STABILIZATION OF LEAD IN LOW-LEVEL RADIOACTIVE WASTE FORM USING LOW-ALKALINITY CEMENTS

T. Sasaki, Y. Miyamoto, and M. Fukumoto
Japan Nuclear Cycle Development Institute
4-33, Muramatsu, Tokai-mura, Ibaraki 319-1194 Japan

ABSTRACT

Leaching behavior of lead from waste forms solidified using low-alkalinity cements was studied to reduce the leachability of lead from low level radioactive waste forms. The low-alkalinity cements used to solidify lead were calcium sulpho-aluminate cement blended silica fume and cement glass. Two kinds of leaching tests and an unconfined compressive strength test were conducted. This study shows that calcium sulpho-aluminate cement blended silica fume effectively decreases the leachability of lead from the cement-solidified waste forms.

INTRODUCTION

130 tons of lead is contained in the low-level radioactive wastes (LLRWs) stored in the Japan Nuclear Cycle Development Institute (JNC). Most of the lead is recyclable, but a part of it should be disposed of because of the difficulty of decontaminating radioactive nuclides. Although regulations on disposal of mixed wastes are not legislated at present in Japan, the Advisory Committee on Nuclear Fuel Cycle Backend Policy of the Atomic Energy Commission of Japan recommended in the report of May 28th, 1998 that disposal of the mixed wastes should meet the regulations on disposal of hazardous industrial wastes in landfills. In Japan, hazardous industrial wastes must pass the leaching test described in Waste Management and Public Cleansing Law before their disposal. Therefore, the LLRW forms including lead should also pass this leaching test. The regulatory level for lead is 0.3 mg/L. Lead in hazardous industrial wastes is generally converted to lead sulfide to reduce its solubility and is disposed of in landfills without solidification. It is difficult for cement-solidified LLRW forms to pass the leaching test, because ordinary Portland cement (OPC) is used to solidify LLRWs and its relatively high pH (12 - 13) increases the leachability of lead from the waste forms due to the formation of plumbite ion. In this study, low-alkalinity cements, calcium sulpho-aluminate cement blended silica fume (LAC-S) and cement glass (CG) were used to decrease the leachability of lead. Calcium sulpho-aluminate cement contains Hauyne ($3CaO \cdot 3Al_2O_3 \cdot CaSO_4$), Gypsum ($CaSO_4$), and Belite ($2CaO \cdot SiO_2$). Cement glass is a mixture of sodium silicate and cement. The pH of these cements is about 11. It is expected that the use of the low-alkalinity cements decreases the leachability of lead from the LLRW forms. In this investigation, leaching tests on crushed waste forms and monolithic waste forms containing lead powder or lead sulfide were conducted to evaluate the effects of the low-alkalinity cements on reducing the leachability of lead.

EXPERIMENTAL

Materials

Japan Industrial Standard (JIS) R 5210 ordinary Portland cement (Taiheiyo Cement Corporation), JIS R 5211 Type C Portland blast-furnace slag cement (Taiheiyo Cement Corporation), calcium sulpho-aluminate cement blended silica fume (LAC-S, Taiheiyo

Consultant), and cement glass (Taiheiyo Consultant) were used for solidifying lead powder and lead sulfide. Lead powder (Kanto Chemical) and lead sulfide (Mitsuwa Pure Chemicals) were used without further purification. Ion-exchanged water was used for the preparation of cement pastes and for the leaching tests.

Preparation of Cement-Solidified Lead Powder and Lead Sulfide

50 mm diameter x 100 mm length cylindrical cement-solidified samples containing lead powder or lead sulfide were prepared for this study. Cement was mixed with lead powder or lead sulfide, and then water was added in the mixture followed by stirring the cement paste in a Hobart mixer for 2.5 minutes. The water-cement ratios of the samples are listed in Table 1. The cement pastes were cast into 50 mm diameter x 100 mm plastic cylindrical molds. The cement pastes are sealed and then cured at 20 °C for 7 days (for unconfined compressive strength tests) or 28 days (for leaching tests and unconfined compressive strength tests).

Table I. Water-Cement Ratios for the Preparation of Cement-Solidified Samples

Cement	Content of Pb or PbS	Water-cement ratio
Ordinary Portland cement	20 wt% Pb powder	0.4
	20 wt% PbS	0.5
Portland blast-furnace slag cement	20 wt% Pb powder	0.4
	20 wt% PbS	0.5
Calcium sulpho-aluminate cement blended silica fume	5 - 20 wt% Pb powder	0.5
	20 wt% PbS	0.6
	30 - 40 wt% PbS	0.7
Cement glass	5 - 20 wt% Pb powder	0.35
	5 - 20 wt% PbS	0.45

Leaching Test for Disposal of Hazardous Industrial Wastes in Landfills

This leaching test was based on Notification No.13 of Ministry of the Environmental of 1973 described as follows. The samples were crushed and then sieved to a size between 0.5 mm and 5 mm. 25 g of the sieved particles were mixed with 250 mL of ion-exchanged water and then the mixtures were shaken for 6 hours. The leachates were filtrated through a 0.45 µm membrane filter. The pH of the leachates was measured using a pH meter. The concentration of lead in the leachates was measured by inductively coupled plasma-atomic emission spectroscopy.

Static Leaching Test

In this leaching test, long term leaching properties of Pb from monolithic solids were measured. A sample having a size of 50 mm diameter x 100 mm length was put in a polyethylene tank with 1.8 L of ion-exchanged water. After 1, 3, 7, 28, and 56 days, the lead concentration of the leachates was measured.

Unconfined Compressive Strength Test

The unconfined compressive strength of sample was determined using a hydraulic compression testing machine according to the JIS A1108. Samples having a size of 50 mm diameter x 100 mm length cured for 7 days and 28 days were used for the test.

RESULTS AND DISCUSSION

Leaching Test for Disposal of Hazardous Industrial Wastes in Landfills

Four kinds of cements, ordinary Portland cement (OPC), Portland blast-furnace slag cement (BC), calcium sulpho-aluminate cement blended silica fume (LAC-S), and cement glass(CG) were used to solidify Pb and PbS. The pHs of leachates were 12.4, 12.1, 11.1, and 10.8 for the PbS solidified with OPC, BC, LAC-S, and CG, respectively. The concentrations of Pb in the leachates are plotted as a function of the pH of the laechates in Figure 1. The use of low-alkalinity cements, LAC-S and CG, decreased the pH of the leachates and significantly decreases the Pb concentration in the leachates.

The only sample that passes the regulatory level of 0.3 mg/L is the LAC-S solidified sample containing 20 wt% PbS. Although PbS has a very low solubility (1.2 mg/L at 25 °C[1]), the leachability of Pb from the cement-solidified PbS increases with the pH of the leachates. This means that PbS is not stable at high pH and PbS changes to a soluble compound that should be plumbite.

In the case of solidified lead powder, the concentration of Pb in the leachates decreases with the pH of the leachates. The high concentration of Pb in the leachates at high pH is due to the formation of plumbite. When Pb was solidified using low-alkalinity cements, the Pb concentrations in the leachates are nearly same to the solubility of PbO (107 mg/L at 25 °C [2]). This is because the surface of lead powder was covered with lead oxide and the surface of lead powder in the crushed samples directly contacted with leaching fluid.

Comparing the LAC-S solidified PbS and the CG solidified PbS, the Pb concentration in the leachate of the LAC-S solidified one is much lower than that of the CG solidified one while LAC-S and CG have nearly same pH. This difference in the Pb concentration in the leachates seems to be due to the difference in the ability of LAC-S and CG to stabilize Pb. Figure 2 shows the concentrations of Pb in the leachates as a function of the content of Pb or PbS in the solidified samples. The concentration of Pb in the leachates from the CG solidified samples does not depend on the the content of Pb or PbS in the samples. The Pb concentrations of the leachates from the CG solidified Pb and PbS are nearly same to the solubilities of PbO and PbS respectively. This means that CG has little effect on stabilizing Pb. On the other hand, The Pb concentration in the leachates from the LAC-S solidified samples decreases with the content of Pb or PbS in the samples. This shows that LAC-S has abilities not only on lowering pH, but also stabilizing Pb in waste forms.

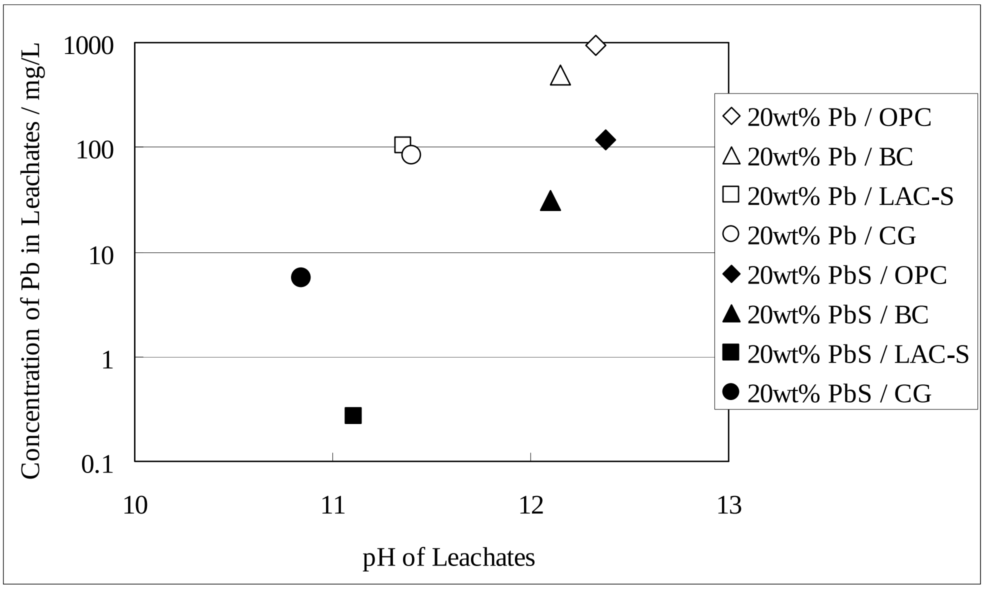

Fig. 1. Concentration of Pb in leachates as a function of pH of leachates

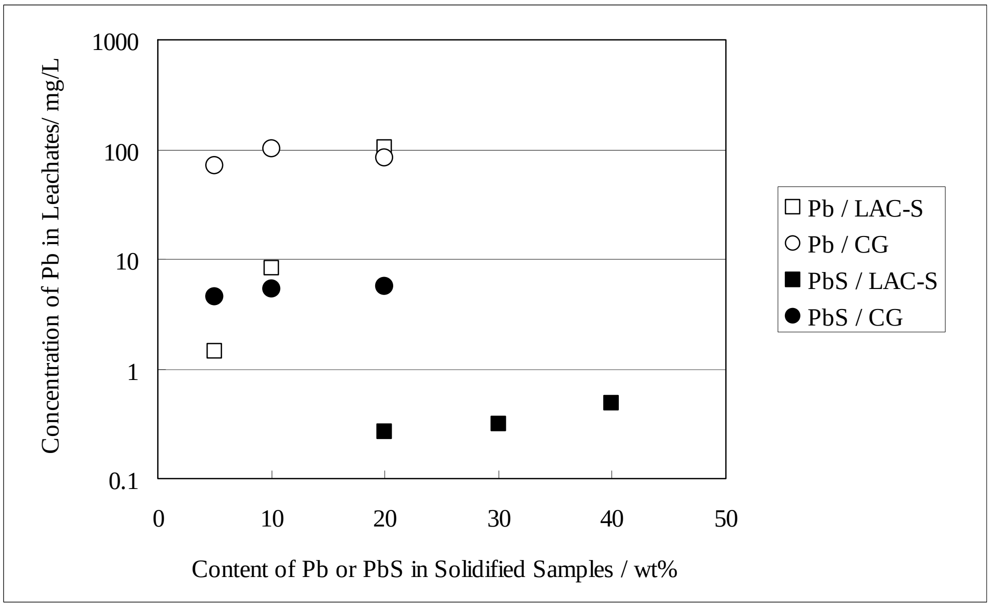

Fig. 2. Concentration of Pb in leachates as a function of content of Pb or PbS in solidified samples

Static Leaching Test

Figure 3 shows the concentrations of Pb in the leachates as a function of leaching time for the samples solidified with OPC, BC, LAC-S, and CG. Pb is easily leached out from the cement solidified samples except the LAC-S solidified samples. This is due to the porous structure of the cement-solidified samples and high content of Pb in the samples. LAC-S has a good performance keeping Pb in the solidified samples for 56 days at least. Further studies on the long term leaching behavior of the LAC-S solidified Pb are required.

The Pb concentration in the leachates from the LAC-S solidified PbS is higher than that from the LAC-S solidified Pb. This result is contrary to the fact that the solubility of PbS is much lower than that of PbO. A possible explanation is as follows. The LAC-S solidified PbS has higher water-cement ratio than the LAC-S solidified Pb for the same workability. Therefore, the LAC-S solidified PbS has a higher porosity than the LAC-S solidified Pb. The porosities of the LAC-S solidified samples containing 20 wt% of Pb and 20 wt% of PbS measured using a mercury porosimeter are 20.8 vol% and 35.1 vol% respectively. The high porosity of the LAC-S solidified PbS allows the leaching out of Pb from the solidified samples.

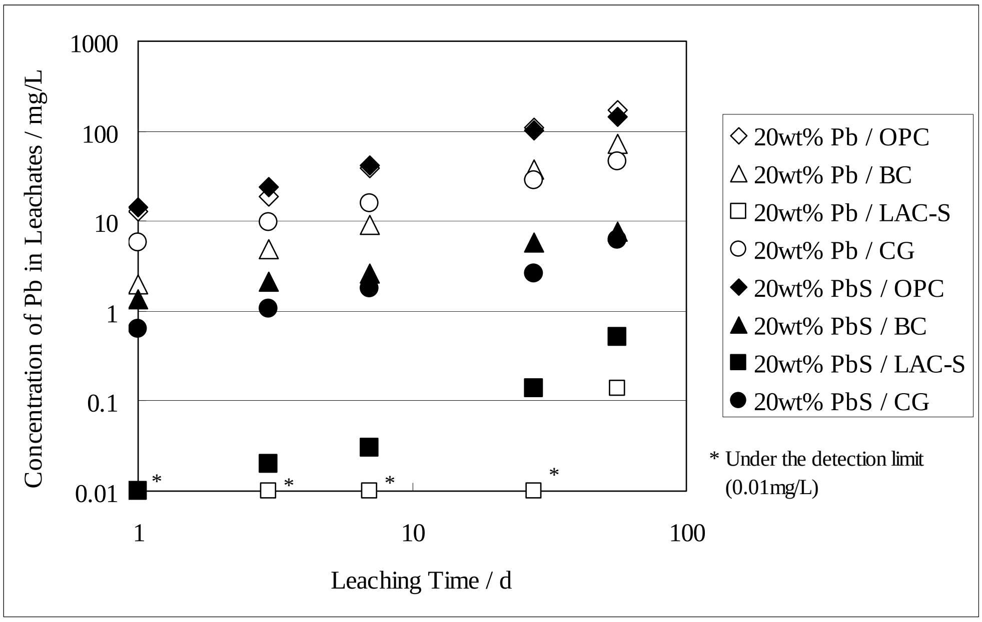

Fig. 3. Concentrations of Pb in leachates as a function of leaching time

Unconfined Compressive Strength Test

The unconfined compressive strengths of the cement solidified samples are listed in Table II. All unconfined compressive strengths of the samples cured for 28 days are sufficiently higher than the unconfined compressive strength in the acceptance criteria of Low Level Radioactive Waste Disposal Center in Rokkasho for homogeneously solidified low level radioactive waste forms (1.5 MPa). LAC-S has a comparable unconfined compressive strength to OPC. Comparing the solidified Pb samples and the solidified PbS samples, the solidified Pb samples have higher unconfined compressive strengths than those of solidified PbS samples. This is because the solidified Pb samples had lower water-cement ratios than the solidified PbS samples.

Table II. Unconfined compressive strengths of samples cured for 7 days and 28 days

Cement	Content of Pb or PbS	Unconfined compressive strength / MPa	
		Cured for 7 days	Cured for 28 days
OPC	20 wt% Pb powder	55.8	82.8
	20 wt% PbS	-*	41.6
BC	20 wt% Pb powder	40.2	73.0
	20 wt% PbS	-*	42.1
LAC-S	20 wt% Pb powder	43.6	61.6
	20 wt% PbS	22.6	36.0
CG	20 wt% Pb powder	15.4	15.8
	20 wt% PbS	8.3	8.1

* Samplewas too soft to measure the unconfined compressive strength.

CONCLUSION

Leaching tests on the cement solidified Pb and PbS were conducted. The low-alkalinity cement, calcium sulpho-aluminate cement blended silica fume (LAC-S), effectively decreases the leachability of lead from the solidified samples. The only sample that passed the regulations on the disposal of hazardous industrial wastes in landfills is the LAC-S solidified sample containing 20 wt% PbS. Static leaching tests shows that LAC-S has a good performance keeping Pb in the cement-solidified waste forms for 56 days at least.

ACKNOWLEDGEMENT

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