# *Watergel (Slurry) Explosives*

## *Watergel Explosives - Background*

ANFO products suffer from poor water resistance and low bulk strengths because of their low density. Explosives were developed in the late 1950's to eliminate these inherent weaknesses.

An interesting discovery was made that permitted watergel explosives to be developed. Pelleted TNT has a critical diameter of 76 mm confined. However in a water-filled steel tube having an internal diameter of 50 mm, it detonates at full velocity of 5800 m/sec. This proved that an aqueous transmission medium could be used to propagate the detonation reaction using TNT as the main explosive ingredient. It was also discovered that an AN solution could be used to oxygen balance the water-based explosive to provide increased energy output.

Thus the fundamental concept of watergel explosives was to dissolve ammonium nitrate in water and mix the solution with fuels and TNT as a sensitizer/fuel so that the product detonated at a high detonation rate when properly primed. The term "fuel" here can include an oxygen deficient explosive (e.g. TNT, or non explosive fuels such as hydrocarbons, carbonaceous and cellulosic materials and heat producing metals such as aluminum). Watergel explosives are made water resistant by means of guar gum which thickened the products, increases the viscosity and prevents flow or retards diffusion of the water into and out of the product.

By the mid 1950's the drilling and blasting of very hard iron formations at Schefferville in North-Eastern Quebec, with its associated high drilling costs and wet conditions, led Cook (IRECO) and Farman (IOC) to try and "tailor make" explosives having good water resistance and high bulk strength. Two systems were developed. One was based on TNT as the sensitizer and the other on aluminum powder. The aluminized watergel however did not find immediate application because of the problems associated to its storage (aluminum and water incompatibility). Later, control of the slow aluminum-water reaction in storage led to the development of watergel explosives with aluminum as the sensitizer. Aluminum increased the weight strength of even very oxygen deficient explosives due to the creation of aluminum oxides as part of the reactants in the detonation reaction. Weight strength can also be increased using TNT. In one formulation, over 40% TNT was used, producing a very high ‘brisance’ type of explosive for use in hard rock formations

TNT watergel was successful in many open pit operations. The initial TNT watergel had the following composition:

- coarse TNT (usually in pelleted or prill form)
- $NH_4NO_3$ solution as an oxidizer
- $NaNO_3$ solution as an oxidizer
- water in above solutions comprised 20%
- guar gum as a thickening agent

The purpose of the guar gum is to prevent the segregation of the ingredients. Initially two systems were developed, both using ammonium nitrate and water with one system based on TNT or alternative high explosives as the sensitizer (such as monomethyl amine nitrate - MMAN or ethylene glycol mononitrate - EGMAN, as well as ethylamine nitrate - EAN), and another totally different non-explosive sensitized system which used fine aluminum (usually paint grade) as the sensitizer. The basic high explosive sensitized watergel consisted of ammonium nitrate, water and thickeners as well as the explosive sensitizer. The quantity of explosive sensitizer used varied depending on the critical diameter desired and the environmental temperatures and pressures likely to be encountered. For example, for a critical diameter of 76 mm at 0 degrees C, a typical composition would be approximately 25 % TNT, 15 % water, 59 % ammonium nitrate and 0.5% -1.0% thickener. The gum thickener served two purposes. First of all it held the coarse high density TNT in suspension and it also formed a jelly-like continuous matrix which imparted good water resistance to the watergel if the gum was suitably crosslinked. Energetic metal fuels such as aluminum were soon added to increase bulk strength further.

A typical TNT watergel has a density of approximately 1.45 gm/cc and weight strength relative to ANFO of 85 so that its bulk strength is 148 relative to free-poured ANFO. Because of this increase in bulk strength, larger drilling and blasting patterns could be laid out. The explosives cost could in some cases be increased but the reduction in drilling costs were such that an overall reduction in drilling and blasting costs was achieved.

Watergel explosives sensitized using aluminum, were not immediately used in open pit mines in Canada because of the severe climatic conditions experienced in the northern part of the country. Borehole temperatures in some instances ran as low as -6 degrees C along with temperatures of -75 degrees C on the benches.

Additional oxidizer salts such as sodium nitrate were introduced to improve the physical consistency of the watergel at low temperatures. Eventually slurries were produced that had jelly-like consistency after standing for long periods of time at very low temperatures.

By the early 1970's watergel explosives had been well tested in many areas and consumption had increased substantially. At such operations, hauling of the packaged explosives, stripping the skins (or polyliners), collecting and removing the garbage produced a labour intensive and costly operation. Transportation was also costly since the explosive manufacturing plants were often remote from the mining operations. This meant that all the ingredients in the packaged product traveled at the high explosive freight rate.

Bulk watergel mix trucks were developed to eliminate the problems associated with pre-packaged watergel products. All trucks had storage bins for oxidizer solutions (liquor made of ammonium nitrate sodium nitrate/water), sensitizer, aluminum additive and guar gum. From these storage bins, auger feeders and pumps (all proportioning systems were calibrated) delivered these ingredients to a mix funnel. On some trucks the mix funnel had mixing paddles driven by hydraulic motors. All fittings were explosion proofed and bearings were kept out of the direct explosives mixing process and feeding environments for obvious safety reasons. Generally, enough material was stored in the trucks bins for consumption for up to 15,000 kg of explosive - loading directly into the borehole.

All mix trucks were classified as mobile mix factories. Tables of distance apply based on the quantity of TNT or other explosive ingredients on board.

Other special purpose trucks such as pump trucks have been produced. These are basically delivery trucks having pre-mixed watergel stored on board. Such trucks can deliver explosives directly to the borehole as well. Mobile mix watergel trucks are not used underground because of the logistics required to get mix ‘factories’ underground.

Watergel explosives are difficult to manufacture because of the number of ingredients involved. There are also virtually no watergel delivery vehicles underground. Any use of watergel explosive on a large scale (large blasts) usually require the delivery of explosive in bins that can be caged underground. Attempts have been made to introduce watergel explosives into drifting underground. There has been little success in this case. Packaged watergel explosives are used extensively in underground operations, particularly in VRM applications when wet conditions are encountered.

Up to this point, mostly large diameter watergel explosives have been discussed. Present watergel explosive technology includes the development of liquid explosive sensitizers such as MMAN, EGMN, and EAN. Apart from gaining improvements in watergel explosive manufacturing operations, liquid sensitizers have the advantage of lowering the critical diameters of watergel formulations to less than 25 mm. With the development of this additional sensitizing system, watergel blasting agents are now manufactured for use in small diameter boreholes such as those found in quarrying, road construction and some underground mining operations. Although much of the small diameter slurries available for use are transported and used in the form of a packaged product (cartridges), bulk loading can be easily done when loading tools such as pneumatic loaders are used.  Such devices are air operated, consisting of a breech mechanism that accepts the explosive cartridges for loading into boreholes. When the breech is pressurized, the cartridge is propelled down a plastic hose (attached to the breech) compacted into the borehole. The most common pneumatic loading system is the Swedish Loader developed by Nitro Nobel (DYNO). Originally developed for dynamites it is now used in several models and can loader several diameters of cartridged explosive products.

Typical small diameter watergel explosives currently in use have excellent water resistance as well high bulk strength.  This added feature permits less drilling, higher blasting efficiency and better rock fragmentation. They are particularly effective in ‘bad ground’ and can be traced with primacord or ‘Bump’ cord. Cost savings are realized in drilling and materials handling.

Advantages of watergel explosives are the following:

- By dissolution, water brings the ingredients into close contact with each other.
- The solution provides a continuous medium through which the detonation wave passes.
- Water desensitizes the explosive against fire, sparks, impact and friction thereby decreasing hazards associated with storage and handling.
- Water is believed to increase the energy of the explosive by taking part in the reaction at the time of explosion especially if Al is present.
- Water affects the products of detonation and suppresses the formation of toxic gases: carbon monoxide and oxides of nitrogen.
- Water acts as a coolant and offers a perspective of using water-gel explosives in underground gassy coal mines. Some slurries have been accepted as permissible explosives to replace dynamites.

A disadvantage with regard to composition is that low percentages of water present a problem in storage. The explosive becomes hard and grainy due to the crystallization of inorganic oxidizer salts. On the contrary a higher percentage of water decreases the sensitivity as well as the strength.  A percentage of water in the range of 8% - 20% seems to alleviate the low water problem..

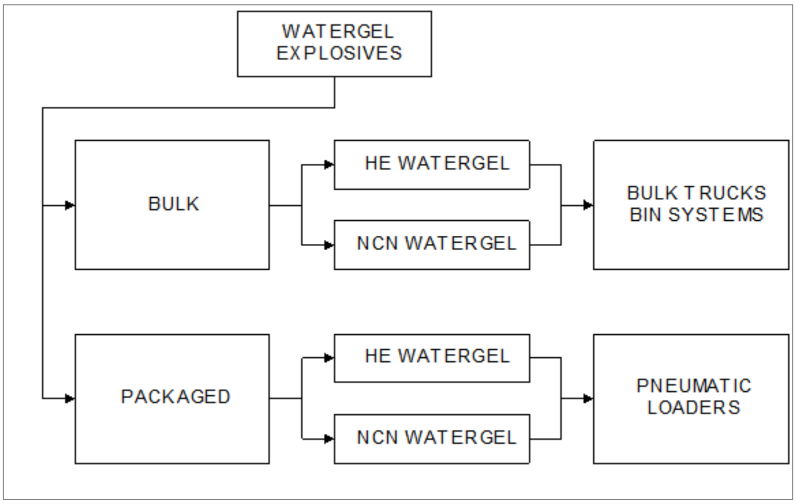
Another problem with watergel explosives has to do with the gel structure itself. Over long periods of time combined with warm magazine conditions the gel will start to tighten up squeezing the salts out of the cartridge package. This process is called synerisis and is most prominent with guar gum of the self cross-linking variety (self-complexing).

## *Watergel Formulations*

A watergel is a continuous liquid containing suspended solid particles. The liquid phase consists of a saturated aqueous solution of ammonium nitrate (65% AN in 20 degrees C). In the liquid phase one finds amounts of undissolved nitrates in suspension, and fuels which react with the oxidizers during the detonation process.
As previously mentioned commercial watergel explosives are thickened and cross-linked using quar gum (in the past - starch).
In the early formulations it was found that the guar gum thickened watergel was not very viscous. As a result the solid particles and the air bubbles would migrate and a deterioration in performance was observed after storage of some days. The viscosity of the guar gum was significantly increased by incorporating cross-linking agents.
Crosslinking agents which are used are:

- borax or other boron compounds
- sodium dichromate
- antimony compounds, potassium antimony tartrate
- semi-synthetic and synthetic polymers (carboxyl cellulose or polycylamide)

Of course the normal oxidizers used are ammonium nitrate and sodium nitrate. In addition, calcium nitrate has been used especially in cold conditions. Another popular oxidizer is ammonium perchlorate. However ammonium perchlorate has the disadvantages of producing chlorine gas as a product of detonation and can produce unstable and very sensitive products.
A variety of fuels are used in slurries. As stated earlier, reactive fuels such as TNT are used with success (TNT can be used as a dual purpose component - a sensitizer and energetic fuel). Non-reactive fuels are however popular since they are cheap and the use of a high explosive sensitizer is eliminated. Aluminum in the form of flakes or granules can be used as air 'trappers' for the purpose of producing 'hot spots'..
However in order to avoid deterioration, aluminum has to be properly coated with stearic or palmitic or oleic acid - sometimes mineral oil.
Liquid sensitizers have been introduced in the formulations of slurries. Alkylamine nitrates (e.g - MAN) increase the sensitivity and reduce critical diameter. Another sensitizer used today is ethylene glycol mononitrate - EGMAN. It should be mentioned that these monomethyl amine (MAN) and Ethyl amine (EAN) are not classified as explosives. Only after they have been nitrated to their explosive components MMAN and EGMAN are they classified as explosive.
However they can be dangerous as a recent experience (1975) has indicated. As ethylene glycol mononitrate was considered safe to handle, no special precautions were taken. A detonation which destroyed a factory in Canada and killed eight people was probably due to friction in the pumping operations of glycol mononitrate.
The chart here shows the various classes of watergel explosives available today.




Watergel Explosive Products

Typical watergel formulations are shown in Tables 1 and 2.

COMPARISONS BETWEEN TNT AND NCN SLURRIES

| TNT WATERGEL | | | NCN WATERGEL | | |
|---|---|---|---|---|---|
| INGREDIENT | WEIGHT and (%) | | INGREDIENT | WEIGHT and (%) | |
| AN | 54 | 54 | AN | 55 | 55 |
| SN | 10 | 10 | SN | 15 | 10 |
| $H_2O$ | 15 | 15 | $H_2O$ | 17 | 16 |
| TNT | 20 | 10 | FUEL OIL | 2 | 0.3 |
| ALUMINUM | - | 10 | ALUMINUM | 9 | 17 |
| GUAR | 1 | 1 | GUAR | 1 | 1 |
| CROSSLINKER | | | CROSSLINKER | | |
| | | | GAS AGENT | 1 | 0.7 |
| DENSITY (g/cc) | 1.45 | 1.5 | | 1.3 | 1.37 |

| SMALL DIAMETER NCN WATERGEL | |
|---|---|
| INGREDIENT | WEIGHT (%) |
| AN | 60 |
| SN | 16.5 |
| H2O | 17 |
| FUEL OIL | 4.8 |
| GUM PLUS CROSSLINKER | 1.0 |
| GASSING AGENT | 0.7 |
| DENSITY (g/cc) | 1.15 |

In order to have a detonable product with reasonable sensitivity the density of the product has to be within limits. Density control can be used to limit the loading density of the top of the hole (top-load) where less explosive is required than in the bottom (bottom-load). Thus top loading and bottom loading is common. Loading surface holes can be single pass or double pass. Single pass is used when formula changes are not

complex whereas double pass is used if there are major changes to the ingredient percentages.
The density can be controlled by using porous solids (perlite) or by using chemical gassing of the aqueous phase of the watergel. In the first method air is locked within the solid grains or is held on the surface of the grains by using naturally or artificially hydrophobic surfaces. Glass microballoons are also used for density control. Microballoons are not compressible and therefore they maintain the sensitivity of the slurries under hydrostatic loads (water in the borehole or long explosive columns). Sensitivity to hydrostatic loading may be reduced for the case in which the solids of the watergel contain the air bubbles within their mass (e.g solid AN prills with about 12% internal free space or porous aluminum which can have up to 20% internal free space).
Another method of controlling the density of the watergel is by mechanical aeration. There is a tendency for natural aeration in all gelled slurries just because of the mixing process. Natural aeration can be used to lower the density by as much as 10%-15%. The density can be decreased further another 15%-20% by artificial mechanical aeration. Further reduction of the density can be achieved by chemical gassing. This is done by acetic acid decomposition of $CaCO_3$ or by slow $NaNO_2$ decomposition. In the first case the gas is $CO_2$ and in the second $N_2$. The solubility of $CO_2$ changes with pressure and pH and for this reason $N_2$ gassing is preferred.

The density-pressure curves of aerated or gassed slurries are calculated from the measured density at atmospheric pressure and the density at a very high pressure. In the second case this is going to be the maximum density of the explosive. The density at different pressures can be calculated by applying Boyle's law:

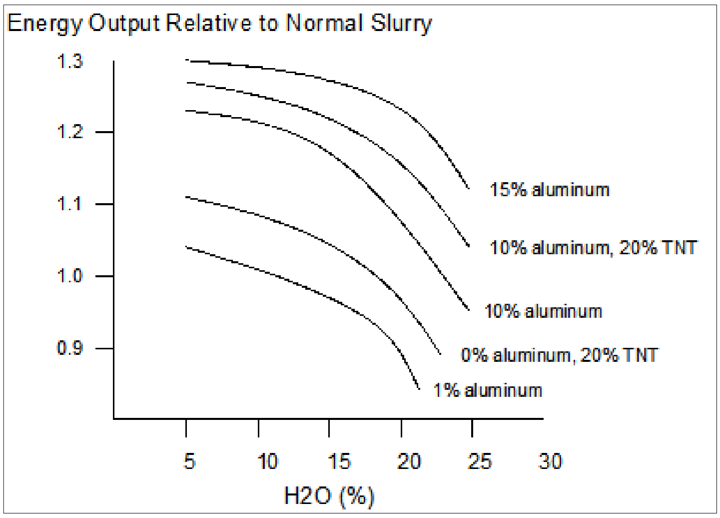
$$P_2 = \frac{\rho_2}{\rho_1} P_1$$

where:

| | | |
|---|---|---|
| $P_1$ | = | initial pressure |
| $P_2$ | = | final pressure |
| $\rho_1$ | = | density at P1 |
| $\rho_2$ | | density at P2 |

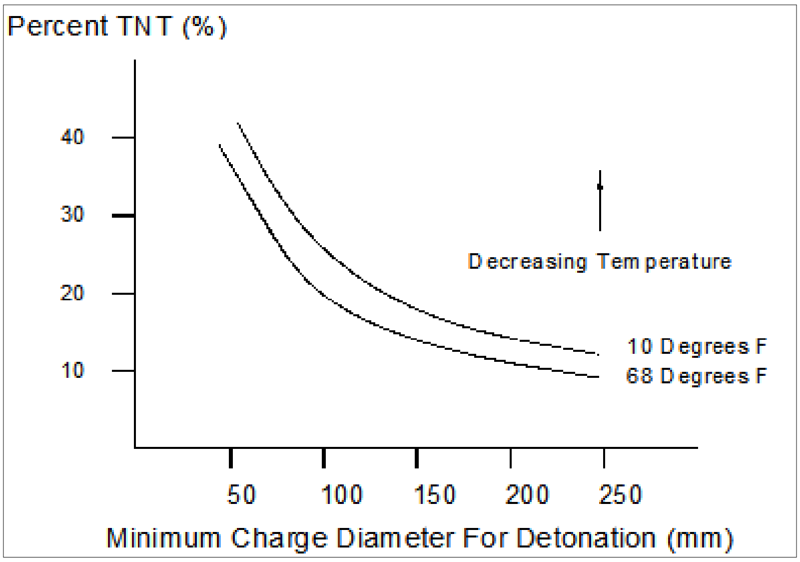
The performance of watergel explosives depends on many parameters, such as high explosive content, water content, density, temperature and pressure. In the following these parameters will be analyzed.
Dependence Parameters

•Effect of Water. Figure below shows the effect of water content and aluminum content on the energy output of TNT slurries and aluminized watergel blasting agents. It follows that water reduces the energy output significantly.

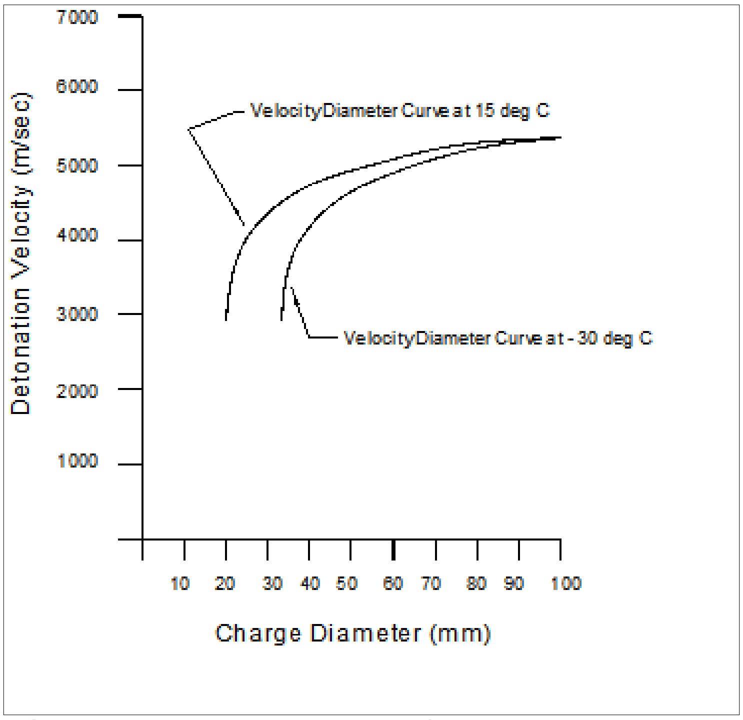


Effect of Water Content on Energy Output on Slurries

•Effect of High Explosive Content. The figure below shows the effect of the TNT content on the critical diameter of TNT based watergels. It follows that in order to achieve small critical diameters large quantities of TNT would have to be used. This is not recommended because of the high cost of TNT. For this purpose small diameter slurries are based on liquid non explosive sensitizers and significant amounts of aeration in order to have adequate sensitivity and detonate in small diameters.



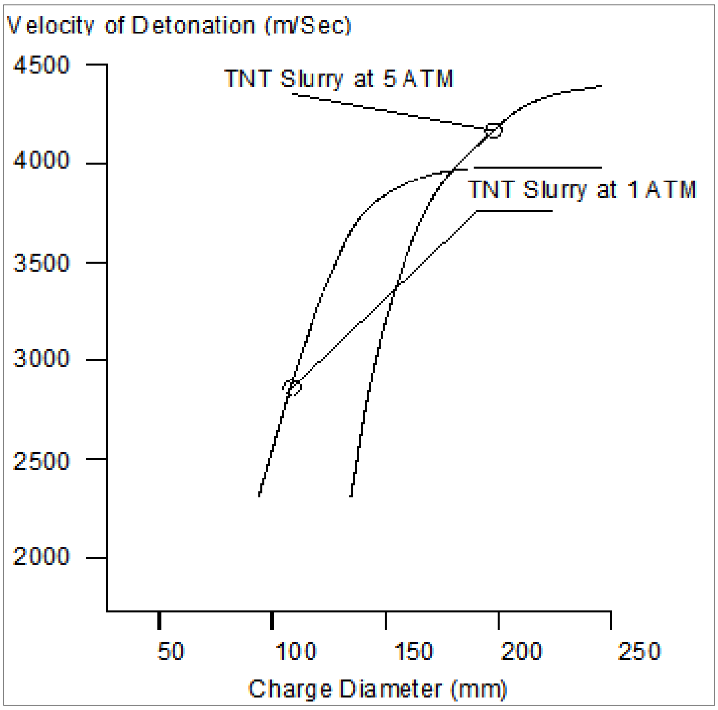
Effect of TNT Content on the Critical Diameter of TNT Slurries




Effect of Temperature on a Small Diameter Watergel Explosive

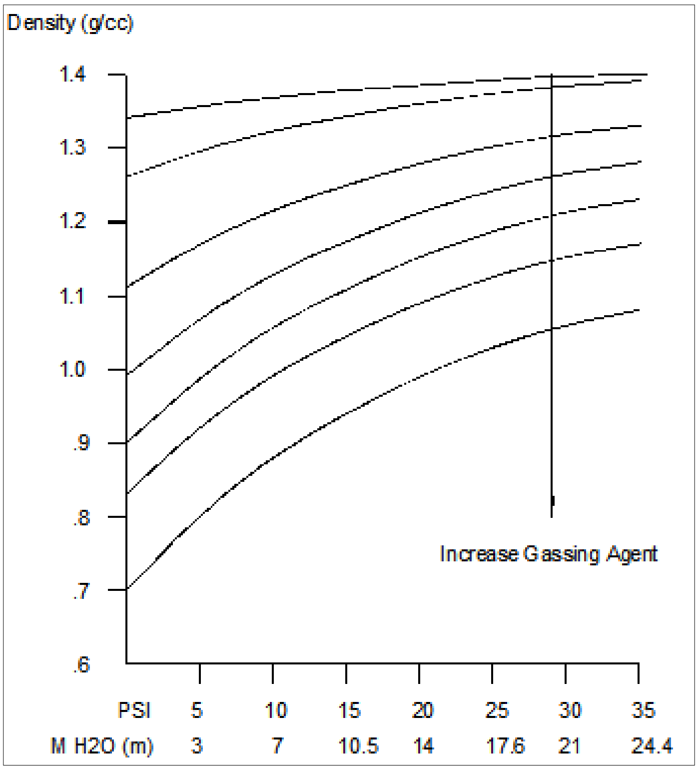
•Effect of Temperature. The graph above shows the effect of temperature on the velocity of detonation-charge diameter curves of typical TNT sensitized slurries. The curves for a typical NCN watergel show that temperature affects affect the critical diameter even more so. It is obvious that the low temperature increases the critical diameter significantly. The effect is more dramatic in the case of the NCN watergel. The same effect can be shown on the critical diameter of a small diameter cap sensitive slurries. The phenomenon has not been explained quantitatively. A qualitative explanation results from the fact that the low temperatures affect the physical state of the products. Crystallization occurs in the solubility of AN in water is dependent upon temperature. This changes the nature and the distribution of the density discontinuities which are responsible for the creation of hot spots. As a result desensitization occurs.

•Effect of Hydrostatic Pressure. The effect of hydrostatic pressures on the critical diameter of an NCN watergel and a TNT watergel is shown in accompanying graph below (for a TNT watergel - the effect is much more marked for an NCN explosive).



Effect of Hydrostatic Pressure on the Critical Diameter of a Watergel Explosive

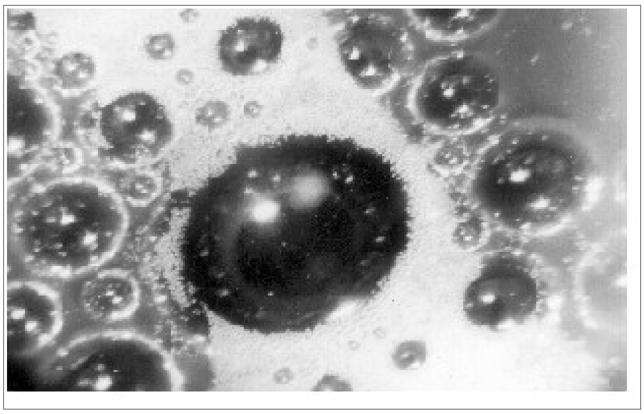
It is obvious that the critical diameter increases and at some point the product fails to detonate. This happens because of the increase of the density of the aerated watergel in the borehole due to the hydrostatic head. This reduces the effectiveness of the air bubbles as reaction centers because of pre-compression and because of the change in their geometry. From the comparison of the previous figures it is obvious that the high explosive sensitized watergel is affected less by the hydrostatic head. TNT as a solid high explosive is not affected by hydrostatic pressures. The increase of the ideal detonation velocity which can be noticed in the curves of the figures is due to the increase in the density of the products. In wet holes the amount of chemical gassing is limited by the ability of the watergel to float. Each gassed watergel composition has a set of characteristic curves indicating density as a function of depth. Each curve represents a different level of chemical gas addition. The figure below is an example for an aluminized watergel.




Effect of Hydrostatic Pressure and Gassing Agent Addition on the Density of an Aluminized Watergel

The critical diameter is also related to density. By knowing the critical diameter at each particular density the amount of gassing required to achieve proper detonation under a particular hydrostatic head can be calculated. If water is present, the ambient density has to be greater than 1.0 g/cc.

•Composition. Apart from the obvious relationship between composition and performance and apart from the previously mentioned relationship between composition and effect of temperatures and pressures, shelf life is strongly dependent on the composition. It has been found that air bubble sensitized watergels which do not contain any explosive sensitizers have shorter shelf lives. This is due to the migration of their ingredients and the coalescence of the bubbles on which their sensitivity is based. The photograph belwo shows the migration of small air bubbles migrating to form larger bubbles.



Air Entrapment and Migration in Watergel Explosive

*References*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- From Dr P. Katsabanis course notes
- From C. J Preston notes from Queen's University Test Site, Dupont field testing