# Detection and neutralization of soil contamination in the event of an emergency leakage of petroleumbased substances from a transmission pipeline

Andrzej PAPLIŃSKI\*, Magdalena PIROS – Faculty of Mechatronics and Aerospace, Military University of Technology in Warsaw, Poland

Table I

Please cite as: CHEMIK 2016, 70, 6, 326-335

#### Introduction

An increasing role of hydrocarbon substances is a feature of contemporary civilizational processes. Hydrocarbon substances are becoming a very common raw material, used in an increasingly wide range of products; they are also a necessary energy source. Technologies using modified hydrocarbon structures allow for manufacture of lightweight products with a durability rivalling metal structures. Manufacturing and social needs promote increased mass transportation of hazardous substances, which is a substantial risk factor for public safety and natural environment. Mass transportation of substances like chlorine, ammonia and others constitutes significant risk; however, petroleum-based materials undoubtedly build-up the biggest volume of transported chemical substances. As demand increases, so does usage of pipelines to transport materials in liquid and gaseous states. Compared to transportation via road vehicles, where safety of transport by a tanker truck depends not only on technical condition of the vehicle but also on traffic and road conditions, taking the principle of limited confidence in respect to other road users into account, transmission via pipelines is a relatively safe mode of transportation. The entirety of the transmission pipeline is usually monitored and controlled to some degree. There is, however, a difference in risk of exposure resulting from damage to a tanker truck transporting a hazardous material versus risk of exposure resulting from a pipeline failure. Until the supply is'nt shut off, the amount of medium leaking is typically many times higher compared to the volume of a leak from a damaged tanker truck.

Table I presents the volumes of leakage and collected active substances in several pipeline failures which occurred in western Europe between 1980 and 2002.

Volumes of leakage and collected active substance in selected pipeline failures which occurred in western Europe between 1980 and 2002 [1]

Incident no.	Year	Diameter of the pipeline	Volume of leakage, m <sup>3</sup>	Volume of recovered active substance, m <sup>3</sup>
169	1980	26"	125	90
170	1981	Pumping station	30	20
200	1984	16"	10	10
217	1986	24"	292	288
232	1987	12"	12	2
241	1988	10"	305	300
275	1991	20"	275	157
305	1992	12"	75	0
314	1993	26"	10	3
326	1994	Pumping station	2	0
402	2002	24``	250	230

Corresponding author:

Andrzej PAPLIŃSKI - Ph.D., D.Sc., (Eng.), Assoc. Prof., e-mail: andrzej.paplinski@wat.edu.pl

**CHEMIK** nr 6/2016 • tom 70

Two aspects of events listed in presented table can be noted. Leakages considered are characterized by considerable volume, in the order of tens or more cubic meters. On the other hand, the amount of substance collected is significant; sometimes it can be as high as 80–90% of the leak. The volume of potential outflow illustrates the scale of the danger which may arise due to spread of hazardous substances in soil or watercourses, while large volumes of collected substances prove that rescue operations were organized and prepared well.

A set of tasks that embrace undertaking and performance of rescue operations is considered in this work. These include legal regulations, rules of planning and organization, cooperation of national and local government bodies, technical conditions stemming from available equipment and preparation of teams and persons who should participate in rescue operations. Determining physico-chemical aspects of harmful effects of spread substances, which is directly related to methods and procedures of eliminating the effects of contamination, also constitutes an organizational element of rescue operations. The danger being considered was related to a chosen location; local crisis response plan was referred to, and taking geographical conditions into account allowed to make the schedule of rescue operations more realistic.

### Legal regulations and monitoring of dangers which may arise due to soil and water contamination with harmful chemical substances

Soil and water contamination is to be understood as an occurrence or excess of a chemical substance in the environment, negatively impacting it and preventing microbiological processes. The Environmental Protection Act of  $27^{\text{th}}$  April 2001 is the basis for defining the tasks of the National Environmental Monitoring [2]. Its text and provisions are adapted to international and European Union rules concerning serious industrial accidents. Units of the State Fire Service and the Chief Inspectorate Of Environmental Protection, supported by Voivodeship Inspectorates of Environmental Protection, are the bodies established to control and supervise in order to prevent accidents and failures leading to soil and water contamination [3÷5]. The National Firefighting and Rescue System, in particular specialized groups of chemical and environmental rescue, is the primary system whose task is to prevent dangers and eliminate soil contamination with hazardous chemical substances in Poland [6÷8].

Cooperation of economic bodies and organizations, state administrative bodies and local government bodies is essential [9, 10]. Starting at the communal level, crisis response plans which take the presence of potentially hazardous technical facilities in the commune and in its immediate vicinity into account should be prepared. Crisis response plans should take symptoms of potentially harmful agents which may be released as a consequence of technical failure as well as mechanisms and scope of their impact on the environment and people living in a given area into account. Prepared scenarios of operations and rules of procedure in case an undesirable situation occurs should take both tasks performed by the rescue services established for this purpose as well as those performed by the teams set up by the local government into account. Adopting an established location of examined catastrophe allows to relate the plan of operations to the means and resources available to a given county (here: Legionowo County) and commune (here: Wieliszew commune).

## Engineering and procedural methods of remedial operations necessary in case of soil contamination with harmful chemical substances

Due to particularity of dangers which are a consequence of environmental contamination with chemical substances it is important for any actions aimed at neutralization to be preceded by an appropriate preparatory procedure. Remedial operations should be a final component in the chain of events in a crisis situation, while elements of rescue operations should be prepared and wellknown to both persons in danger as well as those performing the rescue operations. The Environmental Protection Act imposes requirements concerning compliance with safety and preparation rules as well as implementation of internal and external plans of operations which will be ready to be used in case of a failure or an accident, both within the facility as well as in its vicinity [2].

Standard equipment of rescue units allows to eliminate the contamination using immediate neutralizing agents typically available to rescue teams. In case of a contamination on a larger scale, operations resembling laboratory procedures need to be planned and implemented in order to restore the original properties of the soil. A conceptual plan of operations and appropriate material resources are necessary. Methods of eliminating contamination in planning and undertaking rescue and remedial operations can be divided with regard to the nature of used techniques into engineering methods, which involve collecting and processing (purifying) the contaminated soil off site, and procedural methods, which focus on eliminating and neutralizing hazardous substances in the soil immediately, on site  $[11 \div 13]$ .

Engineering methods include excavation of contaminated soil, using mechanical equipment (e.g. skimmers), sorbents, as well as various barriers. Conversely, procedural methods of eliminating contamination include physical, chemical, biological and thermal treatment processes [11].

Among the most frequently used methods, chemical methods, which include dispersion, reduction–oxidation reactions, alteration of pH or dehalogenation, are highly popular. The purpose of chemical methods is to change the chemical structure of the contamination through chemical reactions, as a result modifying a toxic chemical to a less harmful form, forcing a particular behaviour of the substance in a soil and water environment (decreasing or increasing its mobility in the soil) or ensuring particular conditions promoting microbial degradation of substances [11].

Methods utilizing sorbents play a predominant role in collecting residues of harmful substances during the execution of the plan of operations by rescue units. Means of neutralization frequently used by rescue units include dispersants, also known as surfactants. Dispersants are substances containing surface active agents which are used to remove the contamination through washing the soil.

In case of the task of purifying soil contaminated with hydrocarbon compounds examined in this work, using biological methods of soil purification should be taken into consideration. During the analysis of the task and development of the plan of remedial operations, the following biological methods of soil purification were considered:

- water-stimulated bioremediation
- air-stimulated bioremediation (bio-ventilation), conducted passively or actively
- bioreactor method
- biopile method [13].

332•

The choice of appropriate purification and reclamation technique depends on multiple factors, such as e.g.: properties of the harmful substance, depth of the contaminated soil, hydrological and soil conditions.

Biological purification may be conducted precisely at the location of the contamination – *in situ*, or following excavation and transportation of contaminated soil to the locations where purification will take place – *ex situ*.

Bioremediation involves eliminating contamination by metabolic transformation of harmful substances to carbon dioxide and water compounds through microbial action. The process of bioremediation takes a long time; however, using modern solutions which ensure high bacterial activity (e.g. by increasing the amount of nutrients, soil aeration or by introducing additional microorganisms of different varieties into the environment), these methods allow complete degradation of harmful substances while simultaneously preserving the terrain's infrastructure [13].

Water-stimulated bioremediation involves pumping the contaminated groundwater out, purifying it, aerating, enriching with microorganisms and biogenic substances and pumping it back into the aquifer. Purification of contaminated water takes place in bioreactors. In order to increase efficiency, contaminated soil is subjected to rinsing with water enriched with surface active agents (synthetic surfactants, biosurfactants) which increase solubility of heavy crude oils, creating an emulsion which is easier for microorganisms to degrade and increasing its mobility in the soil [13].

Air-stimulated bioremediation is called bio-ventilation and is used in case a large area is contaminated at a shallow depth. Bioventilation conducted passively involves natural soil aeration using a system of perforated tubes. Active bio-ventilation can be conducted through creating overpressure (injection of air) or underpressure (extraction of soil air). The effectiveness of bio-ventilation depends on aeration, levels of biogenic substances, reduction–oxidation conditions, surface active agents, humidity, pH, temperature. As a result, ventilation of the soil occurs and bacterial activity increases. Injection involves introducing air under pressure (e.g. 2 MPa) via special filters placed below the contaminated zone. Next, the air, along with vapours from petroleum-based substances, is vented via filters placed at the ground surface. Extraction involves creating underpressure (suction pumps) and sucking the contaminated air out of the soil [13].

**Bioreactor method** involves purifying the soil in a special bioreactor to which air, water and microorganisms are provided. Soil purification is aided by surface active agents. This method requires constant control of the degree of degradation of the substance being eliminated and adjustment of the process's parameters (temperature, pH). This method is expensive due to the need to transport the contaminated soil. It is used in cases when immediate decontamination is required [13].

**Biopile method** involves subjecting the soil, formed into  $0,5 \div 1,5$  m high biopiles and placed on a special geomembrane which prevents toxic substances from infiltrating into the ground, to reclamation processes (aerating, adding water, nutrients, microorganisms) [13].

## Emergency contamination of chosen body of water or area with harmful chemical substances – algorithms of remedial operations

Based on the methods of eliminating contamination presented earlier, a selection algorithm for remedial operations concerning soil contaminated with petroleum-based substances was developed. This algorithm is presented in Figures  $1 \div 3$ . The algorithm has been developed in accordance with principles of creating mathematical algorithms; it shows selected factors which significantly affect the processes of soil contamination and elimination of soil contamination.



Fig. I. General selection algorithm for remedial operations



Fig. 2. Selection algorithm for remedial operations in case of well-aerated soil



Fig. 3. Selection algorithm for remedial operations in case of hydrated soil

## A plan of rescue and remedial operations in a situation of an emergency contamination of chosen body of water or area with harmful chemical substances

A plan of rescue and remedial operations in the event of an emergency soil contamination with hazardous substances has been developed as an example of a practical implementation of the rules of procedure in case of a failure or an accident which resulted in a release of hazardous substances. In order to make the model more realistic, the analysis was conducted for an event occurring at a particular location. It was assumed that the soil contamination was a consequence of a rupture in the underground crude oil pipeline running between Mostyska and Emilianów and through the Legionowo county, in the vicinity of the village of Wieliszew. A diagrammatic view of the location of the event is presented in Figure 4. Since a specific location was chosen, the projected analysis of rescue and remedial operations allows to take technical means and projects of operations contained in the local crisis response plan into account. Available crisis response plan for the Wieliszew commune was found to be prepared correctly, and the information and guidelines contained therein proved to be very helpful and have been used in planning of rescue operations. Prepared schedule of operations allows an overview of cooperation between national and administrative bodies during operations conducted in a crisis situation.



Fig. 4. A diagrammatic view of the location of the event (own work)

We assume that the units of the State Fire Service will be the first to arrive at the scene. They take a position within a safe distance from the site of the event and conduct a preliminary evaluation, within their abilities and taking available technical equipment into account, while observing all safety rules. The firefighters have chosen rescue operations procedure no. 128 [10]. The danger zone has been determined and marked with a tape; unauthorized persons have been moved away and the property's owner has been given advice concerning evacuation. At the same time, the necessity to deploy specialized chemical and environmental rescue units has been communicated and the president of PERN [Oil Pipeline Operation Company] has been informed about the situation; the president of PERN then closed the safety valves. When performing rescue operations all safety rules were observed; potential ignition sources have been eliminated (the use of open flame has been prohibited, equipment creating a potential hazard has been grounded, high-voltage lines have been turned off) [10].

The rescue operation under consideration is a local event. A possibility of adverse developments due to potential difficulties in communicating has been therefore assumed; this means that the time between the start of the leakage and the moment it is noticed and closed is fairly long and the volume of released substance is approx. 60 m<sup>3</sup>. Large amount of released substance, coupled with high viscosity and considerable hydration of the area, promotes its spread over long distances with low infiltration in grass-covered areas and greater oil migration into the ground in areas prepared for sowing, not covered with vegetation. Terrain conditions promoting quick spread of the liquid forced – in order to secure private

properties against the spreading spill – the necessity to direct the spill to a single place (a depression in the ground) so as to collect as much of the petroleum-based substance as possible. In order to do that, an embankment was raised and secured using a plastic sheet [6, 9, 10], which allowed to direct the spill to the depression.

Specialized units arrived in the danger zone. The nature and scale of the danger has been re-evaluated and complementary information necessary to implement the concept of rescue operations has been collected. The performance of the operations was being observed with a focus on any significant disruptions in the implementation of the plan. The exact location of the failure has been identified and the access to the ruptured pipeline was made possible through excavation of the soil, which was purified using the *ex situ* bioremediation method in bioreactors, at the cost of the owner of the long-distance underground pipeline [5, 13]. At the same time, collection of the liquid to specially prepared portable tanks, using chemical pumps and node connections, has begun.

The main goal of the operations after the source of the hazard has been eliminated (the inflow of petroleum-based compounds has been shut off and the pipeline has been sealed) is to remove as much of the substance from the ground surface as possible. In order to do that, arable areas have been covered with a sorbent - polyurethane foam, while grass-covered areas, which constitute a layer difficult to permeate, have been covered with a sorbent mat. The residues of the hydrocarbon compound have been broken down using the available surface active agent and the soaked sorbents and mats have been gathered, using intrinsically safe equipment, into special containers. Collected waste has been transferred for treatment, which is the responsibility of the president of PERN  $[10 \div 12]$ . Firefighters were decontaminated, rescue operations were completed and the site of the event was turned over to inspectors from the Voivodeship Inspectorate of Environmental Protection, which supervises operations related to reclamation and restoration of the original properties of the soil [2, 5, 10]. Variants and specific activities of rescue operations are presented in Figure 5.

Assessment of the consequences of the failure is conducted by the Voivodeship Inspectorate of Environmental Protection. Its inspectors conduct tests for presence and concentration of hydrocarbon substances in the soil using atmogeochemical methods<sup>1</sup>. On the basis of obtained results it was found that the permissible concentration of oils (3000 mg/kg) with content of carbon 12 to 35 in the soil designated for cultivation has been exceeded on an area of 224 m<sup>2</sup> at a depth of up to 1 m. The size of the contaminated area and low depth, relative hydration of the soil and high nutrient content led to air-stimulated bioremediation being recommended as the method of reclamation [13]. Conditions promoting acceleration of the processes of biological purification were created. Should the oil reappear, however, wells to which the petroleum-based substances could drain would have to be used; after being extracted using pumps, the substances would be subjected to further neutralization  $[11 \div 13]$ . 6 months later, the Voivodeship Inspectorate of Environmental Protection once again conducts soil analysis and gives an opinion concerning conclusion of remedial operations [5].



Fig. 5. A diagrammatic view of the plan of rescue operations (own work)

#### Summary

Issues concerning the possibility of soil and water contamination with harmful chemical substances have been considered in this work.

The project of anticipated rescue operations has been presented as a complex task, consisting of: statutory regulations and structure of the bodies established to perform remedial operations; cognitive base, which determines the activities and equipment necessary to properly secure the completion of the tasks; warning the local community, which requires preparing local crisis response plans coupled with necessary awareness on the part of a specific set of people connected with local government structures concerning the rules of procedure in emergency situations, communication, ignoring rumours and not giving in to panic.

A model analysis of a crisis situation following the release of petroleum-based substances during transportation of oil products via an underground transmission pipeline has been presented. A plan of rescue and remedial operations was developed and factors affecting the scale of the contamination were analysed. During rescue operations ensuring safety of people is a priority, followed by minimizing harmful effects to the environment through neutralizing contaminated soil or water.

The publication learns from the results of [1] and indirectly shows that a comprehensiveness of tasks developed during planning and preparing for operation as well as ongoing control of safety of transportation of hazardous chemical substances, including petroleumbased materials, are necessary.

#### Literature

- Girgin S., Krausmann E.: Lessons learned from oil pipeline natech accidents and recommendations for natech scenario development. Joint Research Centre, Publications Office of the European Union, Luxembourg, 2015, ISBN 978-92-79-43970-4, doi:10.2788/20737.
- 2. Environmental Protection Act of 27th April 2001.
- 3. State Fire Service Act of 24th August 1991, with subsequent amendments.
- 4. Fire Protection Act of 24th August 1991.
- 5. Environmental Protection Inspection Act of 20th July 1991.
- Rules of Organization of Chemical and Environmental Rescue in the National Firefighting and Rescue System, developed by the National Headquarters of the State Fire Service, Warsaw, July 2013.
- Ordinance of the Minister of Interior of 15<sup>th</sup> September 2014 concerning the scope, detailed conditions and procedure of inclusion of fire protection units into the National Firefighting and Rescue System.
- Ordinance of the Minister of Interior and Administration of 18<sup>th</sup> February 2011 concerning detailed rules of organization of the National Firefighting and Rescue System.
- 9. Crisis Response Plan of the Wieliszew commune, developed by a team of

Atmogeochemical method involves making holes in the soil, collecting a sample of air in the soil using special measuring devices (analyser, detector, gas detector tubes) and analysing for content of hydrocarbon vapours in the air. The number of collected samples depends on the area of the examined region

authors, established by ordinance 22/08 of the Mayor of the Wieliszew Commune, under the leadership of the Chief of the Communal Crisis Response Team – Deputy Mayor of the Commune A. Szczodrowski and Inspector for Defence and Civil Defence R. Bocianowski, Wieliszew, December 2010.

- Rules for Rescue Operations (2008) developed on the basis of The 2008 Emergency Response – Guidebook. Chief Inspectorate Of Environmental Protection. Meritum Comp Consulting in the field of chemicals and environmental protection.
- Rakowska J., Radwan K., Ślosorz Z., Pietraszek E., Łudzik S., Suchorab P: Removing petroleum-based substances from roads and soil. CNBOP-PIB, Józefów 2012, ISBN 978-83-61520-53-5.
- Rakowska J., Radwan K., Ślosorz Z.: Environmental effects of eliminating petroleum-based contaminations. CNBOP-PIB.
- Kołwzan B., Adamiak W., Grabas K., Pawełczyk A.: Introduction to environmental microbiology. Oficyna Wydawnicza Politechniki Wrocławskiej, Wrocław 2006, ISBN 83-7085-992-5.
- 14. Ordinance of the Minister of the Environment of 9<sup>th</sup> September 2002 concerning standards for soil quality and standards for land quality (Journal of Laws No. 165, item 1359).

(recived 16/02/2016)

\*Andrzej PAPLIŃSKI – Ph.D., D.Sc., (Eng.), Associate Professor at the Military University of Technology in Warsaw, graduated in Technical Physics. Presently works at the Department of Safety Engineering of the Institute of Aviation Technology at the Faculty of Mechatronics and Aerospace of the Military University of Technology in Warsaw. Expert in the fields of modelling of processes of conversion of energetic materials, numerical modelling of dynamics of load of homogeneous and multiphase media, analysis of material and dynamic hazards. Author of over 130 works concerning modelling of flow dynamics, analysis of the processes of combustion, explosion and detonation, analysis of safety of technical facilities.

e-mail: andrzej.paplinski@wat.edu.pl

Magdalena PIROS – (Eng.), completed undergraduate studies at the Faculty of Mechatronics and Aerospace at the Military University of Technology in Warsaw, specializing in technical safety engineering (2015).

## Aktualności z firm

News from the Companies

Dokończenie ze strony 330

#### JEC 2016 Innovation Awards

Spółka zależna koncernu LANXESS, Bond-Laminates GmbH, Instytut Inżynierii Produkcji Fraunhofera oraz spółka HBW-Gubesch Thermoforming GmbH wspólnie otrzymały nagrodę w kategorii "Procesy" w konkursie "JEC 2016 Innovation Awards". Uroczystość wręczenia nagród odbyła się w Atlancie. Zwycięska technologia obejmuje lokalne wzmocnienie taśmowe termoplastycznych arkuszy kompozytowych marki Tepex w celu zoptymalizowania właściwości mechanicznych, grubości i masy materiału.

Termoplastyczne materiały kompozytowe wzmacniane włóknami ciągłymi (ang. *Continuous Fiber Reinforced Thermoplastics*, CFRT), zwane również płytami kompozytowymi, oferują ogromny potencjał do wykorzystania w ultralekkich konstrukcjach i bardzo łatwo się je przetwarza. Mogą być wytwarzane w sposób ciągły, mają nieograniczony okres przydatności i dzięki temu zapewniają wymierne korzyści finansowe. Tradycyjne materiały o ułożeniu włókien 0°/90° są doskonałe do większości konstrukcji wymagających wzmocnienia, takich jak części pojazdów silnikowych, obudowy urządzeń elektronicznych czy sprzętu sportowego. Dobrze wyważony materiał nadaje się do wielu zastosowań, znacznie ograniczając masę produktów w porównaniu do materiałów metalowych i plastikowych.

Niemniej jednak, w przypadku wyjątkowych obciążeń i w celu dalszej optymalizacji rozkładu sił, wzmocnienia można zintegrować dzięki wykorzystaniu wieloosiowego materiału Tepex, który jest najnowszym osiągnięciem spółki Bond-Laminates. Dzięki tej metodzie można określić różne ułożenia włókien dla różnych warstw konstrukcji kompozytowej. Pozwala to osiągnąć znacznie lepsze właściwości w relacji do gęstości. Metoda ta sprawia, że projektowanie elementów poddawanych dużym obciążeniom, takich jak dźwignie hamulcowe czy konstrukcje foteli, jest bardzo proste i wydajne. (*kk*)

(Komunikat prasowy LANXESS, 12.05.2016)

### Grupa Azoty ZAK SA partnerem VI Konferencji Nowoczesne Ciepłownie i Elektrociepłownie

W dniach 12–13 maja br. w Opolu odbywał się dialog ekspertów polskiej branży energetycznej. W szóstej odsłonie konferencji Nowoczesne Ciepłownie i Elektrociepłownie istotny udział przypadł największym zakładom Regionu Opolskiego, Grupie Azoty ZAK SA.

Wydarzenie podzielone zostało na panele tematyczne, z udziałem przedstawicieli firm, instytucji państwowych i uczelni wyższych. Głos zabrały m.in. autorytety Politechniki Śląskiej i Opolskiej, a także eksperci Urzędu Dozoru Technicznego.

Jeden z kluczowych tematów tegorocznej konferencji stanowiła największa inwestycja realizowana obecnie w Grupie Azoty ZAK SA – Nowa Elektrociepłownia. Znaczenie projektu dla firmy i regionu, a także stan jego realizacji, zostały omówione zarówno ze strony gospodarza inwestycji, jak i generalnego wykonawcy – firmy RAFAKO SA

W imieniu Grupy Azoty ZAK SA – partnera branżowego VI Konferencji Nowoczesne Ciepłownie i Elektrociepłownie – oficjalnego otwarcia dokonał Prezes Zarządu Mateusz Gramza. Budowa Nowej Elektrociepłowni jest najważniejszą inwestycją prowadzoną obecnie w Grupie Azoty ZAK SA Naszą strategią są innowacje, zwłaszcza w obszarze nawozów i chemikaliów, ale także w obszarze energetyki stosujemy rozwiązania innowacyjne – podkreślał prezes Mateusz Gramza.

Poza wprowadzeniem merytorycznym, na uczestników tegorocznej konferencji czekała gratka w postaci wycieczki tematycznej po terenie kędzierzyńskich zakładów, której najważniejszym punktem była właśnie nowa elektrociepłownia.

Organizatorem VI Konferencji "Nowoczesne Ciepłownie i Elektrociepłownie" jest Agencja Promocji Biznesu. Szczegółowe informacje na temat wydarzenia można znaleźć na łamach serwisu: http://goo.gl/PUxx9t (*abc*)

(http://zak.grupaazoty.com/pl/wydarzenia/883, 13.05.2016) Dokończenie na stronie 338