International Journal of the Physical Sciences Vol. 7(18), pp. 2639-2646, 9 May, 2012
Available online at http://www.academicjournals.org/IJPS
DOI: 10.5897/IJPS12.139
ISSN 1992 - 1950 © 2012 Academic Journals

Review

Procedure for treatment of hazardous waste by MID-MIX procedure in Serbia

Brkljač Nebojša, Šević Dragoljub, Beker Ivan, Kesić Igor and Milisavljević Stevan*

Faculty of Technical Sciences, Novi Sad, Serbia.

Accepted 1 March, 2012

This paper presents adequate treatment characteristics of the problem of hazardous waste while providing a specific example of the problem. Hazardous waste being discussed here is galvanic sludge. Furthermore, not only is the hazardous waste problem within a company discussed, but also on a national level. The MID-MIX® procedure was chosen and described as an optimal solution for adequate hazardous waste treatment, as well as activities and listed documentation on a possible procedure of transporting the waste discussed here to the treatment plant. With a view to demonstrate the problem solving procedure, a flowchart has been used as a graphical representation technique of a realization of a process. Improper waste disposal, especially of hazardous waste, has a tremendously negative effect on the environment. In this particular example it impacts the agriculture, and thereby the food production. Finally, directions for future work on this subject and solutions for the hazardous waste problem on a national level are provided here.

Key words: Best available technology not entailing excessive cost (BATNEEC), MID-MIX® procedure, waste management, hazardous waste, waste generator, sustainability.

INTRODUCTION

All over the world, people have increasingly witnessed nuclear accidents, oil spills, mismanagement of solid and hazardous waste, depletion of resources, environmental deterioration, global warming, environmentally induced deathly diseases and other environmental problems. Also, with mounting awareness along with environmental problems, it was recognized that we are not immune to ecological constraints and that the future generations and ecosystem are in jeopardy (Nazmiye, 2009). One of the most important goals of today is environmental protection at both a local and global level. World population growth and the accelerated economic growth contribute to waste stock increase. Waste matter, especially hazardous waste matter has become a major problem of the modern society. Raising the level of awareness of the necessity of discussing permanent solutions to this problem and their implementation, helps create ideas and solutions with all their characteristics and specifics. The sustainability principle has to be the base for discussion and suggested solutions; it has to be treated as a condition for survival and advancement of manhood. Waste treatment technologies and waste treatment plants have to fulfill the environmental protection and economic criteria. The motivation behind this research lies in the tremendous need for solving the problem of hazardous waste which, according to data of the republic inspectors for environmental protection, can be found in large amounts in Republic of Serbia. This waste is being disposed inadequately and thus represents an environmental problem and potential danger for the citizens. This research was conducted in order to present a way to adequately dispose off company waste and neutralize its toxic and hazardous components on an example of a specific organization with a hazardous waste problem, and all this in order to enhance environmental protection aspects.

Our intention here is to present a solution to serve as an example of adequately treated hazardous waste, and serve as a model to other organizations across the country facing the same waste problems. During the establishment and implementation of the waste management plans, there are several principles that need to be

*Corresponding author. E-mail: steva@uns.ac.rs.

considered, and one of them is the hierarchy principle in waste management. Within this principle, prevention of waste formation and reduction of amounts and hazardous characteristics of the formed waste have been given the highest priority. Vogt (2002) defines reduction of waste generation as arguably one of modern society's greatest challenges. Being more 'green sensitive' throughout the value chain not only brings about economical benefits but also environmental benefits. Waste is an expense for any enterprise. Complicating issues of how to make practices more sustainable are questions of how sustainable our behavior should be. What do we owe future generations? What value should we place on the welfare of others? The fate of future generations is in our hands, and we must decide the toll we will take on their quality of life (Anderson, 2010).

Problem overview

Large industrial plants are the largest hazardous waste generators. In Republic of Serbia, most common sources of hazardous waste are:

1) Energetics.
2) Pharmaceutical industry.
3) Chemical industry.
4) Food processing industry.
5) Packaging industry (Brkljač, 2010).

According to the Serbian National Waste Management Strategy for the 2010 to 2019 period, it is estimated that around 100,000 tons of hazardous waste is annually generated in Serbia. This waste is mainly exported to European countries (such as Austria, Hungary, Germany, Denmark, Scotland, Italy and Czech Republic) where it is subjected to incineration. However, organizations which lack sufficient financial resources to export and adequately test the hazardous waste, tend to storage harmful chemicals in their surroundings or illegally transfer to landfills, and thereby represent danger for the environment. Also, it is very important for these countries to have well-established mechanisms for applying legislation. Our country falls into the category of countries with a relatively good legislation, unfortunately, it lacks well-developed mechanisms. It is certain that there is no difference between the nonexistent legislation and the legislation no one obeys (Šević, 2010). In addition, the construction of the physical-chemical waste treatment plant in Serbia became a legal obligation several years ago and a part of the agreement signed with EU, towards EU integrations. Specifics and difficulties of solving this problem and making the right decision entail a wide range of consequences, and make the beginning of the project realization impossible to determine.

Discussing solution proposals such as plants with or without an incinerator, treatment of only particular sorts of waste, waste inertization technology, etc. is a very complicated procedure. Economic factor, environmental preservation, the effect of the citizens on the decision are only some of the key factors which affect the authorities decision of what general waste problem solving strategy will be, especially concerning hazardous waste. Treatment of hazardous waste with a MID-MIX® procedure is the third potential solution for waste treatment [1) export of waste, 2) construction of a waste treatment plant] and will be presented as follows as a hazardous waste problem solution in a specific organization. As a typical example of hazardous waste problem, let's focus on waste created after the process of galvanization and the same plant halt in the particular organization. This waste (Table 1), in the form of metal salts solution (Figure 1), acids, bases and galvanic sludge (Figure 2) is located in special tubs for galvanization. A possible accident, which could lead to severe environmental pollution, is leakage of chemicals used in the galvanization process. After halting production in the plant, chemicals that are treated as hazardous waste are not being removed from the site. There is a huge risk that these chemicals would be spilled in the nearby river, a risk of soil contamination or both. River pollution would not only lead to destruction of its flora and fauna, but also to contamination of agricultural land because the water from the river is used to supply the irrigation system on the land located downstream from the accident site.

Likewise, in the company's surrounding area, there are residential buildings, and an accident, in the form of the mentioned chemicals would have negative effect on the environment and the people who live in the surroundings.

MID-MIX® TECHNOLOGY

MID-MIX® is a patently protected technology which has been applied since the end of the 1980's. Mobile and stationary plants for industrial waste treatment using this technology are located in multiple European countries (Spain, France, Portugal, Austria, Italy, Poland, Slovenia, Andorra, Croatia, Bosnia and Herzegovina, Serbia).

MID-MIX® is one of the approved and recommended technologies in Europe [BATNEEC (Best Available Technology Not Entailing Excessive Cost)] – the best available technologies which do not entail excessive cost of waste managing and do not pollute environment with industrial waste after treatment. This technology is used for inertization of different sorts of industrial waste (industrial sorts of waste) from almost all basic and processing industries such as refineries, petrochemistry, basic chemistry, pharmacy, food processing industry etc. The most processed waste materials using this technology are:

i) Old oils, industrial residue,

Table 1. List of waste compounds and their amounts within a company discussed.

Waste name	Active matter	Formulation	Amount
Denikal	Nickel(II) hydroxide	$Ni(OH)_2$	1.027 l
Nickel electrolyte	Boric acid	BH_3O_3	5.140 l
	Nickel (II) sulfate hexahydrate	$NiSO_4 \cdot 6H_2O$	
Cyanide copper	Nickel (II) chloride hexahydrate	$NiCl_2 \cdot 6H_2O$	4.391 l
	Copper cyanide	CuCN	
	Potassium cyanide	KCN	
Cyanide brass	Sodium cyanide	NaCN	6.583 l
	Copper cyanide	CuCN	
Cyanide zinc	Zinc cyanide	$Zn(CN)_2$	6.200 l
	Sodium cyanide	NaCN	
	Sodium hydroxide	NaOH	
Acid copper solution	Copper (II) sulfate	$CuSO_4$	4.100 l
	Copper (II) sulfate pentahydrate	$CuSO_4 \cdot 5H_2O$	
	Sulfuric acid	H_2SO_4	
Degreaser	Sodium hydroxide	NaOH	3.878 l
	Sodium metasilicate	Na_2SiO_3	
	Sodium carbonate	$NaCO_3$	
Pickling solution	Hydrochloric acid	HCl	1.092 l
Pasivizator	Nitric acid	HNO_3	864 l
		Total:	33275 l

Figure 1. Galvanic solution (Brkljač, 2010).

Figure 2. Galvanic sludge (Brkljač, 2010).

ii) Soil contaminated by organic waste,
iii) Petrochemical and pharmaceutical residue,
iv) Different industrial and municipal sludges,
v) Colors and varnish,
vi) Tar and phenols,
vii) Paraffin residue,
viii) Waste from separator filters, galvanic sludges, emulsions and solvents,
ix) Sludges from the treatment with wastewater purifiers,
x) Electrofilter ashes (www.yunirisk.com, 2011).

In order to cut costs of industrial waste transportation and avoid the risk of possible emergency situations during the transportation, mobile MID-MIX® plants should be placed inside industrial zones. They are usually set on rectangular plateaus sized 20 × 25 m and 40 × 80 m (Figures 3 and 4), depending on the waste treatment capacity. The only resources used by these plants are electrical power and water.

WHAT IS MID-MIX® PROCEDURE?

MID-MIX® is a physical-chemical oxidoreduxtion process reflected in reaction of waste molecules with additives based on calcium oxide and calcium hydroxide [CaO and $Ca(OH)_2$] and obtaining new solid inert powder–solidificate (www.yunirisk.com, 2011). Inertization of industrial and municipal waste is conducted using this process and solidificate and condensed water from vapor are final products of process, and they do not have harmful effects on human beings and their environment. Term “solidificate” comes from the name of the chemical process - solidification, which is also the basis of MID-MIX® technology. The chemical process conducted during the MID-MIX® technological procedure is called the exothermal vacuum-gas molecular encapsulation. During the MID-MIX® technologic process, using instructed reaction parameters, it comes to so-called TTT equilibrium of parameter’s state:

i) T_1 Temperature T (°C),
ii) T_2 Time t (s) and,
iii) T_3 Transformation Q (kg/s).

Transformation speed (waste + additives = solidificate) is considerable and the process lasts less than 10^{-12} s. This physical-chemical process is characterized by:

i) Intensive contact of waste and the process additives,
ii) Exothermal reaction with water evaporation,
iii) Vacuum-gas molecular encapsulation of waste particles,
iv) Hardening - solidification of the entire content in the reactor and,
v) Nonexistence of waste water and harmful gases.

Solidificate is low density, white-grey to grey-brown powder with extremely hydrophobic and pumpability features. According to EU categorization of waste, it represents an inert, non-dangerous material which can be further processed and used accordingly. Solidificate has the following characteristics:

i) Water non-permeability from 2.0 to $10^{-9} > \kappa > 1.1$ to 10^{-9}

Figure 3. General look of the MID-MIX® mobile plant with capacity of 10 m^3/h for treatment of different sorts of cobble hydrogenised waste placed in the hall (Maribor – Slovenia 2000), (www.grgoni.hr, 2011).

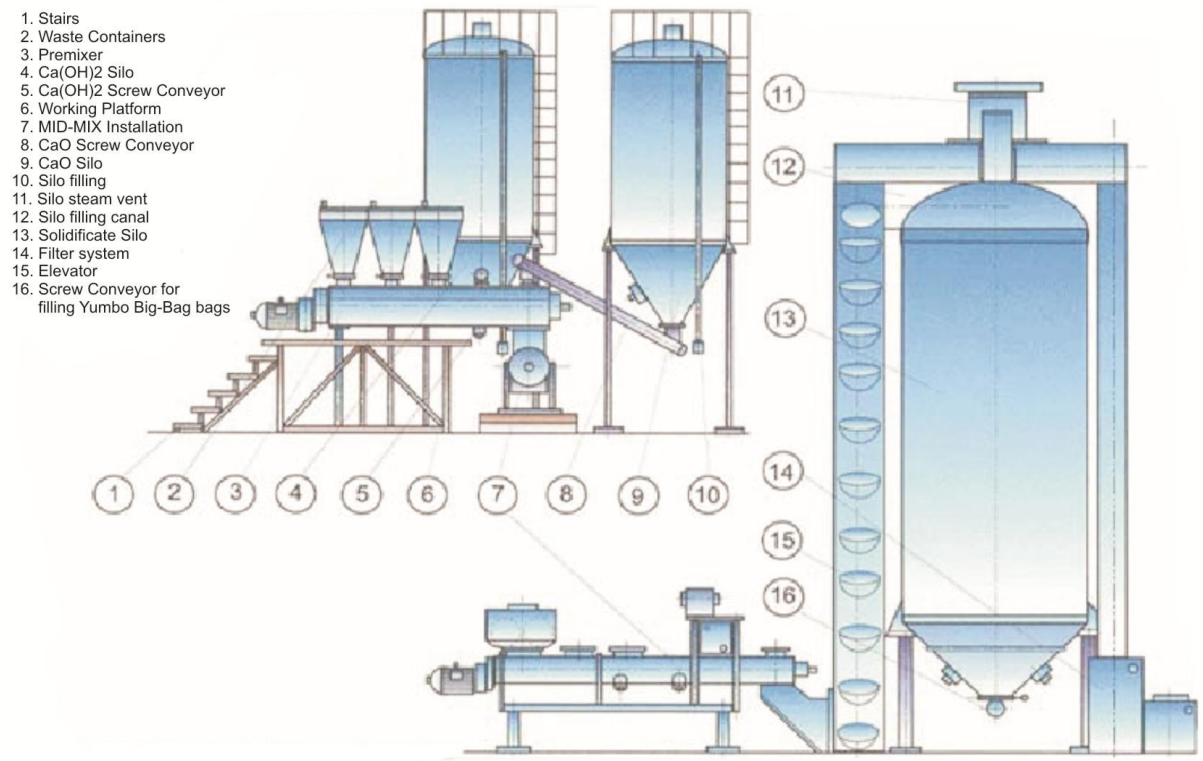

Figure 4. Scheme of the MID-MIX® mobile plant for industrial waste treatment placed on a concrete plateau sized 25 x 20 m, 2006 (www.yunirisk.com, 2011).

m/s, which makes it an almost completely hydrophobic material.
ii) Specific density of solidificate is less than 1 g/l (0.935 to 0.965), it floats on water without mixing with it (it is not soluble in water).

This powder can be stored in big-bag sacks and elevators, or pressed in briquettes they occupy around 3 times less volume from the starting volume, and on landfills for non-dangerous waste (landfills for construction waste). Also, according to EU regulations, it has found a practical application in:

i) Construction industry (concrete and gas-concrete blocks),
ii) Construction waterproofing,
iii) Road construction (sub-alignment, ground areas),
iv) Energetics (solid fuels additive),
v) Process industry (industrial fuels additive),
vi) Cement industry,
vii) Production of asphalt, briquettes, etc (www.yunirisk.com, 2011).

There are various reasons why the MID-MIX® procedure can solve the hazardous waste problem such as creating documentation for hazardous waste movement is significantly simpler compared to transboundary waste movement. Further more, transporting costs and the possibility of an accidental situation could be avoided. Whereas, from the aspect of environmental protection and sustainable development, solidification procedure itself is less harmful than waste incineration. Mobility of plants which are used for the given procedure is considered as a noticeable convenience feature.

PROCEDURE FOR MOVEMENT OF HAZARDOUS WASTE WITHIN STATE BOUNDARIES

If it is impossible to install a mobile plant for waste treatment using the MID-MIX® procedure within the organization, it is necessary to transport waste to the nearest site with the plant installed. Afterwards, activities based on the composed Hazardous Waste Management Plan, and with the reference to valid regulations on a national and international level for hazardous waste management are prescribed, which will lead to the solution of the given problem, and documentation for monitoring these activities is defined, as well as the responsibilities for their conduct which is graphically presented on the flowchart (Figure 5), as a good tool for displaying the conduct of logistic activities (Gourdin, 2006). Waste generator is responsible for conducting waste classification according to its origin (DT – A1), and in consonance with the Waste Catalogue listed in the Rulebook on Secondary Material Classification, Packaging and Storage Conditions and Handling. It inscribes a six digit mark obtained from the catalogue and the marks obtained from the mentioned lists into the **'**waste classification document'. Upon request of the waste generator, an accredited laboratory conducts hazardous waste research (DT – A2), determines its hazardous characteristics and issues a Waste Research Report. Waste classification document monitors the classified waste according to origin, character and category. Using the data from the Waste Classification Document, the waste generator enters the data on packaging, that is, the waste packaging method and the type of transportation to the waste receiver, routes and potential additional information on hazardous waste into the Hazardous Waste Movement Document (DT – A3). For the Hazardous Waste Movement Document to be complete, it is necessary that the waste transporter, as well as the waste receiver fill out all the required fields in the form. All three participants in the process need to certify the validity of the information entered into the form with the seal and signature of the responsible person.

After hazardous waste classification, appropriate packaging is conducted (DT – A4) and in a manner prescribed under national regulations (Waste Management Law, Hazardous Material Transportation Law, Rulebook on Secondary Material Classification, Packaging and Storage Conditions and Handling, Rulebook on Waste Movement Document Form With Filling Instructions, Transportation of Hazardous Waste by Road and Rail Regulation, Decision on Hazardous Waste Shipping Labels). Hazardous Waste Movement Document consists of six identical copies; the first one of them represents prior notice sent by the waste generator (DT – A5) to the Ministry of Environmental Protection and Physical Planning, not later than 3 days before commencement of movement. The second copy will be kept by the waste generator. The third copy will be kept by the transporter and the forth one by the waste receiver. Waste receiver sends the fifth copy to the Ministry. After transportation (DT – A6), hazardous waste is received for treatment by the waste receiver (DT – A7), followed by the treatment procedure and adequate disposal of the remains. Waste receiver is responsible for entering the information about the reception of waste for treatment into the Hazardous Waste Movement Document and to send a copy to the waste generator (DT- A8) as a verification of the procedure's successful completion. After the reception, waste generator archives the document and puts it to permanent storage (DT – A9). Unless the waste generator receives the document within 15 days, with included information that waste is received for treatment, he is liable to inform the Competent Authority.

Waste receiver sends the fifth copy of the Hazardous Waste Movement Document (DT – A10) to the Ministry (and to the competent authority of the Autonomous Province, if the movement is conducted on its territory), and the sixth one to the generator within 10 days from the

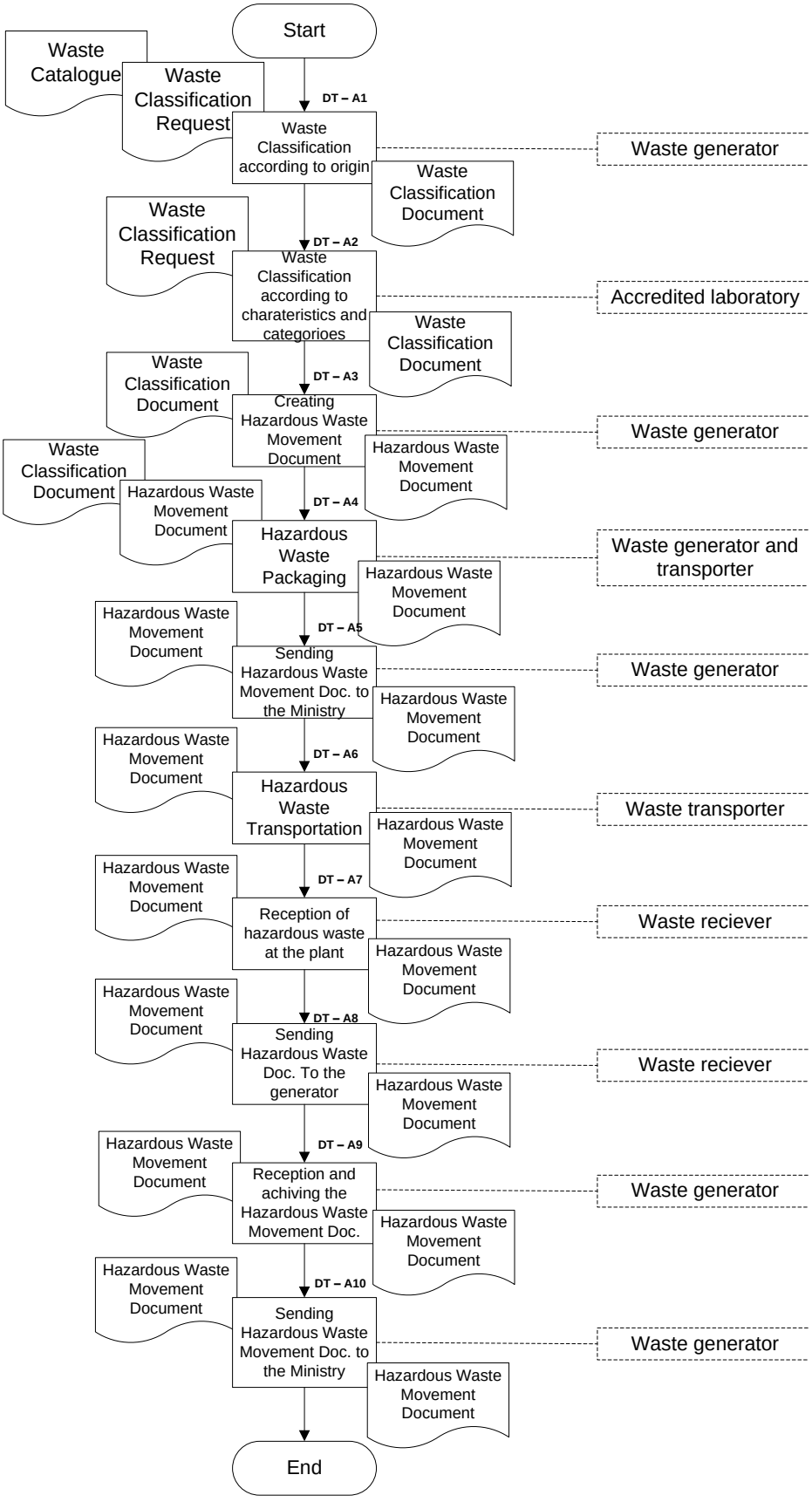

Figure 5. Procedure for movement of hazardous waste within state boundaries (flowchart).

waste reception. This is where obligations of the generator ends when it comes to the procedural of hazardous waste disposal.

PAPER RESULTS ANALYSIS, CONCLUSIONS AND DIRECTIONS FOR FUTURE WORK ON THE SUBJECT MATTER

This paper describes the hazardous waste problem in a specific organization, as well as on the level of Republic of Serbia and the branches of industry which are treated as the largest generators. Treating waste with the usage of the MID-MIX® procedure has turned out to be an acceptable and an efficient solution from the aspect of environmental protection. Besides, solidificate, as a result of the process, can be used in road construction and construction industry. Also, another advantage of this solution is the usage of mobile plants which eliminates waste transportation costs, as well as custom duties in case of transboundary movement. However, waste transportation method is also described, if it is impossible to install a mobile plant within the organization which is the generator of waste. This kind of approach to the problem would ensure that waste, and especially hazardous waste in any way cannot contaminate natural resources, water and agricultural land which are particularly sensitive to this type of contamination and thereby not jeopardize health and safety of the local inhabitants. Further research should be conducted on this field in the direction of improving procedures for adequate waste treatment and disposal in Republic of Serbia, thereby preventing further environmental degradation and ensuring a higher degree of environmental protection on all levels and in all of the company activities. Formation of the ‘integral cadastre of the sources of pollution’ also represents the first very important step towards this goal, because it will detect companies with hazardous waste problems and facilitate the identification of potential sources of pollution hazards.

Creating plans for waste management, providing detailed description of activities of the waste disposal procedure, providing required documentation for waste management and economic aspects of conducting procedures would provide an excellent example and would serve as a universal model for other organizations with similar problems.

REFERENCES

Anderson DA (2010). Enviromental economics and natural resource management, Rotledge, New York.

Brkljač N (2010). The selection of optimal variant of hazardous waste in the organization „SAMA“ Ltd, MSc thesis, Faculty of Technical Sciences, Novi Sad.

Gourdin N (2006). Global logistics management – A competitve advantage for the 21st century, Blackwell Publishing, Oxford.

Nazmiye E (2009). Testing the new ecological paradigm scale: Turkish case. Afr. J. Agric. Res., 4(10): 1023-1031,

Šević D (2010). Development of management model for logistics processes based on process approach, sustainable development and the environmental management, PhD thesis, Faculty of Technical Sciences, Novi Sad.

Vogt JJ (2002). Business Logistics Management – Theory and Practice, Oxford Southern Africa, Cape Town,

http://www.grgoni.hr/images/Docs/STUDIJA%20OBRADE%20AZBESTA.pdf, (date of access 20.05.2011.)

http://www.yunirisk.com/assets/docs/MID-MIX.pdf, (date of access 10.05.2011.)