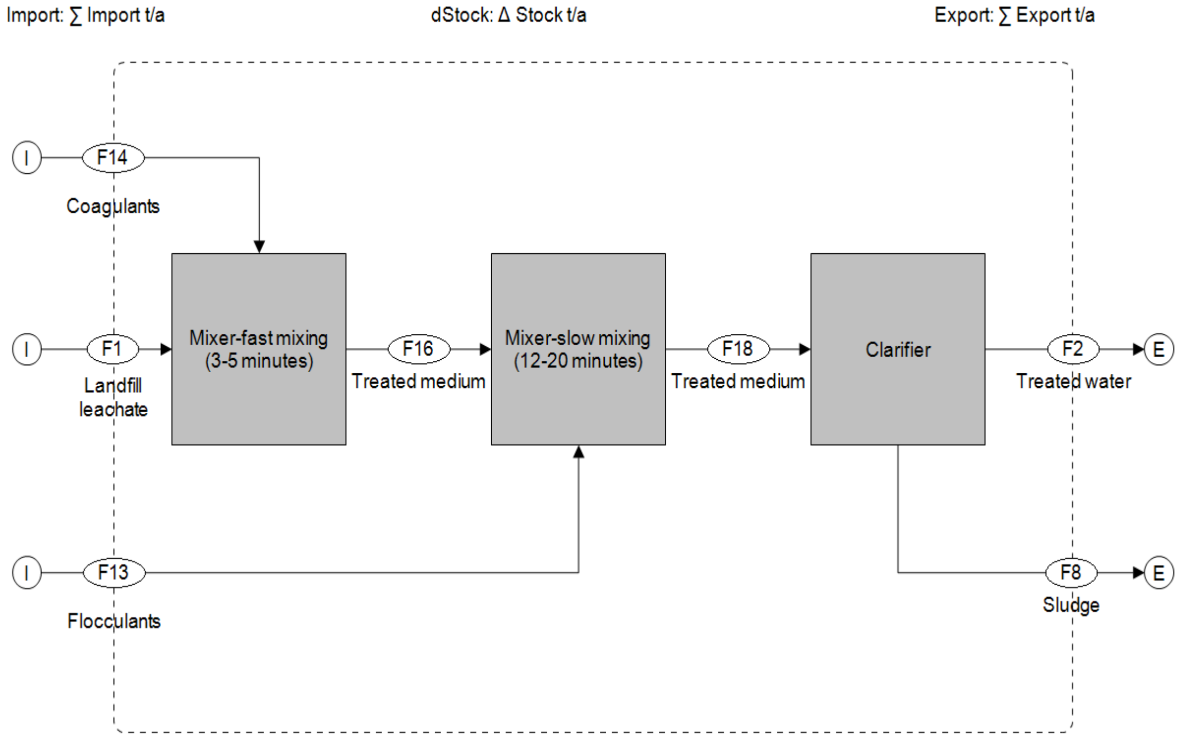

Figure 7. Implementation of physical and chemical method of coagulation/flocculation within the landfill leachate treatment plant

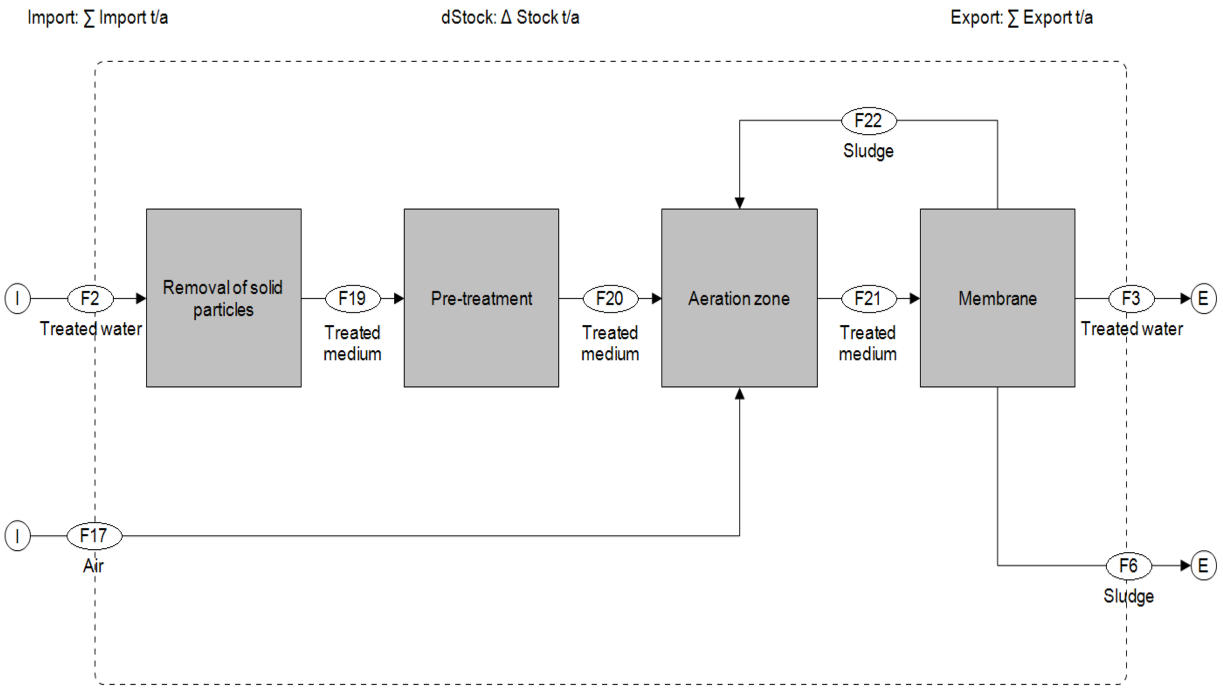

Figure 8. Implementation of biological method of membrane bioreactor with side flow

and it amounts to 647.3 mm/year (Vujić et al., 2009a; Republic Hydrometeorological Service of Serbia, 2010).

When applying the methodology it is necessary to take into consideration the fact that 70 % of precipitation evaporates from the landfill through drying, and 25 % evaporates through biometric processers occurring in the layer of deposited waste at depth of 0.5 to 2 m. Remaining precipitation, as a filtrate, migrates down to the bottom of the landfill by 5-15 % for a sloped area and by 1-10 % for the area which is not sloped. Consequently, the coefficient k for landfill sites on a flat terrain amounts to 0.1, while for sloped landfill sites (mostly 2 %) it amounts to 0.15 (Miloradov, 2006). Also, the total annual volume of water distributed on the surface of waste actually accounts for merely 30 % of total annual precipitation left after evaporation off the landfill site surface.

In calculations the formula (2) applies for conversion of values from the level of mm/year to m^3/year (Berndtsson et al., 2014):

$$mm/year = \frac{10^{-3} m^3}{1\ m^2} year \tag{2}$$

By applying the said formula (2) we have concluded that the annual volume of precipitation per 1 m^2 amounts to 0.6473 m^3. Introducing exploited area of the landfill site “City Landfill” Novi Sad which amounts to 35,381 m^2, we have calculated that the annual volume of precipitation for the given surface amounts to 22,902.12 m^3/year. Therefore, a factor P was determined within the formula (1). On the basis of the obtained results, the factor Q was calculated and it represents the remaining 30 % of total annual precipitation distributed on the surface of waste and it amounts to 6,870.64 m^3/year. On the basis of the presented data an assessment of generating leachate was carried out within the hypothetical landfill site, on a daily (3) and on an annual (4) basis.

$$Q_f = \frac{0.15 \cdot (22{,}902.1213\ m^3/year\ + 6{,}870.63639\ m^3/year)}{365} = 12.24\ m^3\ /year \tag{3}$$

$$Q_f = 0.15 \cdot (22{,}902.1213\ m^3/year\ + 6{,}870.63639\ m^3/\ year) = 4{,}465.914\ m^3/year \tag{4}$$

Concentration of cadmium within the generated volume of leachate was established on the basis of field testing and qualitative analysis of leachate from the landfill site “City Landfill” in Novi Sad. Values of the stated concentration amount to 0.02 mg/L, and 20 mg/m^3 (Vujić et al., 2009b).

Within the *in-situ* system of Scenario 1, the value of efficacy of the reduction of the flow of cadmium through the method of chemical oxidation was adopted on the basis of book values, by applying H_2O_2 as an oxidizing agent, and it amounts to 95 %, while through the method of phytoremediation using plant species *Typha* *domingensis*, *Brassica napus* and *Typha latifolia L.*, amounts to 81 % (Seol and Javandel, 2008; Lavagnolo et al., 2016; Mojiri et al., 2016; Antić et al., 2017; Ferniza-García et al., 2017).

Within the *ex-situ* system of Scenario 2, and based on book values, the value of efficacy of the reduction of the flow of cadmium through the method of soil washing amounts to 55 %, while through the method of vitrification, executed while performing field testing amounts to 70 % (Thompson et al., 1992; Kos and Leštan, 2003; Pociecha et al., 2011; Sung et al., 2011).

Within Scenario 3, the value of efficacy of the reduction of the cadmium flow by applying the method of coagulation/flocculation is ranging between 74 % (field research) to 98 % (laboratory research) (Kurniawan, 2011). For the purpose of Scenario 3, efficacy of the method in the amount of 74 %, established on the basis of field research, was adopted. Efficacy of the reduction of cadmium flow within MBR plant was adopted on the basis of book value and amounts to 84 % (Mahmoudkhani, 2014). Efficacy of the reduction of cadmium flow by applying the phytoremediation method was tested experimentally several times by experts. It was established that efficacy amounting to 81 % was achieved by using plant species *Typha domingensis*, *Eichhornia crassipes* and *Typha latifolia L*. (Mojiri et al., 2016; Antić et al., 2017; Ferniza-García et al., 2017). Within the treatment at the cement plant, 99.98 % of the flow of cadmium was concentrated in clinkers, and the remaining 0.02 % through waste gases are emitted in the environment (Korzun and Heck, 1990; Mitchell et al., 1992).

3. Results and discussion

3.1. Scenario 1

Due to possibly very harmful impact on the environment and people's health, within Scenario 1, the focus is on efficacy of the reduction of the flow of toxic heavy metal cadmium on the level of landfill site soil contaminated with leachate.

The flow of cadmium in remediation of the landfill site soil contaminated with leachate on an annual basis is shown in Figure 9.

The input flow of cadmium was concentrated within generated waste deposited on the landfill site in the amount of 1,464,144 g/year, and 1,464.14 kg/year. Cadmium concentrations were not recorded in remaining input flows, i.e. precipitation and heat input.

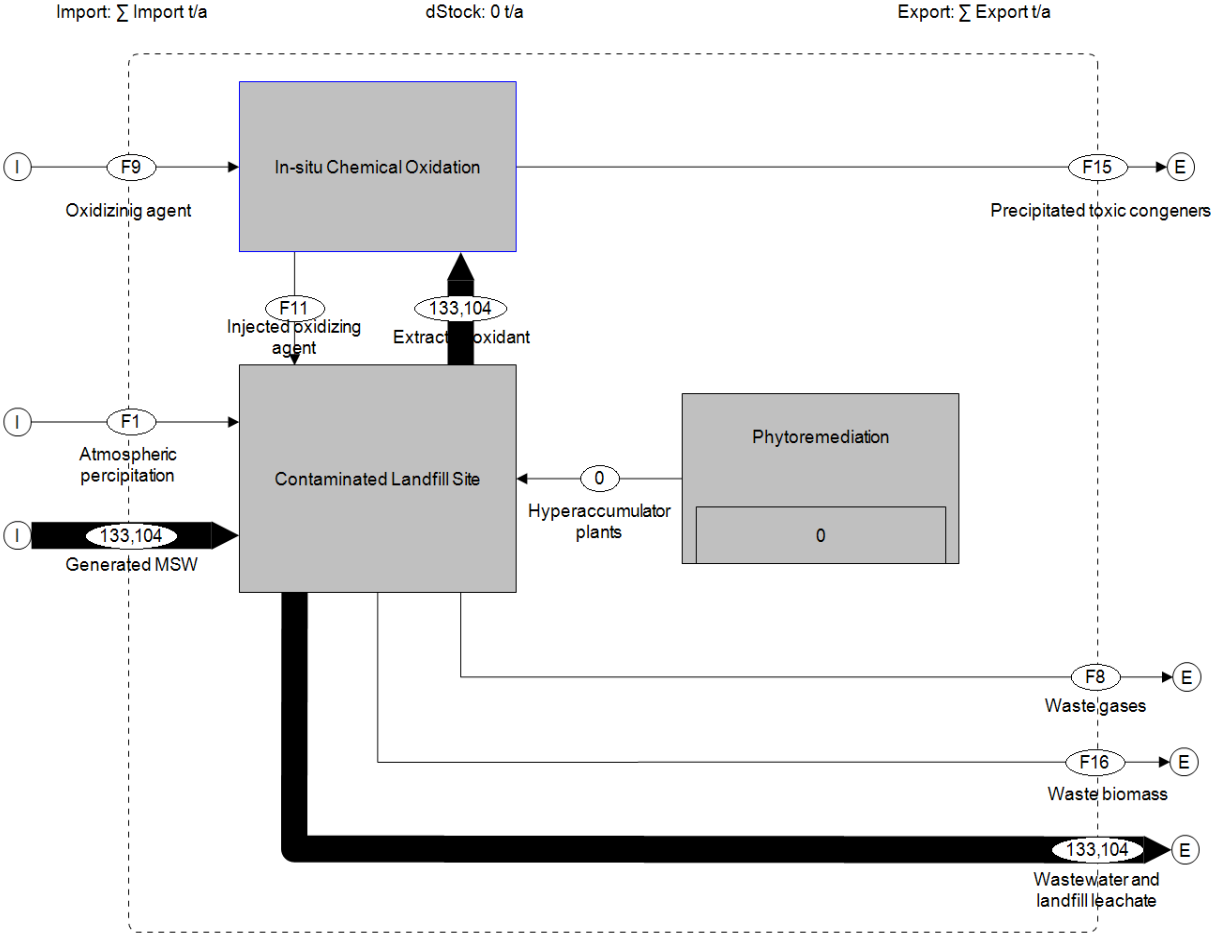

Figure 9. The flow of cadmium within the process of *in-situ* remediation of landfill site soil contaminated with leachate (g/year)

Efficacy of the *in-situ* method of chemical oxidation was adopted on the basis of book data and amounts to 95 % (Seol and Javandel, 2008). Accordingly, 95 % of the initial cadmium flow, namely 1,390,937 g/year or 1,390.94 kg/year, was accumulated and extracted in the form of toxic congeners of cadmium together with the remaining oxidizing agent. The flow of cadmium within the *in-situ* method of chemical oxidation is shown in Figure 10.

After performed *in-situ* chemical oxidation treatment, 5 % of the initial flow of cadmium remains within the landfill site soil contaminated with leachate, primarily in surface layers. Secondary treatment of contaminated soil is carried out by applying the method of phytoremediation using plant species Typha domingensis, Brassica napus and Typha latifolia L. Efficacy of the reduction of the flow of cadmium by applying the method of phytoremediation using the mentioned plant species was adopted on the basis of recorded data and amounts to 81 % (Lavagnolo et al., 2016; Mojiri et al., 2016; Antić et al., 2017; Ferniza-García et al., 2017).

Accordingly, after implementing the method of phytoremediation within the waste mass, 4.05 % of the remaining flow of cadmium is being accumulated, namely 59,298 g/year or 59.3 kg/year. The remaining 0.95 % of the flow of cadmium, namely 13,909 g/year or 13.91 kg/year, through leachate generated within the landfill site is allocated to groundwater aquifer.

Based on the flow of cadmium shown in Figure 4 and the performed calculations, it has been established that the efficacy of the applied *in-situ* methods of soil remediation at the landfill site contaminated with leachate amounts to 99.04 %.

3.2. Scenario 2

Due to possibly very harmful impact on the environment and people's health, the focus within Scenario 2 is on the efficacy of the reduction of the flow of toxic heavy metal cadmium on the level of the landfill site soil contaminated with leachate waters. The flow of cadmium within the remediation of landfill site soil contaminated with leachate on an annual basis is shown in Figure 11.

The input flow of cadmium is concentrated in generated waste deposited on the landfill site and it amounts to 11 mg/kg, whereby the annual flow of cadmium within the municipal waste was obtained and it amounts to 1,464,144 g/year, i.e. 1,464.14 kg/year. Cadmium concentrations were not recorded in remaining input flows, namely precipitation and heat input.

Considering the mechanism of leachate production, in

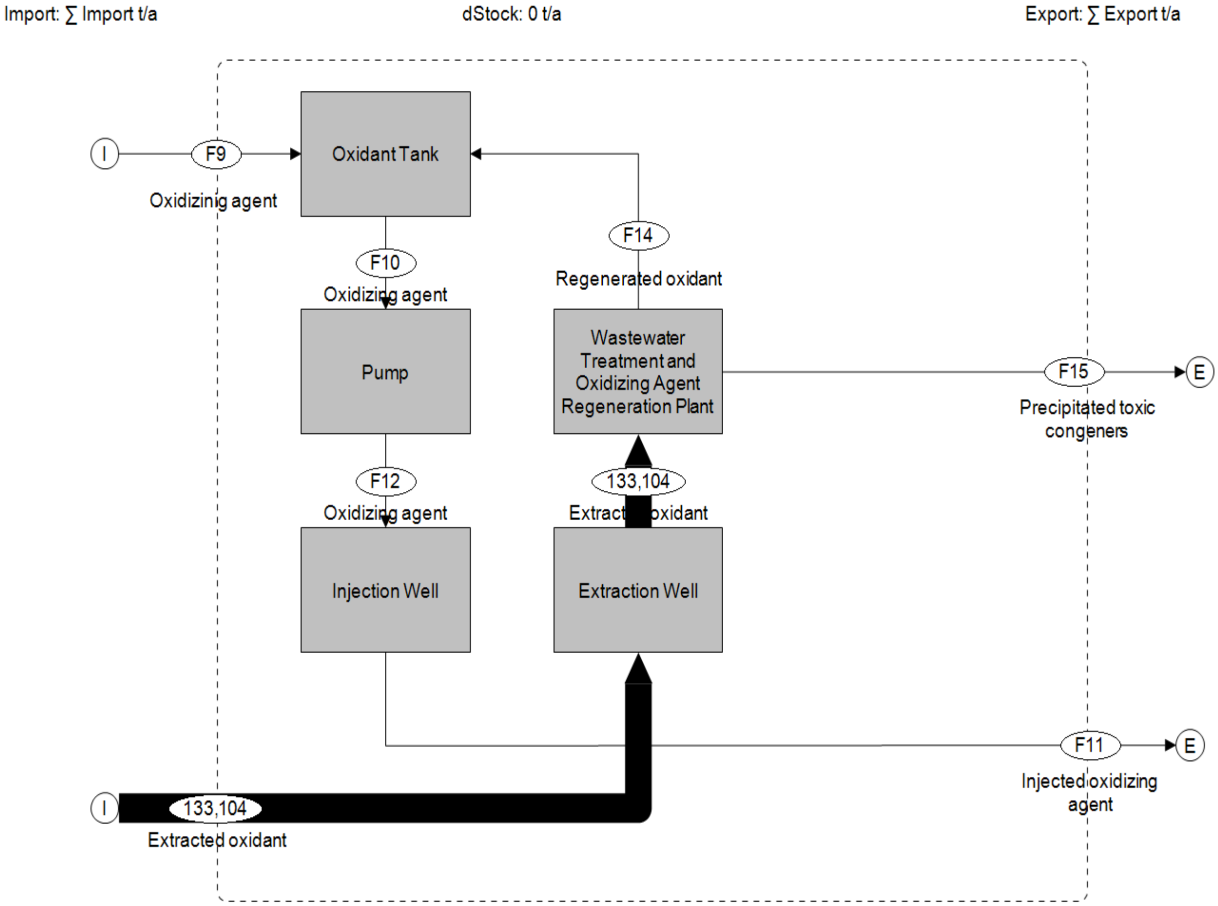

Figure 10. The flow of cadmium within *in-situ* treatment of chemical oxidation of the landfill site soil contaminated with leachate (g/year)

the event of non-sanitary municipal solid waste landfills without the system for its removal and collection, 85 % of cadmium concentration contaminates soil on and in the vicinity of the landfill site through leachate as a transfer medium discharged onto the surface of the landfill site. The mass flow rate within the said stream amounts to 1,244,522 g/year, i.e. 1,244.52 kg/year. Within the landfill body, with potential for collecting and/or infiltration in groundwater aquifer only 5-15 % of the landfill filtrate remains, carrying with it 15 % of the initially generated concentration of cadmium, namely 219,622 g/year or 219.62 kg/year (Miloradov, 2006).

Value of efficacy of the reduction of cadmium concentration by applying *ex-situ* method of washing soil was adopted on the basis of book data, namely the value of efficacy of the reduction of heavy metals achieved through field testing, which amounts to 55 % was applied (Kos and Leštan, 2003; Pociecha et al., 2011; Sung et al., 2011). Accordingly, after implementation and execution of the said treatment, treated land and clean water are obtained as final products. The treated land usually in practice returns to the landfill site carrying with it 45 % of the initial cadmium flow from the treated medium, namely 560,035 g/year or 560.04 kg/year, while the remaining 55 % of cadmium flow, namely 684,487 g/year or 684.49 kg/year, is stored within coarse fractions of soil which are not subject to the applied treatment.

Coarse fraction of contaminated soil which is not subject to *ex-situ* treatment of land washing, within which the flow of cadmium amounts to 684,487 g/year, namely 684.49 kg/year, is sent for *ex-situ* vitrification treatment. The value of efficacy of the reduction of cadmium concentration by applying *ex-situ* vitrification method was adopted on the basis of book data, namely the value of efficacy of the reduction of heavy metals obtained through field testing was applied, which amounts to 70 % (Thompson et al., 1992).

After performing the treatment on vitrified soil the flow of cadmium amounts to 479,141 g/year, namely 479.14 kg/year. Disadvantage of the said treatment is the necessity to perform multi-stage filtering of waste gases. In practice, conditions for the required level of clearing of waste gases typically do not exist, and so the remaining 30 % of cadmium flow, namely 205,346 g/year or 205.35 kg/year are either directly or indirectly emitted in environment.

On the basis of the flow of cadmium shown in Figure 11 and calculations performed, it has been established that efficacy of the applied *ex-situ* methods of remediation treatment of landfill site soil contaminated with leachate amounts to 55 %. The advantage of the presented system is permanent conservation and fixation of 70 % of the flow of cadmium present in coarse fraction of contaminated soil treated by *ex-situ* vitrification

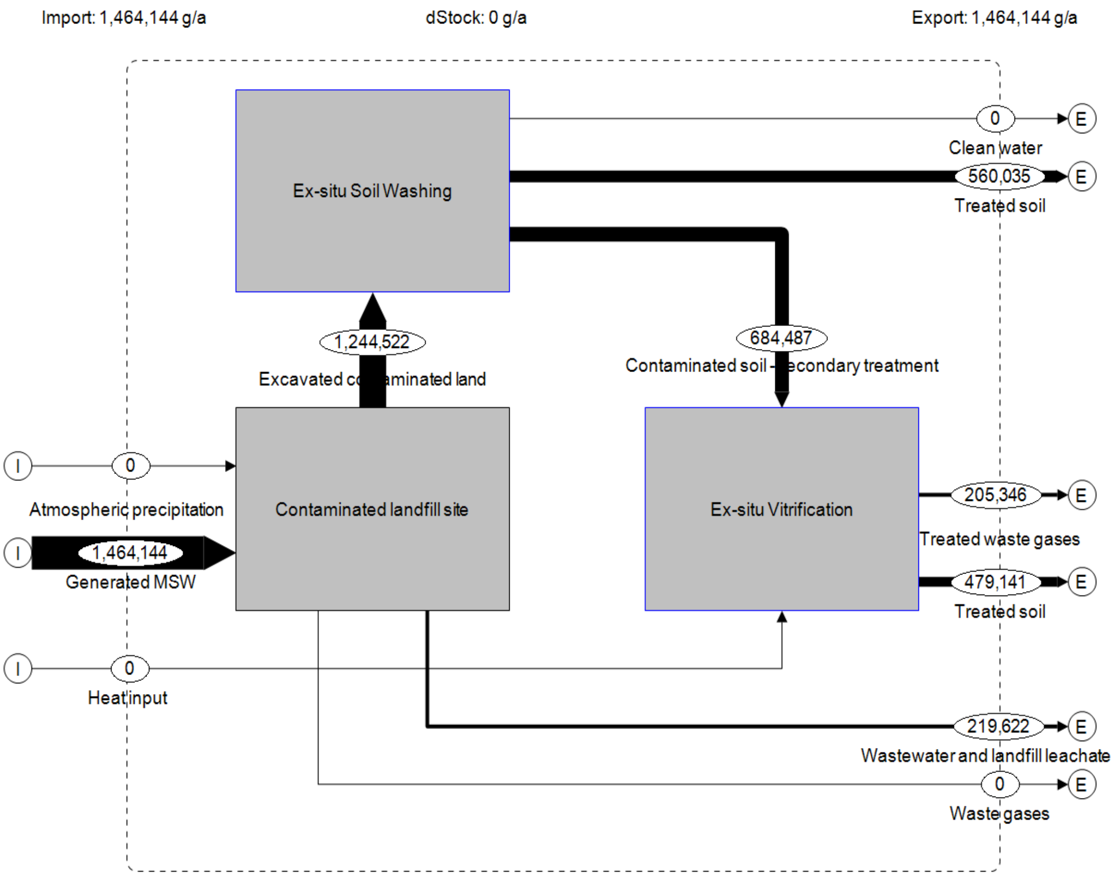

Figure 11. Flow of cadmium within *ex-situ* remediation of landfill site soil contaminated with leachate (g/year)

method. For the purpose of improving the end quality of soil which is after applying *ex-situ* washing process returned to the landfill site, it is necessary to apply additional treatment of the said fraction. Optimum selection in achieving the said goal is thermal treatments, such as pyrolysis or incineration, characterized by high range of efficacy of the reduction of heavy metals, from 93.91 % to 99.9 %, within the treated medium (Debela et al., 2012; US Environmental Protection Agency, 2012).

Long-term financially sustainable option for improving the quality of soil which, after the process of *ex-situ* washing returns to the landfill site, as well as simultaneously long-term maintenance of the quality of surface layers of soil of the landfill site, is the implementation of the method of phytoremediation using wooden plant species such as black alder (*Alnus glutinosa*), silver birch (*Betula pendula*) and black pine (*Pinus nigra*). The use of trees within the phytoremediation method may result in extraction of substantial quantities of metal, due to their high production of biomass. Also, the advantage of implementing the said method is the forming of a new sustainable ecosystem and the green belt, as well as the aesthetic enhancement of the treated site.

3.3. Scenario 3

Due to a possibly very harmful impact on the environment and people's health, within Scenario 3 the focus of attention is on the efficacy of the reduction of concentrations of toxic heavy metal cadmium on the level of generated leachate, removed within sanitary municipal solid waste landfills through implementation and application of systems for collecting leachate.

The flow of cadmium within physical and chemical, biological and alternative treatment of leachate from solid waste municipal landfills on the level of a plant for treatment of leachate is shown in Figure 12.

Cadmium concentration within generated volume of leachate was determined on the basis of field testing and qualitative analysis of leachate from landfill sites of the "City Landfill" in Novi Sad. Values of the stated concentration amount to 0.02 mg/L, namely 20 mg/m3, on the basis of which the input mass flow of cadmium was calculated in leachate which amounts to 89,318 mg/year, and 89.32 g/year.

Efficacy of reduction of heavy metals by applying the method of coagulation/flocculation is ranging from 74 (based on field testing) to 98 % (based on laboratory

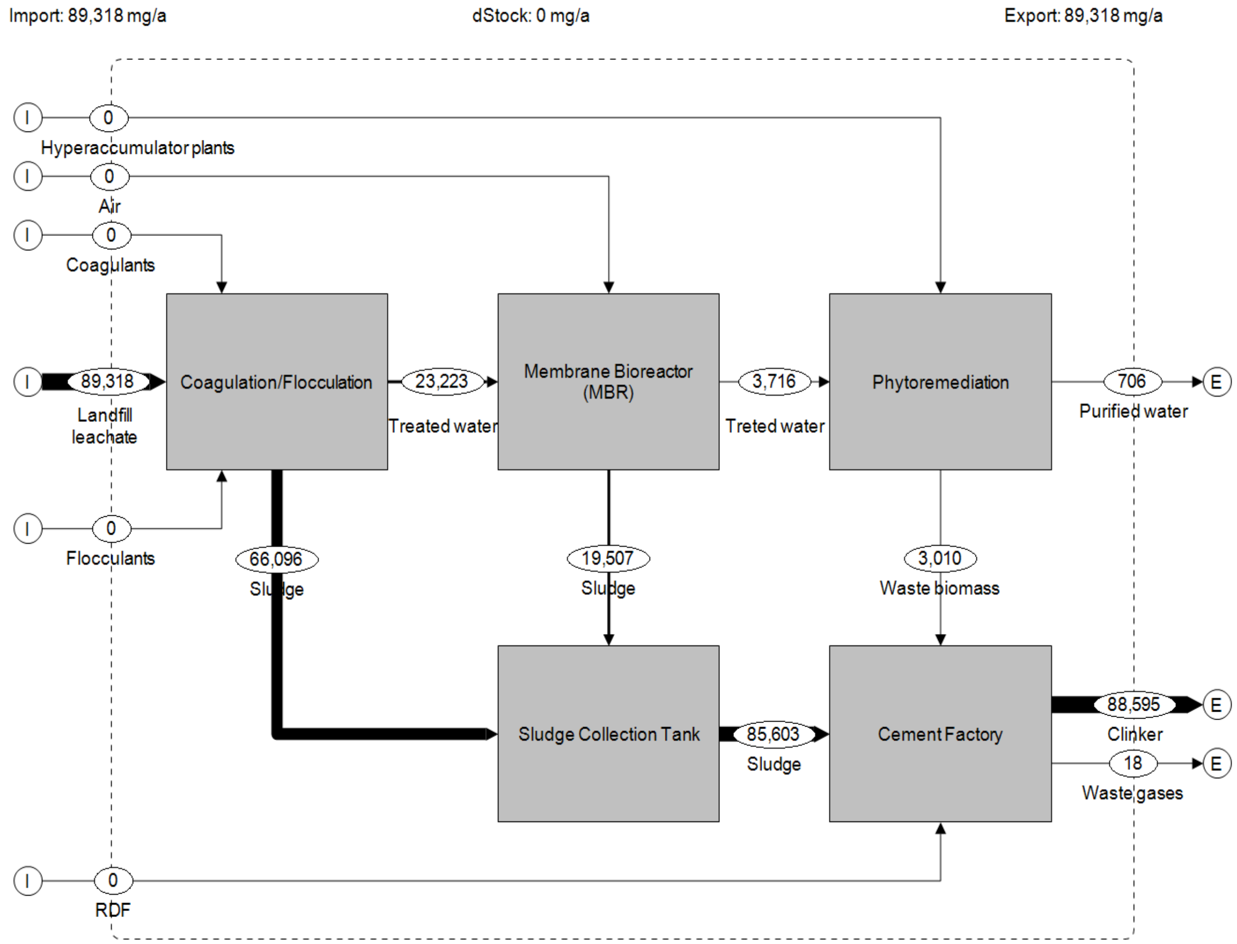

Figure 12. The flow of cadmium within the process of filtering leachate from municipal solid waste landfills in an adequate plant for physical and chemical, biological and alternative treatment (mg/year)

testing) (Kurniawan, 2011). In order to meet requirements of Scenario 3, the efficacy of the method in the amount of 74 %, established on the basis of field research, was adopted. Accordingly, 74 % of cadmium flow is deposited within waste sludge, whereby the flow of cadmium in this amounts to 66,096 mg/year, i.e. 66.096 g/year.

In leachate treated by applying the method of coagulation/flocculation, 26 % of the flow of cadmium remains, so the mass flow of cadmium within the stated stream amounts to 23,223 mg/year, i.e. 23.22 g/year.

Efficacy of cadmium reduction within MBR plant was adopted on the basis of a book value and it amounts to 84 % (Mahmoudkhani et al., 2014). Accordingly, 84 % of cadmium flow from previously treated leachate is concentrated in waste sludge, whereby the flow of cadmium in it amounts to 19,507 mg/year, i.e. 19.5 g/year. 16 % of cadmium flow remains in the secondary treated leachate, so the mass flow of cadmium in the said stream amounts to 3,716 mg/year, i.e. 3.72 g/year.

Efficacy of the reduction of cadmium by applying the method of phytoremediation was tested on several occasions experimentally by experts and it was concluded that efficacy in the amount of 81 % was achieved by using plant species *Typha domingensis*, *Eichhornia crassipes* and *Typha latifolia L.* (Mojiri et al., 2016; Antić et al., 2017; Ferniza-García et al., 2017). On the basis of the said above, 81 % of cadmium from secondary treated leachate is accumulated in biomass applied within the process of phytoremediation, whereby the mass flow of cadmium after the process of phytoremediation in waste biomass amounts to 3,010 mg/year, namely 3.01 g/year. 19 % of cadmium flow remains in tertiary leachate against the influent of tertiary treatment, so the flow of cadmium in leachate after applying the phytoremediation method amounts to 706 mg/year, i.e. 0.71 g/year.

It is possible to use sludge deposited in the tank for sludge storing, as well as waste biomass from tertiary treatment, and/or the process of phytoremediation, as alternative fuel in cement plants. For the purpose of presenting the flow of cadmium in the stated alternative fuels, Scenario 3 does not include the values of cadmium concentration within RDF, and/or primarily exploited fuel in cement plants. On the basis of book values, it is known that 99.98 % of the flow of cadmium is installed in the final product of cement plants, clinkers, while merely 0.02 % of cadmium flow is emitted within waste gases. Expressed in the form of a mass flow, 88,595 mg/year, i.e. 88.6 g/year of cadmium is installed in a clinker, while 18 mg/year, i.e. 0.02 g/year of cadmium is emitted within waste gases from cement plants.

On the basis of the flow of cadmium shown in Figure 12 and calculations performed, it has been concluded that the efficacy of the designed plant for leachate treatment within Scenario 3, including implemented primary - physical and chemical, secondary - biological and tertiary - alternative treatment, amounts to 99.2 % on an annual basis.

4. Conclusion

This paper demonstrates three possible Scenarios for soil remediation of contaminated landfill site, as well as direct treatment of the polluting medium, leachate. *In-situ* treatment of soil of the landfill site contaminated with leachate, shown within Scenario 1, enables a comprehensive treatment of both deep and surface layers of contaminated soil, so the implementation of the mentioned system is recommended primarily at solid waste municipal landfills within which a spacious scattered contamination with heavy metals and with xenobiotic organic compounds was determined through implementation of the Assessment of the condition of the environment. The use of the *ex-situ* system of treating landfill site soil contaminated with leachate, presented within Scenario 2, is recommended primarily in case of concentrated pollution of surface layers of landfill site soil with heavy metals. Treatment of landfill filtrate within the leachate treatment plant is presented within Scenario 3. The shown system represents integration of conventional and alternative treatment methods, namely physical and chemical methods of coagulation/flocculation, biological treatment by applying membrane bioreactor with side flow, and alternative tertiary treatment by using the method of phytoremediation, for the purpose of enhancing efficacy of reduction of heavy metal concentration.

On the basis of the presented cadmium flows and performed calculations, it has been concluded that efficacy of the applied *in-situ* system of treating remediation of landfill site soil contaminated with leachate amounts to 99.04 %, while *ex-situ* system of treatment amounts to 55 %, with the possibility for improving the performances by applying additional thermal and alternative treatments. Efficacy of the reduction of cadmium flow of the projected leachate filtering plant within Scenario 3, with implemented primary - physical and chemical, secondary - biological, and tertiary - alternative treatment, amounts to 99.2 % on an annual basis. The use of a method of collecting and filtering leachate is very suitable and optimal with aim to prevent the overflowing of contamination of the landfill site soil with leachate, as well as maintenance of optimum qualitative composition of generated landfill filtrate.

The models of applying remediationtechnologies as well as the very creation of the Plan for sanitation and remediation of contaminated sites vary depending on a particular case, considering the fact that certain specific factors characterize each landfill site in particular the effects of which either directly or indirectly affect the entire process of remediation of contaminated landfill site. The realization of the research has proven that the treatment of the landfill filtrate within the landfill leachate treatment plant is an essential step in the implementation of landfill leachate management system within the solid waste municipal landfills. Also, the above procedure represents an adequate measure of prevention from contamination of landfill site soil.

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Analiza efikasnosti procesa remedijacije zemljišta deponijskog lokaliteta kontaminiranog procednim vodama primenom analize tokova materijala

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I Z V O D

Kod nesanitarnih komunalnih deponija čvrstog otpada, usled nezadovoljavanja zahteva u pogledu vodonepropusnosti i debljine geološke barijere i odsustva implementacije i primene sistema za upravljanje otpadom i procednim vodama, kao i u zavisnosti od vrste i minerološkog sastava geološke barijere, moguća su dva slučaja. Pri prvom slučaju, u okviru sastava geološke barijere dominira nepropusna glina, kaolinit, te krajnji ishod predstavlja izlivanje procednih voda u zapreminu deponovanog otpada, kao i izbijanje istih na površinu deponijskog lokaliteta. Pri drugom slučaju, propusne gline, smektiti, preovlađuju u okviru sastava geološke barijere, te je dominantna infiltracija procednih voda u podzemni tok. U skladu sa prvim slučajem, primenom softvera *STAN* realizovana je analiza tokova supstanci (SFA), primarno kadmijuma, u okviru tri scenarija. Efikasnost remedijacije zemljišta deponijskog lokaliteta kontaminiranog procednim vodama, sa aspekta redukcije teških metala, sa akcentom na kadmijum, primenom *in-situ* i *ex-situ* sistema, predstavljena je u okviru Scenarija 1 i Scenarija 2. Mogućnost i efikasnost direktnog tretmana procednih voda u postrojenju za tretman istih, u slučaju implementacije i primene sistema za upravljanje procednim vodama, predstavljena je u okviru Scenarija 3. Efikasnost redukcije toka kadmijuma ostvarena u okviru Scenarija 1 iznosi 99.04 %, u okviru Scenarija 2 iznosi 55 %, dok u okviru Scenarija 3 iznosi 99.2 %, respektivno. Prevencija kontaminacije deponijskog lokaliteta procednim vodama primenom sistema za upravljanje istim predstavlja optimalnu opciju i poželjnu praksu, dok u slučaju već postojeće kontaminacije deponijskog lokaliteta i neposredne okoline, primenom *in-situ* sistema remedijacije zemljišta deponijskog lokaliteta, na osnovu dobijenih rezultata, ostvaruje se visoka efikasnost, nasuprot primeni *ex-situ* sistema.

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Recycling spent fluid cracking catalysts for rare earth metal recovery - a review

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ABSTRACT

Fluid cracking catalysts (FCC) are widely used in the petroleum industry and generate significant amounts of waste with rare earth (RE), such as Lanthanum (La) and Cerium (Ce). Therefore, proper recycling of these materials is of paramount importance. This review paper highlights the most recent developments in this field regarding the different leaching and separation processes, such as solvent extraction and precipitation. Leaching of these wastes was found to be more effective using hydrochloric acid (HCl) and higher temperatures. On the other hand, the effectiveness of both solvent extraction and precipitation, as separation methods, are dependent on the end result required and strategy used. Regardless, saponified solvent extraction provides extraction with higher efficiency but also less selective. In terms of precipitation, if a mischmetal of La and Ce is the goal, either the double sulphate or the oxalic acid addition method are equally effective on a HCl pregnant solution. Based on these conclusions, a process flowsheet is herein proposed, adaptable to variations in economic feasibility. In addition, several research gaps are identified throughout this review in order to further advance and explore recycling possibilities for FCC recycling.

1. Introduction

Fluid cracking catalysts (FCCs) are components used for hydrocarbon processing in the petroleum industry. FCCs aid in the cracking of large molecules from feedstocks, such as heavy or vacuum gas oil. Although their constitution can vary, they are mainly made of crystalline microporous aluminosilicates also known as zeolites, which are synthetized in such a way as to increase its potential as a catalyst.

The zeolite is responsible for cracking due to its acid sites that can convert molecules to the shorter and desired gasoline range. However, other components are required to pre-crack larger molecules as well as to act as binding agent (Vogt and Weckhuysen, 2015).

Zeolite Y is one of the main types of zeolites used in the industry and is stabilized with rare earths metals (REEs), such as lanthanum (La) and cerium (Ce). These metals not only enhance the catalyst activity but also prevent loss of acid sites due to metal poisoning, mostly vanadium (V) and nickel (Ni).

After reaction at high temperatures, the FCCs are separated from the products and regenerated by burning off the carbon, also known as coke, that has been deposited; therefore, FCCs are continuously regenerated. However, this process cannot be repeated endlessly; due to the harsh temperature and pressure conditions in the reactor, a complete catalyst deactivation eventually occurs. Thus, fresh catalyst needs to be added to sustain the conversion reactions (Ferella et al., 2016).

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The spent FCCs can be rejuvenated mostly by removing impurities, such as V and iron (Fe), which concentrate in the outer surface and reduce the active surface available for reaction. However, despite several developed methods, rejuvenation is not always an option and has limited commercial application, namely due to associated costs (Marafi and Stanislaus, 2008). Once rejuvenation is no longer a possibility, spent FCCs can be reused in other applications without the need of any further processing.

One such reuse option is its application in cement production. It is estimated that FCCs can replace up to 15–20 % of cement content or 10 % of sand without adverse effect (Al-Jabri et al., 2013) although some disadvantages of this reuse are also reported (Soriano et al., 2016).

As a last resort, spent FCCs are still being sent for disposal in landfills. However, the price of such option has been increasing steadily. As a hazardous waste, spent FCCs require several pre-treatments to ensure its safe disposal and to reduce heavy metal leaching (Marafi and Stanislaus, 2008).

Before opting for landfill disposal, metal recovery of spent FCCs should be considered due to the sheer volume of REEs used in the catalyst; in 2008, 1,980 tons of cerium(IV) oxide (CeO_2) and 17,800 tons of lanthanum oxide (La_2O_3) were used for FCC production and it is expected that these values have increased since then (Akah, 2017).

Recycling these spent FCCs with the intention of recovering REEs (La and Ce) have been the subject of recent research efforts. As a result, this review aims to assess the existing literature with a focus on hydrometallurgical processes, to isolate the most efficient yet simple and cost efficient process flowsheet for an environmentally friendly recovery of REEs from spent FCC.

2. FCC recycling process

The process of FCC recycling can be roughly divided in two major steps. The initial step is the leaching process, in which strong acid solutions are used to transfer the metals into a liquid phase. A second step (or series of steps) involves the separation of the REEs from contaminants and, eventually, between them, if desirable, in order to enable their complete recovery. Aspects such as leaching efficiency and the influence of temperature, type of acid, etc. will be explored in an initial section below. Subsequently, two other sections will focus on the most widely used separation methods, namely solvent extraction and selective precipitation.

2.1. FCC leaching

The first stage of REEs recovery from spent FCC or other derivatives is the acid leaching. There is a variety of numerous inorganic acids studied, which may exhibit different leaching efficiencies.

To better assess the performance of different acids as well as other varying conditions, this study compares the performance of several different works dedicated to this matter. Although not a complete meta-analysis, some screening parameters were used to ensure the quality and relevance of potential comparisons. The studies included in Table 1 all have the following characteristics:

- Studies of leaching of spent FCC or FC slag,
- Studies that have individual leaching efficiency values for La and Ce,
- Studies with original data and present in the Scopus database.

Furthermore, to enable a more comprehensive comparison of the data, the molar quantity of the leachant per gram of waste is also reported. Table 1 summarizes the results compiled from studies on FCC acid leaching, reported by increasing order of molar acid used per g of waste.

By analysing Table 1, it can be seen that the lowest values of Ce leaching efficiencies (25 and 53.5 %, respectively) were obtained when nitric acid (HNO_3) and sulphuric acid (H_2SO_4) were used as leachants. However, the same pattern cannot be found for La leaching efficiency. Furthermore, Zhao et al., (2017) also details that preliminary tests indicate that H_2SO_4 and HNO_3 up to 4 M in similar conditions as described in Table 1 are only able to recover around 70 % of existing rare earth elements while HCl is able to obtain 84.3 %. One possible explanation for this difference presented by Zhao et al., (2017) was that chloride (Cl^-) ions have a higher coordination effect than nitrate (NO_3^-) or sulphate (SO_4^{2-}). Another aspect is that HNO_3 and H_2SO_4 are also reported to lead to Ce precipitation, which would require a secondary leaching in order to increase the recovery of this rare metal (Zhao et al., 2017).

Regardless of the mechanism in question, the data in Table 1 suggests that HCl is the most effective mineral acid that can be used for REEs extraction from FCC. This is further confirmed in Innocenzi et al., (2015) where a second leaching with H_2SO_4 did not significantly increase the leaching of REEs.

Little to no conclusions can be made regarding the time and temperature required for leaching. Based on the results of Zhao et al., (2017), 0.5 hours is clearly insufficient for leaching and higher temperatures (60 ºC) are preferable.

The experimental setup and conditions can be difficult to compare. For instance, Wang et al., (2017b) used a preliminary caustic selective leaching of aluminium before the acid leaching, which seemingly increases the efficiency of the latter.

Other aspects can also be seen in Table 1, like the influence of varying the solid-to-liquid (S/L) ratio.

Table 1
Acid leaching of FCC or FC related wastes for La and Ce recovery

Source	Type	S/L ratio (g/mL)	Leachant	mmol H^+/ g waste	Time (h)	T (ºC)	Initial Concentration (%)	La (%)	Initial Concentration (%)	Ce (%)
(Nguyen et al., 2018)	FCC	0.33	HNO_3 2 M	6	1	80	1.82	88.00	0.06	25.00
(Zhao et al., 2017)	FCC	0.20	HCl 2 M	10	2	60	1.92	84.00	0.29	83.00
(Zhao et al., 2017)	FCC	0.09	HCl 1 M	11	9	25	1.69	76.60	1.57	95.50
(Zhao et al., 2017)	FCC	0.10	HCl 2 M	20	2	45	1.92	83.50	0.29	86.40
(Zhao et al., 2017)	FCC	0.10	HCl 2 M	20	2	30	1.92	76.00	0.29	81.00
(Zhao et al., 2017)	FCC	0.10	HCl 2 M	20	0.5	45	1.92	68.10	0.29	72.80
(Zhao et al., 2017)	FCC	0.10	HCl 2 M	20	2	60	1.92	92.00	0.29	96.00
(Zhao et al., 2017)	FCC	0.09	HCl 2 M	22	9	25	1.69	75.80	1.57	94.50
(Zhao et al., 2017)	FCC	0.05	HCl 1 M	22	9	25	1.69	71.38	1.57	90.30
(Innocenzi et al., 2015)	FCC	0.15	H_2SO_4 2 M	26.70	3	25	3.02	61.20	0.23	53.50
(Innocenzi et al., 2015)	FCC	0.15	H_2SO_4 2 M	26.70	3	80	3.02	89.00	0.23	81.70
(Wang et al., 2017a)	FC slag	0.25	HCl 9 M	36	2	20	1.20	91.00	2.40	92.20
(Wang et al., 2017a)	FCC	0.25	HCl 9 M	36	2	20	0.38	86.18	1.60	82.30
(Wang et al., 2017a)	Rey Zeolite	0.25	HCl 9 M	36	2	20	1.10	97.94	4.00	99.90
(Wang et al., 2017b)	FC slag	-	HCl 3 M	-	3	20	3.80	98.60	0.25	98.80

In Zhao et al., (2017), for the same H^+ content (the same number of H^+ moles), it was found that the efficiency of the leaching of REEs increased with the S/L ratio; i.e., the lower volume of acid, which corresponded to a more concentrated acid but for the same quantity of H^+ originated a higher efficiency. Further studies are therefore needed to confirm that acid concentration, not just its molar quantity, affects the leaching process and how.

Yet another aspect is the prospect of leaching both spent FCC as well as the slag from its production and other wastes of similar characteristics. This aspect was explored in depth by Wang et al., (2017a). These authors found similar recovery values of La and Ce from spent FCC, FCC slag and Rey Zeolite despite their different initial compositions. However, the extremely high HCl concentration used can be unpractical. This might be mitigated by increasing the S/L ratio and/or the temperature.

Most studies do not report the extraction efficiency of other metals (e.g. Al) also present in the spent FCCs. This means that there is almost no information on the selectivity of different leaching tests, which limits the analysis of options for subsequent purification of the REEs from the leachate.

2.2. Separation techniques

Following the leaching step, the recycling process for FCC moves into a separation and recovery step: a series of different processes to separate the REEs from contaminants, such as Al, as well as between the REEs, if needed. The following sections will explore the two most widely used processes up to now; aspects related with their performance will also be discussed.

Firstly, the use of solvent extraction will be explored taking into consideration the specific characteristics of the REEs and how these affect the performance. Subsequently, another section will explore the potential of consecutive selective precipitation as a low cost alternative, detailing the most recent research in this field.

2.2.1. Solvent extraction

The separation of REEs from each other and other elements by liquid-liquid extraction techniques have been applied for decades. However, the processes are more complex than for other metals (as it will be explained below) and even more so considering the impurities that are associated in the pregnant solutions of FCC leaching.

This section aims to succinctly explore existing possibilities to overcome difficulties in liquid-liquid extraction techniques and how these might be incorporated into a flowsheet of La and Ce recovery from spent FCC recycling process.

Simple solvent extraction with commercially available extractants has very limited extraction capabilities when applied to REEs. This is because of the characteristics of the metals and its reactions with most extractants as demonstrated below: using 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHEHPA) as an example, REEs react with simple extractant (represented as H_2L_2) according to the following equation (Hou et al., 2016):

$$REE^{3+}(aq) + 3H_2L_2\,(o) \leftrightarrow RE(HL)_3L_3(o) + 3H^+(aq) \tag{1}$$

Considering that most extractants are acidic, the release of H^+ promotes the reverse reaction; therefore, the formation of the REE complex with the extractant is limited. One way to overcome this problem is to partly saponify the extractant.

For the same example of EHEHPA, Hou et al., (2016) was able to determine the molar ratio and the complex formed when the extractant was saponified with ammonia hydroxide (NH_4OH), enabling the description of the following equation 2:

$$2REE^{3+}(aq) + 3H_2L_2\,(o) + 6NH_4L\,(o) \leftrightarrow 2RE(HL)_3L_3(o) + 6NH_4{}^+(aq) \tag{2}$$

In which NH_4L represents the saponified portion of the extractant.

This reaction leads to the release of NH_4^+ instead of H^+, therefore not limiting the reaction as previously mentioned. Other saponification reagents include magnesium oxide (MgO) and calcium hydroxide [$Ca(OH)_2$] (Liu et al., 2017).

Saponified solvent extraction is one of the most widely used purification method for REEs, including La and Ce from both primary and secondary sources (Wu et al., 2010). However, this approach raises some problems. On the one hand, it leads to the production of wastewaters with high quantities of NH_4^+, which requires treatment prior to discharge into the environment (Chang et al., 2010). On the other hand, this approach is limited by the saponification rates, i.e., the extent of saponification: a low saponification rate might mean that the reaction will remain limited while a high saponification may lead to emulsification of the extractant and, therefore, the formation of a third phase, which is also negative and affects the extraction efficiency (Zhao et al., 2017).

Furthermore, several impurities also affect emulsion formation, leading to lower extraction capacities. Several of these impurities are present in spent FCC wastes, such as SiO_2 as well as Fe and most notably Al, which directly and indirectly (for instance, due to the precipitation as

($Fe(OH)_3SiO_2 \cdot NH_2O$) increase and stabilize emulsification (Wu et al., 2010). Due to the limitations of the saponified solvent extraction method, several other avenues have also been explored in liquid-liquid extraction of REEs. One such possibility is the complex induced extraction. This method aims to replace saponification as a solution to the abovementioned issue of H^+ production by adding a complexing agent.

One such complexing agent is lactic acid, which forms several complexes with the REEs and enables the following extraction reaction - equation 3 (Yin et al., 2013):

$$RE(Lac)_x{}^{(3-x)+}(o) + 3\,H_2L_2\,(o) \leftrightarrow REA_3 3HA\,(o) + (3-x)H^+(aq) + xLAC\,(aq) \tag{3}$$

In which ‘x’ represents the number of the moles of the ligand in the REE complex and ‘Lac’ represents the lactate ion. The higher the ‘x’ the lower the H^+ produced.

Several other compounds have been tested, such as citric acid, acetic acid, ethylenediamine tetraacetic acid (EDTA), etc. to name a few (Kashi et al., 2018).

It is reported that the addition of these complexing agents enhance the selectivity among different REEs as well as improves the overall extraction efficiency. For instance, Zhang et al., (2016) found that the presence of 0.6 mol/L of lactic acid combined with the extractant 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester P507 increased the distribution ratio up to 8 times for Ce (at pH 2) and up to 25 times for La (at pH 3.5).

Another strategy that might even allow the use of unsaponified extractant is the synergetic extraction. As the name suggests, it involves the synergetic combination of two or more different extractants in such a way that the extraction efficiency is improved, being higher than the sum of the individual extractants (Song et al., 2009).

For instance, a combination of the extractant 8-hydroxyquinoline (HQ) with bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301) has a La distribution ratio up to 3.3 times higher than the ones observed for HQ and Cyanex 301 when tested independently (Tian et al., 2013).

Zhang et al., (2014) combined both principles using a complex induced synergetic solvent extraction – a mixture of 2-ethylhexylphosphonic mono-2-ethylhexyl ester (HEHEHP) and di-2-ethylhexyl phosphoric acid (D2EHPA), as extractants, and lactic and citric acids, as complexing agents.

In this study, it was found that lactic acid was able to increase the extraction capacity of Ce and La by two-fold for both extractants separately.

However, this value decreased when the two extractants tested were mixed. However, mixing the two extractants with the lactic acid increases the separation factor.

Only a few recent studies have analysed the potential and limitations of liquid-liquid extractions when applied to FCC recycling and metal recovery (Table 2).

Table 2
Solvent extraction applied to FCC pregnant solutions containing La and Ce (pHe – equilibrium pH; SE – stripping efficiency)

Source	**(Innocenzi et al., 2015)**	**(Zhao et al., 2017)**	**(Nguyen et al., 2018)**	**(Ye et al., 2017)**
Extractant	D2EHPA* 20 % (v/v)	D2EHPA* 16 % (v/v)	D2EHPA* + TBP** (4:1 ratio)	EHEHPA*** (20 % saponified w/ammonia)
Solvent	*n*-hexane	kerosene	*n*-octane	kerosene
pHe	2.25	2.5	< 1	3.17
Time (min)	-	10	10	-
A/O ratio	-	1	-	2
La extraction (%)	95	85	72	100
Ce extraction (%)	98		89	100
Al extraction (%)	-	50	0	100
Stripping agent	HNO_3 4 M	HCl 2 M	-	HCl 1 M
SE (%) - La	82	62.88	-	96
SE (%) - Ce	79		-	

* D2HPA - di-2-ethylhexyl phosphoric acid

** TBP - tributyl phosphate

*** EHEPA - 2-ethylhexyl phosphoric acid-2-ethylhexyl ester

To the best of the authors' knowledge, these 4 studies are the only ones that incorporate liquid-liquid extraction into a spent FCC recycling flowsheet. This obviously represents a data gap in this field that needs to be addressed. Based on Table 2, D2EHPA is the most tested extractant with *n*-hexane being the solvent that seems to enable a better extraction performance when compared to kerosene and *n*-octane. However, with *n*-octane and added TBP, a high extraction is possible even at low pH; this extraction was extremely selective to the REEs with no Al being co-extracted. Saponification, as demonstrated in Ye et al., (2017), leaded to very high extraction, but not selective to REEs; under these conditions, all Al was also co-extracted. Stripping performance varies with the different studies, likely a reflection of the different quantities being extracted in the first stage of the process. The challenge is to explore the incorporation of these techniques into a flowsheet of spent FCC recovery taking into consideration the specific characteristics of the leachates that are formed during the process, particularly its impurities.

2.2.2. Consecutive selective precipitations

Another strategy to recover the REEs present in the FCCs leachates is to selectively precipitate them. However, as is the case for solvent extraction, research on this issue remains scarce.

There are two main issues to be addressed: (i) to separate the REEs, La and Ce, from the rest of the impurities and (ii) separate La and Ce from each other.

The choice of one over the other depends on the end use and the necessary purity; a precipitated containing both La and Ce can still be used as a mischmetal for several applications, whilst specific needs require pure La or pure Ce. To accomplish the second option, Ce^{3+} can be selectively precipitated from La and Al by oxidation whilst Al and La remain in the solution. For a simplified simulation of the potential selectivity of this approach, Medusa software (Puigdomenech, 2004) was applied to draw Pourbaix diagrams for Ce, La and Al using data from Zhao et al., (2017). The concentrations considered in this simplified model were: 0.013, 0.002 and 0.48 mol/L for La, Ce and Al, respectively.

Results are represented in figure 1, which shows that Ce can be easily separated and purified from La and Al by raising the redox potential (Eh) to approximately 1.6 V in the pH range between 1.0 and 2.5; under these conditions, Pourbaix diagrams predict that Ce^{3+} is oxidized to Ce^{4+}, which precipitates as cerium (IV) oxide (CeO_2) while La and Al remain soluble as M^{3+}.

However, this strategy, should only be applied if an appreciable amount of Ce is present in the leachate and the ultimate goal is to recover Ce and La with high purity.

For the separation of La and Ce from the rest of the impurities in the pregnant solution, two main options are described in the literature: (i) the precipitation of double sulphate salts – $NaRE(SO_4)_2 \cdot H_2O$ and oxalate precipitation in the form of $RE_2(C_2O_4)_3$. In this case, the main precipitates are either $NaLa(SO_4)_2$ or $La_2(C_2O_4)_3$ for the double salt precipitation or the oxalate precipitation strategies, respectively.

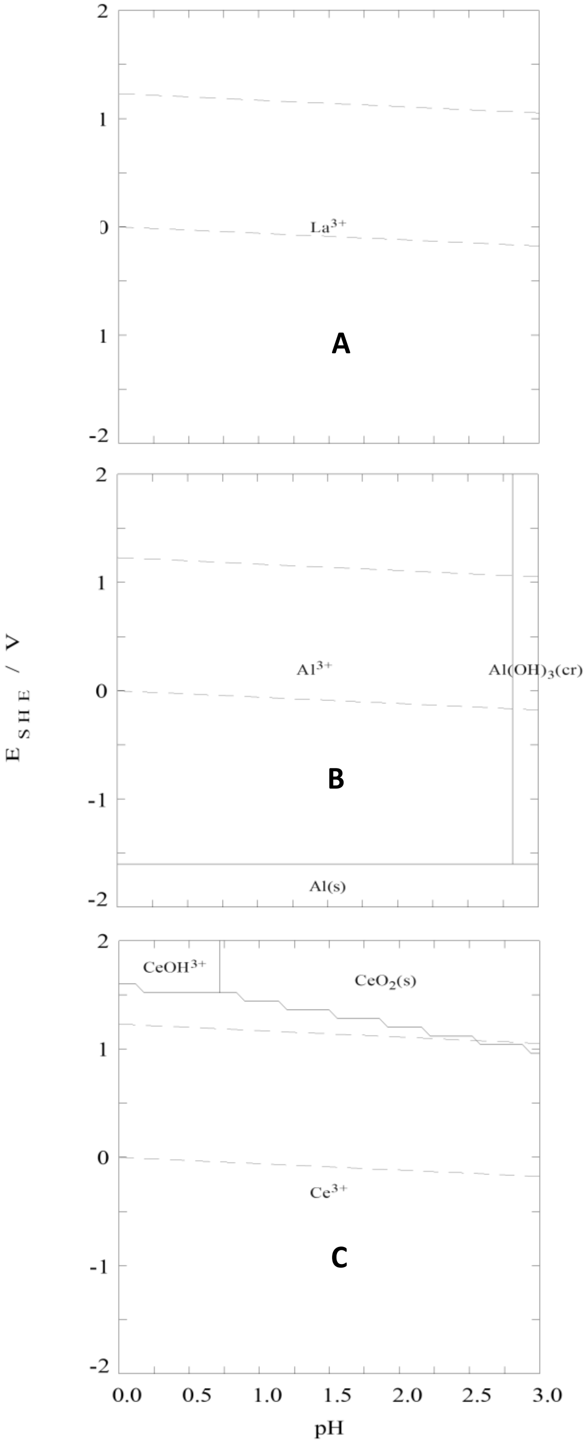

Figure 1. Pourbaix diagrams for Ce (A), La (B) and Al (C) in the pH range 0.0 and 3.0. Initial conditions Al 0.48 M, La 0.002 M, Ce 0.0013 M

Although scarcely, literature describes application of these two precipitation methods for recovering REEs from FCCs leachates. For example, Innocenzi et al., (2015) initially precipitated La and Ce as double sulphate salts by increasing the pH up to 2 after extraction with sulphuric acid. This lead to a precipitation yield of 100 %, with a RE purity between 75 and 80 %.

These authors have also tested oxalic acid precipitation, achieving a precipitate with 37-47 % La and 3.06-3.11 % Ce (w/w) content.

However, this precipitation was only performed after solvent extraction; even though an absolute comparison between the different precipitation approaches is extremely difficult, results suggest that oxalic acid precipitation is capable of yielding a precipitate with higher purity in REEs.

Wang et al., (2017b) performed oxalic acid precipitation prior to any other separation method and was able to achieve a final product with 98.7 % RE purity after calcination. This again seems to confirm that oxalic acid precipitation is capable of producing a final product with very high purity.

Finally, Wang et al., (2017a) tested a sequence of precipitation steps for recovering REEs from a hydrochloric acid leachate. Initially, REEs were precipitated, as $NaRE(SO_4)_2 \cdot H_2O$, using Na_2SO_4 at 300 % of its stoichiometric proportion with 99 % efficiency; under these conditions, only 2 % of Al co-precipitated together with REEs.

Subsequently, this precipitate was converted into $RE(OH)_3$ by reacting with NaOH and then to $RECl_3$ by dissolution in HCl; a final product with a total recovery of 90.2 % of the REEs ready for immediate and direct reuse in zeolite production was achieved. Even though high total REEs recovery with high purity was achieved, the recycling procedure is not simple containing several steps, which consume a huge amount of reagents. In conclusion, further studies seem to be required in order to better assess the potential of consecutive and selective precipitations, particularly considering its potential to substantially simplify the process and reduce operational costs without compromising the final purity of the recycled REEs.

2.3. Process analysis

Potential flowsheet(s) for complete recovery of REEs from spent FCC is shown in figure 2. Initially, an acid leaching step should be implemented in order to extract the REEs from the solid matrix into the aqueous phase as it was mentioned in section for FCC leaching. Literature describes the use of several mineral acids for this purpose but the nature of the anion may affect the yield of the REEs leaching and, consequently, the entire recovery process.

Preferably with HCl, as demonstrated in this article, leaching begins the process creating a solid waste made of zeolite from the FCC (which can, in theory, be reused to produce new FCC if reprocessed) and a leachate containing the REEs, such as La and Ce, plus Al, Si and other minor amounts of other metals, as for example Fe.

This leachate requires further processing with the goal to obtain either pure Ce or La or reusable mischmetals.

As it was discussed throughout this work, solvent extraction can be used either with a single extractant or with a synergetic combination of extractants.

Furthermore, solvent extraction can be also applied through saponified extractants or complex induced to enhance its extraction capacities. However, saponified extractants leads to the production of high-strength wastewater, particularly ammonia, which requires added and more expensive treatment.

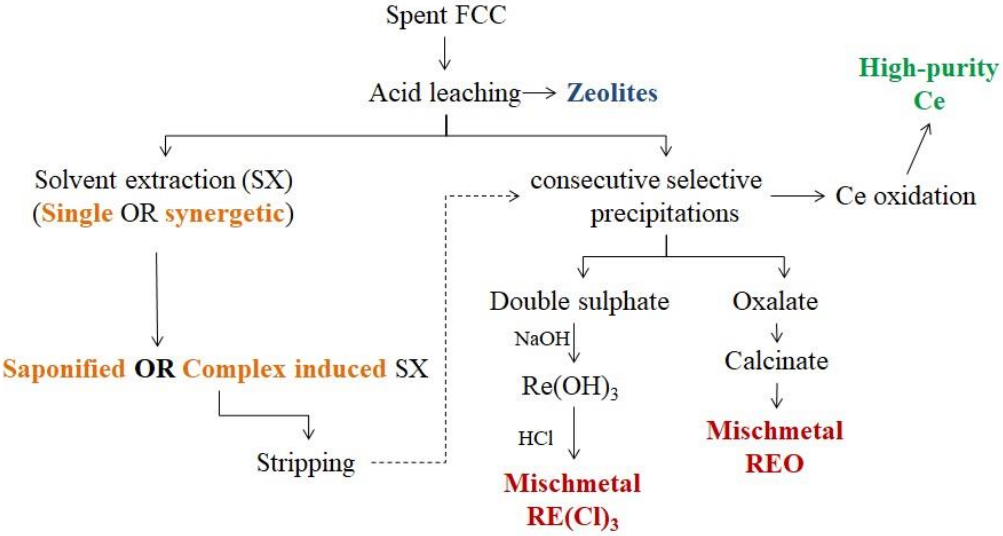

Figure 2. Schematic flowsheet for complete recovery of REE from spent FCC. Legend: Green – final, highly pure products for reuse; Red – final low purity products ready for reuse; Blue – potentially reusable wastes

Regardless of the solvent extraction type, a highly pure solution of La and Ce can be obtained from the stripping step of the solvent extraction, facilitating precipitation.

Alternatively, instead of using solvent extraction, precipitation can be performed directly either by adding Na_2SO_4 to obtain double sulphate salts of Ce and La or by adding oxalic acid or an oxalate salt to precipitate both La and Ce, as well.

Both these strategies required further purification steps. In the case of the double sulphate strategies, one possibility lays on converting the precipitate first to $RE(OH)_3$ (using NaOH) and then finally to an end product mischmetal of $RECl_3$, which is reusable to produce new FCC or other materials (Wang et al., 2017a). In the case of oxalate addition, a calcination step would yield a mischmetal of RE oxides, also directly reusable for FCC production (Geus and D'Appolonia, 2017).

Finally, a selective precipitation to separate Ce from La is also possible, but likely at a higher cost. Through oxidation of Ce^{3+} to Ce^{4+} and consequent precipitation as an oxide, a pure Ce precipitate could be obtained and reused as raw material. The La remaining in the solution could then be precipitated by the other methods referred in this study, preferably through oxalic acid addition plus calcination to obtain a pure La precipitate also ready to be reused as a raw material in the industry.

Considering the current prices of the REEs present in FCC, it seems to be of more practical use to precipitate them at low cost, as oxide mischmetal, to substitute existing mischmetal in the market. However, the proposed flowsheet can adapt to changing prices and market demands, and if prices will increase, the obtainment of pure Ce and/or La may became more advantageous.

3. Conclusion

This review aimed at presenting novel developments in the methodologies of recycling fluid cracking catalysts (FCC) as well as to formulate a tentative process flowsheet.

Regarding leaching and, based on the comparison of different leaching strategies, it can be concluded that hydrochloric acid is the most efficient acid tested across multiple studies. Using this acid, it is possible to extract high quantities of both La and Ce from FCC wastes as well as from FC slag and rey zeolites, two wastes from the FCC production itself.

Furthermore, temperature plays an important role on the extraction efficiency of the REEs during leaching. Some other aspects can be highlighted, although requiring further research, such as the fact that the concentration of acid, and not only its quantity, has a significant impact on the leaching efficiency.

The explored separation techniques for metal selection are characterized by a shortage of recent articles. Still, through a combination of studies in similar fields and the existing studies dedicated to these techniques for FCC recycling, some conclusions can be drawn. Regarding solvent extraction, results suggest that saponified extraction can lead to higher extraction efficiencies but also to a higher wastewater production and lack of selectivity; in this aspect, a compromise between selectivity and extraction capacity will always depend on the subsequent treatments and recycling objectives.

Selective precipitation can also be applied in multiple forms, either through addition of oxalic acid or double sulphate precipitation with similar selectivity, final purity and precipitation yield (although more studies are needed to confirm these aspects further). Similar to solvent extraction, however, the methodology to be adopted depends heavily on the final objectives. Having these multiple possibilities in mind, a process flowsheet was developed and discussed in this study.

The proposed process is adaptable to variations in the price of the commodities to be extracted, in this case the REE La and Ce, with options to increase purity and selectivity, if economically viable, or to precipitate these two metals together into a mischmetal that can be used directly in the industry.

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Dobijanje retkih zemljinih metala recikliranjem istrošenih katalizatora - pregled

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INFORMACIJE O RADU

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Pregledni rad

Ključne reči:
Katalitičko krekovanje u fluidnom sloju
Kiselo luženje
(Saponifikovana) solventna ekstrakcija
Selektivno taloženje
Lantan
Cerijum

IZVOD

Katalitičko krekovanje u fluidizovanom sloju (eng. FCC) koje ima široku primenu u naftnoj industriji proizvodi značajnu količinu otpada koji sadrži retke zemljine elemente, kao što su lantan (La) i cerijum (Ce). Dakle, odgovarajuće recikliranje ovih materijala je od velike važnosti. U ovom pregledu se ističu najnoviji pomaci u ovoj oblasti hemijskih postupaka luženja i separacije, kao što su solventna ekstrakcija i taloženje. Luženje ovih otpada efikasnije je u prisustvu hlorovodonične kiseline (HCl) i na visokim temperaturama. S druge strane, efikasnost solventne ekstrakcije i taloženja kao metoda za separaciju zavisi od traženog krajnjeg rezultata i strategije koja se koristi. Uprkos tome, saponifikovanom solventnom ekstrakcijom se postiže veća efikasnost, ali i manja selektivnost. Što se tiče taloženja, ako je cilj da se dobije mišmetal koji sadrži La i Ce, podjednako je efikasan i metod sa dodavanjem sulfata i oksalne kiseline u rastvor HCl. Na osnovu ovih zaključaka, u radu je predložen dijagram postupka koji je podložan promenama u vezi sa ekonomskom ostvarivošću. Pored toga, u pregledu je uočeno i nekoliko propusta na osnovu kojih mogu da se unaprede i ispitaju mogućnosti recikliranja katalizatora.

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Optimization of biodiesel production from corn oil by methanolysis catalyzed by corn cob ash

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ABSTRACT

The use of low-cost or priceless feedstocks such as byproducts in biodiesel production results in a reduced overall process costs. The present paper reports the use of corn germs and corn cobs as byproducts from corn-based starch production in the biodiesel production by the methanolysis of the oil extracted from corn germs, catalyzed by the ash produced by combustion of corn cobs. The major aim was to optimize the methanol-to-oil molar ratio, catalyst loading, and reaction time in a batch stirred reactor with respect to the content of methyl ester fatty acids (FAME). The statistical modeling and optimization were carried out using a second-order polynomial (quadratic) model developed by the response surface methodology combined with a 3^3 factorial design with 3 central points. The FAME content was determined by a high-pressure liquid chromatography method. The analysis of variance showed that only the catalyst amount, the reaction time, the catalyst amount interaction with reaction time and all three quadratic terms were the significant model terms with the confidence level of 95 %. The optimum reaction conditions (the catalyst amounts of 19.8 %, the methanol-to-oil molar ratio of 9.4 mol/mol and the reaction time of 31 min) provided the FAME content of 98.1 %, which was in an excellent agreement with the predicted FAME content (98.4 %). Thus, both corn germs and corn cobs may be suitable feedstocks for biodiesel production.

1. Introduction

Biodiesel, a mixture of fatty acid alkyl esters (FAAE) that satisfy the prescribed standards, such as EN14240, is commonly produced by esterification of free fatty acids (FFAs) and/or transesterification (alcoholysis) of triacylglycerols (TAG) from various renewable bioresources with methanol or ethanol, in the presence of a catalyst. Because of its growing use (Živković et al., 2017) and almost unchangeable price (Veljković et al., 2018), biodiesel production is expected to expand from $29.7 \cdot 10^6$ m^3 in 2014 to $39 \cdot 10^6$ m^3 in 2024, which is a 27 % increase (OECD/FAO, 2015). The main feedstocks for biodiesel production are oil crops like rapeseed, soybean, and palm oils, which mainly contribute to the high biodiesel production price. Therefore, other oil crops that could grow on marginal lands and produce non-edible oils should be looked for. Besides that, low-

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cost or priceless by-products and wastes of existing production processes, which contains oil, are also interesting as biodiesel feedstocks. Such by-products are, for instance, corn germ in starch production and distillers dry grains with solubles (a part of whole stillage) in ethanol production (Noureddini et al., 2009; Moser and Vaughn, 2012).

So far, corn oil has not been a feasible biodiesel feedstock because of its high value as edible oil and relatively high price despite its huge global production (about 3.2 million tons) (FAO, 2016). However, being a by-product from ethanol or starch production, corn oil is the fastest expanding biodiesel feedstock because its use had increased about ten-fold from 2010 to 2015 (Veljković et al., 2018). The transesterification reaction is most frequently used for the conversion of corn oil-based feedstocks into biodiesel (Veljković et al., 2018).

The transesterification reactions of corn oil over heterogeneous base catalysts are reviewed in Table 1. MgO, ZnO, $Ba(OH)_2$, $ZnAl_2O_4$, KOH, loaded CaO on silica or alumina, and CaO from snail shells have been used as a solid catalyst, while methanol, ethanol, and dimethyl carbonate have been applied as acyl acceptors. Except for the reaction with $ZnAl_2O_4$, the other reactions were conducted at the temperature lower than the boiling point of the acyl acceptor. The highest ester yield (> 96 %) has been obtained from neat and waste frying corn oil with $Ba(OH)_2$ and CaO from snail shells within 2 and 1 h, respectively. The use of cheap but active catalysts is another way to reduce the overall biodiesel production costs, such as ashes generated by combustion of agricultural wastes (Basumatary et al., 2018).

Corn cob ash has been used for preparing silica-based catalysts with potential for complete removal of methylene blue (Velmurugan et al., 2015) or hydrogenation of lignin-derived alkylphenols (Salakhum et al., 2018), but it has not been applied yet as a catalyst in biodiesel production.

The efficiency of biodiesel production processes, leading to the reduction of the production costs, can also be increased by conducting them under the optimum reaction conditions, which are usually determined using the response surface methodology (RSM) in combination with a design of experiment (DoE). This approach has widely been used in recent years for the improvement of the biodiesel production from corn oil. For this purpose, the RSM is usually combined with full factorial (Fernandes et al., 2012; de Lima et al., 2013), central composite (El Boulifi et al., 2010; Ciftci and Temelli, 2011; Moradi et al., 2014; Mustata and Bicu, 2014) or Box-Behnken (Sun et al., 2014) design.

A review of the literature regarding statistical modeling and optimization of biodiesel production from corn oil-based feedstocks are given in Table 2. The present paper deals with the biodiesel production by methanolysis of the oil extracted from corn germs in the presence of the ash produced by combustion of corn cobs; both corn germs and corn cobs are byproducts from corn-based starch production. The major goal of the study is the optimization of the reaction conditions with respect to the methanol-to-oil molar ratio, catalyst loading, and reaction time.

Table 1
A review of the transesterification reactions of corn oil over heterogeneous base catalysts

Catalyst / loading, % to the oil	**Type of acyl acceptor**	**Acyl acceptor:oil molar ratio, mol/mol**	**Temperature, °C**	**Type, volume of reactor, mL / Type of stirrer, stirring rate, rpm**	**Optimal reaction conditions**		**Reference**
					Reaction conditions	**Yield (Conversion), % / Time, h**	
$ZnAl_2O_4$ / –	Methanol	12:1	150–200	Batch reactor – / – 800 (500 kPa)	150 °C	(22.7) / 2	Velázquez, (2007)
	Ethanol				200 °C	(32.5) / 2	
MgO / 2–9	Methanol	10:1 – 30:1	65	Flask, 150 / magnetic, 800	20:1, 5 %	62.61 / 10	Hatefi et al., (2014)
ZnO / 2–11					15:1, 9 %	53.1 / 10	
CaO/SiO_2 / 6	Methanol	16:1	50–65	Flask, 250 / –, 600	60 °C	(85.6) / 8	Moradi et al., (2014)
$CaO/\gamma\text{–}Al_2O_3$ / 6	Methanol	12:1	65	Flask, 250 / –		79.1 / 5	Moradi et al., (2015)
$CaO/\gamma\text{–}Al_2O_3$ / 1–5	Methanol	6:1–12:1	20–65	Flask, 250 / magnetic, 900	12:1, 5 %, 65 °C	(91.58) / 6	Waisi et al., (2015)
$Ba(OH)_2$ / 1.76–4.24	Methanol	5.4:1 – 12.6:1	33	Vessel, 500 / mechanical, 500	11.32:1, 3.6 %	99.15^a / 2	Mustata and Bicu, (2014)
CaO from snails shells^a / 3–9	Methanol	6:1–12:1	60	Flask, 250 / magnetic, 200	6:1, 3 %	96 / 1	El-Gendy et al., (2014)
CaO / 3 %		6:1			–	95 / 1	
KOH / 10–20	Dimethyl carbonate	3:1 – 9:1	65–75	Flask, – / magnetic, –	9:1, 16.3 %, 60 °C	90.9 / 9	Sun et al., (2014)

^{a} Waste frying corn oil

Table 2
The review of the literature regarding to statistical modeling and optimization of biodiesel production from corn oil–based feedstocks

Feedstock[a]	WFCO	CO		CO	CO	CO	CO		CO	CO	
Acyl acceptor[b]	MeOH	MeOH		MeOH	DMC	MeOH	MeOH		EtOH	EtOH	
Catalyst[c]	CaO	CaO/silica		$Ba(OH)_2$	KOH	Lipase	KOH		NaOH	NaOH, KOH	
Design of experiments[d]	D–OD	BBD		CCD	BBD	CCD	FFD	CCD	FFD	fFD	CCD
Number of factors	4	3		3	3	4	2	2	2	6	2
Number of levels	3	3		5	3	5	2	5	3	2	5
Response[e]	EY	EP	EY	EY	EY	EP	EY	EY	EP	EY	EY
Reaction temperature (A)						√	√	√			
Molar ratio (B)	√			√	√	√			√		√
Catalyst amount (C)	√	√	√	√	√		√	√	√		√
Reaction time (D)	√			√	√					√	
Stirring speed (E)	√									√	
Pressure (F)						√					
CO_2 flow rate (G)						√					
Influential factors[f]	B, C, D, B^2, C^2	C, E, C^2	C, E, C^2	B, C, B^2, C^2	ng[g]	A, B, A^2	A, C, A·C	A, C, A·C	B, C, C^2	To screen factors	ng
Reference	El-Gendy et al., (2014)	Moradi et al., (2014)		Mustata and Bicu, (2014)	Sun et al., (2014)	Ciftci and Temelli, (2011)	El Boulifi et al., (2010)		Fernandes et al., (2012)	de Lima et al., (2013)	

[a] CO – corn oil and WFCO – waste frying corn oil. [b] MeOH – methanol, EtOH – ethanol and DMC – dimethyl carbonate. [c] IL – ionic liquid. [d] FFD – full factorial design, fFD – fractional factorial design, D–OD – D–optimal design, BBD – Box–Behnken design and CCD – central composite design. [e] EP – esters purity and EY – esters yield. [f] At the 95% confidence level.[g] ng – not given.

2. Experimental

2.1. Materials

Corn germs, with a moisture content of 3.3 %, were purchased from the ALMEX-IPOK, Zrenjanin, Serbia. Corn germs were ground in a Braun electric grinder for 2 min and sieved through a 0.8 mm screen. The oil was extracted from the ground germs using *n*-hexane. Waste corn cobs were combusted in an oven and the obtained ash was used as a catalyst. Methanol (99.5 %, Zorka-Pharma, Serbia and HPLC grade, Promochem LGC, Germany), *n*-hexane (HPLC grade, Promochem LGC, Germany) and 2-propanol (HPLC grade Carlo Erba, Italy) were used.

2.2. Extraction of oil by maceration

The oil was also extracted from the ground corn germs by maceration. Ground corn germs (200 g) and *n*-hexane (600 ml) were poured into an Erlenmeyer (1000 ml), equipped with a reverse condenser, which was then kept for 15 min in a water bath at 20 °C. After completion of the extraction, the liquid extract was separated from the residual solid material by filtration using a Büchner funnel. The cake obtained after filtration was washed with 200 ml of *n*-hexane. Thereafter, the combined filtrate was evaporated at 50 °C to a constant mass using the rotary vacuum evaporator.

2.3. Methanolysis of corn oil

The base-catalyzed methanolysis of the corn oil obtained by maceration was carried out in a three-necked round-bottom flask (250 ml), equipped with a reflux condenser and a magnetic stirrer, which was placed in a thermostated water bath. The reaction was carried out at the methanol-to-oil molar ratio of 9:1, 12:1 or 15:1, the catalyst concentration of 10, 15 or 20 % (based on oil mass), and 60 °C under atmospheric pressure.

The oil (20 g) and the appropriate amounts of catalyst and methanol were added to the reaction flask and stirred with a magnetic stirrer (900 rpm). The catalyst particles were uniformly distributed in the liquid. At different time intervals during the reaction, samples (0.5 ml) of the reaction mixture were taken to determine the conversion of TAG. The samples were centrifuged (Sigma, Germany) at 3500 min^{-1} (average 700 ×g) for 10 min to separate the ester-oily and alcoholic phases. The upper ester-oil layer was separated and dissolved in a mixture of 2-propanol and *n*-hexane (5:4 v/v) in a ratio of 1:200, and then filtered through a Millipore (0.45 μm) filter for quantitative analysis using an HPLC method (Stamenković et al., 2007). The TAG conversion degree (x_A) was calculated on the basis of the actual and initial TAG contents in the oily-ester phase of the reaction mixture using the following equation:

$$x_A = 1 - TAG / TAG_0 \tag{1}$$

where TAG and TAG_0 are the actual and initial concentration of TAG (%).

2.4. Modeling the experimental results of the methanolysis reaction

The methanolysis of corn oil was investigated at various amounts of catalyst (factor A), methanol-to-oil molar ratios (factor B) and reaction times (factor C) according to a 3^3 factorial design with 3 central points.

The dependent variable (response) was the FAME content in the oily-ester phase of the reaction mixture.

The lower, central and upper coded values of the process factors are designated as (-1), (0) and (1), respectively. The values of the coded and non-coded process factors are shown in Table 3. In order to minimize the error, the experiments were performed in a random order.

The obtained experimental data of the FAME content were modeled by the non-linear regression method using the second-order polynomial equation (Eq. 2), which correlated the dependent variable with the process factors:

$$y = b_0 + b_1A + b_2B + b_3C + b_{12}AB + b_{13}AC + b_{23}BC + b_{11}A^2 + b_{22}B^2 + b_{33}C^2 \tag{2}$$

where y is FAME content, A, B and C are factors, b_0 is the regression coefficient, b_i, b_{ii}, and b_{ij} (i, j = 1, 2, 3) are linear, quadratic, and two-way interaction regression coefficients, respectively. The complete design matrix of the 3^3 factorial design with 3 central points is shown in Table 4, consisted of 30 experimental runs. According to the Kolmogorov-Smirnov normality test, the FAME content data were normally distributed at the 0.05 level of significance.

The obtained experimental data were analyzed by the R-Project software (open source, http://cran.us.r-project.org). Statistical significance of the process factors and their interactions, as well as the applicability of the model, was assessed by the analysis of variance (ANOVA). The influence of the process factors on FAME content was analyzed using the RSM, while the optimal conditions providing the maximum FAME content were determined by solving the regression equation.

Table 3
Process factors

Symbol	Factor	Unit	Level		
			(-1)	(0)	(+1)
A	Catalyst (ash) amount	%[a]	10	15	20
B	Methanol-to-oil molar ratio	mol/mol	9:1	12:1	15:1
C	Reaction time	min	20	30	40

[a] Based on the oil mass

Table 4
Experimental matrix of the 3^3 factorial design with 3 central points

Run	Coded factors			Uncoded factors			FAME, *Y* (%)		
	Factor *A*	Factor *B*	Factor *C*	Factor *A*	Factor *B*	Factor *C*	Actual	Predicted	Relative deviation[a] (%)
1	-1	-1	-1	10	9	20	11.1	8.3	25.2
2	0	-1	-1	15	9	20	42.3	54.3	-28.4
3	1	-1	-1	20	9	20	91.2	81.2	11.0
4	-1	0	-1	10	12	20	17.7	13.6	23.2
5	0	0	-1	15	12	20	59.4	56.03	5.7
6	1	0	-1	20	12	20	73.9	79.2	-7.2
7	-1	1	-1	10	15	20	12.0	5.5	54.2
8	0	1	-1	15	15	20	33.9	44.2	-30.4
9	1	1	-1	20	15	20	64.7	63.8	1.4
10	-1	-1	0	10	9	30	37.6	44.5	-18.4
11	0	-1	0	15	9	30	82.4	81.6	1.0
12	1	-1	0	20	9	30	98.0	99.6	-1.6
13	-1	0	0	10	12	30	44.5	52.5	-18.0
14	0	0	0	15	12	30	96.1	86.0	10.5
15	1	0	0	20	12	30	96.5	100.3	-3.9
16	-1	1	0	10	15	30	43.3	47.0	-8.5
17	0	1	0	15	15	30	77.9	76.9	1.3
18	1	1	0	20	15	30	90.1	87.6	2.8
19	-1	-1	1	10	9	40	69.1	62.5	9.6
20	0	-1	1	15	9	40	92.0	90.7	1.4
21	1	-1	1	20	9	40	98.8	99.8	-1.0
22	-1	0	1	10	12	40	71.0	73.1	-3.0
23	0	0	1	15	12	40	96.6	97.8	-1.2
24	1	0	1	20	12	40	96.5	103.2	-6.9
25	-1	1	1	10	15	40	71.0	70.4	0.8
26	0	1	1	15	15	40	88.9	91.4	-2.8
27	1	1	1	20	15	40	98.2	93.2	5.1
28	0	0	0	15	12	30	80.1	86.0	-7.4
29	0	0	0	15	12	30	94.5	86.0	9.0
30	0	0	0	15	12	30	93.0	86.0	7.5
								MRPD[b] (%)=	±10.3

[a] Relative deviation (%) = (Actual – Predicted) 100/Actual. [b] $MRPD = \sum \left| Relative\ deviation \right| / n$, where $n = 30$

3. Results and discussion

3.1. Development and assessment of the statistical model

First, the adequacy of the possible statistical models was checked by (a) sequential sum of squares, (b) lack of fit and (c) model summary statistic tests. They select the highest order non-aliased polynomial model where the additional terms are significant, the model with insignificant lack of fit and the model maximizing the R^2_{adj} and the R^2_{pred}, respectively. These tests suggested disregarding the cubic models as being aliased (Tables 5-7). Excluding the aliased cubic models, the quadratic model had the highest R^2-value (0.956) among the tested models. This high R^2-value implied the acceptable goodness of fit of the quadratic model. Besides that, the R^2_{pred} -value of 0.895 was in reasonable agreement with the R^2_{adj} -value of 0.936, indicating no problem with the developed model and/or data. Indeed, no outlier was observed in the tested dataset. Moreover, the lack of fit for the quadratic model was insignificant relative to pure error, which confirmed that this model fitted the data well.

Therefore, the quadratic model was accepted for modeling FAME content with the process factors. The ANOVA results are shown in Table 8. The F_{model} - and p -values implied the model was significant, meaning that the model fitted well. The same conclusion was supported by the relatively low *MRPD*–values (±10.3 %, 14 data, Table 4).

According to the ANOVA result, the catalyst amount (A), the reaction time (C), the catalyst amount interaction with reaction time (AxC) and all three quadratic terms (A^2, B^2 and C^2) were the significant model terms with the confidence level of 95 %. On the other hand, the effect of the methanol-to-oil molar ratio (B) and its interactions with the other two process factors (AxB and BxC) on FAME content were statistically insignificant with the confidence level of 95 %.

Table 5
Results of sequential model sum of squares test

Source	Sum of squares	df	Mean square	*F*-value	*p*-value	Remark
Mean vs Total	150,138.6	1	150,138.6			
Linear vs Mean	18,251.3	3	6,083.8	36.90	< 0.0001	
Two-factor interaction vs Linear	1,191.1	3	397.0	2.95	0.054	
Quadratic vs 2FI	2,098.0	3	699.3	14.02	< 0.0001	Suggested
Cubic vs Quadratic	283.9	7	40.6	0.74	0.644	Aliased
Residual	713.6	13	54.9			
Total	172,676.4	30	5,755.9			

Table 6
Results of lack of fit test

Source	Sum of squares	df	Mean square	*F*-value	*p*-value	Remark
Linear	4,125.5	23	179.4	3.34	0.175	
Two-factor interaction	2,934.4	20	146.7	2.73	0.222	
Quadratic	836.5	17	49.2	0.92	0.620	Suggested
Cubic	552.6	10	55.3	1.03	0.556	Aliased
Pure Error	161.0	3	53.7			

Table 7
Results of model summary statistics test

Source	Stand. dev.	R^2	R^2_{adj}	R^2_{pred}	
Linear	12.84	0.810	0.788	0.754	
Two-factor interaction	11.60	0.863	0.827	0.795	
Quadratic	7.06	0.956	0.936	0.895	Suggested
Cubic	7.41	0.968	0.929	0.763	Aliased

Table 8
ANOVA results for the quadratic model

Source	Sum of squares	df	Mean square	***F*-value**	***p*-value**
Model	21,540.3	9	2,393.4	47.99	< 0.0001
A	10,300.9	1	10,300.9	206.53	< 0.0001
B	100.3	1	100.3	2.01	0.172
C	7,850.0	1	7,850.0	157.39	< 0.0001
AxB	157.7	1	157.7	3.16	0.091
AxC	947.0	1	947.0	18.99	0.0003
BxC	86.4	1	86.4	1.73	0.203
$\boldsymbol{A^2}$	633.3	1	633.3	12.70	0.002
$\boldsymbol{B^2}$	310.3	1	310.3	6.22	0.022
$\boldsymbol{C^2}$	567.1	1	567.1	11.37	0.003
Residual	997.5	20	49.9		
Lack of Fit	836.5	17	49.2	0.92	0.620
Pure Error	161.0	3	53.7		
Corrected Total	22,537.8	29			

The quadratic model is as follows:

- Coded factors

$$y = 86.00 + 23.92A - 2.36B + 20.88C - 3.62AB - 8.88AC + 2.68BC - 9.61A^2 - 6.73B^2 - 9.09C^2 \quad (3)$$

- Uncoded (actual) factors

$$y = -406.20 + 24.55A + 18.09B + 9.14C - 0.24AB - 0.18AC + 0.09BC - 0.38A^2 - 0.75B^2 - 0.09C^2 \quad (4)$$

After eliminating the insignificant terms, Eqs (3) and (4) become the reduced quadratic models as follows:

- Coded factors

$$y = 86.00 + 23.92A - 2.36B + 20.88C - 8.88AC - 9.61A^2 - 6.73B^2 - 9.09C^2 \quad (5)$$

- Uncoded (actual) factors

$$y = -394.89 + 22.65A + 17.15B + 10.21C - 0.18AC - 0.38A^2 - 0.75B^2 - 0.09C^2 \quad (6)$$

The R^2-value (0.945) demonstrated a good fitting capability of the reduced quadratic model, which was supported by an acceptable *MRPD*-value (±10.6 %, 30 data). In addition, the R^2_{adj} - and R^2_{pred} -values (0.927 and 0.896, respectively) were high and close enough to each other, implying that the reduced quadratic model represented the experimental data well. This reduced quadratic model was further used for response surface analysis and optimization.

3.2. Response surface analysis and optimization

Figure 1 shows the response surface 3D plots for FAME content as a function of catalyst loading and reaction time at methanol-to-oil molar ratio 12:1 mol/mol resulted from the reduced quadratic model. It was obvious that the FAME content increased with the increase of both catalyst loading and reaction time. The influence of the catalyst amount on FAME content was more significant at a shorter reaction time, while it decreased at a longer reaction time. Such a behavior could be attributed to approaching the reaction to the equilibrium when the FAME formation rate slowed down. The reaction time was more influential at lower catalyst amounts and became less significant at higher catalyst amounts, which was ascribed to the faster reaction rate at a higher catalyst amount because of the higher concentration of catalytically active sites, enabling the completion of the transesterification reaction rate for a shorter reaction time. The significant influence of catalyst amount and reaction time on FAME content was previously reported for the corn oil transesterification over a CaO-based catalyst obtained from snails' shells (El-Gendy et al., 2014) and the corn oil transesterification with dimethyl carbonate over solid KOH (Sun et al., 2014). According to Mustata and Bicu (2014), the catalyst amount had a significant influence, while the effect of the reaction time on the corn oil

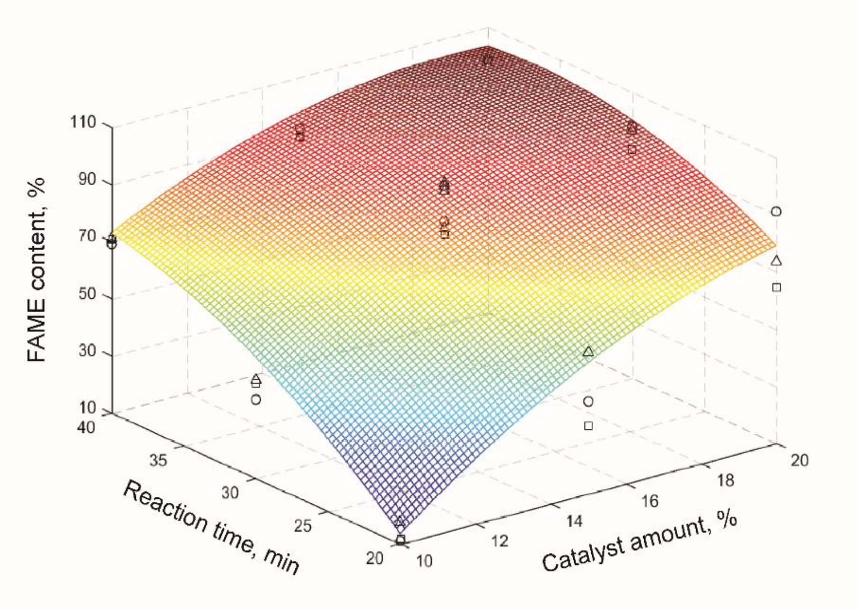

Figure 1. Response surface plot for FAME content as a function of catalyst loading and reaction time (surface corresponds to methanol-to-oil molar ratio of 12:1; actual FAME content at various methanol-to-oil molar ratios: 9:1 – ○, 12:1 – ∆ and 15:1 – □)

conversion was insignificant in the presence of barium hydroxide as a catalyst and dimethyl ether as a cosolvent. Opposite to the present study, the methanol-to-oil ratio was designated in the previous studies as the process factor with a significant influence on the FAME conversion, which could be explained by the differences in the process conditions applied in different studies, such as the presence of cosolvents, the type of acyl acceptor and the range of the experimental conditions.

The optimum reaction conditions for achieving the highest FAME content were determined based on the reduced quadratic model. The FAME content above 98 % could be obtained at the catalyst amount over 15.3 %, the methanol-to-oil molar ratio in the range 9.3 - 14.2 mol/mol and the reaction time longer than 31 min. The optimum reaction conditions were selected as follows: the catalyst amounts of 19.8 %, the methanol-to-oil molar ratio of 9.4 mol/mol and the reaction time of 31 min, under which the predicted FAME content was 98.4 % that agreed well with the experimentally obtained value of 98.1 %.

4. Conclusion

Corn germs and corn cobs as byproducts from corn-based starch production were shown to be the suitable feedstocks for the biodiesel production by the methanolysis of the oil extracted from corn germs, which was catalyzed by the ash produced by combustion of corn cobs. The RSM and the ANOVA showed that only the catalyst amount, the reaction time, the catalyst amount interaction with reaction time and all three quadratic terms had a statistically significant influence on FAME content with the confidence level of 95 %. The optimum reaction conditions were the catalyst amounts of 19.8 %, the methanol-to-oil molar ratio of 9.4 mol/mol and the reaction time of 31 min and provided the FAME content of 98.1 %, which was in an excellent agreement with the predicted FAME content (98.4 %).

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Optimizacija proizvodnje biodizela kukuruznog ulja metanolizom katalizovanom pepelom kurdeljke

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I Z V O D

Upotreba jeftinih ili bezvrednih sirovina, kao što su sporedni proizvodi, u proizvodnji biodizela ima za rezultat smanjene ukupne troškove procesa. U ovom radu su prikazani rezultati upotrebe kukuruznih klica i okrunjenog kukuruznog klipa (kurdeljke, krudeljke) kao sporednih proizvoda iz proizvodnje kukuruznog skroba u proizvodnji biodizela metanolizom ulja izdvojenog iz kukuruznih klica, katalizovane pepelom dobijenim sagorevanjem kurdeljke. Glavni cilj je bila optimizacija molskog odnosa metanol-ulje, količine katalizatora i reakcionog vremena u šaržnom reaktoru sa mešanjem u odnosu na sadržaj metilestra masnih kiselina (MEMK). Statističko modelovanje i optimizacija izvršeni su korišćenjem kvadratnog modela, razvijenog metodologijom odzivne površine, u kombinaciji sa 3^3 faktorijelnim planom sa 3 centralne tačke. Sadržaj MEMK-a je određen metodom tečne hromatografije pod visokim pritiskom. Analiza varijanse je pokazala da su samo uticaji količine katalizatora, reakcionog vremena, interakcije količine katalizatora sa reakcionim vremenom i sva tri kvadratna člana statistički značajni sa nivoom pouzdanosti od 95 %. Pod optimalnim reakcionim uslovima (količina katalizatora 19,8 %, molski odnos metanol/ulje 9,4 mol/mol i reakciono vreme 31 min) dobijen je sadržaj MEMK-a od 98,1 %, koji se slaže sa predviđenim sadržajem MEMK-a (98,4 %). Prema tome, i kukuruzne klice i kurdeljka mogu biti pogodne sirovine za proizvodnju biodizela.

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Micronization of zeolite in vibration mill

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ABSTRACT

Dry micronizing grinding of mineral raw materials is a very complex process and depends on a whole range of parameters such as: shape, particle size, size distribution of the starting and micronized material, hardness, moisture, density, surface properties, structural characteristics of mills, etc. In order to obtain a clear picture of dry micronizing milling process, a good knowledge of the theoretical principles of high-energy mills operation is necessary.

Classical mills are not suitable for micronization to a fine and particularly very fine particles size (upper particle size limit below 5 µm), which is necessary for modern industrial application domains. The intensive fundamental and developmental research of the dry micronizing milling process for the new materials development has also enabled the development of new construction solutions for ultra-fine high-energy mills - mechanics. These mills have found application into the state-of-the-art production technologies of new very profitable materials. For the production of powders - particles of micron dimensions, the mechano-actuators are used and all micronizers - disintegrators, colloidal (perl mills), vibratory, planetary, ultra-centrifugal mill, Jet-current mills and others operate on the principle of impact, shock and friction.

This paper presents the experimentally achieved results of dry micronizing grinding of zeolites in a vibrating mill with rings, as well as the improvement of its reactivity. All experimental micronization investigations were carried out on a previously prepared coarse particle size class (- 3.35 + 0) mm with different starting mass (50 g and 200 g), and carried out in different grinding time intervals (45, 120, 900 seconds), in order to examine the impact of these parameters on the micronization process. Grinding success was evaluated by the particle size measurements and content of class (- 5 + 0) µm, and particle specific surface. It was shown that for a sample of four times larger initial mass it is need longer grinding time to achieve the maximum content of the class (- 5 + 0) µm, but for a sample of the bulk class (- 3.35 + 0) mm with a lower starting mass the effects of amorphization due to prolonged micronizing grinding are very pronounced, and the zeolite minerals in crystalline form are practically in the trace and the largest part is amorphous. Generally, it can be concluded that a vibrating mill with a rings proved to be a good device for efficient ultra-fine micronizing grinding.

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1. Introduction

In the history of humanity non-metallic mineral raw materials were the first natural materials that a man began to use, and most of them until the beginning of the 20th century did not attract attention. Between the two World Wars, and especially during and after the Second World War, there is a significant change in relation to these raw materials, they become increasingly important and necessary to the modern industry. One of such non-metallic mineral raw materials are certainly zeolites that represent precious inorganic material that has a wide range of applications (Andrić, 2014).

Natural zeolites are the most porous crystalline hydrated alumosilicates (tectosilicate) whose structures contain infinite three-dimensional frames. The basis of the three-dimensional network consists of tetrahedral groups SiO_4 and AlO_4 (Johan et al., 2015; Stocker et al., 2017). The adjacent tetrahedrons are bound, at their corners, through a common oxygen atom, making the zeolites structure rich in cavities and channels. The channel opening consists of 6, 8, 10 or 12 oxygen atoms together with the same number of silicon and / or aluminum atoms. Tetrahedral groups are connected in space through common oxygen atoms by constructing secondary polyhedron units whose connection creates a crystalline (alumosilicate) grid (Baerlocher et al., 2007).

The alumosilicate grid is formed by connecting Si(IV)-O and Al(III)-O of the building units, and it is negatively charged. Electroneutrality is provided by the alkali and / or alkaline earth metal cations located inside the channel and the cavity of the grid. These hydrated cations are mainly Na^+, K^+, Mg^{2+} and Ca^{2+} and rarely Ba^{2+} and Sr^{2+}.

Due to poor electrostatic interactions with the alumosilicate gratings, these cations are mobile, and in contact with the solution, they can be easily exchanged with ions from the solution, which gives the zeolites the ion exchanger properties (Jovanović, 2016). Zeolites are actually forms of "molecular sieves" associated with micropores and cavities. Structural empty spaces in the molecular-scale range (3-10 A°) can provide space for receiving cations (Na^+, K^+, Mg^+, Ba^+, Ca^+), and various metal cations, transition metal ions (Co, Fe, Mn, Zn), as well as molecules and ions from the group H_2O, NH_3, CO_3^{2-}, NO_3^-. In the channels and cavities there are also water molecules that can be reversibly desorbed, which gives to zeolites the properties of the drying agents (Alver et al., 2010; Terzić et al., 2017).

Due to their unique structure, zeolites have wide application (Charkhi et al., 2010). Zeolites are inactive in nature, and their adsorption capability and cation exchange capacity are activated by mechanical treatment. Activated zeolites are used as organic products in construction, agriculture and livestock, veterinary medicine, antioxidants and as adsorbents for heavy and radioactive metals, in food, textile and other industries. Zeolites are also used for the separation of gases due to its adsorption potential (Ackley et al., 2003; Wang et al., 2015; Chen et al., 2017), for the collection of unpleasant odors and removing moisture traces from organic solutions, from the rooms and therefore also been used as aquarium filters, purification of water and wastewater containing heavy metals and ammonia (Cooney et al., 1999; Margeta et al., 2013; Kahler, 2014; Ghasemi et al., 2016), gas sorption as catalysts (Tomić, 2016).

2. Micronization milling of non-metallic mineral raw materials

The process of micronizing grinding is intended to grind the mineral raw material to particles of micron dimensions and thus prepare for direct application or for further technological processing. The micronizing grinding process is mainly used for grinding mineral raw materials that have been already crushed and grinded. This process is carried out under the influence of external forces, as is the case with standard grinding (Andrić and Trumić, 2013), and the intensity of the micronizing grinding process depends on the characteristics of the micronized mineral raw material, the purposes and the market requirements regarding the quality of the product. During micronizing grinding there is a decrease in the regularity of particle shape, which reflects in the increase in the content of fine particles at the expense of the large ones. One of the basic factors affecting the shape and interaction of the individual particles content are the type of process and the type of micronizing grinding device which is used (Prziwara et al., 2018). Today, special attention is paid to the effect of micronizing grinding mills, in other words, to the micronized product costs, especially if the mineral resource is low. However, recently, all micronized mineral raw materials, especially non-metallic mineral raw materials, have market value. In the micronizing grinding of non-metallic mineral raw materials, special attention is paid to the following basic parameters of product quality: the content of individual size classes, the specific surface, the average particle diameter, the chemical and mineralogical characteristics. In addition to the bulk, as a basic parameter of the quality of micronizing grinding products, it is necessary to mention other very important parameters: volume mass, surface activity, particle shape, optical properties, etc. The mentioned parameters of the quality of micronizing grinding products depend on the physical, mechanical, chemical and mineralogical properties of the starting materials, such as: structure, texture, resistance, plasticity, durability, hardness, abrasiveness, sagnosticity, elasticity, stickiness (Andrić et al., 2010; Andrić and Trumić, 2013).

3. Material and methods

The micronizing grinding of zeolite was carried out in a laboratory vibrating disc mill „SIEBTECHNIK TS-250“, with rings at 1,000 rpm over a time interval of (45, 120 and 900) seconds. For all laboratory experiments of the zeolite micronization, a grossness class (- 3.35 + 0) mm was used with different starting mass (50 and 200) g and as a characteristic grossness class, the share of the class (- 5 + 0) µm was also monitored. On each micronizing grinding product, the particle size distribution and the specific surface area were monitored all in order to obtain the finest micronized product of improved reactivity.

After analyzing the particle size distribution of micronizing grinding products, X-ray diffraction analysis was carried out to determine and monitor the phase composition of the samples. The samples were analyzed on the "PHILIPS", X-ray diffractometer, the PW-1710 model with a curved graphite monohromator and a scintillation counter. The diffracted CuKα X-ray diffraction intensities (λ=1.54178Å) were measured at room temperature at intervals of 0.02 °2θ and at a time of 1 a in the range of 4 to 65 °2θ. The X-ray tube was loaded with a voltage of 40 kV and a current of 30 mA, while the slots for direct and diffracted beam direction were 1 ° and 0.1 mm.

3.1. Physico-chemical and mineralogical characteristics of the initial zeolite sample

The measured density of the zeolite sample was determined by glass pycnometers, and the average value after three measurements was: ρ=2,186 kg/m^3, which fits the theoretical values for zeolite ρ=2,000 – 3,000 kg/m^3 (Majstorović-Necković, 2015; Mihajlović-Kostić, 2016).

In Table 1, the results of the particle size distribution and the theoretical specific surface area of the initial zeolite sample of the bulk class (- 3.35 + 0) mm are shown.

Table 1
Particle size distribution of the bulk zeolite sample (- 3.35 + 0) mm

	Dry screening		**Wet screening**	
Particle size (mm)	W (%)	D (%)	W (%)	D (%)
- 3.35 + 2.36	17.96	100	14.71	100
- 2.36 + 1.70	14.93	82.04	10.04	85.29
- 1.70 + 1.18	13.21	67.11	9.75	75.25
- 1.18 + 0.85	9.03	53.90	5.18	65.50
- 0.85 + 0.600	7.97	44.87	6.47	60.32
- 0.600 + 0.425	5.93	36.90	4.37	53.85
- 0.425 + 0.300	5.31	30.97	3.82	49.48
- 0.300 + 0.212	3.70	25.66	3.19	45.66
- 0.212 + 0.150	4.18	21.96	3.29	42.47
- 0.150 + 0.106	3.68	17.78	3.36	39.18
- 0.106 + 0.075	3.44	14.10	3.07	35.82
- 0.075 + 0.040	4.56	10.66	5.87	32.75
- 0.040 + 0.030	0.05	6.10	0.29	26.88
- 0.030 + 0.020	0.05	6.05	0.23	26.59
- 0.020 + 0.010	0.15	6.00	0.08	26.36
- 0.010 + 0.005	0.06	5.85	0.17	26.28
- 0.005 + 0	5.79	5.79	26.11	26.11
$\sum$	100.00	-	100.00	-
Calculated theoretical specific surface area, S (m^2/g)	**70.79**		**294.07**	

The particle size distribution of the initial sample of the bulk class (- 3.35 + 0) mm sieving with dry and wet method are significantly different. It can be noticed that when dry procedure is followed, the finest particles formed aggregates (larger particles), which does not occur with wet sieving process. Such a phenomenon leads to a decrease in the content of the finest class (- 5 + 0) µm from 26.11 % to 5.79 %, and therefore, up to four times lower value of the specific surface is obtained.

The determination of the chemical composition of the initial sample of zeolite, was carried out using a standard analytical method. The results of the chemical analysis are given in Table 2.

Table 2
Chemical composition of the initial zeolite sample

Component	**Content, %**
SiO_2	64.05
Al_2O_3	15.29
Fe_2O_3	2.52
CaO	4.82
MgO	1.33
K_2O	0.77
Na_2O	1.27
LoI *	9.86

* LoI - The loss on ignition (LoI) was determined as a weight difference between 20° and 1000° C.

The diffractogram of the initial zeolite sample a polycrystalline powder is shown in Figure 1 and it can be seen that the most prevalent minerals in the analyzed sample are zeolite minerals, while quartz, feldspars and micas are significantly less represented. Of feldspar, plagioclases are more dominant than K-feldspar. From the carbonate minerals the presence of calcite appears in the trace.

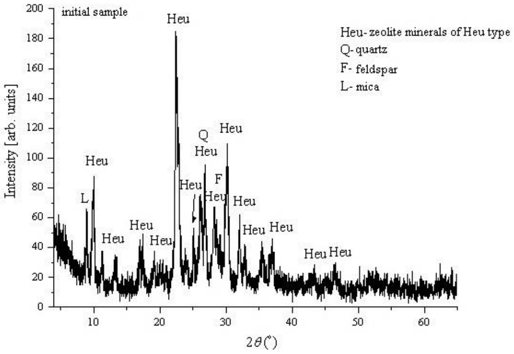


Figure 1. XRD analysis of the initial sample of zeolite

4. Results and discussion

4.1. Micronization grinding of zeolites

The results of the micronizing grinding of zeolite particle size class (- 3.35 + 0) mm are shown in Table 3 and Table 4.

Table 3
Particle size distribution and specific surface of micronized zeolite, bulk class (-3.35 + 0) mm, starting mass 50 g

SAMPLE: **(- 3.35 + 0) mm**	**45 seconds**		**120 seconds**		**900 seconds**	
Particle size, (µm)	W (%)	D (%)	W (%)	D (%)	W (%)	D (%)
- 212 + 150	0.29	100.00	0.80	100.00	3.12	100.00
- 150 + 106	0.29	99.71	0.68	99.20	5.20	96.88
- 106 + 75	0.87	99.42	1.82	98.52	7.69	91.68
- 75 + 30	0.66	98.55	1.55	96.70	2.29	83.99
- 30 + 20	0.45	97.89	0.82	95.15	1.02	81.70
- 20 + 10	0.02	97.44	0.02	94.33	0.12	80.68
- 10 + 5	0.02	97.42	0.23	94.31	0.38	80.56
- 5 + 0	97.40	97.40	94.08	94.08	80.18	80.18
∑	100.00	-	100.00	-	100.00	-
Calculated-theoretical specific surface area, S (m^2/g)	**1.07**		**1.04**		**0.89**	

Table 4
Particle size distribution and specific surface of micronized zeolite, bulk class (-3.35 + 0) mm, starting mass 200 g

SAMPLE: **(- 3.35 + 0) mm**	**45 seconds**		**120 seconds**		**900 seconds**	
Particle size (µm)	W (%)	D (%)	W (%)	D (%)	W (%)	D (%)
- 212 + 150	0.25	100.00	0.54	100.00	7.25	100.00
- 150 + 106	0.97	99.75	0.25	99.46	7.76	92.75
- 106 + 75	2.74	98.78	1.28	99.21	8.85	84.99
- 75 + 30	1.40	96.04	2.16	97.93	1.89	76.14
- 30 + 20	1.83	94.64	1.24	95.77	1.06	74.25
- 20 + 10	0.20	92.81	0.53	94.53	0.69	73.19
- 10 + 5	0.12	92.61	0.61	94.00	1.01	72.50
- 5 + 0	92.49	92.49	93.39	93.39	71.49	71.49
∑	100.00	-	100.00	-	100.00	-
Calculated-theoretical specific surface area, S (m^2/g)	**1.02**		**1.03**		**0.80**	

Based on Table 3, it can be concluded that grinding takes place up to 45 seconds of micronizing grinding. Subsequently, the content of the class (- 5 + 0) µm begins to slowly decrease. Only after 45 seconds of micronizing grinding, the content of the class (- 5 + 0) µm was 97.40 %, but after 900 seconds of grinding the content decreased to almost 80 %, indicating that 17 % of the particles had a larger mean diameter.

Based on the results in Table 4, for a sample of the bulk class (- 3.35 + 0) mm, and the starting mass of 200 g, it can be observed that grinding takes place up to 120 seconds of micronizing grinding. Then, the content of the class (- 5 + 0) µm begins to decrease. After 120 seconds of micronizing grinding, the content of the class (- 5 + 0) was 93.39 %, and after 900 seconds of grinding the content decreased to almost 72 %, indicating that about 21 % of the raw material was reduced.When the particle size distribution of the starting mass 50 g and 200 g (Figure 2) is comparing, it can be noted that for a sample of 50 g a shorter grinding time is required to achieve the maximum value of the class (- 5 + 0) µm. At the starting mass sample of 50 g grinding takes place up to 45 seconds, and the content of the class (- 5 + 0) µm is 97.40 %. For a sample of four times larger initial mass 200 g it is need about 2.5 times higher grinding time to achieve the maximum content 93.39 % of the class (- 5 + 0) µm.

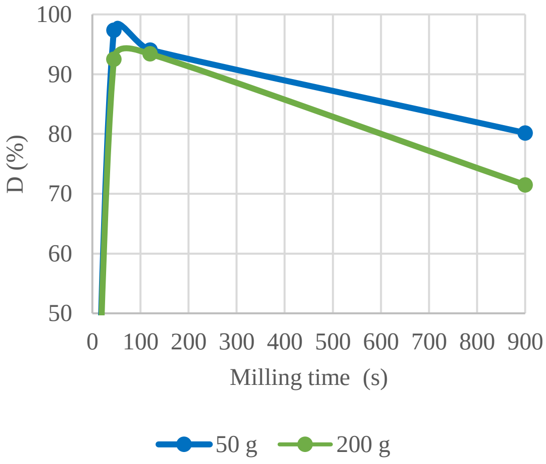
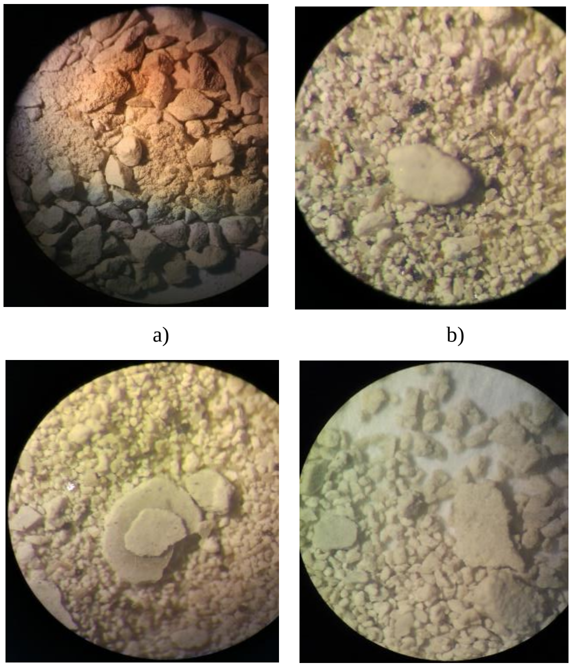


Figure 2. Cumulative mass of the bulk class (- 5 + 0) µm depending on the grinding time

In the ultra-fine micronizing grinding process, the energy consumption is very high. Due to this fact, the ring mill has proven to be an economical device for efficient ultra-fine micronizing grinding. Depending on the starting mass, (50 or 200) g, more than 90 % of the raw material is smaller than 5 µm after only 45 seconds of micronizing grinding, which is better than the results obtained by other researchers. Based on the literature, it was found that various authors in their work came up with the following results: Herceg et al., (2004) carried out tribomechanical micronization of zeolites using equipment designed for tribomechanical micronization and activation (TMA), and only after 60 seconds of grinding, was achieved the 90 % cumulative mass of the class (- 44.12 + 0) µm and of the class (-31.15 + 0) µm at a speed of 16,000 rpm and 22,000 rpm, respectively; Tunç and Demirkıran, (2014) investigated the effects of mechanical activation of the natural zeolite in a planetary mill with balls, and found that after 2 hours of grinding cumulative mass of the class (- 33.16 + 0) µm was 90 %; Burris and Juenger, (2016) performed micronization of zeolites in a gravity mill with balls, and found that after 8 hours of grinding cumulative mass of the class (- 24.3 + 0) µm was 90 %; Terzić et al., (2017) investigated the mechanochemical activation of zeolites in the ultra-centrifugal mill, and found that after 30 minutes of grinding 38.8 % of the raw material, (- 5 + 0) µm, was obtained.

By comparing the obtained results with these from literature it follows that the vibrating mill with rings proved to be a very good solution when ultra-fine micronizing grinding (- 5 +0) µm, is needed.

In Figure 3, a microscopic analysis of the samples before and after grinding were shoved. In Figure 3 c-d, it can be noticed that after micronizing grinding of 120 and 900 seconds the finest particles were formed aggregates.


a) b)

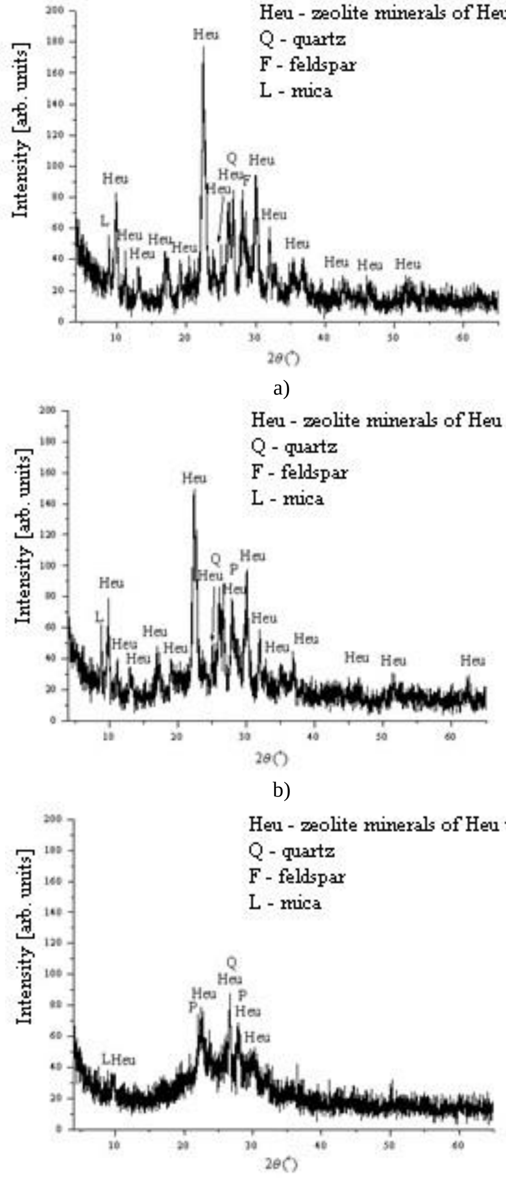
c) d)

Figure 3. Microscopic image of zeolite samples before and after micronizing grinding: a) the initial sample obtained with the x10 magnification; b) the micronizing grinding zeolite sample after 45 seconds obtained at x100 magnification; c) the micronizing grinding zeolite sample after 120 seconds obtained at x100 magnification; d) the micronizing grinding zeolite sample after 900 seconds, obtained at x100 magnification

When comparing the microscopic view of the initial sample of the class (- 3.35 + 0) mm with microscopic images obtained after micronizing grinding of (45, 120 and 900) seconds, it can be noticed that the particles in initial sample has a cubic shape, and after micronization, the majority of the particles changed shape in a spherical, elliptical or irregular shape. The formed agglomerates have a plate shape, which can be seen at Figure 3 c-d.

4.2. XRD analysis

The redgene assay was tested on the initial sample (Figure 1), and on a samples with the starting mass of (50 and 200) g after micronizing grinding (Figure 4 and Figure 5).



a)

b)

c)

Figure 4. XRD analysis of the micronized sample: a) 45 seconds; b) 120 seconds; c) 900 seconds

Figure 4 shows XRD analysis of the micronized sample with a starting mass of 50 g after micronizing grinding process (45, 120 and 900) seconds. It can be noticed that after 45 seconds of grinding the zeolite mineral content has not decreased in relation to the initial sample, and the effects of the amorphization due to grinding are not visible. For micronized sample which was obtained after 120 seconds of grinding, the zeolite mineral content begins to decrease, and the effects of grinding amorphization are poorly expressed. With an increase in grinding time 900 seconds, on the obtained sample, the effects of amorphization due to grinding are very pronounced, and the zeolite minerals in crystalline form are practically in the trace and the largest part is amorphous.

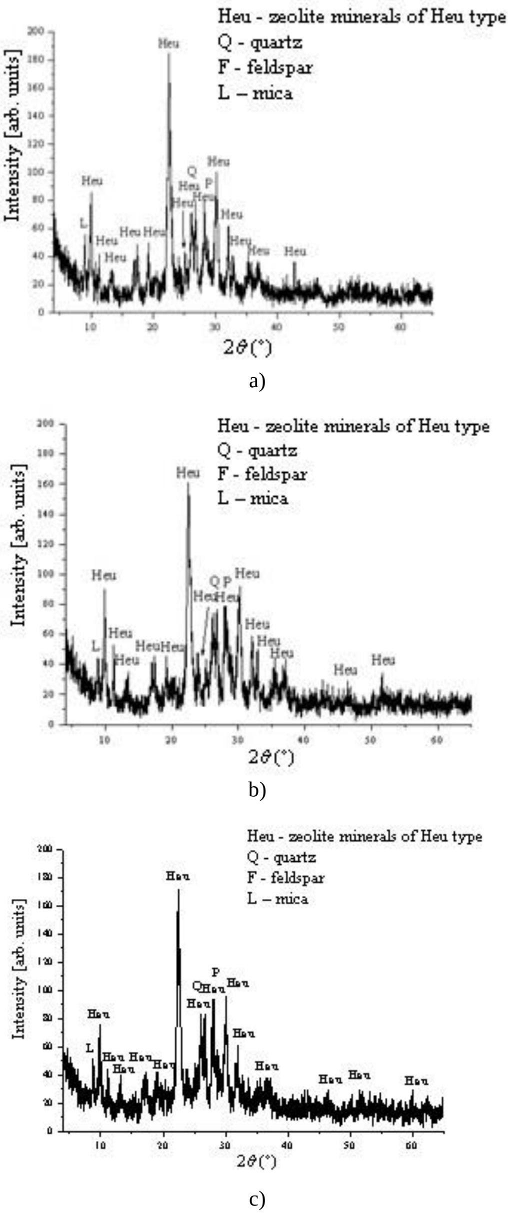


Figure 5. XRD analysis of the sample micronized: a) 45 seconds; b) 120 seconds; c) 900 seconds

Figure 5 shows XRD analysis of the micronized sample with a starting mass of 200 g after micronizing grinding process (45, 120 and 900) seconds.

Figure 5 shows that a micronized samples with 4 times large mass, which were obtained after 45 seconds and after 120 seconds of grinding, have the same zeolite minerals content as well as a sample with smaller mass. The effects of amorphization due to grinding are not visible too. This shows that the sample mass has no effect on the mineralogical composition of the zeolite if grinding takes place in a short time interval. With an increase in grinding time 900 seconds, on the obtained sample, the effects of amorphization due to grinding are not visible unlike a sample of 4 times less mass.

4.3. Reactivity of zeolite during micronizing grinding

By correlation of the operating parameter of the vibratory disc mill and the zeolite micronizing grinding product parameter, the functional dependence of the specific surface area on the micronizing grinding time was formed. This functional dependence shows that as the micronizing grinding time increases, the specific surfaces in all experiments increase to the limit value upon which over time passes into the stationary level, which corresponds to the balance in the ultra-fine micronizing milling.

The results of the functional dependence of the specific surface from the time of micronizing grinding are shown in Figure 6. This analysis also confirms the visual conclusion that after a very short micronization grinding time, particle agglomeration occurs, i.e. the specific surface area decreases.

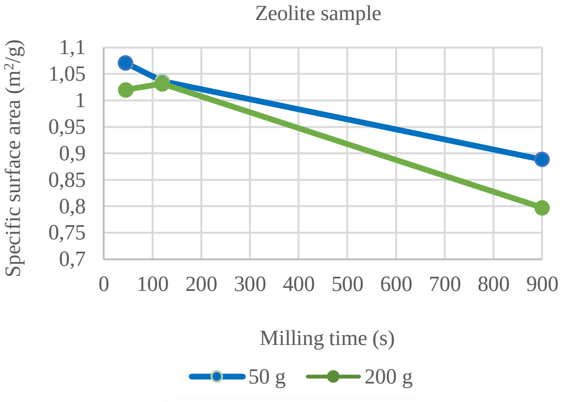


Figure 6. Change of the zeolite specific surface during micronizing grinding

Based on the above, it can be said that the specific surface area parameter is a very important indicator of the micronizing grinding efficiency.

5. Conclusion

Based on experimental research and experimentally achieved results, it can be concluded that the study of micronizing grinding zeolite in the domain of modern technologies is not a simple task, it is complex and very important.

Zeolites after micronizing grinding have wide application, and are especially used as adsorbents, due to the significant power of sorption of metal ions, radionuclides, micotossine. Thanks to their physico-mechanical and physico-chemical properties, as well as their composition and structure, zeolites are also used as ion exchangers, and have been shown to be very powerful detoxicans and antioxidants because of significant capacity to deactivate free radicals.

Based on experimentally achieved results and their analysis, the following conclusions can be made:

- It is important to select a sieving procedure to avoid particle agglomeration. The sieving of micronized products of zeolite should be carried out wet.
- For a sample of four times larger initial mass 200 g it is need about 2.5 times longer grinding time to achieve the maximum content of the class (- 5 + 0) μm.
- For a sample of the bulk class (- 3.35 + 0) mm with a starting mass of 50 g the effects of amorphization due to micronizing grinding (after 900 seconds) are very pronounced, and the zeolite minerals in crystalline form are practically in the trace and the largest part is amorphous.

In this work, complex experimental investigations of the micronizing grinding of zeolite have enabled:

- To determine the kinetic parameters of the vibratory mill with rings in the micronizing grinding process, which influence the appearance of structural defects and the reactivity of zeolites, which can be efficiently used to rationalize process of grinding and the obtaining of high quality zeolites.
- To determine the optimum values of all the most important technological and technical parameters (particle size distribution, mean particle diameter and particle shape, specific surface areas, etc.).
- To establish the correlation of the change in the specific surface and the reaction capacity, determine the changes in the specific surface energy that have a major influence on the flow of the micronizing grinding of the zeolite.

Generally, it can be concluded that a vibrating mill with a rings proved to be a good device for efficient ultra-fine micronizing grinding.

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Mikronizirajuće mlevenje zeolita u vibracionom mlinu

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Aglomeracija
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Zeolit

IZVOD

Suvo mikronizirajće mlevenje mineralnih sirovina je vrlo složen proces i zavisi od čitavog niza parametara kao što su: oblik, krupnoća čestica, granulometrijski sastav polaznog i mikroniziranog materijala, tvrdoća, vlažnost, gustina, svojstva površina, konstruktivne karakteristike mlinova itd. Da bi se dobila što jasnija slika procesa suvog mikronzirajućeg mlevenja, neophodno je dobro poznavanje teorijskih principa rada visokoenergetskih mlinova.

Klasični mlinovi nisu pogodni za mikronizaciju finih i posebno veoma finih čestica (gornja granična krupnoća čestice manja od 5 μm), koja je neophodna za savremene domene industrijske primene. Intenzivna fundamentalna i razvojna istraživanja procesa suvog mikronizirajućeg mlevenja za razvoj novih materijala omogućila su i razvoj novih konstrukcionih rešenja za ultra fine visokoenergetske mlinove - mehano-aktivatore. Ovi mlinovi su našli primenu u najsavremenijim tehnologijama koje se bave proizvodnjom novih profitabilnih materijala. Za dobijanje mikronskih čestica - prahova, koriste se mehano-aktivatori i ostali mikronizeri-dezintegratori, koloidni (perl-atritori), vibracioni, planetarni, ultra-centrifugalni, Jet-strujni mlinovi i dr., koji rade na principu udarnog dejstva, udara i trenja.

U radu su prikazani eksperimentalno postignuti rezultati suvog mikronizirajućeg mlevenja zeolita u vibracionom mlinu sa prstenovima, kao i poboljšanja njegove reaktivnosti. Svi eksperimenti mikronizacije su se izvodili na prethodno pripremljenoj široj klasi krupnoće (- 3,35 + 0) mm sa različitim polaznim masama (50 g i 200 g), i u različitim vremenskim intervalima (45, 120, 900 sekundi), kako bi se ispitao uticaj ovih parametara na proces mikronizacije. Proizvodi mlevenja su praćeni preko granulometrijskog sastava, sadržaja klase (- 5 + 0) μm i preko specifične površine. Pokazalo se da je za uzorak zeolita koji ima četiri puta veću masu u poređenju sa inicijalnim uzorkom, potrebno duže mlevenje za postizanje maksimalnog sadržaja klase (- 5 + 0) μm, ali i da kod uzorka zeolita klase (- 3,35 + 0) mm sa manjom početnom masom su efekti amorfizacije usled mikronizirajućeg mlevenja vrlo jako izraženi, a minerali zeolita u kristalnom obliku praktično su u tragu, odnosno najveći deo je amorfizovan. Generalno, može se zaključiti da se vibracioni mlin sa prstenovima pokazao kao dobar uređaj za efikasno ultra fino mikronizirajuće mlevenje.

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