Chemical Processes of Decontamination in the Treatment of Hazardous Substances

Article *in* Polish Journal of Environmental Studies · January 2015

Short Communication

Chemical Processes of Decontamination in the Treatment of Hazardous Substances

Rade Biocanin[1], Selim Sacirovic[1], Sonja Ketin[2]*, Stevan Canak[1], Nada Vignjevic Djordjevic[1], Semsudin Plojovic[3], Slobodan Neskovic[4]

[1]State University of Novi Pazar, Vuka Karadzica bb, 36300 Novi Pazar, Serbia
[2]Faculty of Technical Science, Trg Dositeja Obradovica 6, 21000 Novi Sad, Serbia
[3]International University of Novi Pazar, Dimitrije Tucovica bb, 36300 Novi Pazar, Serbia
[4]Faculty of Economics and Management, Cvetna 2, 21000 Novi Sad, Serbia

Received: 25 November 2013
Accepted: 21 May 2014

Abstract

When CB (chemical and biological) armor is applied as protection against CB accidents and CB terrorism and to remove the consequences of contamination, one of the principal activities is performing final decontamination. For this purpose, caporit (calcium hypochlorite) in water solution is, we believe, the most frequently used material. This is an inorganic substance with active chlorine. When solution is properly prepared, it is useful, economical, effective, and applicable for decontamination and desinfection activities. Production of this material consists of finding production materials, collecting them, proper equipment use, quantifying, preparing both the production area and the equipment, solution production, effectiveness control, and, finally, the use of product made. Technology depends on quality and quantity of repro material in disposal, aperature, and equipment, employees' education, business organization, and protective measures during the working process. In terms of highly-toxic chemical and biological contamination it is necessary to perform chemical and biological decontamination as soon as possible.

Keywords: CB, decontamination, hazardous substances

Introduction

Should the significance and value of calcium hypochlorite in wartime (the use of chemical and biological weapons), in accidents, and in chemical and bio-terrorism be taken into account, it is very important to enlarge the number of manufacturers of this substance in countries that would be independent and use their own capacities, provide the necessary quantities of it, and accomplish great financial savings. The substance in question is used as a 5-10% solution in water, as a mash (ratio 1:2), and as a powder (approximately 300g/m^2). Several factories in our country produce chlorine and hydrated lime and the consumers are all the water supply networks and construction companies, hence both products are available on the market in adequate quantities. The mass production of the apparatus for the production of the solution $Ca(OCl)_2$ and its distribution into the CB and CD (chemical decontamination) protection units and into companies, and personnel training (PTC BC-D) are necessary.

Obtaining the $Ca(OCl)_2$ solution includes procuring and collecting the means and the raw materials, determining the quantity of the solution and its use, adapting the working space and the apparatus required, the mere process of production, determining the efficiency when used in decontamination purposes, and the use in removing the results of chemical and biological contamination. The technical proceedings depend on the quantity and quality of the means and the equipment available, qualifications of the personnel, and work organization following the safety measures for certain jobs [1-4].

*e-mail: stefanov.sonja@gmail.com

In this paper we analyze mainly purposes of research regarding the production of calcium hypochlorite-inorganic substance with active chlorine for decontamination of hazardous substances in chemical processes. Our paper is organized as follows: Section 2 discusses the characteristics of calcium hypochlorite. Section 3 introduces the experimental. Section 4 presents the results and discussion. Section 5 introduces determining solution efficiency. Section 6 presents conclusions.

Characteristics of Calcium Hypochlorite

Calcium Hypochlorite (caporit) is one of the materials used for the chemical and biological decontamination MTM of soil, roads, fortification and construction structures, equipment, etc. Aside from that, caporit is used for external decontamination of means of protection and of people, and as a strong oxidant caporit could be used for biological decontamination (disinfection). Dry caporit contains 68-72% of active chlorine, but with less than 18% of active chlorine it cannot be used in the process of decontamination. Caporit is a hygroscopic substance because it contains 5-7% of calcium chloride ($CaCl_2$) and the level of humidity does not go over 1% in high-quality caporit.

Calcium hypochlorite [$Ca(OCl)_2$] is calcium salt of hypochlorous acid. The technical product contains calcium hydroxide – $Ca(OH)_2$ calcium chloride – $CaCl_2$, and calcium carbonate – $CaCO_3$. Chemically pure caporit dissolves very well in water and the solution creates an alkaline reaction. The main characteristic of caporit is that it behaves as a strong oxidant and as a chlorinating substance. Caporit is packed in iron or plastic barrels of 60 dm^3 volume and they are filled with 50 kg of caporit. In chemical decontamination of MTM, caporit is applied in a form of 5% water solution and mash in 1:2 ratio. In biological decontamination, caporit is applied as a 0.5-2% solution.

For the decontamination of roads and soil, caporit may be applied in a dry (powder) state following the standard of 300 g/m^2 of contaminated soil. For the decontamination of closed spaces (biological decontamination), most appropriate are 0.2-0.5% solutions and for the decontamination railway facilities and stables 2-5% solutions are advisable. The durability of caporit is five to seven years, although it can be used later if the solution is enriched with active chlorine.

Chlorinated lime ($CaOCl_2$) is a substance used for chemical and biological decontamination, and for the same purposes as caporit. When completely dry, chlorinated lime looks like white powder and has a sharp odor such as chlorine. The technical product is sometimes of faint yellow color due to the impurities of iron salts. The temperature heightening of water decreases its ability to dissolve. In organic solutions it does not dissolve. Chemical composition of chlorinated lime is not constant. The basic compound is $Ca(OCl)_2$. There are also approximately 28% of $CaCl_2$ and 13% of $Ca(OH)_2$ and other substances. Fresh chlorinated lime contains 32-36% of active chlorine and up to 10% of humidity. Chlorinated lime that contains less than 18% of active chlorine is not suitable for decontamination; it is unstable and it crumbles easily. The other characteristics of chlorinated lime are the same as the characteristics of caporit.

Calcium hydroxide can be used for chemical and biological decontamination of leather, metal, wooden, plastic, ceramic, and other surfaces of structures and soil. For chemical decontamination, milk of lime is used after it is taken from one part of pickling lime distilled in three parts of water. It is used for decontamination of soil contaminated with poison gases and biological agents. In biological decontamination, milk of lime is used for decontamination of floors made of earth, brick, asphalt, stone, and concrete, and of walls, carts, motor vehicles, railway cars, and more.

Experimental

Basic raw materials for derivation of calcium hypochlorite solution are: water, liquid chlorine, and limes (hydrated, quick lime). For the preparation of solution the most suitable is hydrated lime (quality is a result of the presence of carbon dioxide, calcium oxide, magnesium oxide, and free water). Hydrated lime is presented on the market in paper bags (33 kg), which are labeled (JUS, type of lime, manufacture date, mass, name of the manufacturer, and attest). As mentioned before, chlorine is extracted using electrolysis on common salt in normal conditions. It is yellow and green and has a sharp odor. Compressed and cooled, it easily turns into a liquid state (critical temperature is 144ºC, critical pressure is 7.7 MPa). In the transport package chlorine is in balance with its pair in liquid state. At 70ºC, liquid chlorine inside a bottle turns into gas followed by the rise of pressure from 3.5 bars to 24 bars. Chlorine is relatively difficult to dissolve in water but with the rise of pressure its dissolvability grows, and the degree of chlorine hydrolysis is 32% of the entire dissolved quantity. The equipment for producing calcium hypochlorite solution are: chlorine bottle, solution production apparatus, ribbed tube for heating the chlorine bottle, mobile decontamination vehicle (MDV), and CB protection tools and equipment (Fig. 1).

The chlorine bottle is under supervision of steam boilers and pressure inspection which, after final hydraulic test-

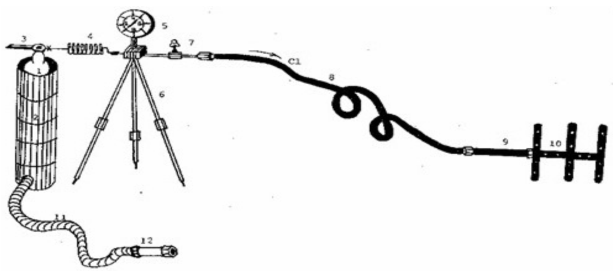

Fig. 1. The apparatus for obtaining the caporit solution.
1 – chlorine bottle, 2 – rubber coat, 3 – wrench for opening the bottle, 4 – spiral tube, 5 – manometer, 6 – tripod, 7 – chlorine valve, 8 – distributive tube reinforced, 9 – extended tube, 10 – slide valve, 11 – hydrant tube, 12 – exhaust extension.

ing and documentation checks, issues a license (certification) for the chlorine bottle use. It is filled to 80% of volume, and at 2/3 of the height of the bottle there must be a "liquid chlorine" label. On the bottle must be: name and type of product, name and location of the manufacturer, gross and net mass, and JUS label. Each bottle is equipped with inlet and outlet valves (tightened at the top of the bottle), and there is a protective cap around it. There is a valve handle on the bottles of lesser volume, and on the larger bottles there is a square extension for opening and shutting the bottle. According to the standard, 0.8ℓ of bottle volume is filled with 1 kg of liquid chlorine and this must not be exceeded. A hand valve of socket (square) wrench is used for opening the bottle, and the valve should be opened to ¼ of the circle. While using the bottle, it must not be stricken with a hammer or other solid object when trying to open the valve. The bottle must not be heated using open flame. For controlling the continued discharge of chlorine (gaseous) from the bottle and introduction of it in MDV a chlorine manometer is used, rotmeter or scale (for measuring full and empty bottles).

For heating the bottle with chlorine (turning it into gaseous state), exhaust gases of MDV are used, ribbed tube (from the kit for filling the cistern with water), exhaust tube extension, and coat (for covering the chlorine bottle during the heating).

As mobile decontamination vehicles, formation means for decontamination are used (MDV), utility trucks, fire department trucks, and other cisterns, which may have an engine of their own, water pump, solution mixer, and pipeline with valves. Considering that the solution of calcium hypochlorite reacts corrosively on metal surfaces, the inside of the cistern should be plated with protective paint, and after expending the newly obtained solution, the cistern should be thoroughly washed, dried, and finally oiled.

In order to pursue safety measures at work, during the preparation of the solution for decontamination a set of safety equipment consists of: protective mask (panorama masks) with filters for chlorine, gloves, boots, coveralls, and aprons. The equipment is as follows: the ammonia bottles, cleaning cloths, mercury thermometer, set of rubber seals, tools, and work manual instruction. The manual instruction provides instructions for preparation, organization, and introduction of chlorine into the solution of hydrated lime, i.e. complete calcium hypochlorite obtaining a procedure, as well as a procedure for testing the quality of solution for decontamination.

Results and Discussion

Chlorine is introduced into the reservoir as fast as reaction conditions and chlorine evaporation from the bottle allow. Chemical kinetics deals with studying the changes of concentration, rapidity of reaction, and mechanisms in which the reaction takes place. The process of the reaction and the conditions:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

As far as the expenditure for this reaction is concerned, it is 100 kg of calcium oxide and 2000ℓ of water

$$Ca(OH)_2 + Cl_2 \rightarrow Ca(OCl)_2 + H_2 + O_2$$

H_2 is released through the exhalation valve.

For the process of obtaining calcium hypochlorite, the basic raw materials are calcium hydroxide and chlorine and the reaction is as it follows:

$$2Ca(OH)_2 + 2Cl_2 \rightarrow Ca(OCl)_2 + CaCl_2 + 2H_2$$

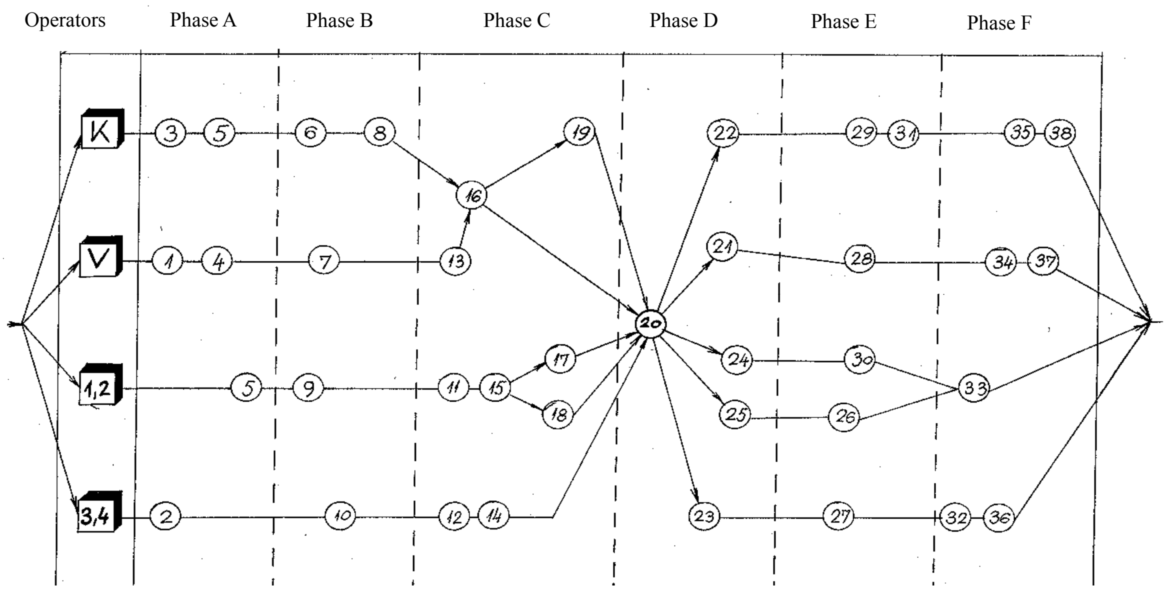

Fig. 2. Phases of calcium hypochlorite obtaining process.
Phase A – preparation of hydrated lime solution, Phase B – end of preparation of the solution, Phase C – preparation for chlorine introduction into the solution of hydrated lime, Phase D – introduction of chlorine, Phase E – end of chlorine introduction, Phase F – packing of the apparatus and tools.
Assistants: C – commander, D – driver 1,2,3,4, - assistants

Table 1. The regime of obtaining calcium hypochlorite.

Experimental No.	$Ca(OH)_2$	Reservoir	Temperature, ºC			Introduction	Chlorine solution
	kg	l	initial	final	t	t	%
1	33.00	500,00	15.00	27.00	12.00	50.00	3.33
2	66.00	1,000,00	16.00	26.5	10.50	60.00	2.91
3	66.00	1,500,00	16.50	27.5	11.00	60.00	3.05
4	99.00	2,000,00	17.50	27.5	10.50	55.00	2.77
5	165.00	2,400,00	17.00	29.00	12.00	60.00	3.33
6	170.00	2,200,00	14.00	25.5	11.50	90.00	3.19
Mean	99.50	1,600,00	16.00	27.00	11.00	60.80	3.05

The dissolving process may be presented using the diagram in Fig. 2.

Obtaining the solution of calcium hypochlorite using the apparatus and capacity of the territory has experimentally proved (in practical use in the process and testing and teaching) that the use of 1-4% of volume of active chlorine in the cistern may effectively perform chemical and biological decontamination of MTM, soil, and structures. The chemical process of obtaining calcium hypochlorite may be presented in the reaction:

$$2Ca(OH)_2 + 2Cl_2 \rightarrow Ca(OCl)_2 + CaCl_2 + H_2O$$

This means that into suspension of hydrated lime gaseous chlorine in an appropriate ratio with constant mixing should be introduced. Chlorine is introduced with rapidity permitted by the reaction conditions and evaporation of chlorine from the bottle. During that procedure, the leakage of chlorine at joints and exhalation valves (cap) of the cistern must be controlled with a measurement apparatus and made environmentally harmless. For each percent of active chlorine in the reservoir of the cistern (where the solution of hydrated lime is prepared), after some time (when reaction conditions are met), a calcium hypochlorite solution with approximately the same percent of active chlorine is obtained.

Mathematical calculus of introduction of chlorine into the cistern could be comparatively presented:

a) If the solution is prepared using calcium format hypochlorite:
   - In MDV with 2000ℓ of water, 200 kg of calcium hypochlorite is introduced in such a manner that overall mass of the solution prepared reaches 2,200 kg.
   - Calculus of percentage of active chlorine in a reservoir should be done.

This was the case when (real) 10% solution of calcium hypochlorite in water is used, but for neutralizing most highly toxic compounds, 5% solution is used so:

$$x= 5.45:2=2.72(\%) \quad x=2.72\%$$

b) With obtaining solution of calcium hypochlorite in suggested manner in MDV in 2000ℓ of water, 100 kg of hydrated lime is introduced so that the overall mass of previously prepared solution reaches 2,100 kg – the percentage of introduced chlorine in 100 kg is obtained using proportion:

Mathematical calculus brings us to the conclusion that the obtained solution of calcium – hypochlorite (which contains 4.76% of volume active chlorine) fulfills the demands of use for chemical decontamination.

During the process of chlorine introduction all safety measures at work must be taken and as protective masks (instead of standard ones), special protective filters for chlorine are used. The introduction of chlorine lasts for approximately one hour, and the time period required depends on the initial temperature of the solution, air temperature, engine work of MDV, etc. The space where the process of obtaining calcium hypochlorite is to be performed, security must be provided. The process of chorine introduction lasts approximately 60 minutes, which depends on the capacity of the reservoir, mixing velocity engine work, season and looseness of the valve for chlorine dosing. If the external temperature exchange is put aside, as well as certain heating of solution in MDV, the heightening of temperature (aside from rot meter, manometer, the extent of freezing chlorine bottle, measurement of bottle mass during chlorine introduction) may be an indicator of process and of the finalization of process of chlorine introduction – introduction of gaseous chlorine into a solution of hydrated lime. According to the thermodynamic equation for each percent of active chlorine, there is an adequate temperature rise of new solution for 3.9ºC.

When the temperature of solution rises for 10-12ºC (measured after 60 minutes of chlorine introduction) then the introduction of chlorine into a cistern is stopped, and the difference in temperature is the proof that the appropriate solution of calcium hypochlorite has been obtained and that it could be used for chemical decontamination. After the procedure the chlorine bottle is closed, the pump and the mixer in MDV are turned off, and then the sample should be taken (Erlenmeyer flask of 200 ml is plunged into the solution) for laboratory testing for the percentage of active chlorine in obtained solution. Basic parameters for obtaining the solution of calcium hypochlorite solution during the experiment (in experiments 1-6) are presented in Table 1.

Table 2. Regime of chlorine introduction in an experiment.

Time of introduction	Temperature of solution, ºC	Quantity of the introduced chlorine, kg	Quantity of applicable $Ca(OH)_2$, kg	Quantity of water in MDV	% Cl	pH
9.30	17.50	77.00				
9.40	18.80		170.00	22,001.00	3.17	12.57

The results, which are obtained by introduction of chlorine in experiment are approximately the same, so they could be approximated to one introduction. The initial temperature of solution (suspension) of calcium hydroxide was 14ºC, and afterward it was measured in 10-minute periods.

In situations when there are no MDVs, other vehicles with reservoirs can be used (preferably with a water pump and mixer due to effective chlorine introduction). The price of materials is 10 times less than the price of formed calcium hypochlorite in the world market. The obtained solution is stable enough so it could be kept for several days in closed reservoirs at room temperature, and when used in the process of decontamination new mixing will be required.

Determining Solution Efficiency

Calcium hypochlorite is a very active compound and its main characteristic (aside from having a high percentage of active chlorine) is that it reacts as a strong oxidant. In water solution (obtained in a manner previously described as a liquid phase of suspension) are several active components (chlorine, chlorine oxide, hypochlorous acid, hypochlorite ions) that are the results of the following reactions:

$Ca(OCl)_2 + H_2O \Leftrightarrow 2HOC + Ca(OH)_2HOCl \Leftrightarrow H^+ + OCl^- \; 2HOCl \Leftrightarrow H_2O + Cl_2O$

The presence of molecular chlorine is conditioned by the presence of chlorine ions in the hypochlorite system.

$HOCl + H^+ + Cl^- \Leftrightarrow Cl_2 + H_2O$

The relations between the components, as presented in the diagram, depend upon the pH environment. In hypochlorite solutions when pH is 8.5, a hypochlorite ion is dominant when pH is approximately of the same concentration of molecules as hypochlorous acid and hypochlorite ion. When pH is 3.5, the basic component is hypochlorous acid and its anhydride Cl_2O, and chlorine dominates when pH is less than 3 (Table 2).

Relative to the pH of solution of calcium hypochlorite, the procedure and the efficiency of the reaction can be altered in hypochlorite solution as well as in some highly toxic compounds. Hypochlorite is usually used for decontamination in the form of mash (1:2) or solution (5-10%). Since there are hypochlorite ions in the mash as well as hypochlorous acid and elemental chlorine, the processes of chlorine introduction and oxidation may proceed regularly (depending on the conditions in which reaction is to occur), and the products of S-yperite gas (S-yperite) are gradually dissolved due to the exothermal reaction while hydrochloric acid is extracted and chlorovinyl products are created [5-7].

During the decontamination process many intermediate products are created which, as final products, do not have the effects of mustard agents on the human organism. The obtained solution of calcium hypochlorite causes oxidation of CW agents with the effect of mustard agents, and dichlorodiethylsulfoxide and dichlorethylsulfate are created in parallel. When the oxidant reacts, sulfoxide transforms into sulfone in the presence of extra hypochlorite, and sulfone dissolves and creates calcium sulphate, carbon dioxide, and other compounds (reference to the stated reaction). The presented scheme of the process proved to be very successful in the experimental work, in decontamination of trophy technology contaminated with drops of S-yperite.

The solution of calcium hypochlorite is very useful in MTM decontamination, plus decontamination of soil, structures, and other CW (chemical weapons) agent types Soman contaminated surfaces due to hydroxyl and hypochlorite ions per mechanism of nucleophile shift: ClO- has a catalytic reaction to the process of CW agents' hydrolysis. In such cases some acidic esters of methylphosphonic acid are created, which in alkali solution create appropriate calcium salts.

The stated equation is presented in alkali environment as a reaction of thioster with solution of calcium chlorite in which, in the initial phase, acidic ester and dialkiltaurine are created, which in the presence of more oxidant transforms into sulfoacetic aldehyde and secondary chloramines. One of the basic characteristics of calcium hypochlorite relevant to the effectiveness of performing chemical decontamination is the percentage of active chlorine, i.e. the percentage of water solution (most commonly used in the process of decontamination). The percentage of active chlorine in the solution is determined judging by the degree of chlorine introduction into lime suspension, and it is analytically processed based on the principle of reductometric titration of chlorine with sodium thiosulfate (weaker oxidants are reduced) according to the scheme: $2\ S_2O_3 \rightarrow S_2O_6 + 2\ e-$

That is the manner of forming the tetrathionate ion. Should the solution of highly oxidant substance be added with potassium iodide, the iodide would oxidize into elemental iodine: S J- V J2 + 2e-

Iodine is easily titrated with the $Na_2S_2O_3$ solution with starch as an indicator. Due to the mediatory reduction with iodide, this method is considerate part of iodine-metry. The analysis of the calcium hypochlorite solution quality may be performed using an LH-M3 mobile chemical laboratory, as well as in a stationary BC-D laboratory, equipped with the necessary tools, equipment, and chemicals for quality and quantity analysis of highly toxic compounds and substances for chemical decontamination.

Conclusions

In terms of highly-toxic chemical and biological contamination it is necessary to perform chemical and biological decontamination as soon as possible. The solution is in rapid production of universal materials for decontamination-calcium hypochlorite, which do not exist on the regional market. The solution is the implementation of our innovations in a short period of time with an inventive device that can prepare a solution of calcium hypochlorite. This paper summarizes the problem and provides a permanent solution.

The basic indicator evaluation of the reactive ability of any system for decontamination is its efficiency, which may be based on the quantity of the decontamination substance necessary for successful decontamination of certain quantities of chemical contaminants per unit of time.

Chemical decontamination of people, materials, technology, clothes, equipment, soil, structures, food, and water is achieved using complex physical and chemical methods (removal, absorption, adsorption, chemisorptions, oxidation, hydrolysis, chlorine introduction, alcoholysis, and others), and chemical reactions may be carried out via various mechanisms.

Mere awareness of the mechanisms of decontamination (for some reactions) is not sufficient for efficiency evaluation, because the concordance with the test data is limited in certain conditions [8, 9]. In practical experiments, teaching and performing exercises to determine the effectiveness of decontamination, exact and less exact methods were used, and the results (summary) obtained were not sufficiently reproducible.

A comparative laboratory method for testing the effectiveness levels of the decontamination of means and structures contaminated with highly toxic substances is presented in this part of the study [10-12].

References

1. STEFANOV S., BIOČANIN R., VOJINOVIĆ MILORADOV M. Ecological modeling of industrial pollutants-Serbian case, Journal of Environmental Protection and Ecology, ISSN 1311-5065, Sofia, Bulgaria **13**, 75, **2012**.
2. STEFANOV S., BIOČANIN R., VOJINOVIĆ MILORADOV M., SOKOLOVIĆ S. Ecological modeling of pollutants in accidental fire at the landfill waste, Thermal Science, Serbia, DOI: 10.2298/TSCI110531161S
3. BIOCANIN R., STEFANOV S., UROSEVIC S., MEKIC S. Modeling of pollutants in the air in terms of fire on dumps, doi: 10.2478/v10216-011-0043-6 Ecol. Chem. Eng. S. **19**, (4), 609, **2012**.
4. BIOČANIN R., STEFANOV S. Environmental Bio-indicators of the Quality System of Eco-monitoring, The International Conference on Bioscience: Biotechnology and Biodiversity – Step in the Future, The Forth Joint UNS – PSU, Novi Sad, **2012**.
5. STEFANOV S., CVEJIC R., BIOCANIN R. Modeling of pollutants at the landfill waste, International scientific and methodological conference "Quality of education" management, certification, recognition, ISBN 978-966-379-516-4, pp. 152-159, Kramatorsk, Ukraine, **2011**.
6. BIOČANIN R., STEFANOV S. Effects and Consequences of Pesticide Use and Biochemical Measures of Protection, 10th Anniversary international scientific conference, III-594-603, ISSN1313-230X, Gabrovo, Bugarska, **2010**.
7. STEFANOV S., VOJINOVIC MILORADOV M., SOKOLOVIC S., BANCOV Š. Monitoring of industrial pollutants in oil and petrochemical industry, Proceedings of the Romanian Academy Serial B: Chemistry, Life Science and Geoscience, Chemistry, ISSN 1454-8267, No. 2-3, **2009**.
8. STEFANOV S., BIOČANIN R., MEHIC S., ADAMOVIC D. Modeling of Pollutants CO, PM, PAH In Accidental Fire At The Landfill Waste, GCGW-12, ISBN 978-605-89885-1-5, pp. 840-849, Istanbul, **2012**.
9. STEFANOV S., VOJINOVICMILORADOV M., BIOCANIN R. Ecological modeliling of pollutants in process industry, ICET 2011 & PEC-9, Faculty of Engineering PSU, Thailand, pp. 202-208, **2011**.
10. BIOCANIN R. Human Ecology, School of Pharmacy and Health University of Travnik, Travnik, Bosnia and Herzegovina, **2014**.
11. STEFANOV S., BIOCANIN R., VOJINOVIC MILORADOV M., BANJANIN B. CALCIUM HYPOCHLORITE – Innovativemethods of neutralization, IUPAC2013, 44th World Chemistry Congress, Istambul, Turkey, Poster Sesion, P921, Chemistry Education, 11-16 August, **2013**.
12. BIOČANIN R., STEFANOV S. Calcium-hipohlorit-innovative aproach in environmental process, 45th International October Conference on Mining and Metallurgy, IOC2013, p.73-76, October **2013**.