



Cape Peninsula
University of Technology

**DEVELOPMENT OF TWO-COMPONENT GASSING SYSTEM TO SENSITIZE
EXPLOSIVE EMULSIONS.**

by

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ABSTRACT

This study investigated explosive emulsions used in civilian mining for breaking rocks. These emulsions were highly concentrated (mass fraction greater than 90 %) and consisted of a dispersion of an aqueous solution of industrial grade ammonium nitrate in a fuel phase containing surface active agents. For such emulsions to detonate, they must be sensitized. This is usually done by generation of gas bubbles (voids) in-situ via a gassing reaction, whereby a gassing component is added to the emulsion to react with ammonium nitrate (present in large quantity), which is a one-component method. In this method, any excess of gassing agent gives rise to an undesired extent of gassing reaction, resulting in poor blasting performance. This study reports an alternative approach to sensitizing explosive emulsions, by using a two-component gassing system, one (KI) that was added to the fuel phase or to ammonium nitrate solution in a pre-determined amount prior to emulsification, and the other (H_2O_2) added to the explosive emulsion after manufacture, when sensitization was required. Thus, the primary goal of this research was to carry out a phenomenological study of the dependence of H_2O_2 and KI concentrations, as well as the effect of pH on the emulsion density over time, with a view to shedding light on the factors controlling the final gassed emulsion density, and on optimizing the process. Blasting experiments were also conducted to compare the performance of the new method to the one currently being used.

Three industrial fuel phases were selected for this study: F800, Bullfinch and R602/45. The H_2O_2 solution (30 wt%) and KI concentrations were varied from 0.09 to 7.80 wt% and 0.004 to 0.1 wt% respectively. The pH values ranged from 4.4 to 6.5.

The research showed that the stoichiometric reaction between KI and H_2O_2 was dominant rather than the catalytic decomposition of H_2O_2 . It was also found that when KI was added to the fuel phase, the rate of density change increased and the final gassed emulsion density decreased with increasing H_2O_2 concentration. As with the effect of H_2O_2 , an increase in rate of density change and a decrease in final emulsion density with increasing KI concentration were observed. For KI concentrations of 0.008 wt% (F800) and 0.004 wt% (Bullfinch and R602/45), the reference density was reached and the excess of H_2O_2 did not affect the extent of gassing reaction or the final gassed emulsion density. Unexpectedly, emulsions in which KI was added to the ammonium nitrate solution yielded exactly the same results.

Interestingly, it was demonstrated that regardless of the phase in which KI is initially added prior to emulsification, the gassing reaction neither occurred in the fuel nor the aqueous phase but at the interface formed by the fuel and aqueous phases.

Blasting experiments showed that emulsions sensitized by the new method (two-component system) yielded velocities of detonation 7 to 11% lower than the current method (one-component system). This was probably due to the differences in porosity of emulsions sensitized by different methods.

The studies conducted have shown that the use of the two-component (H_2O_2 and KI) gassing system is suitable to regulate the extent of the gassing reaction in explosive emulsions for $\text{pH} < 6.0$. The two-component gassing system could be used in the explosives industry where consistent blasting performance is required.

DECLARATION

I, Kabamba Katende Jonathan, hereby declare that, to the best of my knowledge, this thesis represents my own work and has not been submitted previously for examination toward any degree or diploma qualification at any other University. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology.

.....

Kabamba Katende Jonathan

February 2018

DEDICATION

The following have played a vital role in my life and I dedicate this work to them.

- My parents Matthieu Katende Kabamba and Therese Cibangu. I would have never made it this far without their spiritual, moral and financial support.
- My brothers Glory and Daniel Katende, and sisters Patricia and Gracia Katende. When supported by such champions, one is continuously motivated to succeed.
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NOMENCLATURE

| Symbol | Description | Unit |
|----------------|--------------------------------|-------------------|
| d | Diameter | m |
| L | Length | m |
| M | Mass | kg |
| M ₁ | Mass of density cup | g |
| M ₂ | Mass cup + sensitised emulsion | g |
| t | Time | µs |
| V | Volume of density cup | cm ³ |
| ρ | Sensitised emulsion density | g/cm ³ |

Abbreviations

| | |
|-----|---------------------------|
| AN | Ammonium nitrate |
| ANS | Ammonium nitrate solution |
| TNT | Trinitrotoluene |
| VOD | Velocity of detonation |

GLOSSARY

| Terms | Definition |
|--------------------------------------|--|
| Emulsion: | Two immiscible liquids (usually oil and water) with one of the liquids dispersed as small spherical droplets in the other. |
| Explosive Emulsions: | Emulsion that consists of small droplets of oxidiser solution tightly packed in a fuel. |
| Gassed emulsion: | Explosive emulsion in which voids have been introduced using a chemical reaction |
| Gassing: | Use of chemical reaction to produce voids within emulsion explosive |
| Over-gassing: | Phenomenon in which final sensitized emulsion density drops below desired value leading to poor blast performance |
| Sensitization: | Introduction of small, low density voids into emulsion providing hot spots at which an explosion may nucleate |
| Sensitized emulsion: | Explosive emulsion in which voids have been introduced |
| Apparent equilibrium density: | Gassed explosive emulsion density recorded at the end of the first hours of observation (2 to 3 hours) |
| True equilibrium density | Gassed explosive emulsion density recorded after overnight observation |
| Emulsification | Process of dispersing one liquid into a second immiscible liquid |

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CHAPTER 1 INTRODUCTION

1.1 Background

An emulsion is a system comprising two immiscible liquids with one of them dispersed in the other as droplets of spherical shape. The system is stabilized by a surfactant. Emulsions are classified based on the dispersion of oil and aqueous phases (McClements, 1999). They can be simple or multiple. Simple emulsions which are the subject of this study are classified in 2 categories: water-in-oil (w/o) emulsions and oil-in-water (o/w) emulsions.

Explosive emulsions are water-in-oil (w/o) super-concentrated emulsions (90 vol.%). They comprise an oxidizer solution (with ammonium nitrate being the most commonly used) which forms the dispersed phase, an organic liquid which forms the continuous phase, and an emulsifier. Explosive emulsions are used in civilian mining, quarrying and excavation industries for breaking rocks and ore for mining (Rodgers, 1999).

Explosive emulsions require sensitization before detonation. This is done introducing void spaces (hot spots) into the base emulsion. The density of explosive emulsions is usually around 1300 kg/ m³ and has to be reduced to around 1000 kg/ m³ for an efficient blast (Da Silva et al., 2009). Various technologies used to sensitize emulsions include addition of high explosives, incorporation of materials containing entrapped voids and chemical sensitization, which is the subject of this study. Sensitization via addition of high explosive has been largely abandoned because of the high costs attached to this technology; moreover, it requires emulsions to be sensitised at the manufacturing site; in this sense subsequent transportation to the blasting site unsafe (Dlugogorski et al., 2011). The materials containing entrapped voids used in sensitisation of explosive emulsions are known to pose handling problems. Moreover, they must be added to the emulsions at the manufacturing plant; this implies transportation of sensitised material to the blasting site, which is also unsafe.

The use of chemical reactions to produce voids within explosive emulsions is also known as chemical sensitization or gassing. This method was found to be an efficient and cost-effective means to sensitize explosive emulsions (Ngai et al., 1997). Gassing is at present the most commonly used method to sensitising explosive emulsions. During the gassing process, small bubbles of CO₂, O₂, H₂, NO, N₂, C₂H₂, etc are formed in emulsions via chemical reactions thus creating hotspots (Dlugogorski et al. 2011; Da Silva et al. 2009; Lownds 1995; Thornley & Udy 1975; Ferguson & Hopler 1966; Tomic, 1973). Chemical sensitisation is done using cheap reagents and can be performed at the blasting site (for

most technologies). The advantages offered by gassing make it a suitable method for the sensitisation of most bulk explosive emulsions (Dlugogorski et al., 2011).

Over the last 30 years, the most commonly used chemical sensitisation method has been nitrogen gassing via the nitrosation mechanism. In this method, a concentrated solution of nitrite ions from NaNO_2 , HNO_2 or acid solutions of potassium or ammonium nitrites is added to explosive emulsions (Dlugogorski et al., 2011). Currently, gassing of emulsions is done by the addition of sodium nitrite to the explosive emulsion. The addition of the chemical gassing agent to the base emulsion is generally done just before the loading of the explosives into a blast hole. The chemical reaction occurs whilst the emulsion is in the blast hole. This method presents various advantages: NaNO_2 is safe at the levels used; and molecular nitrogen is in the atmosphere and is relatively non-reactive due to the presence of a triple bond. The disadvantage of this gassing technology is that the use of excess NaNO_2 could lead to an undesired extent of reaction since the ammonium nitrate present makes up most of the emulsion in terms of composition. In this sense, the final density of the emulsion will be lower than desired (over-gassing of the emulsion). This phenomenon results in poor blasting performance (lower bulk strength). The current study considered the use of a two-component gassing system that could provide better control of the extent of the gassing reaction.

1.2 Problem statement

The advantages that chemical gassing offers (such as efficiency, cost effectiveness, and sensitization done at the blasting site rather than the manufacturing site for most technologies) make it the method of choice for emulsion explosives sensitization. However, the use of this technology presents a significant limitation which is the difficulty of controlling the extent of the gassing reaction. Most chemical gassing methods rely on the reaction between gassing agent and oxidizer (present in large amounts), and any excess of gassing agent poses a problem. These sensitization methods are greatly affected by the human factor, making the adjustment of emulsion density difficult to regulate. Of all the chemical gassing technologies used to sensitize explosive emulsions, there is none that has successfully addressed the issue of controlling the extent of the gassing reaction.

1.3 Objectives of the study

The main objective of the current research was to develop a two-component system where one component (A), inert to constituents of the explosive emulsion, is added to the fuel phase or ANS in a predetermined amount. The other component (B), the “gasser”, will be added to the emulsion when sensitization is required. The extent of the chemical reaction will be determined by the amount of component (A) present in the emulsion; this will result in the desired gassing reaction extent and required final density. Studies were conducted for the

cases where KI was added to the fuel phase and where KI was added to ANS prior to emulsification. This was done with a view to determining the case that provides better control of the final gassed emulsion density.

To achieve the overall goal of the study, the following specific objectives were defined:

- To select from the literature reactants and their chemical reactions that produce gases based on the following criteria: safety, environmental impact, toxicity, reaction temperature ≤ 50 °C; and to experimentally investigate the compatibility of selected compounds with emulsion components: oxidiser (ammonium nitrate) and fuel phase (hydrocarbon fuels).
- To study the ability of components (A) and (B) to react in the fuel phases and explosive emulsions to generate gas.
- To study the effect of component (B) concentration on the rate of density change and the final sensitized emulsion density using fixed concentrations of component (A).
- To study the effect of component (A) concentration on the rate of density change and the final sensitized emulsion density using fixed concentrations of component (B).
- To study the effect of pH on the final sensitized emulsion density.
- To investigate blasting performance as compared to the current method and implement a newly developed two-component gassing system in different industrial grade fuels.

1.4 Research design and methodology

To achieve the objectives outlined above, the study was conducted in the following manner:

1.4.1 Selection of gassing components

Possible gassing components selected from the literature study were tested in terms of:

- reactivity with the aqueous phase (ANS) and fuel phase (hydrocarbon fuels).
- solubility or dispersion and/or suspension in the fuel phase
- reactivity in the fuel phase and in explosive emulsions to produce gas.

These experiments were of a qualitative nature and visual observations were used as means of generating and interpreting results.

1.4.2 Manufacture of emulsions using Hobart N50 mixer

The prepared emulsions had dispersed phase and continuous phase concentrations determined by AEL Mining Services. Component (A) was to be added to the fuel phase or ANS before emulsion preparation. Emulsions were prepared with the Hobart N50 mixer. Besides emulsions used for blasting experiments which were prepared according to AEL

Mining formulations, the aqueous phase of emulsions was a 60 wt% aqueous solution of AN. The mass fraction of the aqueous phase was 90 wt%. The concentration of component (A) was varied from 0.003 to 0.1 wt%.

1.4.3 Gassing in emulsions

In gassing experiments, gassing component (B) was added to the emulsion containing component (A) with continuous mixing. Component (B) concentration ranged from 0.09 to 7.80 wt%. After mixing, a gassing cup was filled to the brim with sensitised emulsion and the contents were flattened to the rim having recorded the initial mass. The gassing reaction caused emulsions to expand, and at regular intervals excess emulsion was scraped off the rim of the cup and the weight of the cup with its contents was re-measured. The rate of change of the gassed emulsion mass remaining in the cup was used to determine the rate of density change. Results from gassing of emulsions, and graphs of density change over time were plotted with Microsoft Excel.

1.4.4 Effect of pH on gassing rate and final sensitized emulsion density

To investigate the effect of pH on final sensitized emulsion density, emulsions were prepared using the aqueous phase for which pH was varied from 4.4 to 6.5. Emulsions were sensitized, and density evolution was followed. Graphs of density evolution over time were plotted with Microsoft Excel and used to analyse experimental data.

1.4.5 Blasting Properties

For blasting properties studies, explosive emulsions sensitized with new technology were blasted at the AEL Mining Services' far range. Velocity of detonation (VOD) was calculated from readings obtained on a VOD timer.

1.5 Significance of research

The newly developed two-component gassing system will add significant value in controlling gassing reactions in emulsion explosives. For industrial applications, this work could provide information on an alternative and probably better technique for sensitizing emulsion explosives which could solve the problem of over-gassing of emulsion explosives during gassing.

1.6 Research delineation

The project will be limited to emulsion formulations determined by AEL Mining Services. The effects of temperature on the gassing process will not be covered in this study

1.7 Expected outcomes

The outcome of the project is a two-component system where one component (A) is dissolved in the fuel phase at manufacturing site in a pre-determined amount. The other component (B), the gasser will be added at to the matrix the blasting site when the sensitization of the emulsion explosives is required. The chemical reaction will be controlled by the amount of component (A) in the fuel phase and not by the amount of “gasser” (B) added to the emulsion, resulting in an accurate final density.

The thesis is subdivided into the following chapters:

- **Chapter 1: Introduction**

The chapter serves as a background to this thesis.

- **Chapter 2: Literature Review**

Relevant literature on sensitization of explosive emulsions is reviewed in this section of the thesis. This includes different methods of explosive emulsion sensitization with emphasis placed on chemical sensitization or gassing technologies.

- **Chapter 3: Feasibility Study**

In this chapter the selection process of two gassing components that are capable of reacting in the fuel phase, and of emulsions to generate gas bubbles for explosive emulsion sensitization, is presented.

- **Chapter 4: Experimental Work**

The materials used, procedures that were followed to carry out experiments, and instruments used for various measurements are described.

- **Chapter 5: Results and Discussions**

In Chapter 5 the experimental findings from gassing and blasting experiments are analysed and discussed.

- **Chapter 6: Conclusions and Recommendations**

This chapter presents the summary of the dissertation. Conclusions drawn from experimental findings are also presented and recommendations for future research projects are made.

CHAPTER 2

LITERATURE REVIEW

This chapter presents the literature relevant to the subject of sensitisation of explosive emulsions. Fundamental notions of explosives and emulsions are presented to provide the reader a better understanding of the subject matter. Emphasis is placed on the methods or technologies that have been used to sensitise explosive emulsions. The advantages and disadvantages associated with these methods are discussed.

This chapter is divided into the following sections:

- General definition of explosives
- Classification of explosives
- General definition of emulsions
- Explosive emulsions
- Technologies for explosive emulsions sensitisation

2.1 Definition of explosives

Explosives are substances capable of reacting rapidly, releasing heat and gases without intervention of external reagents such as atmospheric oxygen (Zukas & Walters, 1998). Mechanical means (impact, friction), action of heat (sparks, open flame) or detonating shocks (blasting cap, booster charge) can initiate the chemical reaction (Zukas & Walters, 1998). Explosives are mixtures of carbon, hydrogen, oxygen, nitrogen and other additives which confer on them specific properties such as density, viscosity and water resistance.

An explosion can either be a detonation or a deflagration depending on the rate of propagation of shock waves relative to the speed of sound. When the rate of chemical decomposition is higher than the speed of sound, detonation occurs and when the rate is lower than the speed of sound, deflagration occurs (Safetell, n.d.).

2.2 Classification of explosives

According to the Bureau of Alcohol, Tobacco, Firearms and Explosives (2015), explosives are subdivided into 3 categories, namely low explosives, high explosives and blasting agents. Primary explosives can be considered as a separate category.

2.2.1 Primary explosives

Primary explosives, also called initiators, form part of the substances known as explosives. They are used to initiate the combustion or detonation of the main explosive when subjected

to mechanical, thermal or electrical stimulus. Examples of initiators include mercury fulminate, lead azide, nitrogen sulphide, and tetracene (Matyas & Pachman, 2013).

2.2.2 Low explosives

Low explosives, also known as propellants, are combustible materials containing all the oxygen required for their combustion. They normally undergo deflagration and if this happens at high rates, the effects produced are similar to detonation. Black and smokeless powders are examples of low explosives (InfoChimica, n.d.).

2.2.3 High explosives

High explosives are characterized by detonation when initiated. They are more powerful than low explosives and their decomposition occurs within seconds during detonation. Examples include dynamite, nitroglycerin, pentaerythritol tetranitrate (PETN), trinitrotoluene (TNT), etc. (Melane, 2010).

2.2.4 Blasting agents

Blasting agents are explosive used in mining and excavation activities. They are generally cheap, do not pose safety problems and are not used for military purposes (Melane, 2010). Examples of blasting agents include ammonium nitrate fuel oil (ANFO), water gels, slurries and explosive emulsions which will be the subject of the current study. Explosive emulsions belong to a family of dispersions known as emulsions.

2.3 General definition of emulsions

According to the International Union of Pure and Applied Chemistry (IUPAC, 1971), an emulsion is defined as a dispersion of liquid droplets and/or liquid crystals in a liquid. An emulsion comprises two immiscible liquids; one of the liquids is dispersed in the other in the form of small spherical droplets stabilized by a surfactant (McClements, 1999). Emulsions are systems consisting of 2 or more liquid immiscible phases. Emulsions can be classified into 2 broad groups: simple and multiple emulsions. Simple emulsions are further classified in 2 categories: water-in-oil (w/o) emulsions and oil-in-water (o/w) emulsions (Pal, 2011), as shown in Figure 2.1.

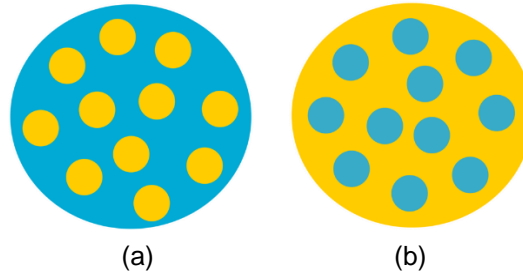


Figure 2. 1 (a) Oil in water and (b) water in oil emulsions

In oil-in-water emulsions, the aqueous phase is the continuous phase in which oil droplets are dispersed. In water-in-oil emulsions, the oil forms the continuous phase in which the aqueous phase in the form of droplets is dispersed. Multiple emulsions comprise water-in-oil-in water (w/o/w) in which w/o emulsion droplets are dispersed in an aqueous continuous phase and oil-water-in-oil emulsions in where o/w emulsion droplets are dispersed in an oil phase (Yaqoob et al., 2006). The dispersed droplets phase is also known as internal phase and the surrounding liquid as external or continuous phase (McClements, 1999).

Emulsions are encountered in a wide variety of industries and applications: food, personal care products, household products, pharmaceutical products, explosives, etc.

Emulsions can be dilute, moderately concentrated or highly concentrated depending on the concentration of dispersed phase droplets usually described in terms of volume fraction (ϕ). An emulsion is referred to as dilute when the volume fraction of dispersed droplets is small ($\phi < 0.02$) (Pal, 2011). In moderately concentrated emulsions, the volume fraction of the dispersed phase ranges between 0.02 and the maximum packing volume fraction of undeformed droplets (Pal, 2011). Highly concentrated emulsions, also known as high internal phase ratio emulsions or gel emulsions, are emulsions in which the disperse phase volume fraction exceeds the maximum packing volume fraction of undeformed droplets (Foudazi et al., 2015; Pal, 2011). Highly concentrated water-in-oil emulsions are the subject of this study.

2.4 Explosive emulsions

Explosive emulsions, developed in the early 1960s (Egly & Neckar, 1994; Gehrig, 1965; Bluhm & Tamaqua, 1969), exhibit high detonation parameters and good safety characteristics which have made them important blasting means (Lee & Persson, 1990; Takahashi et al., 1999). They are water-in-oil super-concentrated emulsions comprising an oxidiser solution which is the phase to be dispersed phase, an organic liquid (continuous phase) in which the oxidiser solution will be dispersed and an emulsifier (Mullay & Sohara, 2000). The components making up the emulsions are inexpensive and this makes the use of

explosive emulsions cost effective. (Rajapakse, 2007). A microscopic image of an explosive emulsion is shown in Figure 2.2.

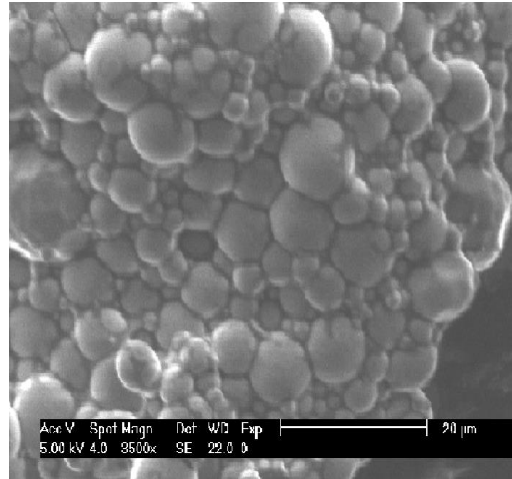


Figure 2. 2 Microscopic image of explosive emulsion (Masalova & Malkin, 2013)

Explosive emulsions are used in civilian mining, quarrying and excavation industries as a principal method for breaking rocks and ore for mining (Rodgers, 2012).

2.4.1 Composition of explosive emulsions

a. Dispersed or discontinuous phase

In conventional explosive emulsions, the dispersed phase consists of a solution of inorganic salts such as alkali and alkaline earth metal nitrates, chlorates and perchlorates, ammonium nitrate (NH_4NO_3), ammonium chlorate (NH_4ClO_3), and ammonium perchlorate (NH_4ClO_4) capable of releasing oxygen (Prest & Yorke, 1989; Curtin & Yates 1985). AN either alone or combined with a small quantity of calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) or sodium nitrate (NaNO_3) is preferred as a salt. The solubility of AN in water decreases as temperature decreases; this results in leaching out from the solution, thus adversely affecting the stability of the explosive emulsion. Using a combination of salts increases the quantity of oxygen that can be supplied, improves the stability of the emulsion and lowers the fudge point (Pradhan, 2007). The concentration of inorganic salt used generally ranges from 45% to 94% by weight of the total emulsion mass (Sudweeks & Lawrence, 1980).

b. Continuous phase

The oil phase forms the continuous phase of the explosive emulsion and acts as a combustion agent; it is one of the essential components of the explosive emulsion capable of making the system consistent resistant to water. The various fuel phases used include

paraffin oils and waxes, mineral and vegetable oils, petroleum, microcrystalline waxes and other petroleum fractions (Curtin & Yates, 1985). To be used as an oil phase material, the hydrocarbon needs to have a proper consistency (Pradhan, 2007). The fuel phase concentration generally ranges from 2% to 15% of the total emulsion mass (Cooper et al., 1999).

c. Emulsifiers

Emulsifiers are molecules comprising hydrophilic/lipophobic and lipophilic/hydrophobic parts; they are categorized according to the hydrophilic/lipophilic balance (HLB). Emulsifiers are able to interact with the interface between two phases; their ability to stabilise mixtures of oil and water comes from their surface activity (Whitehurst, 2004). Emulsions have a normal tendency to go into to a state of lowest free energy, which is the separation into two phases and in the absence of an emulsifier; this results in fluid layers which cannot be used as explosives (Bampffield, 1983; Pearson & Morrison, 2002). In w/o emulsions, the emulsifier molecules will be aligned such that the head with affinity for water (hydrophilic) is in contact with surface of the aqueous droplet, and the tail with affinity for oil (lipophilic) is absorbed in the oil phase (Figure 2.3). The emulsifier forms a molecular layer around the droplet (Figure 2.3); in this sense, the rate of dispersed phase droplets coalescence is greatly reduced (Rajapakse, 2007).

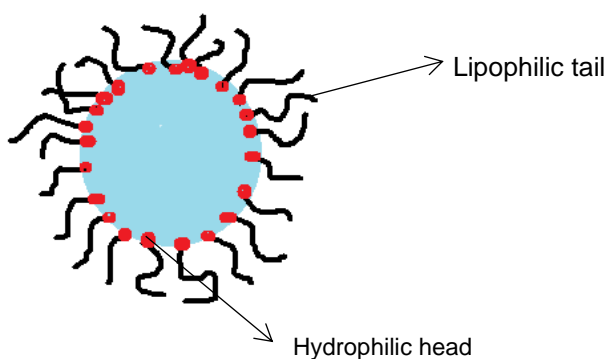


Figure 2. 3 Hydrophilic head group of the surfactant absorbed at the surface of the water and lipophilic tail at the oil surface in W/O emulsion

The performance of explosive emulsions is dependent on the activity of the emulsifiers. They are not only required to facilitate the emulsification process but also prevent crystallization and breakdown through coalescence of the aqueous phase. Under normal conditions the supersaturated aqueous phase used to prepare emulsions would be crystalline. Crystallisation of the oxidiser phase can lead to emulsion breakdown and reduction in

detonation sensitivity (Cooper et al., 1999). The layer of emulsifier surrounding the dispersed phase droplet creates a barrier between droplets such that crystals' growth from one droplet into another is inhibited. Sorbitan monooleates (SMO) were among the first emulsifiers used in explosive emulsion manufacture. Sorbitan emulsifiers include sorbitan fatty acid esters such as sorbitan monolaurate, sorbitan monooleate (Figure 2.4), sorbitan monopalmitate, etc., which provide similar stability in emulsion explosives (Bluhm & Tamaqua, 1969).

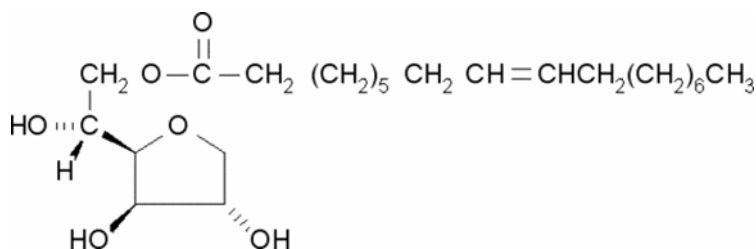


Figure 2. 4 Sorbitan mono oleates

The drawback associated with the use of sorbitan mono oleates is that they are unable to provide long term stability of explosive emulsions (Hales et al., 2002). Research in this area has led to the development of various soaps and oxazolines such as 4,4-bis(hydroxymethyl)-1-heptadecyl-2-oxazoline and 4-methyl-4-hydroxymethyl-1-heptadecyl-2-oxazoline, salts of long chain fatty acids such as calcium oleate, magnesium oleate, aluminum oleate and calcium stearate, sorbitan esters such as polyoxyethylenesorbitan mono oleate, and sorbitan sesquioleate, and ethylene oxide condensates of fatty acids (Egly & Neckar, 1964), all of which were used as emulsifiers. However, their incompatibility with internal and external stabilizers in ammonium nitrate, caused explosive emulsions breakdown, resulting in failure to detonate (Pearson & Morrison, 2002).

Further research on emulsifiers capable of stabilizing emulsions in the long term was carried out (Forsberg, 1987; Yates & Dack, 1987; Chattopadhyay, 1990; Cooper & Baker, 1989) and the finding was a unique class of emulsifiers based on polyisobutenyl succinic anhydride (PIBSA) shown in Figure 2.5 and its derivatives, which are more compatible with the stabilizers in ammonium nitrate.

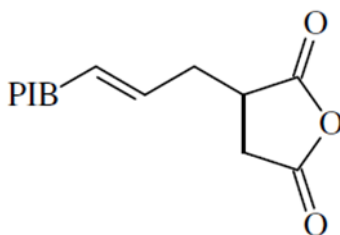


Figure 2. 5 Polyisobutenyl succinic anhydride (PIBSA)

In this new type of emulsifier, the lipophilic nature is provided by PIBSA and hydrophilic nature can be provided by various chemicals such as alcohols, polyol, amines, alkanolamines, etc. Emulsifiers having the composition of PIBSA and amines such as ethylene diamine, diethylene tetramine and mono- and di-ethanolamine were reported by Baker and Cooper (1989). PIBSA with polyethylene glycol or polyethylenimine was reported by Binet et al. (1979). Boer (2002) carried out an experiment in which PIBSA and urea reacted to produce an emulsifier. He found that the adduct produced showed superior performance as an emulsifier in explosive emulsions as compared to known products, such as the adduct of monoethanolamine (MEA) with PIBSA. An explosive emulsion sample containing the adduct of PIBSA and urea showed a longer shelf life, meaning slower crystallisation of oxidiser salts than control samples made at the same time with the adduct of PIBSA and MEA. A blend of PIBSA derivative emulsifiers and SMO in emulsions preparations resulted in emulsions with smaller drops and high stability (Ghaicha et al., 1995). Some PIBSA-based derivatives are shown in Figure 2.6.

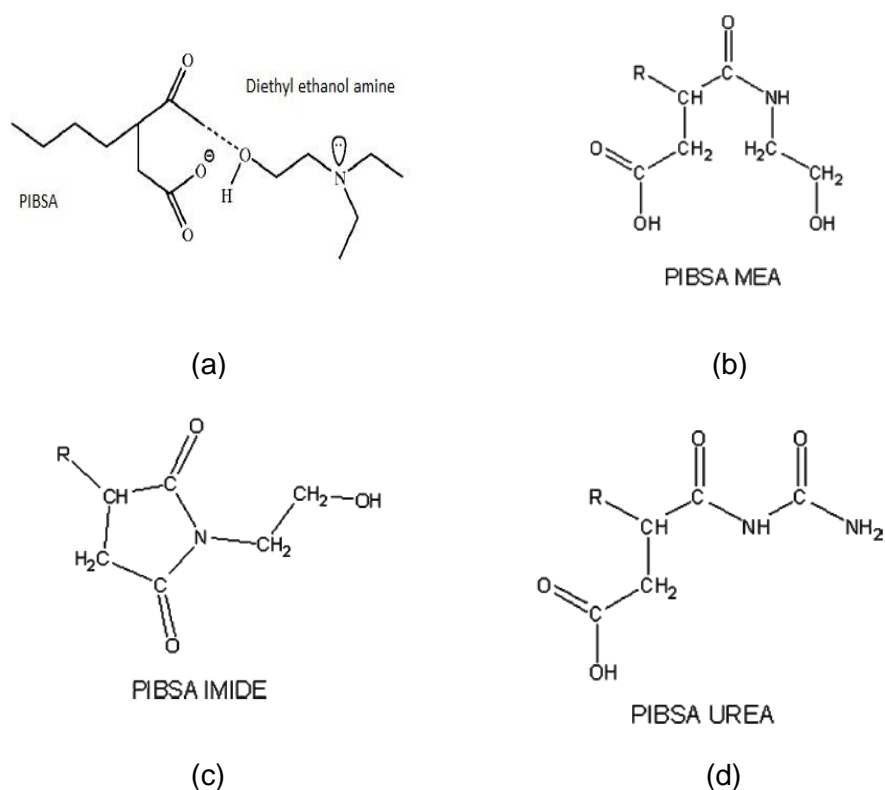


Figure 2. 6 Polyisobutenyl succinic anhydride (PIBSA) based derivatives: (a) PIBSA-Diethyl ethanol amine, (b) PIBSA-MEA, (c) PIBSA-Imide and (d) PIBSA-Urea

Tomic (1972) reported the composition of emulsion with stearate salt (sodium stearate) emulsifier. The stearate salt that causes the emulsion to be formed imparts to the composition properties and characteristics not possessed by other compositions, e.g., blasting agents containing an emulsifying agent. First, and quite surprisingly, the water resistance of compositions emulsified with the stearate salts is substantially higher than those emulsified with other emulsifying agents. Second, the stearate salt emulsified composition is readily pumpable, and, third, it does not adhere to walls of containers in which it can be packaged prior to use.



Figure 2. 7 Sodium stearate (sodium salt of stearic acid)

Explosive emulsion compositions containing selectively hydrogenated copolymers prepared using conjugated dienes as emulsifier have been introduced by Coolbaugh and Mahamat (2003). In this invention, the emulsifiers are generally based on liquid, low molecular weight polymers generated by anionic block polymerization of dienes, such as butadiene and isoprene, and olefins, such as styrene. These emulsifiers showed several advantages such as controlled molecular weight and its distribution, controlled polymer structure, etc.

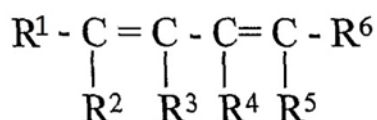


Figure 2. 8 Conjugated diene where R1-R6 are each independently hydrogen or a hydrocarbyl group

The base emulsion itself is generally considered not capable of detonation. The explosive emulsion can only detonate after it has been sensitised. Sensitization involves introducing small low density voids (air, gases or some hollow or porous material) into the base emulsion (Mader, 1965). These become the hotspots making it possible for the explosion to nucleate (Wang, 1994; Sychev, 1997; Sychev, 1985; Sychev, 1995). The hotspots thus formed are compressed adiabatically during detonation; this causes temperature to increase rapidly up to values exceeding the explosive's detonation temperature resulting into the propagation of the explosive shockwave. A typical explosive emulsion's density is about 1,300 kg/m³. Through the introduction of hotspots, the density has to be reduced to around 1,000 kg m³ which is required for an efficient blast (Da Silva et al., 2009).

2.5 Technologies of sensitization

Salts with the ability to supply oxygen such as ammonium nitrate, sodium nitrate and potassium nitrate are commonly used as components of blasting agents (Egly & Neckar, 1964). Though AN can be considered a blasting material, its sensitivity is too low for quick initiation or to sustain sufficient propagation. The production of a highly efficient AN blasting agent requires the use of sensitisers which do not only cover the particles to provide complete sensitisation, but also fill the gaps between particle, thus improving the density of the blasting agent. This results in increased blast hole pressure, increased power, and more complete control, uniformity and predictability for each blasting operation (Egly & Neckar, 1964). Various technologies have been developed to provide sensitization to explosive emulsions, or gel type blasting agents.

2.5.1 Addition of high explosive

Originally, emulsions were sensitised by the addition of high explosives. Egly and Neckar (1964) used organic liquids with low water-solubility to sensitize oxygen-supplying salts such as ammonium nitrate. One of the advantages of this invention is that water is lighter than the sensitising compounds. This causes water to be forced out of wet boreholes thus preventing further contact between the ammonium nitrate to be sensitized. Cook et al. (1967) used smokeless powder as a sensitizer combining it with the basic oxidizer (such as ammonium nitrate, or sodium nitrate, or mixtures thereof, or blends of one or more such nitrates with inorganic chlorates and the like). Explosives including trinitrotoluene (TNT), nitroglycerine, nitrocellulose, nitroguanidine, hexamethylenetetramine, trinitrophenylmethylnitramine, mixtures of TNT and trimethylenetrinitramine, TNT and pentaerythritol tetranitrate, and TNT with ethylene dinitramine have also been employed as means of explosive emulsions sensitisation (Hattori et al., 1982; Berthmann et al., 1967). Some high explosive structures are shown in Figure 2.9.

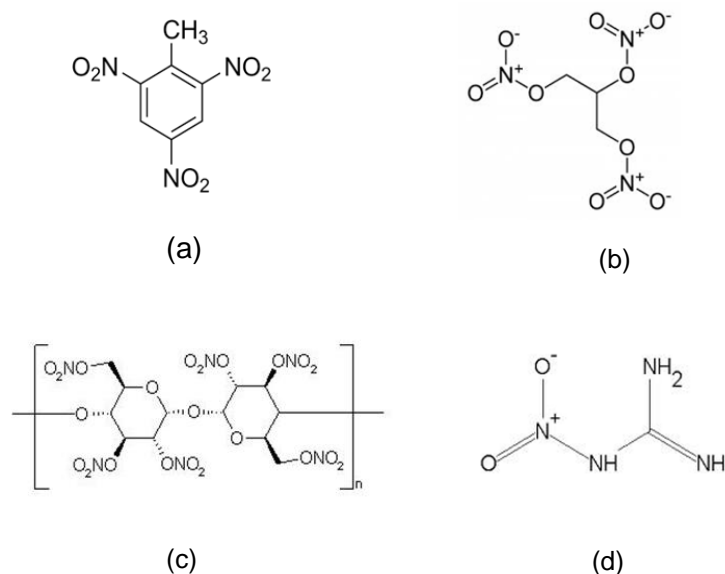


Figure 2. 9 High explosives; (a) Trinitrotoluene (TNT), (b) Nitroglycerine, (c) Nitrocellulose and (d) Nitroguanidine

Sensitization of explosive emulsions via addition of high explosives methods are very costly. Moreover, these methods addition of the sensitizer during emulsion preparation, normally at the manufacture plant (Dlugogorski et al., 2011). Due to these drawbacks, emulsion sensitisation via addition of high explosives has been largely abandoned.

2.5.2 Incorporation of materials containing entrapped voids

This technology is based on creating air voids in an explosive emulsion by addition of hollow microballoons. The use of microballoons with particles containing one or a number of inorganic micro hollow spheres such as obtained from glass (Figure 2.10 a), shirasu (Japanese volcanic ash), sodium silicate (Figure 2.10 b), silicon sand (Figure 2.10 c), carbonaceous micro hollow spheres and synthetic micro hollow spheres is presented in Ehrnstrom & Ekman (1988); Villamagna et al. (1991), and Tanaka et al. (1992).

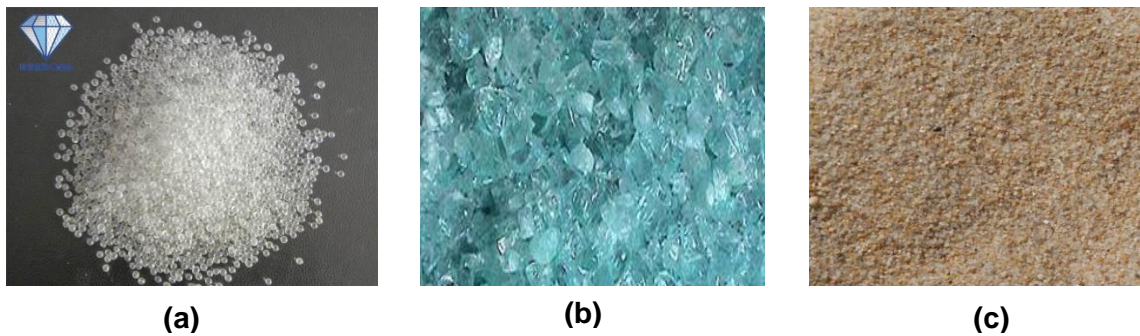


Figure 2. 10 Materials incorporated to explosive emulsions for sensitisation purposes: (a) Glass microsphere (b) Sodium silicate, (c) Silica sand

Wade (1978) used glass hollow microspheres or Saran resin hollow microspheres (with single independent bubbles) as means of explosive emulsions sensitisation. Although this method is suitable in creating voids within the explosive emulsion, the glass microballoons are costly and their bulk density makes the handling of the microballoons difficult. Moreover, the production of a w/o explosive sensitised with glass microballoons having a low velocity of detonation has been technically and economically difficult (Nguyen, 1991).

The shirasu hollow microspheres from volcanic ash have been used to sensitize explosive emulsions (Nippon Oil and Fats Company Limited, 1984). The hollow microspheres can either consist of single independent bubbles or bubble assemblies. However, the use of these microspheres in explosive emulsion sensitization results in explosive emulsions that are difficult to handle, having a low consistency and a poor storage stability (Nippon Oil and Fats Company Limited, 1984).

Sudweeks and Lawrence (1980) used perlite fine particles to sensitize explosive emulsions. The perlite fine particles are neither hazardous nor expensive compared to other commercially used microspheres. However, the major problem associated with the use of these microspheres is that the spheres can collapse if the explosives experience

compression from the shockwave of a neighbouring or adjacent detonation (dead pressing) in a blasting application. Dead pressing results in failure of explosive emulsion to detonate because it does not have the required density for detonation (Sudweeks & Stock, 1984). It is necessary to use a material of greater hardness and to increase the shell thickness to improve the strength of hollow microspheres. The use of hard hollow microspheres of large shell thickness results in a high theoretical density; this means a large amount of hollow microspheres must be used in order to adjust the density of a water-gel explosive to the desired value for an effective blast. However, the use of a large amount of hollow microspheres is not desirable in view of the inexpensive production of explosive emulsions, and it furthermore causes deteriorations of explosion strength, storage stability and detonability of the resulting emulsion.

Sudweeks and Stock (1984) introduced microspheres of sufficient strength to prevent or minimize dead pressing. The spheres are preferably glass, although plastic spheres can be used. Edamura et al. (1988) disclose the use of gas-retaining agents, such as those made from foamed polystyrene, foamed polyurethane and the like. The gas-retaining agents can have a rigid structure similar to inorganic microballoons, and which can be brittle and subject to breakage during handling or can be made soft and spongy so as to be more resistant to inadvertent breakage during handling. However, the route of adding gas voids to the blasting agent requires the initial preparation of a spongy or rigid microsphere structure (gas-retaining agents) which is added to the blasting agent; this results in high detonation velocity, while the production of explosive emulsions with high safety margins against methane or coal dust has been impossible.

The major disadvantages associated with technologies involving materials containing entrapped voids is that they require the sensitisation of emulsions to be done at the manufacturing site; this will mean transportation of detonable emulsions from the manufacturing site to the blasting site, which is unsafe.

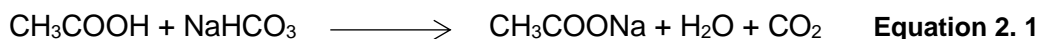
2.5.3 Chemical Sensitisation

Chemical sensitisation or gassing consists in generating voids within the explosive emulsion via a chemical reaction. This sensitisation method been found to be efficient and cost-effective (Ngai et al., 1997). It was introduced in the late 1960s and early 1970s to provide alternative means of sensitizing gel explosives and then emulsion explosives. Gassing is currently the most commonly used means to sensitising explosives. The method involves the formation of CO₂, O₂, H₂, NO, N₂, C₂H₂, etc. gas bubbles in explosive emulsions which provide hotspots on which explosion may nucleate. The reagents used for chemical are relatively cheap and the operation can be performed on the blasting site while loading the

explosive into a blast hole (for most technologies). The advantages offered by gassing make it a suitable method for the sensitisation of the majority of bulk explosive emulsions (Dlugogorski et al., 2011).

Most gassing agents dissolve in the inorganic oxidizer solution (aqueous phase) of the explosive emulsions where they react with the oxidizer under specific pH conditions to produce gas bubbles throughout the emulsion. The timing of gassing agent addition is important; the gassing agent cannot be added to the oxidizer phase before emulsification, as this will result in premature emulsion sensitization during preparation (Cranney & Hansen, 2007).

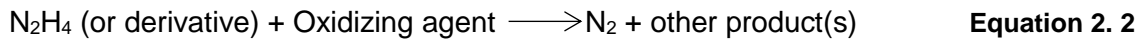
Ferguson and Hopler (1966) disclose a gassing technology whereby the gassing occurs as a result of an in situ reaction of a water-soluble carbonate and an acid that produces carbon dioxide to sensitise aqueous slurry type explosives. This technology could potentially be used for explosive emulsions. Mineral, oxidizing or carboxylic acids such as hydrochloric acid, acetic acid, nitric acid, sulphuric acid and the like were found to be suitable for the technology being developed. The preferred carbonates were ammonium carbonate, sodium bicarbonate and potassium bicarbonate. In the study conducted, sodium bicarbonate and acetic acid were used; they react to produce CO₂ as shown in equation 2.1.



The amount of acid required to completely consume the carbonate was added to the mixing chamber together with the oxidiser solution and the fuel phase. An amount of carbonate within a range from 0.005 to 0.1% of the total composition was subsequently added to the slurry when sensitisation was required. Unfortunately, it is difficult to control the extent of density change of the slurry due to the varying solubility of CO₂ in blasting agents as a function of pressure and blasting agent composition.

Chrisp (1972) has used hydrazine and its derivatives as chemical gassing agents to sensitize water bearing blasting agents. The hydrazine derivatives include substituted hydrazines, especially those with the formula R–NH–NH₂ or RR'–N–NH₂ where R and R' represent alkyl, acyclic radicals and hydrazine salts. The effective hydrazine derivatives that can be used individually or as mixtures include methyl hydrazine, ethyl hydrazine, propyl hydrazine, phenyl hydrazine, diphenyl hydrazine and methyl phenyl hydrazine, cyclohexyl hydrazine, cyclopentyl hydrazine, semicarbazide, hydrazine nitrate, hydrazine sulfate, dihydrazine sulfate, hydrazine chloride, hydrazine phosphite, hydrazine phosphate, hydrazine perchlorate, hydrazine formate, hydrazine acetate, hydrazine oxalate and hydrazine tartrate. Best results were obtained when using hydrazine hydrate, monomethyl hydrazine or phenyl

hydrazine. The amount of hydrazine or derivative used, added first to the emulsion mix, ranges from 0.01 to 3% of the total amount of blasting agent. Hydrazine or its derivatives decompose in the blasting agent in the presence of oxidizing agents such as hydrogen peroxide, chromium trioxide, and the persulfates, permanganates, chlorates, iodates, bromates, dichromates, and chromates of ammonium, alkali, and alkaline earth metals to give off nitrogen gas as shown in equation 2.2, thus sensitizing the blasting agent.

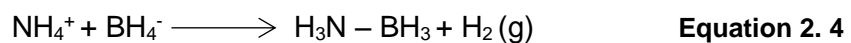


The amount of oxidizing agent used, added when sensitization is required, generally ranges from the stoichiometric amount to 10% in excess. The preferred temperatures of the mix during addition of each gassing component range from 37 to 54°C. Among all oxidizing agents considered, the best results were obtained when using hydrogen peroxide. Equation 2.3 shows the reaction that occurs.



The use of hydrazine as gassing agent has the advantage of nitrogen gas generation which is inert in the atmosphere. The use of this technology is associated with the following drawbacks: first, hydrazines are highly toxic. Second, the reaction with hydrogen peroxide is very slow under normal conditions (Wellman et al., 1976) and require the use of a copper catalyst which poses safety concerns, since it forms an explosive mixture in reaction with AN (Phillips & Hale, 1943). Third, its use involves sensitisation of explosive emulsions at the manufacturing site, which makes the transportation of explosive emulsions to the blasting site unsafe. Moreover, for optimum results, the process requires addition of the gassing agent when the emulsion is still hot. In this sense, if the emulsion has cooled, and sensitization is required at a later time, the explosive emulsion will require subsequent heating which is a practical limitation (Dlugogorski et al., 2011).

Alkali metal borohydrides such as lithium, potassium and sodium borohydrides were used by Tomic (1973) as gassing agents in the sensitisation of water gels and emulsion type blasting agents. The amount of alkali metal borohydride added to the mix ranges from 0.002 to 0.10%, depending on the mass of the total composition. The application of borohydrides is based on the fact that reactions between alkali metal borohydrides and ammonium salts generate hydrogen gas, as shown in equation 2.4.



The hydrogen gas generated makes the emulsion sensitive. Best results are obtained when gassing agent is added to the explosive emulsion with the latter at temperatures ranging from 37° to 65° C. The borohydride ion reacts with ammonium ion in the aqueous phase of the

blasting agent. This gassing technology has not been further developed because of safety concerns associated with metal borohydrides, hydrogen and the possible loss of hydrogen from the explosive emulsion due to its rapid diffusion through the matrix (Dlugogorski et al., 2011); this makes control of the extent of gassing difficult.

Tomic (1973a) used N,N-Dinitrosopentamethylenetetramine as a chemical gassing agent to sensitize water-bearing or emulsion type blasting agents. The concentration of gassing component used ranged from 0.03 to 1 % of the total mass of the composition. The gassing agent was added to the explosive emulsion at temperatures ranging from 60 to 71°C for optimum results. Gassing occurred as a result of the decomposition of N,N-Dinitrosopentamethylenetetramine producing nitrogen. The disadvantage of this technology is that N,N-Dinitrosopentamethylenetetramine is highly toxic; furthermore, this compound is carcinogenic and presents difficulties when gassing is to be done at low temperatures. Moreover, addition of any extra gassing agent amounts due to human factors will result in greater gassing extent than required.

A sensitization technology consisting of the decomposition of a diazonium salt was reported by Vattipalli et al. (2000). Diazonium salts decompose due to heat, producing nitrogen gas; they can be produced by bringing together an amine, an acid and a nitrite salt. In their invention Vattipalli et al. (2000) used two different methods to sensitize explosive emulsions: in the first, an aromatic amine and an acid were added to the aqueous phase of oxidizer salt prior to emulsification; a solution of sodium nitrite was subsequently added after emulsification when sensitization was required. In the second method, an aqueous solution of diazonium salt was prepared by mixing an amine, an acid and sodium nitrite at 0 °C; the resulting solution was subsequently mixed with the emulsion (at temperatures above 35 °C) when sensitization was required. This method offers the advantage of high gassing kinetics. However, the diazonium salts generated are toxic. Moreover, the presence of excess nitrite salt, known to react with oxidizer salts such as ammonium nitrate (Hughes et al., 1958), could result in further generation of nitrogen gas either while the diazonium salts are decomposing or after they have completely decomposed. This could greatly reduce the density of the explosive emulsion below the value required for effective blast.

Da Silva et al. (2007) described an explosive emulsion sensitization method that involves reacting a compound of an enol group (enol compound) with a nitrosating agent. The reaction forms O-nitroso products which decompose, generating nitric oxide (NO) that sensitizes the explosive emulsion. The pH is one of the factors with a major effect on the reaction. The typical enol compound used is lactone, sourced from ascorbic acid. The enol compound concentration typically ranges from 0.005 M to 0.04 M. Dinitrogen trioxide (N₂O₃)

is used as nitrosating agent; this compound can be formed from reaction between nitrite and hydrogen ions. Any suitable nitrite salt (KNO_2 , NaNO_2) could be used as nitrite ion source. The nitrite concentrations used were within a range of about 0.01 to 0.04 M. The gassing solution containing the nitrite salt in water together with the enol compound and a suitable acid (acetic acid, citric acid or other carboxylic acids) is introduced into the explosive emulsion when sensitization is required. In the study conducted, it took about 4 minutes to sensitise explosive emulsions at 25 °C and a pH below 3.9. This sensitization technology offers advantages such as rapid kinetics, making it possible to operate at higher pH values, as well as the use of non-toxic, cheap and readily available gassing agents such as ascorbic acid. However, the gas generated (NO) is toxic and promotes the production of other toxic fumes after blast (Dlugogorski et al., 2011).

Tomic (1974) described a technology in which hydrogen peroxide is used to sensitize explosive emulsions. The amount of sensitizing agent varies from 0.05 to 5 wt% of the total composition. The gassing process consists in the decomposition of hydrogen peroxide in the presence of catalysts such as manganese dioxide, coarse sand, ferrous sulfate, etc. at temperatures above 55 °C; this results in the production oxygen gas bubbles which sensitize the emulsion. The limitation of this technology is that it is difficult to control the extent and timing of the gassing reaction. Moreover, the bubbles formed were not uniformly distributed within the explosive.

Lownds (1995) developed a technology involving the use of an emulsified gassing agent comprising a water-in-oil emulsion of an aqueous solution of hydrogen peroxide, a liquid fuel and an emulsifier. The emulsified gassing agent contains 5 to 30 wt% H_2O_2 , 70-95 wt% fuel and 0.1 to 2 wt% emulsifier. Decomposition of H_2O_2 present in the gassing agent occurs when the latter is added to the explosive emulsion producing oxygen gas bubbles. Manganese dioxide, ferric nitrate, ferrous sulphate, manganese sulphate, aluminium particles and even coarse sand added in proportions ranging from 0.01 to 2 wt% of the total composition are compounds that can be used to accelerate the reaction. The use of this technology offers the advantage of a more uniform distribution of gas bubbles within the emulsion which improves the performance of the explosive. However, the extent of the gassing reaction is difficult to control; in this sense addition of an excess gassing agent due to human factor will result in an undesired extent of gassing, inducing poor blast performance in turn.

Over the last 30 years nitrogen gassing via a nitrosation mechanism has been the most commonly used method to chemically sensitize explosive emulsions. The process consists in

mixing concentrated solution of nitrite ions from NaNO_2 , HNO_2 or acid solutions of potassium or ammonium nitrites with explosive emulsions (Dlugogorski et al., 2011).

Thornley & Udy (1975) disclose a technology for sensitizing blasting slurries using a nitrite gassing agent. Nitrous acid, ammonium nitrite and other nitrites have been found effective for gassing operations. This sensitization technology can also be used for explosive emulsions. The nitrite concentrations found useful for producing the desired final density fell within the range of 0.001 to 1% of the total emulsion mass. Nitrous acid was used as a gassing agent; it was added to the slurry during manufacture. It decomposes, forming nitrogen gas, and thus creating hot spots in the blasting agent. Since the decomposition of HNO_2 is relatively slow at temperatures below 65 °C, thiourea is used to accelerate the reaction. The advantages offered by this method are: the reactants used to generate the gas are soluble in the liquid phase, extremely small gas bubbles which are readily trapped are evolved. Furthermore, only small amounts of nitrous acid are used to generate nitrogen gas; this is not only effective for gassing the slurry, but it also helps to stabilize the thickener system. The disadvantage of this technology is that sensitization is done at the manufacturing site, which makes the transportation to the blasting site unsafe. Moreover, the fact that only one component is used as a gassing agent makes the control of the extent of gassing difficult.

Nitrogen gassing has concentrated on the use of sodium nitrite gassing technology. This technology mainly requires the addition of sodium nitrite (NaNO_2) to the explosive emulsion as gas generating agent. A solution of sodium nitrite is added to the explosive emulsion where it reacts with the oxidiser (ammonium nitrate in most cases) to produce nitrogen gas bubbles under acidic pH conditions (Nguyen, 1991; Dlugogorski et al., 2011). The reaction kinetics of NH_4NO_3 and NaNO_2 have been studied previously (Hughes et al., 1958). Despite the complexity of the reaction pathway, the reaction can be simplified into the scheme below.



This gassing technology presents various advantages: NaNO_2 is safe at the levels used; molecular nitrogen is relatively non-reactive due to the presence of a triple bond. However, the reaction between ammonium nitrate and sodium nitrite is slow even at temperatures around 50 °C. At low temperatures, the gassing solution may not react sufficiently quickly to sensitize the explosive emulsion prior to detonation. Thiocyanate was used to catalyze the reaction in order to increase the rate, which only slightly improved the rate of gassing (Williams, 1977). An alternative chemical sensitization method has been developed utilizing the accelerant thiourea (Pare, 1981), which has improved the rate of gassing. In spite of these developments, the method is subject to human factor. In this sense, any excess sodium nitrite could lead to over-gassing of the emulsion since the oxidizer is present in large

quantities in the explosive emulsion. This phenomenon will result in poor blast performance (lower bulk strength).

Cranney and Hansen (2000) describe a technology whereby the gassing solution consisted of a nitrite salt and calcium ion (Ca^{2+}), strontium ion (Sr^{2+}), and mixtures thereof. The gassing reaction occurred as the nitrite ions (NO_2^-) reacted with ammonium ions (NH_4^+) or other substrates in the aqueous phase to produce nitrogen gas. The gassing solution composition ranged from 0.1 to 0.6 wt% of the total explosive emulsion mass on a dry basis; the ions (Ca^{2+} , Sr^{2+} or mixture) present in the nitrate salt solution constituted from about 2.0 to 10.0 wt% of the nitrate solution mass. The ions acted as gassing enhancers. Dramatic improvements in gassing rates, generation of smaller and finely dispersed bubbles less susceptible to coalescence are some of the advantages associated with this technology. However human or equipment errors easily lead to addition of excessive gasser; this makes it difficult to control the extent of the gassing reaction.

Nguyen (1991) described a technology involving mixing sodium nitrite as dry particles with explosive emulsions at low shearing. A process in which the particle size of the dry gassing agent was regulated in order to control the gassing reaction rate was also presented. The findings show that the gas bubble size and distribution in the explosive emulsion could be readily controlled. The particle size range of the dry material should preferably be between 37 μm and 74 μm . It was observed that the reduction in density increases with decreasing particle size. Although the technology provides better control of the gassing rate, its use does not prevent the effect of human factors on the final density of emulsion.

Pienaar et al. (2014) used a hypochlorite gassing system in an attempt to control the rate of the gassing. Basic head groups on the PIBSA (poly-isobutylene succinic anhydride) surfactant have been used successfully in providing additional stability to the emulsion when oxidizer quality is a problem. These surfactants however have drawbacks in that a sodium nitrite gassing system does not provide sensitisation under normal operating conditions. The independence of a sodium hypochlorite gassing system to pH provides a suitable alternative for sensitising an emulsion system without requiring fundamental changes to operating procedures or equipment. Improvement of the gassing rate in emulsions was observed. Gassing rates could be controlled but this resulted in higher final density of the gassed product. Moreover, the use of only one component as gassing agent made it difficult to control the extent of the gassing reaction.

2.5.4 Research issues identified

This topic - chemical sensitisation of explosive emulsions - must come to the forefront of study. Though there are several published works on chemical sensitization technologies, the results from studies are rather rarely published; most are intellectual properties. Most of the technologies reported are based on the reaction between a gassing agent and oxidizer which is AN in most cases (present in large amount in the emulsion); this has been termed a “one-component system”. In this case, any excess of gassing agent leads to an undesired extent of reaction which poses a final density control problem; further, this will result in the explosive releasing insufficient energy to break rocks, or poor blast performance.

It must also be mentioned that, among the works devoted to chemical sensitisation, only a limited number touch on two-component gassing technology, which is the subject of this study, i.e. emulsions in which two gassing agents are added to one or both phases with the sole purpose of generating gas for sensitisation (control of final density). Meanwhile, the two-component reaction in a multiphase system (emulsion) creates new and very promising features for these colloids.

The interest in such explosive emulsions is great because they have numerous potential technological applications in mining, quarrying and excavation industries. In all these applications, their blasting performance is mainly determined by the final density of the sensitised emulsion.

Of all the two-component gassing technologies developed thus far, none has been able to successfully address the problem of extent of density control, also known as over-gassing. These technologies are subject to problems such as high toxicity of gassing components or dissolution of gas produced in the emulsion making the density adjustment difficult.

There is a gap in the literature which allows the introduction of a two-component gassing system with a pre-determined amount of one component which could be added to the emulsion matrix. In this sense, having a pre-determined compound as part of the emulsion composition could greatly reduce the impact of the human factor, allowing better control of final emulsion density, resulting in turn in an effective blast.

Very little is known and published concerning the phase in which the two-component gassing system reacts in the explosive emulsion. An understanding of the underlying gassing mechanism inherent in the two-component system is important; it will possibly shed light on the process of controlling the final emulsion density, which determines its application value.

The main objective of this study is to investigate the possibility of applying a two-component gassing system in chemical sensitisation to control the extent of the gassing reaction and the

final density of explosive emulsions. One component (A), inert to constituents of the explosive emulsion, is added to the fuel phase or to ANS in a pre-determined amount and the other component (B), the “gasser”, will be added to the explosive emulsion when sensitization is required.

CHAPTER 3

FEASIBILITY STUDY

As demonstrated in the literature review, various chemical technologies are used to sensitize explosive emulsions with generation of one of the following gases: CO₂, O₂, N₂, H₂, N₂O and C₂H₂. Agents used to generate the gases are normally soluble in the aqueous phase of the emulsion (Pienaar et al., 2014) where they react at specific pH to produce gas bubbles in the system. The possibility of generating gas in the fuel phase of the emulsion has not been explored in any of the chemical technologies developed for sensitization of explosive emulsions; there is no systematic information on the compatibility (solubility and reactivity) of reactants generating gas that could be used with oils.

The main objective of this chapter is the selection of gassing components that are capable of reacting in the fuel phase and in emulsions to generate gas bubbles for explosive emulsion sensitisation. To achieve the objective, this section is subdivided into two parts:

- Theoretical study which presents the pre-selection process of gassing components from both a list of commonly used gases in chemistry and the common reactions generating them;
- An experimental part which deals with the selection of gassing components for sensitisation of explosive emulsions.

3.1 Theoretical study: pre-selection of gassing components

The main goal of this section is the selection of gassing components which are compatible with components of explosive emulsions in terms of reactivity. The specific objectives are as follows:

- a) To select from a list of commonly used gases in chemistry those that have the potential to be used in sensitization of explosive emulsions. The selection will be done according to the criteria presented in section 3.1.1.
- b) To select chemical components with their common reactions that produce gases selected in a).
- c) To investigate from the literature the reactivity of chemical components selected in b) with explosive emulsion components.

3.1.1 Selection of potential gases for explosive emulsions sensitization

The most common gases presented in chemistry literature have been considered for this study. Table 3.1 presents a list of common inorganic and organic gases at room temperature from which suitable ones for the current study will be selected.

Table 3. 1 List of common organic and inorganic gases at room temperature presented in chemistry literature

| Gas | Chemical formula |
|-------------------------|---------------------------------|
| Nitrogen | N ₂ |
| Hydrogen | H ₂ |
| Carbon dioxide | CO ₂ |
| Oxygen | O ₂ |
| Ozone | O ₃ |
| Ammonia | NH ₃ |
| Carbon monoxide | CO |
| Chlorine | Cl ₂ |
| Fluorine | F ₂ |
| Hydrogen sulphide | H ₂ S |
| Hydrogen chloride | HCl |
| Sulfur hexafluoride | SF ₆ |
| Phosphine | PH ₃ |
| Dichlorodifluoromethane | CF ₂ Cl ₂ |
| Boron trifluoride | BF ₃ |
| Nitric oxide | NO |
| Nitrogen dioxide | NO ₂ |
| Nitrous oxide | N ₂ O |
| Nitrogen trifluoride | NF ₃ |
| Sulfur dioxide | SO ₂ |
| Arsine | AsH ₃ |
| Helium | He |
| Neon | Ne |
| Argon | Ar |
| Xenon | Xe |
| Acetylene | C ₂ H ₂ |
| Ethylene | C ₂ H ₄ |
| Ethane | C ₂ H ₆ |
| Methane | CH ₄ |
| Propane | C ₃ H ₈ |

To be selected as a possible alternative for explosive emulsion sensitization, the gas must meet the following criteria:

- It should not pose major safety and toxicity concerns;
- It should not have major adverse effects on the environment;
- It should not react with or dissolve in emulsion components because of possible interference with the desired reaction and adverse effects on the overall process;
- It should be generated from a chemical reaction that occurs at temperatures between 0 – 50°C that will make the practical implementation of the technology cost effective in the AEL Mining Services SA context. Should the reaction require higher or lower temperatures, explosive emulsions will have to be heated or cooled before sensitization, resulting in extra costs;

- The chemical compounds reacting to generate the gas should not be gases at room temperature because they might sensitize explosive emulsions at an undesired time.

Application of the above criteria to the list of gases in table 3.1 has sensibly reduced the number of gases: even though hydrogen has been used to sensitize explosive emulsions (Tomic, 1973), safety concerns attached to its use have prevented further development of the technology (Dlugogorski et al., 2011). The use of CO₂ to sensitize emulsion explosives poses a problem: its solubility in blasting agents (aqueous phase of the emulsion) changes with pressure and the agent's composition; this makes it difficult to adjust the emulsion density to desired values, especially for deep boreholes (Dlugogorski et al., 2011). O₃ will not be considered for this study since the methods used to produce it (corona discharge, ultraviolet light, cold plasma, etc.) require the use of oxygen (O'Donnell et al., 2012) which is a gas at room temperature. NH₃ gas will not be considered for this study because it is produced from N₂ and H₂ (Kotz et al., 2012) which are gases at room temperature. Mixing gases with the emulsion during preparation will result in sensitization at a time when it is not required. CO will not be considered for investigations because of its high toxicity (Hanley & Patel, 2017). Cl₂ and F₂ will not be considered because of their high toxicity and strong oxidizing nature that makes them react with flammable materials, and the mixture of chlorine with fuels may cause an explosion (National Center for Biotechnology, 2017). H₂S will not be considered for this study because of its high toxicity (Occupational Safety and Health [OSHA], n.d.). HCl (hydrogen chloride) upon contact with water (an emulsion component) forms hydrochloric acid (Perumalla & Sun, 2012) which is a liquid. This makes it unsuitable for this study since in a sensitized emulsion the gas generated is to remain in the gaseous state. SF₆ is not suitable for this study because of its strong adverse effects on the environment (Malik, 2009). PH₃ gas will not be considered for this study because of its high toxicity (US National Library of Medicine, n.d.). CF₂Cl₂ will not be considered for this study because of its strong adverse effects on the environment (National Center for Biotechnology Information, n.d.). NO and NO₂ are NO_x gases which have severe adverse effects on the atmosphere (US Environmental Protection Agency, 1999). For this reason, these gases will not be considered for this study. Just like NO_x gases, SO₂ will not be considered because of its strong adverse effects on the environment (US Environmental Protection Agency, 1999). BF₃ reacts with water which is one of the components of the explosive emulsion to produce fluoroboric acid (Wamser, 1951). This makes it unsuitable for the current study. When heated NF₃ emits toxic fumes of fluoride and has the potential to explosively react with fuels (Urban & Bretherick, 2016). For these reasons, it will not be considered for this project. AsH₃ gas is extremely flammable, can react vigorously with oxidizing materials, and is extremely toxic (National Center for Biotechnology, 2017). This makes it unsuitable for this project. He, Ne, Xe and Ar are noble gases and cannot be used for the current study because they are

produced by fractional distillation (Schrobilgen, 2017) and not chemical reactions. The technology being developed in this study involves chemical reactions, which is why He, Ne, Xe and Ar are not suitable. C₃H₈ gas is produced from natural gas processing or crude oil refinement (Propane Education and Research Council, n.d.). This makes it unsuitable for the current study.

For the reasons mentioned above, only the gases presented in table 3.2 have been found to be possible options for explosive emulsions sensitization and have been selected for further investigations:

Table 3. 2 List of gases selected for further investigations

| Gas | Chemical formula |
|---------------|-------------------------------|
| Nitrogen | N ₂ |
| Oxygen | O ₂ |
| Nitrous oxide | N ₂ O |
| Acetylene | C ₂ H ₂ |
| Ethylene | C ₂ H ₄ |
| Ethane | C ₂ H ₆ |
| Methane | CH ₄ |

3.1.2 Selection of suitable gassing components for explosive emulsions sensitization: compatibility study

To be selected as possible gassing components for explosive emulsion sensitization, the components must adhere to the following criteria:

- There must be two of them (*two-component system*) designated as components (A) and (B) reacting to generate gas. Gases produced from decomposition reactions (one component) will not be considered;
- Gassing components should not be gases since they have the potential to sensitize the emulsion at an undesired time;
- Both gassing components (A) and (B) should not react with the explosive emulsion components to avoid any interference with the main reaction.

Components adhering to a) and b) for which there is no information on reactivity with aqueous phase will be selected for experimental investigation of criterion c).

Since to the best of my knowledge, no one has considered gassing in the fuel phase, there is no systematic information on the compatibility (in terms of reactivity) between the fuel phase and potential gassing components. Therefore, the theoretical part will investigate only the compatibility between gassing components and aqueous phase.

The most common reaction-producing gases shortlisted (Table 3.2) are discussed (based on the above criteria) below with the aim of selecting components that could be used as gassing agents for the experimental part.

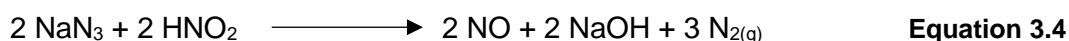
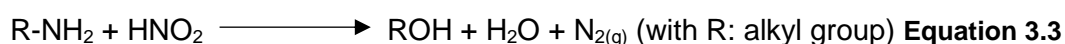
a. Nitrogen gas

- Nitrogen gas can be produced from the reaction between sodium nitrite and ammonium nitrate as shown in Equation 3.1 (Rojey, 1997).



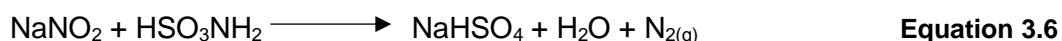
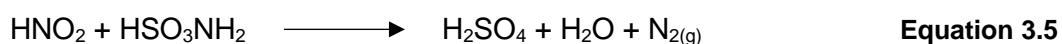
Despite the fact that the reaction above is used in most current gassing techniques for explosive emulsions, it cannot be considered for this study because NaNO_2 reacts with the oxidizer.

- Nitric acid reacts with ammonium nitrate as shown in Equation 3.2 (Thornley & Udy, 1975), with amines as shown in equation 3.3 (Clark, 2004) and with sodium azide as shown in equation 3.4 (US Committee on Prudent Practices, 1995) to produce nitrogen as one of the products.



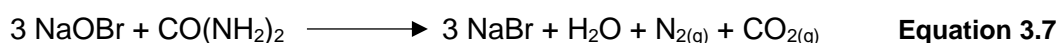
The components involved in the reactions above will not be considered since nitric acid reacts with the oxidizer which violates one of the selection criteria for gassing components.

- Sulfamic acid reacts with nitrous acid according to equation 3.5 (Hughes, 1967) and sodium nitrite as shown in equation 3.6 (Kotz et al., 2012), yielding nitrogen gas as one of the products.



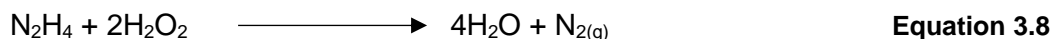
The use of reactants in presented in equations 3.5 and 3.6 shown above is not suitable for this study since HNO_2 and NaNO_2 both react with the oxidizer (Rojey, 1997; Thornley & Udy, 1975)

- Sodium hypobromite reacts with urea and other acid amides to producing N_2 and CO_2 (Menaul, 1921), as shown in equation 3.7.



Components in equation 3.7 will not be considered for this study because NaOBr is capable of reacting with the oxidizer (Dlugogorski et al., 2011). Another disadvantage is the generation of carbon dioxide which is known to make the control of the extent of gassing difficult (Dlugogorski et al., 2011).

- Hydrazine reacts with hydrogen peroxide to generate nitrogen gas as one of the products, as shown in equation 3.8 (Wellman et al., 1976).

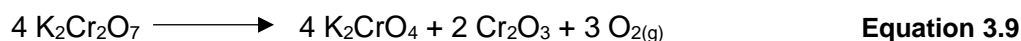


Gordon (1949) studied the reaction represented by equation 3.8 and found that it was very slow under normal conditions. Wellman et al. (1976) were able to increase the reaction rate by using copper as a catalyst. Applying the reaction above to this study will require the use of copper. The drawback involved is that copper reacts with ammonium nitrate (Phillips & Hale, 1943). The other disadvantage is associated with the use of hydrazine which is highly toxic and potentially explosive (Schmidt, 2001).

From the literature investigation conducted on nitrogen gas generation, it was concluded that the common reactions presented above used to generate nitrogen gas are not suitable for this study because most of them involve a component capable of reacting with the oxidizer.

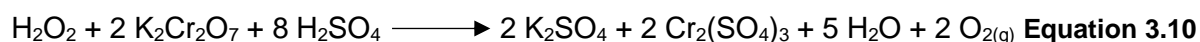
b. Oxygen

- Upon being heated strongly, potassium dichromate decomposes with the evolution of oxygen gas as shown in equation 3.9 (Kumar De, 2007).



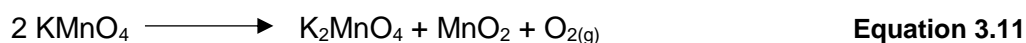
The reaction presented in equation 3.9 is not suitable for the present study since the system only involves one component, but the goal of the study is to develop a two-component system.

- In aqueous medium, potassium dichromate reacts with H_2O_2 in acidic pH to generate oxygen gas as one of the products as shown in equation 3.10 (Robert, 2013).



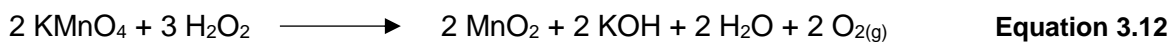
No information about the compatibility of the reactants involved in reaction 3.10 with the explosive emulsions components has been found in the literature. Experimental studies need to be conducted to test the compatibility of reactants in equation 3.10 with explosive emulsion components.

- Solid potassium permanganate decomposes upon heating to produce oxygen gas as one of the products as shown in 3.11 (Robert, 2013).



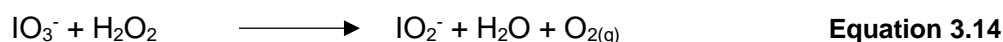
The reactant in equation 3.11 will not be considered for this study since there is only one component involved.

- Potassium permanganate crystals react with hydrogen peroxide to produce oxygen gas with large amounts of steam, and leave black residues of manganese oxide as shown in equation 3.12 (Bowman, 1949). In aqueous solutions, KMnO_4 also reacts with H_2O_2 in acidic media to produce oxygen gas as shown in equation 3.13 (Chang, 2007).



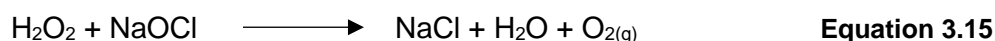
Reactions presented in equations 3.12 and 3.13 will not be investigated because KMnO_4 is known to react with ammonium nitrate and form an explosive mixture (Pohanish & Greene, 2003).

- Potassium iodate reacts with hydrogen peroxide to give off oxygen gas according to equation 3.14 (Bray & Liebhafsky, 1931).



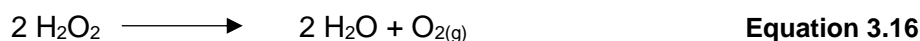
However, there is no information in the literature on the compatibility of the reactants above with the explosive emulsion components. Compatibility studies need to be conducted for reactants in equation 3.14.

- Sodium hypochlorite reacts with hydrogen peroxide to produce oxygen gas as shown in equation 3.15 (Lontsi et al., 2014).



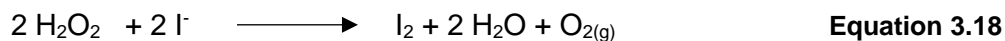
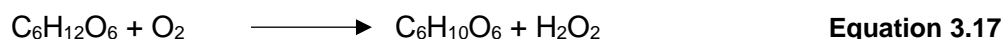
The reaction in equation 3.15 is not suitable for the current study since NaOCl is capable of reacting with ammonium nitrate (Pienaar et al., 2014).

- Hydrogen peroxide is thermodynamically unstable. It undergoes spontaneous decomposition, generating oxygen as one of the products, as shown in equation 3.16 (Dalmázio et al., 2008). The reaction can be accelerated by catalase enzyme, platinum black, Fe^{2+} , Br^- , I^- , MnO_2 , etc (Hansen, 1996). An increase in temperature and/or pH also enhances the decomposition process (Yazici & Deveci, 2010)



The reaction presented in equation 3.16 will not be considered for this study since the system involves one component. Even though a catalyst may be used, it does not affect the stoichiometry of the reaction. The main goal of this study is to develop a two-component system in which gassing components involved *react stoichiometrically*.

- The test for urinary glucose relies on a two-step process represented by equations 3.17 and 3.18 (Robinson, 2016). The reaction presented in equation 3.17 generates oxygen as one of the products.



Components in equation 3.18 will be considered for experimental investigations since no information has been found in the literature about the compatibility of the compounds involved in these reactions with components of explosive emulsions.

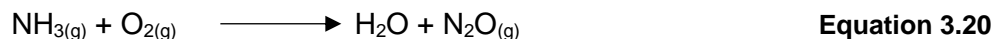
c. Nitrous oxide

- Urea reacts with nitric acid and sulfuric acid to generate nitrous oxide as one of the products as shown in equation 3.19 (Hatabu et al., 1983).



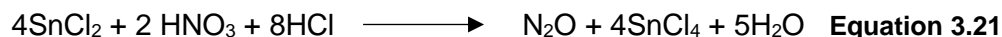
The reaction presented in equation 3.19 requires temperatures above 60 °C in order to proceed (Hatabu et al., 1983). The reaction generates CO₂ which poses density adjustment problems because of its solubility in blasting agents (Dlugogorski et al., 2011). For the reasons noted above, the components involved in this reaction will not be considered for this study.

- Ammonia reacts with oxygen to generate nitrous oxide as one of the products as shown in equation 3.20 (Kobe & Hosman, 1948).



The components in equation 3.20 are both gases at room temperature, which will make their handling difficult. Another disadvantage is that the reaction has to be carried out under very specific conditions so that N₂O is one of the main reaction products (Kobe & Hosman, 1948). These reasons make reactants in equation 3.20 unsuitable for this study.

- Tin (II) chloride reacts with nitric acid and hydrochloric acid to produce nitrous oxide as shown in equation 3.21 (Current, 2008).



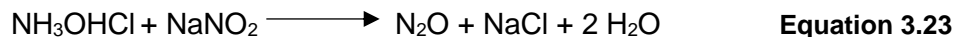
SnCl₄ generated in equation 3.21 forms irritating smoke, and the strong acids used in that reaction have the potential to hydrolyse emulsifiers. This makes the reaction presented in equation 3.21 unsuitable for this project.

- Hyponitrous acid decomposes to N₂O and H₂O as shown in equation 3.22 (Wiberg et al., 2001)



Equation 3.22 only involves one component, which is why the reaction will not be considered for this study.

- Hydroxylammonium chloride reacts with sodium nitrite to generate nitrous oxide as one of the products as shown in equation 3.23 (Current, 2008).

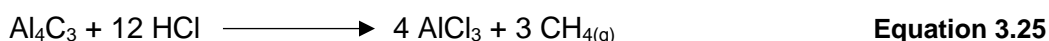
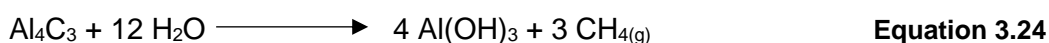


NaNO_2 is capable of reacting with ammonium nitrate. This makes components in equation 3.23 unsuitable for the current study.

No suitable components generating N_2O to sensitize explosive emulsions has been found in the literature. Therefore, N_2O has been rejected as potential gas for sensitization of explosive emulsions in the context of the current study.

d. Methane

- Aluminium carbide reacts with water as shown in equation 3.24 (Ebbing & Gammon, 2010) and hydrochloric acid as shown in equation 3.25 (Kotz et al., 2012) with the evolution of methane gas.

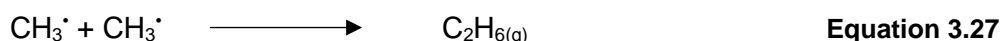
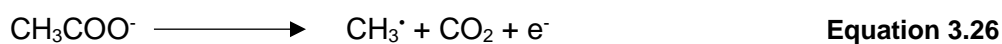


The reactants involved in the reactions above are not suitable for the current study since Al_4C_3 reacts with water, which is a component of the explosive emulsion.

Methane gas will not be considered for this project because the methods used to produce it are not suitable for the explosive emulsion sensitization technology that is being developed.

e. Ethane

- Ethane gas can be obtained as a byproduct of petroleum refining (Solomons & Fryhle, 2009). This method of production is not suitable for the current study since it does not involve chemical reactions.
- Ethane gas can also be produced by a method known as Kolbe electrolysis in which an aqueous solution of an acetate salt is electrolyzed. Oxidation of acetate occurs at the anode accompanied with generation of carbon dioxide and methyl radicals which combine to produce ethane gas. The process can be summarized by equations 3.26 and 3.27 (Holze, 2009).



This method of producing ethane gas will not be considered for this study since it only involves one component.

- Ethylmagnesium bromide, a Grignard reagent, reacts with water to produce ethane gas as one of the products, as shown in equation 3.28 (Parsonage, 2001).

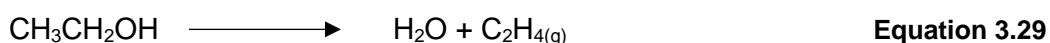


Reactants involved in equation 3.28 are not suitable for the current project since ethylmagnesium bromide reacts with one of the explosive emulsion components to produce the gas.

None of the components involved in the generation of ethane was found to be suitable for this study. Ethane will not be considered as a potential gas for explosive emulsion sensitization.

f. Ethylene

- Ethylene gas is produced by the dehydration of ethanol by heating it in the presence of sulfuric acid or passing it over heated aluminium oxide powder, as shown in equation 3.29 (Infratec Solutions, 2013).



Equation 3.28 only involves one component which is why it will not be considered for this study.

Ethylene is not a suitable gas for explosive emulsion sensitization in the context of the current study.

g. Acetylene

- Calcium carbide reacts with water to produce acetylene as shown equation 3.30 (Malone & Dolter, 2008) presented below:



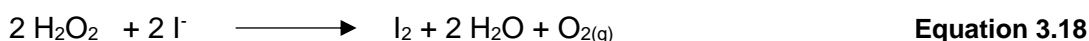
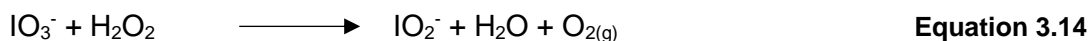
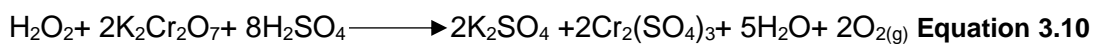
The production of acetylene involves reaction of calcium carbide with one of the explosive emulsion components which makes this reaction unsuitable for the present study.

Acetylene gas is not a suitable alternative because one of the components used to produce it violates one of the selection criteria.

3.1.3 Summary of theoretical study

This research investigated the compatibility of potential gassing components with the aqueous phase of the explosive emulsion based on the available information in the literature. Components to be selected for the experimental part had to adhere to the following criteria: first, there had to be two of them only, reacting to generate gas. **Second**, components should

not be gases. Third, components should not react with the emulsion. Components adhering to the first and second criteria with no information available about the third criteria were tested experimentally. It was shown that only components in the reactions below are suitable for experimental study with a view to selecting the best gassing components for explosive emulsions sensitization.



The experimental studies are presented in the following section.

3.2 Experimental study

The main goal of the experimental study was the selection of gassing components which are compatible with explosive emulsion components in terms of both solubility and reactivity.

The selection process was done according to the criteria outlined below:

- Gassing components must be capable of reacting in the fuel phase.
- One or both gassing components had to be totally or partially soluble in the fuel phase or could possibly be dispersed and suspended in it. This is to ensure that the gassing reaction can be produced in the fuel phase. Should it happen that only one of the components dissolves/disperses in the fuel phases, it will be selected as component (A) (to be added to the fuel before the emulsification process) and the other as component (B) (to be added to the emulsion when sensitization is required). In the event that both components are soluble in the fuel phase, the component exhibiting higher stability at temperatures at which emulsions are manufactured will be preferred as component (A).
- Both gassing components (A) and (B) should not react with the fuel phase. The reaction of any of the components with the fuel phase of the emulsion will possibly have undesired effects on the overall process.
- Both gassing components (A) and (B) should not react with the oxidiser phase in the emulsion matrix for the same reason mentioned above.

To achieve the main objective of this section, the following specific objectives were defined:

- To study the compatibility (solubility and reactivity) of selected gassing components preselected from the theoretical study with the fuel phase;
- To study the reactivity of preselected gassing components with the emulsions aqueous phase;
- To study the reactivity of preselected gassing components *in* the fuel phases;
- To study the reactivity of gassing components in emulsions;

- To select the components to be used as (A) or (B) based on criteria presented above.

It is worth mentioning that detailed information on chemicals used for these experiments is presented in section 4.1.

3.2.1 Solubility/dispersion and suspension in the fuel phases

The pre-selection process (theoretical study) resulted in the choice of potential gassing components which are mineral compounds. It is known that mineral compounds (polar) are not soluble in standard oils (apolar). The fuel phases used for this study contain a wide variety of different molecular species (surfactants, etc.) which confer on them a certain degree of polarity, as shown in Masalova et al. (2013). In this sense one could expect to dissolve, at least partially, some mineral compounds in these oils. The aim of this section is to try to dissolve or both disperse and suspend (for insoluble solid particles) the preselected gassing components in the fuel phases. The rationale behind this was to maximize the specific surface area of particles with a view to obtaining a high gassing reaction rate.

Since only visual observation was used as a means of confirming whether dissolution or dispersion occurred, any significant disappearance (total or partial) of the component added to the fuel phase after stirring, without any noticeable sign of reaction, was considered as total or partial dissolution respectively.

It is known that KI is partially soluble in ethanol, acetone and glycerol (O'Neil, 2001), and can be dispersed in lipids (Draget et al., 2011) which are organic media whilst KIO_3 does not dissolve in organic solvents, and $K_2Cr_2O_7$ does not dissolve in any of the compounds previously mentioned (Weast, 1986). It is based on the information that solubility experiments were first conducted for KI/ H_2O_2 components, as they appear to present more ability to dissolve in organic media than the others, and thus could constitute suitable candidates for this work.

A Mettler Toledo PB303S-2T (Figure 4.1) laboratory balance was used for weighing operations. The dissolution or dispersion was carried out in a beaker. A Silverson L4RT high speed mixer (Figure 4.4) was used to attempt to disperse or dissolve components in oils.

The solubility or dispersion/suspension of KI in the fuel phase was investigated according to the following procedure:

- 100 g of fuel was placed in a beaker. Three fuel phases were provided by AEL Mining Services SA and used for the investigations: F800, Bullfinch and black oils (R602/45).
- 1% by mass of KI was added to the fuel phase.

- Using the up/down control button of the Silverson L4RT mixer (Figure 4.4), the mixing head assembly was placed inside the beaker. It was ensured that the mixing head did not touch the bottom of the beaker.
- The speed regulator of the mixer (Figure 4.4) was used to adjust the speed to 2500 rpm.
- The mixture was stirred at 2500 rpm for 5 minutes and it was ensured that no solid particles remained stuck to the mixer head assembly.
- The mixture was left to rest for 10 minutes and visual observations were made.

The observations made whilst conducting these experiments are shown in Figure 3.1.

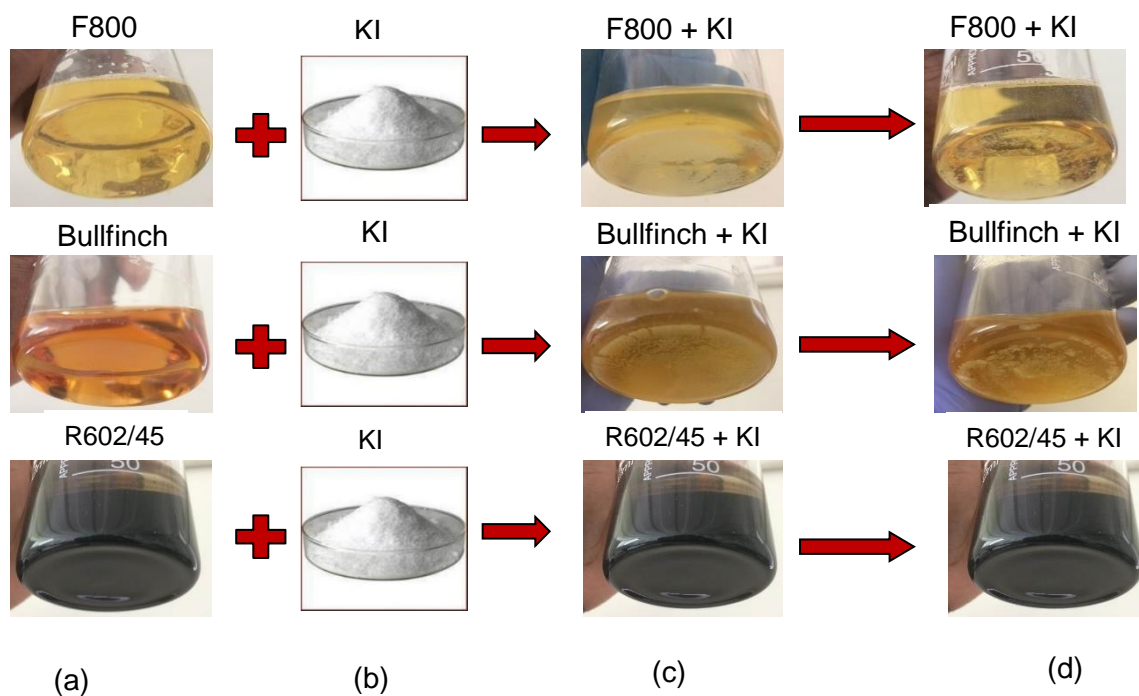


Figure 3. 1 Solubility/dispersion and suspension of KI in Oils; (a) Fuel phases (F800, Bullfinch and R602/45), (b): KI, (c): KI/fuel mixture at $t = 0$ (before stirring), (d): KI/fuel mixture, at $t = 10$ min (10 min after stirring)

Figure 3.1 showed that in contrast to the KI/fuel mixture without stirring (Figure 3.1 c), agitation of the mixture led to a significant change in the stability of the dispersion. It could be seen that 10 minutes after stirring, part of the KI was dispersed and suspended in the fuel phase, whereas the other part settled at the bottom of the beaker (Figure 3.1 d). This was especially evident for F800 and Bullfinch; due to the colour of R602/45 fuel phase, no visual observation in terms of dispersion or suspension could be made. It can be assumed that during mixing, part of KI was dissolved in the oil due to the relatively high polarity of the oils used (Masalova et al, 2013). In this sense, the size of some particles could be reduced,

allowing them to be suspended instead of settling. Furthermore, since the fuel phase contains surfactants, the latter could adsorb onto the particle surface thus further stabilizing the suspension. The observations made for F800 and Bullfinch led to the conclusion that KI was partially dissolved, dispersed and suspended in the fuel phases.

From the results obtained for the solubility of KI in relatively polar oils, it seems reasonable to assume that no improved results can be expected when using $K_2Cr_2O_7$ and KIO_3 ; the latter are more polar than KI. Experimental compatibility in terms of solubility studies was therefore not conducted for these two components.

It is worth mentioning that solubility/dispersion studies were not conducted for H_2O_2 for the following reasons: first, H_2O_2 is an aqueous phase; it is not expected to dissolve in the fuel phase. Second, the fuel phases to be used already contain surfactants, and emulsions could form during the mixing, as mentioned in Lownds (1995).

3.2.2 Reaction between KI and H_2O_2

Before any experimental compatibility study in terms of reactivity was conducted, an experiment was done to confirm the reactivity of KI and H_2O_2 . An Erlenmeyer flask was used as the reaction vessel. Volumetric cylinders were used to measure the amount of solution required to carry out the experiment. A Mettler Toledo PB303S-2T laboratory balance, shown in Figure 4.4, was used to weigh the KI. Stirring was done on a magnetic stirring stove using a magnetic stirrer bar.

The experiment was carried out at room temperature (25 °C) according to the following procedure:

- 20 ml of aqueous solution potassium iodide containing 1 g of KI was transferred into a 100 ml Erlenmeyer flask
- 10 ml of aqueous solution of hydrogen peroxide (30 wt%) was added to the solution while stirring. The observation time was 1 minute
- Visual observations (color and temperature change, precipitate formation, gas evolution) were used as indicators of reaction occurrence. Temperature changes were observed using a thermometer.

The findings from this experiment are presented in Figure 3. 2

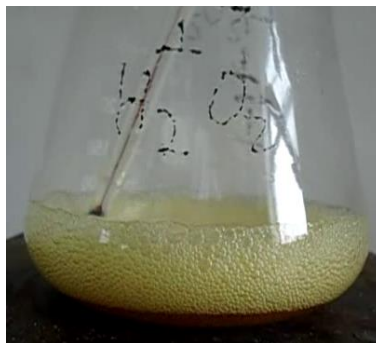


Figure 3. 2 Hydrogen peroxide + Potassium iodide (35 seconds after start of stirring)

It was observed that the Erlenmeyer flask contents turned yellow 5 seconds after stirring had started; this was followed by bubble formation 3 seconds later. The yellow colour was probably due to the presence of iodine in solution (Hildebrand, 1908), and the gas bubbles due to oxygen. This is in line with results presented in Robinson (2016). At the end of the time of observation, the temperature had increased by 5 °C due to the exothermic nature of the reaction.

3.2.3 Reactivity with fuel phases

○ Potassium iodide

The reactivity study was done according to the same procedure as solubility study presented in section 3.2.1. It was observed as shown in Figure 3.1 that KI did not react with the fuel phases considered for these investigations since no temperature, colour change or gas evolution was observed. A slight temperature increase (2 °C) was observed; this was the result of mixing and not chemical reaction.

○ Hydrogen peroxide

An experiment was conducted to study the reactivity of H₂O₂ with the fuel phase (F800 in this case). A beaker was used as reaction vessel. The amounts of H₂O₂ and fuels used for this experiment were measured with a graduated beaker.

Experiments run at room temperature (25 °C) were done according to the following procedure:

- 30 ml of fuel phase (F800) was placed in a beaker
- 20 ml of H₂O₂ was placed in another beaker then poured slowly into the first.
- The reactivity between H₂O₂ and the fuel phase was observed in terms of colour change, temperature change, gas evolution or precipitate formation. This was done for a period of 6 hours.

It is worth noting that the mixture was not stirred since the fuel phase contains surfactants and emulsions might have formed whilst stirring. The observations made are shown in Figure 3.3.

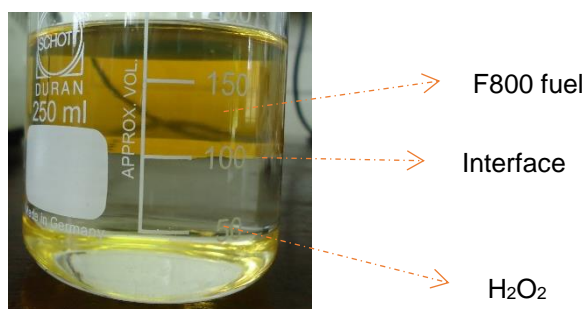


Figure 3. 3 Test of reactivity between H₂O₂ and F800 fuel phase (2 hours after start of experiment)

It was observed that there were 2 layers that formed: a layer of H₂O₂ below and a layer of fuel above. Interestingly, even after 6 hours, no temperature or colour change, no gas evolution, and no precipitate formation were observed at the interface between the two layers where the reaction was expected to occur. This observation led to the conclusion that no reaction occurred between H₂O₂ and the fuel phase.

3.2.4 Reactivity with Ammonium nitrate

o Potassium iodide

The reactivity between KI and AN was also investigated. The reaction vessel was a beaker. Weighing operations were performed using a Metter Toledo PB303S-2T laboratory balance (Figure 4.1). The study of the compatibility of KI with ammonium nitrate was done according to the following procedure:

- o 10 g of KI was added to 90 g of water. The mixture was stirred manually with a spatula to dissolve KI.
- o 20 ml of AN aqueous solution (60 wt%) was placed in a beaker.
- o 10 ml of aqueous solution of KI was measured with a volumetric cylinder and added to the AN solution
- o The mixture was stirred at room temperature (25 °C) on a magnetic stirring stove using a magnetic stirrer bar for 20 minutes and observed for any changes in temperature, colour, precipitate formation or gas evolution.

The findings are shown in Figure 3.4.

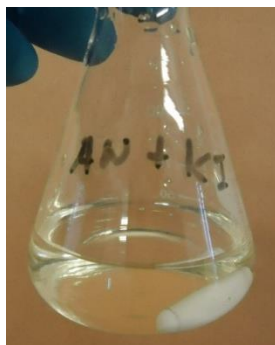


Figure 3. 4 Ammonium nitrate + potassium iodide 10 minutes after stirring

No temperature or colour change, precipitation formation or gas evolution was observed during the experiment, not even two 2 hours after. This led to the conclusion that KI does not react with AN.

- **Hydrogen Peroxide**

An experiment was conducted to test the reactivity of AN and H_2O_2 . A beaker was used as reaction vessel. Weighing operations were performed using a a Metter Toledo PB303S-2T laboratory balance. A pipette was used to measure the required volume of H_2O_2 .

To investigate the compatibility of H_2O_2 with AN, an experiment was conducted according to the following procedure:

- 60 wt% AN was prepared by adding 60 g of AN to 40 g of water in a beaker. The mixture was stirred with a spatula to dissolve the AN.
- 20 ml of the aqueous solution of AN (60 wt%) was transferred into a beaker.
- 20 ml of aqueous solution of H_2O_2 (30 wt%) was added to the AN solution with a pipette.
- The mixture was stirred a magnetic stirring stove using a magnetic stirrer bar at room temperature (25 °C) for 20 minutes and observed visually for any changes in temperature, colour, precipitate formation or gas evolution for 2 hours.

The findings are shown in Figure 3.5.



Figure 3. 5 Ammonium nitrate + hydrogen peroxide 20 minutes after stirring

No visual changes in terms of temperature or colour, precipitate formation or gas evolution were observed during the mixing operation. This led to the conclusion that H_2O_2 does not react with AN.

3.2.5 Reactivity of gassing components (KI and H_2O_2) in the fuel phase

Since the gassing reaction in the fuel phase is under consideration, an experiment was conducted to test the reactivity of gassing components in the fuel phase. Test tubes were used as reaction vessels, and KI was weighed with a Mettler Toledo PB303S-2T laboratory balance; the required fuels and peroxide volumes were measured with a pipette. Mixing operations were performed using the Silverson L4RT mixer described in section 4.2.2.

The investigation was done according to the following procedure:

- 99 g of fuel was placed in a beaker.
- 1 g of KI was added to the fuel phase.
- Using the up/down control button of the Silverson L4RT mixer (Figure 4.4), the mixing head assembly was placed inside the beaker. It was ensured that the mixing head did not touch the bottom of the beaker.
- The speed regulator was used to adjust the speed to 2500 rpm.
- The beaker contents were stirred at 2500 rpm for 5 minutes.
- 4 ml of the fuel-KI mixture were placed in a test tube.
- 1 ml of H_2O_2 (30 wt%) was added to the fuel-KI mixture.
- The experiment was conducted at room temperature (25 °C). The test tube contents were observed visually for any change in colour, precipitate formation, and gas evolution. Temperature changes were observed with a thermometer.

The observations made are shown in Figure 3.6.

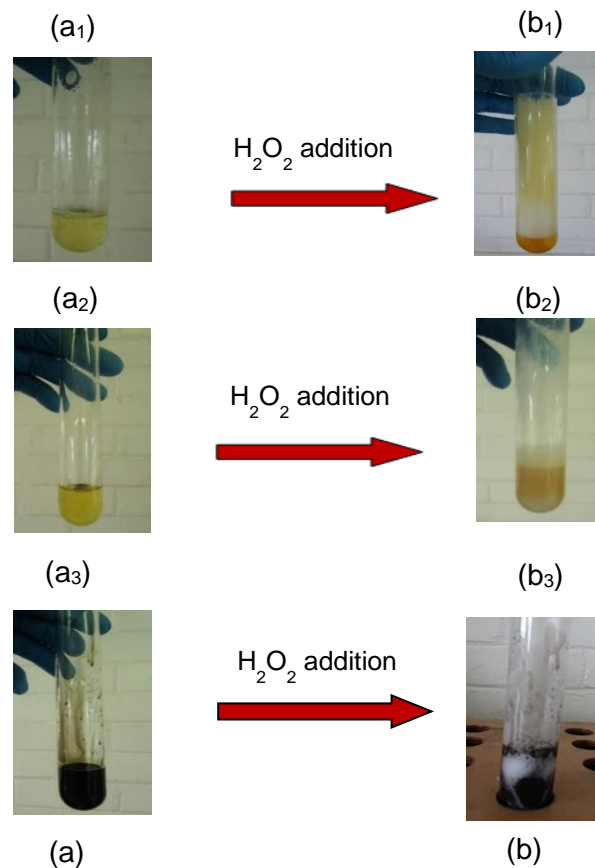


Figure 3. 6 Gassing in fuel phase (a): Fuel phase + KI, (b): Fuel phase + KI + H₂O₂

After peroxide addition to the different fuel phases containing KI, it was observed that gas bubbles had formed. In F800, gas evolution started right after peroxide addition. The bubbles formed in F800 as shown in Figure 3.5 (b₁) were very stable due to the presence of bubble stabilizers. In Bullfinch, gas bubbles were observed 10 seconds after peroxide addition. In R602/45 fuel, gassing started immediately after peroxide addition. From these observations it seems reasonable to assume that KI and H₂O₂ were reacting in the fuel phase.

3.2.6 Reactivity of gassing components (KI and H₂O₂) in explosive emulsions

The study presented in section 3.2.5 showed that KI is probably reacting with H₂O₂ in different fuel phases to generate gas. This section investigated the reactivity between KI and H₂O₂ in explosive emulsions. Emulsions were prepared and sensitized according to the procedures described in sections 4.2.2 and 4.2.3. The selected H₂O₂ concentration was 3 wt% of the total emulsion mass, which falls within the gassing agent concentration range for most applications (Vermaak, 2011; Lownds, 1995). The KI concentration used was 0.1 wt%, which should completely be consumed by H₂O₂ according to the stoichiometry of the reaction between KI and H₂O₂. The results obtained after five minutes of observation are shown in Figure 3.7.

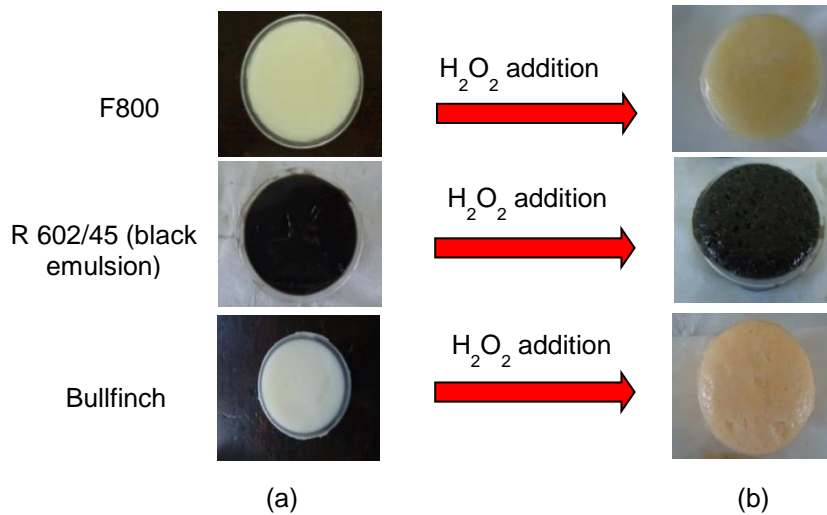


Figure 3. 7 Sensitization of emulsions with new two-component system. (a) Emulsion + 0,1 wt% KI (b) Gassed Emulsion

Figure 3.7 showed that in contrast to KI/explosive emulsion mixture without H_2O_2 , (Figure 3.7 a), addition of H_2O_2 led to a significant change in both the colour and density of the emulsion. It was observed that emulsions turned yellow immediately after stirring. This was especially evident for F800 and Bullfinch based emulsions. This could be due to the formation of iodine which is yellow in diluted solutions (Hildebrand & Glasgow, 1908). On the other hand the cup contents overflowed five minutes after peroxide addition as a result of a formation of a gaseous product. It seems reasonable to assume that gas bubbles due to oxygen gas formation from the reaction between KI and H_2O_2 are responsible for this observation. These observations prove that it is possible to sensitize explosive emulsions with the KI/ H_2O_2 component system.

The reaction mechanism between KI and H_2O_2 in explosive emulsions will be further discussed in section 5.2.

From the experimental studies conducted on the compatibility of preselected gassing components with explosive emulsion components, the following conclusions are drawn:

- KI is suitable for use as component (A): it partially dissolves and disperses/suspends in the fuel phases and does not react with any of the emulsion components.
- H_2O_2 can be used as component (B): it reacts with KI in the fuel phases and in emulsions to generate gas and does not react with any of the emulsion components. It cannot be used as component (A) because it does not dissolve or disperse in the fuel phases.

3.2.7 Summary and conclusion of feasibility study

The feasibility study consisted of two parts: theoretical and experimental investigations which were conducted with the aim of selecting gassing components that are capable of reacting in the fuel phase to generate gas bubbles for explosive emulsion sensitisation. The theoretical investigation allowed preselection of only the pairs KI/H₂O₂, KIO₃/H₂O₂, K₂Cr₂O₇/H₂O₂ as potential gassing agents for explosive emulsion sensitisation. The preselected gassing components were tested experimentally according to the criteria defined in section 3.2. The following tests were done to verify adherence to the defined selection criteria: solubility or dispersion/suspension of gassing components in the fuel phase, reactivity of gassing components with both the fuel or aqueous phases, reactivity of gassing components in the fuel phases and in emulsions. It was found that: first, although the oils used in this study are highly polar, KI is only partially dissolved, dispersed and suspended in the fuel phases. In this sense, it seemed reasonable to assume that no improved results could be expected when using K₂Cr₂O₇ or KIO₃; the latter are more polar than KI. Therefore, experimental compatibility in terms of solubility studies was not conducted for these two components. **Second**, the gassing components KI/H₂O₂ reacted with neither the aqueous phase nor the fuel phases. **Third**, the gassing components KI/H₂O₂ reacted in the fuel phases and in emulsions generating gas, making it possible to sensitize explosive emulsions. It was concluded that KI and H₂O₂ are suitable components for explosive emulsion sensitisation. Moreover, the research showed that KI is suitable for use as component (A): to be dissolved/dispersed in a pre-determined amount in fuels or ANS prior to emulsion manufacturing; H₂O₂ as component (B): to be added to the explosive emulsion when sensitization is required.

CHAPTER FOUR

EXPERIMENTAL PROCEDURE

This chapter gives a description of the materials used, steps that were followed to carry out experiments, and instruments used for various measurements. Highly concentrated water-in-oil emulsions were used for this study. The prepared emulsions consisted of a dispersion of an aqueous solution of AN in fuel, a phase containing surface active agents which stabilize emulsions. The experimental procedure covered the following aspect of this study: materials and matrix of samples, methodology and instrumentation for preparation of emulsions, gassing in emulsions, study of phase in which gassing reaction occurs, investigation of pH effects on gassing rate and final emulsion density, and study of blasting characteristics.

4.1 Materials

4.1.1 Fuel phase

Three different fuel phases used to manufacture the emulsions were provided by AEL Mining Services SA namely: F800, Bullfinch and R602/45; they are mixtures of various hydrocarbon oils and surfactants for emulsion stabilization. For privacy reasons, the exact compositions could not be disclosed. It is worth mentioning that Masalova et al. (2013) demonstrated that unlike conventional oils that are non-polar, industrial oils used in this study are relatively polar for the following reasons: first, the fuel phases contain a wide variety of different molecular species. Second, the fuel phases contain surfactants which lower the surface tension of the oils.

4.1.2 Aqueous phase

Industrial grade ammonium nitrate provided by AEL Mining Services SA was used in the aqueous phase preparation. Except for the emulsions used for experiments involving blasting, the aqueous phase of the emulsions that were prepared was an aqueous solution of 60% ammonium nitrate by mass. Experiments were carried out at temperatures below 60 °C. At these temperatures, 60 wt% aqueous ammonium nitrate remains in saturated state (Masalova et al., 2013). The selected concentration of the aqueous phase was 90 wt%. For blasting experiments, AEL Mining Services SA commercial formulations were used and for confidentiality reasons the compositions could not be disclosed.

4.1.3 Gassing agents

Gassing in oils and emulsions required two components and from the feasibility study, the following were selected: hydrogen peroxide (H₂O₂) and potassium iodide (KI). For this project

H₂O₂ solution (30 wt%) and potassium iodide powder (99.5% purity) purchased from Merck Laboratories were used.

4.1.4 pH adjustments

To adjust the pH to the desired value, acetic acid (assay ≥ 80%) purchased from Sigma Aldrich and/or sodium acetate (assay ≥ 99.0%) from Merck Laboratories were used.

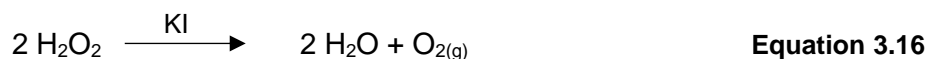
All chemicals presented were used as received without further modification.

4.2 Instrumentation and methodology

4.2.1 Determination of gassing mechanism (reaction)

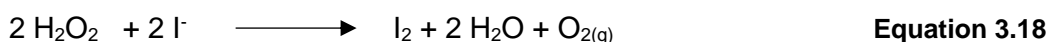
As mentioned in the feasibility study, there are two possible reaction mechanisms between KI and H₂O₂:

- Catalytic reaction: in aqueous solutions, KI can act as a catalyst to decompose H₂O₂ generating oxygen gas (Morgan, 1954).



In a catalytic reaction, the catalyst is regenerated at the end of the reaction. In this sense a non-stoichiometric amount of H₂O₂ can react with KI since the decomposition will be repeated every time an extra amount of reagent (H₂O₂) will be added to the reaction vessel. In this case the reaction cycle is theoretically infinite.

- Stoichiometric reaction between KI and H₂O₂ yielding O₂ and I₂ (Robinson, 2016).



In a stoichiometric reaction between H₂O₂ and KI, if KI is completely consumed, adding extra H₂O₂ will not have any effect on the reaction. In this case, no reaction cycle is expected.

It is worth noting that stoichiometric reaction (equation 3.18) would be preferred as it is in line with the main objective of this study in being able to control the gassing reaction by controlling the amount of gassing component. In contrast, catalytic reaction is non-stoichiometric as the catalyst here identified as KI is regenerated. making the control of the final emulsion density difficult.

To identify the dominant reaction mechanism, a qualitative experiment was conducted. A 20 ml glass test tube was used as reaction vessel. Weighing operations were performed using a Mettler Toledo PB303S-2T laboratory balance shown in Figure 4.1.



Figure 4. 1 Mettler Toledo PB303S-2T balance (error: ± 0.0002 g)

The steps described below were followed:

- 100 ml of 60% ANS was placed in a 250 ml glass beaker.
- 0.020 g of KI was dissolved in the ANS.
- 4 ml of the resulting solution was placed in a test tube.
- 1 ml of H_2O_2 was added to the test tube using a pipette. It is worth noting that the initial amount of H_2O_2 selected was superior to the quantity required by the stoichiometry, assuming that stoichiometric reaction between KI and H_2O_2 occurs.
- The test tube was covered with a cap to prevent evaporation of iodine since it is a volatile compound.
- The mixture was observed visually (color change, gas bubble evolution, precipitate formation) until the reaction stopped. It was assumed that the reaction stopped when no more visible change was observed inside the test tube.
- After the reaction stopped, one ml extra of H_2O_2 was added to the test tube to visually observe the phenomena (color change, gas bubble evolution, precipitate formation) that would occur
- The test tube contents (covered with a cap) were left overnight and the next day another extra one ml of H_2O_2 was added to the reaction vessel to visually observe what would occur.

4.2.2 Emulsion preparation

Emulsions were prepared using the Hobart N50 mixer shown in Figure 4.2 (a). The mixer consists of a D wire whisk (Figure 4.2 b) which is capable of performing mixing operations at three different gears as shown in Figure 4.2 (c), and a jacketed bowl lifted with the aid of a hand lever (Figure 4.2 a). The jacket bowl is heated to the desired temperature with an oil

circulator (Figure 4.2 (d)). The oil flows from the circulator to the bowl through the pipes shown in Figure 4.2 (d).

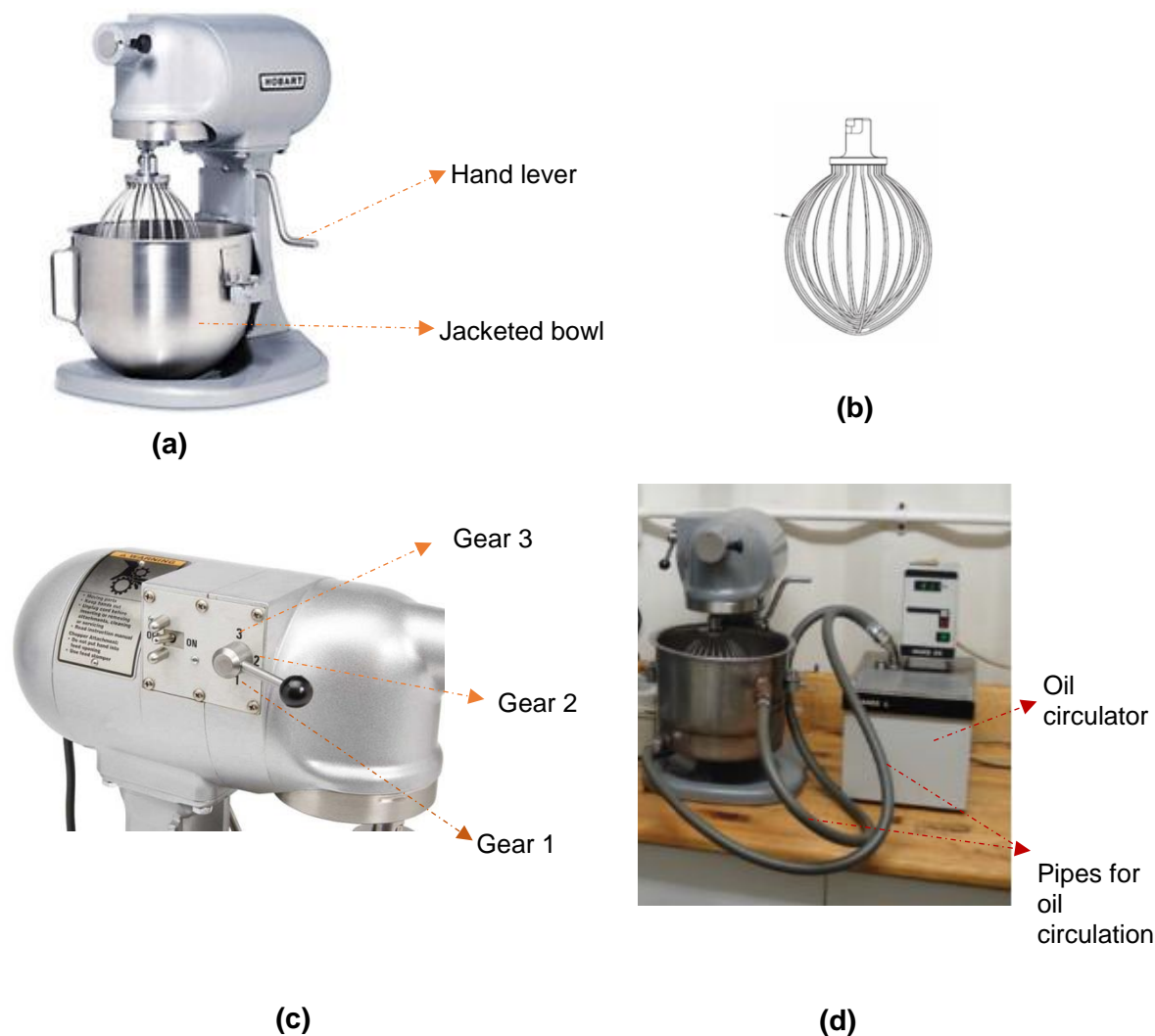


Figure 4. 2 (a) Hobart N50 mixer (b) D wire whisk (c) Gear lever (d) Oil circulator

The mixer speeds corresponding to different gears are summarized in Table 4.1.

Table 4. 1 Speeds of Hobart N50 mixer

| Speed/Gear | Agitator speed (rpm) |
|-----------------------|----------------------|
| Low (gear 1) | 136 |
| Intermediate (gear 2) | 281 |
| High (gear 3) | 588 |

a. Hobart mixer operating procedure

- The oil circulator was switched on and the temperature set to a value of 50 °C. This was done so that all experiments could be run at the same controlled temperature. The selected temperature had to be above room temperature (25 – 30°C) to prevent crystallization of ANS. However, for emulsions used in blasting experiments, the circulator temperature was set according to AEL Mining Services SA specifications.
- It was ensured that the circulator valve was opened to allow oil circulation through the pipes to the bowl, thus warming it up.
- The speed on the mixer was selected by moving the gear shift handle with the motor turned off.
- The D-wire loop whip was firmly attached on the agitator shaft. It was ensured that the whip was safely secured onto the shaft.
- Locating lugs on the bowl were snapped down over the retaining pins.
- The bowl-lift handle was moved to lift or lower the bowl.

b. Preparation of base emulsion

b.1 Aqueous (dispersed) phase preparation

- The aqueous phase components (60 wt% AN and 40 wt% water) were weighed into a metal jug using a Mettler Toledo PB300-S laboratory balance (error: ± 0.003 g) shown in Figure 4.3.



Figure 4. 3 Mettler Toledo PB300-S laboratory balance (error: ± 0.003 g)

- AN had to be dissolved in the water and because of the endothermic nature of the dissolution of ammonium nitrate in water, the operation was performed on a heating stove.
- The metal jug was placed on a heating stove for which the temperature was set to 300 °C to dissolve the AN. The jug contents had to be stirred often to prevent boiling

of the contents on the hot plate. As soon as complete dissolution was observed, the jug was removed from the stove to prevent evaporation.

b.2 Fuel (continuous) phase preparation

Dispersion of KI in the fuel phase was carried out using the Silverson L4RT high speed mixer (Figure 4.4). The mixer is used for mixing liquids or solids and liquids at speeds up to 8000 rpm.

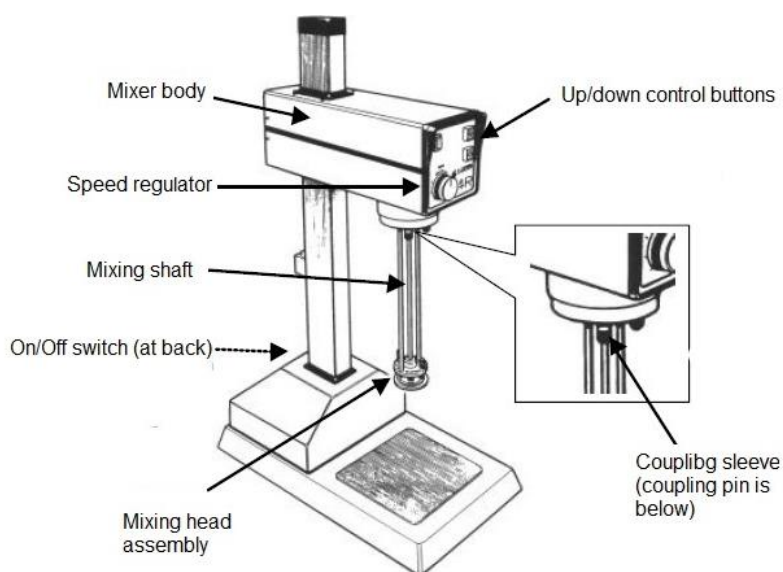


Figure 4. 4 Silverson L4RT Mixer diagram

The mixer consists of a mixer body connected to a shaft with a head assembly at the bottom, and a switch at the back to turn the mixer on or off. The up/down control button is used to lower the body so that the head assembly is in contact with the components to be mixed. The speed regulator is used to control the speed of the mixer.

The fuel phase was weighed using the Mettler Toledo PB303S-2T balance (Figure 4.1) and the KI using the Mettler Toledo PB300-S laboratory balance (Figure 4.3).

The fuel phase preparation was done according to the following procedure:

- The required quantity of fuel was weighed with the Mettler Toledo PB300-S laboratory balance (Figure 4.3) and placed in a beaker.
- The required KI amount was weighed with the Mettler Toledo PB303S-2T balance (Figure 4.1) then added to the fuel phase. The various KI concentrations used are presented in the matrix of samples (section 4.3).

- KI was dispersed in the fuel using the Silverson mixer shown in Figure 4.4.

b.3 Emulsion preparation

- The fuel containing KI was placed in the preheated bowl (temperature ≈ 50 °C).
- The mixer was switched on at speed 1 which corresponds to a speed of 136 rpm (table 4.1).
- The aqueous solution was slowly transferred into the bowl by running the solution by means of a spatula.
- It was ensured that an emulsion was formed at gear 1 to prevent splashing when operating the mixer at higher speeds.
- The mixer was stopped after the aqueous phase was transferred into the bowl; then the mixing bowl was covered with plastic or aluminium foil to prevent splashing of the emulsion.
- The speed was switched to 281 rpm (gear 2) (Figure 4.2 c) for 2 minutes to ensure complete emulsion formation.
- The mixer was stopped then and switched to gear 3 (588 rpm) (Figure 4.2 c) for droplet refinement; it was run at this speed until the desired viscosity was reached (18-21 Pa.s). The viscosity was measured using the Brookfield DV-E (Figure 4.5) described in section 4.2.2.c.
- Emulsions used for blasting were prepared according to AEL formulations. The only difference was that the optimum KI was dissolved in ANS before preparation.

c. Viscosity measurements

To measure the viscosity, the Brookfield DV-E viscometer (Figure 4.5) which measures fluid viscosities at given shear rates was used. The setup includes a laboratory stand from which the viscometer was suspended. The viscometer has a coupling nut to which the spindle is attached.

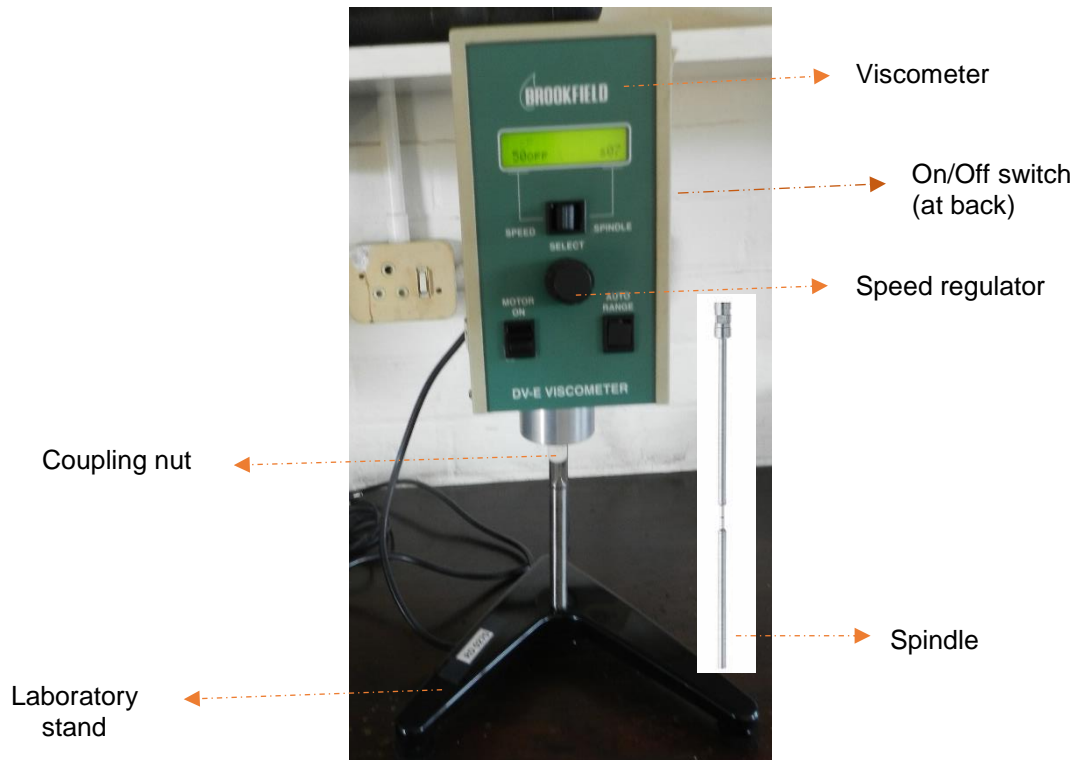


Figure 4. 5 Brookfield DV-E viscometer

The viscometer was operated according to the following procedure:

- The spindle was attached to the coupling nut.
- The fluid for which the viscosity had to be measured was placed in a small container which was filled to the brim.
- The speed was set to 50 rpm using the speed regulator. Measurements were to be carried out under laminar conditions and at the speed selected; the flow is laminar for the viscosity range of explosive emulsions (Brookfield Ametek, n.d.).
- The viscometer was lowered slowly into the sample container using the up/down button and it was ensured that the spindle did not touch the bottom of the container.
- Using the motor on the button shown on Figure 4.3, the measurement was started. When steady state value was reached, the reading was recorded.

The same procedure as described above was followed to prepare explosive emulsions with KI added to ANS, except that KI was dissolved in ANS before emulsion preparation, and no KI was dispersed in the fuel phase.

4.2.3 Gassing in emulsions

a. Measurement of gassing rate and extent

Gassing in emulsion experiments were carried out at AEL Mining Services Research and Development Laboratories. The operation was performed in gassing cups; two cups were

used. In one, emulsions were mixed with H_2O_2 using a spatula to form a homogeneous mixture which was then transferred to the other cup (to be initially filled to the brim) to follow the gassing process. The detailed steps are presented below:

- 130 g of emulsion was placed in density cup 1, shown in Figure 4.6 (a). This amount was selected because it is higher than the maximum mass of emulsion that density cup 2 may hold when filled to the brim.

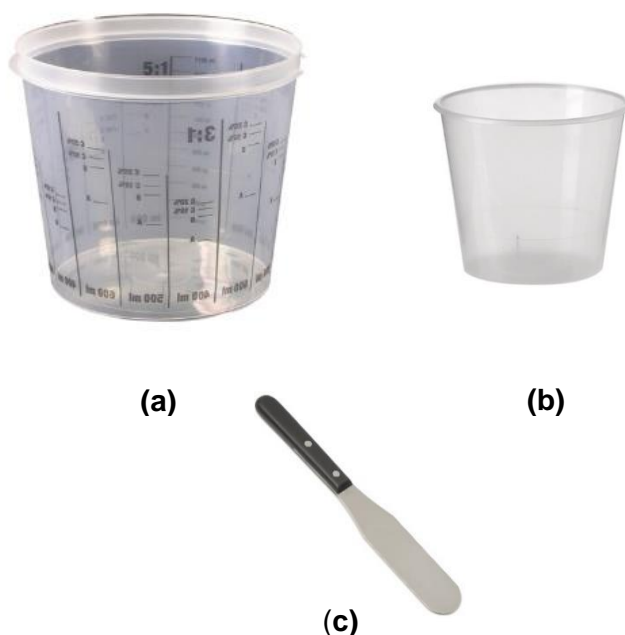


Figure 4. 6 (a) Density Cup 1 (300 ml); (b) density cup 2 (80 ml); (c) spatula used for levelling

- Hydrogen peroxide (30 wt%) was added to the emulsion and a spatula was used to stir the mixture for homogenisation. Studies were conducted for different H_2O_2 concentrations presented in the matrix of samples (section 4.3). The H_2O_2 concentrations selected were superior to the quantity required by the stoichiometry, assuming that direct reaction between KI and H_2O_2 occurs (calculations shown in Appendix A). This was done to ensure the KI present in the emulsion was completely consumed
- The mixture was transferred to density cup 2 shown in Figure 4.6. (b) with a spatula. Cup 2 *had to be filled to the brim* and it was ensured that there were no air gaps inside the cup since their presence at the start of the process could result in major errors. It is worth noting that the time interval between stirring and transfer to cup 2 to had to be less than or equal to 2 minutes. It was observed that exceeding 2 minutes resulted into the first data point being left out.

- In the transfer process from cup 1 to cup 2, there were overflowing contents in cup 2 which were scraped off to the rim with the spatula shown in Figure 4.6. (c).
- The cup contents were weighed with an analytical balance
- The gassing process was followed for 2 to 3 hours. This was done to ensure equilibrium was reached. The gassing process caused the cup contents to rise and overflow and every 5 minutes the overflowing emulsion was scraped off from the rim of the cup, the cup and its contents were then weighed, and the mass was recorded. This was done according to AEL Mining Services SA standard procedure.

The rate and extent of gassing reaction were indirectly measured by following the rate of change in emulsion density and the extent of decrease of the equilibrium density respectively. To achieve this with a high degree of accuracy, the volume of the density cup used for measurements (density cup 2) was calibrated according to the following procedure:

- A 100 ml burette was filled with water and the contents poured into density cup 2 until it was full to the brim.
- The volume of the cup was determined from the volume of water left in the burette.
- The procedure was repeated 5 times and the average volume obtained was used.

The density of the emulsion was then determined using equation 4.31:

$$\rho = \frac{M_2 - M_1}{V} \quad \text{Equation 4.31}$$

where ρ is the sensitized emulsion density, M_1 the mass of the empty cup, M_2 the mass of the cup and its contents after scraping off overflowing emulsion, and V the volume of the cup. Data of density change with time were collected and analysed using Microsoft Excel.

b. Error in density measurement

It is well known that all experiments are subject to errors which may be random or systematic. Parallax errors when using the burette, instrument resolution and the presence of air bubbles in the emulsion being gassed could have been sources of errors in these experiments. To reduce errors due to parallax, the observer was squarely aligned with the instrument used (burette in this case). To prevent the presence of air bubbles in the gassed emulsions, density cup 2 when filled with sensitized emulsions was tapped on a flat surface. The errors that could be due to instrument resolution were determined using the values given by the manufacturer. For the 100 ml burette, the error was ± 0.1 ml and for the balance used it was ± 0.003 g. The estimated error in density calculation did not exceed the value of 0.02 g/cm³ (see Appendix D).

4.2.4 Determination of the phase in which gassing reaction is occurring

The literature review showed that H_2O_2 can react with KI in the aqueous phase and this was confirmed in the feasibility study (section 3.2.2). On the other hand, experiments conducted in the feasibility study demonstrated the possibility of generating gas in the fuel phase from the reaction between KI and H_2O_2 . The question that needed to be answered here was: In which of the phases (aqueous or fuel) did the gassing reaction in the emulsion occur?

To answer the above question an experiment was conducted according to the following procedure:

- 100 ml of 60 wt% ANS was placed in a 250 ml beaker.
- 100 ml of fuel phase was placed in a 250 ml beaker and a small amount of KI was added.
- The fuel – KI mixture was added to the ANS beaker with a pipette. The addition was done slowly with the pipette placed against the wall of the beaker in order not to disturb the interface.
- A few drops of H_2O_2 were added slowly to the same beaker from the fuel phase with a pipette (Figure 7.a).
- The experiment was repeated with KI dissolved in ANS and not added to the fuel phase as previously. H_2O_2 was added from the oxidiser phase with a pipette (the pipette was dipped into the oxidiser phase which was below the fuel phase), as shown in Figure 4.7 (b).
- The gassing process was observed visually in both experiments.

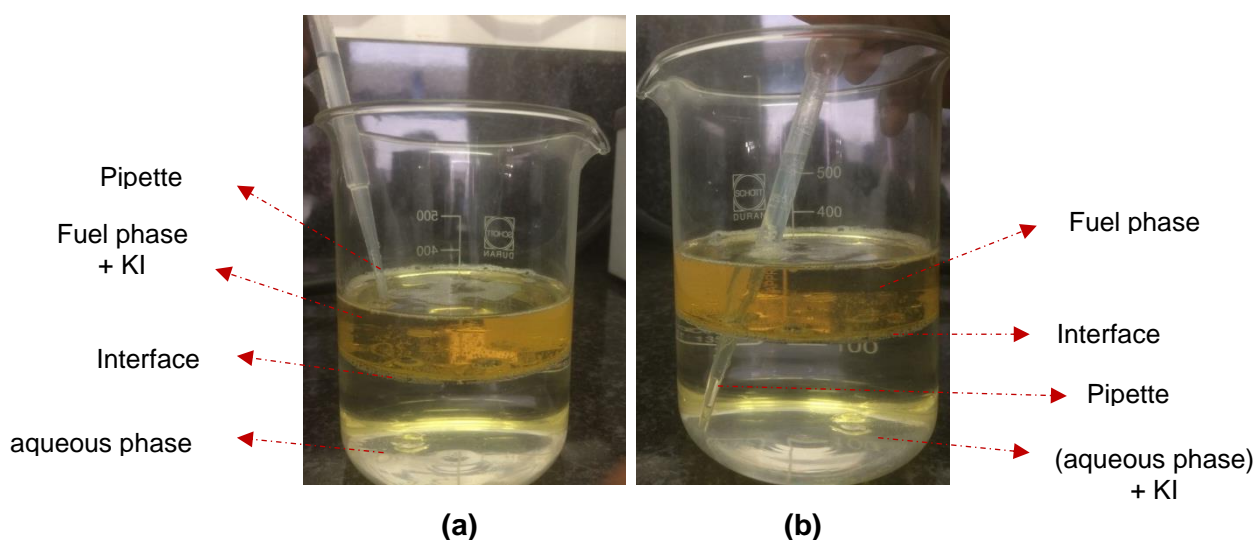


Figure 4. 7 Addition of H_2O_2 (a) from fuel phase (b) from aqueous phase

4.2.5 pH effect on final emulsion density

The gassing reaction between KI and H₂O₂ in aqueous solution is greatly affected by the pH (Bray & Liebhafsky, 1931). In order to study the effect of pH on the gassing reaction in ANS and in emulsions, a set of experiments were conducted.

To measure the pH the Martini Mi 180 Bench Meter shown in Figure 4.8 was used. The pH meter had to be calibrated once every day using buffer solutions of pH 4 and 7.



Figure 4. 8 Martini Mi 180 pH meter

The Martini Mi 180 pH meter measures 6 different parameters: pH, ORP, EC, TDS (Total Dissolved Solids), percentage of NaCl and temperature in a variety of ranges. The instrument measures pH values ranging from -2.00 to 16.00. pH calibration can be done in 1, 2 or 3 points with 7 memorized buffers to provide a very accurate calibration curve.

a. Effect of pH on the gassing reaction in ANS

Although the focus here was to study the effect of pH on the final emulsion density, it was important to first estimate at least qualitatively the influence of pH on the gassing reaction between KI and H₂O₂ in ANS. This would probably give an idea of what could occur in explosive emulsions. The investigations were done according to the following procedure:

- 100 ml of 60% ammonium nitrate solution were placed in a glass beaker; the pH of the solution was then measured using the Mi 180 Bench Meter (Figure 4.6).
- The pH was adjusted to the desired value using acetic acid and/or sodium acetate.
- 0.020 g of KI was dissolved in the ammonium nitrate solution.

- 4 ml of the solution of KI in ammonium nitrate were placed in a test tube with a pipette.
- 1 ml of H₂O₂ was added to the test tube containing 4 ml of KI in ammonium nitrate solution with a pipette to allow the reaction between the KI and H₂O₂ to proceed at a specific pH.
- The gassing process was observed visually to estimate the changes in both the speed and the amount of gas bubbles generated by the reaction.
- Experiments were carried out for various pH values. The values ranged from 4.4 (pH of 60% ANS without addition of any pH modifiers) to 6.5 (maximum pH value reached no matter the amount of pH modifier added).

b. Effect of pH on gassing reaction in emulsions

To investigate the effects of pH on gassing reactions in emulsions, the samples were prepared following the procedure described in section 4.2.2. The ANS pH was adjusted to the desired value using acetic acid and/or sodium acetate before emulsion preparation. Emulsions were sensitized, and density evolution followed according to the procedures described in section 4.2.5.a. Graphs of density evolution over time were plotted with Microsoft Excel and used to analyse experimental data.

4.2.6 Blasting Properties

To investigate the blasting properties, emulsions were manufactured according to AEL commercial explosive formulations, which for confidentiality reasons could not be disclosed.

a. Pipes preparation

AEL Mining services SA uses PVC pipes for emulsions used in underground blasting operations (F800 based explosive emulsions) and cardboard pipes for emulsions used in surface blasting operations (Bullfinch and R602/45 based emulsions). To conduct blasting experiments, pipes had to be prepared: 32 mm diameter and 1 m long PVC pipes (Figure 4.9) for emulsions manufactured using F800 fuel phase; and 80 mm diameter and 0.5 m long cardboard pipes (Figure 4.10) for emulsions manufactured using Bullfinch fuel phase.

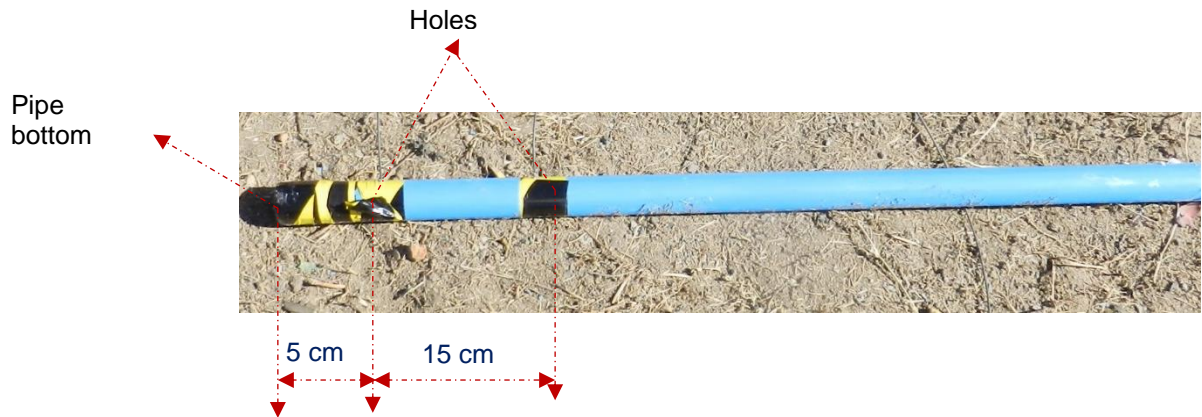


Figure 4. 9 Blasting pipe (32 mm diameter, 1 m long)

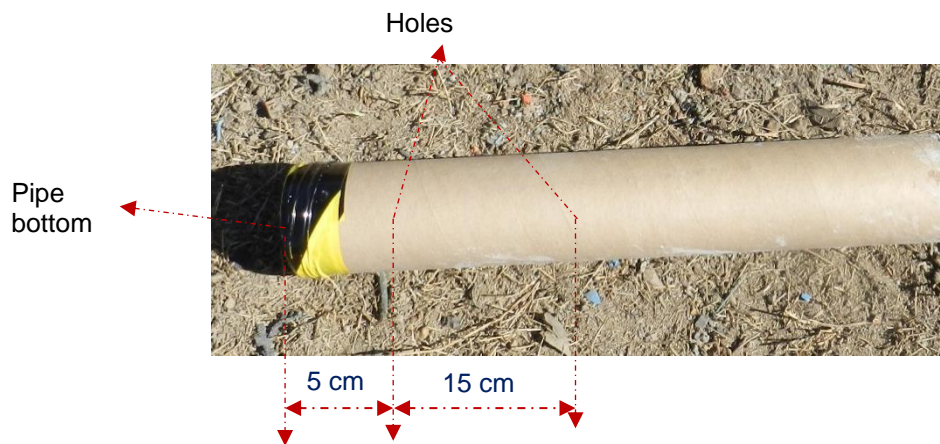


Figure 4. 10 Blasting pipe (80 mm diameter, 0.5 m long)

The pipes were prepared according to the following procedure:

- The pipe lengths were measured with a ruler and cut according to required length.
- 2 holes 15 cm apart at the bottom of the pipes were drilled (AEL standard). The first hole was 5 cm away from the pipe bottom as shown in Figures 4.9 and 4.10. The distance between the holes were used for VOD calculations.
- Prepared explosive emulsions were weighed in buckets according to the amount required for each pipe, then sensitized by addition of the required amount H_2O_2 . To estimate the mass of sensitised emulsions required for each pipe, the density of 1.05 g/cm^3 and the pipe volume (determined from height and diameter) were used; calculations are shown in appendix C.
- The emulsions were carefully placed in pipes using a spatula.
- The pipes filled with emulsions were taken to the blasting site.

c. Measurement of shockwaves travel time during blasting and VOD calculations

The measurements of shockwaves travel times were carried out using a VOD timer model VOG-3 (Figure 4.11 b). A VOD timer tester model VIT 1 (Figure 4.11 b) was used to test the VOD timer before blasting operations. The VOD timer model VOD-3 consists of two identical optical input channels connected to a timer. The time difference between arrival of the first impulse at each channel (start and stop) is measured and displayed on a liquid crystal display, which is easily read in daylight and poor lighting underground.



Figure 4. 11 (a) VOD time tester model VTT-1 (b) and VOD timer model VOD-3

The measurements of the shockwave travel time were done according to the following procedure:

- The VOD timer measurement cables were placed in the drilled holes as shown in Figure 4.12.
- For the 32 mm diameter and 1 m long pipes, an in-hole detonator was placed in the pipe as shown in Figure 4.12. It was connected to an outside detonator and to the initiating system, which is not shown for confidentiality reasons.
- For the 40 mm diameter and 0.5 m long pipes, a booster was placed inside the pipe as shown in Figure 4.13; this was connected to the initiating system.

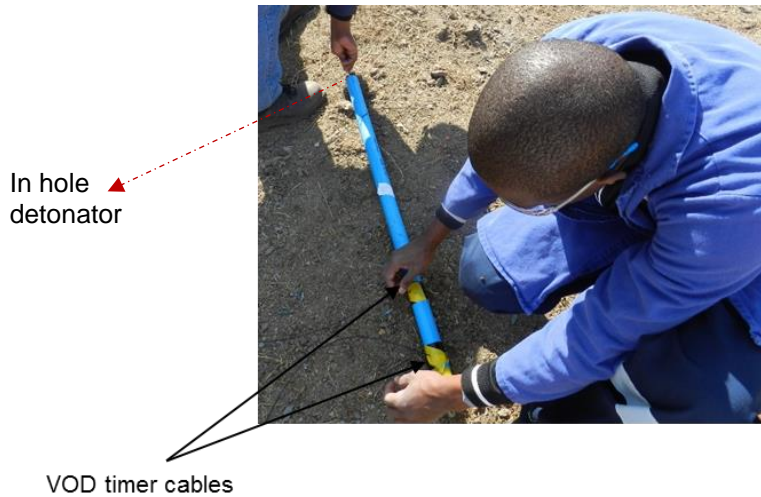


Figure 4. 12 VOD cables placed for time measurements



Figure 4. 13 Blasting pipe (40 mm diameter, 0.5 m long) with booster

- The initiating system was activated to cause blasting to occur.
- The time taken for the shock wave to travel between the 2 drilled holes was measured using a VOD timer (Figure 4.11).

Equation 4.32 was used to calculate the VOD.

$$VOD = \frac{0.15}{t}$$

Equation 4.32

VOD: Velocity of detonation (m/s)

t: VOD timer reading (microseconds) converted to seconds

VODs calculations were done for emulsions gassed with both current (reaction between NaNO_2 and ammonium nitrate) and new (reaction between KI and H_2O_2) methods, and results were compared.

4.3 Matrix of samples

The matrix of samples is presented in Table 4.2. The percentages are given relative to the total emulsion mass. As mentioned earlier, the dispersed phase made up 90 wt% of the emulsion and the balance was the continuous phase containing KI. For emulsions prepared with KI dissolved in the dispersed phase, the continuous phase made up 10 wt% of the emulsion and the balance was the dispersed phase containing KI.

Table 4. 2 Matrix of samples

| Fuel phase | KI, wt% | H ₂ O ₂ , concentration range, wt% | Dispersed phase |
|------------|---------|--|--------------------------------|
| F800 | 0.100 | 0.09 – 6.07 | 60 wt% solution of AN in water |
| | 0.016 | 0.43 – 4.34 | |
| | 0.020 | 0,43 – 4.34 | |
| | 0.025 | 0.43 – 4.34 | |
| | 0.010 | 4.34 – 7.80 | |
| | 0.008 | 4.34 – 7.80 | |
| Bullfinch | 0.100 | 0.09 – 6.07 | |
| | 0.008 | 4.34 – 7.80 | |
| | 0.004 | 4.34 – 7.80 | |
| R602/45 | 0.100 | 0.09 – 6.07 | |
| | 0.008 | 4.34 – 7.80 | |
| | 0.004 | 4.34 – 7.80 | |

4.4 Summary

The materials used to prepare highly concentrated emulsions in which an inorganic salt (ammonium nitrate) solution was dispersed in a fuel phase were described. The methodology used to prepare emulsions, sensitize them, and to study the gassing process and pH effects were presented. The instruments that were used in this study were also described.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Introduction

A comprehensive description of results obtained is presented in this chapter. The main objective of this chapter is the analysis and discussion of test results obtained from gassing and blasting experiments.

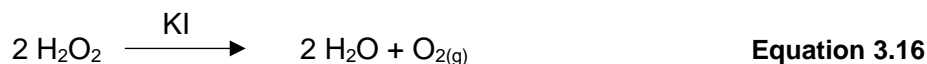
This part of the study is divided into the following sections:

- determination of gassing mechanism,
- sensitization of emulsions with KI added to the fuel phase prior to emulsification,
- sensitization of emulsions with KI dissolved in ANS prior to emulsification and
- blasting characteristics.

5.2 Determination of gassing mechanism

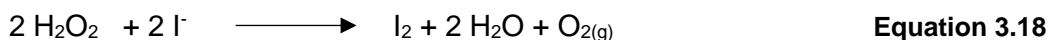
As mentioned in the feasibility study and experimental procedure, there are two possible reaction mechanisms between KI and H₂O₂:

- Catalytic reaction: in aqueous solutions, the catalytic decomposition of H₂O₂ catalyzed by KI can occur. The decomposition is accompanied by generation of oxygen gas (Morgan, 1954).



At the end of a catalytic reaction, regeneration of the catalyst occurs. In this case the decomposition cycle of H₂O₂ will be repeated every time an extra amount of reagent (H₂O₂) is added to the reaction vessel. The reaction cycle is theoretically infinite.

- Stoichiometric reaction between KI and H₂O₂ yielding O₂ and I₂ (Robinson, 2016).



KI is completely consumed by H₂O₂ present in excess, as would be the case in a stoichiometric reaction; no reaction is expected after adding extra H₂O₂ to the reaction vessel. In this case, no reaction cycle is expected.

In line with the main objective of this study, namely being able to control the gassing reaction by controlling the amount of gassing component, the stoichiometric reaction between KI and H₂O₂ (equation 3.18) would be preferred; whereas, the catalytic reaction would make the control of the final emulsion density difficult in terms of the goal of the research.

The visual observations from the qualitative experiment aimed at identifying the dominant reaction mechanism are shown in Figure 5.1.

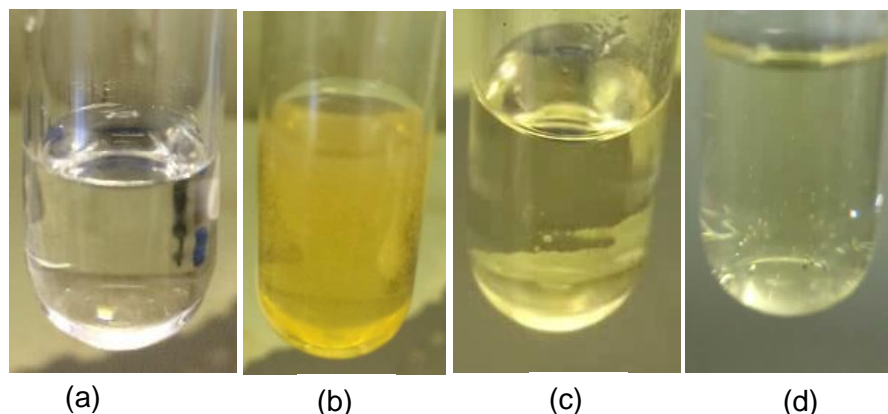


Figure 5. 1 Study of reaction mechanism; (a) AN solution containing KI; (b) 30 seconds after first H₂O₂ addition; (c) 8 hours after first addition; (d) 30 seconds after second H₂O₂ addition

The following observations were made: when 1 ml of H₂O₂ was added to the ANS containing dissolved KI (Figure 5.1 a), the solution immediately turned yellow and gas bubbles formed 15 seconds after the addition (Figure 5.1 b). The yellow colour could possibly be due to the presence of iodine in solution (Hildebrand & Glasgow, 1908). On the other hand, formation of gas bubbles could be due to the production of oxygen in the reaction. Addition of extra H₂O₂ after the reaction had stopped did not have any visible effect on the solution in the test tube (Figure 5.1 c and d); this is in contrast with what would be expected for a catalytic reaction. It was then concluded that under the conditions in which this experiment was conducted, H₂O₂ does not undergo a catalytic reaction in the presence of KI; the stoichiometric reaction (equation 3.18) seems to be the dominant mechanism. This conclusion means that the selected reactants system (KI and H₂O₂) could be suitable in controlling the final density, and thus achieve the overall objective of this study.

5.3 Sensitization of explosive emulsions with fuel phase containing KI

In this section, the results obtained from sensitisation of explosive emulsions prepared with the fuel phase containing KI are presented and discussed.

5.3.1 Effect of H₂O₂ concentration

The effect of H₂O₂ concentration on two parameters, namely the rate of density change and the final gassed emulsion density were investigated. The rationale behind this was to shed light on the extent of the impact of H₂O₂ concentration on the explosive emulsion density. To

conduct the study, emulsions with 0.1wt% KI concentration were prepared and sensitized using H₂O₂ concentrations ranging from 0.09 to 6.07wt% of total emulsion mass. It is worth mentioning that H₂O₂ was used with a view to determining the range in which the chemistry is independent of the H₂O₂ concentration used, which is consistent with the objectives of this study.

5.3.1.1 Effect of H₂O₂ concentration on the rate of density change

The changes in sensitized emulsion density over time for different H₂O₂ concentrations, for emulsions prepared using the 3 different fuel phases, are shown in Figures 5.2 to 5.4.

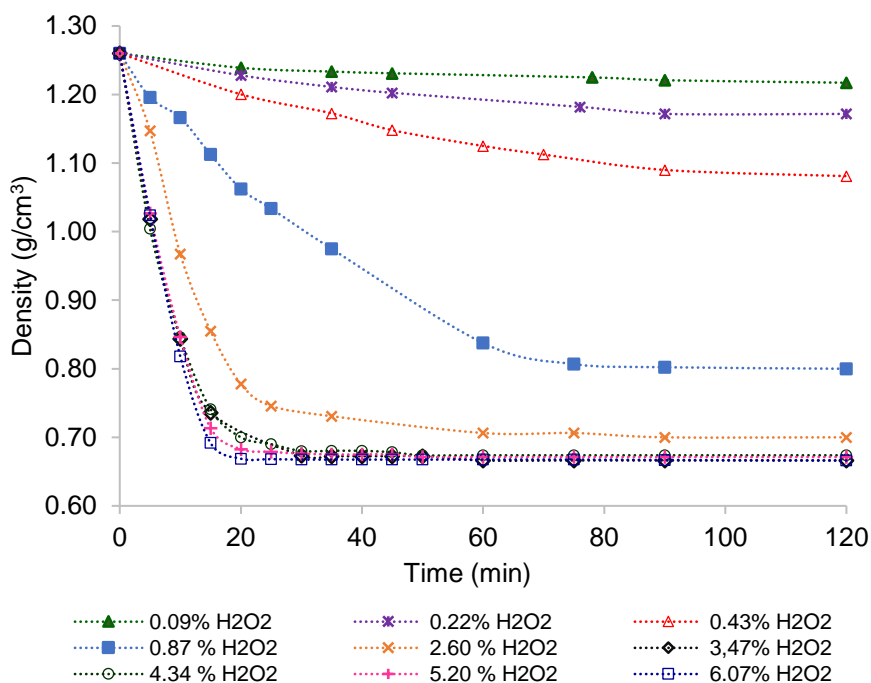


Figure 5. 2 Density variation of sensitized emulsion with time (F800 fuel phase/0.1wt% KI)
0.09wt% < H₂O₂ Conc. < 6.07wt%

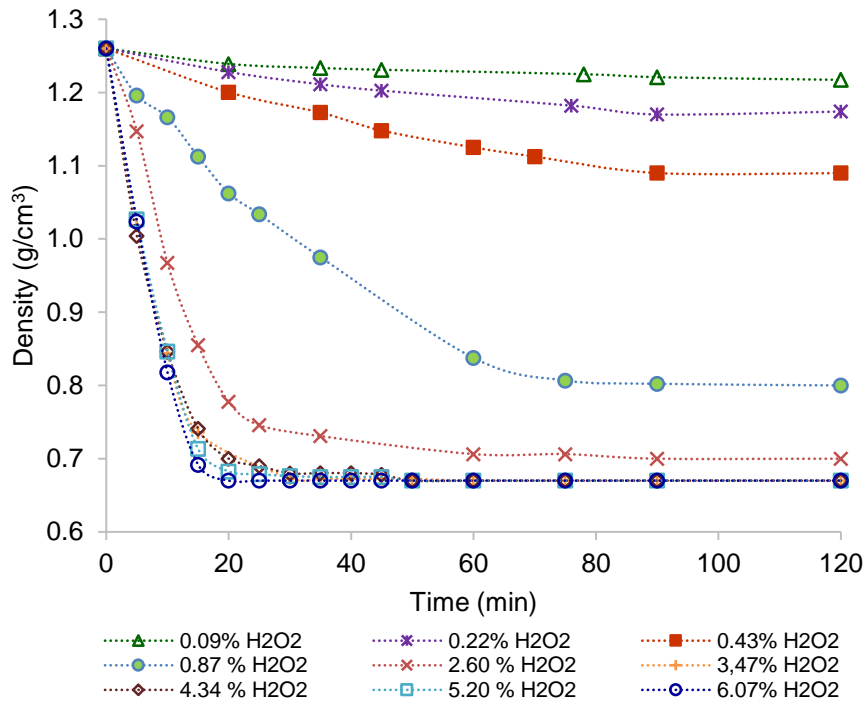


Figure 5. 4 Density variation of sensitized emulsion with time (R602/45 fuel phase/0.1wt% KI) 0.09wt% < H₂O₂ Conc. < 6.07wt%

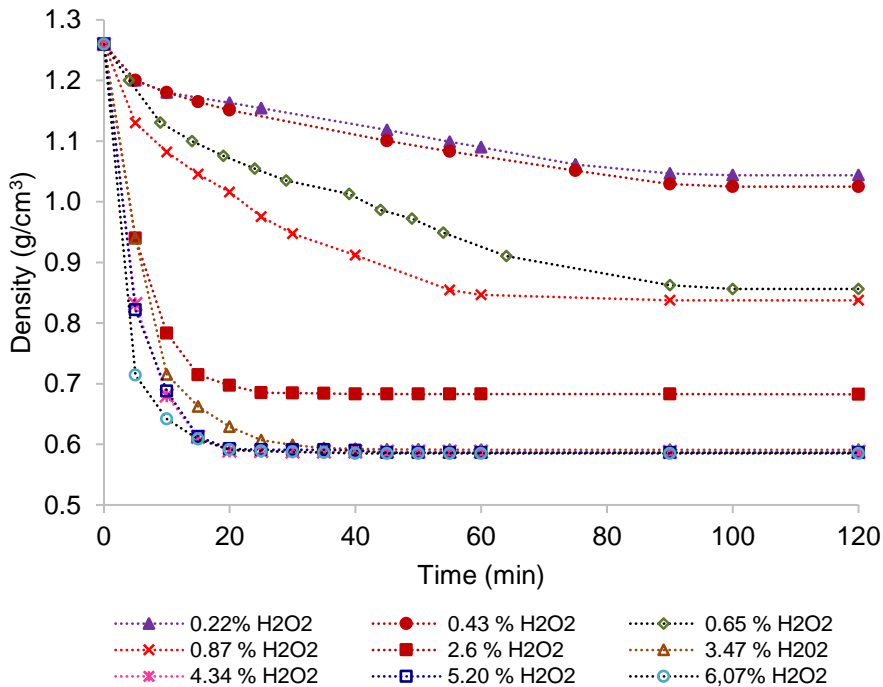


Figure 5. 3 Density variation of sensitized emulsion with time (Bullfinch fuel phase/0.1wt% KI) 0.09wt% < H₂O₂ Conc. < 6.07wt%

Before looking at density variation with concentration, it is worth noting that the density evolution with time presents two regions separated by a transitional point: in the first (left side

of the transitional point), an initial steady decrease of density is observed for all different H₂O₂ concentrations. The steady decrease observed in the first region is followed by a second region (right side of the transitional point) in which the density has reached a plateau since the gassing reaction seems to have reached equilibrium.

The rate of change in density has been found to increase with increasing H₂O₂ concentration. At H₂O₂ concentration of 3.47 wt%, a transition in terms of rate of change in density occurs. Above this concentration, the rate of gassing was subject to very small variations for F800-based explosive emulsions (Figure 5.2) and remained constant for Bullfinch- and R602/45-based explosive emulsions (Figure 5.3 and 5.4).

In table 5.1 the effect of H₂O₂ concentration on gassing time (time taken to reach final density) for emulsions prepared with the 3 different fuel phases is summarized.

Table 5. 1 Effect of H₂O₂ concentration on gassing time

| H ₂ O ₂ conc., wt% | F800 | Bullfinch | R602/45 |
|--|-------------------|-------------------|-------------------|
| | Gassing time, min | Gassing time, min | Gassing time, min |
| 0.09 | 120 | 100 | 90 |
| 0.22 | 116 | 95 | 85 |
| 0.43 | 90 | 90 | 80 |
| 0.87 | 60 | 60 | 75 |
| 2.60 | 50 | 25 | 40 |
| 3.47 | 25 | 25 | 25 |
| 4.34 | 25 | 20 | 20 |
| 5.20 | 20 | 20 | 20 |
| 6.07 | 20 | 20 | 20 |

As expected from the rate of density change curves (Figure 5.2 – 5.4), it was observed that the time taken to reach equilibrium density decreases with increasing peroxide concentration up to a transitional point corresponding to a peroxide concentration of 3.47 wt%. Beyond the transitional point, the gassing times were almost constant irrespective of H₂O₂ concentration.

5.3.1.2 Effect of H₂O₂ concentration on final sensitized emulsion density

Figures 5.6 – 5.8 show the variation of final sensitised emulsion density with H₂O₂ concentrations for emulsions prepared with the 3 different fuel phases with KI concentration of 0.1 wt%.

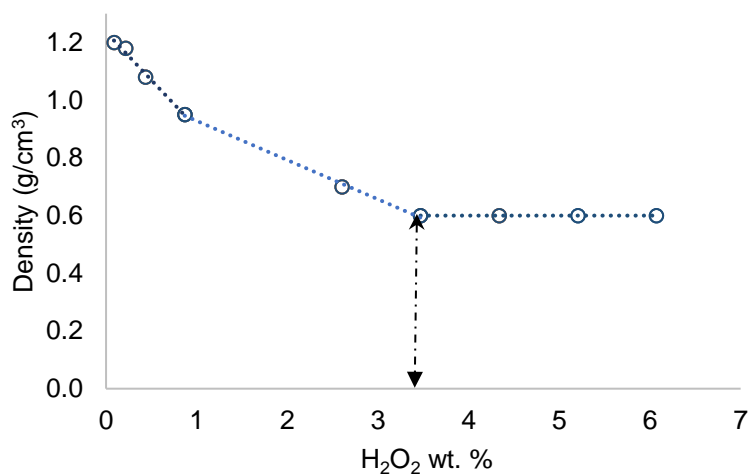


Figure 5. 5 Final gassed emulsion density dependence on H₂O₂ concentration for emulsions prepared with F800 fuel phase/0.1 wt% KI

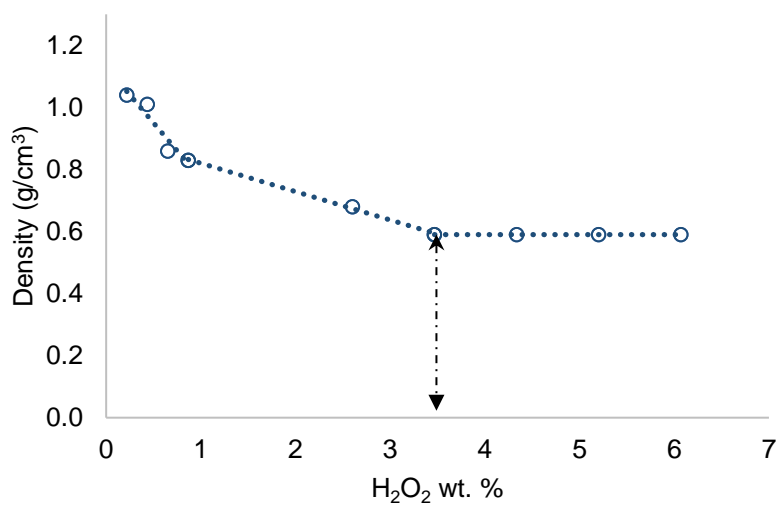


Figure 5. 6 Final gassed emulsion density dependence on H₂O₂ concentration for emulsions prepared with Bullfinch fuel phase/0.1 wt% KI

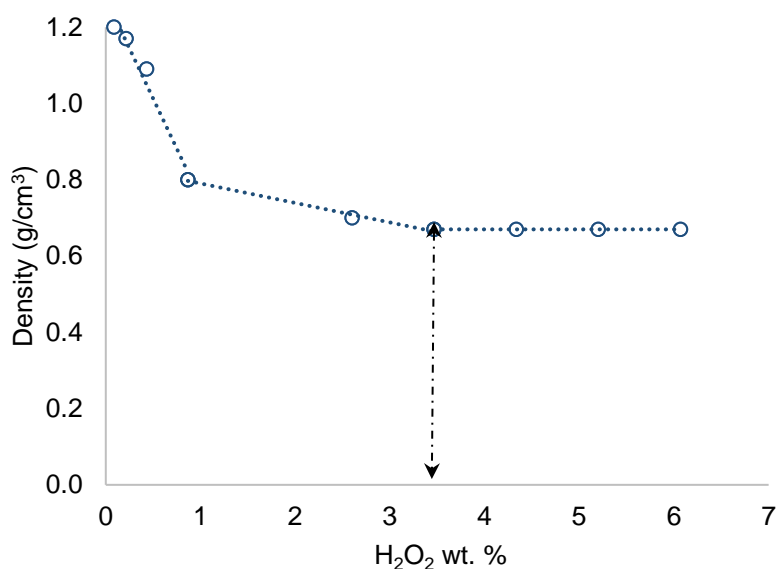


Figure 5. 7 Final gassed emulsion density dependence on H₂O₂ concentration for emulsions prepared with R602/45 fuel phase/ 0.1 wt% KI

The figures show the existence of three regions. The first region (H₂O₂ conc. ≤ 0.87wt%) shows a rapid decrease in density with increasing H₂O₂ concentration. The second region (0.87wt% ≤ H₂O₂ conc. ≤ 3.47wt%) shows a moderate density decrease with increasing H₂O₂ concentration as compared to the first region. In the third region (H₂O₂ conc. ≥ 3.47%) the density remains unchanged irrespective of the H₂O₂ concentration. This indicates that the density dependence on H₂O₂ concentration has been suppressed. Table 5.2 summarizes the final densities as a function of H₂O₂ concentration.

Table 5. 2 Effect of H₂O₂ concentration on final density

| H ₂ O ₂ conc., wt% | F800 | Bullfinch | R602/45 |
|--|----------------------------------|----------------------------------|----------------------------------|
| | Final density, g/cm ³ | Final density, g/cm ³ | Final density, g/cm ³ |
| 0.09 | 1.22 | 1.04 | 1.20 |
| 0.22 | 1.17 | 1.01 | 1.17 |
| 0.43 | 1.08 | 0.86 | 1.09 |
| 0.87 | 0.95 | 0.83 | 0.80 |
| 2.60 | 0.70 | 0.68 | 0.70 |
| 3.47 | 0.60 | 0.59 | 0.67 |
| 4.34 | 0.60 | 0.59 | 0.67 |
| 5.20 | 0.60 | 0.59 | 0.67 |
| 6.07 | 0.60 | 0.59 | 0.67 |

It was interesting to note that the transition in terms of rate of gassing and final emulsion density occurred at 3.47 wt% H₂O₂. Above this concentration, both the final density and rate of gassing did not change. The corresponding KI concentration was 0.1wt%, which led to the conclusion that 34.7 to 1 is the critical H₂O₂/KI ratio for all different fuel phases.

Although above the critical H₂O₂/KI ratio the final sensitised emulsion density dependence on H₂O₂ concentration was suppressed, the density values obtained were lower than the reference value of 1.05 g/cm³ which is required for effective blasting.

5.3.1.3 Correlation between rate of density change (due to H₂O₂ concentration change) and final density of explosive emulsions

The correlation between the rate of gassing reaction and the final emulsion density was investigated with a view to shed light on the parameters affecting the final density in order to have better control of the latter (as stated in the objectives). The procedure used to estimate the rate of reaction is presented in Appendix B. The correlation is presented in Figure 5.8.

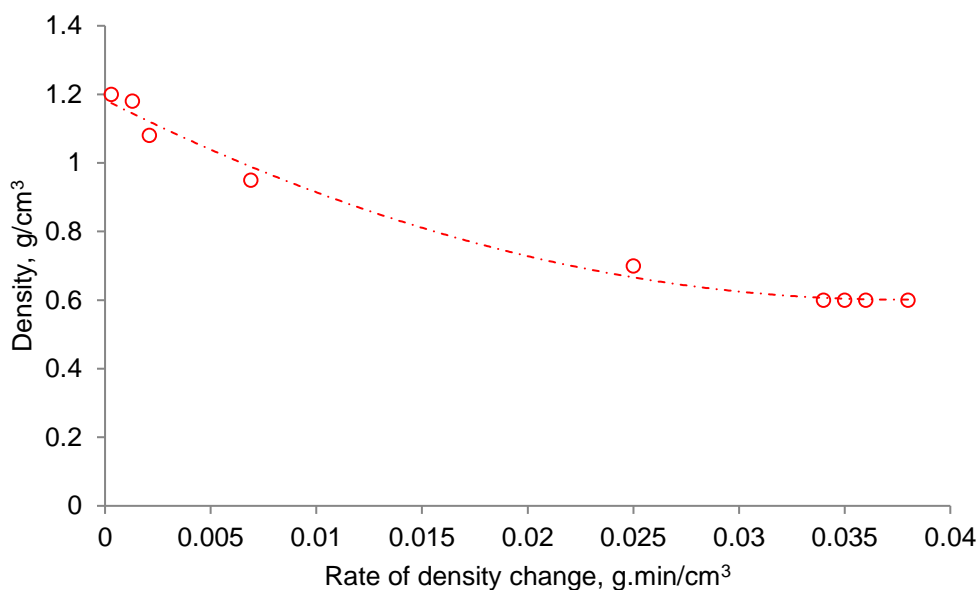


Figure 5. 8 Correlation between rate of density change and final sensitised emulsion density (F800/0.1 wt% KI)

It appears from the Figure above that the rate of the gassing reaction influences the final sensitised emulsion density. The final density decreases with increasing rate of gassing. To elucidate the influence of the rate of gassing reaction on the final density, typical results from emulsions prepared with 0.1 wt% KI and sensitized with 0.87 wt% H₂O₂ (final density = 0.95

g/cm^3) and 2.60 wt% H_2O_2 (final density = 0.70 g/cm^3) after 2 hours of observation are presented in Figure 5.9.

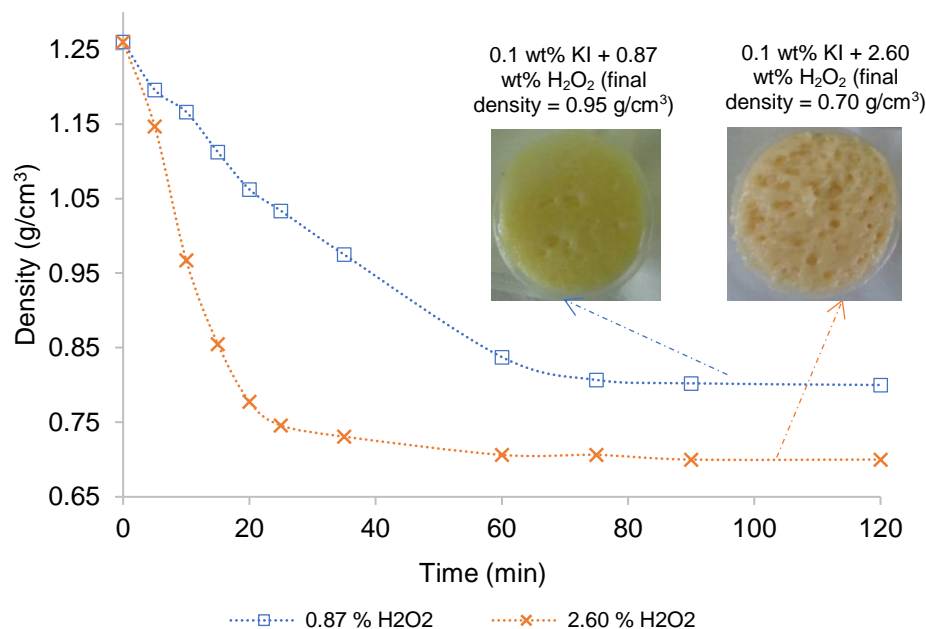


Figure 5. 9 Rate of density variation of sensitized emulsion with time (F800 fuel phase/0.1wt% KI) vs. void size at final density

From Figure 5.9, the following can be observed: on the one hand, as the H_2O_2 concentration increases, the rate of gassing (slope of density vs. time graph in the first region) increases. On the other hand, higher rate of gassing is associated with large void size or lower sensitised emulsion final density. This clearly demonstrates the impact of the rate of gassing on the final density; the latter decreases with increased rate of gassing. In this sense, it seems reasonable to assume that at high rate of gassing reaction, coalescence of gas bubbles is amplified due to the increase of the probability of collisions between them. Since the amount of gas released (which determines the void volume fraction) is assumed to be the same in both cases (constant KI concentration and H_2O_2 is in excess), it can be concluded that higher rate of gassing induces higher rate of bubble coalescence, which in turn generates big voids resulting (at constant void volume fraction) in lower final density.

5.3.2 Effect of KI concentration

The effect of KI concentration on the rate of density change and the final gassed emulsion density were investigated. The rationale behind this was to shed light on the extent of the impact of KI concentration on the explosive emulsion density. To conduct the study, typical emulsions with different KI concentrations (from 0.016 to 0.1 wt%) were prepared and sensitized using the 2.60 wt% H_2O_2 .

5.3.2.1 Effect of KI concentration on rate of density change and the final emulsion density

Typical graphs illustrating the changes in sensitized emulsion density over time for different KI concentrations for emulsions prepared using the F800 fuel phase are shown in Figure 5.9.

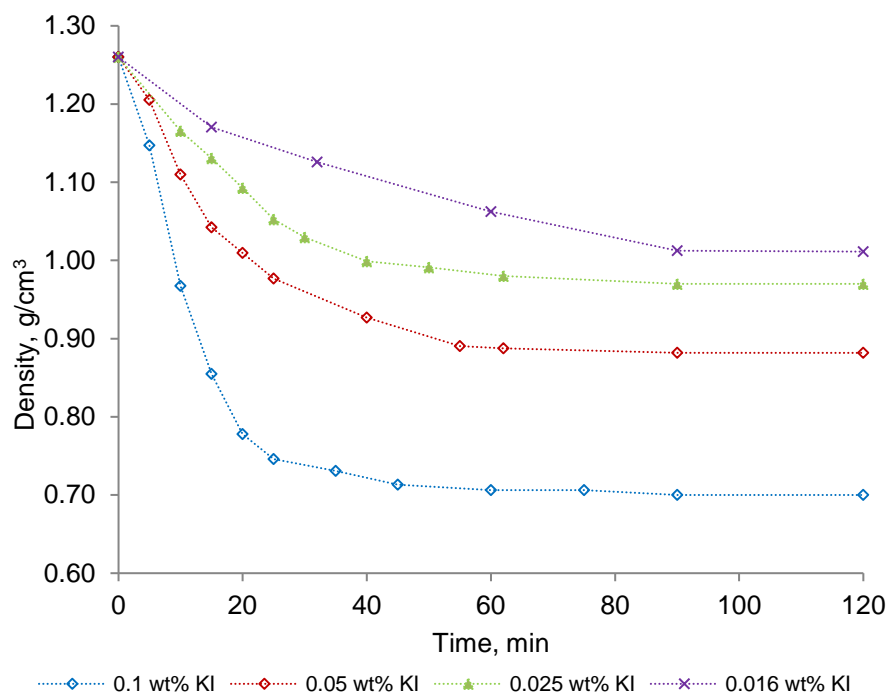


Figure 5. 10 Density variation of sensitized emulsion with time (F800 fuel phase/2.60 wt% H₂O₂) 0.016wt% < KI Conc. < 0.1 wt%

As observed when investigating the effect of H₂O₂ on sensitised emulsion density: first, the density evolution with time presents two regions separated by a transitional point: in the first region (left side), the density decreases with time. This region is followed by a plateau (second region) where no apparent change of density is observed. This is due to the fact that equilibrium has been reached. Second, the rate of change in density was found to increase with increasing KI concentration. This could be an indication that the rate of reaction increases with increasing KI concentration. Third, the final emulsion density decreases with increasing KI concentration. This could be explained by the fact that higher KI concentrations produce greater amounts of gas, inducing a higher void volume fraction, and resulting in lower sensitised emulsion density.

It has been previously demonstrated that there is a correlation between the rate of gassing and the final emulsion density due to H₂O₂ concentration. Now the question to be asked is:

how does KI affect the correlation between the rate of density change and the final emulsion density?

5.3.2.2 Correlation between rate of density change (due to KI concentration change) and final density of explosive emulsions KI concentration

An investigation into the correlation between the rate of gassing reaction as a function of KI concentration and the final emulsion density was conducted in order to understand the factors influencing the final density to better control it (as stated in the objectives). The procedure used to estimate the rate of reaction is presented in Appendix B. The results are shown in Figure 5.11.

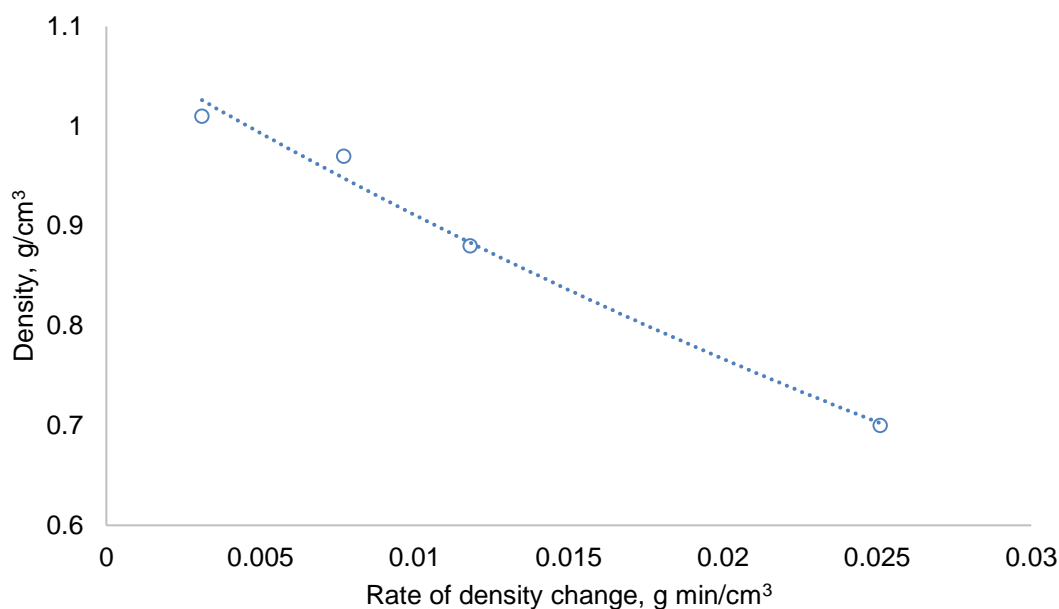


Figure 5. 11 Correlation between rate of density change and final sensitised emulsion density (F800/2.60 wt% H₂O₂)

The final sensitised emulsion density is affected by the rate of the gassing reaction. For increasing rate of gassing, it has been observed that the final density decreases.

To shed light on the influence of the rate of gassing reaction on the final density, typical results from emulsions prepared with 0.1 wt% KI and 0.05 wt%, sensitized with 2.60 wt% H₂O₂ after 2 hours of observation, are presented in Figure 5.12.

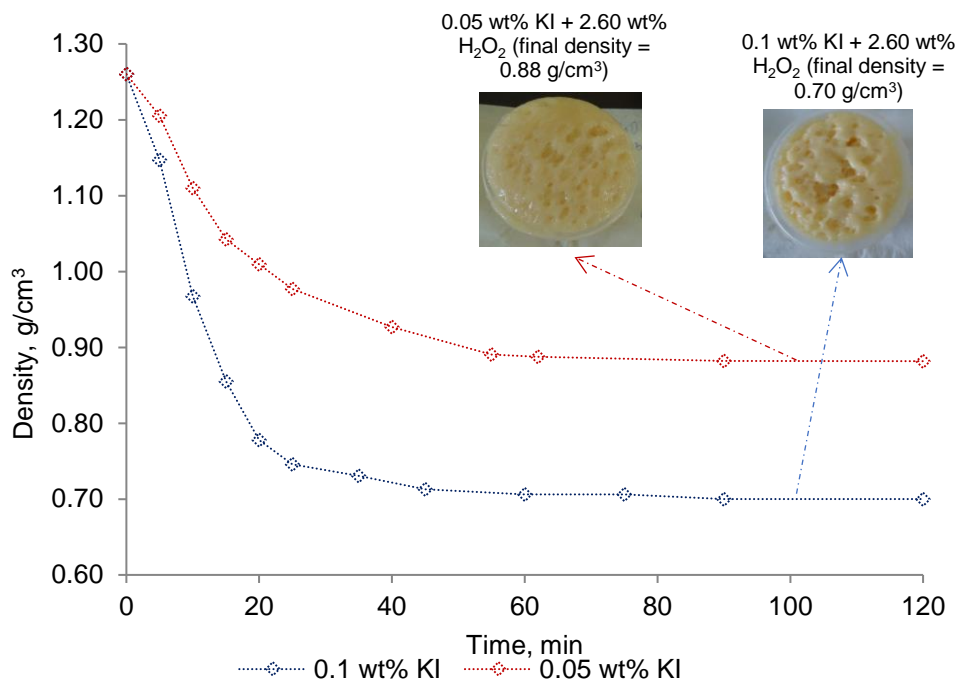


Figure 5. 12 Rate of density variation of sensitized emulsion with time (F800 fuel phase/2.60 wt% KI) vs. void size at final density

From 5.12, the following can be observed: on the one hand, as the KI concentration increases, the rate of gassing (slope of density vs. time graph in the first region) increases. On the other hand, higher rate of gassing is associated with large void size or lower density. This clearly demonstrates the impact of the rate of gassing on the final density; the latter decreasing with increasing the rate of gassing. This is in agreement with the observations made on the effect of H_2O_2 concentration. Once again it can be advanced that at high rate of gassing reaction, coalescence of gas bubbles is intensified due to the increase of the probability of collisions between them. Stoichiometry dictates that the amount of gas released at higher KI concentration (0.1 wt% KI; H_2O_2 is in excess) is expected to be higher than that corresponding to lower KI concentrations (0.05 wt% KI; H_2O_2 is in excess). In this sense, it can be concluded that higher KI concentrations correspond to both higher amounts of gas and higher rate of gassing; this induces higher rate of bubble coalescence which in turn generates big voids, resulting in lower final density.

5.3.3 Factors controlling the final emulsion density

On the basis of the findings on the effect of H_2O_2 and KI concentrations on the final density of gassed emulsions, it is clear that the latter is controlled by two factors:

- Void volume fraction, which is only related to the amount of gas released in the system. In this sense, it is only defined by the amount of pre-determined component which is KI for this study.

- Void size which is related to the rate of gassing and the amount of gas released. It is assumed that the large amounts of gas produced at high rate cause a high degree of coalescence of gas bubbles generating large voids. The latter are very unstable as they collapsed overnight, as shown in Figure 5.13.

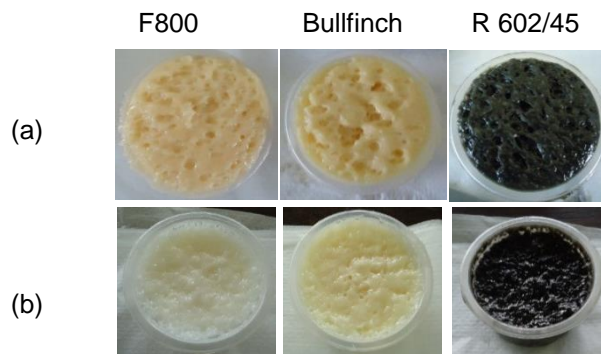


Figure 5. 13 Sensitized emulsion prepared with 0.1 wt% KI (a) just after gassing (b) collapsed emulsion on the next day

This drastic change in the emulsion density observed on the next day of the experiment due to the collapse of the emulsion associated with the presence of very large voids clearly demonstrates that the sensitized emulsion is in a metastable state at the end of the gassing reaction. In this sense, the final density associated with the plateau is apparent, not the true equilibrium density. This component of the density (void size) is affected by both KI concentration, which defines the amount of gas and the rate of gassing, and H_2O_2 influencing the rate of gassing only. It is crucial to find a way to minimize the void size to avoid the metastable state of sensitized emulsion subjected to changes over time. The latter makes it difficult to control the final density of gassed emulsion, which is detrimental for technological applications.

In light of the findings presented above, there are two major problems in the development of the two-component gassing system:

- Sensitized emulsions are in a metastable equilibrium, making the final density unstable (changes over time). KI, a component to be used in a pre-determined amount during emulsion manufacturing, has an influence on both the void size and void volume fraction in the sensitized emulsions. The former (void size) is related to both the rate of gassing and the amount of gas produced, whereas the latter (void volume fraction) is only related to the amount of gas produced. Higher KI concentrations generate large amounts of gas at high speed which induce high rates of bubble coalescence resulting in large voids; these collapse with time after the

gassing reaction, making the control of the final density difficult. H_2O_2 , a gassing component to be used in excess after manufacturing (when sensitisation is required), only influences the density by defining the void size. The latter is closely related to the rate of gassing: higher H_2O_2 concentrations cause higher rate of gassing which induce higher rate of bubble coalescence, which in turn generates large voids (unstable system).

- Although a point has been reached (H_2O_2 to KI concentration ratio = 34.7) above which the final density did not change irrespective of H_2O_2 concentration (one of the objectives of this study), the density reached is below the reference value of 1.05 g/cm^3 required for effective blasting.

To overcome the challenges that arise in developing the two-component gassing system, optimisation of the process is required.

5.3.4 Process optimization

Taking into consideration the observations made above, the optimisation of the gassing process can be done in two ways:

- Optimisation of density based on changing H_2O_2 concentration. This route is not suitable for the current study for the following reasons: first, according to the main objective of this study, the second gassing component, in this case H_2O_2 , must be used in any amount (in excess) without causing over-gassing. Second, in light of the role it plays in this process, it is not expected to be efficient in minimizing the effect of void size on final sensitized emulsion density, as it influences only the speed of the gassing reaction and not the amount of gas released.
- Optimisation of density based on changing KI concentration: this route shows significant promise in achieving the goal of this study. Unlike H_2O_2 , KI which is used in a pre-determined amount, will impact on the two factors (void size and void volume fraction) controlling the final sensitized emulsion density. So it was concluded that KI concentration is the only parameter which will be changed for the optimisation.

5.3.4.1 KI concentration optimisation: F800 based emulsions

The optimisation of KI concentration was done using an iterative method. To obtain the concentration that would be used as a starting point, two methods were used: one based on density vs. H_2O_2 concentration graphs where KI concentration was estimated from density vs. H_2O_2 concentration graphs; and the other based on density vs. KI concentration graphs where the optimum KI concentration was estimated using the density vs. KI concentration graphs. Emulsions were then prepared using estimated optimum KI concentrations and gassed with different H_2O_2 concentrations in an attempt to obtain the desired final gassed

emulsion density (reference density = 1.05 g/cm^3) at reduced void size, to eliminate the time dependant component of the final density.

a. Method based on density vs. H_2O_2 concentration graphs

a.1. Estimation of KI concentration to be used as starting point

The concentration of KI required to reach a final gassed emulsion density of 1.05 g/cm^3 was estimated using graphs of density vs. H_2O_2 concentration for emulsions prepared with three different fuel phases (F800, Bullfinch and R602/45). A typical estimation of KI concentration based on the graph plotted for emulsions prepared with F800 fuel phase (Figure 5.14) is shown below.

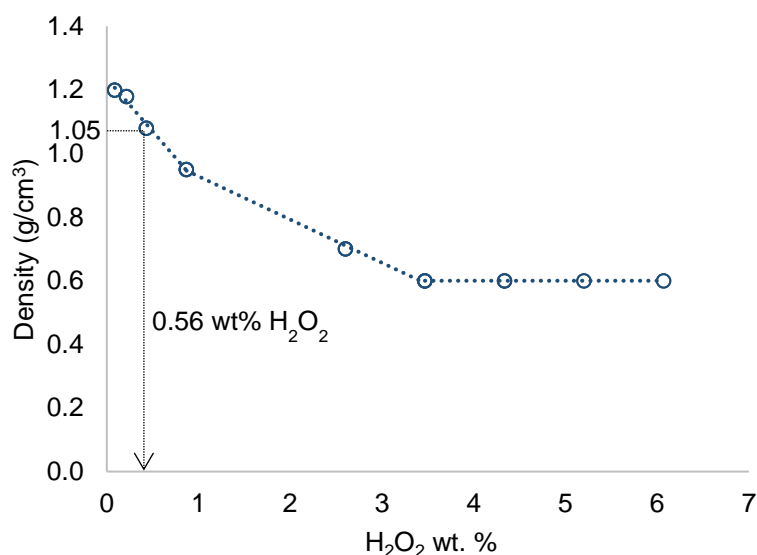


Figure 5. 14 Final gassed emulsion density dependence on H_2O_2 concentration (determination H_2O_2 required to reach final density of 1.05 g/cm^3)/ F800 fuel phase/ 0.1 wt% KI

In Figure 5.14, interpolation was used to determine the peroxide concentration corresponding to a density of 1.05 g/cm^3 . For F800 based emulsions it was found to be 0.56 wt%.

To determine the concentration of KI required, the H_2O_2 concentrations obtained from density concentration graphs was divided by the critical $\text{H}_2\text{O}_2/\text{KI}$ ratio = 34.7: 1 (see section 5.3.1. 2).

% KI required = $0.56/34.7 \approx 0.016 \text{ wt}\%$ KI as mentioned earlier (section 5.3.4); this concentration will be used as starting point for iterations.

The results obtained for all the fuel phases are summarized in table 5.3

Table 5. 3 Estimated KI concentration to be used as starting point for different fuel phases

| Fuel Phase | % H ₂ O ₂ | % KI |
|------------|---------------------------------|-------|
| F800 | 0.56 | 0.016 |
| Bullfinch | 0.22 | 0.006 |
| R 602/45 | 0.44 | 0.013 |

The next set of emulsions was prepared using the estimated KI concentration. In this case, emulsions prepared using F800 fuel phase were the main focus.

a.2. Effect of H₂O₂ concentration on emulsion density

Emulsions prepared with estimated optimum KI concentration (0.016 wt%: starting point for iterations) using F800 as fuel phase were sensitized using H₂O₂ concentrations (0.87 to 4.34 wt%) such that the H₂O₂/KI ratio was bigger than the critical ratio of 34.7 obtained earlier (section 5.3.1.2). The findings are plotted in Figure 5.15 and summarized in Table 5.4, where results associated with 0.1 wt% in the same region (H₂O₂/KI > critical ratio) were added for the purpose of comparison.

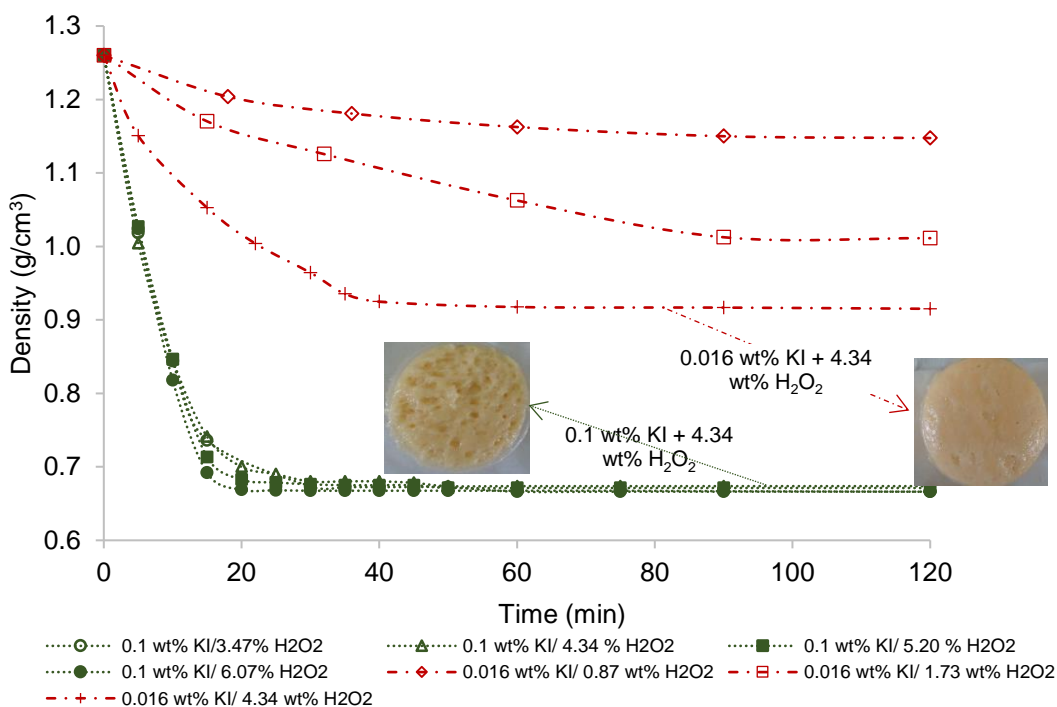


Figure 5. 15 Density change of sensitized emulsion with time (F800 fuel phase/0.016wt% KI and 0.1 wt% KI)

Table 5. 4 Effect of H₂O₂ concentration on final emulsion density and gassing time (0.016 and 0.1 wt% KI)

| KI Conc. wt.% | H ₂ O ₂ Conc, wt% | Final density (g/cm ³) | Gassing time, min | Comment |
|---------------|---|------------------------------------|-------------------|---|
| 0.016 | 0.87 | 1.15 | 90 | Reduction of gassing rate. Density dependence on H ₂ O ₂ conc. observed. Reference density not reached. |
| | 1.73 | 1.01 | 60 | |
| | 4.34 | 0.92 | 40 | |
| 0.1 | 3.47 | 0.60 | 25 | Very high gassing rate. Suppression of density dependence on H ₂ O ₂ conc. observed. Reference density not reached. |
| | 4.34 | 0.60 | 25 | |
| | 5.20 | 0.60 | 20 | |
| | 6.07 | 0.60 | 20 | |

From Figure 5.15, the following can be advanced: first, the gassing rate has significantly decreased for 0.016 wt% KI as compared to 0.1 wt% KI; this is shown by the slope of the graph. Reduction in KI concentration has resulted in a lower degree of coalescence, which in turn produced smaller bubbles, as evidenced by pictures presented in Figure 5.15. Moreover, on the following day, the sensitised emulsions had not collapsed, in contrast with previous observations (see Figure 5.16).

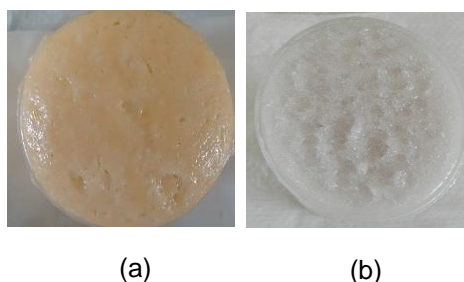


Figure 5. 16 Sensitized emulsion prepared with 0.016 wt% KI (a) just after gassing (b) on the next day

This indicates that the sensitised emulsions were not in a metastable state; therefore, the density value reached on the previous day was an equilibrium value. Second, the density dependence on H₂O₂ concentration suppressed for KI concentration of 0.1 wt% reappears when 0.016 wt% KI is used, even though the H₂O₂/KI proportions exceed the critical value previously obtained. In this sense, it seems reasonable to assume that the critical H₂O₂/KI ratio depends on the concentration of KI; 0.016 wt% KI must have a critical H₂O₂/KI ratio different from 0.1 wt% KI. Third, the density value obtained for 0.016 wt% KI (0.92 g/cm³) is

higher than that obtained when using 0.1 wt% (0.60 g/cm³) for the same H₂O₂ concentration (4.34 wt%). However, the reference density (1.05 g/cm³) was not reached.

The method based on a density vs. H₂O₂ concentration graph was successful in reducing the rate of bubble coalescence, thus eliminating the possibility of density change over time after equilibrium was reached. However, the issue of density dependence on H₂O₂ concentration was not resolved. Furthermore, the reference density was not reached. This method was not used further due to the dynamic nature of the critical H₂O₂/KI ratio, which caused complications in the optimisation of KI concentration.

In light of the above findings, the question to be answered is this: can the use of the method based on density vs. KI concentration graphs both suppress the dependence of density on H₂O₂ concentration and result in a final sensitised emulsion density of 1.05 g/cm³?

b. Optimisation based on density vs. KI concentration graphs

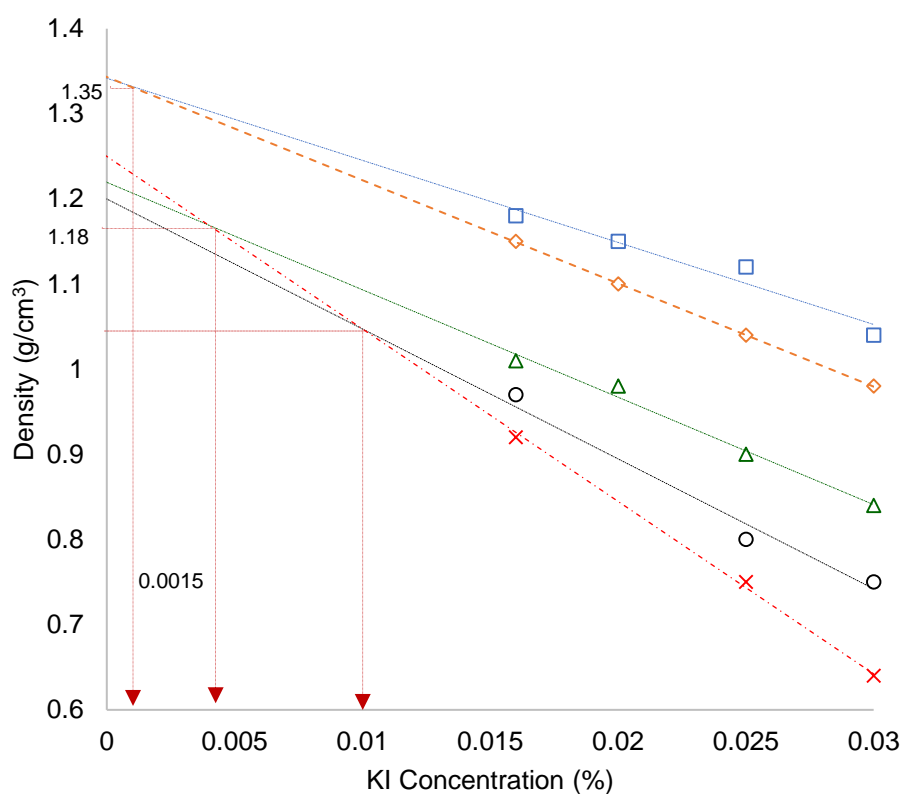
In this approach, emulsions were prepared with different KI concentrations and sensitized using various H₂O₂ concentrations. This was done to generate a graph of density vs. KI concentrations (Figure 5.17) with a view to obtaining a starting point for the iterations.

b.1. Estimation of KI concentration to be used as starting point

Extrapolation was done for non-parallel graphs that showed a tendency to convergence.

The following criteria were used for the selection of the starting point:

- The starting point should preferably be one towards which most of the graphs will converge; in this sense the final density dependence on H₂O₂ concentration would be suppressed
- The point of convergence should be associated with a positive KI concentration; a negative concentration does not have any physical meaning
- The corresponding density should be as close as possible to 1.05 g/cm³ which is the target value; in this sense, few iterations will be required.



□ 0.43wt% H₂O₂ ◇ 0.87wt% H₂O₂ △ 1.73wt% H₂O₂ ○ 2.60wt% H₂O₂ × 4.34% H₂O₂

Figure 5. 17 Equilibrium density of sensitized emulsions vs. KI concentration (F800 fuel phase)

The graph shows a convergence of the trendlines corresponding to 0.43 and 0.87 wt% H₂O₂. But the point towards which they converge corresponds to a low KI concentration (≈ 0.0015 wt%), which will result in a density (≈ 1.35 g/cm³) higher than the reference. The trendlines corresponding to 0.87 wt% and 1.73 wt% appear to be parallel. The 1.73 and 2.60 wt% trendlines converge towards a positive KI concentration, but this one corresponds to a density ≈ 1.18 g/cm³ which is higher than the reference value. The 2.60 and 4.34 wt% H₂O₂ trendlines converge towards a KI concentration at which the reference density can possibly be reached. The equations associated with these trendlines are:

$$2.60 \text{ wt\% Trendline: Density} = -15.26 [\text{KI}] + 1.20 \quad \text{Equation 5.1}$$

$$4.34 \text{ wt\% Trendline: Density} = -20.26 [\text{KI}] + 1.25. \quad \text{Equation 5.2}$$

Where [KI] represents the concentration of KI.

Solving equations 5.1 and 5.2 simultaneously yields a KI concentration ≈ 0.01 wt% and a density ≈ 1.04 g/cm³.

From these theoretical findings, 0.010 wt% KI with H₂O₂ concentrations higher than 2.60 wt% is preferred as the starting point; this will probably reduce the number of iterations needed in the optimisation of KI concentration based on the density vs. KI concentration graph.

b.2. Effect of H₂O₂ concentration on final gassed emulsion density

Emulsions were prepared using 0.010 wt% KI and sensitized using H₂O₂ concentrations above 2.60 wt%. The maximum concentration of H₂O₂ used was 7.80 wt% since above that value, the excess H₂O₂ did not further mix with the emulsion. The density change over time as a function of H₂O₂ concentration is shown in Figure 5.18.

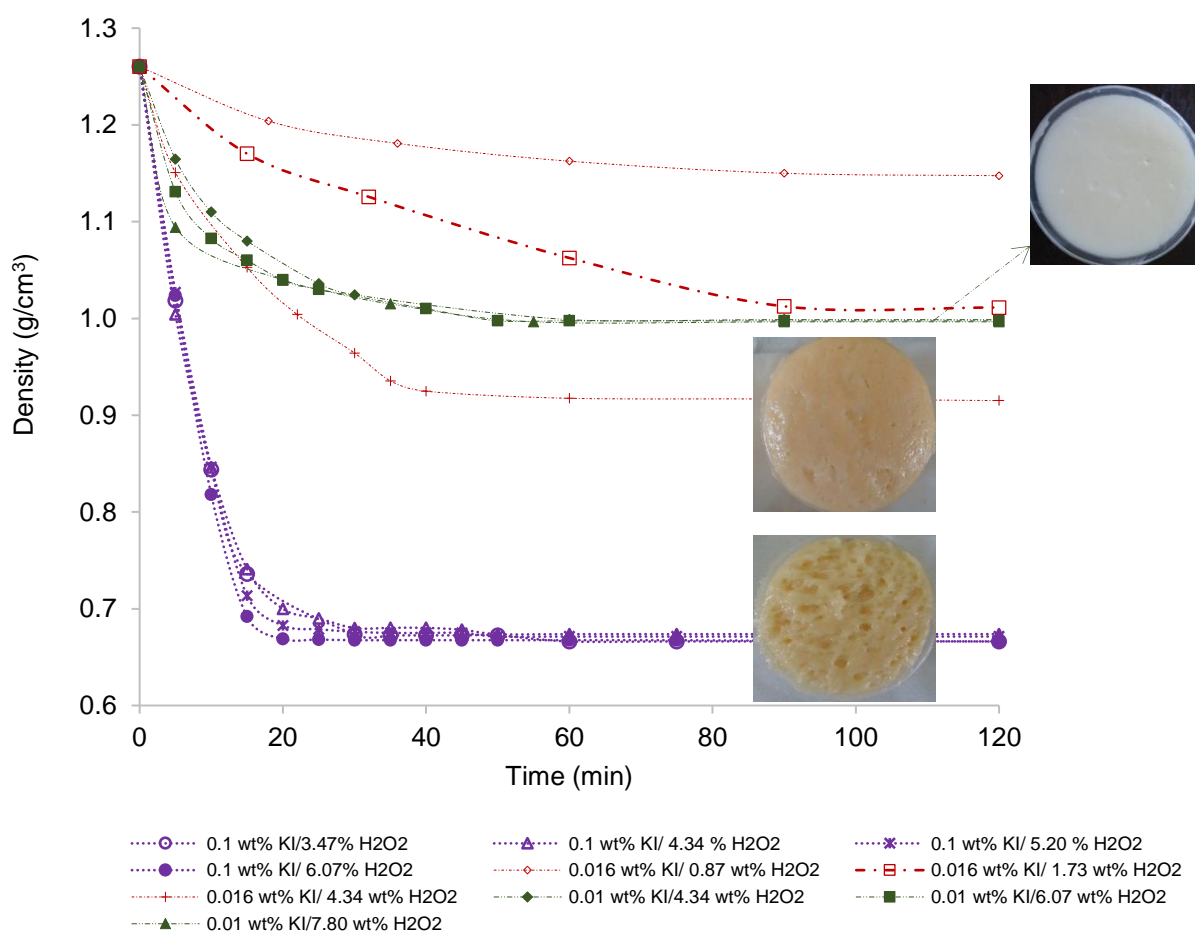


Figure 5. 18 Density change of sensitized emulsion with time (F800 fuel phase/0.016, 0.1 and 0.01 wt% KI)

Interestingly, the gassing rate drastically decreased compared to emulsions prepared with 0.1 wt% KI. This resulted in smaller void size, as shown in Figure 5.18. Moreover, unlike emulsions prepared using 0.016 wt% KI, the dependence of density on H₂O₂ concentration was suppressed for 0.01 wt% KI. The density reached in this case (1.00 g/cm³) is higher than

the cases involving 0.1 and 0.0016 wt% KI; however, the value reached was lower than 1.05 g/cm³.

For the second iteration, emulsions were prepared with a lower KI concentration (0.008 wt%) with the aim of reaching the reference density of 1.05 g/cm³. The emulsions were sensitized with H₂O₂ concentrations higher than 2.60 wt%. Figure 5.19 presents the experimental findings.

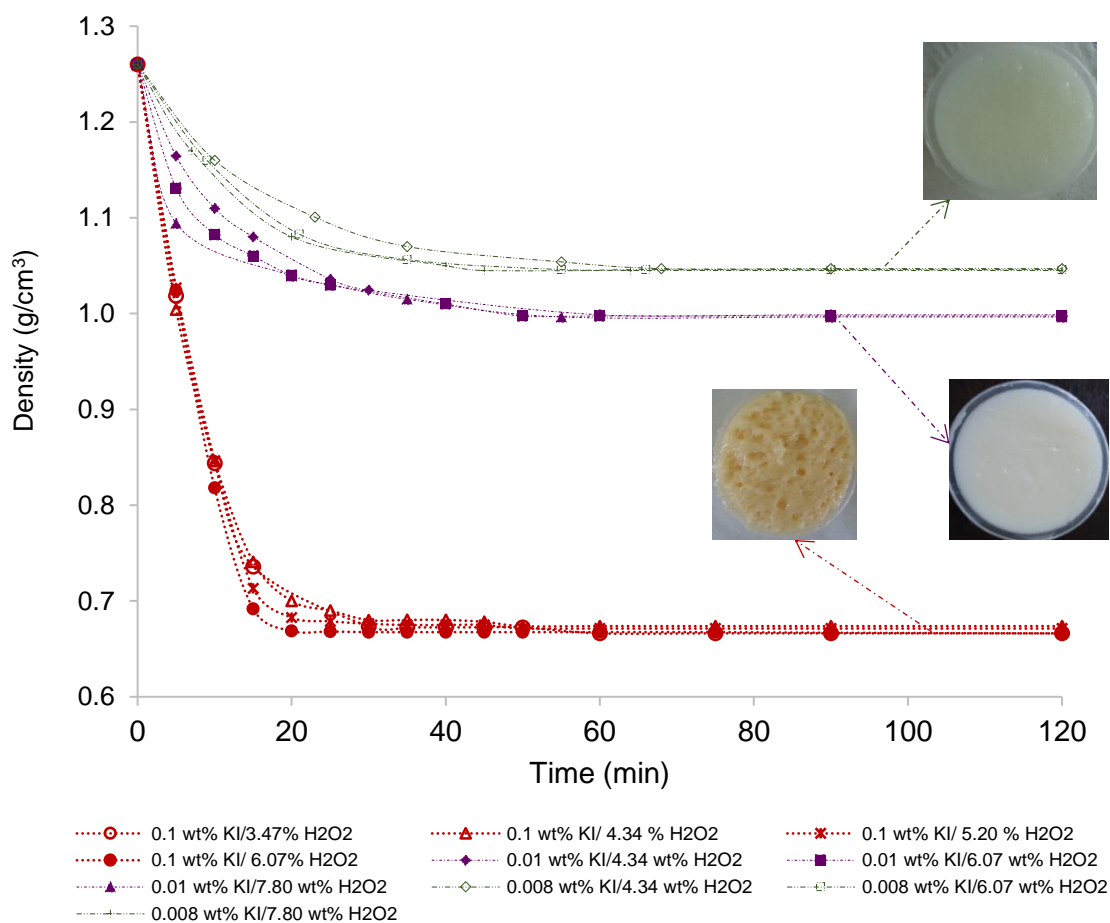


Figure 5. 19 Density change of sensitized emulsion with time (F800 fuel phase/0.008wt% KI) H₂O₂ conc. > 2.60wt%

In this case, it was observed that the gassing rate was lower than in sensitised emulsions prepared with 0.01 and 0.1 wt% KI as shown by the slopes. The voids formed were small as compared to those in emulsions prepared with 0.01 and 0.1 wt% KI. This reduced the probability of bubble coalescence. The sensitized emulsions did not collapse on the following day. The visual observations made are presented in Figure 5.20.

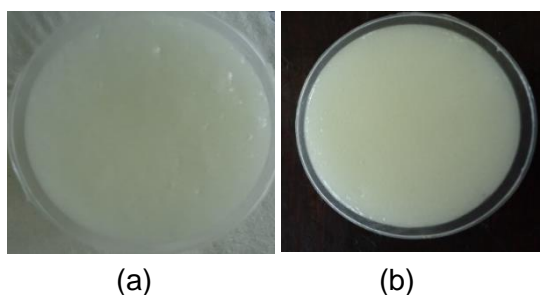


Figure 5. 20 Sensitized emulsion (F800 fuel phase/0.008 wt% KI). (a) just after gassing (b) next day

The graph shows that the density was independent of H₂O₂ concentration and a final gassed emulsion density of 1.05 g/cm³ was reached within 45 minutes.

5.3.4.2 KI concentration optimisation: Bullfinch and R602/45 based emulsions

a. Emulsions prepared using Bullfinch fuel phase

The optimum KI concentration of 0.008wt% obtained for F800 was used as the first iterative point for emulsions prepared using the Bullfinch fuel phase. The H₂O₂ concentrations used were higher than 2.60 wt% H₂O₂ as previously indicated. The results obtained are shown in Figure 5.21.

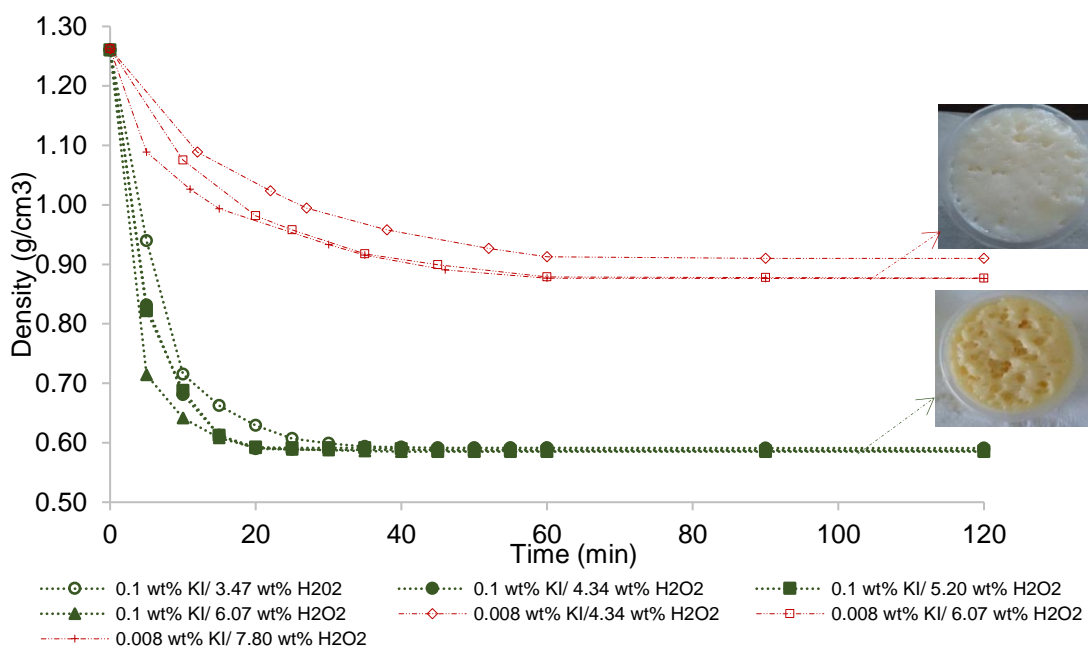


Figure 5. 21 Density change of sensitized emulsion with time (Bullfinch fuel phase/0.008 and 0.1 wt% KI/ H₂O₂ conc. > 2.60wt%)

A significant decrease in the rate of gassing for emulsions prepared using 0.008 wt% KI as compared with 0.1 wt% KI was observed, as shown by the slope of the graph. This resulted in lower degree of coalescence which in turn produced smaller bubbles, as evidenced by pictures presented in Figure 5.21. Moreover, on the next day, the sensitised emulsions did not collapse, in contrast with previous observations (see Figure 5.22).

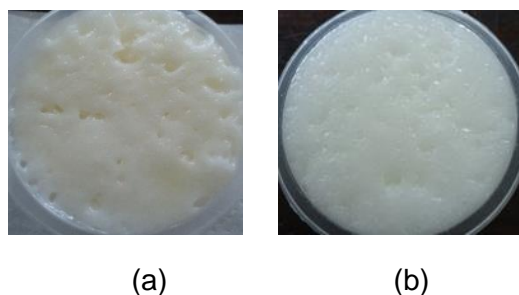


Figure 5. 22 Sensitized emulsion (Bullfinch fuel phase/0.008 wt% KI). (a) just after gassing (b) next day

At H_2O_2 concentrations of 6.07 wt% and above, the final gassed emulsion density remained constant irrespective of the amount of H_2O_2 added. The H_2O_2 concentration dependence was suppressed. Although there was an increase in the final sensitized emulsion density, it was still lower than 1.05 g/cm^3 .

For the next iteration, emulsions were prepared with lower KI concentrations then sensitized. The next selected KI concentration was 0.004 wt%. Results obtained are shown in Figure 5.23.

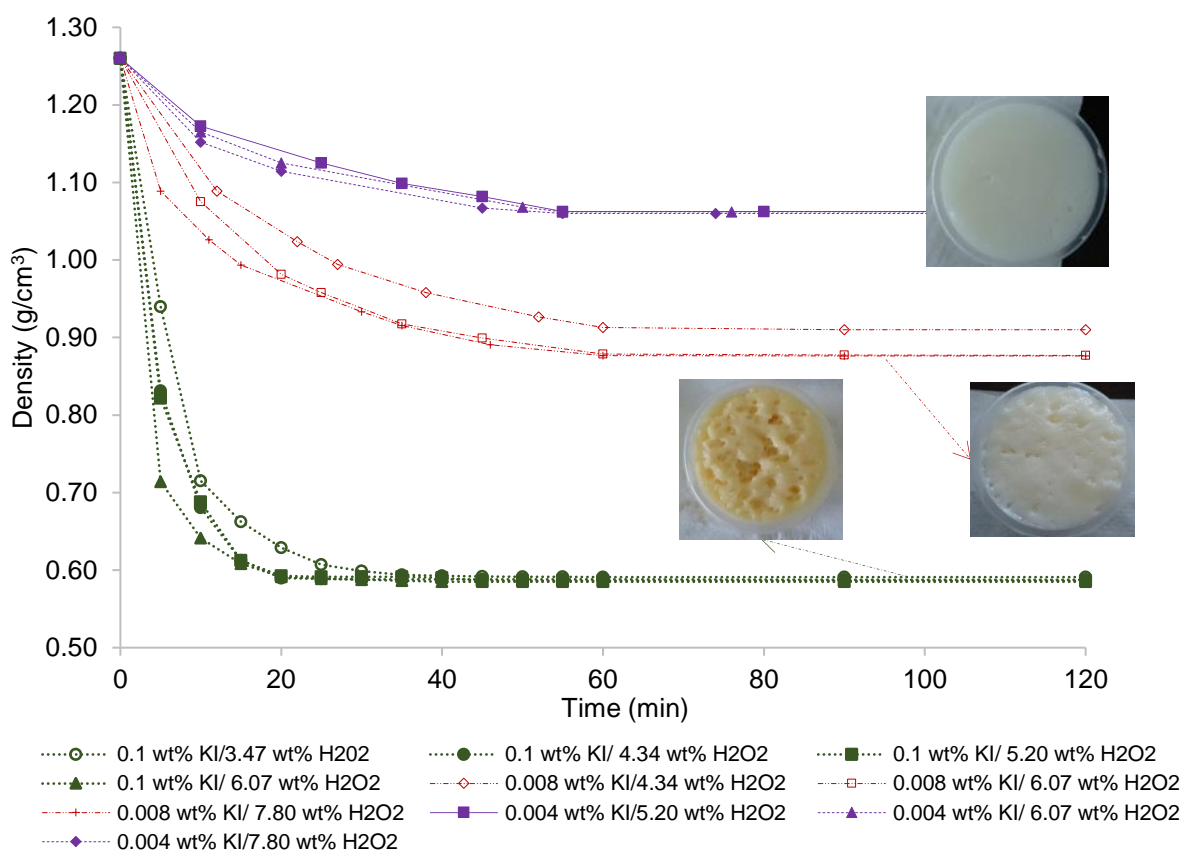


Figure 5. 23 Density change of sensitized emulsion with time (Bullfinch fuel phase/0.004wt% KI). H₂O₂ conc. > 2.60wt%

In emulsions prepared with 0.004 wt%, the gassing rate was observed to be much lower than those prepared with 0.008 and 0.1 wt% KI. The void size was smaller compared to emulsions containing 0.008 and 0.1 wt% KI, as evidenced by pictures in Figure 5.23. The graph shows that the density of 1.06 g/cm³ was reached using an H₂O₂ concentration of 5.20 wt% within about 55 minutes. The addition of more H₂O₂ did not affect the final gassed emulsion density. Moreover the voids did not collapse on the following day (Figure 5.24).

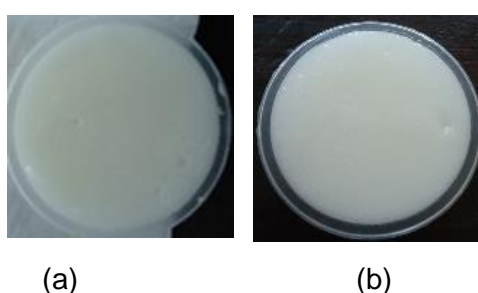


Figure 5. 24 Sensitized emulsion (Bullfinch fuel phase/0.004 wt% KI). (a) just after gassing (b) next day

b. Emulsions prepared using R602/45 fuel phase

The optimum KI concentration obtained for F800 (0.008 wt%KI) was also used in preparing emulsions with the R602/45 fuel phase. The findings from sensitization of these emulsions with H₂O₂ higher than 2.60 wt% are shown in Figure 5.25.

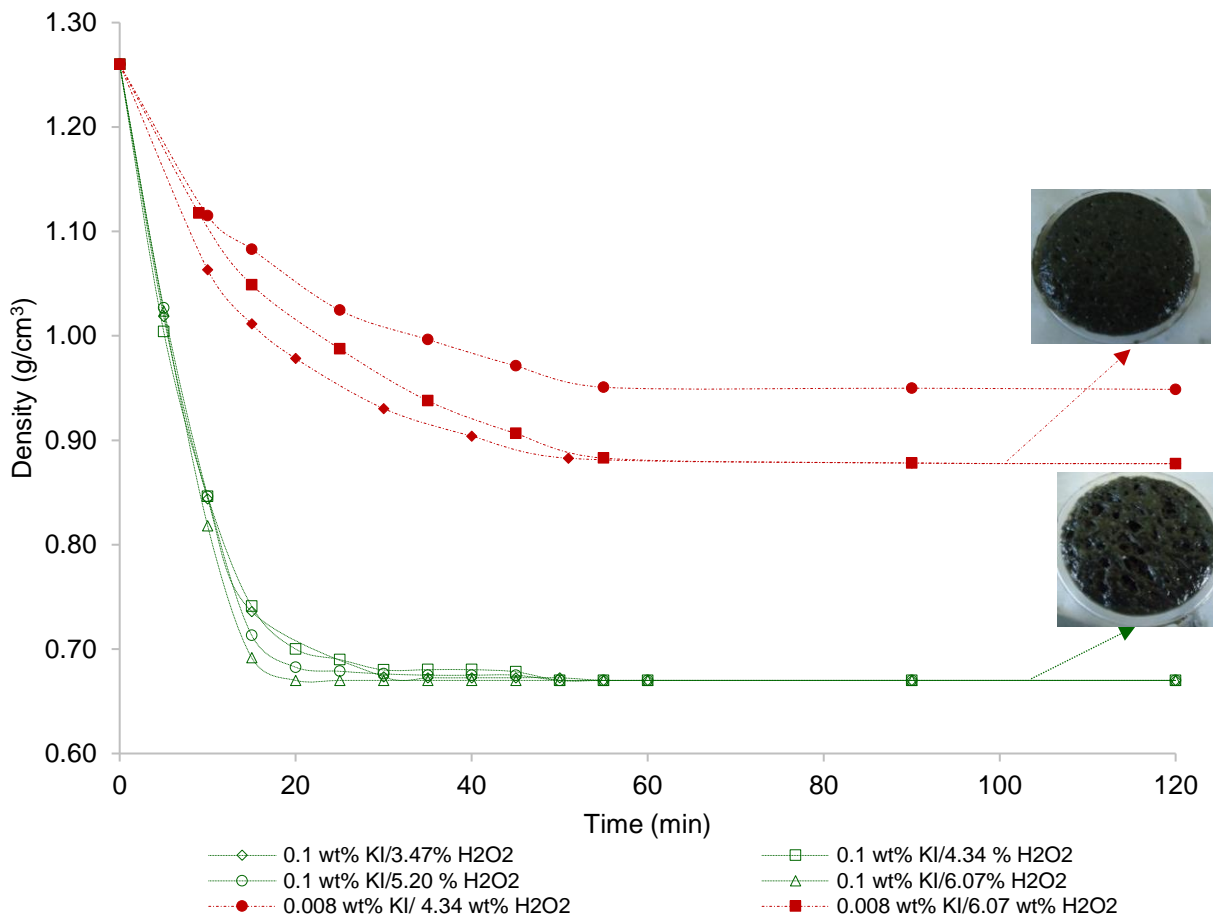


Figure 5. 25 Density change of sensitized emulsion with time (R602/45 fuel phase/0.1 and 0.008wt% KI)

It can be seen, as before, that the gassing rate drastically dropped when the KI concentration was decreased to 0.008 wt%. As a consequence, the rate of bubble coalescence was lower, which resulted in small voids and a density much closer to 1.05 g/cm³ as compared to the case in which 0.1 wt% KI is used. The sensitised emulsions did not collapse on the following day, as shown in Figure 5.26.

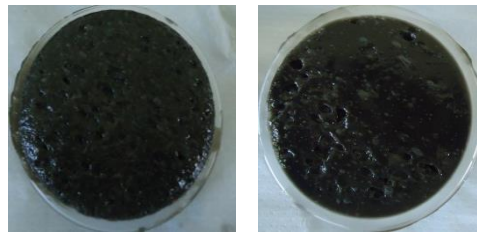


Figure 5. 26 Sensitized emulsion (R602/45 fuel phase 0.008 wt% KI). (a) just after

At H₂O₂ concentrations of 6.07 wt% and above, a suppression of density dependence on H₂O₂ concentration was observed. However, the final density reached when using 0.008 wt% KI was lower than 1.05 g/cm³.

For the second iteration, emulsions were prepared with a lower KI concentration (0.004 wt%) and sensitised with H₂O₂ concentrations higher than 2.60 wt%. The outcome of the gassing experiments is presented in Figure 5.27.

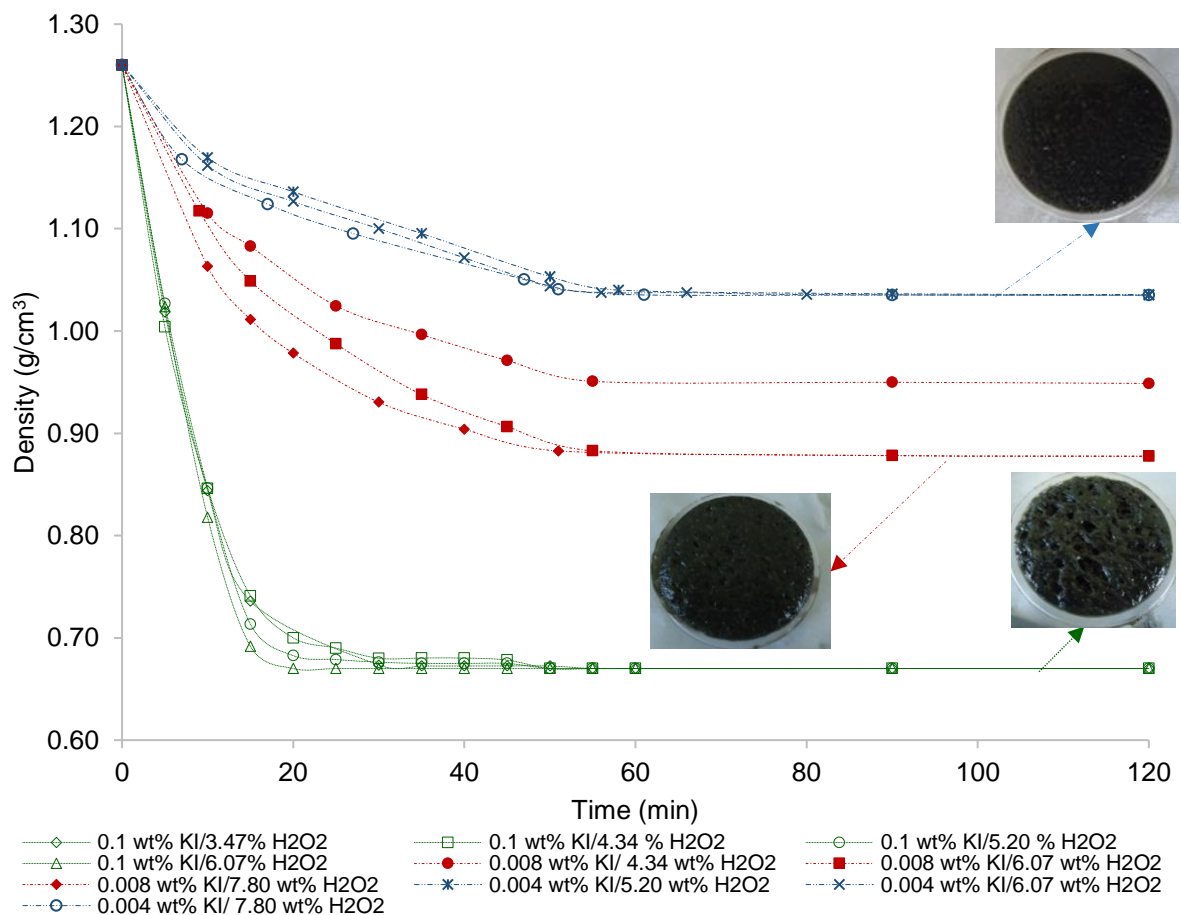


Figure 5. 27 Density change of sensitized emulsion with time (R602/45 fuel phase/ 0.1, 0.008 and 0.004wt% KI)

A significant drop in gassing rate compared to emulsions prepared with 0.008 wt% and 0.1 wt% was observed. This induced a decrease in the extent of bubble coalescence, resulting in smaller void size, as compared to emulsions containing 0.008 and 0.1 wt% KI (see pictures in Figure 5.25). The graph shows that the density of 1.04 g/cm³ was reached using an H₂O₂ concentration of 5.20 wt% within 52 minutes. Addition of extra H₂O₂ did not affect the final gassed emulsion density. Moreover, no emulsion collapse was observed on the following day (Figure 5.28).

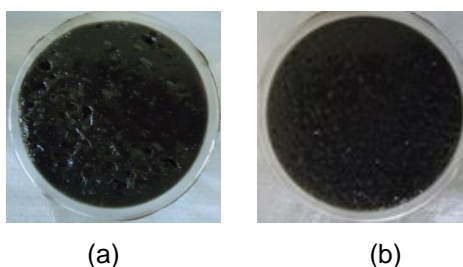


Figure 5. 28 Sensitized emulsion (R602/45 fuel phase). (a) just after gassing; (b) next day

Through the optimization process, the metastable equilibrium challenge encountered earlier was overcome and the reference equilibrium density was reached.

5.3.5 Summary of sensitisation of emulsions with KI added to fuel phase

In light of the results obtained for the sensitization of explosive emulsions prepared with KI dispersed/dissolved in the fuel phase presented above, the following can be advanced:

- Irrespective of the H₂O₂ concentration used, it could be seen from the density profiles that the gassing process started with a region of density variation with time proceeded by a plateau, which indicated that the reaction had come to an equilibrium.
- When using 0.1 wt% KI, the rate of density change increased with increasing H₂O₂ concentration up to a transitional point (3.47 wt% H₂O₂), above which the changes observed were insignificant. For the same KI concentration (0.1 wt%), the final gassed emulsion density decreased with increasing H₂O₂ concentration up to a transitional H₂O₂ concentration of 3.47 wt%, above which value no change was observed, irrespective of H₂O₂ concentration.
- However, the sensitized emulsions prepared with 0.1 wt% were in a metastable state and the voids formed collapsed the next day. Moreover, the reference density required for effective blasting was not reached. It was shown that the density was controlled by 2 factors: the void size and the void volume fraction. The void size is

controlled by both KI and H₂O₂; the void volume fraction is controlled by KI. The final emulsion density had to be optimised based on that information

- An iterative technique based on changing the concentration of KI was used to optimize the final density of the sensitized emulsions. Two techniques were used to determine the starting iteration point: one based on density vs. H₂O₂ concentration graphs, which was unsuccessful, and the other based on density vs. KI concentration graphs. The latter method yielded the desired results which are summarized in Table 5.5.

Table 5. 5 Optimization results summary

| Fuel phase | KI Conc, wt. % | Equilibrium density, g/cm ³ | Gassing time, min |
|------------|----------------|--|-------------------|
| F800 | 0.008 | 1.05 | 45 |
| Bullfinch | 0.004 | 1.06 | 55 |
| R 602/45 | 0.004 | 1.04 | 52 |

After the comprehensive study of gassing of emulsions with KI added to the fuel phase, the gassing of emulsions with KI dissolved in ANS prior to emulsification is now considered.

5.4 Sensitization of explosive emulsions with KI dissolved in ANS

5.4.1 Effect of H₂O₂ concentration on final emulsion density and gassing rate

To study the effect of H₂O₂ concentration on the final sensitised emulsion density and rate of gassing, emulsions were prepared with KI dissolved in ANS prior to emulsification and gassed with H₂O₂. The pH of the ANS before KI addition used to prepare all emulsions was 4.4 (without addition of pH modifiers). The optimum KI concentrations obtained from the sensitisation of emulsions prepared with F800, Bullfinch and R602/45 (with KI in the fuel phase) were used in this case. Typical results obtained are presented in Figure 5.29 (F800 fuel phase).

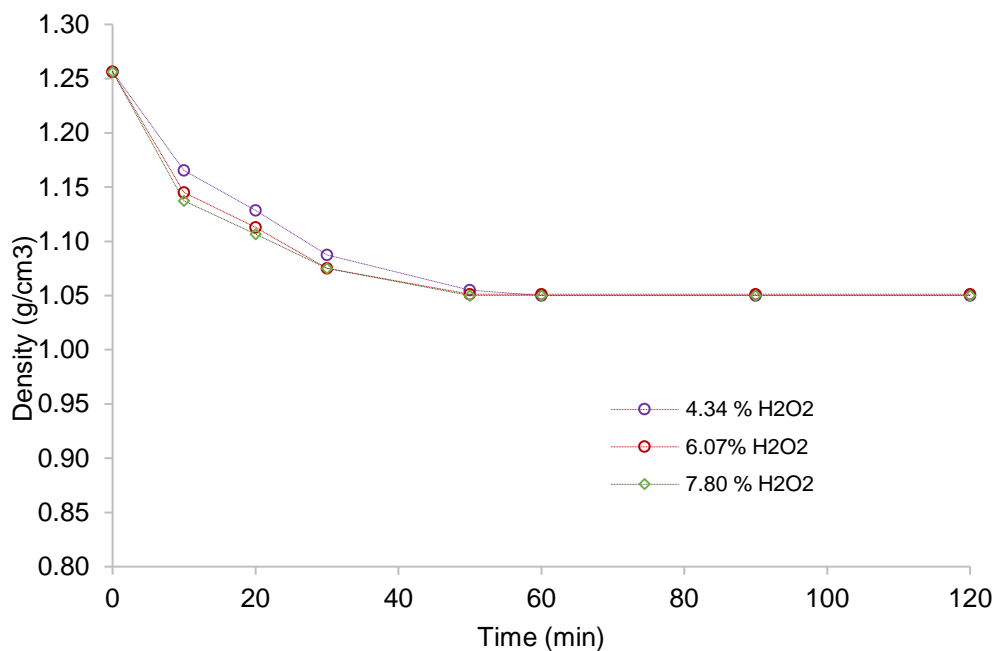


Figure 5. 29 Density change of sensitized emulsion with time (F800 fuel phase/ 0.008wt% KI dissolved in ANS. H₂O₂ conc. > 2.60wt%)

From the graphs above, it can be seen that the density initially decreases steadily with time. The steady decrease is followed by a plateau which indicates that equilibrium has been reached as evidenced by observations made the next day (Figure 5.30).

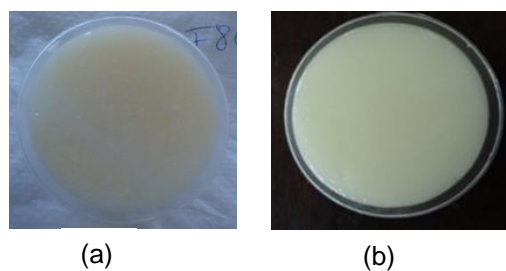


Figure 5. 30 Sensitized emulsion (F800 fuel phase/ KI in ANS). (a) just after gassing. (b) next day

The figure shows that the sensitised emulsions were not in a metastable state as the voids did not collapse the next day.

The results obtained for all three fuel phases are summarized in table 5.6.

Table 5. 6 Effect of H₂O₂ concentration on equilibrium density of sensitised emulsions

| Fuel phase | H ₂ O ₂ Conc, wt% | Equilibrium density, g/cm ³ |
|-----------------------------|---|--|
| F800 (0,008 wt% KI) | 4.34 | 1.05 |
| | 6.07 | 1.05 |
| | 7.80 | 1.05 |
| Bullfinch (0,004 wt% KI) | 5.20 | 1.03 |
| | 6.07 | 1.03 |
| | 7.80 | 1.03 |
| R602/45 (0,004 wt% KI) | 5.20 | 1.03 |
| | 6.07 | 1.03 |
| | 7.80 | 1.03 |

It is obvious from these results that the final emulsion density did not depend of H₂O₂ concentration, and that the reference density was reached for the different emulsions. This is consistent with observations made when KI was dissolved/dispersed in the fuel phase. A quantitative comparison of results was done in the following section.

5.4.2 Emulsions with KI in fuel phase vs. emulsions with KI in ANS

To compare the rate of gassing and the final density of sensitised emulsions with optimum KI concentration, results from emulsions with KI added to the fuel phase and those in which KI is dissolved in ANS prior to emulsification were plotted on the same graph. Typical results are presented in Figure 5.31 (F800 fuel phase), and the data related to all three fuel phases are summarized in Table 5.7.

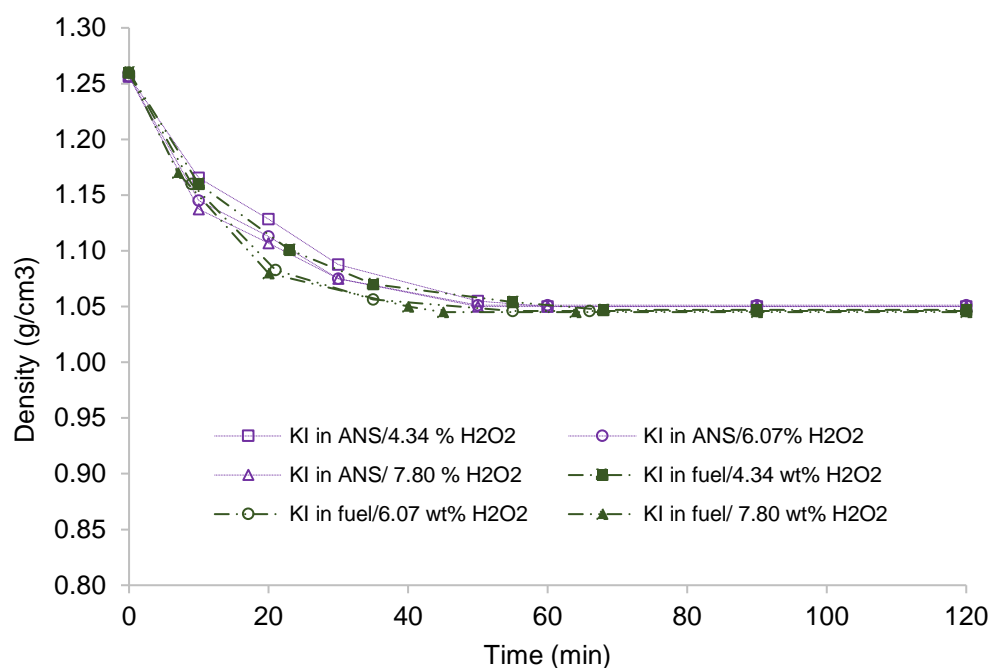


Figure 5. 31 Density change of sensitized emulsion with time (F800 fuel phase/ 0.008wt% KI in ANS vs. KI in fuel phase

Table 5. 7 Summary of results for KI dispersed in fuel phase and KI dissolved in ANS

| Fuel phase | KI dispersed in fuel phase | | | KI dissolved in ANS | | |
|--------------------------|---|--|-------------------|---|--|-------------------|
| | H ₂ O ₂ Conc, wt% | Equilibrium Density, g/cm ³ | Gassing time, min | H ₂ O ₂ Conc, wt% | Equilibrium Density, g/cm ³ | Gassing time, min |
| F800 (0,008 wt% KI) | 4.34 | 1.05 | 50 | 4.34 | 1.05 | 50 |
| | 6.07 | 1.05 | 45 | 6.07 | 1.05 | 50 |
| | 7.80 | 1.05 | 45 | 7.80 | 1.05 | 50 |
| Bullfinch (0,004 wt% KI) | 5.20 | 1.06 | 55 | 4.34 | 1.03 | 55 |
| | 6.07 | 1.06 | 55 | 6.07 | 1.03 | 50 |
| | 7.80 | 1.06 | 55 | 7.80 | 1.03 | 50 |
| R602/45 (0,004 wt% KI) | 5.20 | 1.04 | 52 | 4.34 | 1.03 | 55 |
| | 6.07 | 1.04 | 52 | 6.07 | 1.03 | 55 |
| | 7.80 | 1.04 | 52 | 7.80 | 1.03 | 55 |

Interestingly, the optimum concentration KI when it is dissolved or dispersed in the fuel phase coincides with the optimum KI when dissolved in ANS: First, for emulsions prepared using F800 fuel with KI added to ANS, the final density was 1.05 g/cm³ (second column from the right in Table 5.7); this value did not change irrespective of the H₂O₂ amount added (Figure 5.31). This is in agreement with the case where KI is in the fuel phase (third column

from the left in Table 5.7). The same trend was observed for emulsions prepared with Bullfinch and R602/45 fuel phases (Table 5.6). Second, the changes in rate of gassing for emulsions prepared with F800 (KI added to ANS) were insignificant as the H_2O_2 concentration increased (Figure 5.31). This is roughly indicated by the gassing time of 50 minutes observed, irrespective of H_2O_2 concentration (column 1 from right in Table 5.6). This is consistent with the case where KI was added to the fuel prior to emulsification. Results from emulsions prepared with Bullfinch and R602/45 fuel phases showed a similar trend (Table 5.7).

The similarity of results from the gassing of emulsions with KI dissolved in ANS and those in which KI is added to the fuel phase prior to emulsification gave rise to a question: in which of the phases (aqueous or fuel) is the gassing reaction occurring?

5.4.3 Phase in which gassing reaction is occurs

As described in section 4.2.4, experiments were conducted for 2 different conditions: first, KI was dissolved/dispersed in the fuel phase, then the mixture formed was added to the ANS. Afterwards H_2O_2 was added from the fuel phase with a pipette. Second, KI was dissolved in ANS, then the fuel phase was added to the resulting ANS/KI solution. Afterwards H_2O_2 was added from the ANS (pipette dipped in ANS). The observations made 10 seconds after H_2O_2 addition are presented in Figure 5.32.

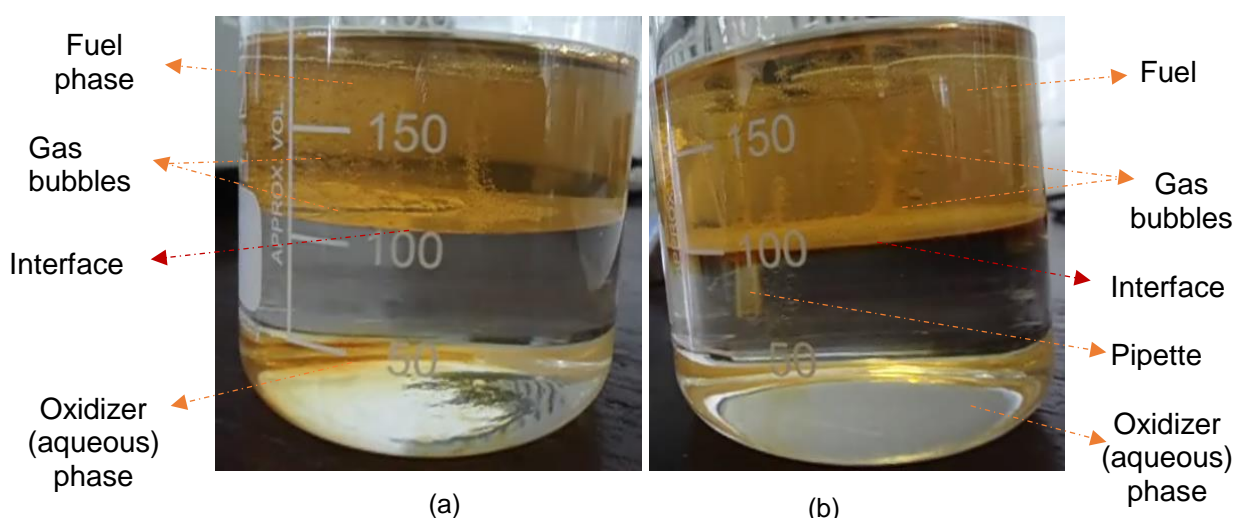


Figure 5. 32 Phase in which gassing is occurring 10 s after H_2O_2 addition: (a) KI added to the fuel phase (b) KI dissolved in ANS

Figure 5.32 (a), the case in which KI was added to the fuel phase, shows gas bubble formation 10 seconds after addition of H_2O_2 . A similar observation was made in the case where KI was dissolved in ANS (pipette containing H_2O_2 dipped in the ANS) as shown in Figure 5.32 (b). Interestingly, the results in Figure 5.32 (a) and (b) show that irrespective of the phase in which KI is added, the gassing reaction occurs at the interface formed by the fuel and aqueous phases. This information is important for the following reasons: first, it sheds light on the gassing reaction between KI and H_2O_2 in the fuel phase reported in section 3.2.5 of the feasibility study: when H_2O_2 was added to the fuel containing KI, a fuel phase/aqueous H_2O_2 interface was created which made the reaction between KI and H_2O_2 added to the fuel phase possible. Second, it offers a plausible explanation of the similarities between the case in which KI is added to the fuel, and KI is dissolved in ANS (in terms of both gassing rate and final emulsion density). Third, it is relevant for further study of the KI + H_2O_2 reaction mechanism in explosive emulsions.

It is worth mentioning that the findings above are associated with an ANS pH of 4.4. It is also important to note the following:

- The behaviour of H_2O_2 is greatly affected by the pH; interference with the reaction between KI and H_2O_2 in the explosive emulsions (due to pH effect on H_2O_2) could negatively affect the equilibrium density.
- Commercial emulsions used for industrial applications are prepared at different pH, depending on the formulation.

In light of the above, the study cannot be concluded without looking at the effect of pH on the gassing process using the two-component system in terms of final sensitised emulsion density (with KI dissolved in the aqueous phase).

5.4.4 Effect of pH on final emulsion density

5.4.4.1 Effect of pH on gassing reaction in ANS

Before conducting the experiment in emulsions which are multiphase systems, a qualitative study was done for a single-phase system (ANS) to shed light on what could occur in emulsions. The reaction between KI and H_2O_2 was carried out in ANS to visually observe the effect of pH on the gassing process. KI was dissolved in ANS, then H_2O_2 was added to the resulting solution. The results obtained 30 seconds after H_2O_2 addition are shown in Figure 5.33.

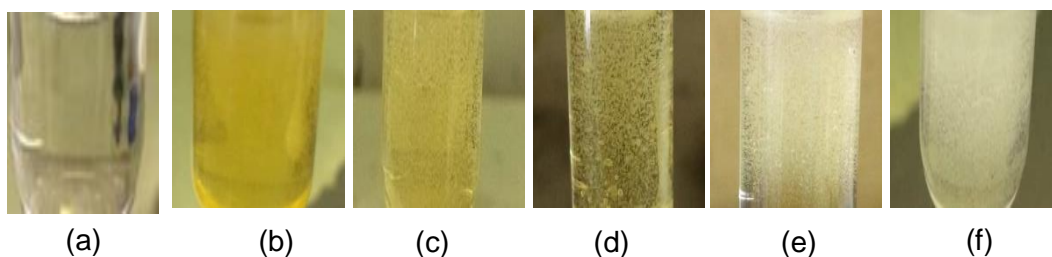


Figure 5.33 Effect of pH on gassing reaction in ammonium nitrate solution 30 sec after of 1 ml H₂O₂ addition to 4 ml ANS (containing 0.2 g KI/L ANS) (a) ANS solution; (b) pH 4.4; (c) pH 5.0; (d) pH 5.5; (e) pH 6.0; (f) pH 6.5

It could be seen that the solutions turned yellow immediately after H₂O₂ addition and bubble formation occurred about 5 seconds after H₂O₂ addition to the ANS containing KI. It is clear from Figure 5.33 that:

- At pH < 6, the yellow colour is more pronounced as seen for ANS pH of 4.4 (Figure 5.a), 5.0 (Figure 5.b) and 5.5 (Figure 5.c) with slight decrease in intensity with increasing pH.
- At pH ≥ 6.0, the yellow colour has almost completely disappeared as seen for ANS pH of 6.0 (Figure 5.33 d) and 6.5 (Figure 5.33 e).
- A transition occurs between pH 5.5 (Figure 5.33 c) and pH 6.0 (Figure 5.33 d) where the solution goes from deep yellow to very light yellow that tends to colourless.
- the gassing reaction became more vigorous with increasing pH values. This was indicated by an increasing amount of bubbles as pH values increased. These observations could be an indication that the rate of gassing increases with increasing pH with a transition around pH 6.0.

5.4.4.2 Effect of pH on gassing reaction in emulsions

The effect of pH on the gassing reaction has been studied for emulsions prepared with optimum KI concentration using F800 fuel phase (KI dissolved in ANS). The results are shown in Figure 5.34.

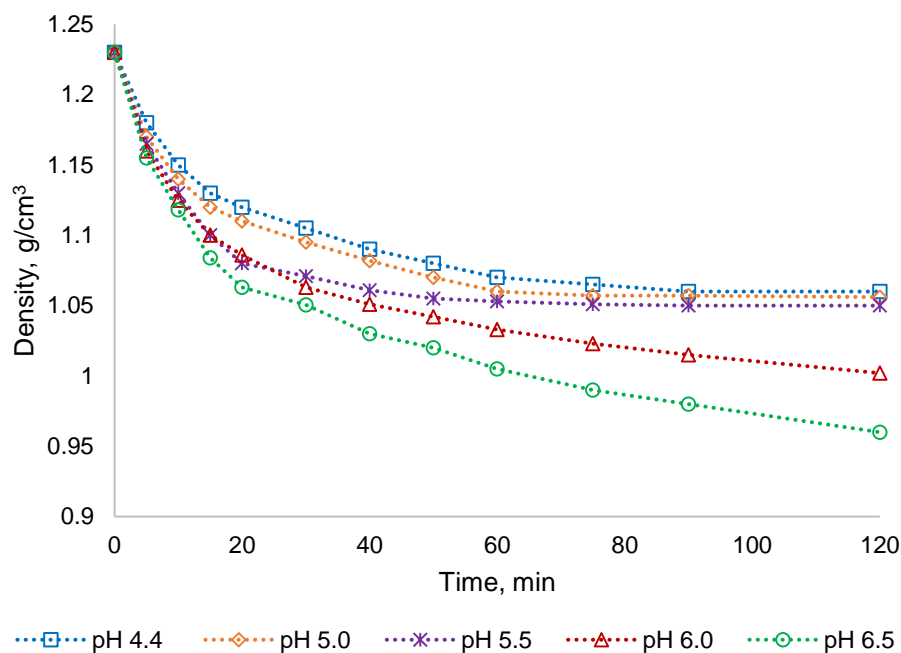


Figure 5. 34 Effect of pH on rate of density change and final density. $4.4 \leq \text{pH} \leq 6.5$

At pH between 4.4 and 5.5, equilibrium density of 1.05 g/cm^3 is reached within 45 - 60 minutes, whereas at pH between 6.0 and 6.5, the equilibrium density was not reached within the time of observation; it continued to drop beyond 120 minutes and the value reached at that time was below the reference value (1.05 g/cm^3). From the observations made, it is clear that a transition occurs at pH around 6.0. This corresponds to the value at which transition was observed for experiments conducted in ANS. Below the transitional point, the final density is not affected by the pH whereas above the transitional value, the pH seems to have an effect on the final density. It seems that the gassing reaction continues even though theoretically all the KI has been consumed. What could be the possible explanation behind these observations? Morgan (1954) reported that in the presence of a catalytic substance (e.g. platinum black, Fe^{2+} , Br^- , I^- , MnO_2) and at solution $\text{pH} \geq 5.0$, H_2O_2 undergoes catalytic decomposition. On the other hand, it is well known that an increase in pH promotes the spontaneous decomposition of H_2O_2 (Yazici and Deveci, 2010).

The question arising is this: in explosive emulsions prepared with ANS at transitional pH value, is there a change of mechanism from stoichiometric reaction to catalytic decomposition of H_2O_2 or is spontaneous decomposition of H_2O_2 greatly enhanced?

5.4.4.3 Catalytic vs. spontaneous decomposition of H₂O₂ at transitional point

In an attempt to answer the question above, two experiments were conducted: in one the possibility of catalytic decomposition was studied and in the other the possibility of enhanced spontaneous decomposition was examined. The experiments were conducted in ANS which had so far given a good qualitative indication of what occurs in explosive emulsions.

a. Catalytic decomposition of H₂O₂ in explosive emulsions

An experiment similar to the one conducted under section 4.2.1 was carried out to test the possibility of a catalytic reaction occurring in explosive emulsions at transitional pH value. 0.02 g KI was dissolved in 100 ml ANS (with pH adjusted to desired value). 4 ml of ANS containing KI was placed in a test tube, and then 1 ml of H₂O₂ was added to the solution. The findings are shown in Figure 5.35.

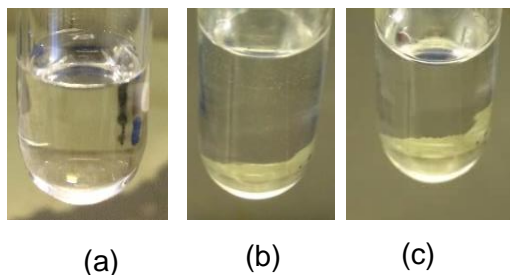


Figure 5. 35 Gassing mechanism at transitional pH (a) ANS before H₂O₂ addition (b) ANS 8 hours after H₂O₂ addition (c) ANS next day after extra addition

It was observed as previously (Figure 5.35 d) that vigorous gassing reaction started 5 seconds after H₂O₂ addition. The gassing reaction rate dropped with time as indicated by a slower motion of bubbles in the solution. Unlike the observations made at pH 4.4 (section 5.3), gas bubbles were still being formed in the solution even 6 hours after the initial peroxide addition (Figure 5.35 b). The solution was left for overnight observation and it could be seen the next day that bubbling was still occurring at a very low rate. After the addition of an extra 1 ml H₂O₂, gas bubble formation continued at the same low rate. This led to the conclusion that the reaction was not catalytic. For a catalytic reaction, it was expected that the gassing reaction would occur as vigorously as on the first day.

b. Spontaneous decomposition of H₂O₂ in explosive emulsions

To study the effect of pH on the spontaneous decomposition of H₂O₂ in explosive emulsions, H₂O₂ solution (30 wt%) was added to ANS at different pH values. The results obtained are shown in Figure 5.36.

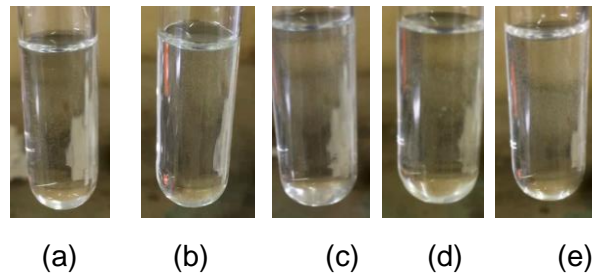


Figure 5. 36 Effect of pH on H₂O₂ decomposition in ANS (a) pH 4.4. (b) pH 5.0 (c) pH 5.5. (d) pH 6.0 (e) pH 6.5

As pH increases, the rate of bubble formation increases. This confirms the information reported by Yazici and Deveci (2010) on the effect of pH on H₂O₂ spontaneous decomposition. The observations made provide an explanation for the continued gassing reaction in sensitized emulsions at pH ≥ 6.0.

5.4.5 Summary of sensitisation of emulsions with KI dissolved in ANS

In section 5.4, the focus was on the sensitisation of emulsions with KI dissolved in ANS prior to emulsification. The optimum KI concentration obtained for emulsions with KI dissolved/dispersed in the fuel phase was used in this case. The following is a summary of the observations made:

- As for emulsions in which KI was added to the fuel phase before preparation, it was found that firstly there was no dependence of final density on H₂O₂ concentration; secondly the reference density was reached; thirdly the sensitised emulsions were not in metastable state as the voids did not collapse the next day.
- The similarities observed between the 2 different cases gave rise to a question: in which of the phases does the gassing reaction occur? To answer the question, an experiment was conducted to determine the phase in which the gassing reaction occurs. Unexpectedly the results showed that the gassing neither happened in the fuel phase, nor in the aqueous phase, but at the interface formed between the two phases.
- Knowing that the increased instability of H₂O₂ with increasing pH could possibly interfere with the reaction between KI and H₂O₂, a study was conducted on the effects of pH on the two-component gassing system. The study showed that at pH ≥ 6.0 the gassing reaction does not reach equilibrium within the time of observation and the density drops below the reference value.

5.5 Blasting Performance

Experiments were conducted to determine the velocity of detonation of explosive emulsions sensitized to give an indication of the blasting performance. Studies were conducted for emulsions sensitised with the two-component system, and results compared with those obtained when using the current technology (one-component system). The findings for F800 and Bullfinch-based emulsions are summarized in Table 5.8. Only a limited number of experiments could be conducted due to time constraints, while other restrictions attached to the use of the blasting site did not allow for extra work on blasting to be carried out.

Table 5. 8 Blasting characteristics for commercial explosive emulsions

| Fuel phase | One component system | | Two-component system | |
|------------|----------------------------------|----------|----------------------------------|----------|
| | VOD timer reading, μs | VOD, m/s | VOD timer reading, μs | VOD, m/s |
| F800 | 33.3 | 4500 | 35.7 | 4200 |
| | 32.6 | 4600 | 37.5 | 4000 |
| | 32.6 | 4600 | 38.5 | 3900 |
| Bullfinch | 37.5 | 4000 | 40.5 | 3700 |
| | 35.7 | 4200 | 39.5 | 3800 |

The equipment used for measurements in blasting experiments was only capable of measuring the time taken for the shockwave to travel 15 seconds. More details about this were presented in section 4.2.6. The VOD was calculated from the time obtained; detailed VOD calculations are shown in Appendix E.

It was observed for explosive emulsions prepared with both fuel phases that the VOD was lower for the two-component than for the one-component system. Mendes et al. (2014) studied the differences between the detonation behaviour of emulsion explosives sensitized with glass and with polymeric micro-balloons. They found that in explosive emulsions with densities ranging between 0.7 and 1.05 g/cm³, for equal sensitised emulsion densities, emulsions sensitised with polymeric microballoons exhibited higher velocities of detonation than those sensitised with glass micoballoons. In a study on the influence of artificial pores on the detonation parameters of explosive emulsions, sensitisation of emulsions was conducted using 5 different materials: glass and polymeric microballons, perlite grains, hollow cenospheres, and a gas generating additive (GGA) that produced nitrogen microbubbles (Yunoshev et al., 2017). It was found that for a sensitised emulsion density of 1.05 ± 0.1 cm³, emulsions sensitised with cenospheres resulted in a VOD of 4200 m/s and those with a GGA 4700 m/s. For a sensitised emulsion density of 1.01 g/cm³, emulsions sensitised with polymeric microballoons, perlite grains and glass microballoons resulted into

VODs of 5200 m/s, 4700 m/s and 4400 m/s respectively. These findings show that the density alone does not determine the VOD of explosive emulsions.

For the present study possible explanations for the observations made are as follows:

- The porosity of explosive emulsions sensitised with sodium nitrite and the new gassing system (H₂O₂ /KI) are different. Mendes et al. (2014) report porosity as an important factor in describing the detonation process of an explosive emulsion. This factor can give an indication of the similarities or differences of VODs at the same sensitised explosive emulsion density.
- The oxygen generated in the new technology could be taking part in fuel combustion during detonation. In this sense the gas bubbles act both as hotspots and as an agent enhancing combustion, as compared to nitrogen gas bubbles that only act as hotspots.

CHAPTER 6

SUMMARY AND CONCLUSIONS

Explosive emulsions are widely used in civilian mining, quarrying, excavation industries, etc. for breaking rocks and ore for mining. In order to increase their sensitivity to a level required for detonation to occur, their density is reduced using methods such as incorporation of materials containing entrapped voids or chemical sensitization (gassing); the latter was the subject of the current study. Most gassing methods rely on the reaction between a gassing agent which is added to the emulsion after manufacturing, and ammonium nitrate (present in large amounts). The disadvantage of this method (referred to as one-component system) is that the presence of any excess of gassing agent (e.g. due to human factors) results in an undesired extent of reaction. This in turn causes the density to drop below the required value for an effective blast thus decreasing the performance of the explosive. In this sense, none of the gassing methods developed so far has successfully addressed the issue of the extent of gassing reaction control.

This study proposed the use of a two-component system where one component (A) inert to constituents of the explosive emulsion was added to the fuel phase or to ANS in a pre-determined amount prior to emulsification. The other component (B), the gasser was added to the matrix after emulsion manufacture, when the sensitization was required. In this case, the presence of excess of component (B) would not affect the extent of the gassing reaction; the final density would solely be controlled by the amount of component (A). The intention was to determine for which case, component (A) added to fuel phase or to ANS, better control of the final gassed emulsion density was obtained. Thus, the overall objective of this research was to develop a two-component gassing system and study its ability to provide control of the extent of the gassing reaction and the final density of explosive emulsions.

The research started with the selection of potential gassing components from a list of 28 chemicals presented in section 3.2.1. A qualitative study of the reaction mechanism of the selected gassing components (KI and H₂O₂) was then conducted. Thereafter, investigations of the effect of H₂O₂ (30 wt% solution) concentration (0.09 to 7.80 wt%) and KI concentration (0.004 to 0.1 wt%) on the density change over time were done. The effect of pH for values ranging from 4.4 to 6.5 on the gassing process was also investigated. Experimental studies were then conducted to determine the phase (aqueous or fuel) in which the gassing reaction occurred. Lastly, blasting experiments were carried out to compare the performance of explosive emulsions sensitized with the two-component gassing system with the current system.

The emulsions used for the study were prepared with 3 different industrial fuel phases namely F800, Bullfinch and R602/45. Two types of emulsions were prepared using an aqueous solution of industrial grade AN: the first type was used for gassing experiments only, and the other type for blasting experiments. The first type was prepared with ANS that consisted of 60% AN prills by mass, and aqueous phase concentration of 90 wt%. The second type was manufactured according to AEL MS formulations.

The following transpired from the gassing component selection process: first, KI was found to be suitable for use as component (A) since it dissolves in ANS, and it was partially dissolved and dispersed/suspended in the fuel phases; it did not react with any of the emulsion components. In this sense KI could be added to either fuel or aqueous phases prior to emulsion manufacture. Second, H₂O₂ was found to be suitable for use as a “gasser” because it reacted with KI in emulsions to generate gas bubbles and did not react with any of the emulsion components.

The qualitative study on the H₂O₂/ KI reaction mechanism revealed that within the experimental window, the stoichiometric reaction (equation 3.18) between H₂O₂ and KI to generate I₂ and O₂ gas was the dominant reaction mechanism, and not the catalytic decomposition of H₂O₂. The reactant system KI (component A) and H₂O₂ (component B) was identified as suitable for achieving the objective of the current study.

The following is a summary of results obtained for the gassing of emulsions in which KI was added to the fuel phase prior to emulsification:

- The evolution of density over time for different H₂O₂ concentrations showed that the gassing process in emulsions started with a region of density variation with time, proceeded by a plateau which indicated that the reaction had come to equilibrium. Similar observations were made for different KI concentrations.
- When using 0.1 wt% KI, the rate of density change increased and the final gassed emulsion density decreased with increasing H₂O₂ concentration up to a transitional point (3.47 wt% H₂O₂), above which the changes observed were insignificant. This led to the conclusion that the density dependence on H₂O₂ was suppressed for an H₂O₂ to KI ratio of 34.7 to 1.
- Emulsions prepared with 0.1 wt% KI gave rise to the following problems: first, the voids formed were very large. Second, observations made on the next day showed that sensitized emulsions were in a metastable state as evidenced by the collapse of voids formed on the previous day. Third, the reference density required for effective blasting was not reached.

- The analysis of results showed that the final emulsion density was controlled by 2 factors: on the one hand the *void size* related to the rate of gassing and the amount of gas released, depended on both KI and H₂O₂ concentrations. On the other hand, the *void volume fraction*, only related to the amount of gas released in the system, was determined by KI concentration only. Large amounts of gas produced at high rates caused a high degree of gas bubble coalescence resulting in large bubbles forming; this led to emulsion collapse overnight. It was based on these findings that the final emulsion density was optimized.
- An iterative technique based on changing the concentration of KI was used to optimize the final density of the sensitized emulsions. Optimization could not be done based on changing the H₂O₂ concentration because: first, according to the main objective of this study, the second gassing component, in this case H₂O₂, had to be used in any amount (in excess) without causing over-gassing. Second, in light of the role it plays in this process, it was not expected to be efficient in minimizing the effect of void size on final sensitized emulsion density, as it influences only the rate of the gassing reaction and not the amount of gas released. Two techniques were used to determine the initial iteration point (KI concentration): one based on density vs. H₂O₂ concentration graphs which was unsuccessful; and the other based on density vs. KI concentration graphs.
- The method based on density vs. KI concentration graphs yielded desired results. The optimum KI concentrations obtained after iterations were 0.008 wt% KI (F800), and 0.004 wt% (Bullfinch and R602/45). In this sense, the density dependence on H₂O₂ concentration was suppressed, the sensitised emulsions were not in a metastable state, and the reference density was reached.

The outcomes from sensitization of explosive emulsions where KI was added to ANS prior to emulsion manufacture can be summarized as follows: as for emulsions in which KI was added to the fuel phase, it was found that: when using 0.008 wt% KI (F800) and 0.004 wt% (Bullfinch and R602/45), the reference density was reached and was not affected by the presence of excess of H₂O₂; the sensitized emulsions were not in a metastable state as the voids did not collapse the next day.

The similarity of results in both cases (KI added to fuel phase and KI added to ANS) led to investigations aimed at determining the phase (aqueous or fuel) where the gassing reaction occurred. Interestingly, studies demonstrated that irrespective of the phase in which KI was added prior to emulsification, the gassing reaction occurred at the interface formed by the fuel and aqueous phases. This information was deemed important for the following reasons: first, it offered a plausible explanation for the similarities between the cases where KI was

added to the fuel and KI was dissolved in ANS. Second, it shed light on the gassing reaction between KI and H_2O_2 in the fuel phase reported in section 3.2.5 of the feasibility study. Third, it is relevant for further study of the KI + H_2O_2 reaction mechanism in explosive emulsions.

Studies conducted in emulsions on the effect of pH revealed that at $pH < 6.0$, the final density of the sensitised emulsion is not affected by the pH. At $pH \geq 6.0$, the density of emulsions decreased with increasing pH; it did not reach equilibrium even 6 hours after the gassing reaction had started and dropped below the reference value. It appeared that the gassing reaction continued even though theoretically all the KI had been consumed, since it was the limiting reactant. This could be due to enhanced H_2O_2 decomposition observed at ANS $pH \geq 6.0$. This information is important for industrial applications; the pH of the aqueous phase should be monitored such that it is always lower than 6.0 prior to emulsion preparation.

Blasting experiments showed that emulsions prepared with F800 detonated at 4000 m/s and those with Bullfinch at 3800 m/s. These velocities of detonation were lower as compared to those obtained for explosive emulsions sensitised with the current method. This could be explained by the difference in porosity between emulsions sensitised with the two-component system and those with the one-component.

The studies above have shown that it is possible to control the extent of the gassing reaction when using the two-component (H_2O_2 and KI) gassing system; the presence of excess “gasser” will not affect the final density of the sensitised emulsions. The gassing system produces desired results for $pH < 6.0$. Implementation of the H_2O_2 /KI gassing technology could possibly provide benefits in terms of consistency in blasting performance in the explosives industry.

The following aspects were not covered in this work and could be investigated for future studies:

- Investigation of the effect of temperature on the gassing process in terms of final sensitised emulsion density and gassing rate.
- A study on the phase in which the gas bubbles are located in explosive emulsions. This could include microscopic observations.
- Comprehensive study of the blasting characteristics; determination of the effect of porosity on the VODs for both gassing technologies.
- The study could be extended to emulsions prepared with other fuel phases.

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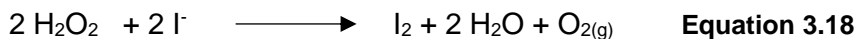
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APPENDICES

APPENDIX A. Determination of stoichiometric H₂O₂ and KI quantities



Mm H₂O₂ = 34 g/mol

Mm KI = 166 g/mol

This is a 1 to 1 reaction therefore:

166 g KI require 34 g pure H₂O₂

Since we are using H₂O₂ (30 wt%):

166 g KI will require $34/0.30 = 113$ g H₂O₂ (30 wt.%)

H₂O₂/KI stoichiometric ratio = $113/166 = 0.68$ g H₂O₂ (30 wt.%) required for 1 g KI

This means 0.68 g of H₂O₂ (30 wt.%) can completely consume 1 g of KI.

APPENDIX B. Estimation of rates of reaction

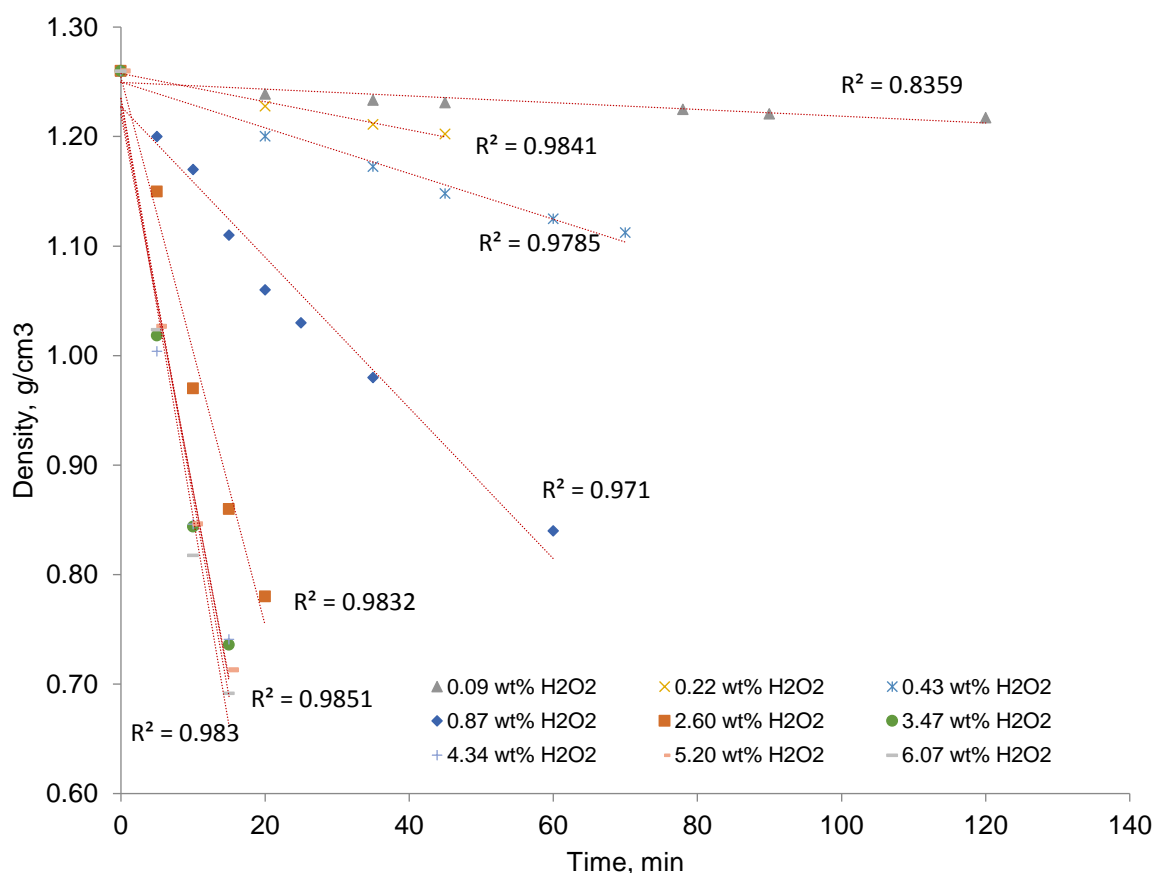


Figure B. 1 Trendlines for rates of reaction determination (emulsions prepared with F800 fuel phase and 0.1 wt% KI)

Table B. 1 Effect of H₂O₂ concentration on rate of reaction and equilibrium density (F800 fuel phase/0.1 wt% KI)

| H ₂ O ₂ Conc., wt% | Rate g/cm ³ .min x10 ³ | Final density, g/cm ³ |
|--|--|----------------------------------|
| 0.09 | 0.3 | 1.20 |
| 0.22 | 1.3 | 1.18 |
| 0.43 | 2.1 | 1.08 |
| 0.87 | 6.9 | 0.95 |
| 2.60 | 25 | 0.70 |
| 3.47 | 34 | 0.60 |
| 4.34 | 35 | 0.60 |
| 5.20 | 36 | 0.60 |
| 6.07 | 38 | 0.60 |

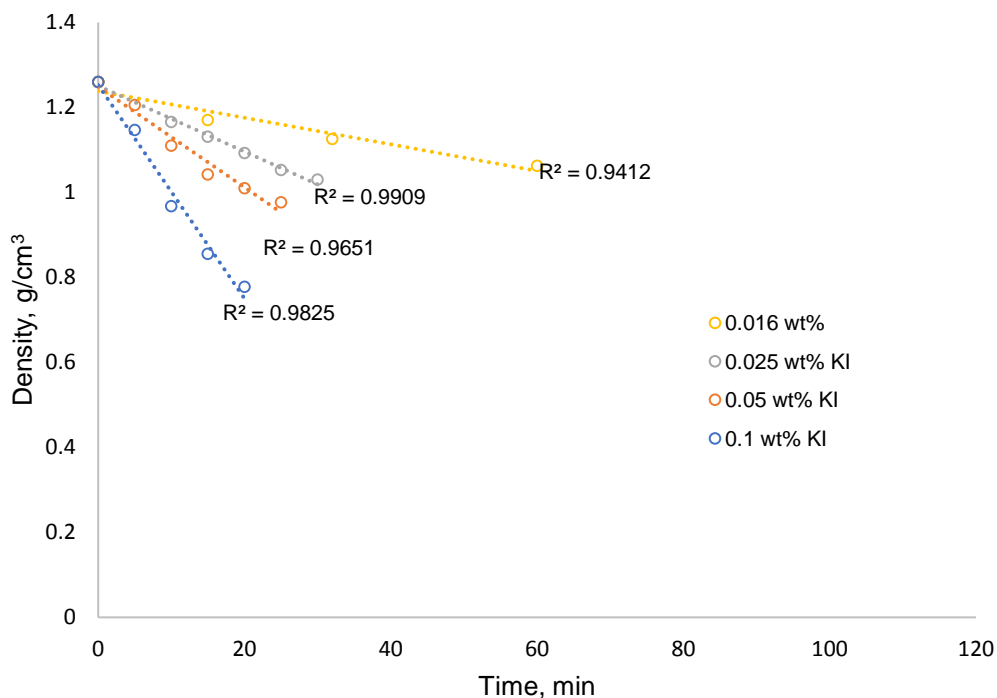


Figure B. 2 Trendlines for rates of reaction determination (emulsions prepared with F800 fuel phase and sensitised with 2.60 wt% H₂O₂)

Table B. 2 Effect of KI concentration on rate of reaction and equilibrium density (F800 fuel phase/2.60 wt% H₂O₂)

| KI Conc., wt% | Rate g/cm ³ .min x10 ³ | Final density, g/cm ³ |
|---------------|--|----------------------------------|
| 0.016 | 3.1 | 1.01 |
| 0.025 | 7.7 | 0.97 |
| 0.05 | 118 | 0.88 |
| 0.1 | 251 | 0.7 |

APPENDIX C. Estimation of mass of sensitised emulsion required to fill blasting pipes

$$M = \rho \times V \text{ and } V = \frac{\pi d^2}{4} L \Rightarrow M = \rho \times \frac{\pi d^2}{4} L$$

The density is taken as $1.05 \text{ g/cm}^3 = 1050 \text{ kg/m}^3$ (reference density)

- If $d = 0.032 \text{ m}$ and $L = 1 \text{ m} \Rightarrow M = 1050 \times \frac{\pi \times 0.032^2}{4} \times 1 = 0.84 \text{ kg}$
- If $d = 0.080 \text{ m}$ and $L = 0.5 \text{ m} \Rightarrow M = 1050 \times \frac{\pi \times 0.08^2}{4} \times 0.5 = 2.64 \text{ kg}$

APPENDIX D. Estimation of experimental error

The error in density measurement can be determined using the expression:

$$\sigma_\rho = \pm \sqrt{\left(\frac{\partial \rho}{\partial M} \sigma_M\right)^2 + \left(\frac{\partial \rho}{\partial V} \sigma_V\right)^2}$$

$$\sigma_M = \pm 0.003 \text{ g} ; \sigma_V = \pm 0.1 \text{ ml} ; \frac{\partial \rho}{\partial M} = \frac{1}{V} \text{ and } \frac{\partial \rho}{\partial V} = -\frac{M}{V^2}$$

For $M = 97.71 \text{ g}$ and $V = 80 \text{ cm}^3$;

$$\sigma_\rho = \pm \sqrt{\left(\frac{1}{80} \times 0.003\right)^2 + \left(-\frac{97.71}{80^2} \times 0.1\right)^2} = \pm 0.02$$

Table D. 1 Error calculation

| Mass, g | Volume, cm ³ | Error σ_ρ , g/cm ³ |
|---------|-------------------------|---|
| 97.71 | 80 | 0.02 |
| 79.70 | 80 | 0.01 |
| 69.03 | 80 | 0.01 |
| 61.54 | 80 | 0.01 |
| 57.58 | 80 | 0.01 |
| 55.00 | 80 | 0.01 |
| 53.25 | 80 | 0.01 |
| 51.00 | 80 | 0.01 |
| 50.50 | 80 | 0.01 |
| 49.50 | 80 | 0.01 |
| 49.50 | 80 | 0.01 |
| 49.50 | 80 | 0.01 |
| 49.50 | 80 | 0.01 |
| 49.50 | 80 | 0.01 |
| 49.02 | 80 | 0.01 |
| 49.00 | 80 | 0.01 |

APPENDIX E. VOD calculation

If the time taken by the shockwave to travel 15 cm is 35.7 μ S,

$$VOD = \frac{0.15}{t} = \frac{0.15}{35.7 \times 10^{-6}} = 4200 \text{ m/s}$$