



# INVESTIGATION ON GASEOUS AND SOLID PRODUCTS FROM DECOMPOSITION OF GALVANIC SLUDGE IN A LABORATORY SCALE TRANSFER ARC LOW THERMAL PLASMA

Bala I. Abdulkarim<sup>1</sup>, Mohd A. Abu Hassan<sup>1</sup>, Raja R. K. Ibrahim<sup>3</sup> and Abubakar M. Ali<sup>3,1</sup>

<sup>1</sup>Faculty of Chemical and Energy Engineering Universiti Teknologi Malaysia Skudai, Johor, Malaysia

<sup>1</sup>Department of Chemical Engineering, University of Abuja, Nigeria

<sup>2</sup>Faculty of Science Universiti Teknologi Malaysia Skudai, Johor, Malaysia

<sup>3</sup>Department of Chemical Engineering, Kaduna Polytechnic, Kaduna, Nigeria

E-Mail: [balisa76@yahoo.com](mailto:balisa76@yahoo.com)

## ABSTRACT

Galvanic sludge was treated in a direct current transfer arc low thermal plasma. The raw sludge obtained from KISWIRE Sdn Bhd was subjected to different operating temperatures (between 1050°C and 1670°C) in a short residence time of 5 and 7 minutes. Treated galvanic sludge at 5 minutes residence time and 1670°C (195A) attained an optimum of 84.83% mass reduction and 91.65% volume reduction, was reached, while at 7 minutes residence time an optimum of 88.35% at 1670°C of mass reduction, and 92.10% at 1546°C of volume reduction were also achieved. The non-homogeneity of the sludge and non-uniformity of the intensity of plasma generated lead to lower values of volume reduction in some instances. The average composition of gaseous product majorly constitutes of 90.063 mol % carbon monoxide (CO) but also there are the presence other gases (CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, NO<sub>2</sub>, SO<sub>2</sub>, NH<sub>3</sub>) in lower concentrations. Aluminium, cadmium, chromium and nickel in galvanic sludge were completely eliminated and Total Organic Carbon (TOC) reduction of 98.11% was achieved.

**Keywords:** galvanic sludge, heavy metals, thermal plasma.

## INTRODUCTION

Sludge generated from galvanizing process is basically a heavy metal laden hazardous waste because only about 30–40% of all metal used are effectively consumed (Leal Vieira Cubas *et al.*, 2014). The constituent of the galvanic sludge depends on the installed process, but the heavy metals commonly found in the sludge are chromium, nickel, zinc, cadmium, tin, lead, copper (Rossini and Bernardes, 2006). These heavy metals are known for several effects on human and the environment. The heavy metal can pollute surface waters through runoff and a leach out into the underground waters. High concentration of heavy metal in plants or animal can bio-accumulate in human when consumed. Apart from the presence of heavy metal found in the sludge, it also contains cyanide, surfactants, oil and grease, hydroxides and hydrate oxides. There is also the possible formation of hydrogen cyanide (HCN), which under ambient conditions is a toxic and poisonous gas. Traditionally, hazardous sludge such as galvanic sludge were directly sent to lagoons and landfills, but in this present generation it is no longer acceptable. This is due to stringent national and international regulation on hazardous waste management, scarcity of land and the need for environmental quality.

Galvanic sludge can be treated by composting, solidification/stabilisation, acid treatment and thermal treatment. During solidification/stabilisation contaminants are immobilised by encapsulating in a durable matrix and converting them into a less soluble form (Hunee *et al.*, 2012; Wiles, 1987). Heavy metal containing sludge/waste has been successfully treated using solidification/stabilisation technique. The addition of

Pozzolanic materials (fly ash and cement clinker dust) to integrated sample containing heavy metal indicate availability of metals leaching from the stabilized sludge were lower than the permissible limit (Katsioti *et al.*, 2008; Lasheen *et al.*, 2013). The addition of bentonite/cement reduced heavy metal concentration in sewage sludge containing heavy metals (Anastasiadou *et al.*, 2012). A mixture ratio of 5:2:3 of wet sludge, bentonite and cement respectively produced a stabilised and solidified material that could be used in construction applications (Katsioti *et al.*, 2008). The effectiveness of H<sub>2</sub>SO<sub>4</sub>, HCl, HNO<sub>3</sub>, which are the most common acids that have been used in the removal of heavy metal in industrial sludge. The removal rate of the metals depends on their solubility and pH values. The application of H<sub>2</sub>SO<sub>4</sub> (20%) for 30 min at 80°C, in eliminating heavy metal in sludge has recorded removal efficiency of 74%, 86%, 99%, 11% and 72% zinc for Ni, Cu, Cr, Pb and Zn respectively (Stylianou *et al.*, 2007). Hydrochloric acid is the most utilised and removal rate could reach 60% but phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) has higher removal efficiency. 42.5% H<sub>3</sub>PO<sub>4</sub> effectively removed chromium and mercury, also cadmium were eliminated with 21.2% H<sub>3</sub>PO<sub>4</sub> (Shiro and Tahei, 2000).

Both solidification/stabilisation and acid treatment has problem of increase in volume of waste and most times non-immobilisation of volatile organic compounds (VOC) and organic pollutants, while incineration also has drawback of hazardous fly ash and bottom ashes that requires further treatment and landfilling (Cedzynska *et al.*, 1999; Chun-Teh *et al.*, 2007). These issues have necessitate for a more efficient and environmentally friendly treatment option such as thermal



plasma that achieve volume reduction, render the hazardous waste inert and produce a material of reusable value. Thermal plasma technique simply involves the creation of sustainable arc by passing electric current through a gas (air, inert gases, CO<sub>2</sub> etc.). Heated gas molecules are initially dissociated into atomic state, but as intensity of heat increases electrons are lost to become ionised (Gomez *et al.*, 2009). As more electrons with electric field continue to bombard other molecules results in more free electrons at exponential rate forming a phenomena referred to as electron cascade. Temperature of 10,000°C and above is attainable using thermal plasma.

## EXPERIMENTAL PROCEDURE

### Characteristics of galvanic sludge

The galvanic sludge sample collected from KISWIRE Sdn Bhd has a moisture content, volatile matter, ash content and fixed carbon of 67.055%, 11.485%, 19.30%, and 2.16% (as air dry basis) respectively. It also has a density of 1.396 g/cm<sup>3</sup> and gross calorific value of -21.4 cal/g. Total Carbon (TC), Total Organic Carbon (TOC) and Total Inorganic Carbon are 2.094%, 2.073% and 0.02031% respectively in the sludge.

### Description of thermal plasma system

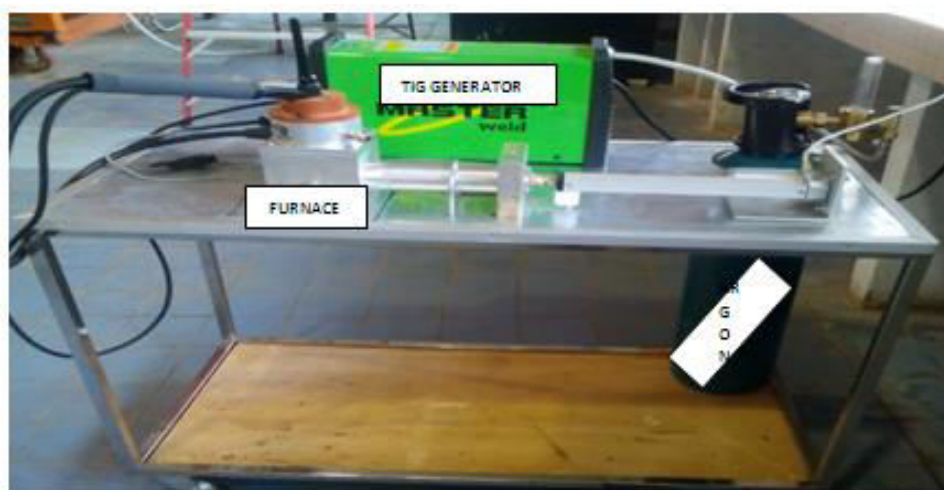
A Direct current transfer arc low thermal plasma consisting of a conical reactor, Direct Current Tungsten Inert Gas (TIG) Inverter master weld generator, Tungsten arc Torch, water cooling system and gas collection system was used to treat obtained galvanic sludge. Table-1 is a description and specification of Direct Current Transfer Arc Low Thermal Plasma.

**Table-1.** Specification/components of items of low thermal plasma system.

Components	Specification/Description
Main reactor	Alumina Conical reactor furnace: Top diameter: 42mm, bottom: 13mm and depth 20mm Reaction chamber: Rectangular shaped of 99mm x 95mm base; 116mm height
Plasma generator	Tungsten inert generator (master weld TP 2000I inverter Input/supply voltage 220/230/240V Power (kW): 4.7 Output voltage: 63V Input current: 31A Output current: 5- 200A
Torch	Cathode tungsten electrode: 4mm diameter; 150mm length Anode tungsten electrode: 10mm diameter; 50mm length
Gas collection system	0.5 litre capacity Teflon gas bag, Flow meter and Heat exchanger.

Twenty (20) grams of galvanic sludge was introduced into the conical alumina furnace. The distance between the electrodes (electrode gap) was adjusted to 3mm for ignition of arc and plasma generation. The sludge was treated at input current range of 160A- 195A, temperature between 1005°C -1670°C and argon flow rate

of 10 l/min for a residence time of 5 and 7 minutes. The temperature was monitored using an infrared thermometer and the cooled treated solid product (slag) was also collected, weighed and analysed. The experimental setup of Direct Current low temperature thermal plasma for treatment of galvanic sludge is shown in Figure-1.



**Figure-1.** Setup of direct current low temperature thermal plasma for treatment of galvanic sludge.

## RESULTS AND DISCUSSIONS

### Gaseous product

Collected gaseous product was analysed in a Gas Chromatographs system (Model: 7820AAgilent technologies) equipped with Flame Ionisation Detector (GC-FID) and Thermal Conductivity Detector (GC-TCD). To analyse Hydrocarbons ( $C_2H_6$ ,  $C_2H_2$ , and  $CH_4$ ), collected gaseous product in Teflon bag was injected manually using 10  $\mu$ l tight syringe into a steel column of 30m x 320 $\mu$ m x 0.25 $\mu$ m, while to analyse for  $NO_2$ ,  $SO_2$ ,

$CO$ ,  $CO_2$ ,  $H_2$ ,  $HCN$  the gas was passed through GS-carbon plot column (30m x 32 $\mu$ m x 1.5 $\mu$ m) fitted with flame ionisation detector. For both GC-TCD and (GC-FID) the carrier gas used was nitrogen at flow rate of 0.5ml/L at oven temperature of 60°C. Result of the average composition of gaseous product from the thermal decomposition of sludge in five (5) minutes treatment time is presented in Table-2. Maximum of three minutes was sufficient to decompose most organic substances presence in the sludge.

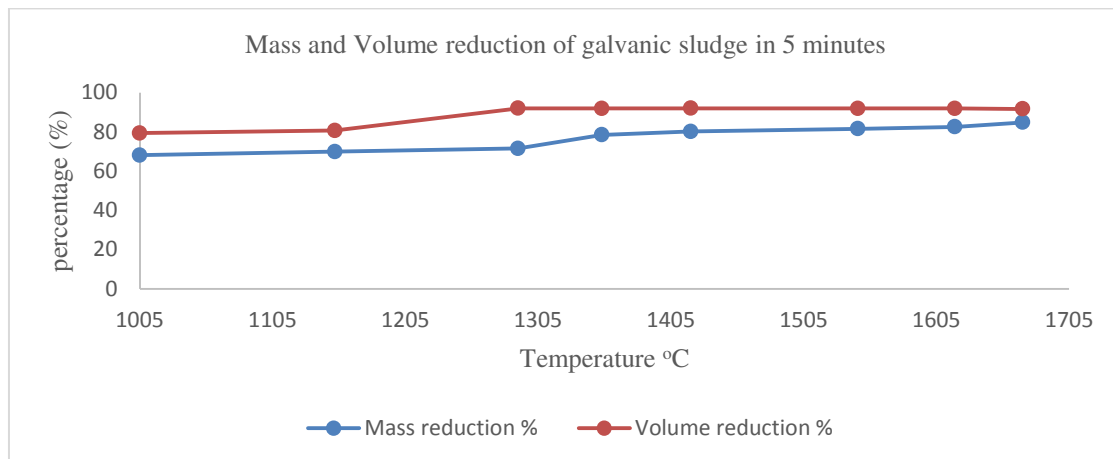
**Table-2.** Average gaseous product composition of thermal decomposition of galvanic sludge at 1005-1670°C.

Component	$CO_2$	$CO$	$NO_2$	$CH_4$	$C_2H_2$	$C_2H_6$	$NH_3$
Conc (Mol %)	1.156223	90.06367	0.002556	0.669392	0.005477	0.030427	0.547684

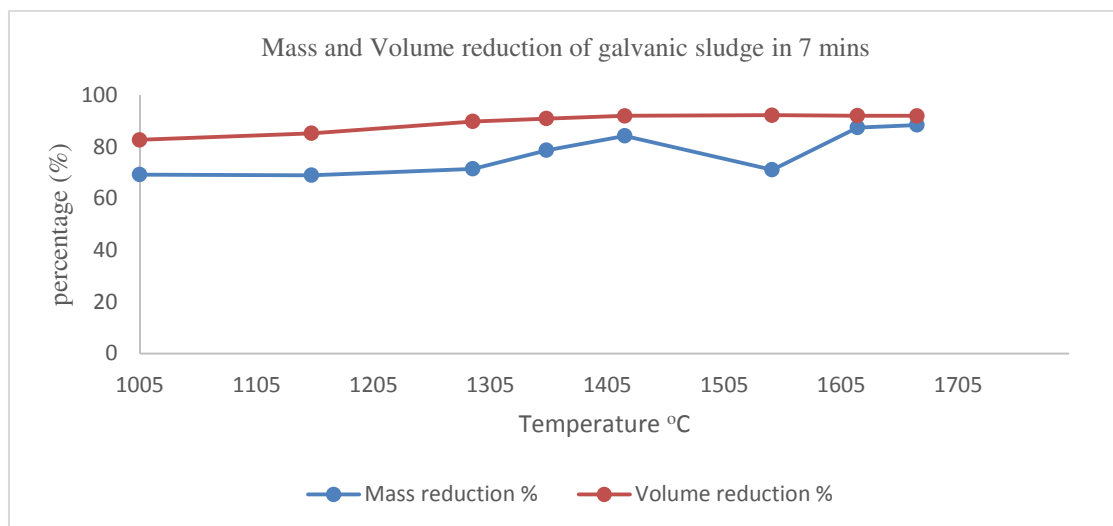
The obtained gaseous product from thermal decomposition of galvanic sludge at 1005-1670°C in 5 minutes residence time majorly constitutes of 90.063 mol % carbon monoxide ( $CO$ ) and other gases ( $CO_2$ ,  $CH_4$ ,  $C_2H_4$ ,  $C_2H_6$ ,  $NO_2$ ,  $SO_2$ ,  $NH_3$ ) in lower concentrations. The high molar concentration of  $CO$  in the gaseous product is a result of existence of  $CO$  at temperatures up to 1500k while  $CO_2$  is not formed because its molecules dissociate at lower temperature.

### Solid products

The thermal treatment of dark brownish untreated galvanic sludge produced a greyish lustrous metallic slag. The Mass and volume reduction of galvanic sludge treated in transfer arc low thermal plasma at different temperature and input current are presented in Figures 2 & 3, while Table-3 is showing metal and carbon composition of the untreated sludge and metallic slag.



**Figure-2.** Volume and mass reduction of treated galvanic sludge at 1005°C to 1670°C and 5 minutes residence time.



**Figure-3.** Volume and mass reduction of treated galvanic sludge at 1005°C to 1670°C and 7 minutes residence time.

Treated galvanic sludge in thermal plasma attained percentage mass reduction of 68% -71% between temperature of 1005°C and 1205°C. Similarly, 64 and 75% weight and volume reduction achieved in treating fly ash in direct current arc plasma furnace was achieved by (Peng *et al.*, 2010), 67.7% (Leal Vieira Cubas *et al.*, 2014), 74.53% (Leal Vieira Cubas *et al.*, 2016) even at temperature 5000oC. Substances and metals of low melting and volatilisation temperature most likely have been eliminated. Higher and almost stable mass and volume reduction indicated between temperatures of 1353°C and 1607°C shows that even at short residence time but high temperature large volume reduction is possible. The lower mass reduction recorded at temperature of 1546°C (Figure-2) during 7 minutes treatment time could be as a result of non-homogeneous heating of the sample in the crucible because initially the

plasma is formed between the two electrodes positioned at the centre crucible then later covering the entire furnace. Therefore the intensity of plasma is non-uniform at this stage.

#### Metal composition

Metals (Aluminium, cadmium, chromium and nickel) in low concentrations in galvanic sludge were completely eliminated or vitrified during 7 minutes residence time as shown in Table-3. The high concentrations of Cu (14873.62mg/kg), Fe (87525.80mg/kg) and Zn (17900.08mg/kg) after treatment is a positive indication of possibility of metal recovery. The thermal decomposition process achieved 99.16% and 98.11% reduction of Total Organic Carbon (TOC) and Total Carbon (TC) respectively.

**Table-3.** Metal and carbon Composition of galvanic sludge and solid product (metallic slag).

Metal concentration			
Heavy metals	Untreated sludge (mg/kg)	Solid product (Metallic slag) (mg/kg)	US EPA Standard, (1993)
Al	54.626	-	-
Cd	2.8708	-	85
Cr	96.5602	-	3000
Cu	5793.44	14873.62	4300
Fe	59290.6	87525.80	-
K	322.104	2162.38	-
Mg	47.636	-	-
Mn	565.754	1185.85	-
Ni	17.558	-	75
Pb	620.046	4290	420
Si	10.2834	-	-
Zn	5411.22	17900.08	7500
Carbon composition of galvanic sludge and solid product			
Total carbon (%)	Untreated sludge	Solid product	Percent reduction
	2.094	0.03958	99.16
Total organic Carbon (%)	2.073	0.01748	98.11

## CONCLUSIONS

The volume and mass of heavy metal laden waste such as galvanic sludge can be reduced to a high degree using thermal plasma technique. At short residence time of 5 minute and temperature of reaction region of 1670°C, optimum percentage mass reduction of 88.35 was achieved, while temperature of 1546°C was sufficient to attain optimal volume reduction of 92.10%. The total carbon and total organic carbon contents of the galvanic sludge was also reduced to 99.16% and 98.11 respectively. This indicates that thermal plasma can serve as an efficient means in reducing the large volume of unpretreated metallic sludge associated with galvanising process and other related industrial sludges.

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