

Characterization of explosive performance parameters: ANFO and explosive emulsion

Caracterização de parâmetros de desempenho explosivos: ANFO e emulsão explosiva

DOI: [10.56238/isevmjv1n2-008](file:///C:/Users/Win-10-Pro/Downloads/10.56238/isevmjv1n2-008) Recebimento dos originais: 03/04/2023 Aceitação para publicação: 24/04/2023

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ABSTRACT

The most commonly used explosives, for civil purposes, in construction and mining are Ammonium Nitrate Fuel Oil (ANFO) and explosive emulsions. Both are ammonium nitrate-based and detonate under the same chemical reaction between nitrate and mineral oil, given that the ANFO is composed of tiny grains of porous nitrate with diffused oil, and the emulsion is in the form of a liquid, continuous, viscous phase oily and the discontinuous aqueous phase. The study of parameters that measure explosive performance is fundamental to understanding the behavior of the explosion. Important parameters are the speed and pressure of detonation, the heat of the blast (energy), and the volume of gas produced. These properties help judge whether a particular explosive is convenient or not for the situation in question because, in some applications, high speed is required to increase the capacity of fragmentation, for example, when you want to fragment hard rocks. However, there is no need to fragment in some moments but to displace. Other properties, such as gas volume, become more relevant in such cases.

Keywords: Explosive, Emulsion, ANFO.

1 INTRODUCTION

Explosives are widely used in mining to loosen rock from exploration of nature, and in civil works such as tunnels to open the passage hole for the same; in transposition works, to open the way of the river, and in road works, to remove/open rocks that are in the form of the road. The most commonly used explosives in construction and mining for civil purposes are ANFO and emulsions. Explosives are based on ammonium nitrate and detonate under the same chemical reaction between nitrate and mineral oil.

ANFO appears as tiny grains of porous nitrate with diffused oil. It has low cost and simplicity of manufacture, safety in handling, and low emission of toxic gases when there is oxygen in stoichiometric quantity. However, if the oxygen balance (OB) is negative, CO formation will form, while for a positive OB, NO_x formation will occur (WANG, 1994). Toxic substances can result in an unhealthy work environment, particularly in underground operations where air circulation is ineffective. Besides, ANFO has a low density and poor water resistance. The OB is according to Equation 1, where O, C, H, and M represent oxygen, carbon, hydrogen, and explosive molar mass (Valença, 2013).

$$
OB = \left(0 - 2C - \frac{H}{2}\right) \cdot \frac{1600}{M} \tag{1}
$$

The explosive emulsion is in the form of a viscous liquid phase, continuous oily and discontinuous aqueous. It has some advantages over other explosives, as they can be applied through the pumpable system, which offers the possibility of preparing and loading the explosive at the fire site, in addition to the proven economic advantages over packaged explosives, mainly in large-scale mining, considering that they do not require packages, load faster and more efficiently, fill the hole, have excellent water resistance and produce little smoke and few gases (Valença, 2013). However, unlike ANFO, the emulsion undergoes oxidative decomposition of the oil phase when in contact with atmospheric air (Jones et al., 1999).

A third explosive is widely used, which is the mixture between ANFO and emulsion, the well-known heavy ANFO or blended emulsion. Mixing can occur in different proportions of each explosive so that the properties of the explosive vary with the balance variation (de MORAES, 2004). For example, ŽGANEC et al. (2016) showed that the higher the emulsion percentage, the higher the detonation velocity (VoD).

Studying the chemical properties of explosives is vital to understanding how to control detonation performance and explosive validity. Different reagents can be used in their composition, whether aluminum flakes or other types of nitrates, such as calcium or sodium, in addition to other compositions that will be exemplified at work. All of them influence performance and explosive validity. The calculation of explosive properties is fundamental to predicting the behavior. It is possible, for example, to predict the explosive energy and gas volume generated after detonation. These properties are essential for decision-making.

Blaster analyzes the rock on which the explosive will be applied and, according to the purpose of discharge, the most suitable explosive. The rock blasting process using explosives

occurs in three stages: The blast hole expands to crack the ho walls in the first stage. This happens due to the high pressure caused by the detonation; In the second stage, compression shock waves emanate in all directions. From the blast hole, with speed equal to the speed of sound in the rock. When this shock wave compression reflects against a free rock front, tensile stresses occur in the rock between the blast hole and the free front. If the tension force of the stone is exceeded, the rock will fragment in this region, which is the case in a correct plane detonation; In the third stage, the release of gaseous volume enters the cracks formed by the high pressures, expanding the cracks (Kabwe, 2018). If the distance between the blast hole and the free face is correctly calculated, the rock mass between the hole and the free face will detach and be designed (Olofsson, 1990).

1.1 PROPERTIES OF EXPLOSIVES

Different working conditions have made it necessary to manufacture explosives with other properties suitable for various requirements and purposes. In this sense, choosing the most suitable explosive requires considering several characteristics.

1.1.1 Velocity of detonation (VoD)

It is the speed at which the explosion travels through the explosive. The detonation speed is more incredible when the explosive is confined than unconfined. High VoD is necessary to generate a powerful impact, to cause the tension responsible for fragmenting the rock, mainly for hard stones (Olofsson, 1990). The higher the VoD, the greater the explosive capacity (Cameron & Hagan, 1996). Explosives such as nitroglycerin and emulsions are suitable for hard rocks such as granite, gneiss, and basalt, while ANFO is suitable for soft stones such as limestone and sandstone. According to Miyake et al. (2001), the detonation velocity of ANFO increases with the particle size reduction, that is, with the surface area increase. \check{Z} ganec et al. (2016) point out that the type of primer also influences VoD.

One aspect that significantly influences the VoD is the stability and size of the emulsion droplets. Since the phase separation process in an emulsion is spontaneous, the use of surfactants is essential to keep the emulsion stable, avoiding coalescence, that is, the increase in droplet size, considering that the smaller the diameter of the drops, the greater the contact area between the phases and, consequently, the greater the reaction rate, resulting in more significant pressure and detonation speed (Zhang et al., 2018).

1.1.2 Detonation energy

The energy or force of an explosive equals the difference between the heat of formation of the explosion products and the heat of the explosive, representing the explosive's theoretical work. In reality, the explosive's efficiency ranges from 30% to 90% of the available energy. At the time of detonation, the explosive's power will result in desirable effects, such as crushing the hole walls, formation of cracks, and rock fragmentation, and undesirable effects, such as ground vibration, noise, and atmospheric overpressure (Hustrulid, 1999).

Initially, the measure of explosive energy was determined as a function of the percentage of nitroglycerin in the explosive, as modern industrial explosives do not have more nitroglycerin, a new standard of comparison. According to Scott et al. (1996), energy is expressed in terms of mass or volume by the parameters: AWS (Absolute Weight Strength): It measures the total energy (in calories) available in each gram of explosive. Typical values range from 2847kJ/kg to 3223kJ/kg for explosive emulsion and 3768 kJ/kg for ANFO; ABS (Absolute Bulk Strength): the total energy (calories) available in each cubic centimeter of the explosive. It is obtained by multiplying the AWS (cal/g) by the explosive density ($g/cm3$). Typical values are 3556 to 4016 kJ/L for the explosive emulsion of density 1.25kg/L and 3071 kJ/L for ANFO. One way to increase the detonation energy of the emulsion is to add aluminum, which acts as an energizer (Crosby, 1998); RWS (Relative Weight Strength): is a measure of the energy available per unit mass of an explosive compared to an equal weight of a standard explosive. The common explosive is typically the ANFO. So, the RWS of any explosive is obtained by dividing the AWS of the explosive by the AWS of the ANFO. The RWS value is always given by multiplying the result of this division by 100. Typical values are 75 to 85 for explosive emulsion; RBS (Relative Bulk Strength): is a measure of available energy per unit volume compared to an equal volume of ANFO with a density of 0.81. It is calculated by dividing the ABS of the explosive by the ABS of the ANFO and multiplying by 100. Typical values are 115 to 130 for explosive emulsion.

When two explosives can be similar in their energy on a mass basis, they may differ in their power on a volume basis due to their densities. For practical applications, the energy on a volumetric basis will be crucial for deciding the explosive used (Mahadevan, 2013).

2 MATERIALS AND METHODS

2.1 CALCULATION OF THE POTENTIAL ENERGY OF THE EXPLOSIVE

The energy released by the explosion was calculated in a formulation as a base with zero oxygen balance. ANFO comprises 94.5% porous ammonium nitrate and 5.5% diesel oil, while the

emulsion consists of 77.3% dense ammonium nitrate, 16.7% water, 4.5% diesel oil, and 1.5% emulsifier. This formulation was developed as a standard for comparing Relative Bulk Strength (RBS) and Relative Weight Strength (RWS). The reaction representing the detonation is shown in Equation 2

$$
C_{16}H_{34} \rightarrow 160_2 + 115H_2O + 49N_2 \qquad \quad (2)
$$

Nitrate is the source of oxygen (oxidizing), and the fuel is the hydrocarbon. Detonations are characterized by high pressures, around 200GPa (Crosby, 1998). According to Bjarnholt (1980), the force is proportional to explosive density plus square VoD. When there is oxygen in the explosive to completely oxidize the carbon and hydrogen to carbon dioxide and water, the oxygen balance equals zero. The heat of the explosion will be optimal, while any deviation from the ideal oxygen balance, positive or negative, will take the heat of the explosion to a lower value (Valença, 2013).

The enthalpy of the reaction was calculated from reaction XX based on the standard formation enthalpy of components (NIST). To calculate energy per unit of mass (RWS), the enthalpy of the reaction for ANFO is divided by the sum of the molecular mass of the reactants. In contrast, for calculating energy per unit of volume (RWS), the enthalpy of the reaction shown for ANFO is multiplied by the density, 0.85. For the relative estimation of RWS and RBS, the energy released by the explosive was divided by the energy released by the ANFO. In the case of emulsion, the calculation of RWS is similar to that used for the ANFO since they detonate through the same chemical reaction. The difference is that the emulsion has inert in the composition, which will not contribute to the detonation. These inerts are water $(16.7%)$ and emulsifier $(1.5%).$ Therefore, to find the energy of the emulsion, multiply the energy associated with the ANFO by the factor of one less inert content.

Similarly, for RBS, the emulsion energy was multiplied by density, which varies from 1 to 1.25 (Valença, 2013). In the case of heavy ANFO, since it is a mixture of ANFO and emulsion, the energy released by the explosion is weighted according to the composition. In the case of the RBS calculation, in which the energy is multiplied by the density, the data of this property as a function of the composition were obtained from the ENAEX company.

2.2 GAS VOLUME CALCULATION

The volume of the gaseous products was calculated at standard pressure and temperature conditions (STP). Once the detonation reaction is complete, 180 moles of gaseous products are

generated. As STP (22.4L/mol) is considered, the gas volume is easily determined by direct proportion. Specifically, as the gaseous volume per unit of volume depends on the specific mass, the gaseous volume per unit of mass is multiplied by this property, which for ANFO is 0.85 kg/L (Valença, 2013).

In the case of the emulsion (which contains water and an emulsifier), considering the mass composition of 4.5% of C16H34 and 77.3% of NH4NO3, the gaseous volume per unit of mass will be 81.8% of the volume determined for the ANFO. In addition, for the gaseous volume per emulsion volume, the gaseous volume per unit mass is multiplied by the emulsion density, which varies from 1 to 1.25 kg/L, depending on its composition. In the case of heavy ANFO, the gaseous volume per unit of mass (L/kg) is a weighted average between the values of gaseous volumes found for the ANFO and emulsion, depending on the proportion of these explosives in the composition of the heavy ANFO. The gaseous volume per unit volume of explosive will also depend on the density, whose value was obtained from the ENAEX company catalog.

3 RESULTS AND DISCUSSION

3.1 ENERGY RELEASED BY THE EXPLOSION: ANFO AND EMULSION

Considering the composition of ANFO mentioned in section 2.1 and the total consumption of reagents, the energy released in the explosion was 3797.2 KJ/kg or 3227.6 kJ/L, and RWS=RWS=1. These values are in accordance with Valencia (2013), which found typical energy values for ANFO by 3768 kJ/kg and 3071 kJ/L.

In the case of the explosive emulsion, the energy released by the explosion was 3160.1 kJ/kg and RWS=0.818. Such values also agree with what was observed by Valença (2013), between 2847 and 3223 kJ/kg. However, the energy per volume varies because the density of the emulsion varies with the awareness. As discussed earlier, the matrix emulsion is not considered the principle of an explosive, only when sensitized by micro balloons, small spaces voids created along with the mass. Therefore, the density decreases after sensitization, ranging from 1 to 1.25 kg/L. The energy corresponding to this density range varies linearly from 3106.11 to 3882.637 J/L, as shown in Table 1. The typical energy for the emulsion is 3556 to 4016 kJ/L in an emulsion of density 1.25 kg/L.

Table 1. Energy by volume according to density

Analyzing the results of Table 1, it is possible to affirm that the higher the density, the greater the energy available per volume of the emulsion. However, the density of the emulsion is directly linked to sensitization. In this sense, the insertion of micro air balloons reduces the density and sensitizes the explosive. Therefore, the denser the emulsion, the more energy activation will need to carry out the detonation, which is less sensitized. The results of Mishra (2018) show that the maximum point detonation velocity for the tested emulsion is at a density of 1.15 kg/L and that explosive failure occurred at a density of 1.27 kg/L due to desensitization caused by high emulsion densities (above 1.20 kg/L), which resulted in a sharp drop in detonation velocity at these densities. When comparing emulsion and ANFO, it is also noticed that the emulsion, even with lower energy per unit mass, may have higher energy per unit volume because it is denser. The energy of the emulsion per unit volume exceeds that of the ANFO in densities above 1.05 kg/L. The emulsion has a higher density than ANFO because it fills the entire shell in which it is contained since its physical form is of a viscous liquid, while the ANFO is in the form of small solid grains, which results in many empty spaces between the grains.

3.2 ENERGY RELEASED BY THE EXPLOSION: HEAVY ANFO

When the emulsion is mixed with ANFO, the density of the ANFO is increased because it fills all the space between the ANFO grains; hence the mixture is called heavy ANFO, which fills all the hole space. Since the energy released by ANFO and emulsion are different, the energy released by the heavy ANFO will depend on the fraction of ANFO and emulsion used. Table 2 shows the energy released by the ANFO weighed as a function of the mass fraction of ANFO in the mixture. The higher the ANFO fraction, the higher the energy per unit mass because the emulsion counts with 16.7% water, inert to the detonation reaction. In ANFO, all the composition participates in the detonation reaction.

Table 2. Energy by kg according to heavy ANFO composition

The energy of the heavy ANFO can also be expressed per unit of volume. However, it also depends on the density, as shown in Table 3. Each heavy ANFO composition has its specific operating density. Most emulsion compositions have wider operating densities because the emulsion varies the density, whereas the majority of compositions of ANFO have densities of operations since ANFO has a fixed density. It is noted that the most energetic conditions are in the dominant mixtures of ANFO, in the emulsion/ANFO ratio of 25/75, 40/60, and 50/50, since the more emulsion there is in the composition, the more inert substances will also be present. It is also possible to observe that the energy per unit volume at high densities is higher than at low densities. At higher densities, more explosives will be contained in the same volume. It is also important to note that the higher the density, the more energy is required to activate the explosive column. In this context, the initiator must be dimensioned to start the entire explosive mass.

Table 3. Energy by volume for heavy ANFO at different compositions according to density

3.3 GASEOUS VOLUME GENERATED BY ANFO AND EMULSION

The volume of the gaseous products developed by the explosion is calculated at a pressure of 1 bar and a temperature of 0ºC (273K). In this way, it is possible to consider 1 mol corresponding to 22.4L. For the ANFO, considering the composition of the ANFO mentioned in the methodology, density 0.85kg/L, and complete reaction of the reagents, the generated gas volume was 979.46 L/kg. In comparison, for the emulsion, the gas volume was 801.37 L/kg. Such results agree with what was observed by Valença (2013) for emulsion (882 L/kg). Comparing emulsion and ANFO, ANFO produces higher gas volume and energy per unit of mass since the ANFO is pure explosive. In contrast, the emulsion has a 16.7% inert (water) composition. The fact that the emulsion varies in density when sensitized implies that the volume of gas generated per unit volume of explosive will vary by density.

In this context, the density varied from 1 to 1.25 kg/L; the results are shown in Table 4. When comparing the ANFO and the emulsion, it is noted that despite the emulsion having a lower volume of gas generated per unit mass, when analyzed per unit volume, the emulsion has a gas volume more significant than the ANFO when at densities above 1.05 kg/L.

Taolo +. Gascous volume generated by emulsion	
Density (kg/L)	Gaseous volume (L/L)
1.00	801.38
1.05	841.45
1.10	881.52
1.15	921.58
1.20	961.65
1.25	1001.72

Table 4. Gaseous volume generated by emulsion

3.4 GASEOUS VOLUME GENERATED BY HEAVY ANFO

Since ANFO and emulsion produce different gaseous volumes, this will depend on the fraction of each component. The gaseous volume per unit mass of the explosive can be calculated from the weighted average of the volume generated by the explosives of its composition. The results are shown in Table 5. As expected, the greater the amount of ANFO, the greater the volume of gas per mass since the ANFO has no inert, while the emulsion does.

In the case of heavy ANFO, the gaseous volume per explosive unit volume will depend on the ANFO/emulsion fraction and the final density of the explosive, which can vary according to the sensitizer inserted in the present emulsion. The gaseous volume per unit of volume generated as a function of density is shown in Table 6. The gaseous volume per unit of explosive is more significant in situations with a greater ANFO fraction in the compositions: 25/75, 40/60, and 50/50. It is also possible to perceive that the volume of gas released at higher densities is more significant because if the explosive is denser, more gases resulting from the detonation will be released. It is essential to mention that high densities also represent a problem in initiating this explosive. Under these conditions, the initiator must have sufficient potency to trigger all this explosive mass without failure.

4 CONCLUSIONS

When comparing the ANFO and emulsion results, it can be seen that the ANFO has higher energy per unit of mass since the emulsion has 16.7% water in the composition, a considerable fraction of inert, while the ANFO is pure explosive. The ANFO has a higher RWS than the emulsion. However, once the emulsion is denser than the ANFO when density is above 1.05 kg/L, it has higher energy per unit volume than the ANFO and larger RBS than the ANFO. When density increases, theoretical energy per volume (RBS) values are higher. Still, not necessarily high densities will lead to a good blasting performance of the emulsion, as the density of the emulsion is directly linked with sensitization since this process is done through the insertion of empty spaces along with the mass. When the explosive is not fully ignited, the performance parameters such as energy, gas volume, and others are reduced.

About the heavy ANFO, since it mixes characteristics of both explosives, it was observed that the majority proportions of ANFO are the ones with the highest energy values, either in mass and volume units, RWS and RBS, respectively. In addition, this majoritarian mixture of ANFO provides higher densities than the practiced in higher emulsion proportions. When comparing the results of ANFO and emulsion on the gas volume generated, it is possible to see that the ANFO has a higher volume of gas generated per unit of mass than the emulsion because the ANFO is a pure explosive. In contrast, the emulsion has inert in the composition. However, when analyzing the gaseous volume generated per unit of the explosive volume, it is possible to notice that the emulsion has a greater gaseous volume than ANFO at densities above 1.05 kg/L.

The mixture between ANFO and emulsion shows that the gas volume grows as the ANFO fraction grows because ANFO is pure explosive and emulsion has inert. The gaseous volume per unit volume of explosive is also higher for proportions majority of ANFO due to the inexistence of inert in the ANFO and the higher densities practiced in these compositions.

ACKNOWLEDGMENTS

The authors thank UFES and OPEX for supporting the research.

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