PERCHLORATES AND INORGANIC PEROXIDES AS GREEN ADDITIVES FOR ANFO

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Introduction

Ammonium nitrate – fuel oil (ANFO) explosives have found extensive industrial application [1,2]. The low detonation parameters in typical explosive charge diameters (e.g. diameters below 46 mm) is a significant disadvantage of this type of explosives, as is the case with the limited sensitivity of ANFO to shock [3]. These two issues have generated considerable research interest in improving the energetic performance of ANFO.

One of the main approaches to improving the performance of ANFO is to modify the oxidising agent itself by adding chemicals or mixtures of chemicals, which readily undergo decomposition and yield significant amounts of gaseous decomposition products [4,5]. This favourably affects the AN decomposition upon interaction with a shock wave, thereby increasing the detonation velocity of ANFO or generating additional hot spots in the material.

In the case of AN, modification of this oxidant with chlorides was found to lower AN's decomposition temperature and increase its self-heating rate, but no overall improvement in detonation parameters was observed [6, 7]. Other additive that have attracted the attention was monoammonium phosphate. The research have shown that when monoammonium phosphate is added to AN, the detonation velocity for 10% of the additive is about 2 km/s. However, as the additive content in the material increases, the detonation velocity begins to decrease sharply once the additive content in the material exceeds 15% [8]. The combination of AN and explosives was also investigated. When combusting mixtures of AN with 15% methylnitrotetrazol (MNT) and 13.3% glycidyl azide polymer (GAP), the low-pressure combustion limits of the fuel oil-free mixtures occurred at pressures of 6–10 MPa. However, the combustion rates of these mixtures were quite low [9].

For the choice of additives to ANFO several criteria were formulated to guide the selection of potentially most beneficial compounds. Among the compounds that have attracted interest as potential additives are those that readily decompose with significant yields of gaseous products under shock wave, compounds that release significant amounts of gaseous products during decomposition, and those that can catalyse the decomposition reaction of ammonium nitrate.

Results and Discussion

Based on activation energy values of decomposition reactions of oxidising agents, as well as their reactivity with AN, magnesium and barium perchlorates, sodium carbonate peroxyhydrate (SPC) and sodium perborate (SPB) were found to be suitable additives for ANFO. Evidence has been provided below that these compounds do not drastically reduce the safety parameters of ANFO while significantly increasing its susceptibility to decomposition (Tab.1) [10].

Table 1 Friction and impact sensitivity testing [10]

Sample Fuel	ANFO	7%$Ba(ClO_4)_2$	7% $Mg(ClO_4)_2$	7%SPB	5% SPC
Friction sensitivity testing according to the standard EN 13631:3 [N]					
Liquid paraffin	>360	216	216	252	252
Naphta	>360	360	120	216	112
Impact sensitivity testing according to the standard EN 13631:4 [J]					
Liquid paraffin	40	3	3	7.5	35
Naphta	>50	10	10	20	7.5

One of the most important parameters to consider when determining the composition of an energetic material is the oxygen balance (OB). For ANFO, the OB should be close to 0% [11], in order to obtain the maximum charge energy with the lowest possible concentration of the post-blast fumes [12].

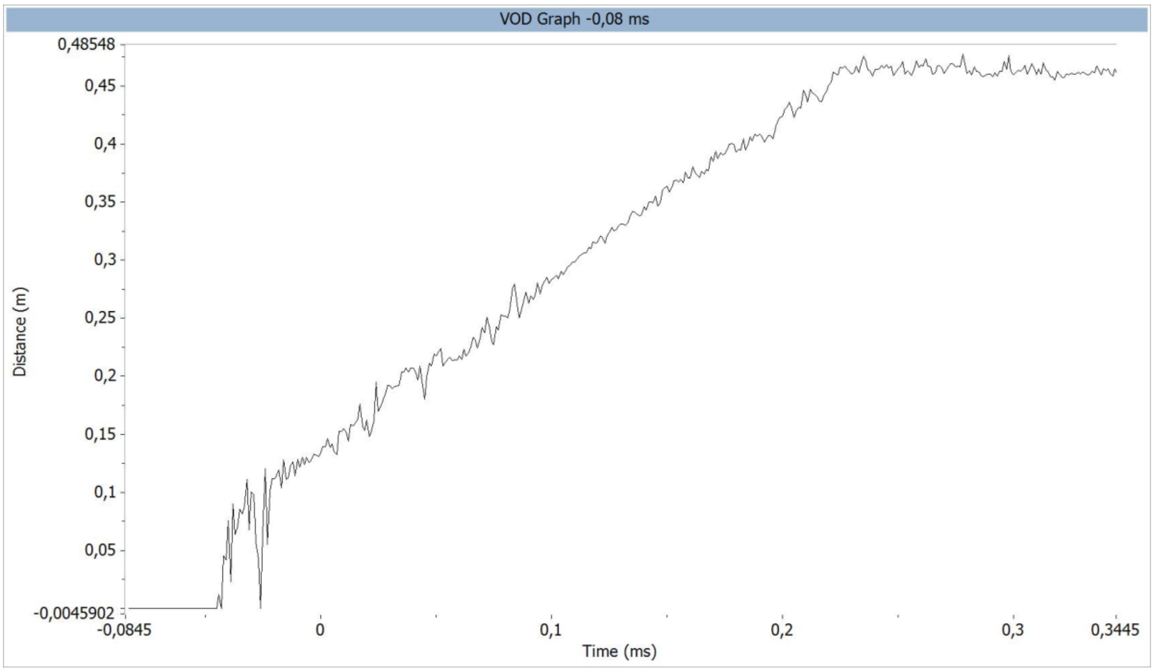
To determine the brisance of the materials obtained, the Hess test was conducted, with three repetitions for each type of additive (Tab.2). The obtained results show an improvement in brisance caused by all of the additives in comparison with traditional ANFO.

Table 2 Experimental results of detonation parameters for modified ANFOs

Type of sample	Charge composition [% mas.]			VOD for ϕ 46 [m/s]	Brisanse [mm]	Critical diameter [mm]
	AN / gAN	FO	Additive			
none	94.00 / 0.00	6	0	1559	2.69	37.1 – 39.8
none	47.00/ 47.00	6	0	2124	6.80	27.7 – 28.8
ClO_4^-	47.00 / 43.73	6	3,27	2098	7.09	22.2 – 31.1
BO_3^-	47.00 / 43.73	6	3,27	2185	7.75	21.7 – 30.0
CO_3^{2-}	47.00 / 44.66	6	2,38	2183	7.96	24.1 - 25.1

The detonation velocity of ANFOs supplemented with the selected additives was conducted using a continuous probe in conical charges. The use of this charge geometry allowed investigating the critical diameter of the modified ANFO, based on the point in which detonation faded in the charges. In the case of all additives, an increase in the detonation velocity and a decrease in the critical diameter was observed (Tab.2).

A



B

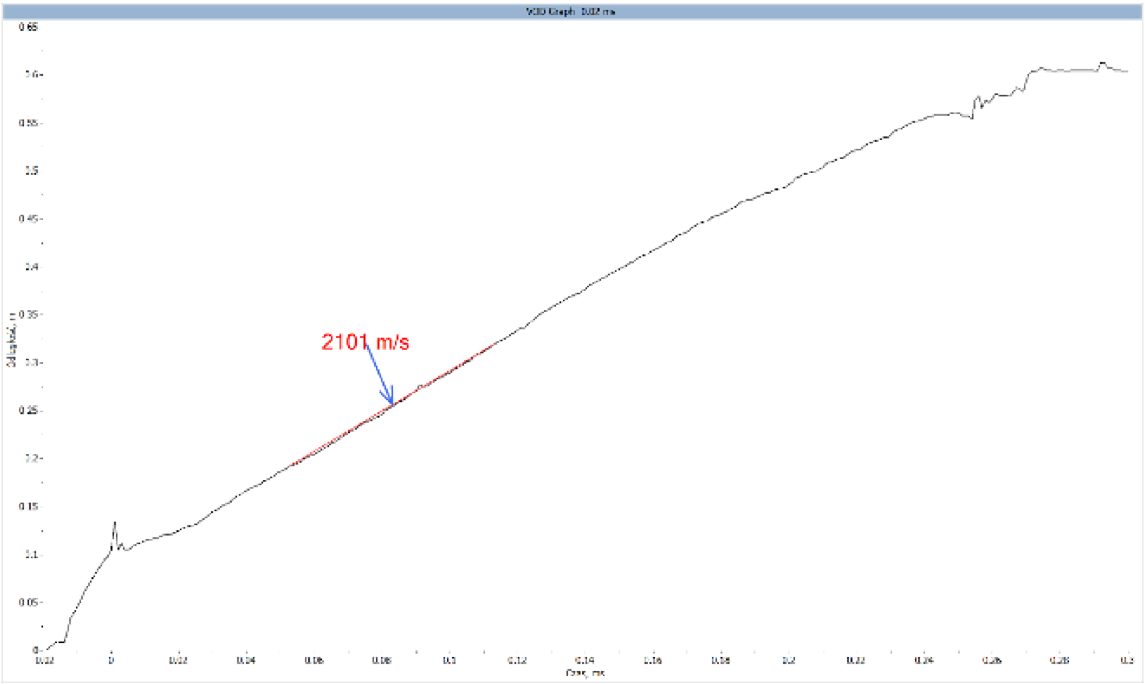


Figure 1 Graph showing measured detonation velocity versus critical diameter (A) for unmodified ANFO, (B) for ANFO with added barium perchlorate

The research has shown that the additives used meet the stated objectives, i.e. increasing the brisance and detonation velocity and decreasing the critical diameter of ANFO, while maintaining only slightly affecting the mechanical sensitivity parameters of the explosives.

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