

Influence of Selected Environmental Management Systems on the Properties and Functional Parameters of Explosive Materials

Andrzej Harat¹

¹ Institute of Civil Engineering, Faculty of Materials, Civil and Environmental Engineering, University of Bielsko-Biala, ul. Willowa 2, 43-309 Bielsko-Biala, Poland
e-mail: aharat@ath.bielsko.pl

ABSTRACT

The article presents the influence of using REACH and LCA systems on the properties and functional parameters of a group of hazardous substances – explosive materials. The most commonly used explosives include dynamite and emulsion explosive materials. Dynamites are generally viewed as dangerous due to the content of nitroglycerin and nitroglycol, whereas emulsion explosive materials are considered safe in environmental terms. However, they have worse functional parameters related to the energy efficiency of the detonation process compared to dynamites. Undoubtedly, the application of REACH regulation will lead to reducing the use of environmentally hazardous substances. On the basis of this principle, an alternative composition of an explosive material consisting of a mixture of emulsion matrix and penthrite with the energy efficiency parameters comparable to those of dynamites was developed. The analysis of research results allows concluding that the criteria for substance qualification specified in REACH regulation are insufficient to thoroughly evaluate the safety of its use, and should be supplemented with LCA analysis elements.

Keywords: REACH system, LCA standard, explosives

INTRODUCTION

Currently, the issues related to the broadly understood environmental engineering are no longer only a scientific and technical problem. It seems that they should be considered as an interdisciplinary issue, in which an important role is played by economic and legal instruments. An excellent example of the latter are management systems – the Regulation of the European Parliament and Council concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) and the ISO 14040 (LCA) standard, being the subject of considerations in this article. Their intended application is aimed at limiting the negative impact of hazardous substances on the environment.

In the article, the influence of REACH and LCA systems on the properties and functional parameters of one of hazardous substances groups – explosive materials – will be discussed. Currently, the most commonly applied explosives include dynamites and emulsion explosives. Emulsion

explosive materials are considered to be safe substances in environmental terms, but they are characterized by considerably worse functional parameters compared to dynamites (lower explosion heat and energy concentration). On the other hand, dynamites have better functional properties than emulsion explosives; however, they contain the substances that are widely recognized as particularly dangerous – nitroglycerin and ethylene glycol dinitrate. The application of REACH in the latter case will lead to a gradual limitation in the usage of these materials.

Given all of the above, it was necessary to develop a new composition of an explosive material which would consist of a mixture of a typical explosive with an additive of penthrite. The work presents a comparison of the properties characterizing the developed compositions and dynamites in accordance with the requirements imposed by REACH. Therefore, the physical, chemical, toxicological and ecotoxicological properties of the substances were taken into consideration. It seems that the criteria for substance classification

specified by REACH regulation need to be supplemented with the LCA analysis elements. Only then will it be possible to obtain full, comprehensive information on all environmental consequences of using a particular substance.

Environmental management systems

The considerations contained in this article are based on the analysis of two management systems – the Regulation of the European Parliament and Council concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) as well as the Environmental Life Cycle, being the subject of the ISO 14040 (LCA) standard, and their influence on the properties and functional parameters of explosives. The systems in question are characterized by considerable differences, which are connected with both the different legal nature and the scope of the conducted analyses.

As mentioned before, REACH is the regulation of the European Parliament and Council (EU). As a result, pursuant to the provision of art. 288 of the Treaty on the Functioning of the European Union (TFEU) dated 13th December 2007, it is applied entirely and directly in all member states of the European Union [TFEU, 2007]. REACH is the most significant piece of environmental legislation ever passed by the EU and is expected to influence the chemical substance flow in the products inside and outside the EU [Spencer Williams et al., 2009, Lee et al., 2013]. It should be emphasized that in this case, the implementation process, which is characteristic of directives, does not apply. On the other hand, LCA is one of the ISO 14000 series standards. The LCA is applied as a methodology to quantitatively compare the overall environmental performance of products and systems over their full life cycle [ISO 14040:2006]. Application of the ISO standards, which, as a rule, are directed to everyone, is based on the voluntary principle. These days, life cycle assessment is used not only to assess the direct environmental impacts of a product system

and compare them with other products but also to influence and initiate policy and marketing decisions [Venkatachalam et al., 2018].

Apart from the above-mentioned legal nature, the discussed systems are characterized by a different scope of the conducted analyses. The REACH system is based on 3 principles – registration, evaluation and authorization. The registration obligation imposes on the producer (importer) the requirement to send electronically comprehensive information regarding the physicochemical, toxicological and eco-toxicological properties of a particular substance to the European Chemicals Agency (ECHA). For the first time, the EU chemical regulatory scheme is now premised on the “precautionary” principle, and dictates that the industry must demonstrate the safety of a new or existing chemical substance before being able to market that substance in commerce in Europe [Steinway, Seitz, 2008].

The provisions contained in the regulation (attachments VII-X) precisely specify the type of data that producers (importers) are obliged to submit. The catalogue of the required information has been presented in Table 1. It depends on the amount of a substance being produced or imported on the community market. In the event the amount of substance placed on the market exceeds 1000 Mg, it is subject to the requirements contained in attachments VII, VIII, IX and X.

The evaluation procedure contained in REACH is aimed at identifying the substances that are particularly hazardous to life and health, constituting the subject of the last of the above-mentioned principles – authorization. As a rule, the effect of implementing the procedure should be a reduction of trade in the substances that are subject to it, because their placement on the market will require the permission granted by the European Commission. REACH has been designed to balance the environmental objectives with competitive aims, and has the scope to induce the development and adoption of eco-innovation as a side effect of the regulation itself [Arfaoui et al., 2014].

Table 1. Data regarding the properties of a substance required for its registration

Turnover range	Attachment VII	Attachment VIII	Attachment VII	Attachment VII
1–10 Mg/year	+			
10–100 Mg/year	+	+		
100–1000Mg/year	+	+	+	
≥1000 Mg/year	+	+	+	+

REACH may be considered a formalized system. Strict cataloguing of information is aimed at creating a unified and comprehensive database of the information on the substances in business trading. However, this can also result in the omission of specific effects of a particular substance. In the case of explosives, an example to quote could be a release of toxic posts-blast gases into the atmosphere during detonation. The large scale of the problem is proven by the fact that a few to several Mg of explosives are detonated each time blasting works are carried out in open-pit mines. Detonation is accompanied by a cloud of gases with an uncontrollable composition and a volume reaching a few hundred and a few thousand m³.

What is more, the regulation disregards the problem of waste. Pursuant to the provisions contained in art. 2 paragraph 2 of REACH, waste is not a substance, mixture or product within the meaning of the regulation [REACH Regulation, 2006]. Moreover, REACH does not take into consideration the problems related to work environment safety. Of course, there are no obstacles preventing such aspects from being included in LCA analysis, as this analysis encompasses all stages of the product life cycle, starting with the exploitation of raw materials, production, use and finishing with post-exploitation stage, which in literature is referred to as “from cradle to grave” [Gu, Bergman, 2017]. For obvious reasons, the LCA methodology can be regarded as more comprehensive and universal than the REACH regulation. LCA is very data-dependent. It requires, in the first place, collection of the inventory information on the identified processes [Tao, Yu, 2018]. Hence, using REACH as a continuously updated and extended data source could be a starting point to improve the current data situation in LCA with several tens of thousands of available ecotoxicity data [Müller et al., 2017].

Currently used explosive materials and their impact on the environment

In literature, an explosive material is defined as a chemical compound in which a strong exothermic reaction can occur due to external stimuli, and the reaction is accompanied by a release of large amounts of gaseous products [Maranda, 2004]. Currently, the most commonly applied explosives include dynamites and emulsion explosive materials.

The technological process of dynamite production involves mixing the compounds contained in so-called dynamite mix. Its main components are: ammonium nitrate (V), sodium nitrate (V), nitroglycerin, nitroglycol, nitrocellulose and dinitrotoluene [Xuguang, 1994].

The production of dynamites has an adverse effect on human life, health and the environment. This is confirmed by the results of analyses based on the provisions of both REACH regulation and LCA standard. In the context of REACH regulations regarding the toxicological and ecotoxicological properties of a substance, the vapours of nitrate esters (nitroglycerin and nitroglycol) are the most harmful to health. Other arduous environmental effects, which are addressed mainly by LCA analysis, include: pollution emissions into the atmosphere, production of waste and sewage.

It is therefore no surprise that other substances which have explosive properties, but, at the same time do not adversely influence the environment, are being sought. The undertaken actions resulted in developing formulations of compounds that were named Emulsion Explosive Materials (EEM). The first materials of this kind were patented by Eagly in 1964 [Patent 3 161 551]. The technological process of emulsion explosive materials production was presented in Fig. 1.

This process can be divided into the following stages: preparation of raw materials (organic phase, emulsifier, solution of nitrates), production of emulsion, mixing, sensitizing process, cooling and packing. As it can be seen based on the data presented in Fig. 1, after the emulsion has been formed, the technological process can go one of two ways. It can result in the formation of an emulsion matrix which does not have explosive properties or lead to the formation of a ready-made explosive material due to the sensitization processes (by adding a high-energy explosive material or forming gas bubbles), cartridge filling, cooling and packing. In the former case, the matrix formed is sensitized in the place where the blasting works are performed.

The obtained emulsion explosive materials are characterized by low sensitivity to mechanical stimuli (friction, shock). Additionally, compared to the latter, the production technology of these materials is practically free of waste. From the point of view of the criteria specified by both REACH regulation and LCA standard, emulsion explosive materials are without doubt safer in manufacturing and application than dynamites.

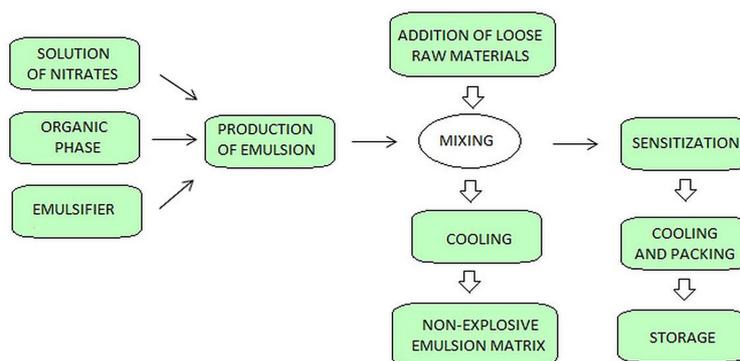


Fig. 1. Diagram of the technological process of emulsion explosive materials' production

The only aspect in which emulsion explosives are worse than dynamites are some of their functional properties related to the detonation process energy efficiency, i.e. explosion heat and energy concentration. Table 2 presents the data regarding selected functional properties of dynamite, the trade name of which is Ergodyn 31E and emulsion explosive material – Emulinit 8M.

For several years, there has been a trend to change the range of offered explosives, which consists in a gradual replacement of classic explosive materials (dynamites) with the compounds that are considered safer to the environment – emulsion explosives.

Alternative composition of an explosive material

The considerable difference in the parameters related to the energy efficiency of the detonation of dynamites and emulsion explosives as well as REACH regulation requirements characterized above provided a starting point for undertaking the works aimed at creating an alternative composition of an explosive material which would be equal to dynamites in terms of the quoted functional properties, and, at the same time, would not contain nitroglycerin and

nitroglycol, characteristic of classic explosives, the use of which will certainly be reduced by the REACH system.

The explosive material that was proposed as an alternative to dynamites contained penthrite (pentaerythritol tetranitrate) in the emulsion matrix.

The emulsion solution is obtained in accordance with the previously presented description. Next, penthrite (PETN) is added to the emulsion.

PETN is considered to be one of the strongest known brisant explosives. The specific volume of the gaseous products of explosion is 780 dm³/kg. The detonation speed reaches 8 300 m/s (with the density of 1.7 g/dm³) [Meyer et al., 2007].

In this way, an explosive with good detonation properties was obtained. Analyses were conducted for the mixtures of the emulsion with penthrite by changing the contents of the latter within a range of 35%-45%. The calculations of the explosive's functional parameters as well as the experimental tests that are commonly conducted for industrial explosives – shock sensitivity and detonation speed measurement were carried out.

Comparative list of properties and functional parameters of dynamites and the developed compositions of an explosive material

Explosive materials can serve as an example of the substances in the case of which the practical implementation of the solutions contained in REACH regulation will force a technological change that will be environmentally friendly and will result in the replacement of the traditional explosives (dynamites) containing nitroglycerine and nitroglycol, which are classified as highly toxic. This type of material, beside emulsion explosives, could be the developed composition, being a mixture of emulsion matrix and penthrite.

Table 2. Selected functional properties of explosive materials [www.nitroerg.pl]

Type of explosive	Parameters	
	Explosion heat [kJ/kg]	Energy concentration [kJ/dm ³]
Ergodyn 31E (Dynamite)	4027	5648
Emulinit 8M (EEM)	3364	4036

Table 3 presents selected properties of nitroglycerin, nitroglycol, i.e. compounds characteristic of dynamites and penthrite, according to the criteria specified by REACH regulation.

Among the physicochemical properties of substances that must be submitted in accordance with REACH regulation, vapour pressure and solubility in water deserve special attention. The latter in the case of nitroglycerin is 1.8 g/dm³, nitroglycol – 5 g/dm³, whereas penthrite is considered to be a substance insoluble in water [Meyer et al., 2007]. Moreover, the vapour pressure values of the analysed compounds are different. They reach – 0.03 Pa (nitroglycerin), 7 Pa for nitroglycol (both values at 20 °C), and penthrite vapour pressure is regarded insignificant [International Labour Organization]. This parameter, which can be defined as gas pressure over liquid at a given temperature, directly shows the exposure of living organisms to the effect of particles of a given substance suspended in the air.

The other group of information about substances which is required by REACH regulation to be submitted are their toxicological and eco-toxicological properties. The toxic effect of penthrite is also lower in this case. The values of acute toxicity of LD₅₀ (orally for mice) noted for penthrite are over 10 g/kg [Huber, 2001], whereas for nitroglycerin – 1.12 g/kg [Bigham, 2001], and

for nitroglycol – 540 mg/kg [Clayton, 1981]. The characterized physicochemical parameter – vapour pressure is directly related to the parameter of toxic effect on skin and airways. It is particularly dangerous in the case of nitroglycol due to the possibility of this compound adsorption through skin [Yinon, 1997]. The characteristics of the described substances are complemented by so-called toxic-kinetic evaluation of the substance behaviour, which is clearly specified in literature. In the case of nitroglycerin, it was found that each form of this compound's effect – through skin, orally or as the effect of the substance vapours – is considered highly toxic [Huber, 2001]. Nitroglycol is considered highly toxic as well. According to Vincoli, the toxicity of nitroglycol is higher than that of nitroglycerin [Vincoli, 1997]. On the other hand, penthrite is described as a slightly toxic substance [Huber, 2001].

Apart from the environmental factors characterized above, the analysis of functional parameters is of great importance in the evaluation of explosive materials. Using a material that is a mixture of emulsion matrix and penthrite could be an interesting alternative solution in this area.

Table 4 presents the selected functional parameters of dynamites, emulsion explosives and the proposed compositions of emulsion matrix and penthrite, containing 35%, 40% and

Table 3. List of selected properties of the substance according to the criteria contained in REACH regulation

No.	Property	Nitroglycerin	Nitroglycol	Penthrite
1.	State of matter	Liquid	liquid	solid substance
2.	Relative density [g/cm ³]	1.6 [Huber, 2001]	1.38 [Huber, 2001]	1.77 [Huber, 2001]
3.	Boiling point [°C]	125 [Huber, 2001]	139 [Huber, 2001]	180 [Huber, 2001]
4.	Vapour pressure [Pa] (20 °C)	0.03 [www.ilo.org]	7 [www.ilo.org]	negligible [www.ilo.org]
5.	Solubility in water [g/dm ³]	1.8 [www.toxnet.gov]	5 [www.ilo.org]	Insoluble [Meyer et al., 2007]
6.	Acute toxicity	LD ₅₀ orally: mouse 1 118 mg/kg rat 822 mg/kg [Bigham et al., 2001]	LD ₅₀ orally: mouse 540 mg/kg rat 616 mg/kg [Clayton, 1981]	LD ₅₀ orally: mouse over 10 g/kg [Huber, 2001]
7.	Effect on skin	LD ₅₀ > 280 mg/kg (for rabbit) [www.gestis.de]	LD ₅₀ : 3800 mg/kg (for rat) [www.gestis.de]	Dose of LD ₅₀ specified only for oral exposure
8.	Effect on living organisms	Toxic effect on skin, eyes and respiratory tract [Yinon, 1997]	Very harmful effect through respiratory track and skin [Yinon, 1997]	No toxic effect [Meyer et al., 2007]
9.	Toxicity for aquatic environment	Highly toxic for aquatic organisms (alga and fish) [www.gestis.de]	No data regarding the effect on aquatic environment	Substance insoluble in water
10.	Evaluation of toxic-kinetic behaviour of the substance	Each kind of effect – through skin, oral exposure, through compound vapours – it is considered highly toxic [Huber, 2001]	Highly toxic compound. Vincoli classifies its toxicity as higher than that of nitroglycerin [Vincoli, 1997]	The compound is not classified as toxic to human body. Huber describes it as a slightly toxic substance [Huber, 2001]

Table 4. Comparison of selected materials' functional parameters

Type of explosive	Functional parameters						
	I [%]	II [kJ/kg]	III [kJ/dm ³]	IV [dm ³ /kg]	V [kJ/kg]	VI [kg/dm ³]	VII [m/s]
Dynamites (Ergodyn 22E, Ergodyn 35E) [www.nitroerg.pl]							
ERG 22E	4.9	3 763	5 260	897	966	1.4	5500
ERG 35E	3.2	4 296	6 014	864	1048	1.4	6000
Emulsion explosives (Emulinit 2, Emulinit GM 1) [www.nitroerg.pl]							
EMU 2	-3.06	3 364	4 036	883	820	1.1–1.3	4700
EMU GM	-3.3	3 762	4 514	904	897	1.05–1.25	4000
Developed compositions (emulsion matrix + penthrite %)							
PETN 35	1.92	4109	5753	852	968	1.4	5440
PETN 40	0.98	4377	6566	841	1011	1.4	6362
PETN 45	0.05	4646	6969	830	1052	1.5	6557

I – oxygen balance, II – explosion heat, III – energy concentration, IV – volume of post-blast gases, V – specific energy, VI – density, VII – detonation speed

45% PETN, respectively (diameter of explosive charge 32 mm).

The results clearly demonstrate that in terms of the functional parameters, the obtained explosive material does not differ from the explosives that are currently on the market. An example could be the data regarding the concentration energy and explosion heat of the explosive material.

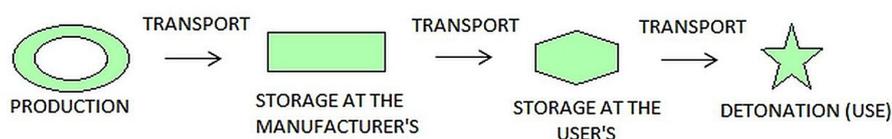
Of course, the above-mentioned criteria of substance evaluation specified by the REACH regulation, regarding the physicochemical, toxicological and eco-toxicological properties of a substance do not reflect the entire influence that it exerts on the environment. Comprehensive information about it, in particular in the case of specific materials, such as explosives, is provided by the LCA analysis, which encompasses the phase of production, storage and use. Fig. 2 presents a diagram of the life cycle stages of explosive materials.

The life cycle stages of explosive materials include production, storage and use as well as the process of transporting the materials between them.

Undoubtedly, the greatest disadvantage of the composition, which consists of a mixture of emulsion – the basic raw material for the production of emulsion explosives and penthrite, will be the lack of mechanical loading into blast holes

of the explosive material obtained. This results from experimental research and the obtained results of shock sensitivity. They reached: 23.5 J for the composition containing 35% of penthrite and 19.6 J for the emulsion matrix with an addition of 40 and 45% of PETN. For safety reasons, the value of shock sensitivity of an explosive material to be mechanically loaded should be higher than 30 J [PN-EN 13631–4:2004]. Such values are reached only by emulsion explosives.

In the case of classic explosives (dynamites) as well as the alternative composition consisting of an emulsion matrix with an addition of penthrite, it is necessary to manufacture a ready-made explosive material in a production plant. As a result, this substance is present all the time, from the moment it has been produced to the time of its use. Storage entails numerous dangers related to fire and explosion threats. In Poland, these problems are subject to the Regulation of the Minister of Economy dated 9th July 2004 concerning occupational safety and health in the process of production, in-house transportation and the trade of explosives. It defines the conditions to be fulfilled by the facilities permitted to store materials and specifies protective zones on the territory of which it is forbidden to carry out the activities described in the Regulation as well as the zones threatened with explosion, which determine the

**Fig. 2** Diagram of the stages of explosive materials' life cycle

location of various kinds of facilities. The process of transporting explosive materials is also an important factor that has an adverse influence on safety. It exposes the substance to the risk of explosion or theft. These threats necessitate conveyed transports of this kind of materials [Regulation of the Ministry of Economy, 2004].

With regard to the safety of application, emulsion explosives should be considered the best. The technical solutions that are applied in the case of these materials eliminate the necessity of producing a ready explosive material in a production factory, as it is possible to manufacture it in mobile plants. In such a case, the explosive material is produced in the loading hose or blast hole. An example of this solution is the UMS system (Universal Mixing System) 2000 [Holmberg, 2000]. As a result, a number of hazards related for instance with the process of storage and transport of a ready explosive from the production plant to the place of its intended use are eliminated.

In consequence, it ought to be concluded that the developed composition of an explosive material, consisting of emulsion matrix with an addition of penthrite, fully complies with the REACH regulation. It should also be noted that in terms of safety parameters, it is not as good as the currently used emulsion explosives, as indicated by the results of the LCA analysis.

CONCLUSIONS

There is no doubt that the currently used chemical substances have a harmful effect on human life, health and environment. The REACH regulation is one of the major community legal acts the application of which should lead to a reduction rather than complete elimination of this type of influences by subjecting them to thorough control. The criteria for the classification of the substances (preparations and products) specified by the REACH regulations are insufficient to thoroughly evaluate the safety of a particular product application. Strict adhering to the principles of registration, evaluation and authorization allows for creating a unified database regarding all the properties of a substance. However, it does not always address the specific effects of substances. A very good example are explosives, being the subject of this article, in the case of which the analysis based solely on the evaluation criteria catalogued by the REACH regulation on

the basis of the physicochemical, toxicological and eco-toxicological properties of a substance does not provide satisfactory results. It seems that the influence of a substance (preparation or product) on the environment can be thoroughly evaluated if elements of both LCA methodology and REACH regulation are taken into consideration in one analysis. Moreover, as mentioned in literature [Adamczyk et al., 2016], it will provide an excellent example of practical implementation of the sustainable development principle as it will combine economic effectiveness with respect for the protection of environment and its resources.

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