

Advanced Gas Cleaning Technology

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REFERENCES

1. Dockery, DW, Pope, CA, Xu, XP, Spengler, JD, Ware, JH, Fay, ME, Ferris, BG, Speizer, FE, An association between air pollution and mortality in six U.S. cities. *New England Journal of Medicine*, 329, 24, p1753-1759, 1993.
2. Hopke, PK, *Advances in Monitoring Methods for Airborne Particles*, 16th International Clean Air & Environment Conference, Christchurch, New Zealand, 2002.
3. Quann, RJ and Sarofim, AF, Vaporisation of Refractory Oxides During Pulverised Coal Combustion, Nineteenth Symposium (International) on Combustion, p1429-1440, 1982.
4. Sarofim, AF, Howard, JB, Padia, AS, The Physical Transformation of the Mineral Matter in Pulverized Coal Under Simulated Combustion Conditions. *Combustion Science and Technology*, 16, p187-204, 1977.
5. Flagan, RC and Friedlander, SK, Particle Formation in Pulverized Coal Combustion - A Review, Recent Developments in Aerosol Science, Shaw, DT, Editor, John Wiley & Sons, p25-59, 1978.
6. Yan, L, Gupta, RP, Wall, TF, A mathematical model of ash formation during pulverised coal combustion. *Fuel*, 81, p337-344, 2002.
7. Linak, WP, Seames, WS, Wendt, JOL, Ishinomori, T, Endo, Y, Miyamae, S, On Trimodal Particle Size Distributions in Fly Ash from Pulverised-Coal Combustion, 29th International Symposium on Combustion, Sapporo, Japan, p441 - 447, 2002.
8. Seames, WS, An Initial Study on the Fine Fragmentation Fly Ash Particle Mode Generated during Pulverised Coal Combustion. *Fuel Processing Technology*, 81, p109 - 125, 2003.
9. Benfell, KE, Assessment of Char Morphology in High Pressure Pyrolysis and Combustion. PhD thesis, Department of Geology, University of Newcastle, Newcastle. p195, 2001.
10. Cohen, D. D. (1998), Characterisation Of Atmospheric Fine Particles Using IBA Techniques. *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials & Atoms*, 138, 14-22.
11. Thurston, G. D. and Spengler, J. D. (1985), A Quantitative Assessment of Source Contributions to Inhalable Particulate Matter Pollution in Metropolitan Boston, *Atmospheric Environment*, 19, 9-25.

HIGH TEMPERATURE FLUE GAS CONTROL SYSTEM WITH GETTER PARTICLES AND CERAMIC FILTER

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ABSTRACT

To reduce the final waste dumping to the land-fill and to reduce hazardous gas such as dioxins, high temperature conditions with ash melting have been required in combustion and gasification processes for solid fuel and waste in Japan. On the other hand, to increase the efficiency of power generation in such combustion and gasification processes, reduction of emissions of corrosive compounds in flue gas or product gas as well as toxic elements will be also required. Then, we have been investigating the emission control technology of hazardous gas and trace heavy metals based on mechanism of capturing metals by sorbent particles in high temperature above 850°C and started the project research on "High Temperature Flue Gas Control System with Getter Particles and Ceramic Filter", which was one of a regional R&D consortium project of METI. In this paper, we report the results concerning sorbent performance, reactivity between getter particles and filter, operation results of pilot tests combined the getter particles and the ceramic filter, and soundness of the system.

BACKGROUND

Air pollutants relating to combustion process have been SO_x, NO_x, and dust in regional environment. Recently, the dioxins and the endocrine disrupters have been paid to attention, and the target of the restriction seems to turn from majors and minor compounds to trace elements. It will take some generations for the finding of the epidemiology and the medicine to understand what influence an increase and decrease of the trace elements and the microorganism exert on the ecosystem of the earth. However, it is necessary to remove hazardous substances that have already appeared the influence. When a large amount of fossil fuel is consumed as the major energy source, especially, it is necessary to consider the element that has been treated as the negligible trace without problem. On the other hand, a highly effective heat recovery and power generation systems are expected to reduce carbon dioxide emission from the viewpoint of global environment, and so the heat recovery in high temperature without corrosion is aspired even for the waste incineration facility.

To understand and solve the above trace element problems, following subjects have been discussed since 2000 by the group of Yokohama trace element workshop [1];

- (1) Specification of emission sources (natural, anthropogenic, harmful or not),
- (2) Contents in fuels (fossil fuels, waste)
- (3) Emission mechanism (itself, fine particles)
- (4) Balance in process (flue gas, waste water, waste solid)
- (5) Environmental impact (air, water, soil)
- (6) Health impact (human being, animals, food, local and global environment)
- (7) Analysis tools (traditional, time, accuracy)
- (8) Monitoring tools (online, real time)
- (9) Abatement technologies (low temperature, high temperature)
- (10) Regulation (foreign, domestic, present, future)

In this paper at the symposium on Gas Cleaning at High Temperatures, the results of the research on "High Temperature Flue Gas Control System with Getter Particles and Ceramic Filter" which is one of a regional R&D consortium project of METI are described [2]. This is a subject of above the abatement technology at high temperature.

TREND OF WASTE MANAGEMENT IN JAPAN

In Japan, the waste management legislation was revised for promotion of the reduction and recycling, the improvements of reliability and safety, and the prevention of illegal disposal, in 1997. Furthermore, to shift from a one-way-use society to a recycling-based society, the Basic Law for Establishing a Recycling-Based Society was enacted in May 2000. In this law, "Recycling-Based Society" defines a society where the consumption of natural resource is kept at a low level and the environmental load is reduced as much as possible by preventing products from becoming waste, promoting the appropriate recycling of products, and securing appropriate disposal. Additionally, restriction by new laws on waste management and pollutant emissions including dioxins has been strengthened since 2000. Municipal waste and industrial waste has been basically treated by incineration and landfill. However, the landfill space is approaching the limitation. To reduce the final waste by the landfill and simultaneously to reduce the dioxins, high temperature condition with ash melting should be effective in combustion and/or gasification processes as well as to increase the efficiency of power generation. However, with increasing temperature, hazardous gases such as toxic heavy metals are also exhausted. On the other hand, to recovery thermal energy efficiently, corrosive gases should be removed at high temperature. The super cleanup flue gas control system with getter particles and ceramic filter was designed as a method of solving the above problems at the same time. Our project covered the range of middle temperature of 600°C to high temperature of 900°C as shown in Figure 1 [2].

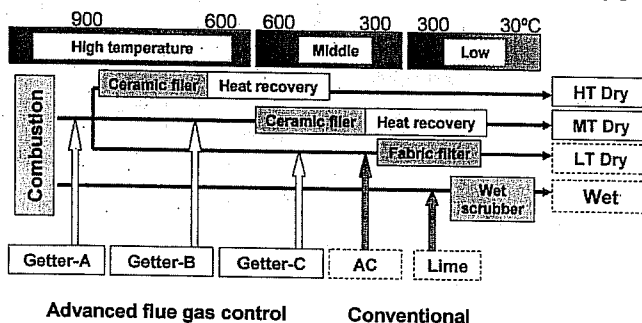


Figure 1 Temperature range of flue gas control

BEHAVIOR OF TOXIC METALS IN CONVENTIONAL INCINERATION FACILITY

In this paper, the behavior of toxic metals in a sewage sludge incineration facility of 40 ton/day shown in **Figure 2** is described as an example of conventional incineration facility for municipal solid waste. The heavy metal concentration in sewage sludge with 80% moisture was about 8 ppm (dry) of lead, 1.9 ppm of arsenic, and 1.1 ppm of mercury, and below the detection limit of selenium and cadmium. **Figure 3** shows the exhaust gas measurement result when this sludge was incinerated in a fluidized bed. The heavy metal concentration in flue gas in each measurement point was 2.7 mg/m³ of lead in the maximum, and a range of 0.12 to 0.76 mg/m³ of mercury. The mercury existed in the state of the gas not of the particulate. As for elements other than mercury and selenium, the concentrations were significantly decreased at the bag house, which suggested that the bag house at low dust collection temperature around 200°C is effective to capture those heavy metal elements. The wet scrubber seems to be effective on capturing the selenium. However, mercury concentration is not so decreased at any equipment and any temperature, which suggests that the mercury appears to exist in gas phase of elemental mercury [3-5].

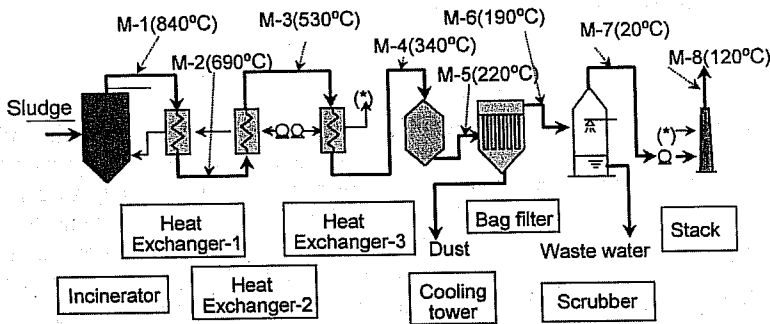


Figure 2 Sewage sludge incineration process (40 ton/d)

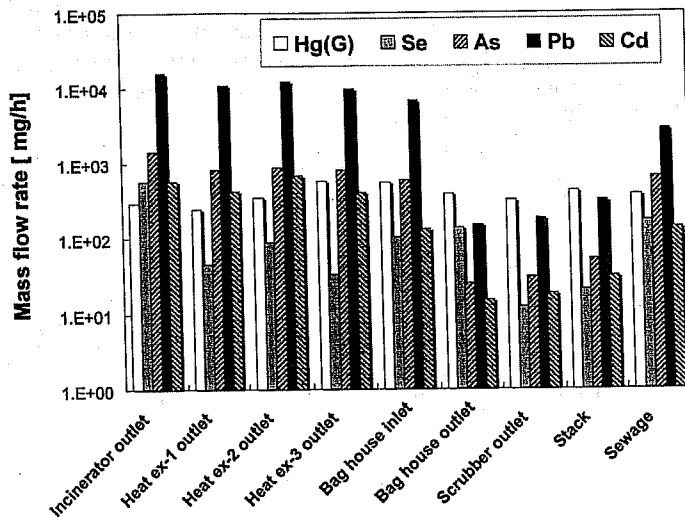


Figure 3 Heavy metal behavior in sewage sludge incineration process in Fig. 2

HIGH TEMPERATURE FLUE GAS CONTROL SYSTEM

Concept of Flue Gas Control System with Getter Particles and Ceramic Filter

To develop the emission control technology for removing corrosive gas and toxic heavy metals, we proposed a system consisting of sorbent injection to capture metals and ceramic filter to capture the sorbent with metals at high temperature condition above 600°C. A conceptual system to capture the metals by getter particles (sorbents) and ceramic filter is shown in Figure 4 [2, 3, 7].

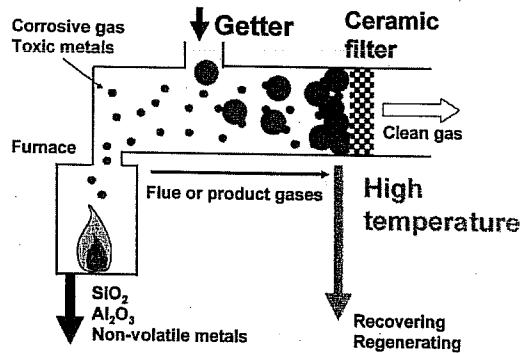


Figure 4 A conceptual system to capture the metals by getter particles and ceramic filter

As candidates of sorbent material, kaolinite, halloysite, limestone and other minerals were tested, how the sorbent reacts with metal vapors and corrosive gases to prevent subsequent nucleation and condensation processes which generate small particles. The cordierite was chosen as a material of ceramic filter over 600°C, though the candidate with high thermal shock resistance in high temperature and in repeating pulse cleaning was cordierite, mullite and silicon carbide [2, 3].

Capturing heavy metals by mineral sorbent

Mineral sorbent has been paid attention as a promising method to remove the volatile metals at high temperature, and the removal performance for typical volatile metals such as lead, cadmium and others has been studied by a lot of researchers [5-11]. It was found that kaolinite which is a kind of clay of alumina-silicate compounds, and lime are very effective for lead and cadmium removal [8, 10]. Such sorbents preferentially capture specified metals under multi-metal coexisting condition and the mixture of lime and kaolinite might be more effective than being applied individually [11]. This viewpoint is much important for the practical application of sorbent particulates because many kinds of heavy metals coexist in flue gas and interactions and competition reactions between them might occur in their removal process by sorbents.

Then, the effect of the multi metal coexistence as lead, cadmium and zinc on the removal performances with sorbent was investigated by comparing with those under single metal conditions. The experimental equipment is shown in Figure 5 [2, 6, 7]. The reactor is cylindrical tube ($\phi 20$ mm x 400 mm) made of quartz which is separable into three parts. A quartz basket ($\phi 10$ mm x 10 mm for single metal system, $\phi 15$ mm x 10 mm for multi-metal system) hooked in the reaction tube central is filled with the heavy metal sample, and the sorbent was put on the silica paper of the lower. The sorbent bed can capture the metals volatilized in the upper basket. Amounts of metals captured by kaolinite and limestone under

single metal condition are shown in **Figure 6**. Lead and cadmium compounds were more captured than zinc, and the addition of steam obviously promotes to capture any metal. On the other hand, in single metal/limestone systems, lead was hardly captured regardless of the addition of steam, while zinc was highly captured. Metal amounts captured under multi metal coexisting condition are shown in **Figure 7**. it was found that the moisture on the performance of heavy metal removal is very effective. In addition, multi-metal coexisting affected to the performance of heavy metal removal, and it was also positive in case of limestone.

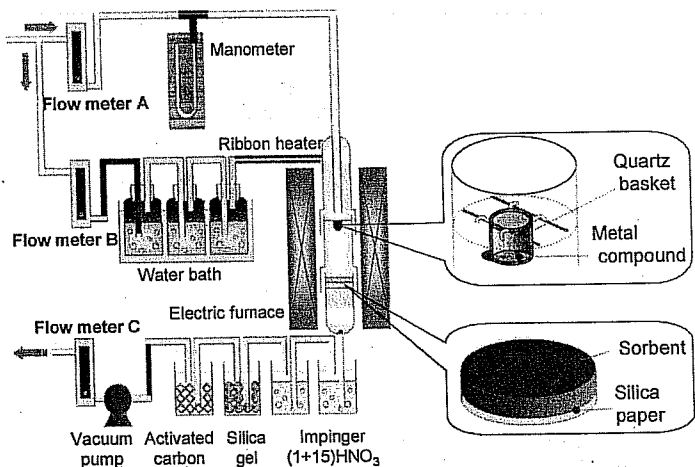


Figure 5 Fixed bed reactor with cell vaporizing metals

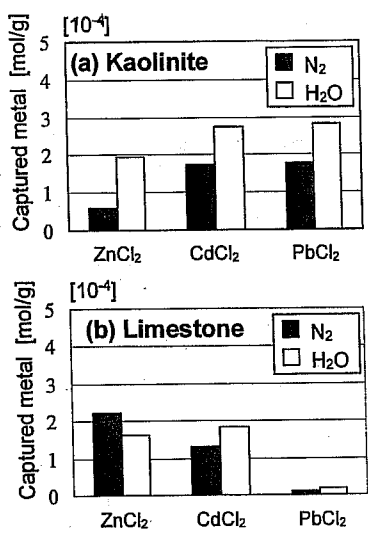


Figure 6 Captured metals in single metal systems under N₂ and H₂O+N₂ conditions for (a) kaolinite and (b) limestone as sorbent

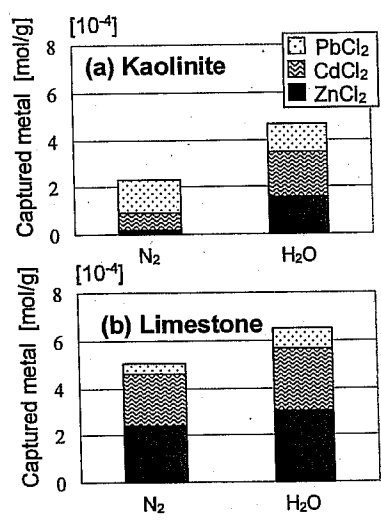


Figure 7 Captured metals in multi-metal systems under N₂ and H₂O+N₂ conditions for (a) kaolinite and (b) limestone as sorbent

Solubility of captured metals

In order to investigate capturing mechanisms of heavy metals, such as physical absorption, chemi-sorption and chemical reaction, the metal captured was separated by dissolution treatment of three steps. Removal efficiencies of three metals under single metal and multi-metal coexisting conditions are shown in **Figure 8**. They are separately expressed according to its different solubility, that is, 'water rinsed metal' (50 mL, 150°C, 1 h), '(1+15) HNO₃ rinsed metal', 'acid soluble metal' (HNO₃/HCl/HF). Any water rinsed metal was not observed under all conditions tested in this study. It means that heavy metals captured by kaolinite are strongly bonded or their chemical forms are changed to water insoluble compounds. The presence of steam is important in kaolinite capturing heavy metals, especially cadmium [3]. On the other hand, removal efficiencies of lead in multi-metal systems was not increased by the addition of steam in contrast with cadmium, although a vaporizing behavior of lead was very similar to that of cadmium due to the almost same melting point. However, 65-70 % of total captured lead in single metal system was acid soluble metal, which suggested that the bonding of kaolinite with lead was considered to be stronger than cadmium and zinc. As a whole, in the multi-metal system, N₂ condition inhibits from capturing cadmium and zinc and N₂ plus steam condition inhibits from capturing lead. The bonding of kaolinite with cadmium becomes tighter due to the effect of multi-metal coexisting, and conversely the bonding with lead becomes looser. Namely, in multi-metal coexisting system, cadmium is dominantly captured by kaolinite via chemi-sorption mechanism.

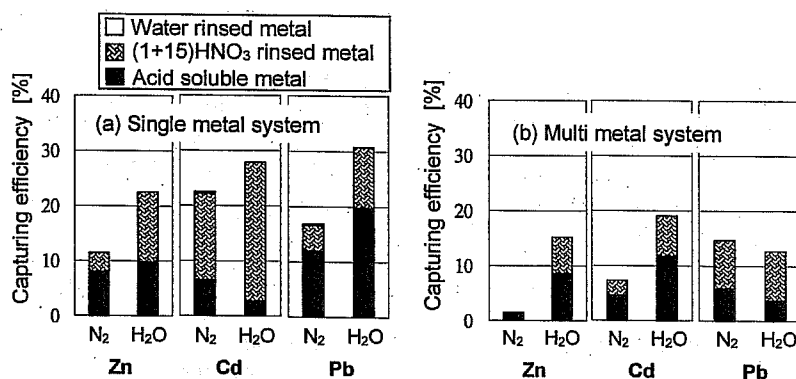


Figure 8 Solubility fractionation of metal compounds captured by kaolinite under (a) single metal system and (b) multi metal systems

Simultaneous Capturing Corrosive gases and heavy metals by Multi-Sorbents

The corrosive gases to be a problem in waste incineration processes are mainly sulfur and chloride compounds. The low melting point compounds with chloride, sulfur and alkali coagulate and deposit on heat exchanger tubes in the cooling process after vaporizing, which promotes corrosion. Such corrosion trouble should be controlled by removing the alkali and the chloride compounds in high temperature conditions. One of the control methods is by using the getter particles to capture the corrosive gases. We concluded previously that lime-silica (CaO-SiO₂) is a useful sorbent to reduce hydrogen chloride [1]. In this reaction scheme, a stable Ca₃SiO₄Cl₂ is formed at 600 to 900°C and the melting point is above 1060°C. In addition, CaO-SiO₂ reacts also with sulfur oxides together with hydrogen chloride to produce stable Ca₁₀(SiO₄)₃(SO₄)₃Cl₂ at above 700°C [1] and the melting point of is above 1100°C to be stable. Kaolinite is confirmed to be a useful sorbent to capture sodium, cadmium, lead and

zinc at high temperature region [3-6]. Based on these previous results, the getter particles composed of multi-sorbents as kaolinite for heavy metals and lime-silica for corrosive gases were made by granulating with binder. Kaolinite, silica and hydrated lime powders were mixed by ball mill, and the getter particles were produced by a spray dryer. The particle diameter as granulated was about 200 μm .

When the getter particles is injected and collected by a ceramic filter in a pilot test plant, if they would be powdered and the fine particles would plug the filter, the pressure drop of the filter would increase, which gives the operating trouble. Therefore, to evaluate the powdering index or the strength and removal efficiency, all of the getter particles with different composition and different binder additives as shown in **Table 1** were tested. Consequently, Getter-A was selected.

Table 1 Compositions of getter particles used for powdering index tests

Getter	Kaolinite	Silica	Hydrated lime	Calcium carbonate	Binder
A	27.7 %	15.2 %	57.1 %		non
B	15.0 %	15.0 %		70.0 %	non
C	15.0 %	15.0 %		70.0 %	PVA
D	15.0 %	15.0 %		70.0 %	water glass

Reactivity of Getter Particles and Ceramic Filter

As the cordierite filter of honeycomb construction is adopted in the pilot test plant, the reactivity between the filter and the getter particles were examined by using the tabular test piece filter. First getter particles or fly ash of sewage sludge was made a slurry with acetone and it was spread on the surface of a ceramic filter in 0.2-0.4g/cm². After dried, it was heated with 250°C/h and held for two hours at 500°C and 900°C. The getter particle after it cooled down flaked off easily from the filter and the reaction between the two was not observed by the SEM. It suggests that there would be no problem on practical use. Furthermore, there should be enough strength on practical use because of being used as a honeycomb structure, though the results on the destruction examination of reacted filters showed that the tabular test piece filter was comparatively destroyed by low pressure when it was plugged,

On the other hand, the relationship between the removal efficiency of heavy metal and pressure drop through the getter particles bed including the tabular test piece filter was investigated by using the fixed bed reactor similar to that in Figure 5. The results on change of pressure drop during capturing metals are shown in Figure 9. It can be seen that an initial peak appears in a few minutes and levels off afterwards and the peak of lead is considerably higher. As a reason, the following reason can be assumed. Because the metal volatilization method is adopted for the experiment, high density metal vapor comes to the surface of the getter particles bed on the filter in the initial stage and forms the primary layer, resulting in increasing the pressure drop. Afterwards, the density of the metal vapor from the basket is decreased and also a part of metal captured escapes through the filter, resulting in decreasing the pressure drop and being stable. In this experiment, the element with the smaller ion diameter in order of zinc, cadmium and lead provides the higher removal efficiency and the higher pressure drop. The relationship between the final pressure drop and the removal efficiency is shown in Figure 10.

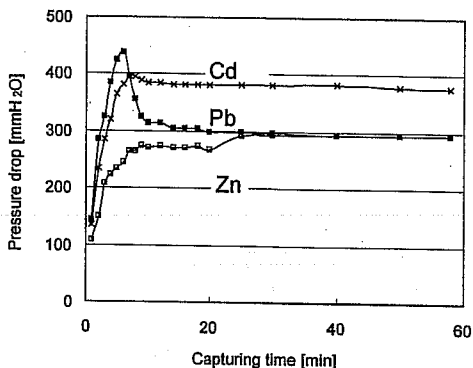


Figure 9 Change of pressure drop during capturing metals

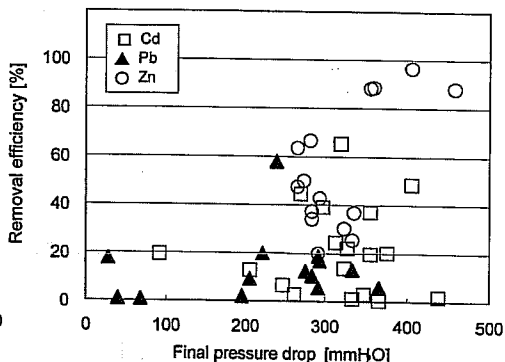


Figure 10 Relationship between final pressure drop and removal efficiency

Results of Pilot Plant Test

Figure 11 shows a schematic flow diagram of the pilot test plant we used. The test plant is consisted of a circulating fluidized bed incinerator (max. 80 kg/h, $\phi 300$ mm x 1,100 mm high), after-combustor ($300 \text{ m}^3\text{N/h}$), a getter feeder, a high-temperature ceramic filter (4 pieces of element with $\phi 200$ mm x 5,001 mm, Cordierite), a flue gas treatment system and an activated carbon tower. The getter particles is of the Getter-A ($\rho: 0.45 \text{ g/cm}^3$, $d_p: 135 \mu\text{m}$). In the tests, four compounds of hydrogen chloride, sodium chloride, lead and zinc were used as the dummy hazardous compounds. Three kinds of tests were carried out, that is, (1) each dummy compound was individually fed, (2) a mixture of four compounds was fed, and (3) the mixture together with actual gas was fed, which was incineration flue gas of sewage sludge. The ceramic filter inlet temperature was 800 to 850°C. **Figure 12** shows removal efficiencies for above three feeding conditions. The removal efficiencies of sodium (CF inlet concentration: (1) 3-5 mg/m^3 , (2) 38-40 mg/m^3) and zinc ((1) 60-100 mg/m^3 , (2) 160-240 mg/m^3) in the actual gas condition are as high as more than 85% and nearly equal to those of the other conditions. Hydrogen chloride ((1) 2000 mg/m^3 , (2) 2000-3000 mg/m^3) is about 45% and equal to that of the single compound condition. Lead ((1) 100-240 mg/m^3 , (2) 90-140 mg/m^3) is decreased from 85% to 14% with increasing other compound. Similar results for lead was obtained by above small fixed bed reactor experiments, suggesting that lead compounds is easily influenced by other heavy metals and the removal efficiency was decreased. Furthermore, as the removal efficiency of sulfur oxides is as high as 90%, the sulfur compounds might prevent the getter from capturing the lead compounds or produce the lower volatilizing temperature compounds related to the lead. Consequently, it was found that the getter used in this tests is effective to capture the hazardous compounds in following order; Na, Zn, SO_x > HCl, Pb. **Figure 13** shows influence of selectivity of lead to zinc or zinc to lead and influence of steam gas on the selectivity when the getter-A captures each metal. The captured amount of zinc when lead was first captured was lower than when zinc was first captured. Then, the captured amount of lead is not so different. The influence of steam gas on the captured amounts of both metals is larger, especially when the zinc is captured regardless of the existence of lead. It could be found out that the getter-A or kaolinite would prefer zinc to lead as well as the result of pilot test plant in **Figure 12**.

Though an increase of differential pressure of the ceramic filter unit above 750°C was monitored in actual conditions without any getter particle, there was no increase of the

pressure with feeding the getter particle, even around 850°C. This suggests that the getter particles could prevent the incineration ash from staying and adhering on the filter surface and promote to wash out the fine dust.

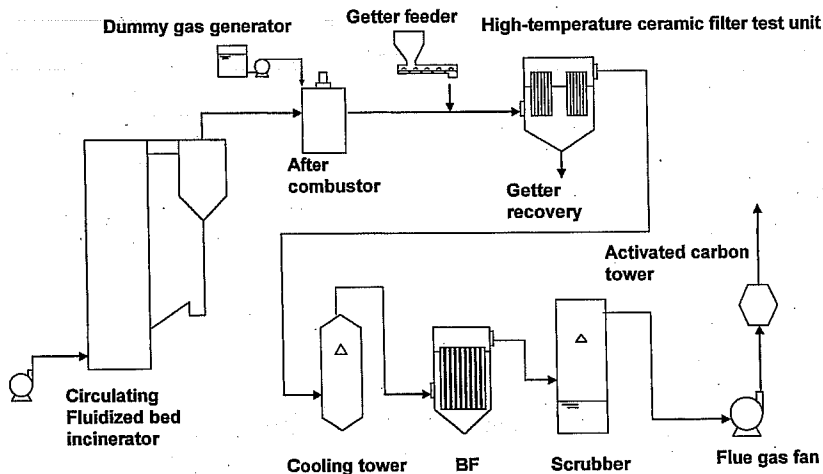


Figure 11 Pilot test plant with CFBC for Sewage sludge (80 kg/h)

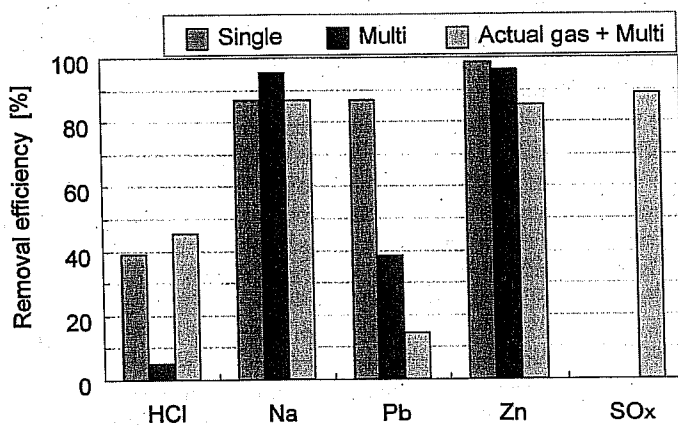


Figure 12 Removal efficiencies for three feeding conditions, (1) each dummy compound was individually fed (Single), (2) a mixture of four compounds was fed (Multi), and (3) the mixture together with actual gas was fed (Actual+ Multi).

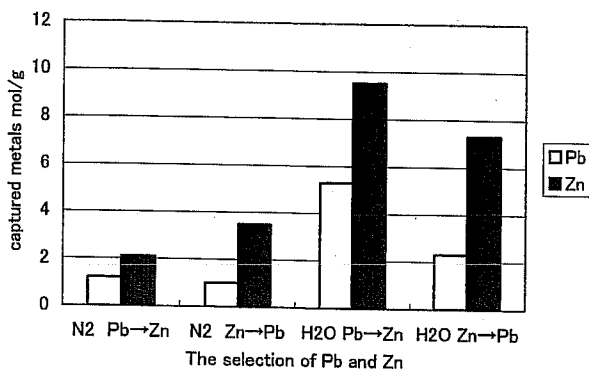


Figure 13 Influence of sequential feeding on capturing metals

CONCLUSIONS

This paper reported mainly the research results of consortium project of "High Temperature Flue Gas Control System with Getter Particles and Ceramic Filter" by the Regional R&D Consortium of Chubu Bureau of Economy, Trade and Industry of METI. As a result, it was confirmed that the combined system with getter and ceramic filter is able to successively work to capture corrosive gases and toxic heavy metals.

REFERENCE

- [1] Proc. of Trace Element Workshop 2000 in Yokohama, 1-45(2000)
- [2] Report of the Regional R&D Consortium of Chubu Bureau of Economy, Trade and Industry of METI, "High Temperature Flue Gas Control System with Getter Particles and Ceramic Filter" by Japan Ultra-high Temperature Materials, Research Institute Corp., 15S4023 (2004)
- [3] Moritomi, H., R. Yoshiie, K. Sonoda and T. Mori, Proc. of 5th Int. Conf. on Technologies and Combustion for a Clean Environment, 12-15 July, Lisbon, Portugal, 39-42(1999)
- [4] Sonoda, K., Trace element workshop 2000, Yokohama, Japan, 13-14 January, 105-110 (2000)
- [5] Sonoda, K., S. Yoshida, T. Tsuboi, H. Moritomi, R. Yoshiie and T. Tsuji, Proc. of the 5th SCEJ Symposium on Fluidization, 2-3 December, Tsukuba, Japan, 302-308(1999)
- [6] Iizuka, M., H. Moritomi and R. Yoshiie; *Kagaku Kogaku Ronbunshu*, 28(5), 575-580 (2002).
- [7] Numata, M., H. Moritomi, R. Yoshiie, M. Nishimura, *Proc. of Int. 6th Conf. on Eco-Material*, Yokohama, Japan, Oct. 8-10 (2003)
- [8] Uberoi, M. and F. Shadman; *Environmental and Science Technology*, 25, 1285-1289 (1991)
- [9] Uberoi, M. and F. Shadman; *AIChE Symposium Series*, 36(2), 307-309(1990)
- [10] Yang, H. C., J. S. Yun, M. J. Kang, J. H. Kim, and Y. Kang; *Korean, J. Chem. Eng.* 16(5), 646-653 (1999)
- [11] Wendt, J. O. L., S. B. Davis and T. K. Gale; *Aerosol Science and Technology*, 32, 142-151 (2000)

