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The Potentials of Aluminium Nanoparticles: Novel High Energy **Density Material for Underwater Explosions**

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Abstract. The destructive parameters of underwater explosives (i.e. shock wave energy, maximum pressure, and bubble radius) are limited to explosion heat; that is comparatively low. One approach for enhanced heat output can be accomplished by integrating reactive metal particles (i. e. Aluminium). However conventional aluminium particles (µm size) would contribute only with combustion gaseous products behind detonation wave front. Underwater, there is no oxygen for such contribution to take place. Furthermore, conventional Al particles could decrease the detonation velocity. So far, full exploitation of aluminium particles in underwater explosions has not been accomplished. Aluminium nanoparticles would combust more efficiently within detonation wave front, offering smaller critical diameter, high reaction rate, and high heat release rate. Consequently, Al nanoparticles could be ideal high energy density material for underwater explosion. Ship model with positive metacentric height, GMT =4.7 cm for ship transverse stability, and GML = 19.3 for ship longitudinal stability was designed. Ship model offers large angle stability (heeling angles= 0-70 deg.). 2 g of explosive charge was detonated underneath the developed naval structure. Upon explosion, the acceleration of the naval structure was measured using shock accelerometer VC tri-axial, high frequency, 5000 ground acceleration, Dytran, Inc. While, Al particles (10 µm) offered an increase in mono-hull acceleration by 16 % compared to TNT; Al nanoparticles offered an acceleration increase by 49 %. This novel finding can be ascribed to the efficient combustion of Al nanoparticles within detonation wave front offering ideal detonation reaction with enhanced destructive effect.

Keywords: Underwater explosion (UNDEX); Metalized explosives; Shock wave.

Introduction

Underwater explosion (UNDEX) is defined as the violent balance disturbance owing to detonation of explosives in water environment. Different weapons can be employed in naval warfare such as naval mines. Such weapons are submerged enough, a passing ship will initiate its firing mechanism [1-2]. Torpedoes are self-propelled guided projectiles that operate underwater [3]. The influence of underwater explosion does not constitute a single impulse but a few large energy pulsations of gas bubbles [4].

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1.1 Underwater explosives

Many trials have been performed to develop more powerful explosive compositions, for underwater explosions (UNDEX). TNT compositions are known to be less sensitive, with extended shelf life [5]. Enhanced performance of TNT compositions for UNDEX is under improvement. Aluminium reaction at the Chapman-Joguet (C-J) plane is relatively slow. Therefore, aluminium could not contribute efficiently to the destructive effect of explosive materials. Aluminium contribution would be limited primarily to gaseous products, offering sustained pressure wave [6-8]. In UNDEX there is no oxygen available for such contribution to take place.

1.2 Shock wave propagation

Cole reported that chemical reaction in UNDEX takes place in two parts: the initial chemical reaction and the detonation process. If initial chemical reaction generated a high pressure; a thermomechanical shock wave "detonation wave" will propagate at supersonic speed through the explosive material producing intense heat [9-10]. The detonation gaseous products can offer a very dense, superheated, and spherical gas bubble; at this instance the detonation process of underwater explosion is complete. Shock wave can be defined as the pressure wave created by the arrival of the detonation wave at the boundary between gas bubble and water. Shock wave propagates in water as a spherical wave at supersonic speed [11]. The shock wave energy (Esw) can be represented as equation 1.

$$E_{sw} = 98000 (W^{1/3}) (W^{1/3}/R)^{2.1}$$
(1)

Where: Esw, W, and R are shock wave energy in (J/m^2) , equivalent weight expressed in kg of TNT (Q_{exp}/Q_{TNT}) , and standoff distance in m. Furthermore the maximum peak pressure (P_m) can be calculated according to equation 2:

$$P_{\rm m} = 52.16 \, (W^{1/3} / R)^{1.13}$$
⁽²⁾

Where: P_m is the maximum peak pressure in MPa, W is the mass of charge expressed in equivalent value of TNT, and R is the standoff distance in meter. It can be concluded that the main UNDEX parameters including shock wave and bubble energy are limited by the explosion heat output that is comparatively low.

1.3 Gas bubble behavior and bubble pulse loading

The gas bubble begins to expand by explosion hot gases. The expansion continues until the internal gas bubble pressure is at its minimum and the diameter is at its largest value [3, 11]. The bubble begins to contract until the compression of the gaseous products stop the contraction, force the bubble to expand again making an oscillating system [3]. Cole and Reid, displayed the shape of the bubble pulses as a gradual rise to the peak pressure followed by a concave shaped decay to hydrostatic pressure [12-13]. The migration of the bubble has a significant effect on the shape of the bubble pulse. It causes the bubble pulse to develop a triangular shape figure 1.



Figure 1. Bubble migration behavior versus bubble expansion.

The velocity of the bubble pulse is similar to the shock wave; it propagates at the speed of sound in water [14-15]. The decay time constant Θ in (μ sec) can be expressed by Equation 3.

$$\Theta = 96.5 \,(\mathrm{W}^{1/3}) \,(\mathrm{W}^{1/3}/\,\mathrm{R})^{0.22} \tag{3}$$

The total impulse can be expressed as equation 4.

$$I = 5760 (w^{1/3}) [w^{1/3}/s]^{0.891}$$
(4)

Where: I, S, and W are specific impulse in Ns/m², Stand of distance in m, TNT equivalent in Kg (Q_{exp}/Q_{TNT}) [16]. The maximum bubble radius can be estimated by Equation 5:

$$A_{\rm m} = (13 \ Q_{\rm v} \ M \ / \ z)^{1/3} \tag{5}$$

Where; Q_v is the heat of detonation (MJ/kg), M is the mass of explosives (kg) [14]. When the frequency of the shock response and bubble pulse response matches the resonant frequency of the ship, whipping occurs. The whipping motion of the ship can break the ship's hull or cause other types of severe structural damage [12-13].

1.4 Damages due to UNDEX

The shock can develop a large hole in case of the small hull thickness and sufficient explosive charge [2]. The hull is heavily deformed; the level of deformation decreased with the increase in

standoff distances. However different portions of the ship will respond at different velocities depending upon the mass per unit area [2]. Another damage mechanism is the bubble collapse. If the oscillating gas bubble is close enough to a rigid body surface such as a submarine or ship hull. The differential pressure created due to bubble volume decrease could result in bubble collapsing onto the hull with the development of a high speed water jet [2].

1.4.1 Surface cut-off phenomena.

Surface cut-off occurs when a plane compressive wave hits a free surface. Compressive wave would be reflected off at that surface as a tensile wave. The reflected wave could interact with (cancels out) the compressive wave. Consequently a slightly negative pressure could be developed figure 2.



Figure 2. Shock wave pressure profiles with cut-off time [17]

Surface cut-off phenomena means that over pressure applied on the hull may be suddenly dropped to negative value; this action could force the hull to move towards the water surface [2].

1.4.2 Cavitation damage.

Cavitation phenomenon occurs when there is a region of negative absolute pressure in water. The phenomenon of bulk cavitations occurs when a shock-wave is reflected off a free surface such as air/water interface. The compression shock-wave reflects off the free water surface as a tensile wave and since water can only sustain a very small level of tension it begins to cavitate figure 3.[18-19].



Figure 3. Bulk cavitation developed during underwater explosion [2]

Cavitations can be divided into two types local cavitations and bulk cavitations. Bulk cavitations is considered as large region of low pressure, at the free surface [18]. Fluid-structure interaction takes place at certain parts of the ship's hull. The overpressure turns out to be negative. Water cannot sustain tension; therefore local cavitations occurs [20].

1.5 Destructive effect measurement

1.5.1 Shock wave measurement.

Measurements for UNDEX are entirely different from air explosions. The main parameter to be experimentally determined is the pressure time period. Pressure sensors can offer measurements of pressure-time profile; therefore shock wave energy can be calculated.

1.5.2 Structure response subjected to underwater explosion.

Displacement and acceleration of naval structure caused by underwater explosion is of immense significance for performance evaluation and in determining the naval structure safety limits.

Explosion heat output is the key parameter affecting UNDEX performance i. e. shock wave and bubble energy. Heat output of common explosive is quite low, and is limited by their heat of formation. Reactive metal particles (i.e. Al) can act as effective high energy density material. Therefore reactive metal particles can propose extended pressure pulse. This improved performance can be correlated to high thermal loading developed behind C. J. plane [21]. The reaction rate of reactive metal particles i. e. aluminium (Al) is relatively slow. Therefore Al particles would act as inert component at the Chapman-Joguet (C-J) plane. Conventional Al particles would contribute with detonation products behind C-J plane [22-23]. Such contribution could not be achieved in UNDEX as there is no air oxygen to react with Al particles. So far, full exploitation of aluminium particles in UNDEX has not been achieved [9, 24-26].

Al nanoparticles can offer an increase in detonation heat and detonation velocity, presumably due to the efficient combustion of Al nanoparticles within the detonation zone. It is expected that Al nanoparticles could be consumed more rapidly in the CHNO reaction zone, as compared to larger particles [27].

Recently, aluminized explosive formulations employing small aluminium particles were developed to produce high initial detonation temperatures, pressures, and velocities. They can offer high expansion blast capabilities [28-29]. Effective development of novel cast metalized formulation based on TNT and Al nanoparticles for UNDEX has been developed. During explosive conversion, aluminum nanoparticles would combust more efficiently within detonation wave front. Consequently this approach could offer ideal combustion process. Naval structure with high floating stability was designed. The effectiveness of developed explosives for UNDX was evaluated via measuring acceleration of floating structure. Upon explosion, the acceleration of the naval structure (mono-hull) was measured using shock accelerometer VC tri-axial, high frequency, 5000 ground acceleration, Dytran,Inc. While, Al particles (10 μ m) offered an increase in mono-hull acceleration by 16 % compared to TNT; Al nanoparticles (100 nm) offered an acceleration increase by 49 %. This novel finding can be ascribed to the reactivity and high interfacial surface area of Al nanoparticles. This manuscript would open the route for the effective development and testing of novel cast metalized formulation where full energy could be released and exploited within the detonation wave front.

Experimental Work

2.1 Development of ultra-fine aluminium particles

Commercial aluminium particles with particle size $\leq 32 \ \mu m$ were dispersed in 250 ml isopropyl alcohol (IPA). The slurry was ground using ball mill Retch 100 for 24 hours. IPA was employed to dissipate any developed heat during grinding. Morphology of developed aluminium particles was visualized TEM. Dry powder morphology was investigated with SEM, Zeiss EVO-10 by Carl Zeiss Corporation. The crystalline phase was investigated with XRD, D8 advance by Burker Corporation over the angle range 20 from 20 to 90 degrees.

2.2 Integration of metallic fuels particles into energetic matrix

Metallic fuel was effectively dispersed in IPA using ultrasonic probe homogenizer, to break down any aggregates and to achieve even dispersed particles. Integration of colloidal particles into energetic matrix is an effective approach for enhanced dispersion characteristics [30-33]. The colloidal particles were integrated into molten TNT under stirring.

2.3 Design of Mono-Hull structure

2.3.1 Geometric model for the ship model.

A 3-D mono-hull model for the ship was developed using Inventor (3D CAD software) as demonstrated in figure 4.

After developing the 3D CAD model, naval architecture software MAXSURF had been employed to for floating stability study.



Figure 4. 3D Geometric model for the ship model: isometric view (a), plan view (b), profile view (c and d).



Figure 5. Stable equilibrium of a ship

2.3.2 Ship model stability

The naval structure can be considered stable if it has the ability to maintain to its equilibrium position after heeling or pitching. Floating stability was investigated to secure stability under sever working conditions during explosions. The ship is considered stable when vertical position of center of gravity (G) is lower than the position of transverse meta-center M figure 5.

Under these conditions, if the ship is heeled with an angle θ , an arm GZ will be developed. GZ arm will creates a righting moment that get equilibrium upright position.

2.3.3 Ship model simulation using MAXSURF

MAXSURF was employed to build ship model and to calculate the model hydrostatics and its stability under severe conditions. The 3D model of the ship was imported in the modeler module to develop the ship model figure 6.



Figure 6. Ship model in modeler module under MAXSURF

a) Ship model initial stability

The hydrostatics was calculated using the MAXSURF Modeler module at design water line (DWL). The vertical center of gravity (VCG) is assigned at 7.4 cm figure 7.

The main hydrostatic results for the ship model are presented in table 1.



Figure 7. Body plan submerged volume at DWL

Displacement	7.147	kg	
Volume (displaced)	6972.7	cm^3	
Draft Amidships	11.36	cm	
Immersed depth	11.35	cm	
Prismatic coeff. (Cp)	0.666		
Block coeff. (Cb)	0.563		
LCB length	16.6	from zero pt. (+ve fwd) cm	
LCF length	19.92	from zero pt. (+ve fwd) cm	
KB	7.12	cm	
KG fluid	7.4	cm	
GMT	4.8	cm	
GML	19.3	cm	

Table 1. Ship model hydrostatic calculations

The ship model displacement =7.147 kg. This model is initially stability, as GM > 0. The main stability criteria include:

The model is transversely stable as GMT=4.8 cm

The Model is longitudinally stable as GML= 19.3 cm

b) *Ship model upright hydrostatics*

As the ship will be to an explosion, it will be subjected to transient motions as follows:

Heaving motion (motion in vertical direction)

Rolling motion (motion about longitudinal direction)

Pitching motion (motion about transverse direction)

Upright stability analysis was conducted. The draft was assigned to be 8-13 cm. The calculated upright hydrostatics at draft=10 cm is represented in Figure 8.



Figure 8. Upright hydrostatics

If the ship is inclined at any draft it tends to maintain its initial position; as the centre of gravity (CG) is below the metacenter (M) figure 9.



Figure 9. Change of GM with draft

The transverse and longitudinal stabilities are conserved as the GMT and GML have positive values. The ship model has upright stability for large draft range (6-15 cm). These severe drafts are expected during underwater explosions.

c) Ship model large angle stability

During explosions, the ship might be subjected to sever heeling (Rolling) conditions. Consequently, large stability angle must be secured. Large angle stability was conducted using stability module for heeling angle range=0 - 70 deg. (Figure 10).



Figure 10. Large angle stability for heeling 20 deg.

Body plan and 3-D isometric view for the ship model simulation during large angle stability calculations at rolling angle =20 deg. Calculations for the large angle stability are represented in figure 11.



Figure 11. GZ curve

Ship model demonstrated positive righting arm GZ for large heeling angles (GZMax at 50 deg.). GZ arm will bring the ship to its initial position after severe rolling during the explosion activities. The

designed model was manufactured and accelerometers were mounded on the ship as represented in Figure 12.



Figure 12. Manufactured ship model

2.4 Underwater explosion strength

UNDEX will produce shock wave in the water as well as bubbles of gaseous products. The explosion strength of different exploding charges was evaluated through the measurement of the acceleration of naval structure subjected to explosion. The acceleration of the ship model was employed as an indication for the strength of explosive charge. Steel tank 1 m (L) ×1 m (W) ×1.5 m (H) was filled with water for conducting the experimental measurements. Floating ship model was assembled with interior accelerometer. 2 g explosive charge was exploded underneath the ship at 50 cm. The target acceleration due to explosion was measured.

3. Results and Discussions

3.1 Characterization of Al particles

The morphology of employed commercial Al particles was investigated with SEM. Al particles in the shape of spheres with 10 μ m average particle size were reported from SEM micrograph figure 13-a. aluminium nanoparticles in the shape of plates of 100 nm were visualized using TEM figure 13-b.

3.2 Theoretical performance evaluation

Detonation heat and volume of gases products represent the ability of explosive charge to develop gas bubble and effective incident shock damage. Al particles could enhance the heat output offering enhanced UNDEX parameters including shock wave energy (Esh), totl impulse (I), decay time constant (Θ) equations 1-3. Table 1 summarize the impact of Al particles on main UNDEX parameters.



Figure 13. Morphology of employed conventional Al particles (10 μm) (a), Al nanoparticles (100 nm) (b) using SEM and TEM respectively.

Shock parameters	wave	TNT	TNT+ Al	Increment (%)
Esh (J/m)		559.0	762.5	36.5%
I (Ns/m)		195.2	236.0	21%
Θ (µ sec)		16.8	18.2	8.2%

Table 2. Impact of Al particles on UNDEX shock wave parameters

However the employed empirical equations do not take into account the particle size. Al nanoparticles could contribute more efficiently within detonation wave front compared with conventional Al particles.

In this study, the impact of reactive metal particles on destructive effect of TNT for UNDEX was evaluated. 2 g of different explosives including pure TNT, Al (10 μ m) / TNT, and Al (100 nm) /TNT were exploded, 50 cm underneath the floating naval structure. The solid loading level of reactive metal



particles was limited to 12 w t%. Shock accelerometer was employed to measure the structure dynamic response. Practical measurement of floating structure acceleration is demonstrated in figure 14.

Figure 14. The impact of Al particles on TNT strength.

Whereas conventional Al particles (10 μ m) offered enhanced ship acceleration by 16 % compared to TNT; Al nanoparticles (100 nm) offered an acceleration increase by 49 %. Furthermore Al nanoparticles offered a broad deceleration peak (circle in red).

This novel finding was ascribed to the reactivity of aluminium nano-particles; as well as efficient combustion within detonation wave front. This could offer higher detonation temperature and could speed up the detonation reaction compared with conventional Al particles. This approach could offer full exploitation of Al particles with UNDEX. It has been reported that Al nanoparticles have tendency to react with not only with oxygen but also with the inert decomposition gases adding additional exothermic reactions [34-35].

$$2Al_{(s)} + 3/2 O_2 \longrightarrow Al_2O_{3(s)} + 1700 \text{ KJ/mol}$$
 (6)

$$2Al_{(s)} + 3CO_{(g)} \longrightarrow Al_2O_3 + 3C + 1251 \text{ kJ/mol}$$

$$2Al_{(s)} + 3H_2O_{(s)} \longrightarrow Al_2O_2(s) + 3H_2(s) + 866 \text{ kJ/mol}$$

$$(7)$$

$$2AI_{(s)} + 3CO_{2(g)} \longrightarrow AI_{2}O_{3(s)} + 3H_{2}O_{3(g)} + 3H_{2}O_{3(g)$$

$$2Al(s) + N2(g) \longrightarrow 2AlN + 346 \text{ kJ/mol}$$
(10)

Al nanoparticles could efficiently initiate this series of secondary reaction. This series of exothermic reactions could take place more rapidly within the detonation wave [36-38]. Therefore, a large amount of heat would be liberated within detonation wave front; excess metal fuel could combust more effectively behind C. J. point [37, 39].

Aluminium nanoparticles would combust more efficiently within detonation wave front, offering high reaction rate, and high heat release rate

3.3 Thermal behaviour of metalized compositions

Differential scanning calorimetry (DSC) can monitor any physical or chemical change which involves the evolution/absorption of heat. The impact of Al particles on TNT thermal behaviour was evaluated using DSC. While micron-Al offered an increase in total heat release by 3 %, nanometric Al offered an increase in total heat release with 78 % figure 15.



Figure 15. The impact of Al particles on TNT thermal behaviour using DSC

Aluminium nanoparticles could combust more effectively within detonation wave front. A serious of secondary exothermic reactions can be initiated. Nanoscopic aluminium particles have the potential to react not only with free oxygen but also with inert gases.

4. Conclusion

Novel approach for UNDEX testing is represented; this was accomplished via measurement of target acceleration upon explosion. A novel design for naval structure with superior stability was represented. The effectiveness of reactive Al nanoparticles as a novel high energy density material to conventional Al particles in TNT for UNDEX was evaluated. Al nanoparticles (100 nm) offered enhanced performance by 49 % compared with 16 % for conventional Al particles (10 μ m). Al nanoparticles could react more efficiently within detonation wave front offering enhanced heat output.

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