

REMOVAL OF URANIUM FROM SIMULATED FLY ASH BY CHLORIDE VOLATILISATION METHOD

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Abstract

Fly ash is generated from LWR nuclear power plant as a low-level waste, which is contaminated with a small amount of radioactive materials, composed mainly of uranium oxide. The constituents of the fly ash are similar to those of the ore; the major components of the ash are oxides of silicon, aluminum, sodium, magnesium, zinc, iron sodium and uranium. In this study, removal of uranium from the simulated fly ash, of which composition was U_3O_8 : 10, CaO:25, SiO_2 : 25, Al_2O_3 : 20, MgO: 10, ZnO:5, Fe_2O_3 : 3 and Na_2CO_3 : 2wt%, by chloride volatilisation method was examined. The simulated fly ash was chlorinated by the same manner as the dry way processing for the ore; namely, the ash was heated in a flow of chlorine in the presence of carbon at high temperatures. In the case of volatilisation of uranium from U_3O_8 and a simulated fly ash by chlorination using chlorine and carbon, it was seen that uranium of both samples showed similar volatilisation behaviour: The volatilisation ratio of uranium (V_U) increased with increasing temperature from 800 to 1100°C. The V_U value attained 99.9% at 1100°C. Iron, silicon and zinc showed similar behaviour to uranium, namely, they vaporised completely. The volatilisation ratio of aluminum, magnesium and sodium were still high in a range 80~90%. The volatilisation ratio of calcium was ~40% under the same chlorination condition, though it changed to chloride. For recovery of uranium from fly ash by chlorination using chlorine in the presence of carbon, high volatilisation ratio of uranium can be achieved at high temperatures. Volatilisation ratio of other components also increases, which decreases the amount of decontaminated residue resulting in the reducing of decontamination effect. Selection of heating condition is important.

Introduction

Since the commercial nuclear power plants are light water type reactors in Japan, UO_2 fuels are used in those plants. In the nuclear fuel cycle for LWR, many types of radioactive wastes are generated from the fuel treatment processes, such as conversion, enrichment, manufacturing and reprocessing. Fly ash is generated by the heat treatment of the low-level waste (LLW) contaminated with a small amount of radioactive materials (mainly uranium oxide). Such LLW's are planned to send to an isolated landfill site at present. If they are decontaminated, namely, the radioactive materials are separated then extracted from the wastes, the residual waste becomes non-radioactive. It could be treated as a general industrial waste. This would lead to reduce the amount of the radioactive waste and to extend the duration time for waste disposal. The fly ash is generated from LWR nuclear power plant as a low-level waste contaminated with a small amount of uranium oxide. The constituents of the fly ash are similar to those of the ore; the major components of the ash are oxides of silicon, aluminum, sodium, magnesium, zinc, iron sodium and uranium. If uranium is removed from the fly ash, it will be handled as a decontaminated waste as mentioned above. To this purpose, the dry chlorination process is supposed to be more hopeful than the wet processes since uranium easily forms chlorides on heating. [1,2] In this report, the removal of uranium from the simulated fly ash by chloride volatilisation method was studied. The effect of chlorination conditions, such as chlorination temperature, reaction time, carbon equivalent amount, oxygen addition, on the chloride volatilisation behaviour of chlorides were investigated.

Experimental

Materials used

The U_3O_8 powder was prepared by heating uranium tunings in air at 873 K for 4 h. The other chemicals of commercial grade, such as CaO , SiO_2 , Al_2O_3 , MgO , ZnO , Fe_2O_3 , Na_2CO_3 and activated carbon, were purchased from Wako Pure Chemicals Ind. and used after drying in the oven for one night. The simulated fly ash was prepared by mixing the above chemicals in a mortar for 30 min. The composition of the ash is given in Table 1. Nitrogen of 99.99% and chlorine of 99.9% gases were obtained from Nippon Sanso Co. Ltd. and Hashimoto Chemical Ind., respectively, and used as received.

Table 1. Composition of the simulated fly ash (wt%)

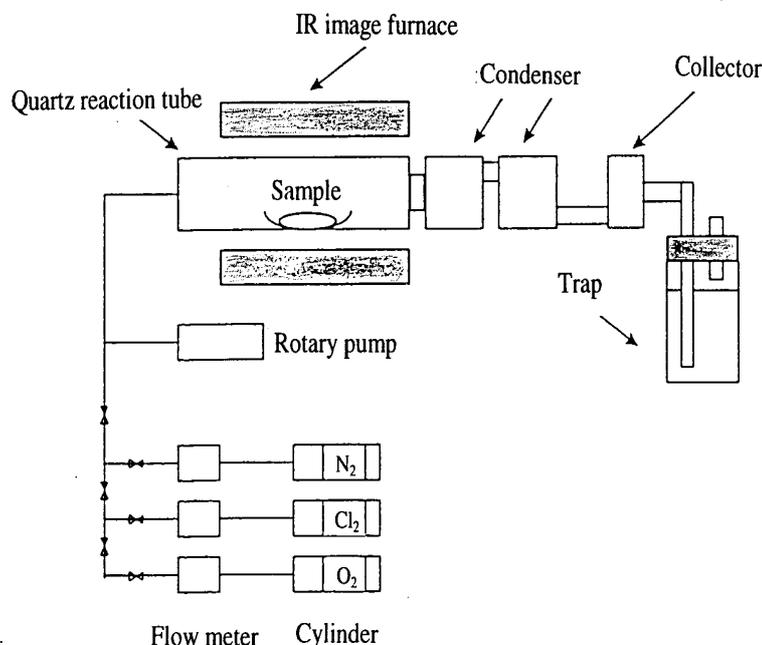
U_3O_8	CaO	SiO_2	Al_2O_3	MgO	ZnO	Fe_2O_3	Na_2CO_3
10	25	25	20	10	5	3	2

Chlorination experiment

The experimental apparatus is shown in Figure 1. A weighed mixture of the simulated fly ash (500mg) was placed on either quartz or graphite boat followed by setting the boat in a quartz reaction tube. The gas inlet tube was inserted to the bottom part of the boat. After the reaction system was evacuated, it was refilled by nitrogen gas to the ambient pressure. Subsequently, the reaction tube was heated by an IR Au-coated image furnace, ULVAC Type MR-H500, to an intended temperature. Then, the chlorine gas was introduced to the reaction part and flowed over the sample for an intended time. After the reaction, the power of the furnace was switched off. When the furnace was cooled down to room temperature, the flow of chlorine gas was ceased. The reaction temperature was changed from 800 to 1100°C. The reaction times were 0.17, 0.5 and 1 h. The flow of gases was

controlled by a float flow-meter (Kusano Type 1/16-160). The flow rates of chlorine were 100 and 200 ml/min. The flow rate of oxygen added to chlorine gas of 100 ml/min was 25 ml/min (11 vol% O₂).

Figure 1. Sketch of chlorinating apparatus



Analysis

After the chlorination experiments, the amounts of metal components in the residue and condensate were analysed by ICP spectroscopy using Hitachi Type AES-P5200 spectrometer. The volatilisation ratio (V) and decontamination factor (DF) were obtained by the equations, $V(\%) = 100(M_i + M_r) / M_r$ and $DF = U_i / U_r$, where M_i and M_r are the amounts of M (M=Si, Al, U, Fe, Na, Mg, Zn and Ca) in the initial sample and residue, respectively, and U_i and U_r are the weight concentrations of uranium for total amount of metals in the initial mixture and residue, respectively.

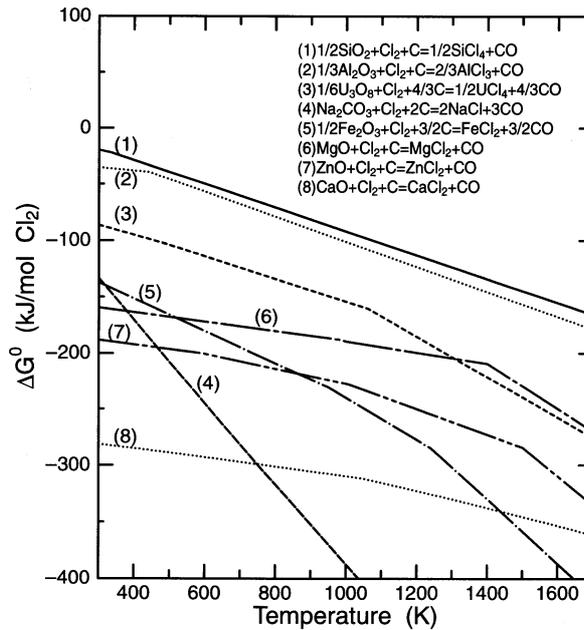
Thermodynamical considerations

When chlorine gas is used for the chlorination of the simulated fly ash containing uranium oxide, it is important to take into account the possible chlorination reactions by using the ΔG° values of the reactions. The formation of chlorides by the direct reaction between oxides and chlorine cannot be expected to take place easily since their ΔG° values is largely positive at temperatures from several hundred Kelvin to more than 1 000 K. Usually, the oxides are chlorinated by chlorine in the presence of carbon with the possible reactions shown in Figure 2 as the following equations per mole of chlorine gas arranged in the order of magnitude from the higher ΔG° value at 300 K: [3]



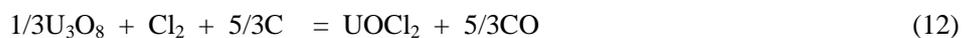
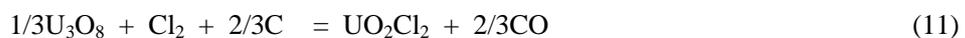
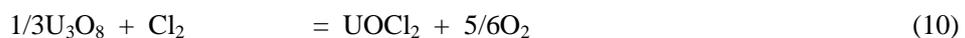
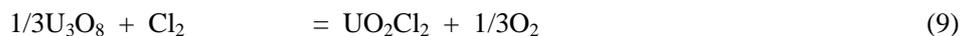


Figure 2. Free energy changes for chlorination reactions of metal oxides at elevated temperatures



The thermodynamic states of the formed chlorides are not written in the equations since they change in the temperature range from 300 to 1 500 K. The kinks in the figure show the transitions. Since all the ΔG° values are negative between 300 and 1 500 K, the above oxides are predicted to convert into the chlorides. It is seen that CaO is most easily chlorinated to CaCl₂ by heating with Cl₂ and carbon below 750 K, while the formation of NaCl becomes easier than that of CaCl₂ over 750 K from curves (4) and (8). The ΔG° value for silicon, aluminum and uranium (curves (1), (2), (3)) becomes higher in this order. The curves for iron (5), magnesium (6) and zinc (7) locate in the middle part of the figure. For uranium and iron, the lower chlorides UCl₄ and FeCl₂ are predicted to form prior to the higher chlorides, such as UCl₆ and FeCl₃, since ΔG° values for the formation of higher chlorides are higher than those for lower chlorides.

In the case of uranium, the formation of oxychlorides is also considered as given in the following equations. The reaction (9) will not occur because of its positive ΔG° values in the above temperature range, while the reaction (10) may occur below 500 K. In the presence of carbon (eqs.((11), (12))), both UO₂Cl₂ and UOCl₂ are predicted to form, however, they decompose to oxides and chlorides over 800 and 1 000 K, respectively.



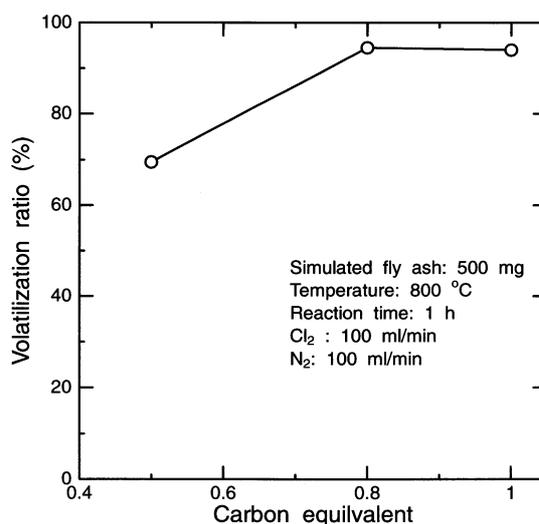
The vapour pressure data of the above metal chlorides [4-6] suggest the possibility of separation of the relatively volatile chlorides of SiCl_4 , AlCl_3 and FeCl_3 from relatively non-volatile chlorides of CaCl_2 , NaCl , MgCl_2 , ZnCl_2 , FeCl_2 and UCl_4 .

Results and discussion

Effect of equivalent carbon amount

In our previous paper, [3] on reaction of uranium ore with chlorine gas in the presence of activated carbon, the volatilisation ratio of uranium increased with increasing amount of carbon. The volatilisation ratios of uranium from the simulated ash are plotted against carbon equivalent in Figure 3. The carbon equivalent 1.0 corresponds to the equivalent carbon amount for the chlorination of the eight components of the simulated fly ash as given in eqs. (1)-(8). It is seen that the volatilisation ratio increases from 70 to 95% with increasing carbon equivalent from 0.5 to 0.8. This increase is considered to be associated with the reaction area of the ash and carbon. However, the volatilisation ratio above carbon equivalent 0.8 does not change.

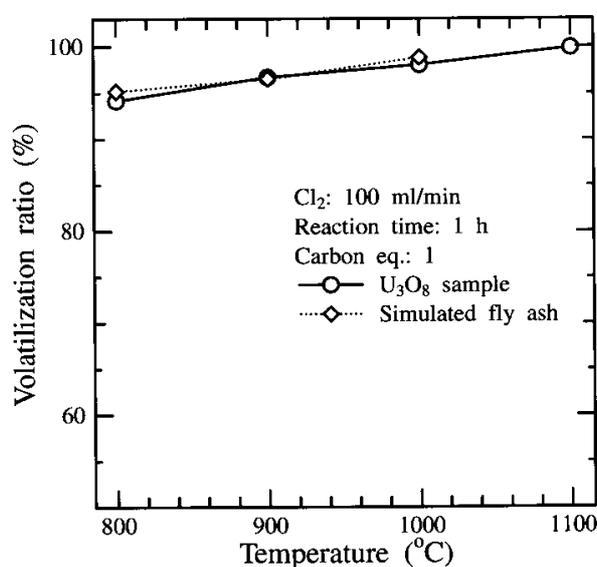
Figure 3. **Effect of carbon equivalent on the volatilisation ratio of uranium**



Effect of chlorination temperature

For the reaction of U_3O_8 and the simulated fly ash with chlorine with a carbon equivalent of 1.0 for 1 h, the measured volatilisation ratios of uranium (V_U) are plotted against reaction temperature in Figure 4. It is seen that the V_U value of U_3O_8 sample is close to 90% at 800°C and it increased with increasing temperature from 800 to 1100°C. At 1100°C, no U_3O_8 sample remained in the boat showing that the uranium was almost completely removed; the V_U value is 99.9%. In the case of the simulated fly ash, the volatilisation behaviour of the uranium in the ash was found to be the same as that of U_3O_8 . From the above result, it is considered that the volatilisation behaviour of uranium is not affected by the presence of other constituents. If the heating temperature is higher, uranium from the ash is removed more completely.

Figure 4. Effect of chlorination temperature on the volatilisation ratio of uranium



Effect of reaction time

Next, the effect of reaction time on the volatilisation of the simulated fly ash was examined. When U₃O₈ sample was reacted with chlorine at a flow rate of 100 ml/min at 1 000°C in the presence of equimolar carbon, the volatilisation ratio of uranium (V_U) increased with increasing reaction time. The ratio exceeding 99% were obtained within 0.5 h and the V_U value of 99.9% was obtained after the reaction time of 1 h. Figure 5 shows the change of the volatilisation ratio of the components of the simulated fly ash as a function of reaction time when the ash was heated with chlorine under the same condition. It is seen that uranium, iron and zinc vaporise completely even in 1 h. The volatilisation ratio of aluminum, magnesium and sodium are high and increased with increasing reaction time. On the other hand, the volatilisation of calcium was less than 50% at 1 h, it increased 64% at 3 h.

In our previous paper, [7] the addition of oxygen to the chlorine gas was found to be effective for suppressing the volatilisation of less-reactive components, such as silicon, aluminum and magnesium. The effect of oxygen addition to the chlorine gas on the volatilisation of uranium and total components was examined. The results are given in Table 2. It is seen that the volatilisation ratio of total components was decreased from 30.5 to 19.5% at 800°C. However, the V_U value also decreased from 94.0 to 71.5%. On the other hand, at 1 000°C, the V_{Total} value decreased from 52.5 to 28.5% by the addition of 11 vol% O₂ to the chlorine gas, while the V_U value only slightly decreased. From the standpoint of the complete removal of uranium, the addition of oxygen seems to be unfavourable but the amount of residue decreased under such condition. For increasing the amount of residue, the addition of oxygen would be effective.

Figure 5. Effect of reaction time on the volatilisation ratio of metal components

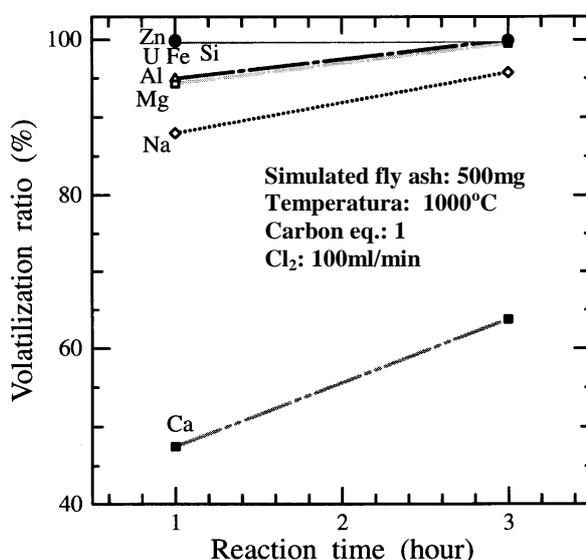


Table 2. Effect of oxygen addition to the chlorine gas on the volatilisation of uranium and total components

Temperature	800°C		1 000°C	
	V _U (%)	V _{Total} (%)	V _U (%)	V _{Total} (%)
O ₂ (vol%)				
0	94.0	30.0	97.2	52.5
11	71.5	19.5	95.5	28.5

Removal of uranium under various chlorination conditions

For the removal of uranium from the fly ash by chloride volatilisation method with a high efficiency, volatilisation of uranium from the simulated fly ash was examined under various chlorination conditions. The results are given in Table 3. In the table, V_U, C_U, R_U and DF are the volatilisation ratio, uranium concentration in total metal amounts of the residue, recovery ratio of uranium in the condenser and ratio of uranium weight concentrations of total metal in the simulated (10%) ash to that in the residue (C_U). From the table, both the volatilisation ratios (V_U) and recovery rates (R_U) are almost 100% suggesting that all the uranium in the simulated ash vaporised by the chlorination and solidified in the condenser. The DF values are seemed to be low at higher chlorination temperatures since the amount of residue is small by the higher vapour pressures of chlorides at higher temperatures. Similar behaviour was observed when the prolonged heating was applied (Runs 4 and 5). The highest DF value of 82 was obtained in the Run 2 case. In the case of carbon equivalent 2 (Runs 1 and 3), the amount of residue decreased resulting in decreasing the DF value. Though the flow rate of chlorine was changed, the same results were obtained. It is considered that the strong chlorinating condition is needed to vaporise the uranium completely, while the short time chlorination with low carbon equivalent seems to be effective for the increase of the amount of residue and DF value.

Table 3. Removal of uranium under various chlorination conditions

Run	Temperature (°C)	Time (h)	Cl ₂ flow rate (ml/min)	Carbon eq.	V _U (%)	C _U (%)	R _U (%)	DF
1	1 000	1	100	2	99.7	1.65	99.5	6
2	1 000	1	100	1	99.9	0.12	100.1	82
3	1 100	1	100	2	99.6	0.46	101.2	22
4	1 000	3	100	2	99.9	0.15	—	68
5	1 100	3	200	1	99.8	0.15	—	67

Conclusion

For the removal of uranium from the fly ash, which is generated from LWR nuclear power plant as a low level waste and contaminated with a small amount of radioactive materials, such as uranium oxide, chloride volatilisation method was applied to the fly ash. The simulated fly ash was chlorinated with chlorine in the presence of carbon at high temperatures. The volatilisation ratio of uranium (V_U) increased with increasing temperature from 800 to 1 100°C, and the V_U value of 99.9% was obtained when the chlorination temperature was higher than 1 000°C or when the reaction time was longer than 1 h. Iron, silicon and zinc also vaporised completely. The volatilisation ratios of aluminum, magnesium and sodium were high of 80~90%. On the other hand, the volatilisation ratio of calcium was ~40% under the same chlorination condition, though it changed to chloride. Furthermore, it was found that high volatilisation ratio of uranium can be achieved at high temperatures, while volatilisation ratio of other components also increase resulting in decrease of the amount of decontaminated residue lowering the decontamination effect.

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