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VEGETATIVE LANDFILL COVERS AND TREATMENT OF LANDFILL LEACHATE

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Abstract

Landfilling is expected to remain as a waste disposal route in the future at least as a means of disposing different wastes that cannot be reused, recycled or burnt. There are also a lot of existing minicipal landfill sites as well as landfill sites of other sort of wastes, which need to be closed properly, to prevent environmetnal pollution. Conventional cover systems usually consist of a membrane liner, which can be connected with high investment as well as maintenance costs. In the last 15 years so called vegetative landfill cover systes have been introduced exhibiting several beneficial properties. These co-natural vegetative covers can be connected also with co-natural way of landfill leachate treatment in constructed wetlands. In this manner LIMNOTOP® system was introduced combining vegetative landfill cover, constructed wetland for leachate treatment and subsuperficial leachate irrigation on vegetative cover. In the paper, the experiences of a pilot project of sustainable rehabilitation of landfill site with innovative approach of leachate management are presented. The technology enabled sustainable landfill closure and elimination of negative impacts of the landfill site on the environment. The results showed that the irrigation with treated leachate not only reduced water stress of vegetative landfill cover, but also added nutrients, particularly nitrogen, to the soil.

Key words: *municipal waste, leachate treatment, willows, constructed wetland, landfilling*

Introduction

Management of solid wastes has undergone substantial changes during the last 50 years to meet higher environmental requirements. Based on the higher awareness of negative impacts of landfill sites illegal and active landfill sites are disappearing where they were numerous decades ago or are replaced with carefully planned landfill sites. However, improperly located landfill sites, operating or closed, represent a constant threat of contamination of groundwater and surface-water due to leachate production for the next 50 to 100 years. There is therefore a constant need for efficient closure as well as collection and treatment of leachate from solid waste landfill sites to avoid surface water and groundwater contamination.

Traditional approaches to landfill leachate treatment (on-site treatment, transport to off-site facilities) are often undesirable because transport may be dangerous and expensive, while commonly used on-site facilities require high capital inputs and energy or can generate large quantities of by-products (Surface et al. 1993; Higgins, 2000; Bowman et al., 2002). In spite of different views on the leachate treatment, many experts agree that an on-site treatment facility is needed which requires little maintenance or power and is financially less demanding (Robinson and Grantham, 1988; Surface et al., 1993; Higgins, 2000, Rosenquist and Ness, 2004). One low-cost “green technology” is the on-site treatment using constructed wetlands (CWs), widely practiced for many years in a number of countries (Vrhovšek et al., 1996; Robinson et al., 1998; Johnson et al., 1998; Justin et al., 2009a, Justin et al. 2009b).

Another example of “green technology” is application of fast growing tree species with elevated rates of photosynthesis and water usage (Zalesny et al., 2007). Besides woody biomass production (Zalesny et al., 2007), environmental benefits of using fast growing poplars and willow have been realised in riparian buffers along streams, as a vegetative filters for phytoremediation applications (Licht & Isebrands, 2005) or as a evapotranspirative landfill covers (Justin et al., 2009b; Bulc & Justin, 2007). Several phytoremediation projects utilized wastewater in the form of landfill leachate as an irrigation and fertilization source (Zalesny & Bauer, 2007).

Vegetative landfill covers or also called evapotranspirative covers (ET covers) display several advantages over traditional covers using membrane liner. The instalation cost savings can be acchieved by using a local available soil material and by elimation of need of use of separate biointrusion and/or gas collection layer (Rock et al., 2012). Besides, these covers can be less prone to cracking and erosion after freez and thawing cycles due to deep soil layer used, compared to membrane covers with shallow soil layer (Rock et al., 2012). Additional ecsystem services that they may provide are sequestration of soil carbon, production of beneficial habitat as well as opened public places for walking or bikepaths, let alone their higher aesthetic value (Rock et al., 2012).

An example of municipal solid waste landfill site rehabilitation applying all above presented approaches of ecosystem technologies is presented in the following parts of the paper. Landfill leachate collected from the landfill site is first treated in the CW. Additionally, leachate treatment from CW is upgraded with the leachate recycling on vegetative landfill cover, to avoid the release of treated leachate into the environment. Leachate recycling in this case represents a phytoremediation of leachate with assimilation of plant nutrients from leachate into biomass, as well as a sustainable approach toward landfill rehabilitation by enabling leachate infiltration into the landfill body. The technology comprises leachate treatment and recycling to achieve faster landfill stabilization and easier public acceptance of a reclaimed site. The final aim is the reduction of landfill impact on the environment with the closed hydrological and pollution cycle within the landfill site and usage of leachate as nutrient source (LIMNOTOP® technology).

Landfill leachate as an important pollution factor of landfills

In addition to biogas, landfill leachate is a long-lasting and disturbing factor among landfill emissions (Kjeldsen et al., 2002). Landfill leachate is difficult to characterize because its composition and concentrations depend on a variety of factors, such as waste composition, landfilling technology, waste age, closure, geology, temperature, moisture content and other seasonal and hydrological factors (Kjeldsen et al., 2002; Connolly et al., 2004). Leachate is characterized by a very complex composition, including high concentrations of several parameters, such as COD, BOD_5, organic carbon, ammonia nitrogen, chlorides, iron, manganese, phenols, and AOX, but little or no phosphorus. Other compounds may be found in landfill leachate, e.g., borate, sulphide, arsenate, selenate, barium, lithium, mercury and cobalt. In general, these components are present in very low concentrations and are considered only of secondary importance. Leachate may also carry a range of organisms, i.e. bacteria and viruses (Jones et al., 2006). In the early stages, acetogenic liquors have high BOD_5 and COD values, together with high concentration of ammonia nitrogen, posing a serious pollution treat to the environment. In later methanogenic phases of decomposition, these organic compounds are effectively converted to landfill gas, but high ammonia concentrations remain in liquor containing relatively low levels of biodegradable organic material.

Alternative ways of landfill leachate treatment

A very wide range of leachate treatment processes have been applied to leachate treatment, such as extended aeration activated sludge biological SBR processes, reverse osmosis, trickling filters, membrane bioreactors, air/ammonia stripping, chemical precipitation, etc. Each method has its strengths and weaknesses. In the case of the treatment of leachate from old landfill sites with a high COD level, the application of biological methods is only partially efficient. Likewise, it is difficult to reduce the high salinity of leachate by standard biological treatment plants. Commonly used conventional leachate treatment processes therefore require high energy and capital inputs and can generate large quantities of by-products, thus forcing the managers of landfill sites to look for alternative possibilities, especially if the extent of pollution and the volume of emerging leachate are relatively low. Consequently, the managers are searching for and developing sustainable and affordable leachate treatment methods. In such cases, robust, sustainable and affordable facilities enabling on-site treatment of leachate with little labour are more than desirable (Cureton et al., 1991; Bowman et al., 2001; Nixon et al., 2001; Rosenqvist and Ness, 2004; Dimitriou et al., 2006; Llicht and Isebrands, 2005). Moreover, today the principle of sustainable waste management is to apply natural ecological processes to the maximum possible extent and to achieve a closed system with a minimum loss of matter and energy (Bramryd, 1999). Natural processes can be utilized both for the stabilization and detoxification of polluted fractions and for the recovery of energy and nutrients.

Phytoremediation of Landfill Leachate with CW Systems

Constructed wetlands are one of the rapidly developing landfill leachate treatment technologies (Mæhlum 1995; Kinsley et al., 2006). As the numbers of CW grow, an increasing amount of research thought the world is being conducted in order to evaluate the efficiency of treatment wetlands.

Constructed wetlands are known to be effective in removing nitrogen from wastewaters through nitrification/ denitrification, plant uptake and volatilization (Brix, 1993; Sawaittayothin et al., 2007), but compared with the organic matter, NH_4-N is more difficult to remove in CW as nitrification bacteria are autotrophic microorganisms that have a slow respiration rate and require a considerable amount of oxygen to function. Removal of NH_4-N in CW treated with strong landfill leacahte is therefore extremely complicated. It involves a series of physical, chemical and biological processes such as adsorption inside the bed matrix, filtration, pollution sedimentation, ion exchange, plant sorption and microbiological reactions (Connolly et al., 2004). The main treatment mechanisms of nitrification and aerobic removal of organic material are oxygen-limited processes. Studies have shown that plant-mediated oxygen-transfer rates are very small relative to the oxygen demand exerted by the wastewater under common loading conditions. As a result, many current wetland designs neglect plant-mediated oxygen transfer altogether. The limited oxygen transfer capability of standard subsurface flow wetlands has led to the development of enhanced treatment system, that are capable of providing sufficient oxygen transfer for nitrification and removal of organic material, introducing oxygen to the system through frequent water level fluctuation, passive air pumps or direct mechanical aeration of the water in the gravel bed (Nivala et al., 2007).

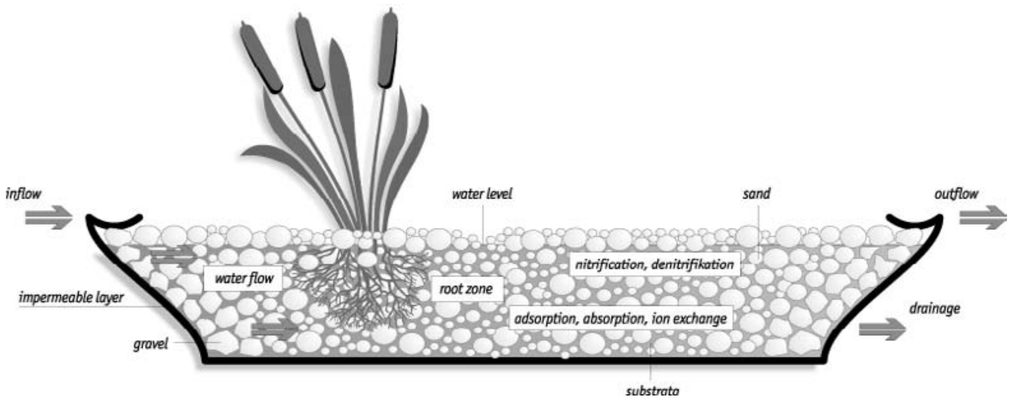

Figure 1. Treatment processes in CW.

Phytoremediation of Landfill Leachate with Dry Land-Based Systems

The treatment of leachate by means of its input into the soil has been examined and practiced in many countries, including Sweden, Finland, Canada, USA and Hong Kong (Bramyrd, 1999; Trapp and Karlson, 2001; Alker et al. 2002; Pulford et.al. 2002; Bowman et.al. 2002; Rosenquist 2004; Pulford and Dickinson, 2005; Licht and Isebrands, 2005; Dimitriou et.al. 2006). Leachate irrigation to land can provide an opportunity for closing the nutrient cycling loop and simultaneously producing effluent of a suitable quality for discharge (Jones et al., 2006). Research has shown that, if grass and wood areas are properly watered with leachate, no contamination of groundwater and nearby watercourses takes place, while substantial removal of ammonium from leachate is achieved (Alker et al., 2002). Moreover, the condition of trees and grass areas does not deteriorate. A controlled input of leachate results in a better provision of soil with nutrients and organic substances, improved growth of vegetation and intensified microbiological activity in soil, including the oxidation of methane (Maurice et al., 1999). No bioaccumulation of heavy metals in plant tissue has been observed to have a negative effect on plant growth (Alker et al., 2002). Today, the phytotechnology employing ligneous plants is used for the treatment of various forms of pollution. In addition to landfill sites, the planting of trees is used for the remediation of watercourse banks, abandoned and polluted industrial areas, at the margins of intensive agricultural areas and other polluted areas, as well as for the treatment of wastewater and sludges (Labrecque et al., 1997; Aronsson et al., 2002; Pulford and Watson, 2003; Mant et al., 2003; Vervaeke et al., 2003; Rawlinson et. al., 2004; Licht and Isebrands, 2005; French et al., 2006). With a large water uptake from soil pores, plants take up also water pollutants and create a new capacity for water accumulation in soil. Poplars and willows take up various pollutants and nutrients (nitrate, ammonium, phosphorus), metals, metalloids, petrochemical compounds (fuels, solvents), pesticides and soluble radionuclides (Licht and Isebrands, 2005; Justin et al., 2005). The rhysosphere and the roots environment are populated by microorganisms and soil fauna, which degrade organic substances and in this way produce a source of plant nutrients, while plant roots provide essential nutrients and organic carbon for the growth of microorganisms. The methods used for the treatment of leachate are vegetation filters, vegetation caps and short rotation coppices (SRC) with fast growing tree species.

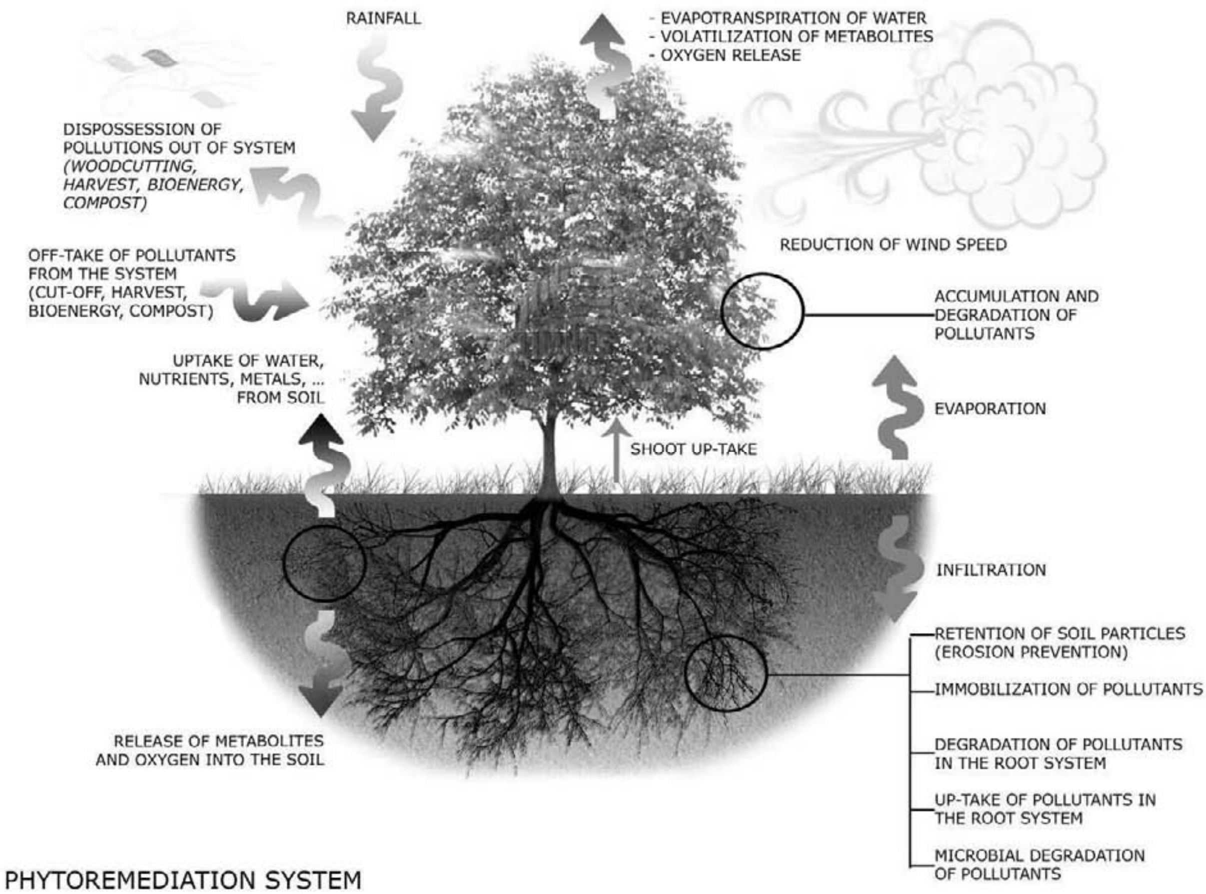

Figure 2. Phytoremediation processes on dry land-based systems like vegetative covers.

Demonstration Of Sustainable Landfill Site Rehabilitation

Rehabilitation steps

Presented below are the results of 18-month monitoring of the municipal landfill site Ormož, in the southeastern part of Slovenia, where the rehabilitation of 1.1 ha of landfill area has been carried out.

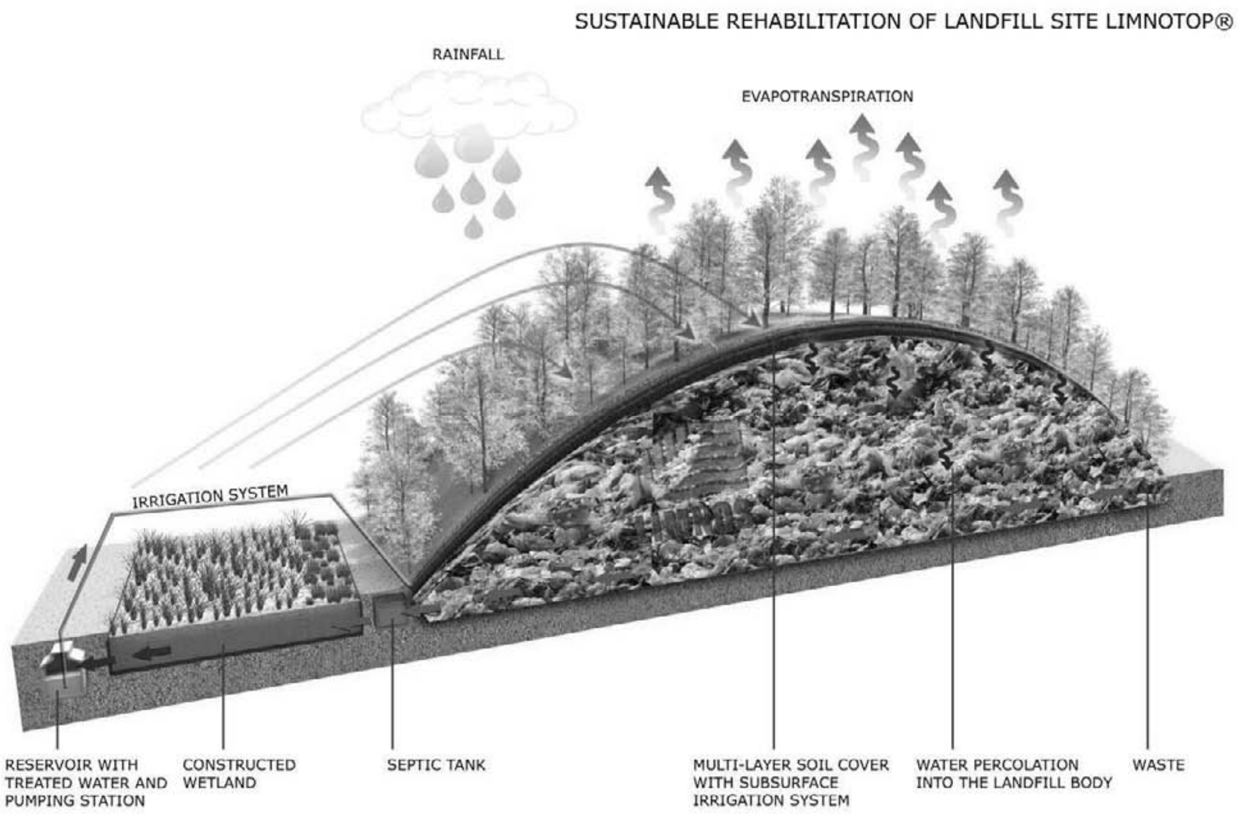

Figure 3. Demonstration of sustainable landfill leachate management, Ormož, Slovenia.

Complete rehabilitation of municipal landfill site was composed of (1) excavation and transposition of old wastes, (2) installation of underground water drainage, (3) sealing of the landfill bottom, (4) installation of collection and drainage system for leachate on the landfill bottom, (5) refilling of landfill body with wastes, (6) compaction of wastes, (7) surface sealing of wastes with surface water and landfill gasses drainage, (8) establishment of final soil and evapotranspirative cover with planting of trees, and (9) installation of irrigation system for the recirculation of treated leachate for irrigation of trees. Collected leachate from the landfill body flowed from the drainage system into the compensation tank and then into the beds of the CW. Treated leachate from the CW outflow was collected in a reservoir equipped with a pump for recycling. Water form collecting reservoir flowed to the pumping system from where it was pumped through the gravel filter onto the landfill site. The pipes of the irrigation system were placed in the depth of 30 cm. The landfill cover consisted of several soil cover layers. Willows (Salix spp) were planted with planting distance of 3 m between rows and 1 m within rows. In-between grass mixture was planted with 5% of white clover.

Analysis of leachate composition

Composition of raw leachate collected from the landfill site is presented in the Table 10 as influent concentration entering on CW. The same table presents the effluent concentrations from CW, its treatment efficiency and average concentrations of leachate parameters, recycled back on the vegetated landfill cover which are important for dry land-based phytoremediation system. Mass load of parameters was calculated upon measured monthly amounts of recycled leachate, which ranged between 9 – 87 l/m^2.

The concentration of other metals, not presented in the table were low, with calculated monthly mass-load for Cr 0.08 kg/ha and for Ni, Cu and Zn 0.03 kg/ha, while for Cd, Pb and Hg mass-load could not be calculated due to their concentration in leachate below detection limit. The concentrations of xenobiotic organic compounds (heavy volatile lipofilic substances, BTX, AOX, volatile chlorinated hydrocarbons, polar organic solvents, phenols, tensides, and pesticides) were also measured and were always below the required normative for the outflow into the running waters; pesticides were never detected.

Table 1. Composition of leachate entering (influent) and leaving (effluent) the CW presented in concentration ranges, treatment efficiency (%) and average concentrations of parameters in leachate used for irrigation during 18-month period. In the last column calculated monthly mass-load of parameters with leachate on the landfill cover is given based on ten-month measurements of irrigation rate. All values are in mg l^{-1} except pH.

	Influent	Effluent	Efficiency (%)	Irrigation average	Mass-load (kg ha^{-1} $month^{-1}$)
pH	7.31-9.73	7.5-8.2			
COD	501-3300	264-2300	34.5	842.13	
BOD_5	34-490	13-280	55.2	74.4	
NH_4^+	110-488	44-466	37.2	184.44	58.52
tot-N	151-616	734-440	36.6	234.45	79.36
tot-P	0.44-6.8	0.44-2.5	48.6	1.05	0.46
Na^+	363-1310	253-1360	22.7	518.07	157.97
K^+	290-1594	210-1634	27.9	577.0	214.89
Ca^+	20-157	20-147	16.3	64.47	12.51
Mg^+	21-124	20-126	18.7	54.13	9.761
Cl^-	296-1994	271-2227	25.1	836.47	331.68
B	1.25-10.68	0.55-5.70	33.8	2.77	0.79
Fe	1.64-16.41	0.53-23.54	38.2	5.6	1.12

Evaluation of the plant respons on irrigation with landfill leachate

To evaluate plant response on leachate irrigation, a remote sensing of the canopy reflectance was performed by ground-based monitoring of vegetation indices of the phytoremediation system with a multispectral camera (Tetracam, USA). Images were taken in regular monthly intervals during one vegetation season, from April to October after two years of leachate irrigation. The images were processed with computer software (PixelWrench, USA) to calculate average Soil Adjusted Vegetation Index (*SAVI*, Huete 1988). Vegetation indices were designed to enhance the vegetation signal from measured spectral responses by combining two (or more) different wavebands, often in the red (0.6-0.7 μm) and near-IR wavelengths (0.7-1.1 μm). Stress is indicated by progressive decrease in near-IR reflectance due to water loss and increase in red reflectance due to lower rates of photosynthesis. One of the most commonly used vegetation indices is *SAVI*, which was designed to minimize the effect of the soil background (Equation 1). The resulting images were analyzed to evaluate the performance and vitality of the vegetative cover at a given time and to monitor its temporal dynamics by comparing different images.

$$SAVI = \frac{(NIR - R)(1 + L)}{NIR + R + L}$$

Equation 1. SAVI: Soil Adjusted Vegetation Index; NIR: Near-IR reflectance, R: red reflectance, L: arbitrary parameter (for high vegetation cover, the value of L = 0.0, and L = 1.0 for low vegetation cover; for intermediate vegetation cover L = 0.5, and that is the value which is most widely used).

The dark green on the color scale indicates high vegetation indices, pointing to high photosynthesis rates and that plants are well provided with water. A photo in the upper part of Figure 4 shows the remediated part of the landfill planted with willows and irrigated by landfill leachate, shown in the central part of the photo. The right side of the photo shows a natural growth of ligneous plants on the same soil as used for covering the landfill site. The lower part of Figure 1 presents two SAVI snapshots from the beginning and the end of growth period (June, September). The dark green color of the remediated part of the landfill site irrigated by leachate indicates that vegetation in this part has significantly higher indices than the vegetation in the ruderal site. The index of vegetation watered by leachate exceeded 0.8, which is characteristic of forest stands at the peak of growth season. The SAVI indices of irrigated vegetation indicate the vegetation growing on nutrients rich soil with no evident seasonal variations in temperature and precipitation. The SAVI values in the ruderal site were constantly low, with a characteristic fast growth in spring and decreasing evenly in subsequent months.

In spite of high mass and hydraulic load during the remote sensing observation period, which followed previous two years of leachate irrigation on the rehabilitated landfill site, *Salix spp*. showed high plant vigor estimated from SAVI indices. The obtained results confirmed the findings that leachate can be a good fertilizer for short rotation coppice produced elsewhere for energy crops. The macronutrient requirements of willow, in relation to nitrogen set to 100, were found to be for N:P:K in relation to 100:14:72. The N:P:K ratio usually found in leachate range from 100:0:54, respectively (Duggan, 2005) to 100:1.5:103 (Dimitriou et al. 2006). The N:P:K ratio calculated from the average concentration of nitrogen, phosphorous and potassium in our leachate analyzed during 18-month period was 100:0.5:246, respectively. The potassium concentration was found in excess and phosphorous concentration was low as it is common for leachate. The lack of phosphorous on plant growth is usually expressed in long term period (>10 years) and its deficiency could therefore not had been expressed during our observation.

Beside macronutrient imbalance, the strength of leachate applied to the landfill vegetative cover with an electrical conductivity (EC) between 3.38 and 11.75 mS/cm was also high. While Cureton et al. (1991) observed detrimental effects on willows (chlorosis of early season foliage, extensive necrosis, leaf desiccation) after applying leachate over two seasons with an EC of 8.89 mS/cm. No such symptoms have been observed in our case. The reason can be in an underground irrigation system applied in our case, instead of spray irrigation for which negative effects were found on plant growth.

The amount of precipitation and leachate recirculation also during the winter period enabled sufficient salt leaching to the deeper waste layers and prevented accumulation of salt ions in the soil which could cause ionic or osmotic stress. Regarding the EC, already lower concentrations (2 - 4 mS/cm) were considered detrimental when irrigated onto tree crops (Dobson and Moffat, 1993). Our observation indicates that it is difficult to predict which concentration will become harmful to plants in a field situation, where the plants have access to sufficient water supply and a large pool of plant nutrients in the soil. Additionally, a range of factors interact with each other in the soil, like precipitation with diluting effect upon the leachate and buffering capacity of the soil, which would allow undiluted leachate to be applied to vegetation cover (Duggan, 2005; Dimitriou et al., 2006).

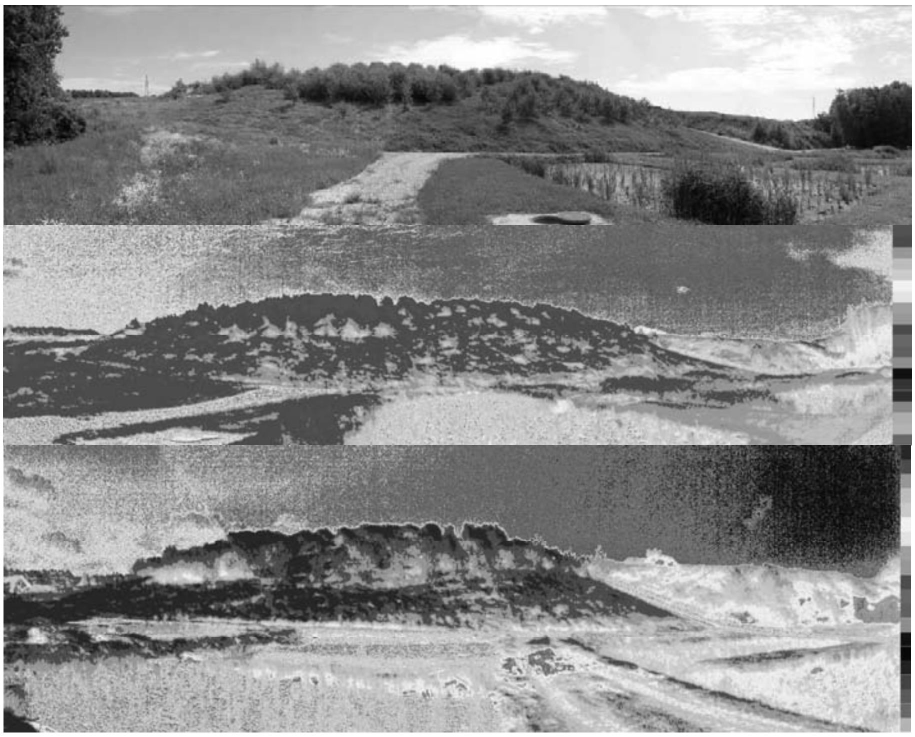

Figure 4. Photography of rehabilitated part of landfill site planted with willow trees with CW in front from July and SAVI image taken in June and September.

Cost analysis

Profound economic analysis of leachate purification through willow-coppice vegetation filters has been performed by Rosenquist and Ness (2004) for a 24 ha willow-coppice plantation site purifying an average annual quantity of 195,000 m^3 of leachate with an average nitrogen content of 24 g/m^3. Their results showed that facility leachates could be purified at 0.34 US$/$m^3$ compared with 0.62 US$/$m^3$ for that of conventional leachate treatment at wastewater treatment plant. Income from willow growing and sale of the biomass chips additionally decreased costs to 0.326 US$/$m^3$. Leachate irrigation was performed in their case only during the vegetation season due to winter dormancy of trees and sensitivity analyses demonstrated that, because of large holding pond expense, only a fraction of facility leachate should be treated through a vegetation filter. In the case of presented LIMNOTOP® system leachate was recycled all year round, using the water-holding potential of soil landfill cover, landfill body and CW during the low evapotranspiration period of the system. The construction cost of CW (1000 m^2), the establishment of an irrigation system on the landfill cover and the vegetation cover per 1 ha was calculated at 92,515 US$, 44,215 US$ and 23,128 US$, respectively. Annual maintenance and operational costs for leachate treatment with CW were 0.483 $/ m^3 and the annual costs of maintenance of vegetation cover were calculated at 1,633 US$ per 1 ha landfill cover.

Conclusion

Experiences with leachate treatment in CW using a simple gravitational subsurface flow (vertical and horizontal) showed that the system can be efficiently used for low strength leachate of closed landfill sites (Bulc et al., 1997). However, the system's efficiency is greatly influenced by environmental conditions (amount of precipitation and temperature), conditions within the CW (maturity of the system), and leachate composition (Bulc, 2006; Mæhlum, 1995). In the case of high leachate strength and high ammonium concentrations, the system can not always reach the normative for discharge into the environment. In this case CW should be upgraded with additional aeration steps in the purification system (Pendleton et al., 2005), used as a tertiary system (Higgins, 2000; Connolly et al., 2004), or as a system for conditioning the leachate and retention of hydraulic peaks before the irrigation of vegetative landfill cover as it was presented with LIMNOTOP® system.

Considering the state of landfill sites in Slovenia as well as in the other parts of the world, there are many possibilities for the application of the presented LIMNOTOP® approach to landfill closure and leachate management. The establishment of a vegetative landfill cover with closed-loop leachate management system provided a multi-purpose ecoremediation system, contributing to: (1) the removal of excess landfill leachate generated in the landfill site; (2) the purification of landfill leachate by phytoremediation of plants, by geochemical processes and by bioremediation of the microbial population in the substrate and soil; (3) the usage of leachate as a nutrient source to create potentially useful biomass, which can represent a renewable source of energy, soil amendment for landfill caps or simply a carbon sink for atmospheric CO_2; (4) the improvement of the landfill mineralization processes by allowing further anaerobic decomposition of waste and its stabilization; and (5) the establishment of a diverse biological community and an acceptable landscape appearance. The results provided an environmentally and economically-viable solution, with large buffering capacity and simple in concept. It is easy to adapt the system for different hydraulic loads, is inexpensive to construct and easy to operate and maintain, with little or no energy demand. The presented methods won several international and national awards (2001 Lillehammer Award – EUREKA – the industrial developing program, Madrid, Award for the environmental technology, Chamber of Commerce, Ljubljana, Slovenia, 2005).

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STATISTICAL MODELING OF FUTURE MUNICIPAL SOLID WASTE ENERGY POTENTIAL IN MONTENEGRO

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Abstract

This paper predicts and evaluates a municipal solid waste (MSW) energy potential in Montenegro produced by modern European (EU) integrated waste management system for the next 25 years. Nowadays growth of gross domestic product (GDP) leads to the higher generation of MSW, which must be handled in a proper and prudent manner. Thus it is very important to utilize integrated waste management system; it's not enough to just collect and dispose MSW to landfill. Based on EU directives such handling is not enough, because the waste needs to be treated properly and full advantage of its potential must be employed before disposal on landfills. The most appropriate way is material and energy utilization of MSW after mechanical – biological treatment (MBT). The combustible or light fraction of residual waste produced in MBT process can be used for energy generation. This domestic energy source saves other conventional types of energy, reduces emissions of pollutants and greenhouse gases.

Key words: *MSW, energy from MSW, incineration, environmental protection, integrated waste management system, statistical modeling.*

Introduction

Nowadays the increasing living standard of the society and thus a larger GDP reflects the increasing amount of MSW. Currently every inhabitant in Montenegro produces a little less than a kilogram of MSWdaily andin the future this amount will increase. Taking into account the average heating value of MSW this equals to around a quarter of liter of heating oil daily or almost one-hundred liters annually per capita. This is currently in Montenegro the untapped energy potential, which is partially disposed of in landfills across the country, a part of these MSW end up on illegal dumps where causes problems with greenhouse gase production and leachate, which heavily pollutes the groundwater. The utilization of this energy source represents a great challenge at national level. Waste-to-energy processes represent an important step towards utilization of available energy sources and reduction of energy import dependence. EU and national legislation provide accurate definitions and requests how to use this valuable resource, which is also partly a renewable source of energy.

In modern societies all citizens and its MSW are included in the process of integrated waste management system. For average citizen the waste management system ends when MSW is slipped into a container but a lot still need to be done. The waste management hierarchy should be followed, which dictates several steps and the first step in reducing the quantity of MSW, second is reuse and third recycling. Forth step is the energy utilization, yet at the end is disposal at landfills.
Currently, his disposal in the whole Montenegro is the only waste management system beside collection, which means that the total amount of collected MSW is disposed of on landfills, because landfill is the simplest, cheapest and most cost-effective method of disposing waste [1]. Utilization of MSW energy is environmentally and energetically justified. However, it is necessary to meet all legal requirements. Generated heat can be used for power (electricity) generation, hot water production for heating and coolness medium production for cooling. Establishing a comprehensive regional management system for MSW and its energy utilization in Montenegro is now inevitable and it is only a matter of time when it actually build.

Potential future integrated waste management system in Montenegro

The purpose for the construction of regional recycling centers in Montenegro is to provide the conditions that will allow modern and environmentally friendly waste management in all regions. The common solution for the problem of MSW has to be approached in a comprehensive manner. In the designing of environmentally acceptable and economically efficient MSW management it is necessary to integrate and coordinate all processes of the waste management. The integrated waste management system should be designed in such way that it in ecological and economic rational way meets the requirements of the legislation with regard to environment protection, which are:

- ✓ waste reduction,
- ✓ reuse and recycling,
- ✓ energy recovery (thermal treatment with efficient use of energy)and,
- ✓ disposal of treated residual waste at the appropriate landfill.

In accordance with these guidelines best available technology (BAT)must be designed specific for the region conditions. At the same time it is necessary to respect the current situation and predict the future state, when the project is implemented and in operation. Thus, it is necessary to provide adequate technological and logistical support:

- ✓ separate collection,
- ✓ sorting separately collected fractions,
- ✓ composting of separately collected biodegradable waste,
- ✓ MBT of residual waste and production of light (combustible)fraction and heavy (inert) fraction,
- ✓ incineration of light fraction,
- ✓ disposal of ash, slag and biologicaly stabilized heavy fractions.

Light fraction of waste, which is interesting as a fuel, is made from a variety of basic fractions (paper, cardboard, plastic, foil, textiles, wood, etc.) are separated in the MBT facility and represents a fuel for waste – to – energy (W-t-E)combined heat and power (CHP) plant for heat and power generation, or a substitute for conventional fuels in large industrial boilers and furnaces.
The scheme in figure 1 represents the material flow of MSW through generalized integrated waste management system. Technological processes in practice follow themselves as shown in Figure 1.

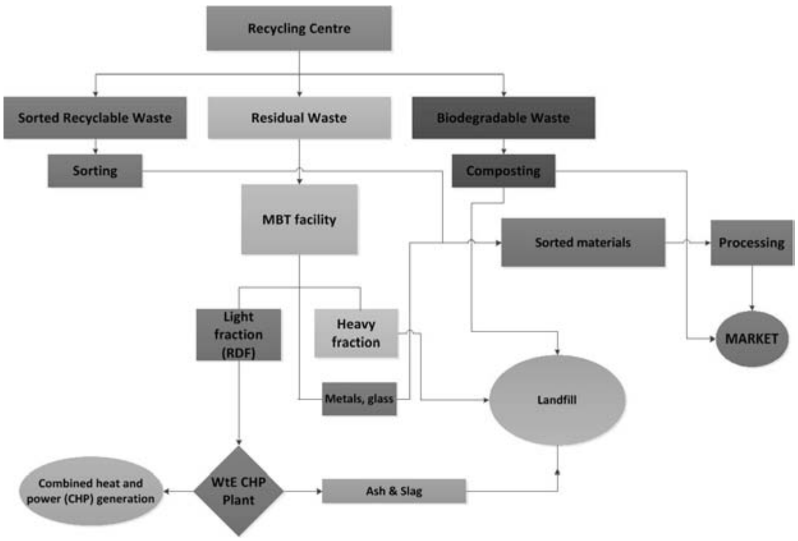


Figure 1: Generalized scheme of proposed future integrated waste management system in Montenegro

Proposed network of recycling centers

In Montenegro seven regions for MSW collection with recycling center (Figure 2) are proposed as the optimal network [2].

The collection of MSW is optimal, if [2]:

- ✓ the radius of the collection is not greater than 40 km, and
- ✓ the annual processing volume fraction of the MSW in recycling center exceeds 5.000 tons.

Region of Montenegro	Recycling Centre	Involved Municipalities
Northern	Recycling Centre 1	Pljevlja i Žabljak
	Recycling Centre 2	Berane, Rožaje, Plav, Andrijevica, Bijelo Polje, Kolašin i Mojkovac
Central	Recycling Centre 3	Nikšić, Plužine i Šavnik
	Recycling Centre 4	Cetinje, Danilovgrad, Podgorica
Southern	Recycling Centre 5	Herceg Novi
	Recycling Centre 6	Budva, Kotor i Tivat
	Recycling Centre 7	Bar i Ulcinj

Figure 2: Proposed network of recycling centers in Montenegro [2]

For separately collected MSW fractions is considered next treatment [2]:

- ✓ the preparation of dried separately collected fractions (paper, metal, glass and packaging waste) for the submission to further processing,
- ✓ processing of the separately collected biodegradable(green) waste, and
- ✓ the preparation of the residual waste (mixed MSW)for treatment in the MBT plant.

The recycling center can perform the following activities [2]:

- ✓ the preparation of separately collected waste paper for the transport to the plants for waste paper treatment,
- ✓ sorting of the separately collected packaging waste by type of material: paper, plastic and metal,
- ✓ the preparation of paper, plastic and metal, obtained by sorting waste; packaging of processed waste for transportation to the plants for waste paper, plastic and metal treatment, and
- ✓ the preparation and composting of the biodegradable waste (kitchen waste and green waste from garden), and sewage sludge.

Statistical prediction of generated MSW in the future

In Montenegro the specific maximum daily amount of MSW generated in the southern region of Montenegro by the data in the Master Plan. This is in accordance with greater economic potential of this area, mainly as a result of tourism, economic activities and in this connection, a number of commercial buildings. For the central region of Montenegro is assumed slightly lower rate of specific MSW generation. Much lower value of specific amount of MSW is in northern region of Montenegro, which, on one hand is less economically developed, and on the other hand has more reuse of MSW fractions in households [3] than in other parts of Montenegro.

On the basis of EU practices for waste management in tourist areas, statistically proposed daily amount of waste is about 1.50 kg/tourist/night. This generation of MSW is a result of tourism nature (higher consumption of disposable products). For refugees are expected very low rate of consumption and MSW generation thus the generation of MSW is estimated at about 0.25 kg/refugees/day [3].
The future increase of generated MSW is expected as a result of higher GDP, higher development of individual municipalities in

Montenegro by 2035, which consequently has impact on increased consumption of population and higher level of communal services.

Figure 3 below shows an estimated specific MSW generation in households for the period 2011-2035 in all regions of Montenegro.

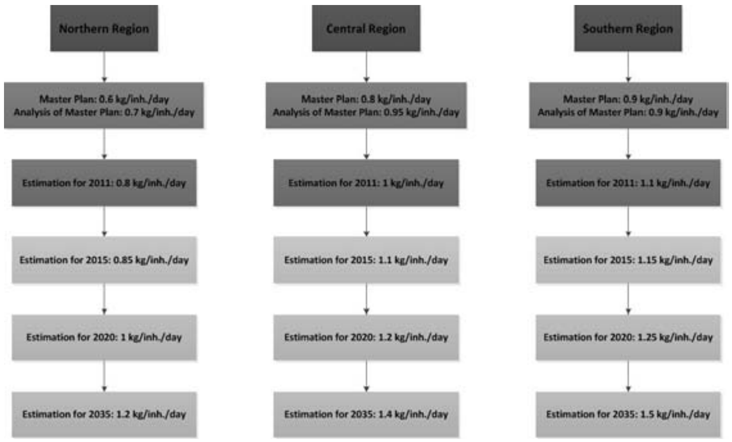


Figure 3: Estimation of specific MSW generation in households for the period 2011 – 2035

MSW composition is changing and depends on the environment, in which it arises and depends also on many factors such as living standard, type of settlement, quality of communal infrastructure, etc. On the other hand, the differences in the percentage of MSW composition are often caused by determining the composition based on estimates and not on the basis of the standardized procedures. Specifically, Montenegro does not keep records of MSW composition and percentage share of its components in accordance with the EU standards.

Generally, the MSW consists of the following main fractions:

- ✓ biodegradable waste (food scraps, yard waste, grass, leaves, cut off branches, trees);
- ✓ paper and cardboard (newspapers, books, magazines, commercial printing, office paper, wrapping paper, paper towels, corrugated paper);
- ✓ plastic (packaging materials, boxes, bottles, plastic bags, sheets and other plastic products);
- ✓ glass (bottles, jars, containers for beverages, flat glass);
- ✓ metal (tin cans, cans, aluminum, iron and other metals);
- ✓ textiles and leather;
- ✓ other (dirt, ashes, street sweepings, dust, unidentified materials).

On the changes of MSW composition in the period 2011 - 2035, the highest affect will have the following factors:

- ✓ higher consumption of goods will lead to more packaging waste, which will mostly effect of the increase in the percentage of paper, plastic and metal in MSW,
- ✓ increase of composting kitchen and green waste (biodegradable waste), which will cause that the amount of processed biodegradable waste in MSW by 2035 will not change, and
- ✓ increase in percentage of bulky waste due to the greater citizen purchasing power – the increase of the domestic waste like furniture or electrical and electronic equipment requires separate collection of the waste.

The assumptions concerning the evaluation changes of MSW composition in the period 2011 - 2035 are shown in Figure 4. The data for the MSW composition in every region of Montenegro in 2011 are taken from the Master Plan [3].

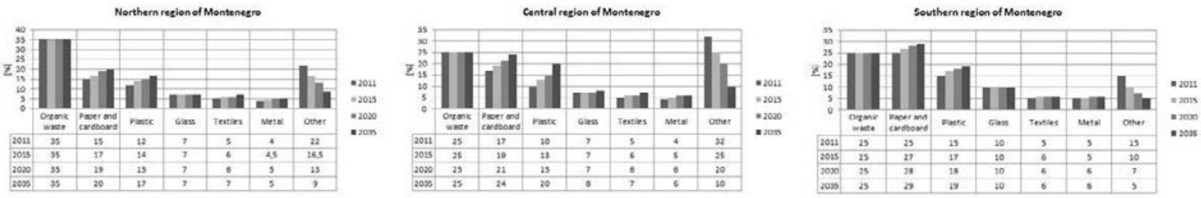


Figure 4: Estimation of the composition change of MSW in the period 2011 - 2035

It is realistic to expect, that the GDP in municipalities of Montenegro will increase, number of inhabitants and tourist`s overnights will increase, and that the gradual decline of refugees occur; it is expected that they will return home or become regular citizens of Montenegro until 2020 with more or less same living habits.

Based on current demographic data and other assumptions [4-5] including the number of inhabitants, the number of tourists overnight stays, the number of refugees, the annual generated MSW in the period 2011 – 2035 is shown in Table 1

Table 1:Estimation of MSW generation for Montenegro regions in the period 2011 – 2035

Year	Region	Recycling Centre	Waste producers			Estimated total generated MSW [t/year]
			Inhabitants	Tourists (overnight stays)	Refugees	
2011	Northern	Recycling Centre 1	34.659 [3]	63.445[5]	805 [2]	10.289
		Recycling Centre 2	141.195[3]	69.650[5]	12.656 [2]	42.488
	Central	Recycling Centre 3	78.187[3]	20.123[5]	2.640 [2]	28.809
		Recycling Centre 4	221.520[3]	127.998[5]	13.447 [2]	82.274
	Southern	Recycling Centre 5	30.992[3]	1.915.346[5]	4.000 [2]	15.681
		Recycling Centre 6	56.080[3]	4.569.917[5]	4.815 [2]	29.810
		Recycling Centre 7	62.633[3]	2.008.692[5]	8.551 [2]	28.940
2015	Northern	Recycling Centre 1	34.200	78.000	475	10.771
		Recycling Centre 2	139.800	90.000	6.485	44.100
	Central	Recycling Centre 3	79.699	25.000	1.370	32.162
		Recycling Centre 4	224.105	140.000	6.723	90.802
	Southern	Recycling Centre 5	32.792	2.200.000	2.000	17.247
		Recycling Centre 6	61.924	5.100.000	2.407	33.862
		Recycling Centre 7	65.370	2.600.000	4.275	31.729
2020	Northern	Recycling Centre 1	35.500	104.000	0	13.114
		Recycling Centre 2	143.300	116.000	0	52.479
	Central	Recycling Centre 3	82.530	40.000	0	36.208
		Recycling Centre 4	231.242	185.000	0	101.561
	Southern	Recycling Centre 5	33.492	3.300.000	0	20.231
		Recycling Centre 6	64.791	6.700.000	0	39.611
		Recycling Centre 7	67.852	4.300.000	0	37.407
2035	Northern	Recycling Centre 1	37.700	141.600	0	16.725
		Recycling Centre 2	152.300	156.000	0	66.941
	Central	Recycling Centre 3	93.788	50.000	0	48.001
		Recycling Centre 4	250.245	270.000	0	128.280
	Southern	Recycling Centre 5	36.492	4.300.000	0	26.429
		Recycling Centre 6	73.067	7.800.000	0	51.704
		Recycling Centre 7	74.885	5.700.000	0	49.550

The projection of population growth was calculated for the medium-fertility variant, which was chosen as the most realistically achievable [5].

In accordance with the Strategic master plan for waste management in the period 2005-2009, the following level of waste collection was anticipated:

- ✓ in the urban areas gradual increase from 85 % in 2004 from to 92 % in 2009, and

- ✓ in other settlements gradual increase from 15 % in 2004 to 27% in 2009 excluding settlements with fewer than 190 inhabitants.

The average level of waste collection in cities in Montenegro was 85.6 %, which is about 6% less than anticipated in the Master Plan [7].
The expected level of MSW collection will be increasing in the period 2010 - 2014 by data in the Strategic master plan. All producers of waste in Montenegro are still not covered by communal services. On the basis of information provided by competent services, 85% of MSW is collected in the urban areas, whereas no information on the collection of MSW in rural areas is available. This document in long term predicts the collecting increase of MSW with the rate of 5% per year in all rural areas of Montenegro starting in 2010. Figure 5 shows the assumed level of MSW collection in urban and rural areas for the period 2011 - 2035 and is valid for all regions in Montenegro.

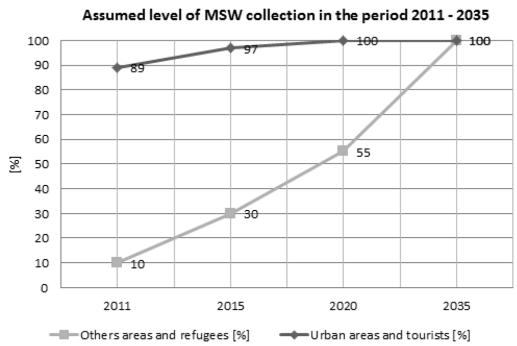


Figure 5: Assumed level of MSW collection in Montenegro

Projections and estimation of generated and collected MSW and the level of MSW collection in each recycling center is shown in Table 2.

Table 2: Estimation of collected MSW and the level of MSW collection in recycling centers

Year	Region	Recycling Centre	Generated MSW [t/year]	Collected MSW [t/year]	The level of MSW collection [%]
2011	Northern	Recycling Centre 1	10.289	6.031	59
		Recycling Centre 2	42.488	17.439	41
	Central	Recycling Centre 3	28.809	19.943	69
		Recycling Centre 4	82.274	59.482	72
	Southern	Recycling Centre 5	15.681	10.060	64
		Recycling Centre 6	29.810	20.702	69
		Recycling Centre 7	28.940	14.332	49
2015	Northern	Recycling Centre 1	10.771	7.716	72
		Recycling Centre 2	44.100	25.015	56
	Central	Recycling Centre 3	32.162	25.936	81
		Recycling Centre 4	90.802	75.668	83
	Southern	Recycling Centre 5	17.247	13.324	77
		Recycling Centre 6	33.862	27.498	81
		Recycling Centre 7	31.729	20.649	65
2020	Northern	Recycling Centre 1	13.114	10.860	83
		Recycling Centre 2	52.479	38.460	73
	Central	Recycling Centre 3	36.208	32.192	89
		Recycling Centre 4	101.561	92.053	91
	Southern	Recycling Centre 5	20.231	15.963	79
		Recycling Centre 6	39.611	32.341	82
		Recycling Centre 7	37.407	25.316	68
2035	Northern	Recycling Centre 1	16.725	16.725	100
		Recycling Centre 2	66.941	66.941	100

	Central	**Recycling Centre 3**	48.001	48.001	100
		Recycling Centre 4	128.280	128.280	100
	Southern	**Recycling Centre 5**	26.429	26.429	100
		Recycling Centre 6	51.704	51.704	100
		Recycling Centre 7	49.550	89.550	100

The objectives of MSW recycling

In order to make the proper collection of MSW in all municipalities of Montenegro, it is necessary in the next five years to perform the organized selective collection of MSW. Realistically it is not be able to fully implement the selective waste collection by 2015, but it is possible to reach a very high level of separate collection, which will be very at the end of 2020 in accordance to the aims of the EU directive. For the implementation of the separate collection special (additional) funds should be planned for the purchase of equipment and to provide the space for containers for separate collection.

6a) Unsorted MSW – practical example 1 **6b)** Unsorted MSW – practical example 2

Figure 6: Present state of unsorted MSW in Montenegro

In Montenegro it is realistically to expect the following rate of recycling individual fractions of MSW by 2035 (Figure 7), which will have to be in compliance with EU directives[8-10].

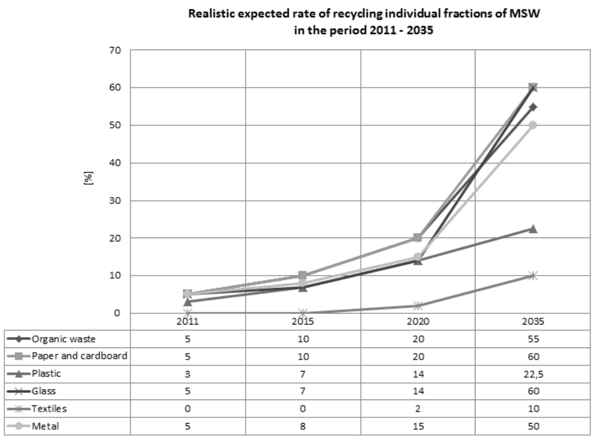
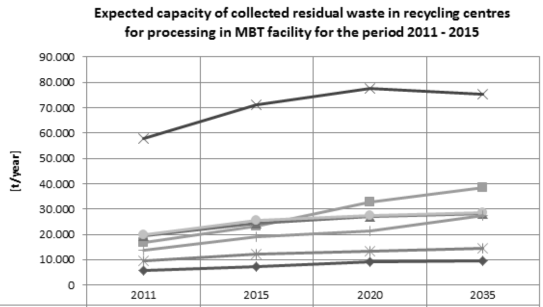


Figure 7: The rate of recycling of individual MSW fractions in the period 2011 – 2035

As shown in the Figure 7 it is realistic to expect a gradual increase in efficiency of the recycling of individual MSW fractions by the year 2020. The larger increase of recycling rate and complete fulfillment of the EU directive objectives is expected in the period 2020-2035.Expected capacity of recycling centers for treating collected waste is shown in Figure 8, where expected waste recycling is incorporated into the account (smaller quantity of residual MSW).



	2011	2015	2020	2035
Recycling Centre 1	5.826	7.174	9.258	9.621
Recycling Centre 2	16.844	23.256	32.787	38.508
Recycling Centre 3	19.354	24.328	27.106	28.248
Recycling Centre 4	57.728	70.976	77.509	75.493
Recycling Centre 5	9.688	12.326	13.483	14.530
Recycling Centre 6	19.936	25.438	27.315	28.424
Recycling Centre 7	13.801	19.102	21.382	27.240

Figure 8: Estimated capacity of residual waste in recycling centers for processing in MBT facility for the period 2011 – 2035

Estimated quantity of collected residual waste by each recycling center is planned for processing in MBT facility where RDF is produced.

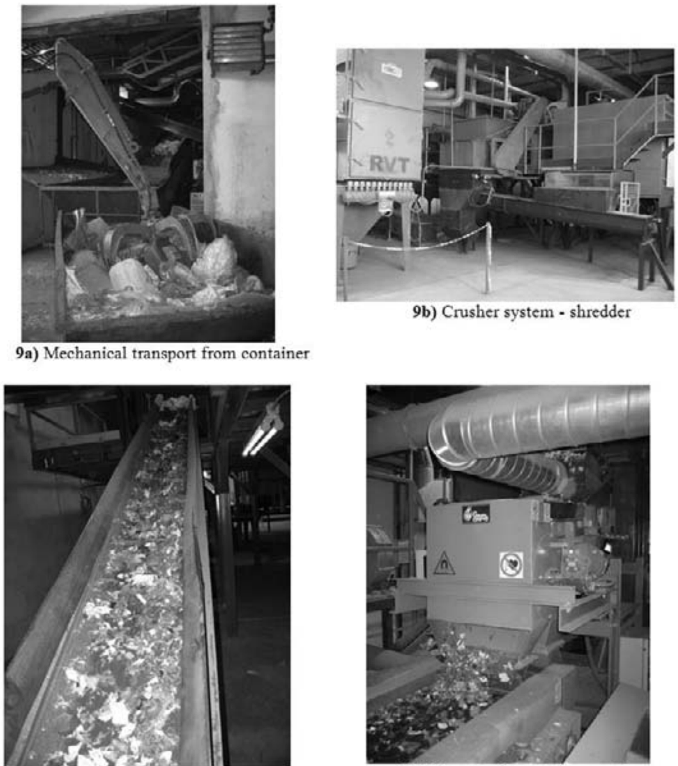
Mechanical – biological treatment (MBT) of residual waste

MBT is a process for residual waste treatment p that involves both mechanical and biological treatment processes. The first MBT facilities were developed with the aim to reduce the environmental impact of landfilling residual waste. MBT therefore compliments, but does not replace, other waste management technologies such as recycling and composting as part of an integrated waste management system. A key advantage of MBT is that it can be configured to achieve several different aims. In line with the EU Landfill Directive[9] and national recycling targets, some typical aims of MBT plants include:

- ✓ pre-treatment of waste going to landfill,
- ✓ diversion of non-biodegradable and biodegradable MSW going to landfill through the mechanical sorting of MSW into materials for recycling and/or energy recovery as RDF;
- ✓ diversion of biodegradable MSW going to landfill by:
  - reducing the dry mass of biodegradable municipal waste (BMW) prior to landfill,
  - reducing the biodegradability of BMW prior to landfill,
- ✓ stabilization into a compost-like output for (limited) use on land,
- ✓ conversion into a combustible biogas for energy recovery; and/or
- ✓ drying materials to produce a high calorific organic rich fraction for use as RDF.

MBT consists from the three base processes:

- ✓ waste preparation (hammer mill, shredder, rotating drum, ball mill, bag splitter),
- ✓ waste separation (trommels and screens, manual separation, magnetic separation, air classification, optical separation,...) and
- ✓ biological treatment (aerobic, anaerobic).



9a) Mechanical transport from container

9b) Crusher system - shredder

9c) Conveyor belt

9d) Magnets for metal separation

Figure 9: Mechanical - biological treatment (MBT) of residual waste–practical example

Facilities for complete residual waste management are transfer stations, MBT and W-t-E facilities and landfills. Based on an analysis of the generation and evaluation of increasing amounts of MSW in the future there are proposed next facilities to be built in Montenegro:

- ✓ transfer stations for transport residual waste and separately collected individual fractions to recycling centers in each region of Montenegro,
- ✓ one MBT facility with landfill for deposition of heavy fraction of treated residual waste in each region of Montenegro (total three MBT facilities) – Figure10.

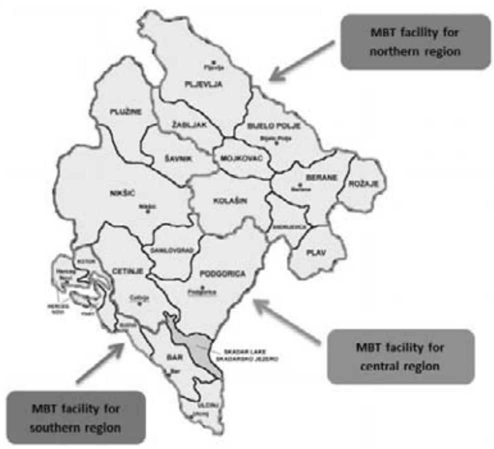


Figure 10: Proposal network of MBT facilities in Montenegro

The Table 3 below shows indicative capital expenditure (Capex), operational expenditure (Opex) and estimated capacity for MBT facilities. There are a wide range of costs that dependent upon the complexity of the technology and the degree of mechanization and automation employed.

Table 3: Estimated treatment capacity and costs for MBT

Region	Treatment capacity [t/year]	Treatment method	Costs	
			Capex [€/t/year]	Opex [€/year]
Northern	40.000	aerobic	70 - 150	do 140
Central	100.000	aerobic	28 - 225	20 - 69
Southern	60.000	aerobic	28 - 225	20 - 69

The costs provided in Table 3 are predominantly based on EU examples. Costs are different from country to country influenced by the cost of permitting, labor, taxes, emission controls and other requirements.

MBT systems are financially sensitive to the recycled materials and RDF markets that are produced by different processes. It is likely that many of the material outputs from MBT will have a negative value and these are not included in the above costs. Partnerships between MBT operators and potential users of outputs should be established at the earliest possible opportunity and care should be taken to ensure plant can deliver materials in desired quality for the required market outlet.

The operation of the MSW is optimal from economical aspect, if:

- ✓ MSW is collected in the region of each recycling center,
- ✓ separately collected biodegradable waste is composted in each recycle center (composting is a part of recycling center),
- ✓ residual waste is treated in MBT facility in recycling center which collects continuously residual waste of the entire statistical region (one MBT facility in each region of Montenegro),
- ✓ heavy fraction of treated residual waste is deposited on the landfill which is built for landfilling the quantity of entire statistical region. The light fraction is used as a fuel in the W-t-E CHP plant for heat and electricity generation or in large combustion plants and industrial furnaces.

RDF production from residual waste

The combustible fractions with higher calorific value are led from residual waste such as plastic, paper or textiles which represents the input components for RDF (Refuse Derived Fuel). Metal materials are led from heavy fraction and additionally, the mechanical-biological stabilization is come after this. The RDF production is not the standard process and the technology equipment depends on the type of residual waste which is treated and father usage of the produced fuel.

Figure 11: RDF– light fraction of residual waste

Master plan does not indicate that the separately collected fraction of residual waste with higher calorific value is suitable for RDF production (plastic, textile...). Furthermore, the utilization of RDF is neither stated (incineration in W-t-E plants, export,...).The main materials for RDF production (figure 11) are:

- ✓ residual waste,

- ✓ separately collected fraction of plastic, paper, cardboard and textiles, which are not suitable for recycling,
- ✓ the rest of the sorting process after separately collected packaging waste which are not suitable for material recycling.

RDF represents a sort of solid fuel which is produced from non-hazardous waste (Solid Waste Fuel).

It is possible to get around 43 - 64 % of light fraction (RDF) from residual waste and represents the fuel for W-t-E CHP plant. Estimated input capacity of residual waste for processing in MBT facility and capacity of RDF production for the period 2011 – 2035 is shown in Figure 12 by regions in Montenegro.

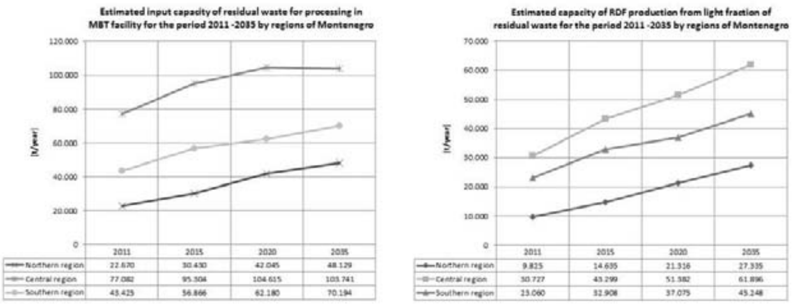


Figure 12: Estimated quantity of residual waste for processing in MBT facility and quantity of RDF production for the period 2011 – 2035 by regions in Montenegro

Energy potential of RDF and comparison with standard fuels

Energy potential(calorific value) of certain types of heating fuels are shown in Table 4.

Table 4: Energy potential of different types of heating fuels

Type of fuel	***Calorific value [MJ/unit of measure]***
RDF	***16 – 20 MJ/kg***
LignitePljevlja[11]	***10,4 – 12,3 MJ/kg***
Brown coalBerane[11]	***13,7 MJ/kg***
Woodchips – mix G30/W40	***2106 MJ/npm****
Hardwood(beech) W30	***6948 MJ/prm†***
Softwood(spruce) W30	***4896 MJ/prm***
Heating oil (extra light)[12]	***38,52 MJ/l***
Natural gas[12]	***36 MJ/m³***
1 kWh of electricity	***3,6 MJ***

* npm–cubicmetres in bulk
† prm – cubicmetres

Figure 13 shows a comparison of consumption of certain types of fuels for heating to get the same amount of energy as from 1 ton of RDF.

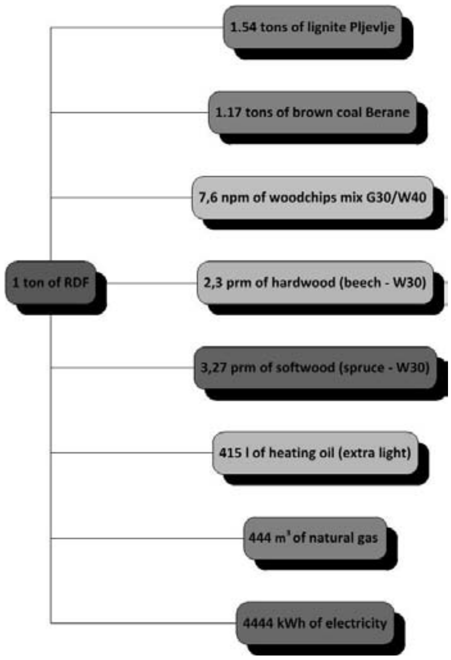


Figure 13: Equivalent energy from1 ton of RDF

Table 5 shows the approximate annual replacement of certain types of heating fuels if RDF is used. According to projections in Montenegro it is possible to produce approximately 100.000 tons of RDF in the year 2020.

Table 5: Estimation of annual replacement of certain types of heating fuelswith RDFin 2020

Region	RDF [t]	Lignite Pljevlja [t]	Brown coal Berane [t]	Woodchips – mix G30/W40 [npm]	Hardwood (beech) W30 [prm]	Softwood (spruce) W30 [prm]	Heating oil (extra light) [l]	Natural gas [m^3]
Northern	18,000	27,720	21,060	136,800	41,400	58,860	7470,000	7992,000
Central	48,000	73,920	56,160	364,800	110,400	156,960	19920,000	21312,000
Southern	34,000	52,360	39,780	258,400	78,200	111,180	14110,000	15096,000
Total	100,000	154,000	117,000	760,000	230,000	327,000	41500,000	44400,000

The utilization of RDF has the following the potential of next positive effects:

- ✓ from 1 ton of RDF can be obtained about 4,444 kWh of heat energy,
- ✓ yearly heating energy consumption for heating one two bedroom apartmentis4,200 kWh per year (55 m^2 * 96.77 kWh/m^2) [13] which can be produced by 1.2 tons of RDF,
- ✓ 100,000 tons of RDF-a is enough to heat 83.427 two bedroom apartments,
- ✓ to produce heat energy equivalent to 1.2 tons of RDF is required:
  - 9,1 m^{3}of woodchips - mix G30/W40,
  - 2,76 prm of hardwood(beech - W30),
  - 3,91 prm of softwood(spruce - W30) or
  - 497 liters of heating oil (extra light).

Conclusions

Correctly processed MSW is a low-cost form of alternative energy with a large potential for future expansion and represents a useful material and energy source. It is possible to use it in adequate devices with the proper organization of integrated waste management system and do not have negative impact on the environment.

As discussed it this paper it is possible to produce useful heat and power from the processed MSW Power is sent to the electric power grid system and the produced heat through district heating is used for heating buildings and industry in all range of heating networks. In the same way it is also possible to produce and transport the cooling media to the users. Such energy utilization of MSW means a significant reduction of greenhouse gas emissions, rational management of energy and reduction of problems with limited space, which is available for MSW disposal.

Additionally, the following positive effects are:

- ✓ the quantity of the MSW which is currently disposed of in landfills, is reduced by 65%,
- ✓ the amount of greenhouse gases and the total organic carbon is radically reduced (up to less than 4%),
- ✓ the heating energy can be used for the district heating system,
- ✓ fossil fuels, solid fuels and in some cases even crude oil can be replaced by the energy produced from the RDF, and the main result will be significant emissions reduction of harmful substances into the air which are caused by the mentioned fuels.

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ELEKTROHEMIJSKO POLIRANJE POVRŠINA ALUMINIJUMA

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IZVOD

U ovom radu, koristeći dosadašnja iskustva iz ove oblasti, kroz eksperimentalni rad, ispitivani su odgovarajući elektroliti za elektrohemijsko poliranje (glačanje) aluminijuma i optimalni uslovi za njihovu primenu. Pre elektrohemijskog poliranja potrebno je uzorke aluminijuma hemijski pripremiti i ukloniti zaštitnu oksidnu opnu. Za uklanjanje oksidne opne korišćena su četiri rastvora, a za elektrohemijsko poliranje ispitivano je pet rastvora. Svi rastvori za elektrohemijsko poliranje aluminijuma daju zadovoljavajuće rezultate, jer se nakon elektrohemijskog poliranja, na osnovu vizuelne procene, povećava sjaj površine uzoraka, tj. površinska refleksija svetlosti i dolazi do smanjenja površinske hrapavosti. Poslednju konstataciju dokazuju izvršena merenja površinske hrapavosti svih uzoraka aluminijuma.

Sa povećanjem vremena elektrohemijskog poliranja dolazi do smanjenja hrapavosti aluminijuma. Od pet korišćenih rastvora za elektrohemijsko poliranje aluminijuma, najbolje rezultate pokazali su rastvori 5(II) i 5(IV). Uzorci aluminijuma obrađeni u ovim rastvorima imaju najmanju hrapavost i najveći stepen refleksije. Na osnovu vizuelnog izgleda najveći sjaj ima uzorak aluminijuma glačan u rastvoru 5(IV).

***Ključne riječi**: Elektrohemijsko poliranje, površinska hrapavost, anodna obrada*

UVOD

Aluminijum je veoma zastupljen metal na zemlji, oko 8,5%. U odnosu na druge elemente, po količini, nalazi se na trećem mestu, odmah iza kiseonika (47%) i silicijuma (28%). Zbog svoje reaktivnosti, ne postoji kao slobodan metal, već je tesno povezan sa drugim elementima, pa se većina njegove mase na planeti nalazi u aluminosilikatima [1-3].

Dosadašnja istraživanja su pokazala da je brzina korozije aluminijuma u rastvorima sa pH vrednostima od 4 do 8 vrlo mala (nekoliko $\mu A/cm^2$). Do znatnog povećanja brzine korozije dolazi pomeranjem pH vrednosti rastvora u kiselu i alkalnu oblast, pri čemu je u alkalnim rastvorima to povećanje veće. U isto vreme je i stabilnost oksidnih filmova u alkalnim rastvorima manja u odnosu na kisele rastvore. Da bi se oblast primjene aluminijuma proširila, neophodno je poboljšati njegove mehaničke, fizičke i hemijske osobine obradom aluminijuma (npr. legiranjem) i/ili obradom same površine aluminijuma [4-10].

Aluminijum spada u grupu metala koji se u industrijskoj praksi mogu malo elektrohemijski obrađivati kako katodnom tako i anodnom polarizacijom. Površina aluminijuma se može elektrohemijski polirati (glačati) njegovim anodnim rastvaranjem u pogodno izabranom elektrolitu pri dovoljno velikoj gustini struje i odgovarajućoj temperaturi [8-14].

Cilj ovog rada je bio da se, koristeći dosadašnja iskustva iz ove oblasti, kroz eksperimentalni rad, da doprinos u iznalaženju nekih od elektrolita i optimalnih uslova za elektrohemijsko poliranje (glačanje) aluminijuma i njegovih legura. Takođe cilj je bio da se pokaže kako odabrani rastvori za elektrohemijsko poliranje utiču na vizuelni izgled i hrapavost površine aluminijumskih uzoraka.

EKSPERIMENTALNI DEO

Eksperimenti su rađeni na aluminijumskim pločicama nepoznatog sastava površine 0,5dm^2 u laboratorijskoj elektrohemijskoj ćeliji zapremine 500cm^3. Pre elektrohemijskog poliranja urađena je hemijska priprema uzoraka aluminijuma. U elektrohemijskoj ćeliji izvođeno je elektrohemijsko poliranje (glačanje) aluminijuma. Sastavi rastvora za pripremu uzoraka aluminijuma koji su korišćeni i radni uslovi pri izvođenju eksperimenata su [13]:

1. Rastvor za odmašćivanje: 50% Na_2CO_3, 50% $Na_3PO_4 \cdot 10H_2O$, t=60-70^{0}C, τ = 15min, 5% vodeni rastvor, pH = 7,5- 8,5.
2. Rastvor (I) za nagrizanje : 20% NaOH + 2% NaF, t=70-75^{0}C, τ = 2-3min,
3. Rastvor (II) za nagrizanje: 550 cm^3/dm^3 HNO_3, 200 cm^3/dm^3 H_2SO_4, 140 cm^3/dm^3 NaF, temperature sobna, τ = 5min
4. Rastvor za osvijetljavanje: 20% HNO_3, 10% HF, temperatura sobna, τ = 5minZa elektrohemijsko poliranje površine aluminijuma, nakon hemijske pripreme, korišćeni su sledeći rastvori [11]:

Rastvor 5(I) **:** 15% Na_2CO_3 (bezvodni), 5% $Na_3PO_4 \cdot 12H_2O$, 80% H_2O,

U = 10-15V, j = 4-6 A/dm^2, t = 80-95 ^{0}C, τ = 8-15 min, katoda nerđajući čelik

Rastvor 5(II): 400cm^3 H_2SO_4, 600cm^3 H_3PO_4, 5cm^3 glicerina

U = 5-15V, j = 11-16 A/dm^2, t = 60 ^{0}C, τ = 15min, katoda nerđajući čelik

Rastvor 5(III): 34% H_2SO_4, 34% H_3PO_4, 4% CrO_3, 28% H_2O,

U = 10-15V, j = 20-30 A/dm^2, t = 85-90 ^{0}C, τ = 5-8min, katoda nerđajući čelik

Rastvor 5(IV): 70% H_2SO_4, 1% HNO_3, 15% H_3PO_4, 14% H_2O,

U = 10-25V, j = 10-15 A/dm^2, t = 75-100 ^{0}C, τ = 2-10 min, katoda nerđajući čelik

Rastvor 5(V): 500cm^3 H_3PO_4, 500cm^3 $CH_3COOH_{(konc)}$

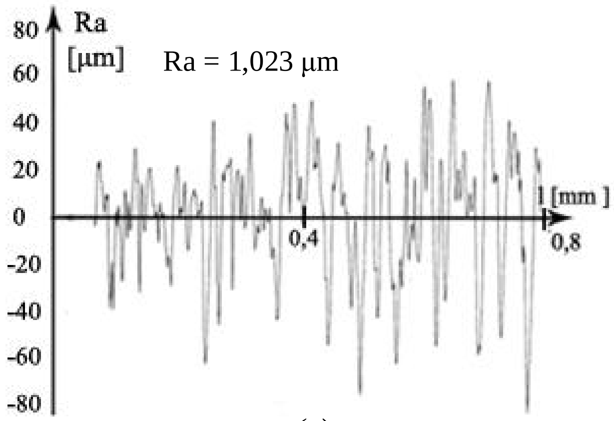
U = 1-2V, j = 3-6 A/dm^2, t = 50-80 ^{0}C, τ = 5-15min, katoda nerđajući čelik

Hemijska priprema svih uzoraka pre elektrohemijske obrade rađena je na sledeći način: hemijsko odmašćivanje 15 minuta, nagrizanje u rastvoru (I) 3 minuta, nagrizanje u rastvoru (II) 5 minuta, osvijetljavanje 5 minuta. Između svake ove operacoje vršeno je ispiranje uzoraka protočnom i destilovanom vodom.

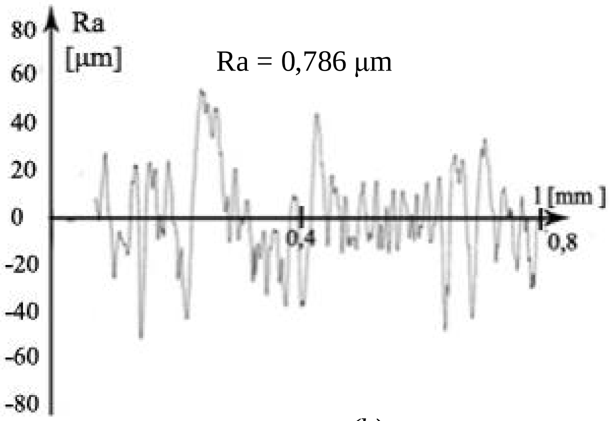
Ovako hemijski pripremljeni uzorci su podvrgnuti elektrohemijskom glačanju u rastvorima 5(I-V) uz mešanje elektrolita. Uzorci su potom isprani u protočnoj destilovanoj vodi, sušeni i merena je površinska hrapavost poliranih uzoraka aluminijuma pomoću ručnog uređaja *TR200* proizvod kompanije Time Group Inc. Korišćena je dužina mernog puta 0.8mm. Uređaj ima i mogućnost softverske podrške i upravljanja preko računara. Mogućnost multiparametarskog merenja sledećih parametara hrapavosti površine: *Ra* (aritmetička sredina devijacije profila), *Rz* (maksimalna visina profila**)**, *Ry* (DIN maksimalna visina profila), *Rq* (kvadrat devijacije profila), *Rp* (maksimalna visina vrha profila), *Rm* (maksimalna dubina dna profila), *Rt* (ukupna visina vrha, dna), *Sk* (kosina profila), *S* (središnji razmak lokalnih vrhova profila), *Sm* (srednji razmak elemenata profila), *tp* (odnos ležišta profila i dužine).

REZULTATI I DISKUSIJA

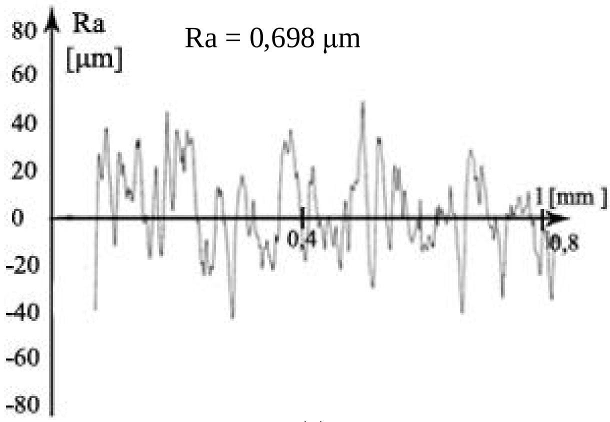
Na slici 1(a-c) dat je grafički prikaz izmerene hrapavosti elektrohemijski poliranih uzoraka aluminijuma u rastvoru 5(I): (a) τ = 8 min; (b) τ = 11,5 min; (c) τ = 15 min. Uslovi elektrohemijskog glačanja za rastvor 5(I) su: I = 2,5 A; U = 2 V; t = 82,5 ^{0}C.



(a)



(b)



(c)

Slika 1. Grafički prikaz izmerene hrapavosti površine aluminijuma glačane u rastvoru 5(I), u zavisnosti od vremena: (a) τ =8 min; (b) τ =11,5 min; (c) τ =15 min.

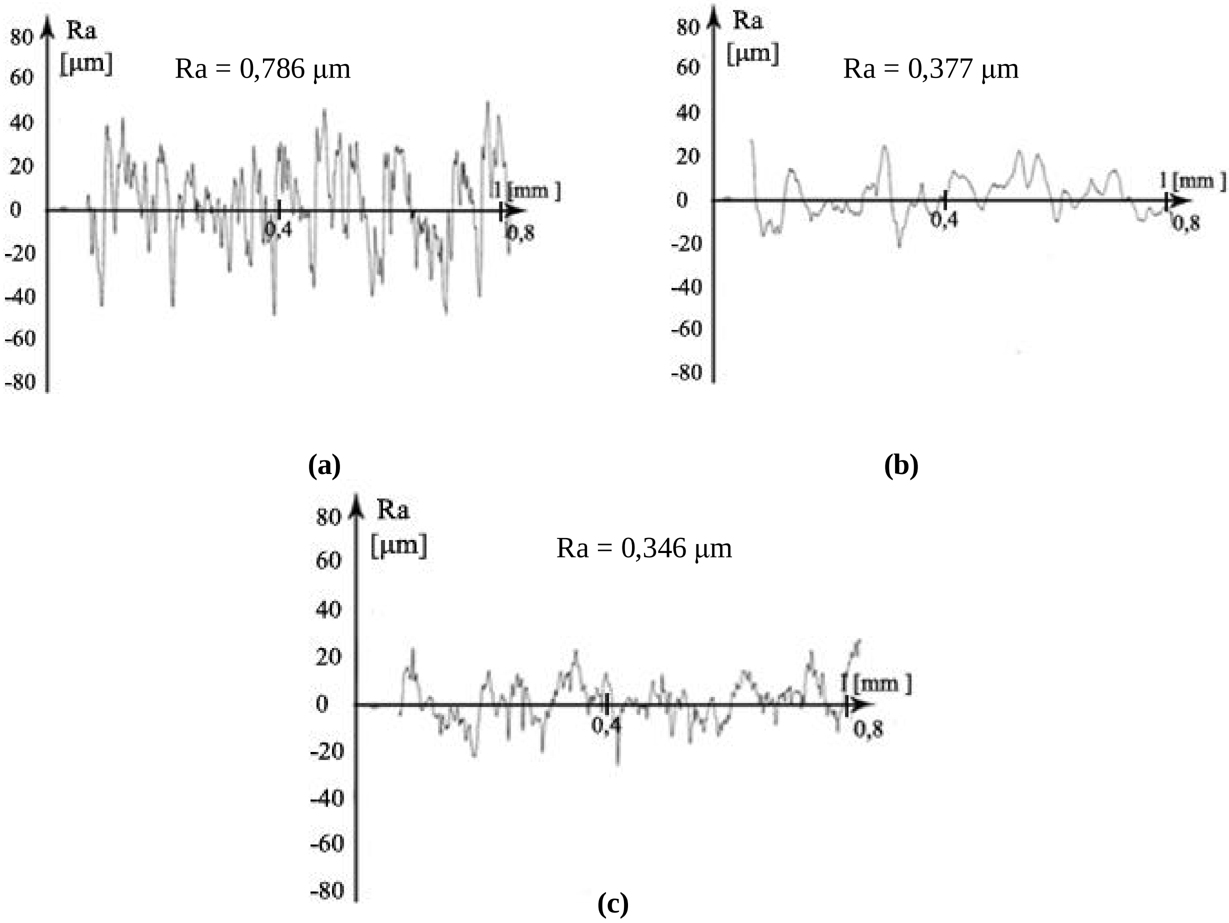
Sa slike 1(a-c) se vidi da se sa povećanjem vremena elektrohemijske reakcije smanjuje hrapavost. Najveća hrapavost je na slici 1(a) pri trajanju elektrohemijske reakcije 8 min, a najmanja hrapavost na slici 1(c) gde je pločica tretirana 15 min, u elektrohemijskoj ćeliji.

U tabeli 1 dat je prikaz svih izmerenih parametara hrapavosti elektrohemijski glačanih uzoraka aluminijuma u rastvoru 5(I).

Tabela 1. Parametri hrapavosti nakon obrade u rastvoru 5(I)

Parametri hrapavosti	Vreme (min)		
	8	11,5	15
Ra (μm)	1,023	0,768	0,698
Rq (μm)	1,270	0,964	0,852
Rz (μm)	3,503	2,053	1.191
Ry (μm)	5,667	4,127	3,772
Rt (μm)	7,219	5,420	4,619
Rp (μm)	2,299	1,820	1,834
Rm (μm)	3,367	2,308	1,927
S (mm)	0,1000	0,1111	0,1176
Sm (mm)	0,1428	0,1666	0,2105
Sk	-0,584	0.244	0,182

Na slici 2(a-c) dat je grafički prikaz izmerene hrapavosti elektrohemijski poliranih uzoraka aluminijuma u rastvoru 5(II): (a) τ = 5 min; (b) τ = 10 min; (c) τ = 15 min. Uslovi elektrohemijskog glačanja za rastvor 5(II) su: I = 5,5 A ; U = 11 V ; t = 61 ^{0}C.

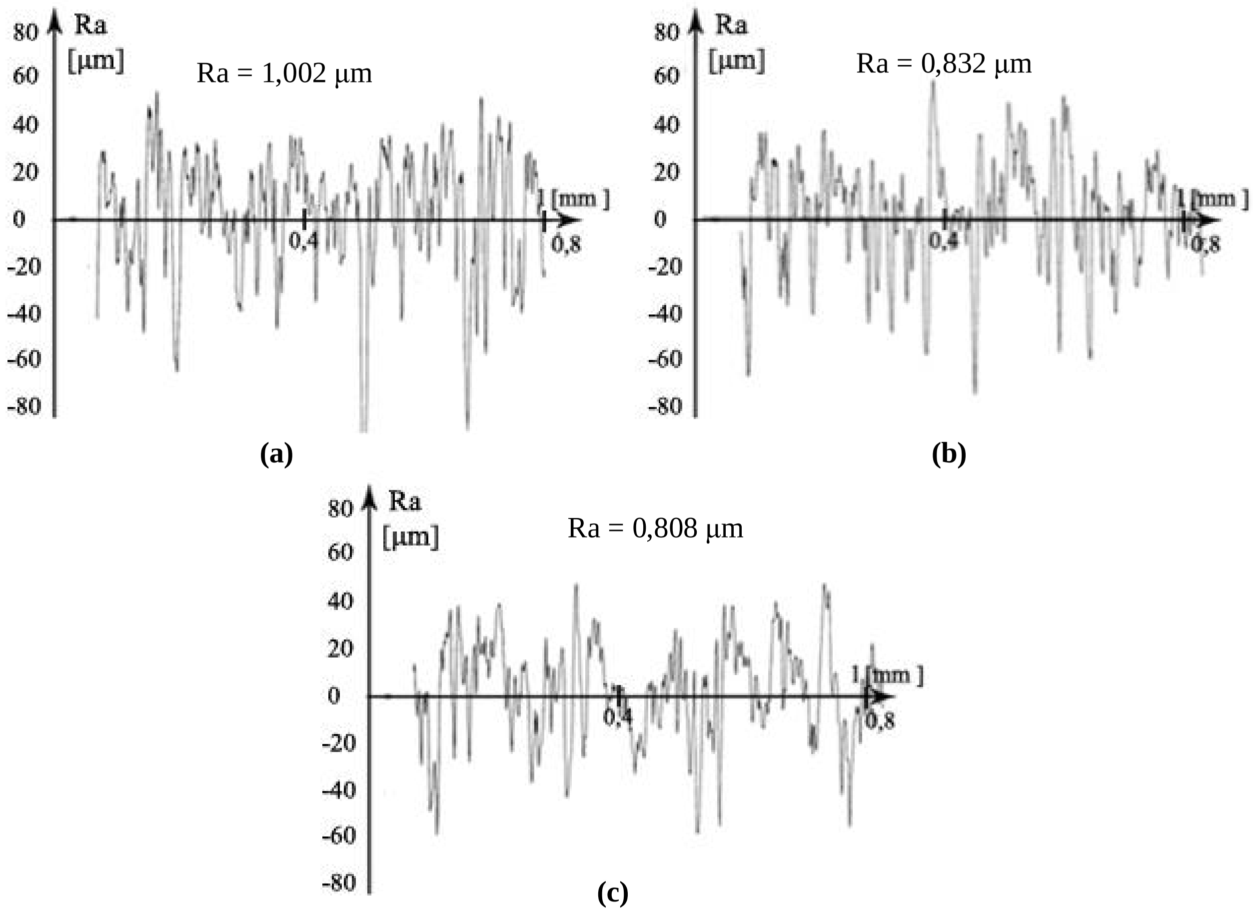


Slika 2. Grafički prikaz izmerene hrapavosti površine aluminijuma glačane u rastvoru 5(II), u zavisnosti od vremena: (a) τ =5 min; (b) τ =10 min; (c) τ =15 min.

Sa slike 2(a-c) je uočljivo da se hrapavost površine elektrohemijski poliranih uzoraka u rastvoru 5(II) smanjuje sa vremenom. Za vreme elektrohemijskog poliranja: τ = 5min, Ra = 0,786µm; τ = 10min, Ra = 0,377µm; i τ = 15min, Ra = 0,346µm. Očigledno je da se površinska hrapavost bitno ne smanjuje za vreme elektrohemijskog poliranja od 10 i 15 min.

Na slici 3(a-c) dat je grafički prikaz izmerene hrapavosti elektrohemijski poliranih uzoraka aluminijuma u rastvoru 5(III): (a) τ = 3 min; (b) τ = 5,5 min; (c) τ = 8 min. Uslovi elektrohemijskog glačanja za rastvor 5(III) su: I = 4 A ; U = 9,5 V ; t = 86,5 ^{0}C.

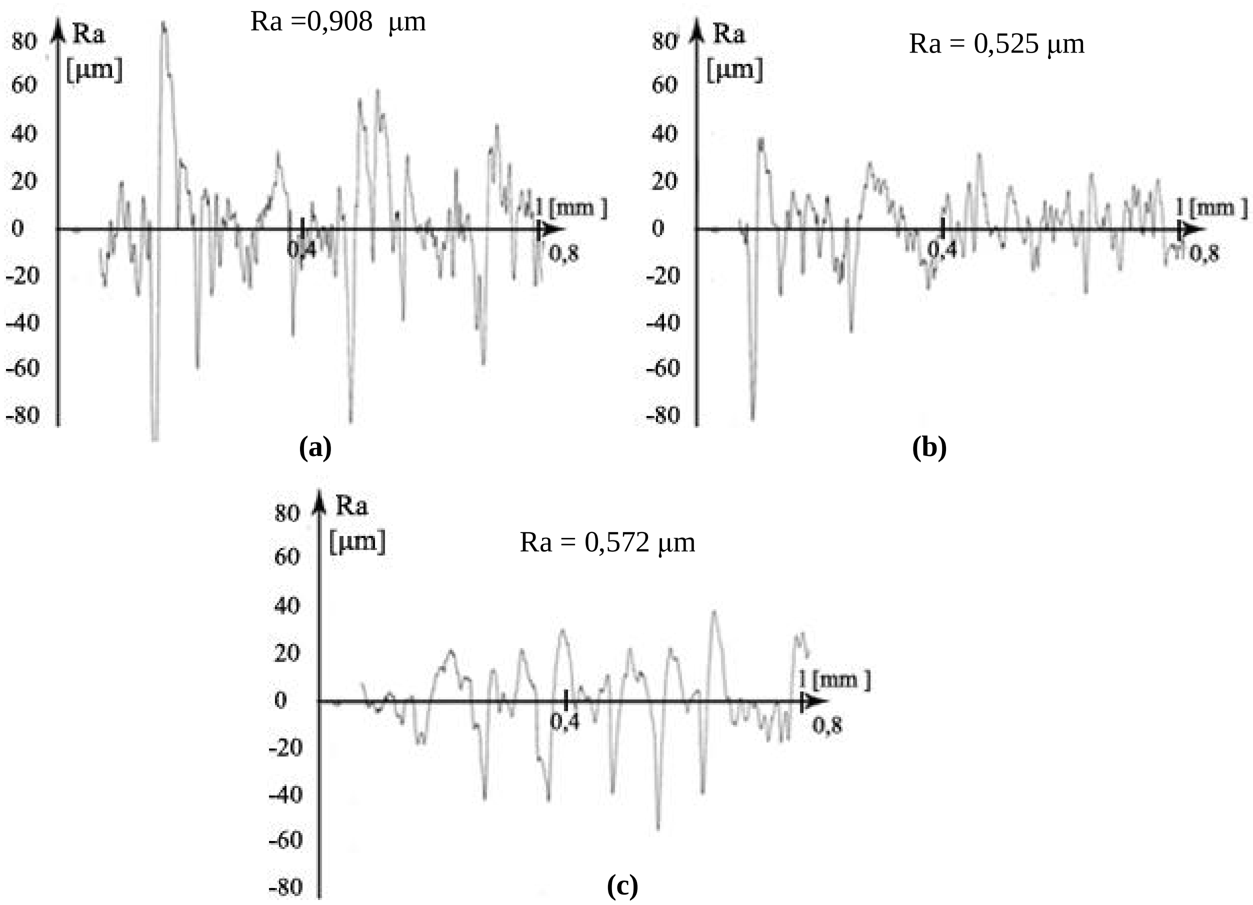
Sa slike 3(a-c) se zapaža da se hrapavost površine elektrohemijski poliranih uzoraka u rastvoru 5(III) smanjuje sa vremenom. Za vreme elektrohemijskog poliranja: τ = 3 min, Ra = 1,002 µm; τ = 5,5 min, Ra = 0,832 µm; i τ =8 min, Ra = 0,808 µm.



Slika 3. Grafički prikaz izmerene hrapavosti površine aluminijuma glačane u rastvoru 5(III), u zavisnosti od vremena: (a) τ =3 min; (b) τ =5,5 min; (c) τ =8 min.

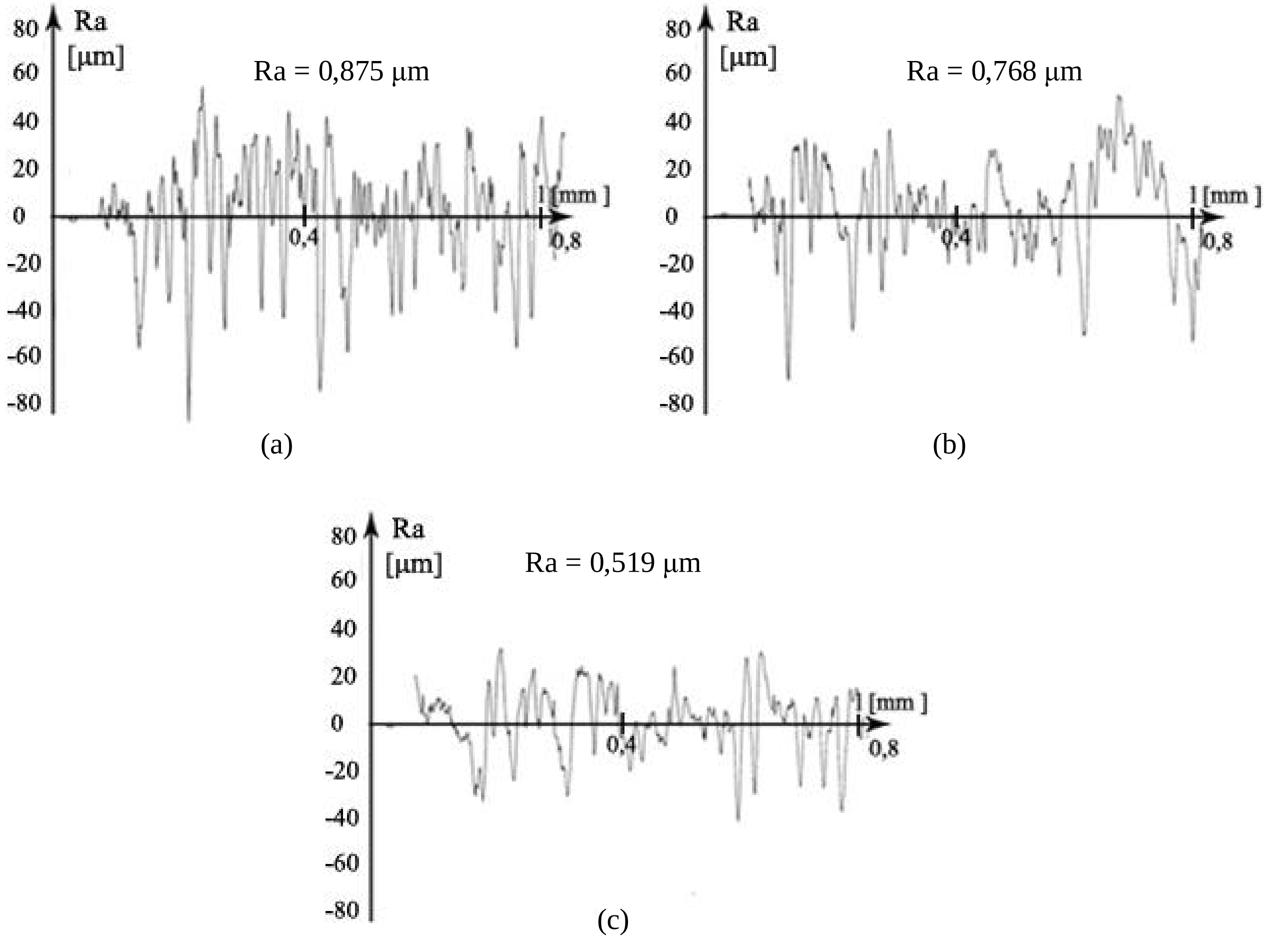
Na slici 4(a-c) dat je grafički prikaz izmerene hrapavosti elektrohemijski poliranih uzoraka aluminijuma u rastvoru 5(IV): (a) τ = 2 min; (b) τ = 6 min; (c) τ = 10 min. Uslovi elektrohemijskog glačanja za rastvor 5(IV) su: I = 6,25 A ; U = 7,5 V ; t = 86 ^{0}C.

Analizirajući slike 4(a-c) zapaža se da se hrapavost površine elektrohemijski poliranih uzoraka u rastvoru 5(IV) smanjuje sa vremenom. Za vreme elektrohemijskog poliranja: τ = 2 min, Ra=0,908 µm; τ = 6 min, Ra = 0,525 µm; τ = 10 min, Ra = 0,572 µm.



Slika 4. Grafički prikaz izmerene hrapavosti površine aluminijuma glačane u rastvoru 5(IV), u zavisnosti od vremena: (a) τ =2 min; (b) τ =6 min; (c) τ =10 min.

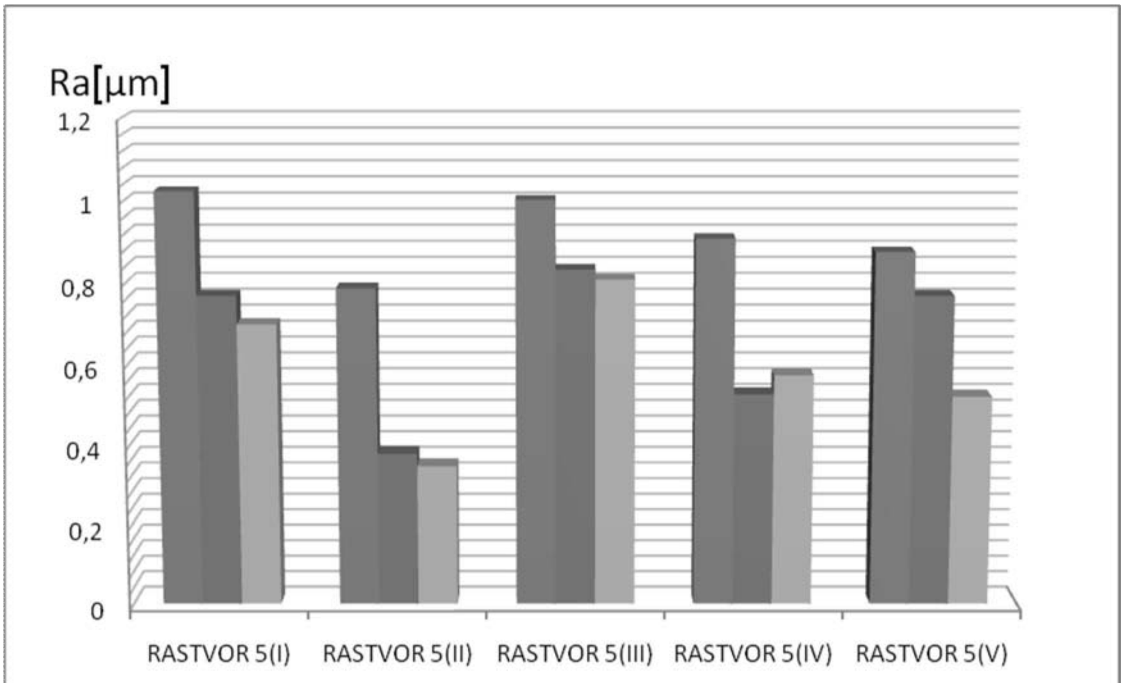
Na slici 5(a-c) dat je grafički prikaz izmerene hrapavosti elektrohemijski poliranih uzoraka aluminijuma u rastvoru 5(V): (a) τ = 5 min; (b) τ = 10 min; (c) τ = 15 min. Uslovi elektrohemijskog glačanja za rastvor 5(IV) su: I = 2,25 A ; U = 16,6 V ; t = 68 ^{0}C.



Slika 5. Grafički prikaz izmerene hrapavosti površine aluminijuma glačane u rastvoru 5(V), u zavisnosti od vremena: (a) τ =5 min; (b) τ = 10 min; (c) τ =15 min.

Sa slike 5(a-c) se vidi da se hrapavost površine elektrohemijski poliranih uzoraka u rastvoru 5(V) smanjuje sa vremenom. Za vreme elektrohemijskog poliranja: τ = 5 min, Ra = 0,875μm; τ = 10 min, Ra = 0,768 μm; τ = 15 min, Ra = 0,519 μm.

Na slici 6 dat je grafički prikaz hrapavosti površine aluminijuma nakon glačanja u svih pet korišćenih rastvora za elektrohemijsko poliranje.



	RASTVOR 5(I)	RASTVOR 5(II)	RASTVOR 5(III)	RASTVOR 5(IV)	RASTVOR 5(V)
τ (1)	1,023	0,786	1,002	0,908	0,875
τ (2)	0,768	0,377	0,832	0,525	0,768
τ (3)	0,698	0,346	0,808	0,572	0,519

Slika 6. Grafički prikaz hrapavosti površine aluminijuma nakon elektrohemijskog glačanja u rastvorima 5(I-V).

Iz dobijenih rezultata hrapavosti (slika 6) za rastvore 5(I-V), može se videti da nakon obrade uzoraka aluminijuma u rastvoru 5(II) površina ima najmanju hrapavost u odnosu na ostale rastvore, a dobre rezultate daje i rastvor 5(IV). Takođe, i na osnovu vizuelnog izgleda uočeno je da najbolju refleksiju imaju uzorci aluminijuma elektrohemijski glačani u rastvorima 5(II) i 5(IV).

ZAKLJUČCI

Na osnovu rezultata izmerene hrapavosti površine aluminijuma nakon elektrohemijskog poliranja aluminijuma u pet ispitivanih rastvora, može se zaključiti da svi korišćeni rastvori za elektrohemijsko poliranje daju dobre rezultate, jer se nakon elektrohemijskog poliranja smanjuje površinska hrapavost, a vizuelno se primećuje i povećanje refleksije svetlosti. Takođe, sa povećanjem vremena elektrohemijskog poliranja u svim korišćenim rastvorima dolazi do smanjenja površinske hrapavosti uzoraka. Od pet ispitivanih rastvora za elektrohemijsko glačanje aluminijuma, najefikasniji su rastvori: ***rastvor 5(II):*** *(400 cm^3) H_2SO_4 ; (600 cm^3) H_3PO_4; (5 cm^3) glicerina* i ***rastvor 5(IV):*** *70% H_2SO_4, 1% HNO_3, 15% H_3PO_4 i 14% H_2O.*

Uzorci aluminijuma obrađeni u ovim rastvorima imaju najmanju hrapavost $Ra_{(5(II))}$ = 0,346 µm i $Ra_{(5(IV))}$ = 0,525 µm i vizuelno najveći stepen refleksije. Na osnovu vizuelnog izgleda najveći sjaj ima uzorak aluminijuma glačan u rastvoru 5(IV) u vremenu od 10 minuta.

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ELECTROCHEMICAL POLISHING OF ALUMINUM SURFACES

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ABSTRACT

In this paper, using past experience in this field, through experimental work, the corresponding electrolytes for electrochemical polishing of aluminum and the optimum conditions for their implementation are examined. Aluminum samples must be chemically prepared and protective oxide membrane must be removed before electrochemical polishing. Four solutions were used to remove the oxide film, and five solutions were investigated for electrochemical polishing. All solutions used for electrochemical polishing of aluminum provide satisfactory results, since after electrochemical polishing, based on visual assessment, the surface gloss of the samples increased, i.e. surface reflection and reduction in surface roughness. The last statement was proved by performed measurements of surface roughness on all aluminum samples.
The increase in time of the electrochemical polishing leads to reduction in roughness. Of the five solutions used for electrochemical polishing of aluminum, the best results showed solutions 5(II) and 5(IV). Aluminum samples treated in these solutions have the lowest roughness and the highest level of reflection. Based on the visual appearance, the greatest reflection has the aluminum sample polished in a solution 5 (IV).

Keywords: *electrochemical polishing, surface roughness, anodic treatment*

Zaštita materijala i životne sredine 1 (2012), broj 2

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ANIONIC SURFACTANTS DETERMINATION IN INDUSTRIAL EFFLUENTS BY SEQUENTIAL INJECTION ANALYSIS WITH POTENTIOMETRIC DETECTION

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ABSTRACT

Sequential Injection Analysis (SIA) was used in these investigations for determination of anionic surfactants (AS) in diluted detergent formulations, used as model effluents.
A flow through home-made potentiometric detector, implemented into a home-made SIA system, recorded the electromotive force changes as a function of the AS concentration investigated. Sodium dodecyl sulfate and sodium dodecyl benzensulfonate were used for the calibration purpose. The specific software was developed for the data acquisition and elaboration, as well as for the instrument control. The detector exhibited almost Nernstian response toward the surfactants investigated down to 10^{-6} M. A 1,3-didecyl-2-methylimidazolium-tetraphenylborate ion-pair was applied as electroactive material in the detector sensing element. The standard addition methodology was used for testing the method, whereas the potentiometric titration was used as a reference method.
Keywords: *microfluidics, sequential injection analysis, anionic surfactant, model, effluent*

INTRODUCTION

Sequential Injection Analysis (SIA), [1,2]), the second generation of Flow Injection Analysis (FIA) techniques, was used in these investigations for determination of anionic surfactants (AS) in diluted detergent formulations, used as model effluents. One of the most important advanteges of SIA is its versatility and the drastic reduction of sample and reagent volumes used, good repeatability and reproducibility.
Anionic surfactants (AS) are the largest group of the surfactants and represent 70% of the annual surfactant production. They are widely used in the industrial and domestic fields; therefore, it is very important to determine the amount of AS in product formulations for quality control, in industrial samples for process control, and in food products and the environment for contamination control [3].
The low concentration of anionic surfactants in effluents and surface waters are usually determined using MBAS (Methylene Blue Active Substance) method which uses the complexing of anionic surfactants with cationic dye Methylene Blue [4].
The use of surfactant selective electrodes for potentiometric determination of low levels of anionic surfactant has been described in several papers [3, 5-8].
In this investigations a liquid-membrane electrode containing ion-pair 1,3-didecyl-2-methylimidazolium-tetraphenylborate (DMI-TPB) as surfactant sensing material was applied for potentiometric determination of the low levels of anionic surfactants in pure systems and modelled effluents.

EXPERIMENTAL

Reagents and Solutions

- sodium dodecylsulfate (NaDDS, Sigma Aldrich),
- sodium dodecylbenzene sulfonate, technical grade (NaDBS, Saponia, Croatia),
- 1,3-didecyl-2-methylimidazolium chloride (DMIC, Sigma Aldrich),
- cetylpyridinium chloride (CPC, Merck, Germany),

- sodium sulfate anhydrous (EBH PROLABO),
- hydrochloric acid (HCl, Merck, Germany).

All of the reagents used, except of NaDBS, were of analytical reagent grade. Deionized water was used through the experiments.
A 1,3-didecyl-2-methylimidazolium-tetraphenylborate (DMI-TPB) used as sensing material, *o*-nitrophenyloctylether (*o*-NPOE), and high molecular weight poly (vinyl chloride) (PVC) were purchased from Fluka (Switzerland) and were used for the preparation of the sensor membrane.

Apparatus
An all-purpose titrator 808 Titrando (Metrohm, Switzerland) combined with a Metrohm 806 Exchange unit (Metrohm, Switzerland) and controlled by the Tiamo software was used as the dosing element to perform the potentiometric titrations. During titrations and measurements, the solutions were magnetically stirred using an 801 Titration stand (Metrohm, Switzerland).
A Metrohm 780 pH meter, a 728 Stirrer, a Metrohm 765 Dosimat (all from Metrohm, Switzerland), in-house software, and the DMI-TPB sensors were all used for the response measurements. A silver/silver (I) chloride electrode (Metrohm, Switzerland) was used as a reference.
Home-made Sequential injection analyzer combined with home-made flow-through potentiometrc detector. SIA system was controlled by home-made software.

Sensor
A detailed explanation of the preparation of the DMI-TPB ion-exchange complex has been described previously [9]. Sodium chloride at a concentration of 3 M was employed as the internal filling solution. A silver/silver (I) chloride reference electrode (Metrohm, Switzerland) with a 3 M potassium chloride electrolyte solution was used as a reference.

SIA analyzer
The scheme of instrument is shown in Figure 1.

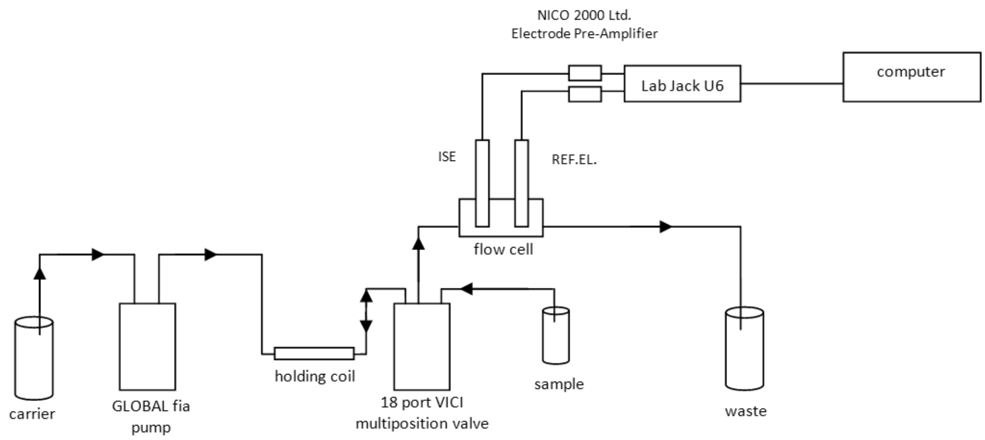

Fig. 1. Schematic diagram of SIA

Procedure

The stopped-flow sequence measurement started with washing with the carrier solution at the beginning of each measurement cycle. The system was filled with carrier solution, the multi position valve position was changed toward sample and sample was aspirated into the holding coil thorough the sample port. The multi-position valve position was then changed toward the potentiometric flow cell and the sample was transported from the holding coil into the potentiometric flow cell. The flow was stopped at the moment when the maximum concentration was reached, and was kept in the cell for 2 minutes. Finally the sample was transported into the waste to empty the cell.
The continuous flow sequence measurement started with washing with the carrier solution at the beginning of each measurement cycle. The system was filled with the carrier solution, the multi-position valve position was changed toward sample and sample was aspirated into the holding coil through the sample port. The multi position-valve position was then changed toward the potentiometric flow cell and sample was

transported from the holding coil through the cell into the waste to empty the cell.

RESULTS AND DISCUSSION

Response characteristics

The response characteristics of the DMI-TPB potentiometric detector toward DBS and DDS were investigated by conventional calibration procedure using pH/milivoltmeter (Table 1). Besides the calibration procedure for DDS was more detailed investigated in the region of 10^{-5} - 10^{-4} M by using of SIA system developed (Figure 2, Table 2).

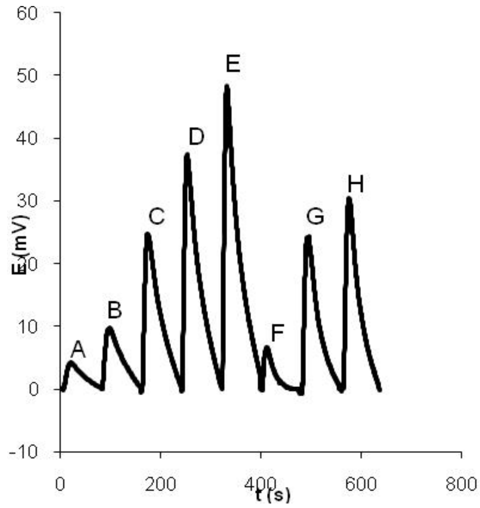

Fig. 2. SIA recorded signals for standard solutions of DDS: (A) 1x10^{-5} M, (B) 2,5x10^{-5} M, (C) 5x10^{-5} M, (D) 7,5x10^{-5} M, (E) 1x10^{-4} M, SIA recorded signals for various effluents (F-H)

Table 1. Response characteristics of DMI-TPB based sensor to the anionic surfactants given together with ± 95 % confidence limits.

PARAMETERS	DBS	DDS
Slope / (mV/decade)	57.8 ± 0.6	56.9 ± 0.4
Correl. coeff. (R^2)	0.9995	0.9998
Detection limit (M)	3 x 10^{-7}	3 x 10^{-7}
Useful conc. range (M)	4 x 10^{-7} - 5 x 10^{-3}	5 x 10^{-7} - 5 x 10^{-3}

Table 2. Response characteristics of DMI-TPB based potentiometric detector to DDS and the corresponding statistics, obtained by developed SIA system.

Series	**Slope mV/decade**	**Intercept**	**Correl. Coef. (R^2)**
1	54,7	229,9	0,9915
2	56,3	220,7	0,9976
3	55,7	211,7	0,9886
4	56,3	228,7	0,9984
5	56,1	227,3	0,9978
Average	55,8	223,6	0,9899
SD	0,67	7,60	0,00665
CV (%)	1,19	3,40	0,67228
CL (p = 0.95)	0,58	6,66	0,00412

It can be seen from Table 1, that DMI-TPB sensor exhibits highly sensitive pure Nernstian response for both, DDS and DBS in a wide concentration range. The sensor reveals a similar response characteristics for DDS in the region of 10^{-5} - 10^{-4} M by using of SIA system (Table 2). This concentration range corresponds more closely to the AS concentration in industrial effluents.

Determination of anionic surfactants in modeled effluents

SIA system was tested for determination of AS content in modeled effluents (diluted complex detergent solution with known AS content). The resulting responses are shown in Fig. 2 and the results of determinations with corresponding statistics are given in Table 3. The satisfactory accuracy and precision were obtained in the whole concentration ranges investigated.

Table 3. *The results of determination of DDS content in modeled effluents obtained by developed SIA system using DMI-TPB based potentiometric detector.*

AS added (mg/L)	**AS found (mg/L)**	**Recovery (%)**	**AS added (mg/L)**	**AS found (mg/L)**	**Recovery (%)**	**AS added (mg/L)**	**AS found (mg/L)**	**Recovery (%)**
6	6,27	104,5	15	14,32	95,5	30	30,29	101,0
6	5,81	96,9	15	15,57	103,8	30	28,76	95,9
6	5,87	97,8	15	14,28	95,2	30	32,43	108,1
6	5,73	95,6	15	14,73	98,2	30	31,20	104,0
6	5,92	98,7	15	15,90	106,0	30	28,55	95,2
Average	5,92	98,68		14,96	99,73		30,25	100,82
SD	0,19	3,09		0,74	4,92		1,64	5,47
CV (%)	3,13	3,13		4,94	4,94		5,42	5,42
CL (p = 0.95)	0,16	2,71		0,65	4,31		1,44	4,79

CONCLUSIONS

A flow through home-made potentiometric detector, implemented into a home-made SIA system, recorded the electromotive force changes as a function of the investigated AS concentration. Sodium dodecylsulfate and sodium dodecylbenzensulfonate were used for the calibration purpose. The specific software was developed for the data acquisition and elaboration, as well as for the instrument control. The detector exhibited Nernstian response toward the surfactants investigated down to 10^{-6} M. A 1,3-didecyl-2-methylimidazolium-tetraphenylborate ion-pair was applied as electroactive material in the detector sensing element.

Sample and reagent injection as the initial input parameters were investigated and optimized. A special attention was paid to the controlled dispersion process as well as to the reproducible timing. The method was tested in pure surfactant solutions as well as in modeled effluent solutions. The standard addition methodology was used for testing the method, whereas the potentiometric titration was used as a reference method. The described SIA device was tested in stopped-flow mode too.

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ODREĐIVANJE ANIONSKIH TENZIDA U INDUSTRIJSKIM EFLUENTIMA SEKVENCIJALNOM INJEKCIJSKOM ANALIZOM S POTENCIOMETRIJSKOM DETEKCIJOM

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IZVOD

U opisanim ispitivanjima korištena je sekvencijska injekcijska analiza (SIA) za određivanje anionskih tenzida (AS) u razrijeđenim otopinama detergenata, upotrebljenim kao modelni efluenti. Protočni detektor ugrađen je u SIA sistem (oboje vlastite konstrukcije) poslužio je za registriranje promjena elektromotorne sile kao funkcije koncentracije ispitivanih AS. Za kalibraciju su korišteni natrijev dodecilsulfat i natrijev dodecilbenzensulfonat. Razvijen je i specifičan softver za prikupljanje i obradu eksperimentalnih podataka, kao i za kontrolu rada instrumenta. Detektor je ispoljio gotovo nernstovski odziv prema ispitivanim tenzidima do 10^{-6} M. Kao elektroaktivni materijal u senzorskom elementu detektora korišten je 1,3-didecil-2-metilimidazolijev tetrafenilborat ionski par. Metodologija standardnog dodatka primijenjena je za testiranje metode, dok je kao referentna metoda korištena potenciometrijska titracija.

Zaštita materijala i životne sredine 1 (2012), broj 2

UDC 669.715:620.18

ISPITIVANJE PONAŠANJA LIVAČKIH LEGURA SISTEMA Al-Si U RASTVORIMA HLORIDA BEZ I SA PRISUSTVOM INHIBITORA

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IZVOD

Sa aspekta korozione stabilnosti legure aluminijuma se mogu podijeliti na koroziono stabilne i koroziono nestabilne (protektorske). Ispitivanja korozione stabilnosti legura aluminijuma zavisno od dobijenih rezultata u velikoj mjeri predodređuju njihovu namjenu. Međutim, treba istaći da sama koroziona svojstva nijesu jedini mjerodavni faktor njihove namjene, jer na njihovu namjenu utiču i dobijeni rezultati mehaničkih karakteristika koji su prije svega značajni u konstruktivnom smislu. Generalno, na ove osobine veliki uticaj ima hemijski sastav legura, koji utiče na formiranje njihove strukture, zavisno od prisustva i koncentracije legirajućih elemenata.
Obzirom da su sa aspekta korozionog ponašanja u agresivnim sredinama veoma interesantne legure sistema Al-Si uz dobra kombinaciju ostalih legirajućih elemenata, to je u ovom radu prikazan manji broj legura sistema Al-Si koji predstavlja nastavak dosadašnjih ispitivanja u ovoj oblasti. Ostali legirajući elementi su: željezo, magnezijum, bakar, nikal, kobalt, mangan, molibden i berilijum.
U ovom radu se pošlo od činjenice da se koroziona stabilnost legura sistema Al-Si korišćenjem neorganskih inhibitora može dovesti na viši nivo.
Ključne riječi: *inhibitori korozije, korozija metala, gustina struje, vodeni rastvori.*

UVOD

Kompleksne legure aluminijuma sa silicijumom spadaju u grupu nedovoljno izučenih livačkih legura aluminijuma, na osnovu čega se stvaraju široke mogućnosti kompleksnih istraživanja različitih faktora koji utiču na strukturu i osobine legura, a samim tim i na mogućnost njihove primjene u praksi.
U tom smislu vršena su ispitivanja korozione stabilnosti u rastvoru 0,51 M NaCl bez i uz prisustvo neorganskih inhibitora ($NaNO_2$, Na_2CO_3 i Na_2HPO_4) koja treba da pokažu uticaj legirajućih elemenata prisutnih u legurama sistzema Al-Si na korozionu stabilnost, kao i da se pokaže da li je njihov uticaj povoljan u tolikoj mjeri da se može govoriti o primjeni ovih legura kao koroziono stabilnih materijala.
Prema tome, cilj rada je bio da se utvrdi brzina korozije navedenog sistema legura i efikasnost zaštite u prisustvu neorganskih inhibitora ($NaNO_2$, Na_2CO_3 i Na_2HPO_4).

EKSPERIMENTALNI DIO

Sve ispitivane legure na bazi sistema Al-Si dobijene su topljenjem u elekroootpornoj peći snage 5,5 (KW), radne temperature 1100°C, livenjem i hlađenjem na vazduhu u laboratoriji za Livarstvo Metalurško-tehnološkog fakulteta.
Prilikom izrade legura posebna pažnja je posvećena tome da se dobiju homogene legure sa što manjim stepenom nehomogenosti. Iz ovih razloga je kao osnova korišćena legura AlSi10Mg kojoj su dodavane različite količine legirajućih elemenata u različitim kombinacijama.

Hemijski sastav dobijenih legura ispitivan je na X-RAY kvantometru u Kombinatu aluminijuma Podgorica, metodom bez razaranja.
Zatezna čvrstoća (Rm) i relativno izduženje (A) mjereni su i ispitivani na proporcionalno kratkim epruvetama. Epruvete su obrađene po JUS - u. Ispitivanja su vršena u laboratoriji KAP-a, na elektronskoj univerzalnoj kidalici tipa -1195 „INSTRON“ čiji se opseg opterećenja kreće od 20 N do 20.000 N.
Tvrdoća je ispitivana u laboratoriji KAP- a. Uzorci su urađeni od iskidanih glava epruveta. Mjerenje tvrdoće je vršeno po BRINELU.

Koroziona i elektrohemijska istraživanja vršena su na opremi za ubrzana ispitivanja-sistem PAR koji čine: potenciostat-galvanostat model 273, diferencijalni elektrometar, koroziona ćelija K0047, standardna zasićena kalomel elektroda, pomoćne elektrode-valjkasti elektrografit, računar sa korozionim softverom SOFTCORR 352 II i štampač.

Eksperimentalni dijagrami dobijeni su korišćenjem metoda:

- metoda polarizacionog otpora, Rp;
- potenciodinamička metoda.

REZULTATI I DISKUSIJA

Hemijski sastav dobijenih legura sistema Al-Si dat je u tabeli 1.

Tabela 1. Rezultati hemijskog sastava sa kvantometra (mas %)

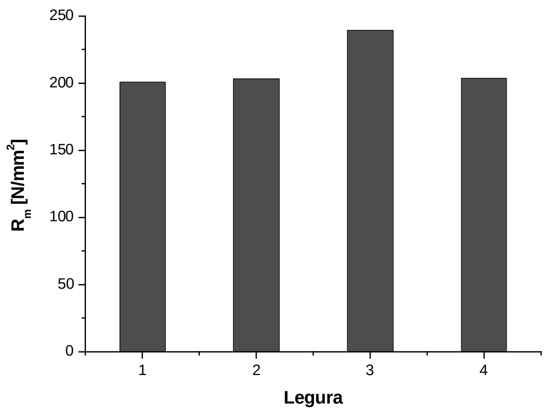
Legura	Si	Fe	Cu	Mg	Ni	Co	Mn	Mo	Be
1	11,76	1,77	1,37	2,96	0,85	0,75	0,44	0,25	0,25
2	11,81	1,64	1,37	0,91	0,78	1,00	0,44	0,30	0,25
3	12,50	1,64	1,21	1,02	1,29	0,70	0,09	0,45	0,25
4	12,45	1,72	2,20	0,95	1,41	0,95	0,09	0,55	0,25

Iz tabele 1 se vidi da se radi o kompleksnim legurama aluminijuma sa velikim brojem legirajućih elemenata.

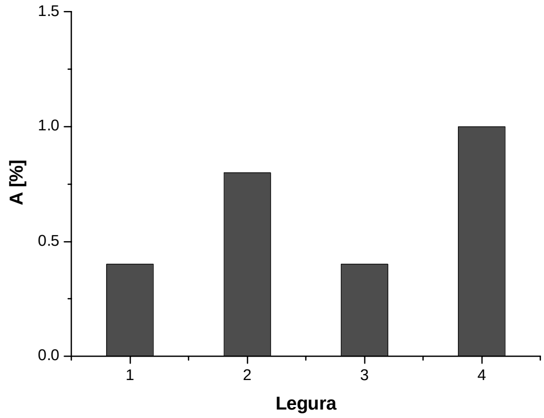
Mehaničke osobine ispitivanih legura prikazane su u tabeli 2 i na slikama 1 – 3.

Tabela 2. Rezultati ispitivanja mehaničkih osobina u livenom stanju

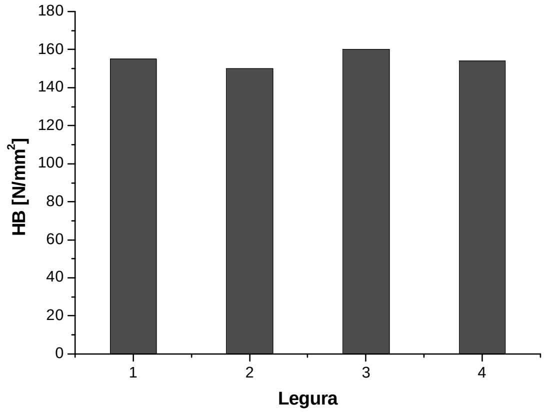
Legura	R_m [N/mm^2]	A [%]	HB [N/mm^2]
1	200,7	0,4	155
2	203,2	0,8	150
3	239,5	0,4	160
4	203,6	1,0	154



Slika 1. Histogramski prikaz vrijednosti zatezne čvrstoće (R_m) ispitivanih legura u livenom stanju

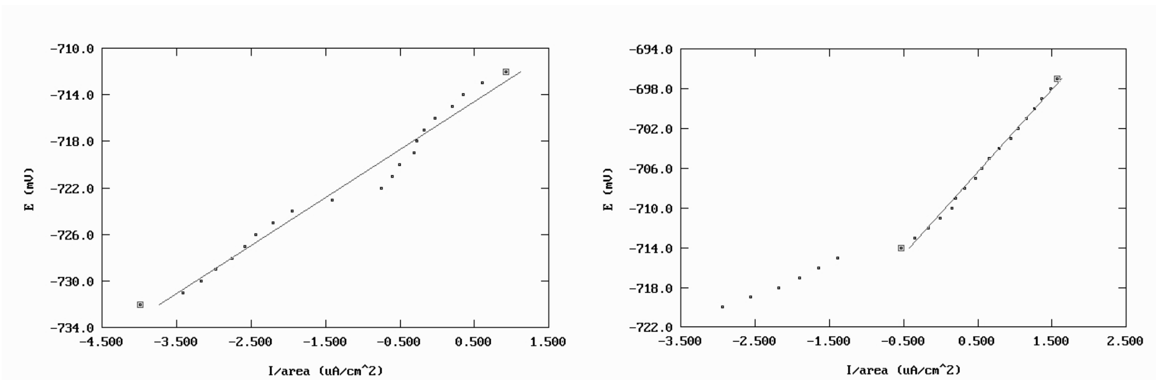


Slika 2. Histogramski prikaz vrijednosti relativnog izduženja (A) ispitivanih legura u livenom stanju

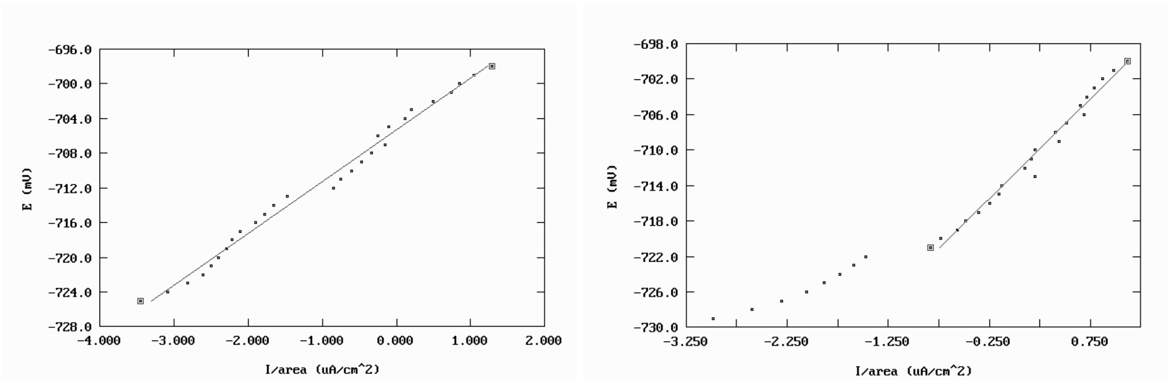


Slika 3. Histogramski prikaz vrijednosti tvrdoće (HB) ispitivanih legura u livenom stanju

Na slikama 4 i 5 prikazani su eksperimentalno dobijeni dijagrami polarizacionog otpora i potenciodinamičke katodne i anodne krive za leguru 1 bez i sa dodatkom neorganskih inhibitora u osnovni rastvor (0,51M NaCl).

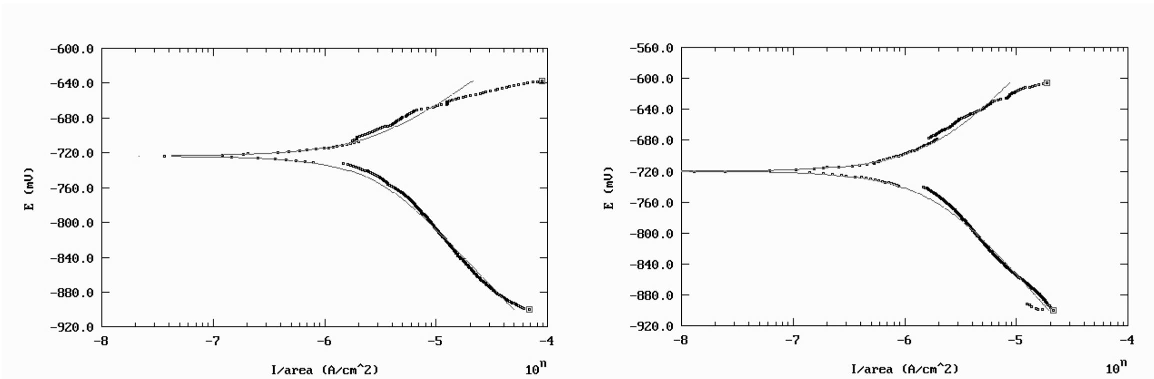


a) *b)*

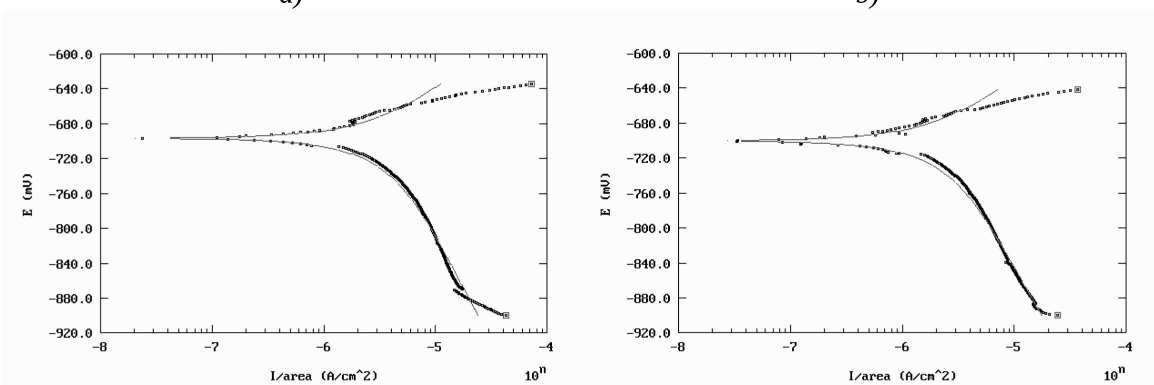


c) *d)*

Slika 4. Dijagrami polarizacionog otpora legure 1:
a) bez dodatka inhibitora
b) u prisustvu 10^{-4}M Na_2CO_3
c) u prisustvu 10^{-4}M $NaNO_2$
d) u prisustvu 10^{-4}M Na_2HPO_4



a) *b)*



Slika 5. Potenciodinamičke katodne i anodne polarizacione krive legure 1:
a) bez dodatka inhibitora
b) u prisustvu 10^{-4}M Na_2CO_3
c) u prisustvu 10^{-4}M $NaNO_2$
d) u prisustvu 10^{-4}M Na_2HPO_4

U tabelama 3-9 prikazane su eksperimentalne vrijednosti polarizacionog otpora (R_p), gustine struje korozije (j_{corr}), potencijala e(j=0) i efikasnosti zaštite. Istraživanja su obavljena u 0,51M rastvoru NaCl uz dodatak neorganskih inhibitora $NaNO_2$, Na_2CO_3 i Na_2HPO_4, koncentracije 10^{-4}M.

Tabela 3. Vrijednosti Rp, j_{corr} i e(j=0) dobijene metodom polarizacionog otpora u prisustvu inhibitora Na_2CO_3

Legura	Bez inhibitora			10^{-4} M Na_2CO_3		
	e(j=0) [mV]	Rp [Ω]	j_{corr} [μA/cm^2]	e(j=0) [mV]	Rp [Ω]	j_{corr} [μA/cm^2]
1	-716,6	4,131	5,257	-710,5	8,316	2,611
2	-748,0	5,465	3,974	-730,4	9,375	2,316
3	-720,3	5,268	4,122	-711,5	10,43	2,083
4	-739,9	4,983	4,358	-733,0	11,44	1,898

Tabela 4. Vrijednosti Rp, j_{corr} i e(j=0) dobijene metodom polarizacionog otpora u prisustvu inhibitora $NaNO_2$

Legura	Bez inhibitora			10^{-4} M $NaNO_2$		
	e(j=0) [mV]	Rp [Ω]	j_{corr} [μA/cm^2]	e(j=0) [mV]	Rp [Ω]	j_{corr} [μA/cm^2]
1	-716,6	4,131	5,257	-705,3	5,976	3,634
2	-748,0	5,465	3,974	-702,1	7,307	2,972
3	-720,3	5,268	4,122	-708,3	8,345	2,602
4	-739,9	4,983	4,358	-727,5	7,132	3,045

Tabela 5. Vrijednosti Rp, j_{corr} i e(j=0) dobijene metodom polarizacionog otpora u prisustvu inhibitora Na_2HPO_4

Legura	Bez inhibitora			10^{-4} M Na_2HPO_4		
	e(j=0) [mV]	Rp [Ω]	j_{corr} [μA/cm^2]	e(j=0) [mV]	Rp [Ω]	j_{corr} [μA/cm^2]
1	-716,6	4,131	5,257	-712,7	11,25	1,930
2	-748,0	5,465	3,974	-729,1	6,758	3,213
3	-720,3	5,268	4,122	-709,9	8,972	2,420
4	-739,9	4,983	4,358	-721,5	6,328	3,432

Na bazi eksperimentalno dobijenih vijednosti polarizacionog otpora i gustine struje korozije (tabele 3-5), uočava se da sva tri inhibitora u koncentraciji 10^{-4}M utiču na smanjenje brzine korozije Al legura u 0,51M rastvoru NaCl. Dodatkom inhibitora u osnovni rastvor došlo je do smanjenja vrijednosti gustine struje korozije, odnosno na povećanje polarizacionog otpora.

Efikasnost zaštite na osnovu podataka iz prethodnih tabela izračunava se po jednačini:

$$\eta = \frac{j_{corr} - (j_{corr})_{inh}}{j_{corr}}$$

gdje je j_{corr} gustina struje korozije u neinhibiranom, a $(j_{corr})_{inh}$ u inhibiranom rastvoru. Izračunate vrijednosti efikasnosti zaštite prikazani su u tabeli 6.

Tabela 6. Efikasnost zaštite ispitivanih Al legura u prisustvu neorganskih inhibitora

Legura	10^{-4}M Na_2CO_3	10^{-4}M $NaNO_2$	10^{-4}M Na_2HPO_4
1	50,33%	30,87%	63,28%
2	41,72%	25,21%	19,15%
3	49,46%	36,87%	41,29%
4	56,44%	30,12%	21,25%

Tabela 7. Vrijednosti e(j=0) dobijeni potenciodinamičkom metodom u prisustvu inhibitora Na_2CO_3

Legura	Bez inhibitora	10^{-4} M Na_2CO_3
	e(j=0) [mV]	e(j=0) [mV]
1	-723,8	-720,1
2	-757,1	-730,4
3	-721,0	-712,6
4	-754,3	-740,1

Tabela 8. Vrijednosti e(j=0) dobijeni potenciodinamičkom metodom u prisustvu inhibitora $NaNO_2$

Legura	**Bez inhibitora**	**10^{-4} M $NaNO_2$**
	e(j=0) [mV]	**e(j=0) [mV]**
1	-723,8	-696,8
2	-757,1	-726,7
3	-721,0	-718,7
4	-754,3	-741,5

Tabela 9. Vrijednosti e(j=0) dobijeni potenciodinamičkom metodom u prisustvu inhibitora Na_2HPO_4

Legura	**Bez inhibitora**	**10^{-4} M Na_2HPO_4**
	e(j=0) [mV]	**e(j=0) [mV]**
1	-723,8	-700,4
2	-757,1	-737,8
3	-721,0	-712,5
4	-754,3	-729,6

Rezultati dobijeni potenciodinamičkom metodom (misli se na vrijednost e(j=0)) koji su dati u tabelama 7-9, pokazuju da dolazi do pomjeranja potencijala e(j=0) ka pozitivnijim vrijednostima kada se u osnovi rastvor dodaju neorganski inhibitori. Vrijednosti potencijala e(j=0) kreću se u intervalu od -696,8 mV do -754,3 mV.

ZAKLJUČAK

Na bazi svih rezultata ispitivanja, kao i zapažanja do kojih se došlo tokom izrade ovog rada može se zaključiti sljedeće:

1. Livenjem legura aluminijuma, dobijene su legure sa različitim karakteristikam, što je posledica različitog hemijskog sastava. Prema tome izabrani i dobijeni hemijski sastav ispitivanih legura imao je direktan uticaj na osobine legura, kako sa aspekta mehaničkih karakteristika, tako i sa aspekta korozionog ponašanja.
2. Vrijednosti mehaničkih karakteristika ispitivanih legura u livenom stanju su u očekivanim granicama. Najveću vrijednost zatezne čvrstoće imala je legura 3 (239,5 N/mm^2), a najmanju legura 1 (200,7 N/mm^2). Vrijednosti relativnog izduženja su se kretale od 0,4 % za legure 1 i 3 do 1,0 % za leguru 4, dok su se vrijednosti tvrdoće kretale od 150,0 N/mm^2 za leguru 2, do 160,0 N/mm^2 za leguru 3.
3. Analizom rezultata korozionih ispitivanih legura može se zaključiti da se sve ispitivane legure ponašaju koroziono stabilno i da je legura 1 ima veću korozionu stabilnost, što je posljedica dobijenog hemijskog sastav. Prisustvo sva tri inhibitora u osnovom rastvoru pokazalo se veoma izraženim obzirom da se efikasnost zaštite kreće u intervalu od 21,25% (legura 4 u prisustvu 10^{-4} M Na_2HPO_4) do 63,28% (legura 1 u prisustvu 10^{-4} M Na_2HPO_4).

ZAHVALNOST

Autori se zahvaljuju Ministarstvu nauke Crne Gore na sredstvima dodijeljenim za naučno-istraživački projekat „Ispitivanje uticaja inhibitora na brzinu korozije materijala na bazi željeza i aluminijuma u vodenim rastvorima“.

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INVESTIGATION OF THE BEHAVIOR OF CASTING Al-Si SYSTEM ALLOYS IN CHLORIDE SOLUTIONS WITH AND WITHOUT THE PRESENCE OF INHIBITORS

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ABSTRACT

From the standpoint of corrosion stability of aluminum alloys can be divided into corrosion stable and corrosion unstable (protectorate). Corrosion stability testing of aluminum alloys depending on the results largely predetermine their purpose. However, it should be noted that the corrosion properties alone are not the only relevant factor in their purposes, because of their influence, and use the results of mechanical properties that are particularly important in a constructive way. Generally, these properties have a great influence chemical composition of alloys, which affects the formation of the structures, depending on the presence and concentration of alloying elements.
Given that in terms of corrosion behavior in aggressive environments very interesting alloy system Al-Si with a good mix of other alloying elements, in this paper is presented small number of alloys of the Al-Si, which is a continuation of previous research in this area. Other alloying elements are: iron, magnesium, copper, nickel, cobalt, manganese, molybdenum, and beryllium.
In this paper started from the fact that the corrosion properties of alloys of the Al-Si using inorganic inhibitors may result to a higher level.

Keywords: *corrosion inhibitors, corrosion of metals, the current density, aqueous solutions*

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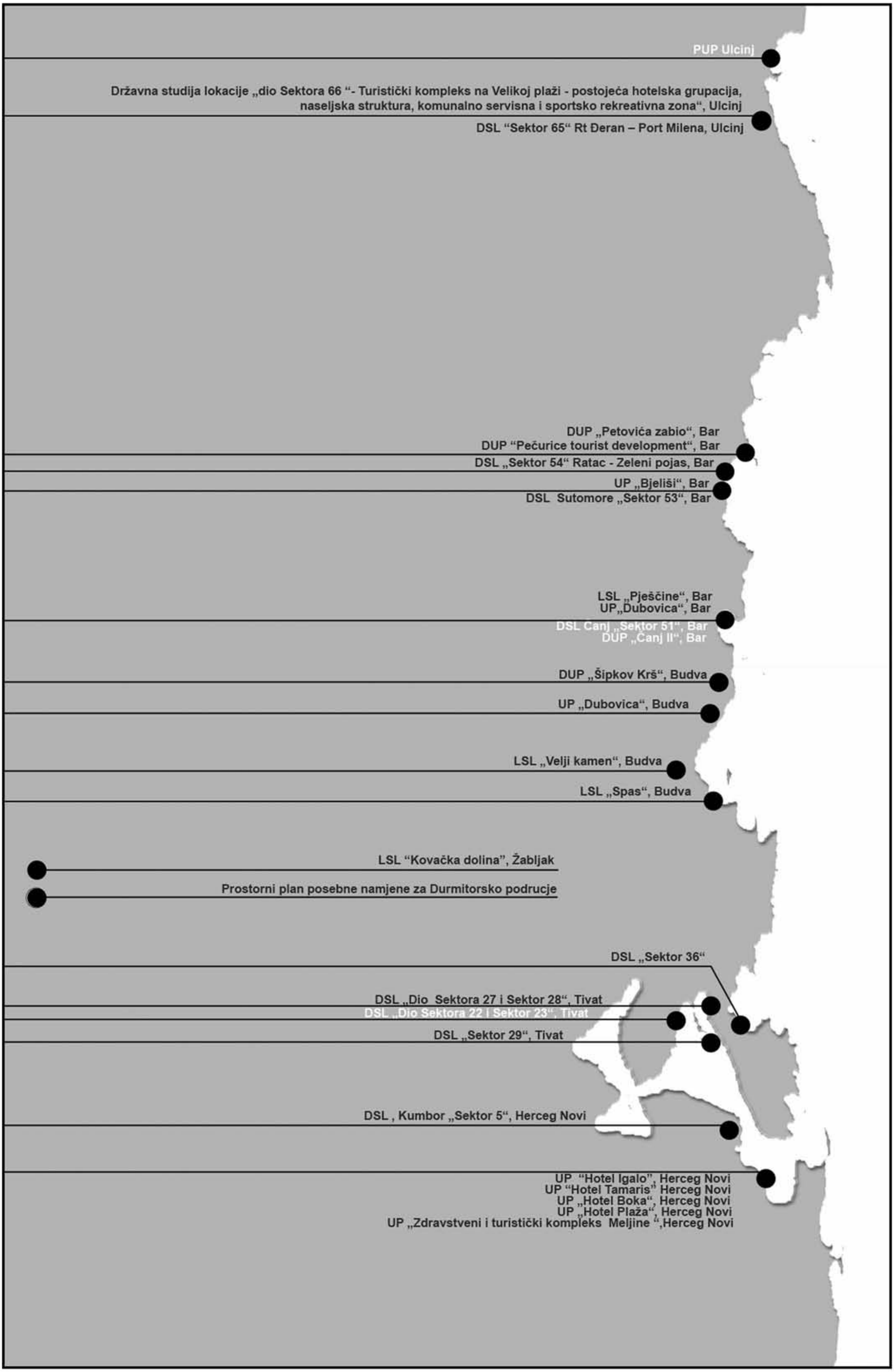
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EGK kao novi proizvod AD»Poliex» Berane po svojim karakteristikama, osobinama i načinu primjene predstavlja napredak u odnosu na sva dosad poznata sredstva korištena za razbijanje, rezanje i cijepanje građevinskih materijala (betoni, armirano-betonske konstrukcije, graniti, mermeri,kameni blokovi).Za razliku od klasičnih eksploziva EGK u zatvorenom prostoru stvara kvazistatički pritisak gasova što dovodi do cijepanja homogenih struktura stijena bez eksplozije i rasipanja materijala.

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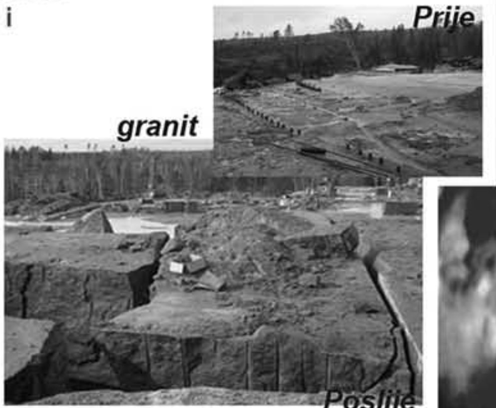

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Preduzeće YU BRIV je nastalo spajanjem dvije porodične firme. Do danas smo prerasli u efikasnu kompaniju sa 120 stalno zaposlenih. Pored inžinjeringa i gradjevinske djelatnosti, obavljamo poslove projektovanja, ugostiteljstva, unutrasnje i spoljne trgovine, unutrasnjeg i medjunarodnog transporta, turizma. Usmjerili smo se na djelatnosti i konačne rezultate naših napora – izvedene objekte. Velika je odgovornost gledati u budućnost i nastojati opravdati ukazano povjerenje, ali je veliko zadovoljstvo pogledati unazad i vidjeti kako su se ostvarile naše poslovne želje, zahvaljujući vjerovanju da se uvijek može postići više.

Spoj tradicije i novih dostignuća i iskustva, tehničko-tehnološke i stručne osposobljenosti, omogućio nam je da u periodu koji je iza nas izgradimo veliki broj objekata visokogradnje, hidrogradnje, niskogradnje i specijalizovanih građevinskih radova.

Sa posebnim zadovoljstvom ističemo radove na:

- II fazi Sanacije i rekultivaciji jalovišta rudnika olova i cinka čime smo dali značajan doprinos saniranju jedne od najvećh crnih ekoloških tačaka u našoj državi.
- Hidrotehnički radovi na izgradnji marine „Porto Montenegro“
  Sistemi za vezivanje mega jahti
  Izgradnja Gata III, IV i kejskog zida
- veliki broj stambenih objekata, drugih objekata visokogradnje, niskogradnje i hidrogradnje

U izvođenju dosta zahtjevnih i složenih građevinskih objekata, posebnu pažnju posvećujemo primjeni i korišćenju najnovijih tehničkih dostignuća nanošenja premaza otpornih na visoko temperature, zaštita građevinskih objekata, uticaja morske vode na izgrađene objekte, ugradnja uređaja i njihova zaštita u sistemima vodosnabdjevanja, uz praćenje stanja i procesa u životnoj sredini.

Veliki broj uspješno realizovanih projekata, dugogodišnje iskustvo omogućili su da postanemo respektabilna firma, razvijana i građena samo sa prijateljima . Graditeljska tradicija je i naša tradicija.Prateći nova tehnološka rješenja posebnu pažnju u realizaciji projekata posvećujemo kvalitetu naših usluga.

U Kompaniji je uveden sistem kvaliteta ISO 9001:2008, i sistema ISO 14001:2008 što je dokaz naše privrženosti uspostavljanja međunarodnih standarda za sisteme upravljanja kvalitetom i zaštitom životne sredine i potvrđuje da je uspostavljen i da se primjenjuje sistem upravljanja zaštitom životne sredine.

LUKA KOTOR
PORT OF KOTOR

Kotor, odnosno Luka Kotor se nalazi neposredno uz Jadransku magistralu i njom je povezana sa mjestima uz obalu, kao i sa gradovima u unutrašnjosti.

Dužina operativne obale kojom raspolaže Luka Kotor u luci iznosi 665 m, od čega se 512 m nalazi na zapadnom djelu dok je 153 m okrenuto prema rijeci Škurdi. Operativna obala se može funkcionalno podjeliti na 5 vezova i to:

- Riva I, vez u dužini od oko 150 m. Operativna obala na ovom vezu je opremljena sa 11 bitava.
- Riva II, vez u dužini od 100 m. Uz ovu operativnu obalu postoji samo uska traka širine od 6 do 9 m koju brodovi mogu koristiti.
- Riva III, obuhvata južni dio rive u dužini od oko 250 m.
- Rijeka I je vez na sjevernom djelu prema rijeci Škurdi u dužini od oko 80 m.
- Rijeka II je vez u dužini od oko 70 m.

LUKA KOTOR

PORT OF KOTOR

Luka Kotor je morskim putem od važnijih luka udaljena kao je prikazano:

	Nm
Kotor-Bar	42
Kotor-Bari	125
Kotor-Otrant	151
Kotor-Trst	334
Kotor-Ankona	254
Kotor-Pirej	715
Kotor-Dubrovnik	40

Operativna obala Rijeka I i Rijeka II su opremljeni sa 10 bitava. Operativna obala je ukupno opremljena sa 61 gumena bokobrana.

Na južnom djelu obale prema moru postoje priključci za vodu, telefon i električnu energiju koji su na raspolaganju plovilima.

S+E TEHNIKA - D.O.O.
BAR

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PIB: 02068095, PDV: 80/31-00222-3

Preduzeće "S+E Tehnika" d.o.o. postoji od 1995. godine.

Preduzeće se bavi :

- crpljenjem septičkih jama, crpljenje separatora masnoće, sakupljanje iskorišćenih jestivih ulja iz friteza (u planu je pravljenje biodizela od ovih ulja za sopstvene potrebe),
- očepljenje svih vrsta kanalizacije i cjevovoda specijalnim vozilima vodom pod visokim pritiskom,
- snimanje cjevovoda specijalnim kamerama i davanje CD-a sa snimljenim materijalom naručiocu. Kamere pored vizuelnog prikaza stanja u cjevovodu mjere i NIVELIRUNG, tj. pad cijevi koja je postavljenja pod zemljom,
- posjedujemo frezu za kidanje korijenja u cijevima ili na primjer skidanje ostataka betona u cijevima i slično,
- takođe, posjedujemo opremu za sanaciju lomova cijevi pod zemljom oblaganjem specijalnom dvokomponentnom plastikom unutrašnjosti cijevi na mjestu loma ili loših spojeva cijevi, tako da ne mora da se kopa, lomi asfalt ili neka druga podloga,
- posjedujemo specijalni kamion sa četkama za pranje zidova tunela.

Kamion za crpljenje i očepljenje kanalizacije

Kamera za snimanje cjevovoda

Komandni pult u kombiju za snimanje kanalizacije

CDKZM

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