Recent Development of Waste Treatment by Reactive Thermal Plasmas in Japan

Takayuki Watanabe

Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, Tokyo, Japan

Abstract

Attractive waste treatments by plasmas under atmospheric pressure have been proposed, because atmospheric pressure plasmas offer unique advantages. In this paper, the application for destruction of hazardous and waste materials, such as low-level radioactive waste, ion-exchange resin waste, and ozone-depleting substances, will be reviewed. Also selective separation mechanism by reactive thermal plasmas will be discussed for waste treatment.

1. Introduction

Attractive material processes by thermal plasmas have been proposed especially for waste treatments, because thermal plasmas offer unique advantages; these advantages include high enthalpy to enhance reaction kinetics, high chemical reactivity, oxidation and reduction atmospheres in accordance with required chemical reactions, and rapid quenching (10^6 K/s) to produce chemical non-equilibrium materials. However, thermal plasmas have been simply used as high temperature source. This indicates that thermal plasmas may have more capability for waste treatment, if thermal plasmas are utilized effectively as chemically reactive gas. In this paper, the application for destruction of hazardous and waste materials will be discussed. Melting and solidification of incineration ash by thermal plasmas will not be discussed in this paper, because these systems have been already commercially operated at several sites.

2. Low-Level Radioactive Waste Treatment

Low-level radioactive wastes (LLW) are generated from nuclear power plants and will be generated from decommissioning of nuclear power plants in future. In Japan, there are three facilities for volume reduction of LLW by thermal plasmas. Thermal plasma process offers attractive advantages for treatment of LLW because of high heat transfer rate from plasmas to wastes.

Two facilities of LLW treatment by thermal plasmas are being conducted at Tokai Research Establishment of Japan Atomic Energy Research Institute (JAERI). One is twin torch transferred arc system with the capacity of 4 tons/day, and another is induction thermal plasmas with induction melting furnace [1]. The melting furnace with induction thermal plasma torch is presented in Fig. 1. Three torches of induction plasmas (200 kW x 3) with an induction furnace up to 800 kW are used for melting and volume reduction for LLW. Capacity of LLW treatment is 4 tons/day. Compared with DC transferred and non-transferred arc, air and oxygen can be used as the plasma gas of induction thermal plasmas. Therefore, complete combustion of the waste can be achieved, resulting in stabilization of radionuclide.

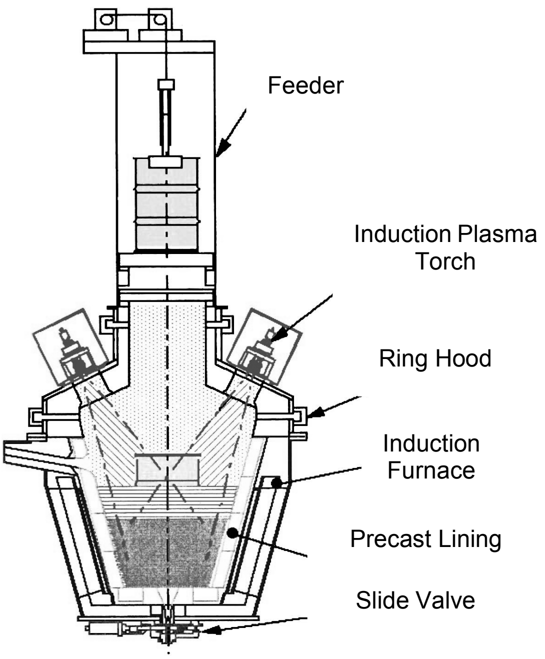

Fig. 1 Plasma – induction melting furnace [1].

The Japan Atomic Power Company (JAPC) has decided to construct LLW treatment facility by the Plasma Arc Centrifugal Treatment (PACT) system at the Tsuruga Power Station [2]. The PACT system with an 8 ft rotating hearth and 1.2 MW transferred arc torch was developed by Retech, Inc., USA. The treatment capacity for LLW is 600 kg/hr.

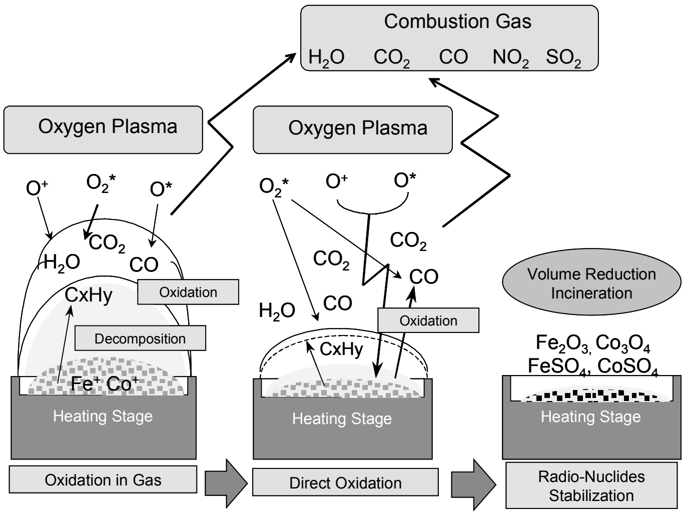

Fig. 2 Ion-exchange resin treatment mechanism by induction oxygen plasma generated at low pressure [4].

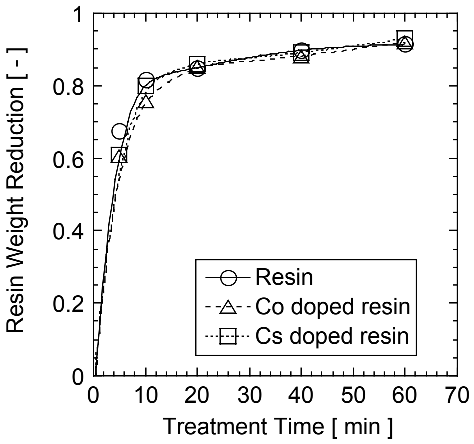

Fig. 3 Weight reduction of ion-exchange resin by thermal plasma treatment.

Radionuclide can be stabilized in the slag generated from the melted LLW by the thermal plasma treatment. Especially cesium entrapment in slag layer is important for LLW treatment. The effect of waste components on the vaporization behavior of Cs was investigated using simulated waste materials [3]. The vaporization rate of cesium increases with an increase in the slag basicities defined as (CaO+FeO+MgO) / (SiO_2+Al_2O_3). Entrapment of Cs into the slag can be enhanced by an increase in the content of Al_2O_3 or SiO_2 in the waste.

3. Treatment of Waste Ion-Exchange Resin

The amount of the waste ion-exchange resins adsorbing of radionuclide is increasing, therefore the effective method to reduce the volume of the waste is required. Fuji Electric Co. Ltd. developed volume reduction system for resin waste using low pressure plasma [4]. The concept of ion-exchange resin by an oxygen plasma is shown in Fig. 2. The process consists of two stages; the first stage is the low volume-reduction (1/4-1/5) by gas-phase plasma oxidation, and the second stage is the high volume-reduction (1/10-1/20) by direct oxidation on the ion-exchange resin. The reduction ratio achieved is 1/20 of the original volume at the treatment rate of 2 L/hr. The migration ratio of radionuclide in the exhaust gas generated in the process is below 10^{-6} under the pressure of 1-10 kPa..

The reactive thermal plasmas were also used to reduce the weight and volume of ion-exchange resins [5]. In the experiment, cation exchange resins (SKN-1) doped with Co and Cs were used as simulated waste resins. Oxygen or air used as reaction gas was injected in the downstream of the anode under atmospheric pressure. Figure 3 shows the weight reduction of waste resins by thermal plasma treatment. The weight was reduced to 80 % after 10 min treatment. After 40 min treatment, the weight was reduced to 95 %. Small difference in the weight reduction was found among the undoped resins and Co and Cs doped resins. XRD analysis indicates that Co in resins remains as CoO and Co_3O_4, while Cs in resins remains as Cs_2SO_4. Retention of Co after the treatment was approximately 100 %. Retention of Cs was approximately 100 % except for large flow rate of oxygen injection. Thermal plasma treatment provides the effective and rapid reduction in weight and volume of ion-exchange resins. The treatment has also good advantages for the stabilization of radionuclide.

4. Plasma Direct Melting Furnace

Waste treatment requires dioxin destruction, landfill-site life extension, material recycling and effective use of waste heat from high-temperature off-gas. A system of gasification of waste with ash melting should meet those requirements. A plasma direct melting furnace for waste gasification was developed by Hitachi Metals, Ltd [6]. Figure 4 shows the pilot-scale of 24 tons/day for municipal solid waste by thermal decomposition and melting using a vertical shaft furnace. This system meets environmental requirements for slag recycling and dioxin destruction. The advantage of this system is smooth and continuous extraction of melted waste with quick starting-up. In this system, crushing, drying and other waste pretreatment are not necessary. The melting section of the furnace maintains at 1,500-1,700°C through the injection of a flame from a plasma torch. The condition of the plasma torch can be controlled to respond the fluctuations in the waste quality, and the coke bed maintains a high temperature in the melting section, enabling stable operation.

The plasma torch consists of a closely spaced pair of tubular water-cooled electrodes. The generated arc discharge is magnetically rotated at extremely high speeds. During operation, a process gas is injected into the heater through a space between the electrodes.

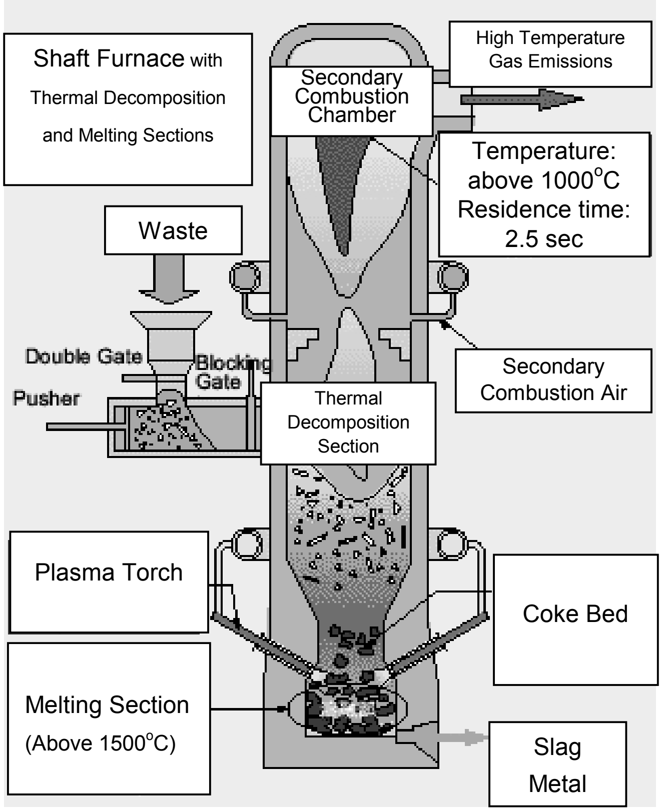

Fig. 4 Schematic diagram of plasma direct melting furnace for waste gasification [6].

5. Selective Separation by Reactive Plasmas for Waste Treatment

Plasma enhanced vaporization is well-known method for production of ultrafine particles of metal. The plasma-enhanced vaporization can be applied to the selective separation for waste treatment. Hydrogen in arc plasmas enhances the vaporization of particular metals on the anode. In Si-Ti system, the vaporization rate of Ti is enhanced selectively by hydrogen in the arc [7]. An increase in H_2 concentration in the arc leads to an increase in Ti fraction in the prepared particles.

The dissociated hydrogen in arc plasmas enables the dissolution of a large amount of hydrogen into molten metals as well as the generation of metal vapor from the molten metals. The vaporization enhancement is attributed to the following four factors; recombination of hydrogen atoms in molten metals; high thermal conductivity of hydrogen; formation of intermediate products such as hydride; activity modification by hydrogen in molten metals. The first and second factors have small effect on the vaporization enhancement, therefore the third and/or fourth factors were considered to be the main factors. However hydride produced from molten metals with hydrogen arcs has not been identified yet. Instability and unknown properties of hydride give rise to difficulty in the quantitative examination.

Investigation of reaction mechanism of molten metals with chlorine or fluorine in arc plasmas would lead to the alternative solution, because chloride and fluoride are more stable and their properties have been known compared with hydride. Arc plasma reactions with chlorine was investigated for the separation of particular elements from alloys since chlorine atoms react with particular elements to form chlorides that have high vapor pressures and are especially separated from alloys [8,9]. The components of the fumes produced by changing O_2 flow rate are shown in Fig. 5. The component using Ar plasmas is almost identical to the initial KOVAR alloy (Fe=53, Co=17, Ni=29 mass %). The concentration of Fe in the fumes is highest by Ar-Cl_2 and Ar-Cl_2-O_2 (0.25 NL/min) plasma treatments. The concentration of

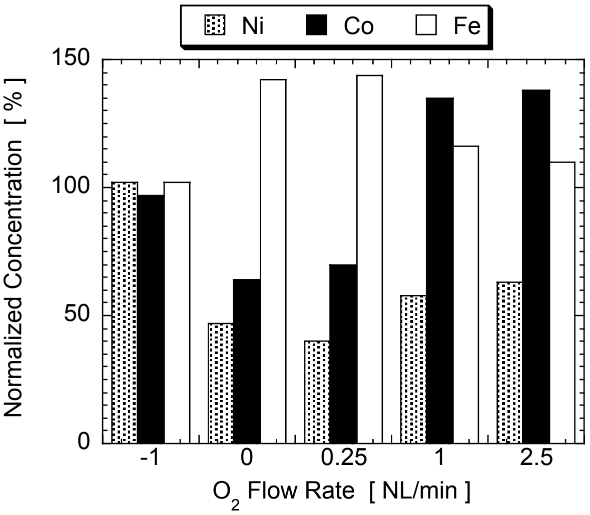

Fig. 5 Selective separation of particular elements from alloy by chlorine thermal plasma with oxygen addition.

Co increases with O_2 flow rate of the plasma gases, while the concentration of Ni using Ar-Cl_2 and Ar-Cl_2-O_2 plasmas is low since Ni compounds are difficult to vaporize. The reaction mechanism using these plasmas with Cl_2 and O_2 can be correlated to Gibbs free energy changes of chlorination and oxidation.

6. Plasma Decontamination

The highly effective decontamination process is required for the treatment of material generated from a decommissioned nuclear reactor as well as from the nuclear reprocessing plant and nuclear waste processing plant. Many wet processes for the decontamination have been proposed, but the wet process has the drawbacks due to the large volume production of secondary waste such as the contaminated solvent and ion-exchange resin. Therefore the plasma methods were proposed owing to the small secondary waste production. The decontamination researches have been carried out under the low pressure plasma conditions, however the low pressure condition is not favorable considering the practical application.

Decontamination process by microwave plasma under atmospheric pressure was developed for the removal of deposition of radionuclide on the surface of stainless steel [10]. The decontamination reaction is based on the formation of volatile compound such as fluoride produced by CF_4/O_2 plasma. Using the stainless steel sample prepared in water in autoclave simulated BWR condition, the surface oxide film was removed by irradiation of CF_4/O_2 plasma, resulting from the fluorination of the oxide.

7. Fly Ash Detoxification

Incineration of municipal waste generates incineration ash and fly ash. Induction thermal plasma system for fly ash treatment was proposed to recover the useful metals and materials from fly ash generating from melting furnace [11,12]. Fly ash fed into the induction thermal plasma was completely vaporized and decomposed during thermal plasma process.

After thermal plasma treatment of fly ash, the components were recovered separately owing to the difference of each condensation temperature. The H_2 injection into the induction thermal plasma strongly influences the difference of each condensation temperature, especially Zn compounds. The atomic fractions of the heavy metals of Zn and Pb included in the recovered materials increase under 800°C with Ar-H_2 plasma treatment, as shown in Fig. 6. More amounts of heavy metals than initial fly ash are included in the materials recovered at lower temperature. On the other hand, the materials recovered at higher temperature are detoxified because they contain extremely less heavy metal components than in initial fly ash.

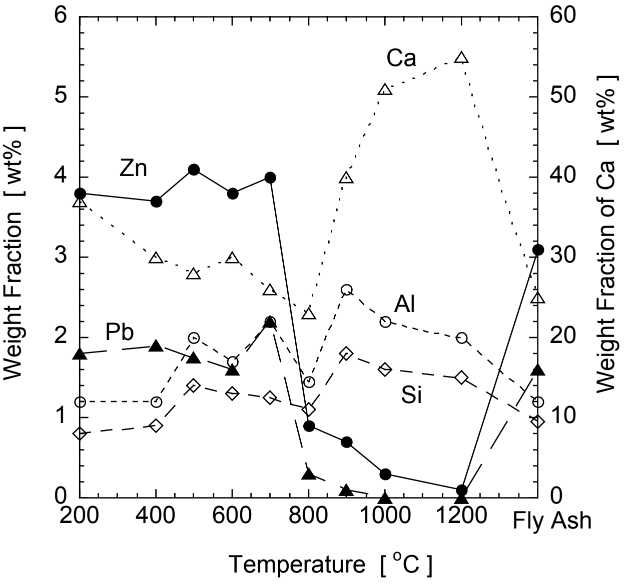

Fig. 6 Recovered materials with changing of the temperature after induction Ar-H_2 plasma treatment.

8. CFC and Halon Destruction

The destruction of ozone-depleting substances (ODS) such as chlorofluorocarbons (CFCs) and halons was developed by using steam thermal plasmas. The use of steam as oxidizing gas has the advantage for the destruction of CFCs and halons. Steam plasmas are successfully utilized to decompose ODS. In Japan, there are two commercial facilities for ODS decomposition by induction thermal plasmas with 100%-steam. The total system for ODS decomposition is shown in Fig. 7. In the first facility, a 200 kW plant under reduced pressure is operated by the Clean Japan Center [13]. ODS fed into a 100%-steam plasma are completely decomposed and converted to CO_2 and hydrogen halides. The feeding rate for CFC-12 and halon 1301 is more than 50 kg/hr under the pressure at 26 kPa. The second facility in Japan, ODS has been decomposed by atmospheric pressure induction plasmas. The second system has important technology for waste treatment;

generation of 100%-steam plasma under atmospheric pressure at 70-90 kW with the steam feeding rate at 14-20 kg/hr. The treatment capacity for CFCs is 30-40 kg/hr.

The small commercial facilities for CFCs decomposition were developed by Mitsubishi Heavy Industries [14]. The CFCs are decomposed by a 100%-stream microwave plasma. In the plasma, The CFCs are injected into the plasma at the concentration of 23-33 vol% under atmospheric pressure. The treatment capacity is 2 kg/hr at the power of 1.8 kW for CFC-12, 1.4 kg/hr at 2.0 kW for HCFC22, 1.5 kg/hr at 2.0 kW for HFC134a. Besides, the destruction of ODS by DC plasmas have been already operated at several sites in Japan. An Ar plasma jet is generated with the injection of oxidizing gas such as steam and oxygen to suppress the formation of soot [15,16]

Treatment of exhaust gas after the decomposition of CFCs and halons is the major concern, because the exhaust gas contains toxic and corrosive gas such as fluorine, chlorine, bromine, fluorohydride, chlorohydride and bromohydryde. In the above-mentioned process, hydrogen halides are quenched and neutralized in a scrubber to convert into calcium halides. Recently, dry process to recover these corrosive gases was developed [17]. Solid alkaline carbonate and hydrate made from dolomite were used as the reactant to adsorb these gases. This dry process of hydrogen halides into calcium halides would be applied to ordinary exhaust gas treatment for combustion.

9. Medical Waste Treatment

Medical waste treatment system for volume reduction and detoxification was developed by several companies in Japan. Figure 8 shows the schematic diagram of the medical waste treatment system by non-transferred arc developed by Chubu Electric Power Co. Inc [18]. This system can treat medical wastes containing a large volume of polyvinyl chlorides, which may cause production of dioxins. This system heats waste without oxygen until the waste breaks down. Then thermal plasma (50 kW) is applied to remaining injection needles, bottles, and other unburned substances to melt and solidify them into stable slag. The volume reduction ratio is 1/250 for treatment capacity of 100 kg/day. The field test has been conducted at Nagoya Daini Red Cross Hospital for a year to check the operability, durability, economy, and other properties of the product.

Another field test of medical waste treatment was conducted at The University of Tokyo Hospital by Koike Sanso Kogyo Co. Ltd. Twin Torch system, which uses two electrodes of opposite polarity connected in series to form a single circuit, was adopted in this system.

10. Conclusions

Thermal plasmas have been simply used as high temperature source. If thermal plasmas are utilized effectively as chemically reactive gas, thermal plasmas would provide more capability for waste treatments. The advantages of thermal plasmas, such as high enthalpy to enhance reaction kinetics, high chemical reactivity, oxidation and reduction atmospheres in accordance with required chemical reactions, and rapid quenching rate, should be utilized effectively for waste treatment. The researches about the reaction mechanism in the plasmas as well as sophisticated numerical analysis of reactive plasmas are important for the development of attractive waste treatment.

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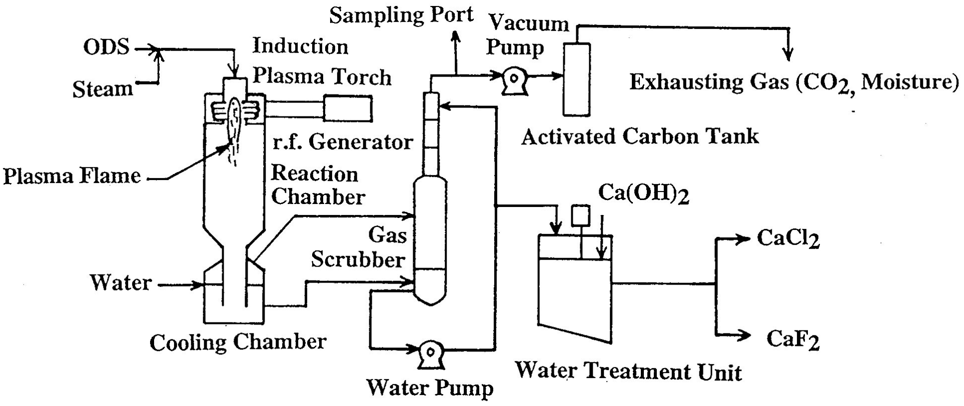

Fig. 7 The total system for ODS decomposition by induction steam plasma [13].

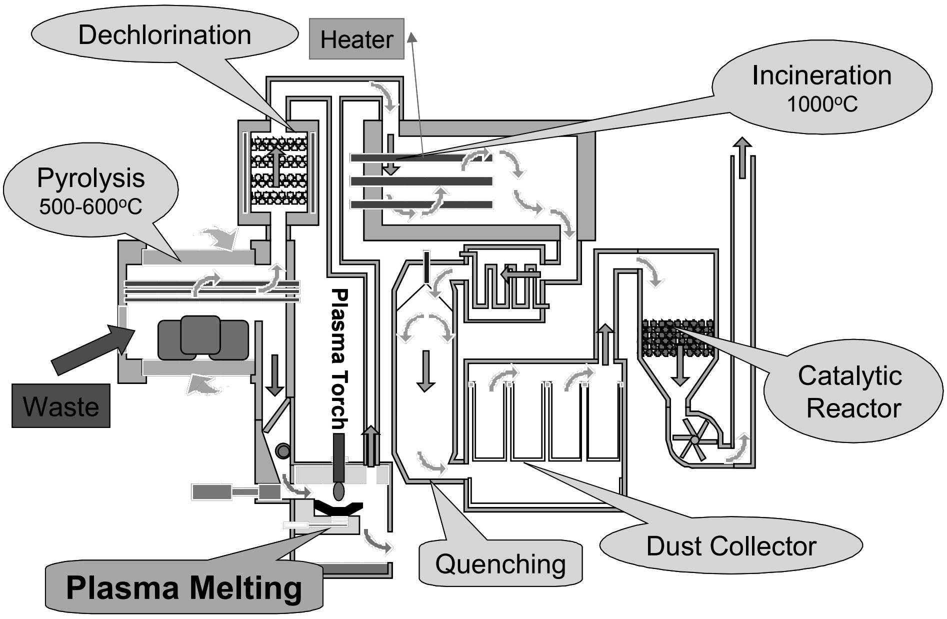

Fig. 8 Medical waste treatment system for volume reduction and detoxification [19].