A-2.2.1 Research on Existing Use and Development and Evaluation of Technologies for Recovery and Destruction of Methyl Bromide

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1. Introduction

Though the regulation of the methyl bromide(MB) was established by the Montreal protocol at 1995, the regulation was excluded for use to the quarantine and the shipping pretreatment. On the other hand, it advised to apply the technologies of recovery and destruction of MB after fumigation and to use the substitute materials and technologies to reduce atmospheric emission of MB. But, there are no economical technologies for the recovery and the destruction. Therefore, development and realization of the economical technologies become a pressing need.

2. Research Objective

The objectives of the research project are to evaluate the efficiency and the economy of various technologies, and to develop efficient and economical technologies for recovery and destruction of MB used for the fumigation of the import crops, vegetables and fruits.

3. Research on Existing Use and Emission

3.1 Amounts of production and consumption to each application

Though the amount of production in Japan had been increased gradually and it exceeded 10,000 tons in 1993, it decreased gradually to 8,713 tons in 1995 and 7,908 tons in 1997. Seventy per cent of MB is used soil fumigation, and a little under 30% for the quarantine fumigation, and the rest is used for the fumigation of airplane, ship, flour mill, museum and etc. Though the consumption amount for the quarantine had been continued c.a. 3,000 tons, it was a little decreased to 2,450 tons at 1995 and 2,200 tons at 1996. The recovery and the destruction technologies of the MB for fumigation of log and cereal should be prior developed because the consumption amounts for them are abundant.

3.2 Crop fumigation procedure and emission of MB

(1) Summary research on procedure of quarantine crop fumigation by literature

The standard application amount of MB for 1 m^3 space is decided for various conditions of fumigation. There are width of 32.5 ~ 48.5g/m^3 in the log tents, 10 ~ 83g/m^3 in the cereal silos, 7 ~ 67g/m^3 in the cereal storehouses and 16 ~ 48.5g/m^3 in the vegetables and fruits storehouses by the gas leakage levels, the existence of stirring or recycle apparatus, the fumigation crops, the accommodation ratios (the amount of fumigation crops, ton / storehouse content volume, m ^{3}), and the temperature. In the case of larger accommodation ratios, smaller stellar magnitude of the facility, higher fumigation temperature, longer fumigation time and facilities equipped a stirring or recycle apparatus, the standard application amounts could be decreased.

(2) Research on tent fumigation of log by hearing comprehension

The import amount of log which was fumigated was 2,587 million m ^{3} at 1995. It is expected that the fumigation rate may be decreased from April 1997 because a fumigation didn't need to do in the case of only the insects which live in Japan. If tent volumes are 400 - 600 m ^{3} and the mean application amount is 40g/m ^{3} , the used amounts of MB are 16 - 24kg as for 1 tent hit. The MB of 80-360kg may be used if fumigation of 5 - 15 tents is done at once. Since there are measurement data of 6,700 - 9,100 ppm after the fumigation, it can be considered c.a. 5,000 - 10,000 ppm.

The humidity in the log tent is high and the gas must be exhaust within two hours. These conditions should be considered when MB is recovered after the log fumigation.

(3) Research on silo and storehouse fumigation by questionnaire

We sent questionnaire to 138 dealer who owned concrete or steel storehouses or silos managed by vegetation prevention of epidemics place in Yokohama. The effective numbers of the answer of the questionnaire are 69, and the effective recovery rate was 50%. The numbers of the silo and the storehouse are about 1/5 of the all numbers in Japan. Though 37 dealers who owned silos treated cereals such as corn, wheat and beans. Twenty four dealers (65%) treated corns, 22 dealer (59%) treated wheat, 11 dealer (30%) treated beans. As for the primary goods of 39 dealers who owned storehouses, 22 dealers (56%) treated cereals, 12 dealer (31%) treated vegetables and fruits, and 5 dealers (13%) treated cereals, vegetables and fruits. The average annual fumigation frequency of 58% of the silos dealers and 72% of the storehouses dealers were under 50 times. But, the storehouse dealers treated vegetables and fruits do fumigation more times than 50 per year, and 3 dealers do fumigation more than 200 times per year. The dealers used more than 100kg of MB at once were 30% of the silo dealers, but 10% of the storehouse dealers. Many storehouses treated cereals have comparatively large volumes, and many storehouses are larger than 2,000 m ^{3} . Many storehouses treated vegetables and fruits had smaller volumes than 500m ^{3} . If a blower is equipped, MB can be easily recovered from the flue gas. As a result of the research by questionnaire, it was found that 49 facilities of the silo had blowers and the effluent flowrates of 70% facilities were under 50m ^{3} /min, 20% facilities were 50 - 100m ^{3} /min, and there were few enormous blowers. In 35 facilities of the storehouse, the flow rates of blower were in the wide range, though most of them were under 50m ^{3} /min. The exhaust times were shorter than 5 hours for 50% of the silos and the storehouses, but some facilities treated only cereals exhausted the gas for about eight hours, one day or two days. On the other hand, many storehouses treated vegetables and fruits exhausted the gas in a shorter time than 5 hours such as 0.5-1.5hours from the reason mentioned before.

The concentrations of MB after the fumigation in 85% of the silos were lower than 7,500 ppm, but they varied with the kinds of crop and the fumigation conditions, and 2,500 ppm in 35%, 2,500 ppm ~ 5,000ppm in 23%, and 5,000 ppm ~ 7,500 ppm in 27% of silos. On the other hand, in much numbers of the storehouses treated only vegetables and fruits, the concentrations after the fumigation were high, and all of the facilities above 10,000 ppm were the storehouses treated vegetables and fruits.

The answers to the question whether the recovery system will be installed, when the flue gas recovery system was developed, were not considered to be eager. Enlightenment of the owners was necessary for the emission control of MB from the fumigation facilities.

(4) Estimation of possible amounts of reduction

Though MB for the soil fumigation had increased until 1994, it became to 5,742 tons which was less than the international regulation value in 1995. Therefore, it may be able to reduce to the regulation levels if it use adequately and employ the substitutive technologies. Because 20% of MB might be lost with sorption in the log fumigation, if only higher concentration gas (about 60%) is recovered with the recovery equipment (recovery efficiency of 80%) before emission, that is, 80x0.6x0.8=38% of 1,318 tons, namely about 500 tons can be reduced. On the other hand, 70% might be lost with sorption in the cereal fumigation, and 30x0.8 =24% of 817 tons namely about 196 tons can be reduced. Furthermore, 20% might be lost with sorption in the fumigation of vegetables and fruits, and 80%, 80x0.8=64% of 235 tons namely 150 tons can be reduced. Consequently, if MB for the quarantine is recovered, about 850 tons of MB, that is 36% of all the used amounts was estimated to be reduced.

4. Research on Recovery and Destruction Technologies

4.1 Requirements

Requirements for the recovery and the destruction technologies are summarized in Table 1 for each the fumigation material. We must think about drying operation before introducing flue gas into the recovering system. The flue gas must be recovered within c.a. 2 hours in case of log and within c.a. 1.5 hours to avoid influence of MB to the qualities of vegetables and fruits.

Table 1 Conditions for technologies for recovery and destruction of methyl bromide(MB)

Products	Log	Cereals		Vegetables fruits
		Loose	Baged	
Institution for fumigation	Tent	Silo	Storehouse	Storehouse
Blower	No	Attached	Attached	Attached
Gas flowrate of blower(m^3/min)	—	<50	<50	<50 or >200
Humidity	High (70～90%)	Low	Low	High
Time for work	In 2 hours	—	—	In 1 hour
Concentration of MB in institution after fumigation (ppm(v/v))	5,000～10,000	1,000～7,500	<7,500	>7,500
Quantity of MB for recovery and destruction(kg)	10～18	17～46 or 110～260	6～45	4～59
Power supply	×	○	○	○
Steam supply	×	×	×	×
Water supply	×	○	○	○
Style of Equipment	No fixed, parallel	Fixed	Fixed	Fixed
Others	No fire	No fire	No fire	No fire

4.2 Present status and problem of technologies for recovery and decomposition of MB

The technologies doesn't reach to practical use in Japan, because there was no regulation. The principles and characters of conventional studies for recovery and decomposition are shown in the Tables 2 and 3. It thinks about four methods as the recovery and decomposition systems for the MB in the fumigation gas. (1) Recovered MB is utilized again for another fumigation, (2) Recovered MB decomposed in another place, (3) Recovered MB decomposed in the used spot, (4) MB in the flue gas is decomposed directly in the used spot. Though the recovery efficiency of the adsorption/desorption method is high. It is necessary to select the adsorbent and treatment of the recoveried MB. A efficiency of high temperature decomposition technology may be high, and the equipment cost is few by using the industrial waste incinerators, though the transportation cost is in need if the facility is not near here.

Table 2 Examples and characteristics of technologies for recovery of methyl bromide(MB)

Technology	Principle	Recovery efficiency	Grade of work	Grade of economy
Adsorption	MB is adsorbed with adsorbant such as activated carbon, zeolite.	○	○	△
Condensation	MB gas is condensed to liquid with refrigerator.	△	○	△

Table 3 Examples and characteristics of technologies for destruction of methyl bromide(MB)

Technology	Principle	Destruction	Grade of work	Grade of economy
Heating	MB gas or adsorbant with MB is heated and products such as HBr, Br_2 are neutralized by alkali.	○	△	△
Chemical	MB is hydrolysesed, oxidized or reduced by chemicals.	△	△	○
Catalyst	MB is catalysesed and products such as HBr, Br_2 are neutralized by alkali.	△	△	×
Ozone	MB is oxidized by ozone and products such as HBr, Br_2 are neutralized by	△	○	×

5. Evaluation for Adsorption Efficiency of Activated Carbons and Basic Design of Recovery Equipment

5.1 Evaluation for adsorption capacities of activated carbons

Four kinds of activated carbon such as the crushed coal base carbon (CQS), the cylindrical coconut shell base carbon (Sx), the crushed coconut shell base carbon (HC), the fiber pitch base carbon (A20) were evaluated by the experiments. The packed density of CQS, Sx and HC were near 0.5g/cm ^{3} , A20 was 0.1g/cm ^{3} . It was confirmed that the obtained adsorption equilibria of the MB were analyzed well by the Dubinin-Polanyi equation shown in the following.

$$W\ (cm^3/g\text{-}AC) = W_0 \exp(-\kappa A^2)\ ;\ A = -RT \ln(P/P_0)$$

Where, W_0 : limit adsorption capacity (cm ^{3} -liquid MB/g-AC), κ : parameter depend on activated carbon, A: adsorption potential (J/mol), R : gas constant, T: adsorption temperature (K), P: vapor pressure of adsorbate, P_0 : saturated vapor pressure of adsorbate. In the concentration range from several thousands to one million ppm in the facilities after the fumigation, the adsorption capacities of MB were in the order of HC, CQS, Sx, A20, and it was found that 15 - 20% of MB in weight could be adsorbed. When humidity was more than 70%, the adsorbed amounts of the water increased rapidly, and the adsorbed amounts of the MB were decreased much.

5.2 Basic design of recovery system and equipment

(1) Recovery system

In the concentration range from several thousands to one million ppm in the facilities after the fumigation, most suitable recovery system is thought that MB is adsorbed with the HC, desorbed with steam indirectly, and recovered by cooling the desorbed gas.

(2) Determination of necessary amount of activated carbon and scale of equipment

The necessary amount of the activated carbon and the scale of equipment are caluculated from the results of this research as followings. If the initial concentration of MB is C_o (ppm), the gas volume of the fumigation facility is V(m^3), the equilibrium adsorption capacity of MB at the final concentration C(ppm) is W(cm^3-liquid MB/g-AC), the liquid density of MB is 1.7(g/cm^3) and it break through at about 60% of equilibrium adsorption capacity, the amount of the activated carbon X(kg) should be the following range.

$$X \geqq 4.0 \times 10^{-6} (C_o - C) V/W$$

For an example, when the MB of 5000ppm in the storehouse of 1000m^3 of the space volume recover by adsorption until 500ppm, the necessary amount of activated carbon X should be more than 450kg, if W is c.a. 0.04 (cm^3/g-AC). And the equipment volume become more than about 1.8m^3, and a flow rate F should be less than 150m^3/min.

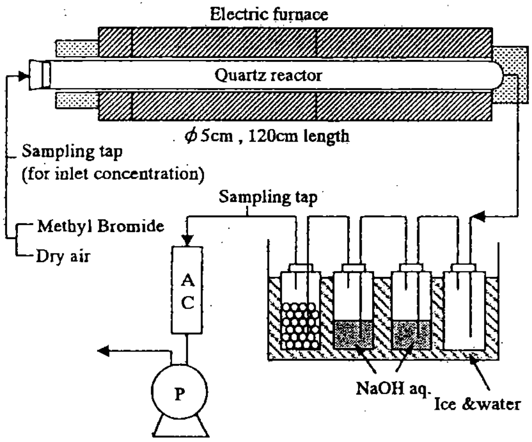

Fig.1 Schematic of the experimental apparatus

6. Development of Destruction Technology

6.1 Experiments of high temperature decomposition in laboratory

As a basis of the destruction technology by incineration, the decomposition efficiencies of MB in each temperature and residence time were measured and characteristic of decomposition was examined by the laboratory experiments.

(1) Apparatus and experimental method

The apparatus whose decomposition temperature and residence time could be changed easily was designed and made as shown in Fig.1. The residual concentration of MB after the decomposition was determined with ECD-GC or GC-MS.

(2) Results of experiment

Changes of the residual ratio of MB by the temperature in each the residence time were shown in Fig.2. It was estimated that MB could be decomposed more than 99.99% at higher temperature than 750 °C in 4 seconds and higher than 700 °C in 8 seconds.

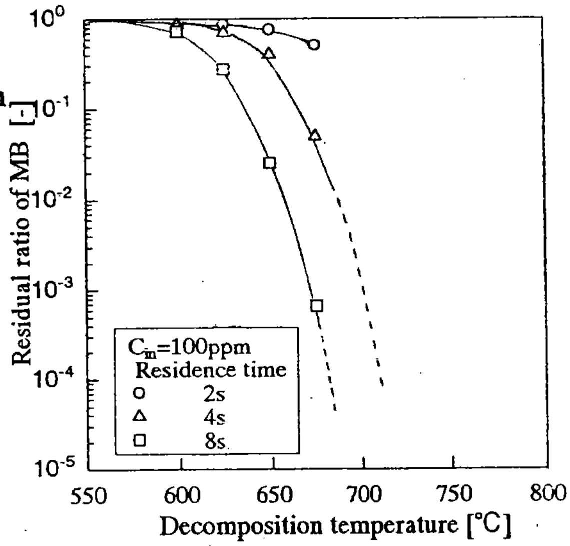

Fig.2 Experimental data for MB decomposition

6.2 Experiment of destruction in an industrial waste incineration facility

(1) Experimental condition

A rotary kiln in an industrial waste incineration facility was selected for the

Table 4 Conditions of incineration and concentrations and decomposition effficiency of MB

	MB	Blank
MB feed rate (kg/h)	10	
Waste feed rate (kg/h)	919	
MB feed ratio[a)] (wt%)	1.1	
Combustion temperature of Rotary kiln at outlet (°C)	970	
Combustion temperature of Secondary combustion chamber at outlet (°C)	870	
Residence time (s)	1.7	
Flue gas rate (m^3_N-dry/h)	9610	
CO concentration (ppm)	16	
MB (ppb)	<10	<10
Decomposition efficiency (%)	>99.996	—

a) Ratio to the waste feed

(2) Results of experiment

The results in Table 4. The destruction efficiency of MB was more than 99.996%, that is, the concentrations of MB in the stack gas were below ca.10 ppb which is the same level in the blank when MB didn't introduce. It is confirmed that the pollutants such as HBr in exhaust gas could be removed by existing the treatment system in the facility.

7. Conclusion

1) The pruduced amounts of MB in Japan was a little under 10,000 tons, and the ones for quarantine 2,400 tons. Of amount of them for quarantine fumigation, above half is for log, 30% is for cereals, the rest is for vegetables and fruits and others.
2) By literature, hearing and questionnaire, realities of quarantine fumigation and necessary conditions for recovery and destruction technologies are clarified.
3) Though the recovery efficiency of the adsorption/desorption method is high, it is necessary in the design carefully that influences of gradation of the gas concentration and the water vapour coexistence.
4) A efficiency of high temperature decomposition technology may be high, and the equipment cost is few by using the industrial waste incinerators.
5) It was confirmed that the obtained adsorption equilibria of the MB in four kinds of activated carbon of CQS, Sx, HC, A20 were analyzed well by the Dubinin-Polanyi equation. In the concentration range in the facilities after the fumigation, the adsorption capacities of MB were in the order of HC, CQS, Sx, A20, and 15 - 20% of MB in weight could be adsorbed. When humidity was more than 70%, the adsorbed amounts of the water increased rapidly, and the adsorption amounts of the MB were decreased.
6) A basic design method of the recovering equipment of MB with activated carbon was proposed by consideration of the above researches and the experiments.
7) It was estimated that MB could be decomposed more than 99.99% at higher temperature than 750 ℃ in the residence time of 4 seconds from the laboratory experiments.
8) It was confirmed that destruction efficiency of MB was more than 99.99% in an industrial waste incineration facility. Therefore it was demonstrated that MB could be destructed safely and reliably in existing facilities.

8. References

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