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APPLICATIONS OF DEMILITARIZED ENERGETIC MATERIALS IN BLASTING TECHNIQUE

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The paper mentions the basic ways of disposal and/or utilization of demilitarized energetic materials (EMs). Direct application of military explosives or propellants in blasting technique is undesirable at present, primarily because of their sensitivity to outer stimuli, the markedly negative oxygen balance, and impossibility of application of mechanized charging of boreholes. One of economically effective, safe and environmentally friendly methods of utilization of these EMs lies in their application as fuel and sensitizing components of commercial explosives with approximately zero oxygen balance. It can be stated that the approach to demilitarized EMs shows how advanced a particular country is from the standpoint of both expertise and legislature.

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Introduction

The recent policy of détente and replacement of old armament systems by modern technologies have led, during the last fifteen years, to a large accumulation of useless ammunition. While the metal components of this ammunition represent attractive raw materials, its active components, which means high explosives, propellants and pyrotechnics components (i.e. military energetic materials) form, from the standpoint of their vast amounts, problematic waste materials classified as Hazardous Waste. This energy-rich waste is predominantly liquidated by the following ways:

- Chemical conversion to higher value products for both civil purposes (raw materials for production of chemicals and plastics [1], but also fertilizers [2,3]) and military purposes (LOVA secondary explosives [4]).
- Open burning (OB) of the explosives alone (particularly propellants [1]) or their mixtures with water and colloidal coal [5,6].
- Open detonation (OD), particularly realized in areas with low population density (Finland, see Refs. [7,8]).
- Storage and disposal by ocean or land burial [9].
- Direct application in blasting (see Refs. [10–12]).
- Reformulation to industrial explosives (e.g., see Refs [2,9,13–22]) or to propellants (smokeless powders).

The interest in chemical conversion of demilitarized energetic materials (EMs) appeared as far back as early 1920s [2]; at present, only economically advanced countries can afford to use this way of treatment. OB/OD are a potential source of air and water pollution. Deposition of old ammunition on the bottom of oceans, which has been practiced already since World War I, is illegal at present (UN Law of the Sea) [9]. Direct application of these EMs in blasting technique is problematic and it is dealt with in this paper along with the problem of their reformulation to industrial explosives.

Military Secondary Explosives and Propellants in Blasting Technique

Military high explosives and propellants are characterized by distinctly negative oxygen balance. In the case of rocket propellants it is even desirable to obtain the explosion burning products of the lowest possible average molecular weight (that means the highest possible content of carbon monoxide, hydrogen etc.). With gun propellants, oxygen deficiency leads to excessive muzzle flash. Direct application of these materials in blasting technique is thus connected with potential pollution of the environment with carbon monoxide and other products of imperfect oxidation. Dismantled military EMs are also generally much more sensitive to

outer stimuli as compared with modern commercial secondary explosives. This is especially true of propellants, whose sensitivity to impact and particularly to friction and electric spark is generally considerably high [19,23].

The EMs of propellant type (as indicated by their name, by the way) are exclusively constructed as propelling and/or spotting charge; hence they are able of deflagration at speeds of 1000 – 1800 m s^{-1} [24,25]. However, depending on their composition, shape, specific surface, porosity, surface treatment, perforation of grain, and on the diameter and confinement of charge, some propellants can detonate at speeds of 4880 – 7800 m s^{-1} (see Refs. [12,24–26]).

Unsuitable grain size of both military high explosives (usually compact filling) and propellants does not make it possible to fill boreholes sufficiently. Mechanical disintegration of these EMs (grinding) in order to obtain suitable grain sizes represents a problematic and considerably risky operation. The unsuitable grain size of propellants often causes their incomplete decomposition in the process of explosion transformation with subsequent post-combustion in the debris, which is another risk factor of direct application of propellants in blasting technique.

However, the capability of rapid gas generation exhibited by gun propellants is exploited to fracture geologic formations containing fossil fuels (reactivation of oil and gas wells) – this procedure is called Tailored Pulse Fracturing [3]. Disruptive high explosives of TNT type, hexolites and pentolites can be used, after a slight modification of composition, to produce booster charges [17]; however, they are unsuitable for direct application in modern blasting techniques.

The most appropriate solution to the problem of application of demilitarized EMs in blasting technique (from the point of view of environmental protection, safe handling, and economy) seems to be in their addition to modern slurry explosives in amounts of 25 – 35 % by wt. [4,9,13,15–22], the resulting mixture being characterized by approximately zero oxygen balance. A survey of a broad assortment of commercial explosives containing demilitarized EMs is presented in papers of Kalatsey *et al.* [17]. An addition of fine-grain powders e.g. to emulsion explosives can increase the working capacity of the resulting mixtures by up to 20 % [27]. It was found [28] that a critical amount (i.e. about 30 % by wt.) of additive of high explosives exists in the slurry or other explosive mixtures with salpeter oxidizing system. Explosive decomposition is not influenced by structure of the oxidizing system (solution or crystalline) of thus fortified mixtures only in the case when the content of the additives is above the critical value [28]. This fact is important for construction of reliably detonating commercial industrial secondary explosives containing demilitarized EMs.

New Trends in Blasting Technique and Industrial Explosives

The 2nd World Conference on Explosives and Blasting Technique held in Prague in 2003 clearly showed [29] that the epoch of trial-and-error empirical blasting operations is over, and a new trend is generally winning, which uses technological-scientific approach based on computational planning of all types of blasting operations with perfect monitoring of all undesirable effects of the operation (seismism, air-pressure effects, fly rock). That guarantees viability of blasting operations also in future even with proper respect to strict environmental regulations. Complex computer programs are tailored for particular sites, and used by competent experts, which guarantes carrying out safe and effective blasting operations. Effective blasting technique is thus becoming teamwork involving experienced specialists from various fields (mechanics of rocks, properties of explosives and their parameters inclusive of preparation and charging, computational models of the optimum parameters of blasting operation, reliable measurement of fragmentation and undesirable effects). It is only such a team that can provide reliable and functional service for customers and fully satisfy their requirements. In developed countries such teams successfully operate, and the management of the respective mine/ quarry can fully concentrate on their main task, i.e. how to best exploit the materials obtained.

In the field of commercial explosives at present the dominating role is played by ANFO explosives and W/O emulsions prepared at the site of consumption and charged mechanically into the boreholes [29]. A highly promising trend of R&D with already realized outputs is the nano-structured EMs (in the form of aerogels or xerogels) [30]. The direct application of demilitarized EMs, particularly smokeless powders, in blasting technique [10–12] stands in sharp contradiction with the above-mentioned trend, and at present it rather represents a sign of misinterpretation of the problem by both experts and legislators. The reuse of energy of these materials added as fuel and sensitizing components to commercial explosives [4,9,13,15–22] is one of effective, safe, and environmentally friendly methods of their liquidation, which is to a considerable extent compatible with the present trends in blasting technique. It should be emphasized that the liquidation of present military EMs is accompanied by ongoing R&D in the area of their replacement by new, so-called green EMs (GEMs) with easier disarmament and reusing [31].

Conclusion

Military energetic materials (EMs) are characterized by distinctly negative oxygen balance and relatively high sensitivity to outer stimuli, as compared with modern commercial explosives. From the point of view of contemporary environment-

protection regulations, aspects of work safety, intensification and mechanization of blasting operations, the direct application of these materials as commercial explosives is undesirable. Their application as fuel and sensitizing additives to commercial explosive mixtures with approximately zero oxygen balance represents one of effective, safe, and environmentally friendly ways of their liquidation. It can be stated that the approach to demilitarized EMs shows how advanced a particular country is from the standpoint of both expertise and legislature. It can be expected that gradual introduction of the so-called Green EMs as charges in armament systems will facilitate the solution to problems of reuse or disposal of demilitarized EMs in the future, as compared with the present situation.

References

[1] Wanninger P.: Chem. unserer Zeit **29,** 135 (1995). (Je to správná zkratka ???)

[2] Anonymous writer, *The Commercial Utilization of Smokless Powder,* Army Ordnance **2**, 233 (1922); Chem. Abstr. **16,** 7745 (1922).

[3] Burch D., Johnson M., Sims K.: *Value Added Products from Reclamation of Military Munitions,* in: Proc. of the 22nd Int. Pyrotech. Seminar, IIT Res. Inst., pp. 69 – 73, Chicago, July 1996..

[4] Mitchell A.R., Coburn M.D., Schmidt R.D., Pagoria P.F. and Lee G S.: *Conversion of Demilitarized Explosives and Propellants to Highe Value Prodcts*, in: Aplication of Demilitarized Gun and Rocket Propellants in Commercial Explosives (Machacek O. Ed.), Nato Sci. Series II., Mathematics, Physics and Chemistry - Vol. 3, pp. 49 – 57, Kluwer Acad. Publ., Dordrecht, 2000.

[5] Delyagin G.N., Erokhin S.F., Karabasov Yu.S., Kurunov I.F., Isteev A.I., Oleinikov D.V.: Chernaya Metallurgiya, Bull. Nauch.-Techn. Ekonom. Inf., (2003), No. 6, 29-36; Chem. Abstr. **140,** 131 419 (2004).

[6] Karabasov Yu.S., Oleinikov D.V., Kurunov I.F., Isteev A.I.: Metallurgist (New York) **45**, 350 (2001).

[7] Hagforts M.: *Environmental Impact of the Disposal of Old Ammunition in Open Surface Detonation,* in: Proc. of the FINNEX 2002 Seminar (Kantolahti E., Kariniemi A., Pääkkönen E., Eds), pp. 163 – 175, Levi, Kittilä, Sept. 2002.

[8] Latvala T.: *Mass Detonations in Finland* , in: Proc. of the FINNEX 2002 Seminar (Kantolahti E., Kariniemi A., Pääkkönen E., Eds), pp. 176–180, Levi, Kittilä, Sept. 2002.

[9] Wulfman D.S.: Canad. Chem. News **76,** 15 (1998).

[10] Munroe C.E., Howell S.P.: *Comminuted Smokeless Powder as a Blasting Agent,* Bur. of Mines, Repts. of Investigations, No. 2386 (1922); Chem.

Abstr. **6**, 1995 (1922).

[11] Klusáček J.: *An Exploitation of Demilitarized Military Explosives in the Civilian Blasting Technique (in Czech)*, Proc. of the Int. Symp. „Ecological Liquidation of Explosives (Especially Propellants for Missiles)", p. 11– 13, Pardubice, Sept. 1996.

[12] Machacek O., Eck R., Gilion J.B.: *Alternative Use of Military Propellants as Novel Blasting Agents*, U. S. Pat. 5,608,184, Universal Tech. Corp., Dallas, Texas, March 1999.

[13] Wulfman D.S., Sitton O.C., Worsey P., Johnson M., Burch D.: *Commercial Reformulation, an Economic Environmentally Benign Means of Using Explosives and Solid Propellants*, Proc. of the 21st Annual Conf. on Explos. & Blasting Techn., pp. 248 – 256, 1995.

[14] Morgan M.E., Miller P.L.: *Recycling Propellants and Explosives into the Commercial Explosive Industry*, in: Challenges in Propellants and Combustion: 100 Years after Nobel (The 4th Int. Symp. on Spec. Topics in Chem. Propulsion, Stockholm, May 1996) (Kuo K.K., Ed.), pp.199 – 204, Begell House, New York, 1997.

[15] Machacek O., Gilion J., Brent E., Eck G., Lipkin J., Michalak R., Perry R., Mckenzie A., Morgan A.: *Recycling of Excess and Demilitarized Energetic Materials in Commercial Explosive Application*, in: Challenges in Propellants and Combustion: 100 Years after Nobel (The 4th Int. Symp. on Spec. Topics in Chem. Propulsion, Stockholm, May 1996) (Kuo K.K., Ed.), pp. 177 – 188, Begell House, New York, 1997.

[16] Wulfman D.S., Sitton O., Nixon F.T., Podzimek M., Worsey G., Beistel D., Worsey P., Burch D., Johnson M.: Canad. J. Chem. Eng. **75**, 899 (1997).

[17] Kalatsey V.I., Matseevich B.V., Glinskii V.P., Plekhanov N.I., Shalygin N.K., Mardasov O.F., Fridman A.G.: Bezop. Truda Promst. No. 12, 32 (1975).

[18] Rabotinski N.I., Sosnin V.A., Iliukhin V.S., *The Application of Reclaimed Explosives in Commercial Emulsion Explosives*, in: Aplication of Demilitarized Gun and Rocket Propellants in Commercial Explosives, (Machacek O., Ed.), Nato Sci. Series II., Mathematics, Physics and Chemistry - Vol. 3, pp.193 – 198, Kluwer Acad. Publ., Dordrecht, 2000.

[19] Salygin N.K., Matseevich V., Glinskii V.P., Mardasov O.F., Plekhanov N.I.: *Use of Converted High Energy Value Explosive Materials as Industrial Energetic Materials*, in: Aplication of Demilitarized Gun and Rocket Propellants in Commercial Explosives, Nato Sci. Series II., Mathematics, Physics and Chemistry, (Machacek O. (Ed.), Vol. 3, pp. 175 – 180, Kluwer Acad. Publ., Dordrecht, 2000.

[20] Wulfman D.S.: *Environmentally Neutral Reformulation of Military Explosives and Propellants*, Appl. Canadian Pat. CA 2,157,059, CIPO, Jan. 1997.

[21] Zabelin L.V., Snigir N.M., Kosarev V.V., Grafova L.A., Talalaev A.P., Ibragimov N.G., Ivanova N.P., Kuzmitskii G.E., Fedchenko N.N., Gilik G.B.: *Water-containing Blasting Agent,* Rus. Pat. RU 2,217,401 (2003); Chem. Abstr. **140**, 220 219 (2004).

[22] Maranda A., Lipinska K. and Lipiński M.: *Analysis of Possibility of Waste Energetic Material Application in Mining Blasting Agents,* in: Proc. of the 5th Seminar "New Trends in Reserach of Energetic Materials" (Vagenknecht J., Ed.), pp. 145 – 149, University of Pardubice, Pardubice, 2002.

[23] Šelešovský J., *Evaluation of Stability and Lifetime of the Military Explosives,* Diploma project, University of Pardubice, Pardubice, 2002.

[24] Urbanski T.: Zeitschrift Gesamte Schiess- und Sprengstoffen **34,** 103 (1939).

[25] Kast H.: Zeitschrift Gesamte Schiess- und Sprengstoffen **15**, 195 (1920).

[26] Schubert H., *Detonation Properties of Gun Propellants and Slurry Explosives and their Combination,* in: Aplication of Demilitarized Gun and Rocket Propellants in Commercial Explosives, Nato Sci. Series II., Mathematics, Physics and Chemistry (Machacek O., Ed.), Vol. 3, pp. 111 – 114, Kluwer Acad. Publ., Dordrecht, 2000.

[27] Odintsov V.V., Pepekin V.I.: Khim. Fizika **13**, 131 (1994); (see also Khim. Fizika **14**, 132 (1995)).

[28] Zeman S., Kohlíček P., Maranda A.: Thermochim. Acta **398,** 185 (2003).

[29] *Explosives and Blasting Technique,* Proc. of the 2nd World Conf. on Explos. & Blasting Techn. (Holmberg R., Ed.), A.A. Balakema Publ., Lisse, 2003.

[30] Vávra P., Jalový Z. and Zeman S.: *Energetic Materials, Trends and Requirements*, Proc. of the Conference "New Trends in Technology of Ammunition Assembling and Present Aspects of Dismantling and Reusing of Ammunition", pp. 127 – 134, Konštrukta Ltd., Trenčín, Slovak Rep., 2003 (in Slovak).

[31] Anonymous writer, *National Policy Dialogue on Military Munitions,* Final Rep., The Keystone Center, Keystone, Colorado, 2000.