Research paper

Study on controlled detonation chamber system of chemical weapons (III): A study on destruction efficiency of chemical warfare materials by controlled detonation

Kiyoshi Asahina*[†], Ryusuke Kitamura*, Masato Katayama*, Tsuyoshi Imakita**, and Masaya Ueda*

*Engineering Department, Nuclear and CWD Business Unit, Machinery & Engineering Company, Kobe Steel, LTD., 2-7,4-chome, Iwayanakamachi, Nada-ku, Kobe 657-0845, JAPAN
[†] Corresponding address: k.asahina@engnet.kobelco.co.jp

**Environment and Chemistry Division, Kobelco Research Institute, Inc. 1-5-5 Takatsukadai, Nishi-ku, Kobe 651-2271, JAPAN

Abstract

As a destruction method of chemical weapons, the controlled detonation system named DA VINCH was developed. Over 99.9999 % Chemical Warfare Materials (CWM) Destruction Efficiency (DE) or DRE (Destruction and Removal Efficiency) is achieved solely by detonation processes.

The high pressure of 10 GPa and high temperature of 3,000 K generated by detonation are the causes of high efficiency and the phenomena is completely different from that by incineration process. Optimization of amount of donor charge to the CWM is also studied.

CO and H_2 gases in detonation product gas are treated by a plasma oxidizer.

Keywords: Controlled detonation, Chemical weapons, Detonation chamber, Destruction efficiency, Destruction and removal efficiency

1. Introduction

The Prohibition of Chemical Weapons Convention defines "Destruction of chemical weapons" as "a process by which chemicals are converted in an essentially irreversible way to form unsuitable for production of chemical weapons, and which in an irreversible manner renders munitions and other devices unusable as such." This means destruction of toxic chemicals is not sufficient. Destruction of chemical weapons by neutralization has fundamental problems to confirm by analysis that decomposition products do not contain reversible product, as well as toxic chemicals. Thiodiglycol is an example of non toxic reversible product for mustard.

There are three major processes to destroy chemical warfare materials (CWM), neutralization, incineration and detonation.

Neutralization is a batch-wise process and the degradiate compounds of CWM can be checked before release, but the time-consuming analysis of necessary composition of liquid causes low throughput.

Incineration is an alternative process which is continuous with higher throughput for destruction of chemical weapons. But continuous process with near real time analysis/monitoring of off-gas has a potential risk of releasing unacceptable off-gas to the atmosphere. This is also a disadvantage.

A detonation, as is a batch-wise process, can avoid potential risks of releasing unacceptable substance to the atmosphere by "Hold, Check and Release" operation, and has a higher throughput than neutralization, due to quick analysis of gas compositions.

The authors studied and developed detonation system of chemical weapons destruction named DA VINCH and its general explanation and optimization of detonation system were described in the previous papers [1,2].

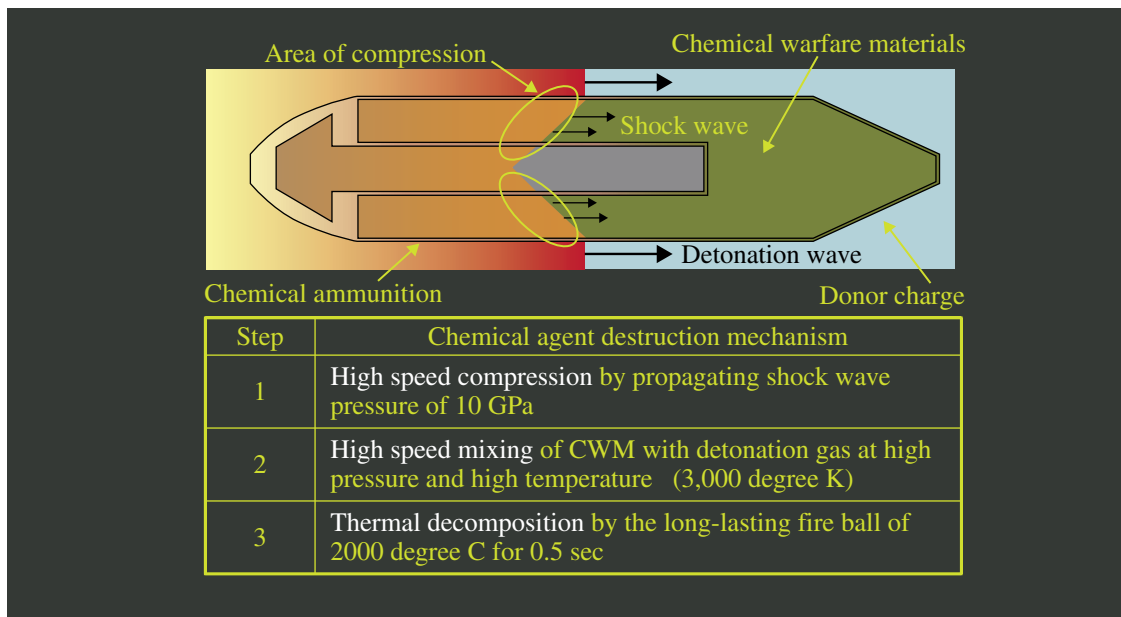The 3rd paper discusses the destruction mechanism of CWM

Fig. 1   Destruction mechanism by detonation.

by detonation, its destruction and removal efficiency as well as a suitable process for detonation product gas treatment.

2. Destruction mechanism of chemical warfare materials

As mentioned in the 2nd paper [2], emulsion-type donor charge around munitions produces high brisance (destruction power) to implode the munitions and keeps the fragments velocity as low as possible to extend the fatigue life of the inner chamber.

The explosive has an enormous power enough to destruct the chemical agent, which generates high compression and high temperature. A special element in the emulsion explosive extends the duration of the fireball, and which secondarily contributes to the destruction of chemical agent.

Figure 1 shows the mechanism in its sequential order.

Fundamentally, the detonation process utilizes the explosive energy itself to destroy CWM, i.e. high pressure of 10 GPa and high temperature of 3,000 K.

1) The 1st step: High compression at the front of propagating shock wave caused by detonation destroys CWM. Similar phenomenon is observed in cavitation bubbles when they collapse, which is known in the field of sonochemistry.

2) The 2nd step: High speed mixing of CWM with detonation product gas at high pressure and high temperature of 3,000 K destroys CWM.

3) The 3rd step: Long-lasting fireball of 2,000 °C for duration of 0.5 sec destroys gasified CWM. Aluminum component of donor charge contributes duration time of fireball.

An efficient CWM destruction is ensured when the above-mentioned three steps are properly operated, given that sufficient donor charge containing adequate Aluminum is provided. This mechanism is completely different from that of incineration, which is single oxidization within the range of 800 °C and 1,200 °C.

3. Destruction and removal efficiency (DRE)
3.1 Definition of DE and DRE

DRE (Destruction and Removal Efficiency) is a very important index to evaluate a total system to destroy organic compounds. DRE is the ratio of the quantity of CWM that is destroyed and removed by a process to the quantity of CWM initially fed to the process, therefore defined generally by the formula below.

DRE=(M-M') / M
Where;
M: quantity of the CWM initially fed to the process
M': quantity of the CWM remaining in the exhaust gas from the stack (final emission after off-gas treatment).

As for incineration process used to destroy CWM, additional CWM destruction and removal equipment like a secondary combustion furnace, scrubbers and charcoal filters are necessary due to insufficient destruction efficiency of the incinerator itself. Detonation process of DA VINCH, however, has sufficient destruction efficiency as is shown later, no additional CWM removal process is necessary in the off-gas line.

For DA VINCH detonation chamber, however, two different definitions of Destruction Efficiency (DE) were defined by the authors, in place of DRE, to evaluate its destruction performance precisely.

DE (gas) = (M-M'(gas)) / M
DE (all)   = (M-M'(all)) / M
M'(all)   = M'(gas) + M'(solid) + M' (surface)
Where;
M'(all)   = quantity of the CWM in the detonation chamber after detonation
M'(gas)   = quantity of the CWM in the detonation product gas

M'(solid)　　=　quantity of the CWM in the solid wastes (fragments and dust)

M' (surface) =　quantity of the CWM deposited on the inner surface of the detonation chamber

DE (gas) is used to evaluate the performance for gas phase, which is, of immediate importance for off-gas treatment, emission and working environment, while DE(all) is used to evaluate the overall destruction performance of the detonation chamber.

3.2 Detonation test using surrogates

"Surrogates" are alternatives to CWM which are used at a simulation test, because CWM is strictly controlled by OPCW. In actual operations, the initial quantity of the yellow agent in a 50 kg-Yellow bomb recovered from the sea is difficult to measure because the bomb shell is corroded and a certain part of the agent is lost. Therefore, a series of test using simulated 50 kg-Yellow bombs filled with surrogates were conducted in order to determine DE (gas) and DE (all).

1) Simulated munition

Simulated 50 kg-yellow bomb is shown in Table 1. The surrogates for yellow agent (mixture of Mustard (HD) and Lewisite (L)) were selected from a perspective of the chemical bonds; the oleic acid has a double bond that is in L. Dicyanobenzene has triple bonds of $C \equiv N$, which is stronger than the bonds in HD and L, and is selected to further examine the potentiality of the detonation. Octanol was added to disperse them.

Another important substance to simulate is degraded chemical agent, i.e. heel of HD and L. Heel is often observed in old chemical munitions and is hard to destroy by neutralization or incineration. Figure 2 shows a typical heel from 50 kg yellow bombs found in Lake Kussharo. The simulated heel was prepared according to the recipe obtained from the analysis of the actual heel in the yellow bombs [3].

CEES (Chloro-Ethyl-Ethyl-Sulfide) was added into the simulated heel as the indicator of destruction, and is a surrogate of HD as well.
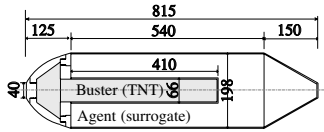
2) Procedures

Three simulated 50 kg-yellow bombs were detonated separately, with different quantity of donor charge in order to find the optimum amount of donor charge. Cleansing shot was carried out after the second shot. Following the cleansing shot, the detonation product gas was swept by the air and the fragments were kept in the closed detonation chamber overnight, then the air inside the chamber was analyzed in order to confirm that the HD surrogate level was lower than the General Population Limit (GPL) for HD of the new US airborne exposure limits (AEL's) [4]. And as long as the air readings in the chamber have not exceeded GPL values, solid materials like fragments in the chamber are considered uncontaminated. GPL is defined as concentration that the unprotected general population can be exposed to 24 hours a day, seven days a week, for a long time.

Table 1　Simulated 50 kg-yellow bomb.

Simulated 50 kg-yellow bomb		
Diameter	0.198 m	
Length	0.815 m	
Thickness	0.003 m	
Empty weight	24 kg	
Total weight	39.6 kg	
Explosive (TNT)	1.5 kg	
Agent (surrogate)	Oleic acid	4 kg
	Dicyanobenzene	4 kg
	Octanol	4 kg
Fill weight	Simulated heel	2 kg
	CEES	0.1 kg

Fig. 2　Heel in 50 kg yellow bombs.

Calcium peroxide was added as chlorine scavenger. In order to determine the agents (surrogates) remained after detonation and to evaluate the DRE, the gas inside the detonation chamber, fragments and debris were sampled, and the deposition on the inner surface of the detonation chamber were sampled by wiping. These samples were analyzed by using GC-MS (Gas Chromatograph Mass Spectrometer). The sampling and analysis methods with the determination limits are shown in Table 2.

3) Results

The obtained DE and surrogate concentration in the detonation product gas are shown in Table 3 and Table 4. As Table 3 indicates, high DE were demonstrated; more than 99.9999 % for DE (gas) and 99.99 % for DE (all) the total of detonation product gas, fragments, debris and dusts on the wall surface. The lower DE of CEES results from the small initial quantity.

HE/CWM, the ratio of explosive weight in donor charge and shell to CWM is a primary factor that influences DE. HE/CWM has been proved out to be sufficient at 1.27 with regard to DE (gas) (See HE/CWM ratio at Yellow-03 in Table 3). Efforts are being made in order to optimize the

Table 2   Sampling and analysis.

	Components	Sampling	Analysis	Determination limit
Gas	Oleic acid	Gas inside DA VINCH chamber was directly sampled	GC-MS	0.08×10^{-6} kg m^{-3} 0.005×10^{-6} kg m^{-3}
	Dicyanobenzene			
	CEES***			0.1 mg m^{-3}* 0.00002×10^{-6} kg m^{-3}**
	O$_2$, N$_2$, H$_2$, CO		GC-TCD****	0.01～2 %
	HCl, NOx, etc.		Detector tube	0.2～4 ppm
Wall surface	Oleic acid, Dicyanobenzene, CEES	-Wipe sampling by cloth dipped in acetone-5 Square areas of 0.15 m × 0.15 m each on 4 segments (door, back and both sides) of the inner surface of the chamber (total 20 areas)	GC-MS	0.03～0.15 mg m^{-2}
Fragments	Oleic acid, CEES, Dicyanobenzene	Sample was taken from collected fragments (all of fragments were collected)	GC-MS	$0.1～1 \times 10^{-6}$ kg kg^{-1}
	As		Fluorescent X-ray	0.1×10^{-6} kg kg^{-1}

*   When organic compounds such as CH$_4$ act as interfering substance.
**   When interfering substance is negligible.
***   CEES: Chloro-Ethyl-Ethyl-Sulfide.
**** GC-TCD: Gas-Chromatograph-Thermal-Conductivity-Detector.

Table 3   Destruction efficiency (DE).

Simulated 50kg-yellow bomb	Conditions			DE of surrogates**					
				DE (gas)			DE (all)		
	Surro-gates (kg)	NEQ* (TNTeq. kg)	Ratio of NEQ/ surrogate	Calculated for agents remaining in detonation product gas			Calculated for all**** remaining agent		
				Oleic acid %	Dicyano-benzene %	CEES %	Oleic acid %	Dicyano-benzene %	CEES*** %
Yellow-01	14.65	22.93	1.57	>99.9999	99.9999	>99.997	99.998	99.95	>99.992
Yellow-02	14.7	32.79	2.23	>99.9999	99.9999	>99.997	99.996	99.978	>99.985
Cleansing shot	0.1	11.33	-	>99.9999	>99.9999	>99.999	>99.999	>99.999	>99.995
Yellow-03	14.1	17.9	1.27	>99.9999	99.9999	>99.997	99.99	99.886	>99.991

* NEQ: Net Explosive Quantity.
** DE: Detonation Efficiency of Detonation process only, surrogate is an alternative chemical to CWM for the test.
*** CEES: chloroethlethylsulfide.
**** Detonation product gas, fragments and dust.

DE by reducing the donor charge.

The heel was successfully destroyed by detonation. DE was further improved by cleansing shot with no remaining agents detected. The concentration of CEES in the air inside the chamber after one night was lower than 0.00002 mg m^{-3}N, that is the General Population Limit (GPL) for HD, thus fragments are considered to be free from surrogates and can be removed from the chamber without additional treatment.

HCl concentration in the detonation product gas (< 0.5 ppm) was far lower than the values monitored in Kanda for actual yellow bombs and red bombs (1 to 50 ppm), therefore the chlorine scavenger was considered to be effective.

4. Detonation product gas and its treatment
4.1 Plasma oxidizer in off-gas system

Hereinafter, the treatment system of detonation product gas to release to the atmosphere is called "off-gas system." Usually, DRE of incineration for destruction of chemi-

Table 4   Concentration of surrogates in detonation product gas.

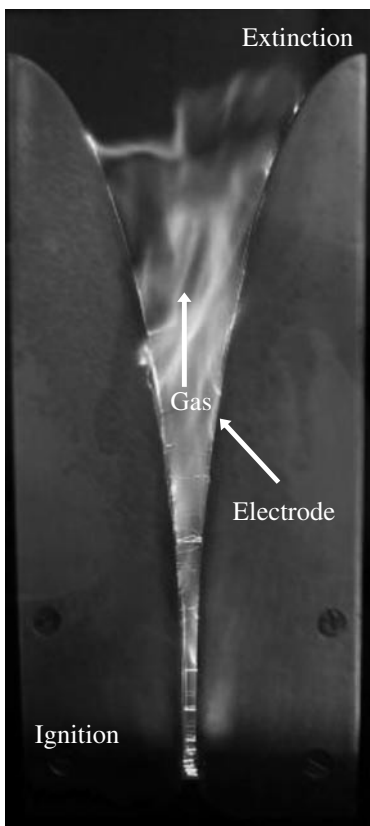|	Oleic acid (double bond) 10^{-6} kg m^{-3}N	Dicyanobenzen (triple bond) 10^{-6} kg m^{-3}N	CEES 10^{-6} kg m^{-3}N
Yellow-01	<0.08	0.013	<0.1
Yellow-02	<0.08	0.02	<0.1
After cleansing shot	<0.08	<0.005	<0.02
After replacing of detonation product gas by air and sealed for one night	-	-	<0.00002
Yellow-03	<0.08	<0.005	<0.1

Fig. 3   Schematic view of plasma oxidizer.
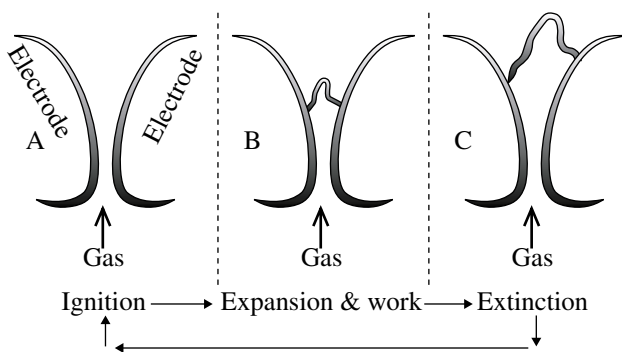
Fig. 4   Plasma oxidizer operating principle.

Table 5   Gas composition ranges of real detonation product gas.

Gas	Concentration (vol %)
Hydrogen	30〜40
Carbon monoxide	20〜30
Nitrogen	20〜30
Methane	1〜 5
Carbon dioxide	5〜15

cal weapons is at most 99 % and additional secondary combustion chamber is necessary to reduce the CWM remained in the off-gas before releasing to the atmosphere. As the DRE (gas) of DA VINCH after the detonation, however, has adequate value of 99.9999 %, and no CWM is detected in the detonation product gas, there is no need to place a secondary combustion chamber in off-gas system, from the view point of CWM.

Nevertheless, detonation product gas of DA VINCH has another contents with the range shown in Table 5, due to the detonation in reduction condition caused by detonation in vacuum.

To reduce the CO content etc. to the adequate level of releasing to the atmosphere, a new designed plasma oxidizer is used. It is not for destruction of remaining CWM but for oxidizing CO and H_2.

The image of the word "plasma" is high energy plasma to heat up and/or melt materials with Mega-Watts of energy. Yet the plasma used for the oxidizer is called cold plasma and its power consumption is in the range of 100 watts used at home.

4.2 Plasma oxidizer operating principle

The principle of plasma oxidizer is to generate plasma arc to keep H_2 and CO gas to burn by their own energy. It is a self burning system.

Figure 3 shows the schematic view of the plasma oxidizer and Fig. 4 shows its operating principle.

4.3 Test results

The test was carried out at a laboratory scale. Fig. 5 shows the plasma oxidizer unit used for the test.

Table 6 shows the gas composition used at the test, determined on the actual detonation product gas composition of Table 5.

Figure 6 and Table 7 show the comparison of CO in the reactor output as a function of the oxidizer temperature. A strong dependence on temperature and gas flow rate. i.e. residence time is seen.

To reduce CO concentration to 50 ppm for releasing to the atmosphere, optimization test of residence time was carried out considering the operating temperature is above 900 °C.

Figure 7 shows that residence time, within the range of 0.65 to 0.8, is appropriate to keep CO concentration below 50 ppm after the oxidizer.

H_2 becomes as low as non detective level and no other hazardous materials were detected in the off-gas, after the oxidizer.

Table 6   Gas composition used.

Gas	Concentration (vol %)
Hydrogen	37.92
Carbon monoxide	29.6
Nitrogen	19.94
Methane	4.68
Carbon dioxide	7.86

Table 7   CO concentration after oxidizer.

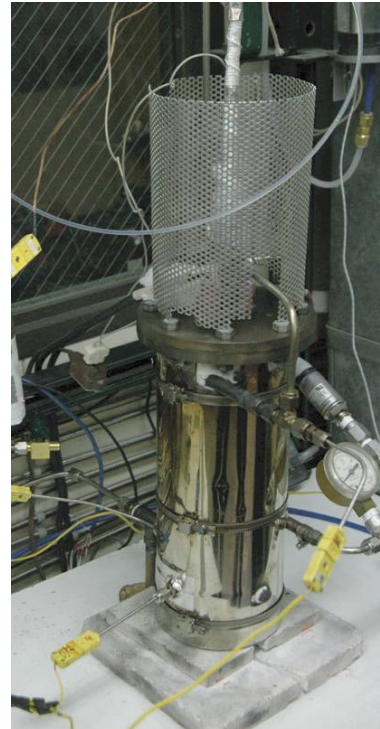| Air flow 10^{-3} m³ s⁻¹	Test gas flow 10^{-3} m³ s⁻¹	Reactor temp K	CO concentration %
0.417	0.047	1080	0.352
	0.047	1094	0.264
	0.049	1169	0.076
	0.047	1163	0.064
	0.052	1224	0.038
	0.052	1225	0.031
0.183	0.032	1068	0.423
	0.032	1069	0.394
	0.033	1164	0.038
	0.033	1159	0.050
	0.043	1227	0.031
	0.043	1233	0.026
	0.048	1233	0.046
	0.048	1248	0.036
	0.043	1235	0.027
	0.043	1233	0.027
	0.042	1231	0.024
	0.042	1228	0.025
0.150	0.041	1233	0.031
	0.041	1232	0.029
0.133	0.040	1226	0.037
	0.040	1226	0.041
	0.040	1225	0.044

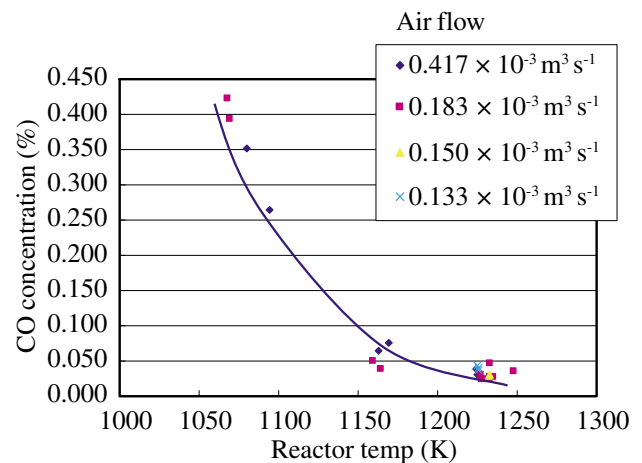Fig. 5   Plasma oxidizer unit and monitor used.

Fig. 6   CO concentration after oxidizer as a function of reactor temperature.
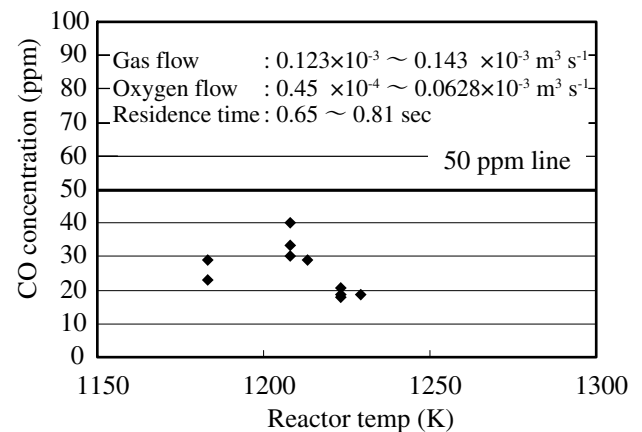

Fig. 7   Optimization of temperature and residence time for CO concentration.

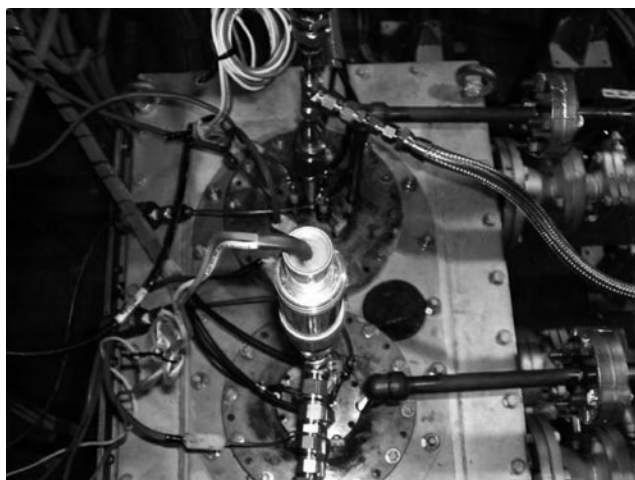Fig. 8   Plasma oxidizer unit at Kanda.

Fig. 9   Plasma oxidizer at the top of the body.

4.4 Operation records

A full size plasma oxidizer was installed as an off-gas treatment equipment of DA VINCH chamber DV60 (with a maximum capacity of 60 kg TNTeq), as is shown in Fig. 8 and Fig. 9.

The actual operation is carried out at 900-950 °C with residence time of 1 sec. No CO and no H_2 are detected in the off-gas, after the oxidizer

5. Conclusions

Under appropriate condition of detonation procedure, controlled detonation has very effective process to destroy chemical weapons.

Through the operations of destruction of chemical weapons at Kanda, the following results were obtained;

1) No Chemical Warfare Materials (CWM) are detected in detonation product gas in the detonation chamber. Therefore, no further treatment is necessary for destruction of CWM.

2) CO and H_2 in detonation product gas are self-burned by a plasma oxidizer to the acceptable levels to release to the atmosphere. No other hazardous components are detected.

3) CWM on fragments of munitions or in soot in the chamber can be destroyed to non detective level by cleansing shot before removal of fragments from the detonation chamber.

6. Acknowledgement

References

1) K. Asahina and K. Tamai,"Study on controlled detonation chamber systems of chemical weapons (I) General description of controlled detonation systems", submitted to Sci. Tech. Energetic Materials.

2) K. Asahina, K. Koide and T. Tada, "Study on controlled detonation chamber systems of chemical weapons (II) A study on optimization of controlled detonation", submitted to Sci. Tech. Energetic Materials.

3) K. Ishiyama, T. Imakita and J. K. Woosley, "Treatment Study of simulated mustard and Lewisite Heel" The International Chemical Weapons Demilitarization Conference, May, 2002, Den Hague, Holland.

4) Current and Revised Chemical Warfare Agent AELs, FACT SHEET, U.S. Army Chemical Materials Agency.

化学兵器の制御爆破チャンバーシステム（第三報）： 制御爆破による兵器用化学剤の破壊効率の研究

朝比奈潔 *†，北村竜介 *，片山昌人 *，今北　毅 **，植田雅也 *

　化学兵器の爆破処理プロセスとして，DA VINCH という名の制御爆破方法が開発された。爆破処理のみによって化学剤の破壊率（DE）は，99.9999 % 以上であることが模擬剤を用いた実験によって確認された。

　また 1000 発以上の化学弾の処理において，爆発後ガス中の化学剤はすべて検出限界以下であった。この高破壊率は爆発時に発生する 10 GPa，3000 K という高圧，高温の爆発エネルギーによるもので，燃焼プロセスによる破壊メカニズムと全く異なる。化学弾を破壊する場合の補助爆薬（ドナーチャージ）の量の最適化についても述べる。

　還元雰囲気での爆発後ガスに含まれる CO と H_2 は，プラズマ酸化炉により自燃処理される。

*（株）神戸製鋼所　機械エンジニアリングカンパニー　エンジニアリング事業部プロジェクト本部技術部
〒657-0845　神戸市灘区岩屋中町４丁目２番７号
†Corresponding address: k.asahina@engnet.kobelco.co.jp

**株式会社コベルコ科研　環境化学事業部　〒651-2271　神戸市西区高塚台１丁目５番５号