HEALTH, SAFETY AND ENVIRONMENTAL CONSIDERATIONS IN USE OF HPE EXPLOSIVES

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ABSTRACT: Hydrogen peroxide (HP) has been the main nitrogen-free alternative to ammonium nitrate (AN) in recent explosives development. This new application as a raw material for bulk explosives in mining and quarrying brings up new aspects regarding occupational health, safety and environment. Exposure of workers to HP is very different from stationary industrial process facilities. From environmental point of view this application for HP is also something new. HP is directly toxic to aquatic life so releases into environment must be noted even if HP decomposes into water and oxygen. HP is very reactive chemical so it's expectable that there's some reaction products from reactions with minerals. These potential issues must be studied and clarified before large scale utilization of HP based formulations. In this presentation our experimental observations are summarized giving some answers to these questions and some findings from literature also reviewed.

1. HYDROGEN PEROXIDE (HP) AND HYDROGEN PERXODE EMULSION (HPE)

HP is a powerful oxidizer and widely used in process industry. Technical grade HP is usually available up to 60 w-% solution. Properties of aqueous HP solutions are well known. HP is very reactive chemical, much more reactive than AN. Contamination usually leads to fast exothermic decomposition of HP. This reaction produces large volume of oxygen gas and vaporized water leading to pressure build-up or even to explosion. In this connection it must be mentioned that sometimes term oxygenated water is misleadingly used parallelly with HP. This is of course a serious mistake. HP is a chemical compound and oxygenated water is a mixture of oxygen and water. These two having completely different chemical characteristics and risks.

Explosive compositions based on HP can be formulated in many ways. In this context the focus is on mixtures with fuels, not molecular explosives even if HP is easily capable of forming those too. Types of mixtures with fuel are 1) absorbed in solid material, 2) water gel and 3) water-in-oil emulsion. The last one (HPE) being the most obvious because continuous fuel phase protects HP droplets from contamination to some degree.

Technically speaking usability and performance of HPE is comparable to common ANE products with some exceptions. HPE viscosity and pumpability can be adjusted so that standard ANE loading technology can be converted for HPE. Detailed risk analysis is of course in the center of the conversion. Energy output of HPE is calculated and compared to standard ANE products. Basically hydrocarbons in fuel phase are oxidized by oxygen released from HP. Based on this principle a relation can be made between concentration of HP and ideal energy output of HPE. For example oxygen balanced HPE made of 50% HP solution energy is ca 2,4MJ/kg and in case of 60% HP ca. 3,7MJ/kg calculated with Explo 5.0 software. Standard ANE like FORCIT's Kemiitti 810 has 2,9MJ/kg. FORCIT has tested performance of Kemiitti HPE in development blasts. Fragmentation and advance was at least as good as with ANE and measured VOD was 4400…5300m/s in Ø51mm horizontal holes. HP concentration used in this test was 56%.

Technical differences to ANE comes mainly from lower density range of HPE. Ungassed HPE has density of 1,15-1,20g/cc depending on HP concentration. Typical density window for gassed HPE is 0,8-1,0g/cc. So in water containing vertical boreholes there's a risk of getting part of the explosive column loose and floating on top. Another feature with the lower density window may be a limitation is vertical hole depth. Gassed product compresses itself to higher density in the bottom of borehole and if density gets too high initiation sensitivity is probably lost. Theoretically estimated critical column height is about 20m but experimental verification by VOD measurements is needed to confirm the estimate.

2. OCCUPATIONAL HEALTH

According to ECHA (European Chemicals Agency) long term (8h) exposure limit in air is 1ppm and short term (15min) exposure limit is 2ppm. Some of the first symptoms of exposure to HP vapor are itching and burning feeling on skin, airways and eyes. Later dizziness. Repeating long term exposure can lead even to permanent lung damage. Study shows that fine particulate matter helps HP entering deeper in lungs causing more severe damage. This may be a relevant factor in mining environment.

During our pilot and field scale testing HP concentration in air has been monitored continuously with Dräger X-am 5100 sensor. This sensor is capable of measuring HP concentration up to 20ppm. The readings have been repeatedly over 2ppm whenever HP or HPE is handled. We haven't observed any differences if HP was 50% or 60% concentration. The measured values are presented in the table 1.

Table 1. Measured HP concentrations in workplace air.

Measurement point	HP concentration in air, ppm
Refilling loading unit tank, hatch open, in 1m radius	10-15
Refilling loading unit tank, hatch open, in 5m radius	1-2
During early stage of loading tunnel round	0-0,3
After ca 30min from start of loading tunnel round	1,0-1,5ppm
In vapor cloud coming from reactive HPE	>20

We have observed that reactivity evolves and spreads very fast through the whole mass of HPE. When the first signs of vapor cloud and bubbling appear the reactivity spreads through whole mass in minutes. Probably this is due to sharp temperature increase (up to ~100°C), strong convection and chemically aggressive radicals released from decomposing HP. The high concentration of HP in vapor is caused by increased vapor pressure of HP in boiling HPE but also strong convection of oxygen gas and vaporized water that carries HP as aerosol. Whenever HP sensor is brought close to vapor cloud the readings immediately jump over the scale. Yet another detail increasing potential consequences from exposure to fumes from reactive HPE is that with some reactants oxygen released from decomposing HP can be in excited molecular state, so-called singlet-state. This singlet-oxygen is classified as a reactive oxygen species which can damage DNA ie. shows carcinogenic effects.

Contamination is an everyday risk in loading with bulk products. Both ANE and HPE have similargreasy and sticky consistency. From a long experience using ANE products in industry we have learned how easily stains of emulsion are spreading all around. ANE contamination is an annoyance without any severe consequences. In case of HPE the contamination and spreading takes place similar way but the consequences can be more serious. The mildest one is getting skin contact causing some itching and stinging/burning pain. Potentially an infection of damaged skin later. In more serious case HPE gets in eye causing permanent damage. Contaminated working clothes and other combustible materials can get in fire spontaneously. We have seen HPE spreading for example on car seats and detonator boxes. During the years of our experimental work with HPE we have had two cases where organic material used to clean HP/HPE stains has ignited spontaneously.

FORCIT's solution to these risks at this stage of development is proper PPE, very careful working methods and keeping volumes at manageable level. The key points are protecting breathing, preventing skin contact and avoiding any spreading of HPE. A motorized full-face mask with suitable gas filter, chemical resistant coveralls, long-sleeved chemical resistant gloves and rubber boots (leg sleeves on boots) is seen as an adequate set of PPE.

FORCIT has arranged three campaigns of blast fume measurements for Kemiitti HPE product. Two of them in 35m3 blast chamber with 1kg charges and one in underground mine. Tests proved the obvious result that no NOx exist in blast fumes. But from occupational health point of view concentration of CO has been comparable to levels gotten from ANE product. Also some ppm of HP was detected. This means that proper venting after HPE blast is as important as is in case of ANE. HPE formulation can be optimized so that CO production is minimal, this is one development goal for the future work.

The blast chamber results were presented in EFEE 2023 in Dublin by LTU. The full scale test in underground mine was done in co-operation with VTT (Technical Research Centre of Finland Ltd) in 2024 and the results will be presented in EFEE 2025 by VTT.

3. SAFETY

HPE contains more than 90 weight-% HP solution hence HPE has similar potential for reactivity as HP. W/O structure hinders the reactivity because water immiscible fuel phase is continuous. But as already mentioned the emulsion structure doesn't remove reactivity. Reaction releases large volume of oxygen gas and water vapor and a lot of energy is released which heats up HPE accelerating the reaction further. According to our observations reactive HPE gets very slippery so it may fall out from downward inclined holes very easily causing a risk of heavy contamination for workers and surroundings and of course affects negatively to blast result. Upholes being the extreme case in this respect.

Compatibility with other explosive components requires risk assessment and test data. The industry has gotten used to compatibility of common materials and components with ANE. In case of HPE the chemistry is different and especially in case of thermal runaway reaction it's critical to know are detonators and primers/boosters commonly used compatible with HP. In worst case reactivity in HPE in combination with other explosive components can lead to premature detonation. A special case of compatibility issues is capability of HP forming initial explosives with certain chemicals. Reaction with acetone or hexamine proceeds easily and products are triacetone triperoxide and hexamethylene triperoxide diamine respectively. These are very powerful and very sensitive compounds. Risk analysis should cover this kind of factors too. No compatibility data found so far and consequences can be intolerable so these issues needs to be experimentally verified.

Another aspect of risk management is to understand the nature of HPE from viewpoint of classification. It may be tempting to make a direct comparison to ANE. But by definition UN3375 isn't usable for HPE. According to UN Manual of Tests and Criteria point 20.2.1b mixtures of oxidizing substances which contain 5,0% or more combustible organic substances shall be subjected to the classification procedure for self-reactive substances. Testing and analysis to possibly include HPE in framework of ADR is future work. All this is on a condition that HPE doesn't change during transport or storge. In ADR vented packages and tanks are required for HP because it decomposes spontaneously and oxygen gas must be released without pressure build-up. In case of HP solution oxygen gas bubbles can escape from liquid. In case of viscous HPE the oxygen bubbles can't escape. This means that there's a possibility that HPE becomes spontaneously transformed into explosive. HPE may be classified initially non-explosive but after certain time it spontaneously transforms into explosive. Time for this transformation is dependent on temperature, formulation details and potential contamination. In some early tests for gassed HPE we used this phenomenon to make samples for VOD measurements. HP grade without special stabilizers was used to make HPE samples in plastic pipes. Pipes were filled with fresh HPE and then density was followed on daily basis. After three days we had a cap-sensitive HPE. With improved stabilizers in HP this process can be slowed down significantly. Spontaneous gassing is observed and reported also elsewhere. For example in Australian tests sensitivity to detonation was observed after 29 days. Limiting transport and storaging temperature and batch age control may help with this issue. But from experience of ANE handling we know that there's always layers of older material in tank walls, corners and pipes. So there's always a risk on existence of older potentially sensitized material in HPE system. A common estimate for decomposition of HP is less than 1% in a year. In figure 1 some estimated densities vs. time are shown with different decomposition rates for HP. In density below 1,05g/cc HPE is detonable for sure. To keep classification and risk management under control the supplier should provide test data showing that spontaneous sensitization doesn't occur if HPE is to transported or stored as a nonexplosive material.

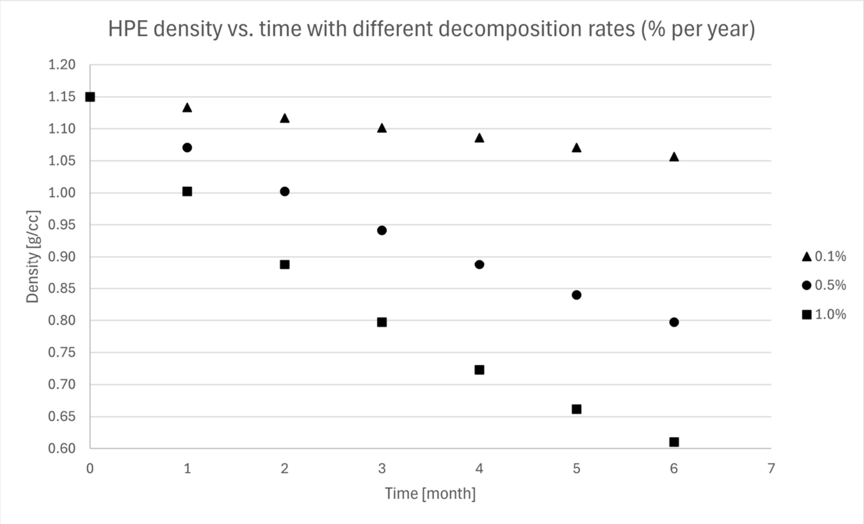

Figure 1. Estimated density of HPE with different annual decomposition rates.

Finally there's a question of waste handling. From experience we know that in bulk emulsion system it's very hard to avoid waste completely. In mine conditions mineral dust is everywhere so hard to avoid contamination. Contaminated HPE can start a thermal runaway decomposition at any second. This means that firstly creating any HPE waste must be avoided and if waste is created it must be converted in safe (unreactive) form immediately. No storage of HPE waste. There's no simple solution to this issue but at least it must be acknowledged and understood before entering any practical scale loading. Demulsification may be the first step to reduce risk level. At least fuel and oxidizer are separated then. Still concentrated HP solution remains and as an aqueous liquid it is even more reactive with contaminants.

4. ENVIRONMENTAL IMPACT

HP is marketed as a green chemical because decomposition products are oxygen and water. In use as a raw material for bulk explosive the release scenario should be re-evaluated. In form of w/o emulsion HP is protected against external factors to some degree. Many studies show that 5-20% of bulk explosives used stay unreacted in muck after blast. This would create a significant source for HP into environment. Depending on further handling of rock material and mine water varying amounts of HP can enter surrounding waters. According to recent studies HP is toxic to aquatic life. There's no results showing the consequences of large scale use of HPE to surrounding waters so studies are needed to avoid any negative surprises.

When HP/HPE reacts with minerals some metals in water soluble form can be expected. In table 2 analysis results of two tests are shown. Other sample was drill cuttings from pyrite mineral (sample Py) and other was drill cuttings from granite-based mineral (sample Gr). Py-0 = pyrite sample washed with water, Py-HPE = pyrite sample reacted with HPE and washed with water. Gr-0 = granite sample washed with water, Gr-HPE = granite sample reacted with HPE and washed with water. Pyrite sample was very reactive with HPE. In just minutes after contact a violent fast spreading decomposition of HPE took place. In contrast with granite reaction was very slow and just notable after strong mixing. In case of Pyrite sample the filtered water was blue-green when sample wasn't in contact with HPE and the sample reacted with HPE had deep brown color in water. This may be due to different oxidation states of iron. The metal analysis from filtered water samples was done with ICP so it can't make any distinction between different oxidation states of the metals. The goal of this test was to see does something new appear in reaction with HPE. The results show that only in case of granite nickel appears in the analysis results when sample had reacted with HPE. All the other metals existed in water soluble form before reacting with HPE. The tests arrangement wasn't very accurate so more tests are needed for estimating actual potential for metal releases.

Sample Al	Al	Ca	Cd	Co	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	S	Zn
	452	516	9	4	1363	1147		1253	103	4	1	52	5528	3360
Py-HPE	539	538	6	4	1472	3955		926	73	3	1	56	6506	2388
Gr-0		468					71	50		1335			122	
Gr-HPE		196					39	21		514	1		56	

Table 2. Metal concentrations ppm in water.

As a powerful oxidizer HP is capable of transforming oxidation states of metals. One case of special concern is chromium. In slightly alkaline environment HP can oxidize harmless Cr(III) into very toxic Cr(VI). Spray concrete, filler used in underground production areas and limestone create this kind of alkaline environment. Test results are lacking but chromate is such highly toxic pollutant that this topic needs to be studied thoroughly before large scale use of HPE especially in areas where chromium containing minerals exist.

5. CONCLUSIONS

HPE has shown promising results in field tests from blasting technical point of view. The main challenge is safety. A new level of personal protection is needed. Working methods needs to be developed to avoid spreading and contamination. The ultimate solution will be mechanized loading where operator is located in cabin of a loading unit.

From material safety point of view reactivity of HP/HPE and consequent effects of it and spontaneous sensitization of HPE are the main challenges. One solution to transport and storge risks is on-site production integrated with loading unit.

Environmental issues require more studies before large scale utilization of HPE. The risks are potential releases and toxic effects of HP in surrounding waters, products from reaction of HP with minerals and ground, especially potential oxidation of harmless chromium (III) into very toxic Cr(VI).

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