# Destruction of Chemical Agents in a Plasma Reactor with Working Gas of Hydrogen\*

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Abstract: In this paper, an AC plasma arc reactor with working gas of hydrogen is applied to destruct chemical agents. The temperature attains 6000°C in the arc area and over 2000°C in the other space of the crucible. The Arsenic (As) contained chemical agent - Adams (DM) used in the experiment, was added into the plasma reactor with the additives: Fe, CaO, and SiO<sub>2</sub>, etc. Pyrolysis and destruction of chemical agents occurs very quickly in the high-temperature reactor. Gaseous hydrogen was injected into the reactor to form a reductive environment, to reduce the formation of  $As_2O_3$  etc. In the bottom of the crucible, the solid residues of toxicant and additives were melted and formed as vitrified slag. The off-gas was treated by a wet scrubber. The amounts of arsenic distributed in the off-gas, vitrified slag, waste water and solids (soot) were measured. The result shows DM is completely destructed in the plasma reactor. The Arsenic content in the off-gas, vitrified slag, waste water and soot are 0.052 mg/l, 3.0 %, 10.44 mg/l, and 5.1% respectively, which will be disposed as the pollutant matters. The results show that the plasma technology is an environmentally friendly technology to destruct chemicals.

Keywords: AC plasma, chemical agent destruction1.

#### INTRODUCTION

Five thousand tons of chemical weapons were abandoned in China at the end of the second world war. Then these fearfully dangerous weapons were hastily and simply buried into the soil and have been seriously corroded after about sixty years. How to destruct the abandoned chemical weapons is becoming an urgent issue in China.

The incineration and pyrolysis both are possible technologies. But the chemical agents have many Halogen elements, which are fire-resistant elements. So, for incineration, the energy consumption is very large and the amount of off-gas has to be treated before release to atmosphere is huge. This causes the treatment process is very expensive and un-efficiently. Plasma generator can produce very high temperature, so it was developed to destruct the chemical weapons and low radiation wastes in developed countries (1,2). The Plasma Pyrolysis with Vitrification (PP/V) technology is a better choice, since the working gas in plasma generator can be chosen according to the features of chemical agents and the proper additives can be added in to reactor, so the toxic organic constituencies and heavy metals can be fixed in the glassy slag. And the off gas from plasma reactor is only 5-10% of incineration if hydrogen is employed as working gas, and the off-gas treatment system is a low cost and low energy consumption system. The metals in electronic waste can be recycled to re-use in this case.

The following is a list of some manufactures of plasma equipment used to dispose chemical weapons and hazardous wastes:

- Mannesmann, a Germany company, and MGC, a Swiss company, have developed the mobile plasma equipment PLASMOX<sup>®</sup>-RIF-2 for chemical weapon destruction. The output power of DC plasma torque is 200 kW, and Nitrogen and Argon are employed. The Munster II is the commercial plant of these companies, with a capacity of 1500kW.
- Startech Environmental, an American Company, manufacturers of technology to safely and economically process solid, liquid, and gaseous wastes; organic and inorganic, hazardous and non-hazardous, including

nuclear wastes and weapons.

- Integrated Environmental Technologies, LLC developed Plasma Enhanced Melter (PEM) System, and the plasma arc technology was applied with Three Joule Heating Graphite Electrodes (3 Phase AC).
- French Astronautic Group has developed the plasma technology for chemical weapon destruction.
- Russia has plasma technology to destroy the chemical warfare agent containing organic Phosphorus. An AC air plasma torch technology was developed by Institute of Problems of Electrophysics, Russian Academy, in Saint Petersburg.
- Thermal Conversion Corp develops magnetic, induction-coupled, plasma technology for waste conversion, co-generation and industrial materials processing.
- Westinghouse Plasma Corporation, develops and manufactures industrial grade thermal plasma systems..

AC plasma arc metallurgy technology (3-phase, 50Hz) was developed in our institutes in later 1980's to 1995, which is very different from them mentioned above. After 1995, this technology was applied to treat hospital waste, waste polymers (plastics and rubber), waste oil, pulp mill slurry, waste scoria and hazardous waste with higher arsenic and sulfur constituents (3, 4, 5). The gaseous emissions can meet the most stringent environmental standard. This paper will introduce the results of the experimental study of destruction of chemical agents in a 3-phase plasma reactor.

## 2. EXPERIMENTAL FACILITY

A plasma reactor with working gas of hydrogen has been developed to destruct the toxicant weapons. The reactor is based on AC 3-phase 50Hz plasma arc metallurgy technology, and the experimental equipment is schematically shown in Fig.1. The plasma arc reactor system has following sub-systems: raw material feeding system, hydrogen supply system, plasma generator, reactor, residual discharging system, off gas scrubber and cleaning system, special transformer and control system.

<sup>\*</sup> This Paper is supported by Chinese National Hi-Tech Project - 863, No. 2003AA644040.

The operating voltage is  $70 \sim 80$  V AC, and the power is about  $100 \sim 150$  kW. The positions of 3 electrodes are moveable individually by three sets of driving wheels. And there is also a water- cooling jacket to cool the reactor surface and an I.D. fan and control system to keep the correct internal pressure.

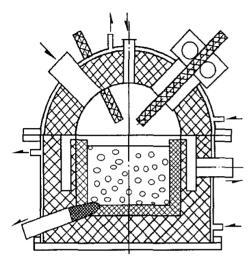


Fig.1 Sketch of AC Plasma Reactor

This reactor is applied to pyrolyse the chemical agents. The temperature attains 6000°C in the arc area and over 1800°C in the other space of the crucible. The arsenic (As) contained chemical agent – Adams (DM), destructed in the experiment, was added into the plasma reactor with the additives, such as SiO<sub>2</sub>, CaO, and Fe, etc. to form DM mixing. The formula of DM is C<sub>6</sub>H<sub>4</sub>(AsCl)(NH) C<sub>6</sub>H<sub>4</sub>, and the molecular weight is 277.57, the icing point is 195°C and boiling point 410°C, the disassociation start-temperature is also 195°C. Pre-process is not necessary.

## **3. EXPERIMENTAL RESULTS**

Pyrolysis and destruction of chemical agents occurs very quickly in the high-temperature reactor. The very high temperature in the furnace will let the hazardous organic waste decompose very fast to harmless simple molecules, such as, Carbon, Hydrogen, Nitrogen, etc. and some less harmful substances, such as, Chlorine, Sulphur, etc. Hydrogen gas was injected into the reactor to form a reductive environment, to reduce the secondary synthesis of toxicant oxide, e.g.  $As_2O_3$  etc. The major constituent of the off gas is combustible gas, Hydrogen. There are no suitable conditions for the reconstruction of PCDDs and  $As_2O_3$ . In the bottom of the crucible, the solid residues of toxicant and additives were melted and can form vitrified slag if the cooling speed is high enough.

Both batch process and continuous process were applied.

In batch test, the prepared material (DM mixing with powders of Fe, CaO and SiO<sub>2</sub>, refer to Table 1) was put in the crucible as lower layer, the middle layer was a Ferrous plate of 50 grams, and the upper layer was the mixing of Fe, CaO and SiO<sub>2</sub> (Fig.2). Then the reactor was closed to start the arc, the total process time was 8 minutes, the temperature wais up to  $1600-1700^{\circ}$ C. When the temperature in the reactor dropped to 200°C after turned down the power, opened the cover of reactor to get slag (177 grams) and iron (152 grams). In this test, the cooling speed was not very fast, so the slag is not very good vitrified.

Constituences	Fe	CaO	SiO <sub>2</sub>	DM
Upper Layer	15	110	65	0
Middle Layer	50	0	0	0
Lower Layer	77	130	77	122
Wt %	22.0	37.1	22.0	18.9

The glassy slag get from batch test is 177 grams, and the constituencies are listed in Table 2.

Table 2 Elements in Glassy Sla
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Sample No.	As %	Si %	Ca %	Fe %
1	7.8	13.0	78.2	1.0
2	6.4	13.1	79.5	1.0
3	2.8	14.5	82.3	0.4
4	4.5	14.2	80.8	0.5
Average	5.4	13.7	80.2	0.7
Wt (g)	9.6	24.2	142	1.2

The elements in glassy slag is almost unified, and the Fe plays as boiling liquid role in reaction. Most of Ca (83%) can be found in the slag, and 99% of CaO is disassociated. Part of Si is in the slag and another is associated within Fe compound. About a half of arsenic content is captured by the slag. The slag is shown in Fig.4. Figure 5 is the spectrum of slag.

To improve the stability of vitrified slag, and the slag capture e fficiency to fix more arsenic content in the slag to reduce the a



Fig.2 Prepared DM Mixing

rsenic emission to off gas, the constituencies of additives were optimized. Finally, a kind of waste ore was used to form the a dditives. In continuous process, 3.05 kg DM mixing (11.5% of DM, 23% of CaO and 65.5% of waste ore) was put in the cru cible, and turn on the arc. When the temperature reaches 1800 °C, input the DM mixing by spiral machine. The total destruct ed DM mixing (the same proportion as the DM mixing in the c rucible) is 18.5 kg during 22 minutes. In this period, the melte d slag was discharged once (Fig.3). The melted slag was quenc hed very quickly and formed very good vitrified slag.

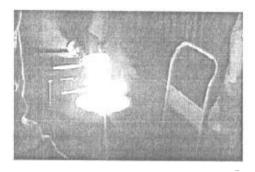


Fig. 3 Discharge of Melted Slag

The productivity of the experimental facility is 50 kg/hr with 60 kW AC power supply in the continuous operation. The energy consumption is about 1.0-1.2 kW-hr/kg waste. There is no air/Oxygen and other gas supply to the process except a little Hydrogen supply. The Hydrogen supply is only 50 liters per hour, so the volume of off gas is only 5 % of conventional incineration, which is much easier to be scrubbed.

Solution of 0.01~0.1 mol/L Na OH was applied to absorb the arsenic compound in off gas, as the cleaning method, the volume of Na OH is 16 L.

To verify the DRE, the glassy slag, the Na OH solution, the

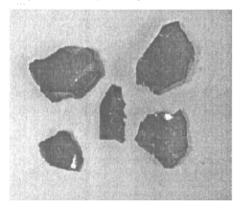


Fig. 4 Vitrified Slag

sediment in continer and off-gas were analysed. The JSM-840 Scan Electronic Microscope and VANTAG Eenergy Spectrometer were employed. The sampling rate of off gas was is 6 *L/min*, and the total gas volume is 36 L.

The amounts of arsenic distributed in the off-gas, vitrified slag, waste water and solids (soot) were measured. The result shows Adams (DM) is completely destructed in the plasma reactor. The Arsenic content in the off-gas, vitrified slag, waste water and soot are 0.052 mg/l, 3.0 %, 10.44 mg/l, and 5.1% respectively, which will be disposed as the pollutant matters. The emissions show that the plasma technology is an environmentally friendly technology to destruct chemical weapons.

The vitrified slag is shown in Figure 4 and the spectrum of slag is shown in Figure 5.

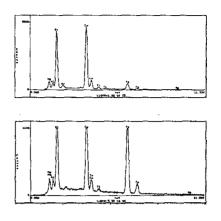


Fig. 5 Spectrum of Vitrified Slag

### 4. CONCLUSIONS

AC (3-phase, 50Hz) plasma arc reactor with working gas of hydrogen is applied to destruct chemical agents. The Arsenic (As) contained chemical agent was processed in the reactor with the additives Fe, CaO, and SiO<sub>2</sub>. Gaseous hydrogen was injected into the reactor to form a reductive environment, to reduce the formation of As<sub>2</sub>O<sub>3</sub> etc. The result shows DM is completely destructed in the plasma reactor. The arsenic content in the off-gas, glassy slag, waste water and soot are 0.052 mg/l, 3.0 %, 10.44 mg/l, and 5.1% respectively. The results show that the plasma technology is an environmentally friendly technology to destruct chemicals.

# ACKNOWLEDGMENTS

The authors gratefully acknowledge the National 863 project 2 003AA644040 for support.

# REFERENCES

- G. S. Pearson, R. S. Magee, "Critical Evaluation of Prov en Chemical Weapon Destruction Technologies", *Pure A ppl. Chem.*, Vol.74, No.2, pp187-316, 2002.
- U.S. Congress, Office of Technology Assessment, "Disposal of Chemical Weapons: Alternative Technologies", Background Paper, OTA-BP-O-95 (Washington, DC: U.S. Government Printing Office, June 1992).
- [3] Hong-zhi Sheng, Yong-xiang Xu and Yong-xian Cao, "Plasma Based Pyro-Incinerator for Hazardous Waste Disposal", IT3-2002.
- [4] Yongxian Cao and Yongxiang Xu, "Hospital waste treatment by a plasma furnace based on AC 3-phase 50Hz plasma arc metallurgy technology", Internal Report, Institute of Mechanics, CAS (1997), in Chinese
- [5] Hongzhi Sheng, "Test report on hazardous waste treatment by a AC plasma arc pyro-furnace", Institute of Mechanics, CAS (2001), in Chinese