The effects of void size and volume on the detonation characteristics of the emulsion explosives such as detonation velocity, detonation pressure and critical diameter were experimentally investigated. Plastic balloons of five different sizes ranging from 0.05mm to 2.42mm in average diameter were used as void. The experimental results showed that detonation velocity, detonation pressure and critical diameter were strongly affected by void size and volume. The fraction of the emulsion explosives reacted in reaction zone was estimated from the comparison of observed detonation velocity and pressure with those theoretically calculated. For the emulsion explosives containing large voids, the fraction of the emulsion explosives reacted in reaction zone was considerably low. This is due to the rarefaction not only from the lateral but also from void itself. A linear relationship between critical diameter and the web thickness of bulk explosives was observed for each void size. This suggests that the reaction in the emulsion explosives sensitized with large voids proceed basically by hot spot and grain burn process in which the reaction starts at the surface of hot spots.

INTRODUCTION

Explosives for civil use, such as emulsion explosives, slurry explosives and ANFO (Ammonium Nitrate-Fuel Oil) are ammonium nitrate (AN)-based. Those explosives are well known to show non-ideal detonation behavior due to its slow reaction rate compared to high explosives for military use. Detonation pressure and detonation velocity is much lower than those for infinite charge diameter. It is well known that detonation behavior can be widely controlled by the selection of size and volume of void contained in the emulsion explosives. The effect of void size and volume on the detonation velocity, critical diameter and sensitivity of the emulsion explosives were reported in many investigations [1-7]. In those studies, glass microballoons (GMB) of diameter smaller than 0.15mm were mainly used as void. To study the effect of void size and volume on the detonation characteristics of the emulsion explosives in detail, detonation velocity and detonation pressure as well as critical diameter were determined for the emulsion explosives sensitized by plastic balloons of five different sizes widely ranged between 0.05mm and 2.42mm in diameter. It was suggested the reaction rate in the bulk explosive is dominant factor which affects the critical diameter especially for the explosive sensitized by large size of voids.

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TABLE 1. PLASTIC BALLOONS USED AS VOIDS.

<table>
<thead>
<tr>
<th></th>
<th>Average diameter (mm)</th>
<th>Standard deviation (mm)</th>
<th>Particle density (kg/m³)</th>
<th>Structure</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB-1</td>
<td>0.053</td>
<td>0.023</td>
<td>27</td>
<td>Mono-cell</td>
<td>Acrylonitrile / Vinylidene Chloride</td>
</tr>
<tr>
<td>PB-2</td>
<td>0.472</td>
<td>0.062</td>
<td>51</td>
<td>Multi-cell</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PB-3</td>
<td>0.795</td>
<td>0.129</td>
<td>77</td>
<td>Multi-cell</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PB-4</td>
<td>1.728</td>
<td>0.273</td>
<td>32</td>
<td>Multi-cell</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PB-5</td>
<td>2.420</td>
<td>0.403</td>
<td>64</td>
<td>Multi-cell</td>
<td>Polystyrene</td>
</tr>
</tbody>
</table>

SAMPLE EXPLOSIVES

The formulation of the emulsion matrix used in this study is ammonium nitrate /sodium nitrate /water /wax and emulsifier = 77.66/4.68/11.22/5.40 in weight ratio. The emulsion matrix is oxygen balanced and its density is 1390kg/m³. A certain amount of plastic balloons of mono- cell or multi-cell structure shown in Table 1 were added into the emulsion matrix to achieve the desired explosive density. PB-1 is the smallest balloon of mono-cell structure with the average diameter of 0.05mm, and others are the balloons of multi-cell structure with average diameter ranging from 0.47 to 2.42mm.

EXPERIMENTAL

DETONATION VELOCITY MEASURE-MENT

Sample emulsion explosives of various bulk density were loaded into a plastic film tube of 20, 30, 40 and 50mm in diameter and 300mm or longer in length to measure its detonation velocity Dv by ionization gap method at 20°C.

DETONATION PRESSURE MEASURE-MENT

To measure detonation pressure, the emulsion explosive loaded into PVC pipe of 51mm in inner diameter, 60mm in outer diameter and 200mm in length was placed on a PMMA block as shown in Figure 1. A PVDF film of 10 µm in thickness and 5mm squares was sandwiched with polyimide films together with electrodes made of copper foil. The PVDF gauge was put onto a PMMA block and then covered and glued with a PMMA plate of 1mm in thickness. The output of the pressure gauge was recorded with a digital oscilloscope at sampling rate of five nanoseconds. Calibration of PVDF pressure gauge was carried out by measuring electric charge created under hydraulic pressure and by comparing with the pressure measured with a manganin pressure gauge that has been preliminarily calibrated. Pressure profile observed is that transmitted into PMMA plate, which exists among the explosive and a PVDF gauge. Detonation velocity was also

![Figure 1. Experimental setup for detonation pressure measurement.](image-url)
measured with ionization gaps.

DETERMINATION OF CRITICAL DIAMETER

Critical diameter $d_C$ of the emulsion explosives was defined as the mean value of minimum charge diameters at which the detonation wave propagated and maximum charge diameter at which the detonation wave failed to propagate in the detonation velocity measurement experiment previously described. The value of 55mm was taken as $d_C$ when the charge of 50mm in diameter failed to propagate. For the diameter smaller than 20mm, certain diameter of charge with length 200mm were prepared to determine the detonation wave propagation.

RESULTS AND DISCUSSIONS

DETONATION VELOCITY

Good linear relationships between measured detonation velocity $D_v$ and the reciprocal charge diameter were observed for each void size (Eyring plot). $D_i$, detonation velocity at infinite charge diameter, are plotted against $[1 – \phi]$ in Figure 2, where $\phi$ is voidage or void volume fraction. The theoretical detonation velocity $D_{CJ}$ calculated with KHT hydro-thermodynamic calculation code is also shown for comparison. Plastic balloons were treated as reactive in the calculation. $D_i$ for the emulsion explosives sensitized by small void size of 0.05mm and 0.47mm agree fairly well with $D_{CJ}$ at the voidage down to 0.25, whereas the larger voids give lower $D_i$ than $D_{CJ}$. Yoshida et al showed that $D_i$ of the emulsion explosives sensitized by GMB presents good agreement with $D_{CJ}$ calculated by KHT code. In this work, it is shown that $D_i$ in the emulsion explosives containing voids size of 0.47mm or smaller is very close to theoretical value for voidage larger than 0.25. When the size of voids contained in the explosives is larger than about 0.5mm, $D_i$ is much lower than $D_{CJ}$. This is due to the incomplete reaction of the explosives in the reaction zone. It is considered that cooling down of the long reaction zone not only by the lateral rarefaction waves but also by the rarefaction from the void itself may cause such incomplete reaction.

The fraction of the emulsion explosives reacted in the reaction zone was estimated by comparing $D_i$ with $D_{CJ}$ and the results are shown in Figure 3. Ingredients other than AN were assumed to be completely reactive and the weight fraction of AN reacted was taken as fraction of the emulsion explosive reacted. The fraction of the emulsion explosive reacted in reaction zone is 85-90% and 60-75 % for the voids of 0.8mm and 1.7mm respectively at the voidage of 0.5-0.7. This

FIGURE 2. DETONATION VELOCITY IN INFINITE CHARGE DIAMETER.

FIGURE 3. FRACTION OF EXPLOSIVES REACTED IN INFINITE CHARGE DIAMETER.
poor reactivity of explosive gives smaller energy release in the reaction zone leading longer reaction zone.

DETONATION PRESSURE

Figure 4 indicates pressure profiles observed for the emulsion explosives of voidage 0.25 (explosive density 1050 kg/m³) sensitized by voids of five different sizes. The pressure rises up sharply to reach its peak pressure within about 75 nanoseconds in the emulsion explosives sensitized by voids smaller than 0.80 mm. The pressure rise time of about 75 nanoseconds can be explained by the passing time of shock front in PVDF film of 10 µm thick taking the front curvature into consideration. Pressure decrease in the reaction zone behind leading shock and following pressure decay in Taylor wave can be observed in the emulsion explosives sensitized by voids of 0.05 mm and 0.47 mm. Whereas the emulsion explosives sensitized by voids larger than 1 mm require longer time to reach its peak pressure. This is due to the important irregularity of detonation front of the emulsion explosives containing large voids, which was measured in optical observation. The peak pressure is fairly low compared with the cases of smaller voids. The reaction zone thickness estimated from the measured pressure profile is about 1.5 mm for the emulsion explosives sensitized by voids of 0.05 mm. This value agrees well with the reaction zone thickness estimated from the diameter effect of detonation velocity in the same emulsion explosive.

The emulsion explosives of voidage 0.37 (explosive density 900 kg/m³) and voidage 0.14 (explosive density 1190 kg/m³) were additionally prepared by adding voids of 0.05 mm and 0.47 mm in diameter respectively for the detonation pressure and detonation velocity measurements. Pressure profiles obtained are shown in Figures 5 and 6. The time axis in the Figure 6 is arbitrary for easy comparison of profiles. These pressure values are plotted as a function of

![Figure 4](image1)

FIGURE 4. PRESSURE PROFILES OF THE EMULSION EXPLOSIVES OF VOIDAGE 0.25.

![Figure 5](image2)

FIGURE 5. PRESSURE PROFILES OF THE EMULSION EXPLOSIVES SENSITIZED BY VOIDS OF 0.05MM.

![Figure 6](image3)

FIGURE 6. PRESSURE PROFILES OF THE EMULSION EXPLOSIVES SENSITIZED BY VOIDS OF 0.47MM.
The pressure observed in this experiment is that transmitted into PMMA plate of 1mm in thickness. The detonation pressure was therefore determined from the impedance match method. The Hugoniot of PMMA was based on the reference\(^\text{10}\), and that of the un-reacted emulsion explosive was supposed to be same as Universal Hugoniot\(^\text{11}\) for AN solution.

The theoretical detonation pressure and velocity were calculated with KHT code in which the ingredients other than AN were assumed to be completely reactive.

The fraction of explosives reacted in the reaction zone was evaluated based on the comparison between the measured and calculated detonation pressure as well as detonation velocity (Figures 9 and 10). The fraction of explosives reacted in the reaction zone evaluated from pressure agrees well with that estimated from detonation velocity. The fraction reacted is as high as 0.87 for the emulsion explosives sensitized by void of 0.05mm. On the other hand, the fraction reacted is as low as 0.30 for the emulsion explosives sensitized by large voids of 2.42mm. This result is due to small number of voids, which act as hot spots, and this

**FIGURE 7. DETONATION PRESSURE FOR VOIDAGE 0.25 AS A FUNCTION OF VOID SIZE.**

**FIGURE 8. DETONATION PRESSURE AS A FUNCTION OF VOIDAGE.**

**FIGURE 9. FRACTION OF EXPLOSIVE REACTED IN THE REACTION ZONE AS A FUNCTION OF VOID SIZE.**

**FIGURE 10. FRACTION OF EXPLOSIVE REACTED IN THE REACTION ZONE AS A FUNCTION OF VOIDAGE.**
leads to longer reaction zone thickness, and poor reactivity of explosive. The poor reactivity of the emulsion explosives containing large voids is due not only to the lateral rarefaction waves but also to the rarefaction waves from void itself.

The detonation pressure observed in the emulsion explosives sensitized by voids of 0.05mm is close to that calculated showing rather ideal detonation behavior. On the other hand, the emulsion explosives sensitized by voids larger than 0.47mm give large discrepancy between the detonation pressures observed and calculated especially at low void volume fraction. It is considered that small number of voids that act as hot spots lead lower detonation pressure due to lower reactivity in the explosives.

**REACTION ZONE THICKNESS**

As previously mentioned, there is a linear relationship between detonation velocity and the charge diameter as follows.

\[
D(d) = D_i [1 - A/d] 
\]

(1)

where, \(D(d)\) is detonation velocity for the charge diameter \(d\), \(A\) a constant related to the reaction zone thickness. The constant \(A\) for the emulsion explosives containing voids of different sizes can be logistically plotted as a function of voidage as shown in Figure 11. Figure 12 shows the dependence of \(A\) on the void size for voidage of 0.14-0.37 (explosive density 900-1200kg/m\(^3\)). The reaction zone thickness \(A\) is roughly proportional to the square root of void size, and it is apparent that the reaction zone thickness is large for the explosive sensitized by large voids.

**FIGURE 11. RELATION BETWEEN REACTION ZONE THICKNESS AND VOIDAGE.**

**FIGURE 12. RELATION BETWEEN REACTION ZONE THICKNESS AND VOID SIZE.**

**CRITICAL DIAMETER**

As voids in the explosive are considered acting as hot spots, the critical diameter \(d_C\) decreases as the chemical reaction rate \(R\) increases. Assuming that \(d_C\) is inversely proportional to the reaction rate at the void surface (\(R_{SURF}\)) and the reaction rate in the bulk explosive (\(R_{BULK}\)), then \(d_C \propto 1/[R_{BULK} + R_{SURF}]\). When \(R_{SURF}\) is much larger than \(R_{BULK}\), then \(d_C \propto 1/R_{SURF}\), the reaction rate is proportional to the surface area of hot spots or voids. It is plotted in Figure 13 the relationship between \(d_C\) and the surface area of voids contained in the unit volume of the emulsion explosives.

Khasainov et al. showed that the linear relationship mentioned above exists for the heterogeneous explosives independent of size or the amount of the voids based on the grain burn concept. Lee and Person showed that the critical diameter of the emulsion explosives is linearly proportional to the void spacing (distance between void centers) by the experiment in which GMB of average diameter smaller than 153µm was used. The results obtained for five different void sizes used in this study present five different lines.
FIGURE 13. RELATION BETWEEN CRITICAL DIAMETER AND RECIPROCAL SURFACE AREA OF VOIDS INCLUDED IN THE UNIT VOLUME OF THE EMULSION EXPLOSIVES.

The void size is considered to be the major reason that gives five independent lines. The voids larger than about 0.5mm affect the reactivity of the emulsion matrix due to the rarefaction from void itself. When the void size is as small as around 0.1mm, $d_C$ should be inversely proportional to the specific surface of voids. Provided that voids are of the average diameter and are regularly dispersed with a certain distance, the spacing of voids can be estimated.

The relationship between $d_C$ and such spacing is shown in Figure 14. Each line crosses with the x-axis approximately at the value of void diameter. For certain size of voids, $d_C$ is proportional to the distance between each adjacent void surface, the web thickness of bulk explosive, and this suggests that $d_C$ depends on the reaction rate of the bulk explosive. When the voids are large, $R_{BULK}$ seems to be dominant in the reaction and $R_{SURF}$ is negligible compared to $R_{BULK}$. Critical diameter is therefore proportional to the web of bulk explosives provided that the reaction rate of the bulk explosive is constant independent of web thickness.

Assuming that voids in the emulsion explosives are regularly dispersed to keep the same spacing with adjacent voids, and that those voids act as hot spots, the number of hot spots in a unit explosive volume is inversely proportional to the size (diameter) of the voids for the same explosive voidage.

Although the detonation front in the emulsion explosive should be curved concave due to the lateral rarefaction wave, we consider the model for the adjacent shock front as shown in Figure 15 in which the voids are regularly located. The numbers $n$ of voids with diameter $d_B$ are regularly dispersed in a unit volume of explosive and the spacing (distance between the void centers) is indicated as $L_C$ and the web of the voids surface $L_S$.

The voids are considered to act as hot spots whose size is as same as the original voids when the detonation front passed by. Under the assumption that the reaction of explosive starts at the void surface after certain induction period, and the void expands as the reaction proceeds until the...

FIGURE 14. RELATION BETWEEN VOID SPACING (DISTANCE BETWEEN VOID CENTERS) AND CRITICAL DIAMETER.

FIGURE 15. VOID ARRANGEMENT MODEL IN FRONT OF AND BEHIND THE SHOCK FRONT IN THE EMULSION EXPLOSIVES.
surface reaches to the next void, critical diameter \( d_C \) can be expressed as follows.

\[
d_C \propto L_S^{[a + m]} \quad (2)
\]

where, \( a \) and \( m \) are constants that respectively relates to the time duration for the surface temperature of hot spot to reach its steady one and the time required for the detonation front to reach to the adjacent hot spot.

As \( L_S \) is inversely proportional to square root of \( \phi \), critical diameter should therefore inversely proportional to square root of \( \phi \) as shown in Figure 16.

\[
\text{FIGURE 16. CRITICAL DIAMETER AS A FUNCTION OF VOIDAGE.}
\]

For the explosives with constant voidage, it is considered that \( a \) is dominant for the small voids, and \( m \) is dominant for the large voids in equation (2). Critical diameter can be expressed as functions of void surface distance or bulk explosive web as shown in Figure 17.

The relation between critical diameter and reaction zone thickness will be discussed here. Assuming that critical diameter is proportional to reaction zone thickness, the values of \( A \) in the following equation is taken as reaction zone thickness \(^8 \) and are plotted in Figure 18.

\[
\frac{D}{D_i} = 1 - \frac{A}{d} \quad (3)
\]

Cooper showed that the critical radius and the constant \( A_R \) derived from equation (4) could be linearly plotted against many kinds of explosive \(^{16} \).

\[
\frac{D}{D_{\infty}} = 1 - \frac{A_R}{R} \quad (4)
\]

where \( D \) and \( D_{\infty} \) are detonation velocity at charge radius \( R \) and infinite diameter respectively. The results of our work are plotted in Figure 19 together with Cooper’s results. The explosives investigated by Cooper are those categorized as group 1 defined by Price \(^{17} \), and critical diameter or reaction zone thickness is thought to be fairly small. The line of this work is positioned upper to Cooper’s data and this means that reaction zone is much longer than those for military explosives. The “Ireco Mix” in his work seems to be industrial explosives, and its result is on the line we obtained.
CONCLUSION
The reactivity of the explosives were evaluated from the results of measurements of detonation velocity, detonation pressure and critical diameter in the emulsion explosives sensitized by certain volume of voids sized between 0.05mm and 2.42mm in average diameter. The reaction zone thickness was also estimated from the diameter effect on detonation velocity. Following results were obtained.
(1) Detonation velocity in the emulsion explosives estimated for the infinite charge diameter Di agrees well with calculated value DCJ when the voids are smaller than about 0.5mm, but Di is lower than DCJ for the voids greater than about 0.5mm.
(2) A linear relationship between critical diameter and void surface distance (web thickness of bulk explosives) was observed dependent of void size. This means that the reaction rate of bulk explosive is a dominant factor for the critical diameter of explosives sensitized by large voids.

REFERENCES
Critical Diameter of Condensed Explosives”, Proceedings of the Tenth Symposium on Detonation, pp.749-757, 1993