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Technical report

Suppression of Hydrogen Gas Evolution from Cement-Solidified MSWI Fly Ash

Tsuneki Ichikawa[1*], Kazuo Yamada[2], Masahiro Osako[3] and Kazuko Haga[4]

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Abstract

Cement solidification/stabilization is an effective way of suppressing the leaching of hazardous materials from municipal solid waste incinerator (MSWI) fly ash, though the solidification of the fly ash from fluidized bed incinerators has been difficult because it causes the evolution of hydrogen gas by the reaction of contained metallic aluminum and alkaline water and results in the formation of porous and brittle solid. We found that the evolution of hydrogen gas is possible to be suppressed by improving the mixing method of the ingredients and controlling the amount of $CaCl_2$ in the mixture. Thorough mixing of the fly ash and cement powders with a drum-type mixer and subsequent addition of water at once scarcely induces the mechanical destruction of protective oxide layers surrounding metallic aluminum particles during the mixing process, so that the aluminum particles are protected from the attack of alkaline water. Water soluble $CaCl_2$ externally added and/or contained in the fly ash helps not only the homogeneous penetration of water into the powder mixtures but also reduces the alkalinity of water, so that it suppresses the evolution of hydrogen gas.

1. Introduction

Incineration is one of the most distinctive features of waste treatment in Japan. Of 43 million tons of municipal solid waste generated in 2014, about 80 % by mass (wt%) was incinerated (Ministry of Environment 2014). The incineration reduces the volume down to 5%, the weight down to 10%, and breaks down several hazardous substances. Solid residues from the municipal solid waste incinerator (MSWI) can be categorized as bottom ash and fly ash. Bottom ash residues are large particles removed from the bed of the incinerator whereas fly ash residues are fine particles entrained in the flue gas and captured by filters. The main components of MSWI fly ash are water-insoluble inorganic particles and water-soluble particles of alkali metal chlorides which are volatile at high temperature. MSWI fly ash also contains a significant amount of calcium hydroxide added for neutralizing the flue gas and calcium chloride that is generated by the reaction of the calcium hydroxide and hydrogen chloride in the flue gas. Although the amount of the fly ash is less than 24 wt% of the total ash, the fly ash is more hazardous than the bottom ash, because volatile hazardous substances such as lead and cadmium are concentrated in it (Lam 2010). Stabilization of hazardous heavy metals is therefore necessary for safe disposal of MSWI fly ash.

One of the simplest methods for the stabilization of MSWI fly ash is cement-based solidification. Solidification involves the mixing of MSWI fly ash, cement (usually Portland cement) and water to form a hard solid after hydration, thereby suppresses the leaching of the hazardous substances. The cement-based solidification is also effective for reducing the solubility of hazardous heavy metals, because many heavy metals form poorly water-soluble hydroxides under an alkaline condition. Although the cement-based solidification has been widely used for stabilizing MSWI fly ash, application of this treatment to MSWI fly ash containing metallic aluminum is difficult, because it causes the evolution of hydrogen gas by the reaction of aluminum and the alkaline solution in the mixture, as

$$2Al + 2OH^- + 6H_2O \rightarrow 2Al(OH)_4^- + 3H_2 \quad (1)$$

and results in the formation of porous and brittle solid (Husain and Krasznai 1994; Aubert *et al*. 2004). Evolution of hydrogen gas takes place not only during the solidification process but merely by absorbing water, since the absorbed water becomes an alkaline solution by dissolving $Ca(OH)_2$ that has been added for neutralizing the flue gas. Even explosive accidents have been reported so far at incineration facilities in Japan (Mizutani *et al*. 2000).

The content of metallic aluminum depends on the type of an incinerator. MSWI fly ash from the Stoker-type incinerator, the most popular incinerator in Japan, scarcely contains aluminum, whereas the fly ash from the fluidized bed incinerator, the second most popular incinerator, contains significant amount of me-

[1]Professor Emeritus of Physical Chemistry, Hokkaido University. *Corresponding author,
E-mail: tsuneki@eng.hokudai.ac.jp
[2]Senior Researcher, Center for Material Cycles and Waste Management Research, National Institute for Environmental Studies.
[3]Director, Center for Material Cycles and Waste Management Research, National Institute for Environmental Studies.
[4]Senior Researcher, Research Center, Taiheiyo Consultant, Co. Ltd.

Table 1 Contents of metallic aluminum, $Ca(OH)_2$, and water-soluble salts in MSWI fly ash.

Fly ash[a]	Metallic Al	$Ca(OH)_2$	$CaCl_2$	NaCl	KCl
F-1	1.4 wt%	24.0 wt%	5.8 wt%	4.0 wt%	2.7 wt%
F-2	1.1 wt%	23.7 wt%	6.2 wt%	3.9 wt%	3.8 wt%
F-3	1.3 wt%	22.0 wt%	5.7 wt%	3.0 wt%	4.5 wt%
S-1	0.0 wt%	32.1 wt%	16.1 wt%	3.6 wt%	8.8 wt%

[a] F and S denote fly ash from fluidized-bed and Stoker-type incinerators, respectively.

tallic aluminum (Sato 2015), because the fluidizing air carries away light aluminum particles from the combustion chamber. For safe disposal of fluidized-bed incinerator fly ash, it is necessary to find a cement solidification process in which the reaction of metallic aluminum with an alkaline solution is suppressed. Suzuki *et al.* proposed two successive processes for preventing the formation of brittle solid (Suzuki *et al.* 2009). They first solidified MSWI fly ash by adding ground granulated blast furnace slag, coal fly ash, NaOH and water. Since the concentration of NaOH was as high as 5 mol/dm^3, all the aluminum reacted with water to converted to stable $Al(OH)_4^-$. The solidified MSWI fly ash was crushed, and then solidified again with Portland cement. Although their method gave a rigid and stable product, the solidification process was complex; a significant amount of hydrogen gas was evolved in the first process, and the volume of the resultant solid was much larger than the original one. A new process of cement solidification without evolution of hydrogen gas has therefore been desired.

Solidification of MSWI fly ash with cement is generally achieved by mixing the fly ash and cement powders with a mixer, adding water slowly to the mixture while mixing, and mixing the ingredients thoroughly. We found that the evolution of hydrogen gas during the cement solidification process is possible to be suppressed by improving the mixing method and controlling the amount of $CaCl_2$ in the ingredients. The details of the process will be mentioned in the following section.

2. Experimental methods

Three kinds of MSWI fly ash from different fluidized-bed incinerators and one MSWI fly ash from a Stoker-type incinerator were used for cement solidification. The contents of water in these ashes were less than 2 wt%. The content of $Ca(OH)_2$ was determined by analyzing the X-ray diffraction pattern. For determining the content of metallic aluminum in MSWI fly ash, 10 g of the fly ash was added to 100 g of a 5 mol/dm^3 NaOH solution in a 250 cm^3 glass Erlenmeyer flask. Hydrogen gas evolved by Reaction (1) was collected in a 1 dm^3 gas sampling bag made of a laminated aluminum foil, and the volume of the gas was determined by measuring the weight of home-made separable volumetric flask in which the bag was immersed in water.

For determining the amount of water-soluble component in MSWI fly ash, 100 g of distilled water was mixed with 10 g of the fly ash for 1 hour and then filtrated through a 0.45μm membrane filter. The content of Cl^- ions in the filtrate was determined by Morh's titration. The content of Ca^{2+} ions was determined by EDTA titration. The contents of Ca^+, Na^+ and K^+ ions were determined with an inductively coupled plasma optical emission spectrometer. The weight of the residue of the filtrate after drying for overnight at 230 °C was in good accordance with the total weight of Cl^-, Ca^{2+}, Na^+ and K^+ in the filtrate, so that the dissolved species were mainly $CaCl_2$, NaCl and KCl. The concentration of Cl^- in the filtrate was also in good accordance with the total concentration of Na^+, K^+ and $2Ca^{2+}$.

The effect of $CaCl_2$ concentration on the pH of $Ca(OH)_2$-saturated $CaCl_2$ solution was measured with a TOA MH-7E pH meter.

MSWI fly ash was solidified by mixing the fly ash with ordinary Portland cement and distilled water or the aqueous solution of $CaCl_2$. Unless otherwise stated, the mass ratio of MSWI fly ash, cement and water was kept at 2 : 1 : 1.35, respectively. They were mixed with two methods. One was a traditional mixing method in which 50 g of the fly ash and cement in a pan was mixed with an electrical mixer for two minutes. Water was then continuously added for approximately two minutes while mixing vigorously. Four fifths of the resultant slurry was transferred into an Erlenmeyer flask for measuring the volume of hydrogen gas evolved. The amount of the fly ash in the flask was 40 g. The other was an improved mixing method in which 40 g of the fly ash and cement in an Erlenmeyer flask was thoroughly mixed by tumbling the flask for two minutes. Water or a $CaCl_2$ solution was then added at once without tumbling. The resultant homogeneous slurry was thoroughly mixed by gently tumbling the flask for approximately two minutes. Although $CaCl_2$ in MSWI fly ash is deliquescent (Ichikawa *et al.* 2017), clumping of the fly ash by the moisture absorption of $CaCl_2$ was not observed during the dry mixing processes.

3. Results and discussion

3.1 Hydrogen evolution by water addition

Table 1 shows the contents of metallic aluminum, $Ca(OH)_2$ and water-soluble components in MSWI fly ash. MSWI fly ash from the stoker-type incinerator contains no metallic aluminum, whereas the fly ashes from the fluidized-bed incinerators contain a significant amount of metallic aluminum. 1 kg of the fluidized-bed incinerator fly ash examined is possible to generate more than 13 dm^3 of hydrogen gas.

Table 2 Relation between the amount of water added (kg/kg dry ash), pH of the resultant fly ash slurry, and volume V (dm^3/kg dry ash) of evolved hydrogen gas.

Water		0.5	0.75	1	1.5	2
F-1	pH	11.56	11.73	11.82	12.0	12.2
	V	0	0	0.9	2.7	3.48
F-2	pH	11.46	11.65	11.8	11.93	12.03
	V	0	0	0	0	5.5
F-3	pH	11.48	11.7	11.86	11.98	12.05
	V	0	3.5	5.0	5.0	6.6

Table 2 shows the amount of hydrogen gas evolved from 40 g of the fluidized-bed fly ash by the addition of distilled water. No generation of gaseous product was observed for Stoker-type fly ash. The evolution of hydrogen gas was started within one day and was terminated within 8 days after the addition of water. Although the amount of hydrogen gas was different, the chemical composition of the fly ash and the pH of the slurry were not much different. The difference might arise from the tolerance of protective oxide layers on aluminum particles to the attack of alkaline solutions. The surface of metallic aluminum is generally covered with a protective oxide layer preventing the attack of water. Evolution of hydrogen gas therefore necessitate the dissolution of the protective oxide layer by reaction

$$Al_2O_3 + 2OH^- + 3H_2O \rightarrow 2Al(OH)_4^- \quad (2)$$

The dissolution rate generally increases with increasing pH of the solution. The pH and the amount of hydrogen gas increased with increasing the amount of water, which was due to the decrease of the concentration of $CaCl_2$ in water. Since the solubility of $CaCl_2$ is more than 40 wt% at ambient temperature, $CaCl_2$ was completely dissolved in the fly ash slurry. On the other hand, the solubility of $Ca(OH)_2$ is very low (0.17 wt% in pure water), so that the dissolved $CaCl_2$ suppresses the dissolution of $Ca(OH)_2$, as

$$Ca^{2+} + 2OH^- \rightarrow Ca(OH)_2 \quad (3)$$

The pH of the solution thereby increases with decreasing the concentration of $CaCl_2$ (**Fig. 1**), or with increasing the amount of water added.

3.2 Hydrogen evolution by cement solidification

Figure 2 compares the evolution of hydrogen gas after solidifying F-1 fly ash with the traditional and the improved mixing methods. Solidification of F-1 fly ash by the improved method did not show the evolution of hydrogen gas, whch suggests that the protective oxide layer was not damaged during the mixing process. As shown in **Table 2**, metallic aluminum in F-1 fly ash was tolerant to the attack of alkaline water up to 0.75 water/dry ash. Although the addition of cement might increase the alkalinity of the mixture, the above result indicates that the pH of cement-solidified fly ash was not much different from that of water-fly ash mixture. Solidification of F-2 fly ash with the improved mixing method did not induce the evolution of hydrogen gas, either.

As shown with open circles in **Fig. 2**, solidification of F-1 fly ash with the traditional mixing method caused the evolution of hydrogen gas, whch suggests that the protective oxide layer was damaged during the mixing process. The mixing process can be devided into three periods, dry mixing without water, semi-wet mixing with insufficient water and wet mixing with sufficient water for fluidizing the mixture. The protective oxide layer may not be significantly broken in the dry and the wet mixing processes, because the mixture contains enough amount of lubricants, air for the former and water for the latter, for reducing the friction between solid particles. Addition of a small amount of water to the dry mixture expells air, sticks the particles together, and makes the

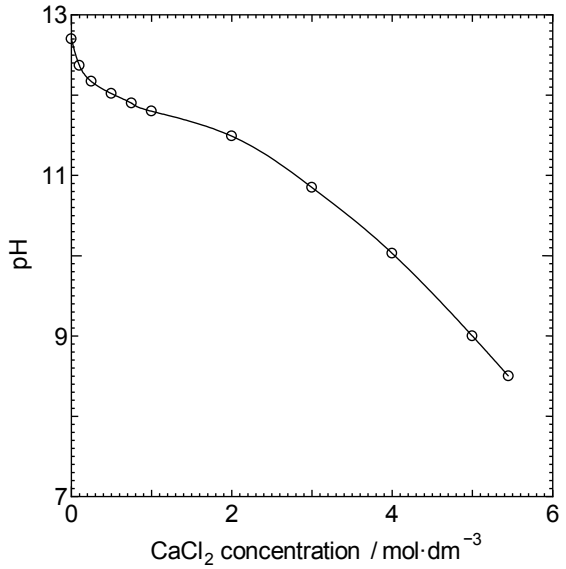


Fig. 1 Effect of $CaCl_2$ concentration on the pH of $Ca(OH)_2$-saturated $CaCl_2$ solution.

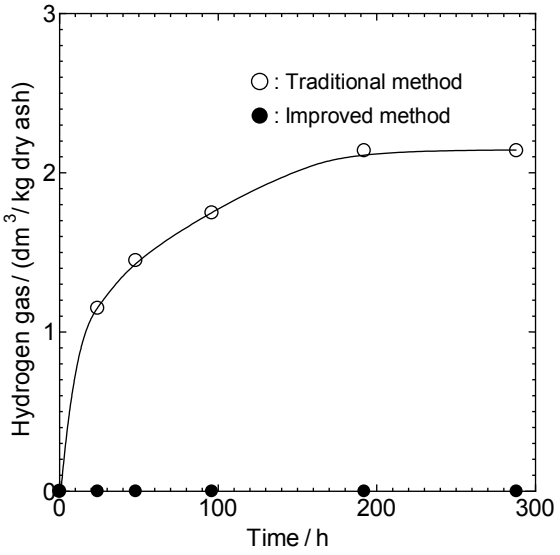


Fig. 2 Evolution of hydrogen gas from cement-solidified F-1 fly ash prepared by traditional and improved mixing methods.

mixture stiff. The protective oxide layer may therefore be broken during the semi-wet mixing. Although this mixing process is necessary for preventing the segregation of ingredients particles in ordinaly mortal and concrete, this is avoidable for the solidification of MSWI fly ash. After the dry mixing, insoluble fly ash particles and cement particles in the mixture are surrounded by highly water-soluble salts particles, so that water added at once is homogeneously penetrated into the mixture while dissolving the salts. The water-soluble salts helped the smooth penetration of water, because the addition of water at once to the mixture of cement and water-washed dry fly ash did not give homogeneous and fluid slurry even the amount of the water was doubled.

Figure 3 shows the evolution of hydrogen gas from cement-solidified F-3 fly ash prepared by using the improved mixing method. Addition of water to the mixture induced the evolution of a significant amount of hydrogen gas, so that the improved mixing method alone was not enough for preventing the evolution of hydrogen gas. However, addition of $CaCl_2$ solutions instead of distilled water suppressed the evolution of hydrogen gas. The concentration of the $CaCl_2$ solution for stopping the evolution of hydrogen gas was 6.9 wt%, which implies that the addition of 5 g of $CaCl_2$ to 100 g of dry F-3 fly ash completely suppressed the formation of hydrogen gas. Since MSWI fly ash from the Stoker-type incinerator contains a significant amount of $CaCl_2$ but not metallic aluminum, Stoker-type incinarator fly ash can be used as a $CaCl_2$ source for suppressing the evolution of hydrogen gas.

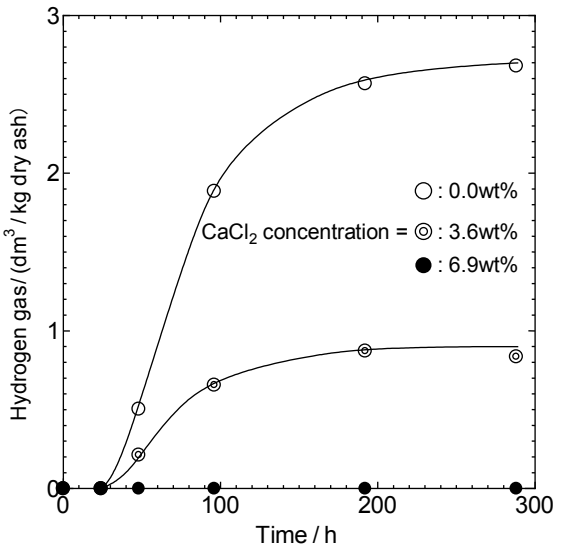


Fig. 3 Effect of $CaCl_2$ concentration on the evolution of hydrogen gas from cement-solidied F-3 fly ash prepared by improved mixing method.

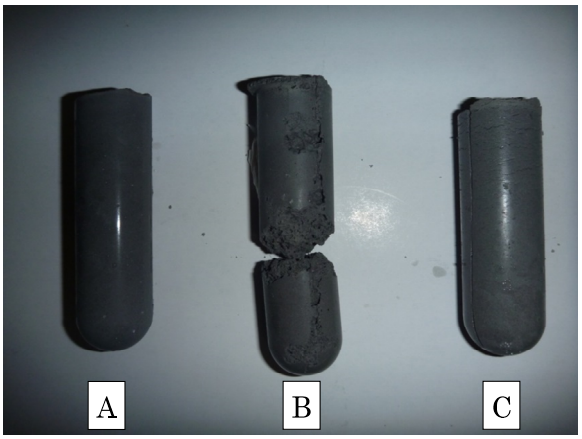


Fig. 4 Photo images of cement-solidified MSWIfly ash prepared from ordinaly Portland cement, water, and (A) F-1 fly ash by improved mixing method, (B) F-1 fly ash by ordinaly mixing method, and (C) F-3 fly ash by improved mixing method.

Figure 4 shows the appearance of cement-solidified MSWI fly ash after removing plastic mold tubes of 27 mm inner diameter and 90 mm height. Solidification of F-1 fly ash with the improved mixing method gave a robust solid, whereas the ordinary mixing method gave a porous solid which was broken during the removal. Solidification of F-3 fly ash with the improved method alone gave a solid with many cracks. Although the total amount of hydrogen gas evolved from the solidified F-3 fly ash was larger than that from F-1 fly ash that was solidified by using the traditional mixing method, since the evolution of hydrogen gas was suppressed for 18 hours after the mixing, the resultant solid was more robust than the latter one.

4. Conclusion

Cement solidification of MSWI fly ash containing metallic aluminum has been considered to be difficult, because it induces the evolution of explosive hydrogen gas and results in the formation of porous and brittle solids. We found that the evolution of hydrogen gas is possible to be suppressed by reducing the mechanical and chemical destructions of a protective oxide layer covering metallic aluminum. The mechanical damage is reduced by tumble-mixing the fly ash and cement powders, adding water at once and wait for a while, and then gently tumble-mixing the resultant fluid. The chemical damage, dissolution of the oxide layer, is reduced by reducing the pH of water which is attained by adding $CaCl_2$ to the mixture. Although the present study deals with a small amount of MSWI fly ash, the proposed cement solidification process can be scaled up by using a conventional drum-type mixer (Ferraris 2001). A commercially-available drum-type mixer can produce about 100 dm^3 of cement-solidified fly ash at once. It should be noted that mixing with a pan-type mixer while slowly adding water gives the worst result.

References

Aubert, J. E., Husson, B. and Vaquier, A., (2004). "Metallic aluminum in MSWI fly ash: quantification and influence on the properties of cement-based products." *Waste Management*, 24, 589-596.

Ferraris, C. F., (2001). "Concrete mixing methods and concrete mixers: State of the art." *J. Res. Natl. Inst. Stand. Technol*., 106, 391-399.

Husain, A. and Krasznai, J. P., (1994). "Compaction of radioactive incinerator ash: gas generation effects." *Waste Management*, 14, 521-530.

Ichikawa, T., Yamada, K. and Osako, M., (2017). "Estimation of the time of cesium leaking by moisture absorption of radiologically contaminated municipal solid waste incinerator fly ash." *J. Soc. Remed. Radioact. Contam. Environ*, 5, 177-190.

Lam, Ch. H. K., Ip, A. W. M., Barford, J. P. and McKay, G., (2010). "Use of incineration MSW ash: A review." *Sustainability*, 2, 1943-1968.

Ministry of Environment, Japanese Government, (2016). "Waste management in Japan, 2014." Available from: <http://www.env.go.jp/recycle/waste_tech/ippan/h26/index.html >.(in Japanese)

Mizutani, S., Sakai, S. and Takatsuki, H., (2000). "Investigation of hydrogen generation from municipal solid waste incineration fly ash." *J Mater Cycles Waste Manag*., 2, 16-23.

Sato, M., (2015). "Cement solidification of incineration ash - Effect of hydrogen gas evolution." Available from: <http://www-cycle.nies.go.jp/magazine/top/201502.html> (in Japanese)

Suzuki, K., Fujii, T., Ayano, T. and Ono, Y., (2009). "Solidification technology for incineration ash using cement materials." *Journal of the Japan Society of Material Cycles and Waste Management*, 20, 320-331. (in Japanese)