Emulsion Explosives

Emulsion Explosives - Background

NG dynamites possess poor safety properties during their manufacture transportation and use. For this purpose, the use of dynamites is diminishing with time. Safer explosives are gradually replacing them. Replacement products have been ANFO, slurries and emulsions. ANFO has a low density which limits its blasting energy. Also, it has poor water resistance and cannot be used in boreholes containing water, unless it is packaged in water tight containers.

Watergels came out in the 1960's because of the need for explosives having good water resistance and high bulk strength. Various kinds of watergel explosives have been developed, from high explosive sensitized slurries to non-explosive, non-metal sensitized products. Some of these slurries contain non-explosive liquid sensitizers (monomethylamine nitrate, ethylene glycol mononitrate, ethylamine nitrate).

A serious disadvantage of watergel explosives is the fact that they detonate non-ideally even in very large diameters. This is a result of mixing and the fact that most of the solid ingredients have large grain sizes. This makes the reaction process incomplete inside the detonation wave since larger portions of the solid ingredients react outside the detonation wave. It must also be pointed out that watergel explosives are multi-component explosives and are difficult to manufacture because of the number of ingredients. This adds cost to the final delivered product.

The next step in the development of commercial explosives was the rise of emulsion explosives.

Composition of Emulsion Explosives

An emulsion explosive comprises mainly inorganic oxidizing salts, water-insoluble organic fuels, an emulsifier and a bulking agent. The fuel oil phase is the external or the continuous one, while the oxidizer salt phase is discontinuous. This phase comprising small supersaturated droplets is suspended in the continuous oil phase. The bulking agent is added for density control as a third phase dispersed in the basic emulsion. It can be either ultra-fine air bubbles or artificial bubbles made of glass, resin, or plastic.

The emulsifying agent reduces the surface tension and the energy required to create new surfaces. Therefore it aids the process of subdivision and dispersion of the droplets in the continuous phase. The emulsification agent also reduces the rate of coalescence by coating the surface of droplets with a molecular layer of emulsifying agent.

A typical composition of an emulsion type explosive is given in the following:

Discontinuous aqueous phase

Water	10 - 22 %
Inorganic salt	65 - 85 %
Closed cell, void containing material	2.5 - 15%

Continuous phase

Fuel	3.5 - 8%

Fuel Emulsifier 0.8 - 1.2%

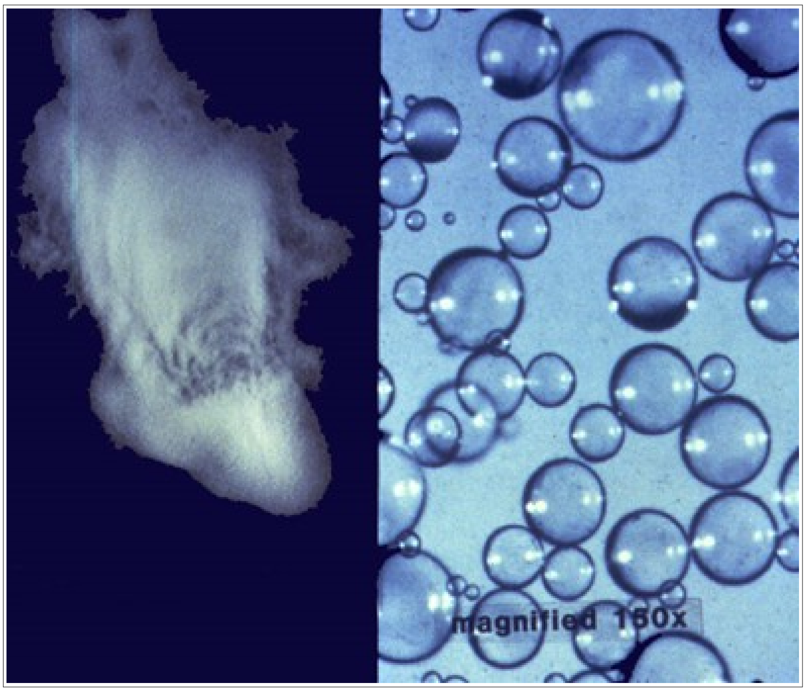
The carbonaceous fuel component of the continuous phase can include paraffinic. olefinic, naphthenic, aromatic, saturated or unsaturated hydrocarbons. In general, the carbonaceous fuel is a water immiscible, emulsifiable fuel that is either liquid or liquefiable at a temperature of the order of 90 degrees C. However a certain percentage of the fuel component is either a wax or oil, or a mixture of both of them. Waxes having sufficiently high melting points can be used. Such waxes include microcrystalline waxes, paraffin waxes and mineral waxes. It has been found that more shelf stable emulsions can be obtained by using a blend of a microcrystalline wax and a paraffin wax.

Suitable oils used are the various petroleum oils. The viscosity of the oil is not critical for the emulsion explosives. The emulsion can contain auxiliary fuels such as aluminum, aluminum alloys, or magnesium.

The emulsifiers used are water-in-oil emulsifiers, such as sodium oleate, sorbitan monolaurate, sorbitan monostearate and sodium tristearate.

The discontinuous aqueous phase contains inorganic oxidizer salts dissolved in water. The inorganic oxidizer salt consists principally of ammonium nitrate. However another inorganic nitrate such as sodium nitrate or an inorganic perchlorate such as ammonium perchlorate or a mixture of them can be used in the formulation. It is generally found that the presence of a material such as sodium nitrate permits greater quantity of oxidizer salt to be dissolved at a given temperature while influencing the final density of the emulsion.

Gas forms a discontinuous phase in the emulsion. It may be in the form of gas bubbles, which are introduced by stirring, injection or chemical means, or in the form of a closed cell, void containing material such as plastic spheres, perlite or hollow glass microspheres.



Microballoons (Hollow Glass Spheres) - 1st at normal magnification, 2nd at 160X

The function of the gas or the gas entrapping material is to reduce the density of the emulsion and provide a sensitization mechanism. Any gas can be used for that purpose. However, if a combustible gas or combustible gas entrapping material is used, it should be included in the calculation for the total fuel.
The usual size of glass microballoons is about 60 microns-70 microns. Their size distribution is between 40 microns and l00 microns. Very small microballoons do not act as hot spots, during detonation, but as solid ingredients because of the thickness of the glass bubble wall. If too small they don’t react at all. Similarly thick walled microballoons are more difficult to collapse and are not as efficient as thin walled ones.
Plastic microballoons can be used in emulsion explosives but preferably not in a continuous process. The reason for this is that a continuous process requires a blender with shearing action which may destroy this type of microballoon.
The aqueous oxidizer phase is protected by a continuous oil phase. Therefore evaporation of water during storage is prevented and the penetration of external standing water into the basic emulsion is inhibited. The process has been so effective that emulsions have excellent water resistance and do not depend upon a package for their ability to function in boreholes containing water. There have been some instances where emulsions have been left in boreholes for years and have detonated even after such a long storage time.
The physical consistency of emulsions is due mainly to the properties of the continuous phase. The water immiscible fuels can be chosen in such a way that the emulsions can be manufactured in a variety of forms. Stiff putty-like compositions suitable for packaged products or almost fluid, pumpable ones, suitable for bulk loading, can be manufactured.
Emulsions have long shelf lives, high bulk strength and good safety properties. Therefore emulsion type explosives contain a flexibility that can permit application in open pit and underground operations under a wide range of conditions.
One explosive supplier has pioneered the use of emulsion explosives in borehole diameters up to 115 mm typically in underground sublevel cave (SLC) operations.
Emulsion explosives also provide the base for another general class of explosives using ad-mixtures of ANFO. This popular class of explosive has been labeled heavy ANFO or HANFO. It is also referred to as either an ANFO blend or an emulsion blend.

Emulsion Explosives Method of Manufacture

In the process of manufacturing emulsion explosives, two basic pre-mixes are formed. The first comprises an aqueous solution of inorganic oxidizing salts, and the second, hydrocarbon fuel components, which provide the oil phase of the water-in-oil emulsion.
The aqueous solution of oxidizing salts is heated to a temperature above the crystallization point of the solution and is maintained at that temperature until the emulsion matrix is formed. To avoid crystallization when mixed with the aqueous solution, due to a temperature drop, the hydrocarbon fuel components are heated to approximately the same temperature. The emulsifier is added to the oil just before the mixing of the two premixes. The reason for this is that the emulsifier can be degraded if it is subjected to high temperatures for long periods of time.
The emulsion matrix is formed in a mixer capable of subjecting the hydrocarbon fuel component, the aqueous solution of inorganic salts and the emulsifier, to emulsifying high shear rates. The emulsion prepared in this manner is fed on a continuous basis to

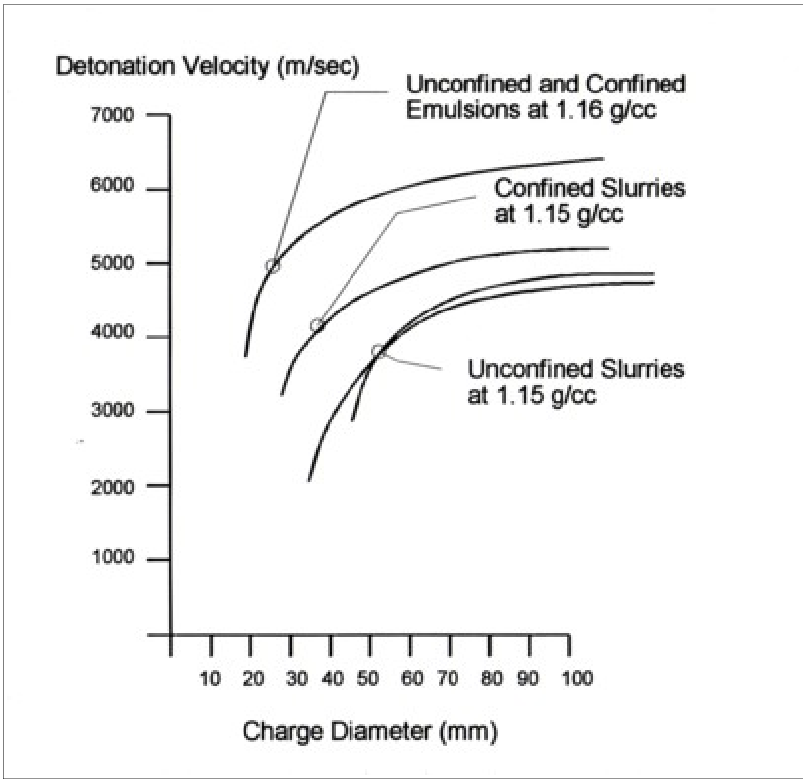
a blender where glass microballoons, and, if desired, auxiliary metal fuels are mixed to form the final products.

Performance of Emulsion Explosives

The detonation velocities of the emulsion explosives approach those obtain by thermohydrodynamic calculations even when the explosive charges are of relatively small diameters. This indicates performance close to ideal even at these small diameters. The graph below shows velocity of detonation charge diameter curves for a typical small diameter emulsion and typical small diameter slurries having similar compositions at relatively the same density under ambient conditions. It is obvious that the non-ideal region is extensive in the case of slurries and short in the case of emulsions.

This is due to the intimacy of mix which is achieved by the emulsification process. This reduces the effective particle size of the product and the time to react in the detonation head. On the other hand slurries are a crude mix of an oxidizer solution phase, droplets of fuel and solid oxidizer and fuel components. Since emulsions reach ideal performance in small diameters, they are ideal for use in secondary blasting, for blasting of hard rock formations and for use as primers.

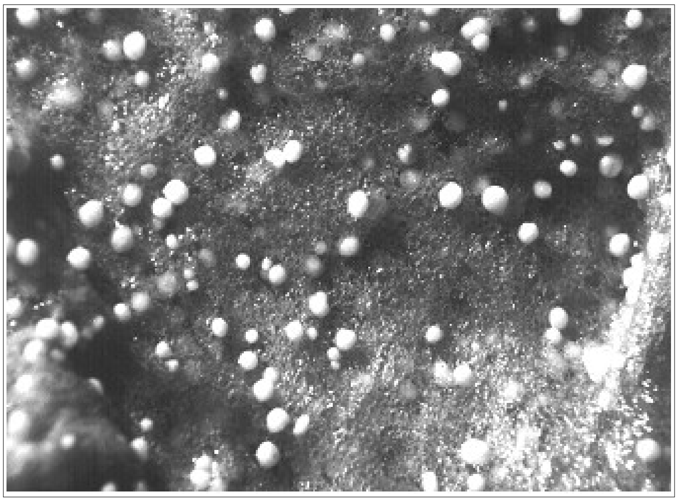
Although emulsions have close to ‘ideal’ operational characteristics, all is not rosy. Emulsifiers are expensive especially those considered for long shelf life. Also because of the



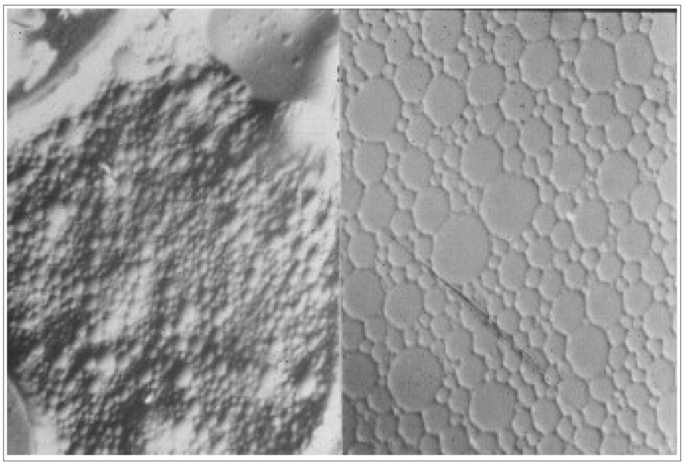
Confined and Unconfined Velocities for Both Slurries and Emulsions Having Similar Densities Under Ambient Conditions

nature of manufacture of emulsion explosives, there is much potential energy stored up in the formation of the re-combinant discontinuous and dispersed phases. Emulsions are cooled rapidly from roughly 100 degrees C to ambient temperatures. With this much stored energy, emulsions will quickly crystallize into a solid product

that has a high critical diameter. Special formulations are required if emulsion products are to be used for pneumatic loading through Swedish loaders.
Emulsions have better cold weather detonation characteristics than watergel explosives because of the more intimate combination of oxidizer and fuel. Note that in the figure below the AN prills appear to be very large compared to the dispersed droplets shown in the bottom figure with the picture on the right having been magnified 100 times.

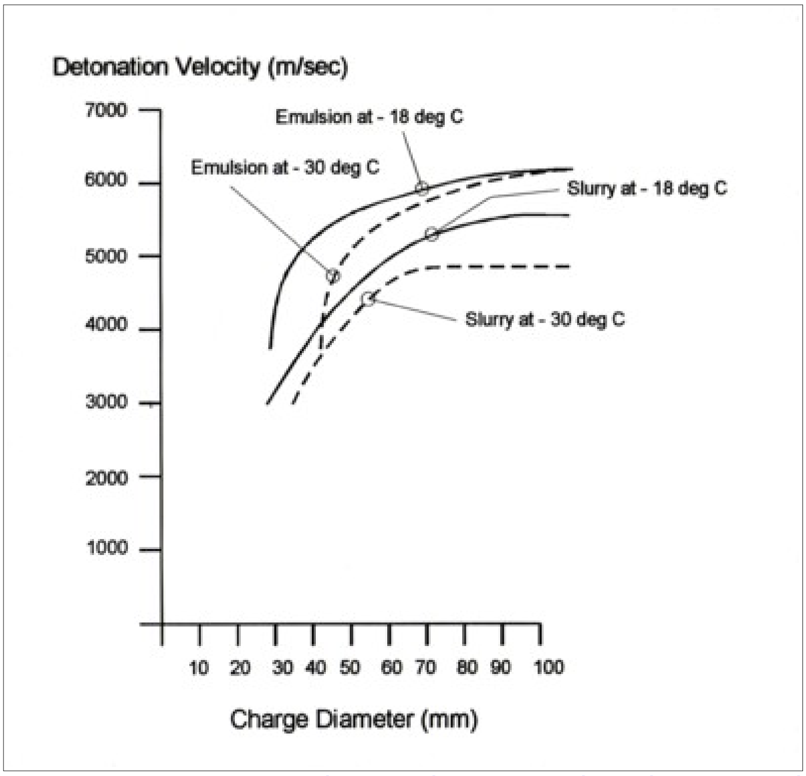


Watergel Explosive Showing AN Prills - No Magnification



Emulsion Explosive Showing Normal Cell Size No Magnification on Left, 100X Magnification on Right

The effect of low temperature on small diameter emulsions and slurries is compared in figure below. Low temperatures increase the critical diameters of both products. However the effect is more pronounced in the case of NCN slurries (shown in the watergel explosives section).

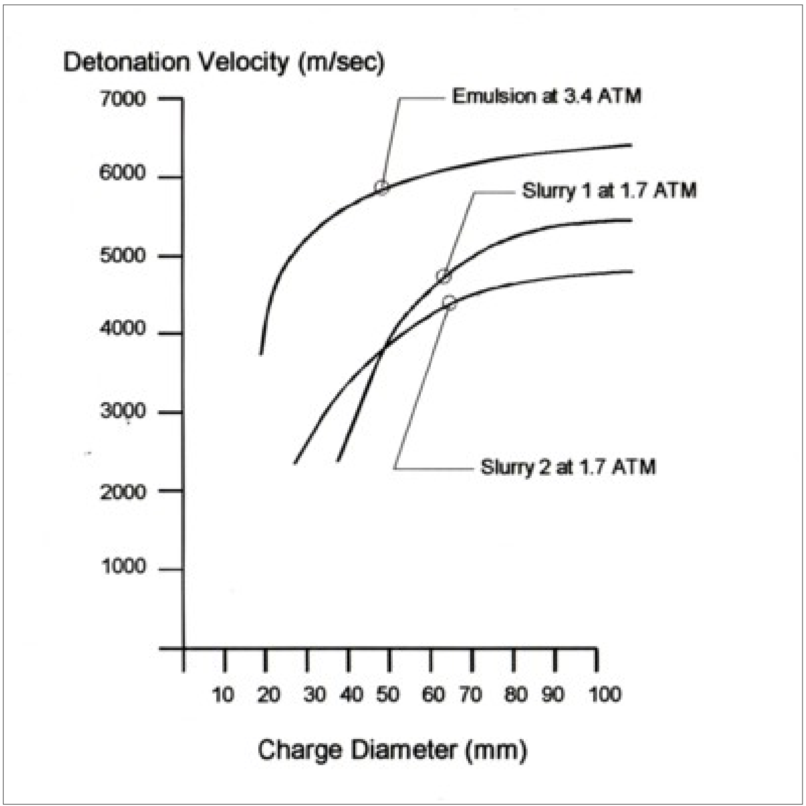


Effect of Temperature on Watergel and Emulsion Explosives in Small Charge Diameters

Furthermore the difference in the performance of the various products can be explained by the graph shown in the below which shows how density and thus detonation velocity behave as a function of the hydrostatic pressure. The density of the emulsion does not change significantly because it contains microballoons which are not compressible at moderate hydrostatic pressures (typically less than 689 kPa). The small difference in the density is a result of the compression of bubbles which were included in the ingredients of the product during the manufacturing process. Watergel (slurry) 2 contains some microballoons and air bubbles while watergel (slurry) 1 contains only air bubbles. This is why the effect of pressure is more pronounced in this case.
A problem which has been found with microballoon sensitized products is the desensitization effect of detonating cord downlines or neighboring holes detonating at a previous delay. Shock pressures (assumed to be of a strength lower than that required for direct initiation of the product) can rupture the microballoons or break the product down and cause desensitization.

Available Products

A variety of emulsion products are offered to meet the needs of the mining industry. Small diameter cap sensitive packaged products have been developed for use in underground operations. The density of these products is between 1.1 and 1.22 g/cc.



Effects of Hydrostatic Pressures on Watergel and Emulsion Explosives

Large diameter products have been developed for open pit applications and large diameter underground blasting. These products require larger primers or boosters for initiation. The density of these products is between 1.2 and 1.35 g/cc.
Small and large diameter products are made as cartridged products or as pumpable products for bulk loading. Bulk applications are exclusively used in open pit large diameter applications. Re-pumpable emulsions have found application in underground mines.

Underground mining is worthy of some additional comments. For example, in sublevel cave operations, emulsion explosives are virtually the only explosive types that can be pumped in toe and collar loading situations. Sublevel heights in most mines are typically less than 25 m. Therefore hole lengths can be in the order of 33 m. Hole diameters can range from 50 mm to over 100 mm.
ANFO would not be economical in these cases since the blasthole pattern would be tight reflecting the decreased bulk strength of ANFO. Waste would complicate matters further with the result of increased nitrates in the mine water.
Emulsion explosives on the other hand have resulted in the ability to increase pattern dimensions with the dropping of holes within the ring thus increasing production capability. However more sophisticated loading equipment is required. The next step would be to investigate the use of emulsion blends. One big advantage that emulsions have over uphole loading using ANFO is the ability to stay in the hole - a consequence of strict viscosity control.

References

•From Dr. Alan Bauer course notes
•From Dr P. Katsabanis course notes
•From C. J Preston notes from Queen's University Test Site, Dupont field testing