

PRACTICAL METHODS TO REDUCE AMMONIA AND NITRATE LEVELS IN MINE WATER

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ABSTRACT

Most commercial explosives contain 70 to 94% ammonium nitrate, by weight. When portions of these explosives end up in shot rock and ore, through spillage or incomplete detonation, ammonia and nitrates leach out of them and into ground water. In recent years, State and Federal regulators have been applying more stringent water quality standards, particularly at new mines and development projects. Bulk ANFO, a mixture of ammonium nitrate and fuel oil, is the explosive of choice at most mines, when mining conditions allow it. ANFO use is desired because it is less costly than other explosives, but when spilled it dissolves readily in water. Several case histories in the United States and Canada show a clear connection between uncontrolled losses of bulk explosives and high nitrate levels in mine effluents.

Mining companies have tried several approaches to reduce ammonia and nitrate levels in groundwater. They either control explosive losses, or they treat mine effluents at the end-of-pipe. This paper addresses the former solution -- controlling explosive losses. For both packaged and bulk explosives, guidelines designed to limit losses during storage, handling and use, are described in detail.

AMMONIA AND NITRATE TOXICITY

Relatively small concentrations of ammonia in water are very detrimental to fish, and particularly to most trout species. The toxicity of ammonia varies with pH and temperature. Researchers have found that, at lower temperature and pH, the toxicity of free ammonia increases (Wiber, M., et al, 1991). In aqueous solutions, ammonia exists in two forms: free ammonia which carries no ionic charge (NH_3) and ammonium which carries a positive charge (NH_4^+). The free ammonia is the more toxic of the two. The U.S. EPA ambient water quality criterion is 0.02 mg/l free ammonia. For U.S. mines NPDES permits commonly include a limit of 10 mg/L total ammonia as N in end-of-pipe effluents. The U.S. EPA drinking water criterion for nitrate as nitrogen (NO_3^- -N) is 10 mg/l. In warm blooded animals, nitrate can be reduced to nitrites in the gastrointestinal tract. The nitrite reaches the bloodstream where it reacts directly with hemoglobin to produce methaemoglobin that impairs oxygen transport.

AMMONIA AND NITRATE SOURCES

Many mines have learned that there is a direct relationship between ammonia and nitrate levels in water and the amount of undetonated explosives in the rock through which the water flows. Most commercial blasting agents contain from 70 to 94% ammonium nitrate. ANFO, the most commonly used blasting agent, is usually a mixture of 6 percent #2 diesel fuel oil (DFO) and 94 percent ammonium nitrate. ANFO readily dissolves in water, releasing both ammonia and nitrate. Emulsion and watergel based explosives also contain a large amount of ammonium nitrate and other oxidizing salts that can leach nitrates to ground water. The rate at which nitrates leach from different explosives varies dramatically, based on the explosive's composition.

In tests conducted at the ICI Explosives Technical Center in McMasterville, Quebec, nitrate leaching rates were established for:



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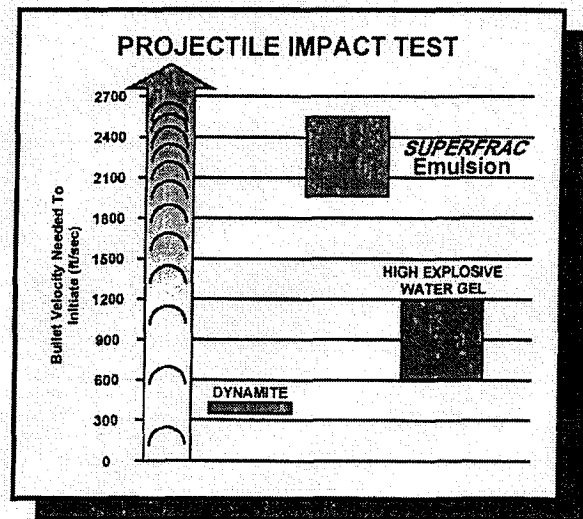
- 1) Standard ANFO
- 2) WR "Water Resistant" ANFO
(ANFO with additives to inhibit the ingress of water)
- 3) Detonator sensitive watergel
- 4) Detonator sensitive emulsion

PERCENTAGE OF NITRATES LEACHED FROM EXPLOSIVE*				
Time (hrs)	ANFO	WR ANFO	WATERGEL	EMULSION
0.1	~ 25	-	-	-
1	> 50	~ 25	-	-
6	-	-	24.6	0.6
144	-	-	> 75	1.2

* When 25% of the nitrates are dissolved, the explosive is probably no longer detonable.

As expected, the emulsion did not release nitrates as readily as the ANFO or watergel explosive. The leaching rate for emulsion explosives is much lower because the ammonium nitrate is contained in an aqueous phase that is surrounded by an oil, or oil and wax, fuel phase. Hence, when water contacts undetonated emulsions, the ammonium nitrate is protected by the relatively impervious oil and wax matrix. Despite their very slow leaching rates, emulsions--when given enough water exposure time--can produce significant levels of nitrates and ammonia. In comparison, spilled ANFO will quickly dissolve in water and release all its ammonia and nitrates. If continuously spilled, the daily level of nitrates and ammonia released by any type of explosive--exposed to water--will eventually become significant. The ammonium nitrate leaching rate for packaged explosives will vary based on the integrity of the package. However, this is usually a moot point because packages of undetonated explosives are almost always ruptured by the violent rock movement within the blast. Despite being ruptured, the packaged explosive can often be recovered from shot rock. Nitroglycerin (NG) based dynamites will also leach ammonia and nitrates at varying rates based on their composition. In addition, NG sensitized products are much more sensitive to shock impact; for this reason, as well

as environmental concerns, the occurrence of unfired dynamite in shot rock should be prevented.



In underground metal mines, noxious levels of ammonia gas often occur when undetonated explosives mix with alkaline water draining from cemented fill or grouting operations (Joyce, D.K., 1992). This parallel ammonia problem is another reason to control explosive spills.

The conclusion from this analysis is that losses of all types of explosives must be controlled, regardless of their composition or packaging.

MANAGING EXPLOSIVE LOSSES

There are several ways that undetonated explosives end up on the ground or in shot rock. First, sloppy handling, storage, and loading practices may cause a significant amount of explosive spillage, particularly when bulk explosives are used. Poor drilling and loading practices can also create significant amounts of undetonated explosives. Charges are often disrupted or torn away by premature rock movement caused by earlier detonations. Drill patterns, stemming or collar length, explosive selection, priming methods, and delay timing are the elements of blast design that can be adjusted to control charge cut-offs or failures.

In a paper presented at the 1991 Northwest Mining Convention in Spokane, Washington, the authors present water monitoring case histories from three separate underground mines in Canada (Wiber, M., et al, 1991). In all three cases, the levels of ammonia in mine water were lowered by at least 50 percent after rigorous explosive management programs were started.

Storage And Handling Controls

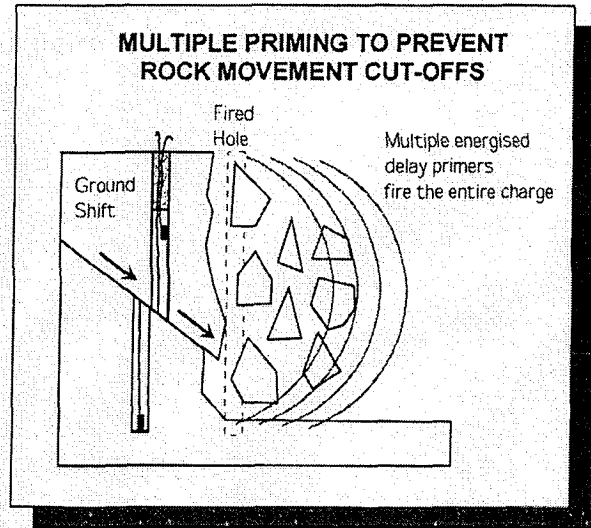
In both surface and underground mining, ANFO and bulk emulsion blasting agents are often spilled during storage, transfer or loading. Bulk ANFO commonly spills out of poorly designed or damaged bins, rail cars, and transfer augers. Bulk emulsion spills are often seen at storage tank outlets and at pump transfer areas. Maintenance employees are an important part of a complete explosives management program. They should understand that all bins, tanks, storage trailers, and loading equipment should be regularly maintained to prevent explosives spills. Employees who understand the importance of preventing explosive spills can greatly reduce their occurrence. However, no level of training will completely prevent all spills; so it is important to develop spill containment and clean-up procedures. To contain spills, some surface mines have placed their bulk explosive bins in concrete containment tanks or they have built rock berms around tanks and bins. Explosive manufacturers can usually provide spill clean up recommendations for their products, and in many areas they can provide special mobile clean-up crew and equipment services.

Blast Design Considerations

For safety, environmental, and economic reasons, blast designs should include measures that ensure complete detonation of all explosives. For this analysis, any charge or portion of a charge that fails for any reason is considered a misfire. Some common causes of misfires, along with design practices that will prevent them are:

Cut-offs: We can not control ground conditions, but we can control drill patterns, explosive loads, and initiation methods. In ground with weak seams or joints, the gasses and shock from early firing charges can cause premature movement of the rock containing adjacent, unfired holes. When the rock moves it separates or cuts off the explosive columns within it. The portions of the columns that

do not contain energized primers will misfire and contribute ammonia and nitrate to ground water. Many of these misfires can be prevented by using multiple in-hole delay primers.

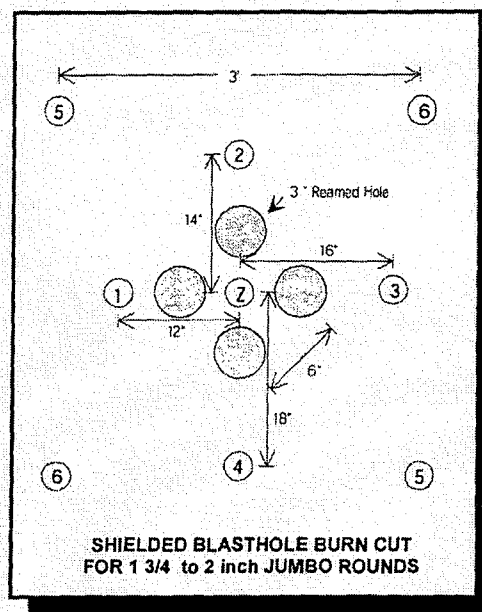


Some failures occur because there is too much delay time between adjacent holes, or rows of holes. In these situations, reducing the delay time between holes can reduce cut-offs. Cut-offs and explosive losses often occur when detonating cord downlines and surface delays are used in bench blasting. When detonating cord is used without a delay detonator in the hole, the ground swell that occurs when the first row of holes fires, can tear cord and delay connections before they fire, hence causing multiple hole failures. This type of cut-off can be prevented by using Fully Activated Sequential Timing (FAST) systems that use relatively long in-hole delays in combination with short surface delays.

The goal with these systems is to have all of the in-hole initiators sequentially energized before the first charges fire and rock starts moving. In very large shots that can not be fully energized, try to have at least two rows energized behind the row that is firing. FAST sequential timing can be achieved with either nonelectric or electric initiation systems.

Precompression Failures: Several blasting problems can occur when hole-to-hole shock pressures are too high. High blast induced pressure in rock can cause sympathetic detonation (propagation) of dynamite charges, and pre-compression failure in emulsion and watergel explosives. Many blasting incidents, often with severe damage to nearby structures, have been caused by propagating dynamite. In critical blasting areas, the propagation hazard is virtually eliminated by substituting less sensitive explosives for dynamite. However, under certain conditions, packaged emulsion and watergel explosives can fail when rock or gas pressure from an adjacent charge squeezes them to a density above their critical limit. This pre-compression or "dead-pressing" phenomenon is caused by several conditions or combinations of conditions. When ground is very seamy and wet, the magnitude of hole-to-hole shock is greatly increased. Shock also increases when holes are very close together which is always the case in underground tunnel and surface ditch blasting, where the application demands tightly spaced holes. If precompression failures occur, try spacing blastholes farther apart, or switch to an explosive that can withstand higher pressures. In tunnel rounds, the holes in the burn cut are usually spaced very closely together. The hole-to-hole pressure transmitted to the charges in these holes can be reduced by placing unloaded relief holes between the loaded holes.

Poor explosive choice: The type of explosive used can have a dramatic effect on overall losses. For instance, if bulk instead of packaged explosives are used, spillage losses will be relatively high. If bulk ANFO is used in wet holes, losses caused by complete failures or partial detonation will be high. At one underground metal mine in the northwest U.S., their total daily limit of nitrates in ground water is 100 pounds. To meet this limit they can not tolerate any spillage, so they use only packaged explosives. Moreover, they use a special emulsion product with a distinctive orange color that can be seen and removed from shot rock.



When conditions that cause very high hole-to-hole shock pressures exist, only explosives that can resist pre-compression should be used.

Loading Controls

Without specific controls, mines using bulk ANFO typically lose 2 to 5 percent to spillage, or blow back -- during pneumatic loading underground. Surface auger-loading trucks with poorly designed -- or aimed -- discharge hoses spill ANFO prills onto the ground around hole collars during loading. Blowing wind can also add to losses by carrying some prill away from the hole if the discharge hose is too high in the air. Blasters that are conscientious and aware can prevent most spills by simply adjusting their loading practices.

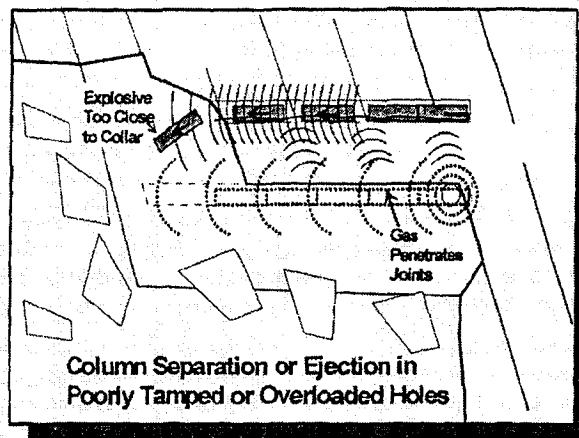
Moreover, when spills do occur, they must know how to clean them up and also understand the importance of doing it.

For some loading applications, explosive makers are developing specialized equipment and products designed to reduce explosive losses. For instance, pneumatic ANFO metering devices can reduce blow loading losses by metering a preset amount of explosives into a blasthole, thus preventing overloading.

Explosive manufacturers have also developed specially formulated tacky ammonium nitrate and fuel mixtures that reduce blow back losses.

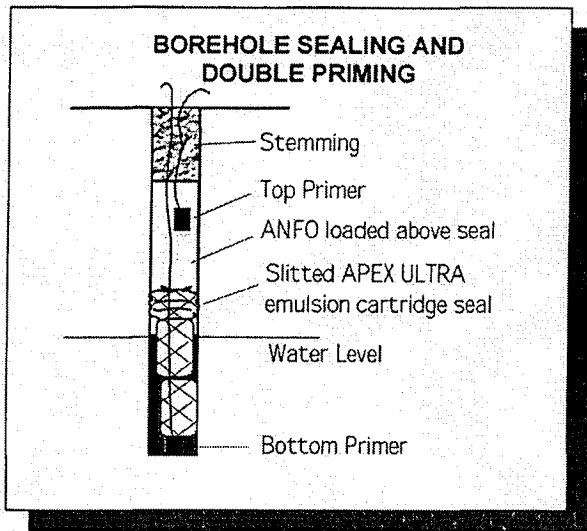
In many underground blasting applications, overloading is the greatest cause of explosive losses. When long period delay detonators are used to delay tunnel and other development rounds, the charges in the later firing holes are subjected to tremendous shock and gas pressure generated by the earlier firing charges. This shock and pressure often tear away the rock around the collars of adjacent and yet unfired holes. Any explosive, whether in stick or bulk form, that is in this collar region is cut off and ends up -- undetonated -- in the shot rock. To control these losses, minimum open collar lengths should be established for all underground blast loads, based on geological conditions and application. Cartridge ejection from hole collars will also cause explosive losses. Ejection losses can be reduced by firmly tamping the cartridges near the hole collar. However, remember to never tamp the primer stick; this practice is dangerous and it is prohibited by MSHA. When charge tamping will cause overloading, the explosive column can be secured by some type of hole plug. To accurately implement good blast designs, operations must have proper loading equipment and trained employees. Loading equipment should be well maintained and in some cases, mines should consider using computerized bulk loading equipment that meters preset weights of explosives into blastholes.

Sometimes during loading, packaged explosives columns are separated when rock chunks fall in the hole or a cartridge becomes stuck. When this occurs, the separated portion should be separately primed with the same delay detonator used in the initial primer. Use of the same delay will prevent one part of the separated charge from disrupting the other, and the desired firing sequence will be maintained.



Loading bulk ANFO into wet holes, or letting ANFO sleep too long in wet or damp holes, is another common cause of explosive loss. When water comes into contact with ANFO, it either dissolves it or wicks into it and desensitizes it. In either case the ANFO charge partially or completely fails to detonate. In underground development rounds, static drill water should be blown out of holes with compressed air before pneumatically loading ANFO. In top loaded vertical holes, water resistant cartridge or bulk explosives should be substituted for ANFO.

In wet holes, packaged explosives are often loaded until out of water and the load is finished with ANFO. If the hole is not sealed, the ANFO will sift past the packaged ANFO and dissolve in the water. The water will cause further ANFO loss when it wicks up the sifting ANFO and into the main column. This problem is a common cause of misfires in bench blasting applications. Holes should be sealed with a fully coupled and waterproof explosive before loading ANFO. A good seal can be made by dropping a cut stick of an emulsion explosive into the hole, before pour loading ANFO.



CONCLUSION

At all mines, significant reductions of ammonia and nitrate in mine water can be achieved by developing an aggressive and ongoing explosive management program. At three different mines in Canada, the implementation of rigorous explosive management programs reduced ammonia levels by at least 50% in all cases.

As responsible stewards of our environment, mining companies and explosive suppliers should work together to establish products, loading equipment, and training programs aimed at lowering toxins in mine effluents. Explosive manufacturers, aware of these environmental concerns, are developing new explosive products and loading equipment specifically designed to reduce explosive losses. Excellent slide and video training programs for explosive handlers are also available. Please accept this call to action and work with your explosive suppliers to prevent ammonia and nitrate compliance problems. Mines that wait to act until ammonia and nitrate limits have been exceeded, will pay huge remedial control costs.

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