Plasma-Arc Technology for the Thermal Treatment of Chemical Wastes

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Abstract

Plasma-arc technology was developed to dispose of chemical wastes from a chemical plant by the Institute of Mechanics, Chinese Academy of Sciences (CAS-IMECH). A pilot plant system with this technology was constructed to destroy two types of chemical wastes. The system included shredding, mixing, and feeding subsystems, a plasma-arc reactor of 150 kW, an off-gas burning subsystem, and a scrubbing subsystem. The additives (CaO, SiO₂, and Fe) were added into the reactor to form vitrified slag and capture the hazardous elements. The molten slag was quickly quenched to form an amorphous glassy structure. A direct current (DC) experimental facility of 30 kW with plasma-arc technology was also set up to study the pyrolysis process in the laboratory, and the experimental results showed the cooling speed is the most important factor for good vitrified structure of the slag. According to previous tests, the destruction and removal efficiency (DRE) for these chemical wastes was more than 99.999%, and the polychlorinated biphenyls (PCBs) concentration in the solid residues was in the range of 1.28 to 12.9 mg/kg, which is far below the Chinese national emission limit for the hazardous wastes. A simplified electromagneto model for numerical simulation was developed to predict the temperature and velocity fields. This model can make satisfactory maximum temperature and velocity distributions in the arc region, as well as the results by the magneto hydrodynamic approach.

Key words: plasma arc; pyrolysis; chemical waste; vitrified slag; numerical simulation

Introduction

PUBLIC HEALTH AND ENVIRONMENT POLLUTION have become a strong concern in China, especially after the 2003 Severe Acute Respiratory Syndrome (SARS) epidemic (Sheng *et al.*, 2004, 2005). It is tremendously important to dispose of the hazardous waste with high efficiency and no secondary pollution. Plasma pyrolysis with vitrification (PP/V) technology has many advantages for the efficient destruction of hazardous wastes; great DRE for the hazardous waste treatment, highly stabilized glass-like residue, smaller reactor and auxiliary equipment, lower capital cost, fast startup and shutdown, and competitive processing cost for the mixed hazardous wastes (Pfender, 1999; Kim *et al.*, 2003). Because of these potential advantages, PP/V technology has been developed for the destruction and removal of various hazardous waste, such as PCBs (Kim *et al.*, 2003), medical waste (Nema and Ganeshprasad, 2002), metallurgical wastes, incineration fly ash (Katou *et al.*, 2001; Cheng *et al.*, 2002), and low-level radioactive wastes. The results show that the PP/V technology is a state-of-the-art technology for the destruction of hazardous waste.

CAS-IMECH developed a three-phase alternating current (AC) plasma-arc furnace for metallurgy in the 1980s, and then used the equipment to dispose of hazardous wastes in the 1990s (Sheng *et al.*, 2004, 2005). Many trials have been carried out for the treatment of organic wastes, including hospital wastes, dead animal bodies, waste polymers (plastics and rubber), waste oil, pulp mill slurry, waste scoria, and hazardous waste with high arsenic and sulfur concentrations. The furnace-feed waste stream can be solids, liquids, gases, or slurries, and all types of wastes can be treated. The volumetric reduction after treatment is up to 99% for organic wastes (Sheng *et al.*, 2004, 2005).

A 150-kW DC pilot system with the modified plasma-arc reactor has been constructed in a chemical plant of ZCRICI, which is located in Zigong City in Sichuan Province of western China, to destroy two types of chemical wastes from the production process in the plant. Furthermore, a 30-kW DC plasma-arc reactor has been also built up in the laboratory to study the mechanism of the formation of vitrified slag and optimize the operating parameters for waste destruction processes.

Three different mixtures of chemical wastes and additives have been destroyed by the 150-kW reactor and the 30-kW reactor. The thermodynamic equilibrium product distribution of initial reactants is calculated by CHEMKIN-III EQUIL subroutine, and the numerical simulation is made to predict

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FIG. 1. Picture of plasma reactor of 150-kW DC pilot system in ZCRICI.

the temperature and velocity fields. A simplified electromagnetic model is also developed to simulate the temperature and flow fields of the plasma-arc reactor, including the arc region and the plasma reaction region.

Materials and Methods

Experimental facilities

Figures 1 and 2 show the reactor of the 150-kW DC pilot system in ZCRICI and the 30-kW reactor in the laboratory, respectively. The 150-kW DC plasma reactor is based on a 150-kW three-phase AC plasma reactor developed in our laboratory in the 1990s, and a rectifier was employed to get stable arc characteristic. Figure 3 shows the schematic description of the pilot pyrolysis system. The 150-kW DC system includes shredding, mixing, and feeding subsystems, a plasma-arc reactor system, an off-gas burning subsystem, an acid-gas recovery subsystem and a scrubbing subsystem. The plasma-arc reactor system is composed of seven subsystems: a power supply, an argon gas supply system, a plasma generator and a reactor, a residue discharging system, a cooling subsystem,

FIG. 2. Picture of the 30-kW plasma reactor in the lab.

and a special transformer and control system. The 30-kW system is simpler than the 150-kW one, but the plasma-arc system is complete.

Experimental materials

The two types of solid chemical wastes from chemical production lines of Second Chemical Plant of ZCRICI are marked with CW-1 and CW-2, of which compositions are shown in Table 1. The elemental analysis of unknown organics (including PCBs) of CW-2 shows that it contains carbon (62.84 wt.%), hydrogen (4.28 wt.%), chloride (32.78 wt.%), and sulphur less than 0.1 wt.%.

To form the vitrified slag, some additives, such as CaO, SiO₂, Fe, etc., are added into the reactor. Table 2 shows three different mixtures of wastes and additives that have been treated in this study.

The mixture 1 and the mixture 2 are destroyed by the three-phase AC plasma reactor in the laboratory. The experiment lasts 260 with 60 kW power for mixture 1 and 330 for mixture 2. Mixture 3 is pyrolyzed and vitrified by the 30-kW DC

FIG. 3. Schematic description of the pilot plasma pyrolysis system.

TABLE 1. MAJOR CHEMICAL COMPOSITION OF WASTES

<i>Chemical wastes</i>	<i>Composition</i>	<i>Wt. %</i>
CW-1	Biphenyl	80–85
	PCBs	10–15
CW-2	Silicon powder	~ 60
	Copper powder	~ 2
	Carbon compounds	25–30
	Unknown organics (including PCBs)	~ 10

CW-1, the first kind of chemical waste; CW-2, the second kind of chemical waste; PCBs, polychlorinated biphenyls.

plasma reactor. The average temperature in the reaction space is controlled at 1,670–1,870 K. During the plasma process, hazardous organic wastes are rapidly pyrolyzed and additives are heated up to molten status to capture the hazardous elements, then the molten slag is quickly quenched to form an amorphous glassy structure.

Experimental Results and Discussions

The gas chromatography-mass spectrometer is used to analyze the off-gases and the residues, and PCBs are the target compounds. The analytical methods used for PCBs in this paper are followed as written in the U.S. EPA SW-846 methods (U.S. EPA, 1997). The detection limit for PCBs is 0.5 ppb for the off-gas and 0.2 ng/kg for the residue. The off-gases of mixture 1 and mixture 2 were sampled by the Chinese National Research Center for Environmental Analysis and Measurements, and PCBs are not detected in the samples. The solid residue content of mixture 1 and mixture 2 are also detected and the analytical results of solid waste residue samples are provided in Table 3. DRE of chemical waste is more than 99.999%. The solid residues contain PCBs in the range of 1.28 mg/kg to 12.9 mg/kg (Table 3), which is far below the Chinese national emission limit value for hazardous wastes.

The waste mixture is heated up to molten state during the PP/V process. The heating process is long enough to ensure that the mixture reacts with each other completely, after which the molten slag is quickly quenched to form an amorphous glassy structure. It has been found that quenching rate is the main parameter for the formation of good vitrified slag because a fast quenching rate can prevent the molten slag from forming a crystal phase. The slag of mixture 2, shown in Fig. 4, is composed of many small chips, which reveals that

TABLE 3. SOLID RESIDUE CONTENT OF MIXTURE 1 AND MIXTURE 2

<i>Content</i>	<i>Residue of mixture 1 (mg/kg)</i>	<i>Residue of mixture 2 (mg/kg)</i>	<i>Detection limit (ng/kg)</i>
Chlorobiphenyl	1.26	12.8	0.2
Dichlorobiphenyl	0.0217	0.122	0.2
Trichlorobiphenyl	ND	0.0131	0.2
Total PCBs	1.28	12.9	0.2

ND, not detected.

the additives with inappropriate proportion fail to form a vitrified slag. The slag of mixture 3, shown in Fig. 5, is covered by soot, which is produced through pyrolysis reaction of chemical wastes.

Because of the high temperature generated by the plasma arc, it can be assumed that the pyrolysis reaction during the PP/V process gets to chemical reaction equilibrium very rapidly. According to the principal of Gibbs free energy minimum, when a system reaches an equilibrium state at constant pressure, the total Gibbs free energy of all the equilibrium substances is minimized (Zainal *et al.*, 2001; Xie, 2002; Mountouris *et al.*, 2006). For a system that element components are given, all the products (especially the main ones) that are formed by these given elements are chosen. For CW-1, elements used in the calculation are C, H, and Cl, and the amounts of them are inputted according to the data of Table 1. The 135 products are chosen in the calculation, including Carbon (solid state and gas state), H, H₂, CH₄, C₂H₂, C₂H₄, C₂H₆, C₃H₄, CH₃Cl, C₂H₅Cl, CCl₄, CCl₂, CCl₃, CCl₄, HCl, etc. The thermodynamic data of these products (e.g., enthalpy, entropy, specific heat at constant pressure) is known or can be

TABLE 2. MIXTURES OF CHEMICAL WASTES AND ADDITIVES

<i>Composition</i>	<i>Mixture</i>		
	<i>Mixture 1 (g)</i>	<i>Mixture 2 (g)</i>	<i>Mixture 3 (g)</i>
CW-1	100		20
CW-2		150	20
SiO ₂		120	15
C	100		
CaO	300	150	5

FIG. 4. Slag of mixture 2.

FIG. 5. Slag of mixture 3.

obtained from some thermodynamic books or websites (Barin, 1995; Burcat, 2008; NIST Chemistry WebBook). To determine the equilibrium state of CW-1, the CHEMKIN-III EQUIL subroutine was used, which iteratively minimized the Gibbs free energy subject to specified atomic constraints (Lutz *et al.*, 1996). Although temperature profile in the reactor is not uniform, such calculation still provides some important and useful information on predicting the pyrolysis products. The calculation result is shown in Fig. 6, which shows that the main products are C, CH₄, H₂, and HCl, and their mol fractions vary with temperature greatly below 1,000 K and slightly between 1,000 K and 2,500 K. The mol fraction of H₂ increases with increasing temperature from 0 to 0.28, while the mol fractions of C, CH₄, and HCl are decreased from 0.785 to 0.74, 0.19 to 0, 0.03 to 0.02, respectively. In fact, the amounts of both C and H₂ increase with temperature, the amount of HCl is almost constant and the amount of CH₄ decreases.

In the experiments, pyrolysis temperature is above 1,800 K and quantity of carbon is produced after the plasma pyrolysis process is completed. HCl is produced in the pyrolysis gas and can be neutralized by NaOH solution (refer to the schematic description of the system). The test result shows that

FIG. 6. Calculation result of CW-1.

FIG. 7. Simulation region.

plasma pyrolysis technology can perfectly meet the most stringent emission standard for the hazardous waste.

Numerical simulation

Numerical simulation of the 30-kW DC plasma-arc reactor is made to predict the temperature and velocity fields. The simulation region including the arc region and the plasma reaction region (Fig. 7) is for a half reaction zone of the reactor because it is symmetric.

In the previous studies, the magneto hydrodynamic approach is normally introduced to simulate the small arc region, but it is difficult to be applied in the reaction region for the waste treatment. In the present work, a simplified electromagneto model is developed to simulate both the arc region and the reaction region, which can reduce not only the number of governing equations but also CPU time greatly, especially for employing waste numerical simulation of the chemical reaction. The governing equations in the simplified model for the plasma-arc reactor (Fig. 7) can be written in cylindrical coordinates as follows (Hsu *et al.*, 1983):

$$\frac{1}{r} \frac{\partial}{\partial r} (r \rho v_r) + \frac{\partial}{\partial z} (\rho v_z) = 0 \quad (1)$$

where the parameters, r and z are the cylindrical coordinates, ρ is the density of the fluid, and v_r and v_z are the velocity vector components. Because the simulation region is symmetric, the continuum equation is simplified into a Two-dimensional equation in cylindrical coordinates.

$$\begin{aligned} \frac{1}{r} \frac{\partial}{\partial r} (r \rho v_r^2) + \frac{\partial}{\partial z} (\rho v_r v_z) = & -\frac{\partial P}{\partial r} + \frac{1}{r} \frac{\partial}{\partial r} \left(2r \mu \frac{\partial v_r}{\partial r} \right) \\ & + \frac{\partial}{\partial z} \left[\mu \left(\frac{\partial v_z}{\partial r} + \frac{\partial v_r}{\partial z} \right) \right] - 2\mu \frac{v_r}{r^2} + S_r \end{aligned} \quad (2)$$

where the parameters, P is the pressure of the fluid, μ is the viscosity of the fluid, and S_r is a volumetric source of

FIG. 8. Water-cooling model.

momentum in radial direction which represents the Lorentz Force effect to velocity field in radial direction.

$$\frac{1}{r} \frac{\partial}{\partial r} (r \rho v_r v_z) + \frac{\partial}{\partial z} (\rho v_z^2) = - \frac{\partial P}{\partial z} + \frac{\partial}{\partial z} \left(2\mu \frac{\partial v_z}{\partial z} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left[r \mu \left(\frac{\partial v_z}{\partial r} + \frac{\partial v_r}{\partial z} \right) \right] + S_z \quad (3)$$

where S_z is a volumetric source of momentum in axial direction that represents the Lorentz Force effect to velocity field in axial direction.

$$\frac{1}{r} \frac{\partial}{\partial r} (r \rho c_p v_r T) + \frac{\partial}{\partial z} (\rho c_p v_z T) = \frac{1}{r} \frac{\partial}{\partial r} \left(r k \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial z} \left(k \frac{\partial T}{\partial z} \right) + S_R \quad (4)$$

where the parameters, c_p is specific heat at constant pressure, T is temperature, k is thermal conductivity, and S_R is a heat source which consists of the Joule-heating term, the radiation term, and an additional term that represents the transportation of electron enthalpy due to the drift of the electrons.

In the simplified model, the temperature profile along the arc boundary is as a known parameter according to the measured data (Olsen, 1959). Based on the constant electrical conductivity assumption of the arc channel theory, by transforming the Maxwell equations, the electric current density profile of the arc region can be obtained, and hydrodynamic

FIG. 9. Contours of temperature in the whole reactor (left) and the arc region (right zoomed).

approach combining of additional sources is applied to simulate the temperature and velocity fields. In this simplified model, the electric current density along the cathode can be assumed to obey the distribution function as described by Equation (5) (Wei-Hong, 2000).

$$j_z = j_{\max} \exp(-br) \quad (5)$$

where j_z is the electric current density, and $j_{\max}$ and b are constant.

In this model, the electric potential along the anode is set to zero. The ambient gas is argon, and the plasma properties are taken from (Olsen, 1959). The κ - ϵ model that is a two-equation model is used to simulate turbulence, where κ represents turbulence kinetic energy and ϵ represents dissipation rate of turbulence kinetic energy (Chen and Jaw, 1998).

The radiation heat transfer is the main phenomenon in the plasma-arc reactor and the discrete transfer radiation model (DTRM) where the gray radiation is assumed is used to simulate this phenomenon. Some of the boundary conditions for the enthalpy are defined in terms of temperature and they are then converted into the enthalpy of the appropriate gas. The cathode temperature is set as about 3,000 K, approximating the free-burning arc cathode temperatures measured by Haidar and Farmer (1993). The electric potential along the cathode is defined by specifying the electric current density.

FIG. 10. Velocity vector in the whole reactor (left) and the arc region (right zoomed).

FIG. 11. Comparison of maximum temperature in the arc region.

The boundary conditions of the outer wall and the inner wall are illustrated in Fig. 8. As expected, the heat loss is a sensitive parameter due to cooling the inner wall by water. Simulation result shows that 65% of the energy is transferred to the inner wall, so it is important for the reactor to line the refractory materials to reduce the heat loss across the inner wall.

Several preliminary numerical studies were carried out in order to choose the optimum parameters for tests. Figure 9 shows the temperature simulation results where the temperature of the arc region is very high, while the temperature in the reaction region is about 1,400 K and is almost uniform. The temperature along the radial aspect decreases rapidly. The results show that the velocity is about 2 m/s in the reaction region, and the maximum velocity in the arc region can reach 300 m/s (refer to Fig. 10).

Figures 11 and 12 show a comparison of the maximum temperature and the maximum velocity in the arc region between the magneto hydrodynamic approach and the present simplified model, respectively. The simulation results of the maximum temperature and maximum velocity distributions in the arc region are very good in agreement with the experimental results reported by E. Pfender *et al.* (Hsu *et al.*, 1983).

FIG. 12. Comparison of maximum velocity in the arc region.

The maximum temperature for the magneto hydrodynamic approach is 18,250 K at 100 A, 20,089 K at 200 A and 23,429 K at 300 A, respectively. For the simplified model, the maximum temperature is 18,411 K at 100 A, 21,250 K at 200 A, and 23,036 K at 300 A, respectively. The difference percent between the two approaches is below 5.46% for the maximum temperature, and 6.1% for the maximum velocity. The most important is that the CPU computing time for the simplified model is about three orders of magnitude smaller than the magneto hydrodynamic approach, which is significantly reduced (Huang, 2008). These results indicate that the simplified model can be a useful tool for further study.

The numerical results presented in this paper are preliminary results. The next step for the process simulation is in the model to account for chemical kinetics.

Conclusions

1. A pilot system with PP/V technology was constructed to destroy two types of chemical wastes that are containing primarily biphenyls and PCBs, and the other containing PCBs and inorganic constituents. The destruction of hazardous chemical waste was studied by using a 150-kW three-phase AC plasma-arc reactor. A 30-kW DC experimental facility with plasma-arc technology was also set up to study the pyrolysis process.
2. During the plasma pyrolysis process, the hazardous organic waste is rapidly pyrolyzed into some simple molecules and the major products are hydrogen, hydrochloride, methane, and carbon. DRE of these chemical wastes is more than 99.999%, and the PCBs concentration in the solid residues is in the range of 1.28 to 12.9 mg/kg, which is far below the Chinese national emission limit for the hazardous wastes.
3. For the plasma vitrification process, additives are added into the reactor. It is found that the quenching rate is the main parameter for the formation of dense vitrified slag with glassy structure. However, some of vitrified slag produced in the experiments is not dense and mat, which reveals that the additives with inappropriate proportion fail vitrification process.
4. A simplified electromagneto simulation was made to predict the temperature and velocity fields in the arc region of the reactor. The results of the simplified simulation process were below 5.46% for the maximum temperature and 6.1% for the maximum velocity different from predictions made with a more rigorous magneto hydrodynamic approach.

The results of this work show that plasma-arc technology can be used to reduce the concentrations of PCBs in solid waste to below regulatory requirements, and that a simplified electromagneto simulation model can be used to provide reasonably accurate temperature distributions and velocity fields in the reactor compared to more rigorous and time consuming modeling methods.

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Author Disclosure Statement

The authors state that no competing financial interests exist.

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