2000

Vol. 26

EVA CHMIELEWSKÁ*

MANAGEMENT AND DISPOSAL OF WASTE CHEMICALS BY INCINERATION

Waste chemicals produced predominantly by textile industry and stored as unuseful waste for decades are disposed by thermal treatment. Because basic matrices of waste chemicals consist of printing colour residues and organic pigments, their disposal by incineration is decisive. Pilot tests with the charging dose of 40 kg of waste mixture per hour were carried out in order to evaluate their combustion efficiency and to analyse the content of waste chemicals and flue gases before their combustion on an industrial scale. Final, commercial disposal of the waste was carried out in pyrolytic combustion chamber equipped with alkaline scrubber and electrostatic dust separator.

1. INTRODUCTION

The aim of this paper was to propose the most convenient method for disposing chemicals. Waste products of textile industry have been stored for several decades as an unuseful waste. If we want to dispose such wastes we have to determine their composition, to evaluate the worthwhileness of the process and its environmental impacts.

Table 1

Code No.	Name	Waste categories
555 09	printing colour residues	special [*] , hazardous ^{**}
555 14	waste organic pigments and colours	special, hazardous
593 02	residues of organic chemicals	special, hazardous

Waste chemical categorization according to waste catalogue

*Special waste requires special mode of handling, mainly because of the economic and environmental reasons.

**Hazardous waste represents special waste with such characteristics as toxicity, infectiousness, irritability, explosiveness and combustibility; they are also carcinogenic, teratogenic and mutagenic agents.

^{*}Comenius University, Faculty of Natural Sciences, 842 15 Bratislava, Slovak Republic. E.mail: Chmielewska@fns.uniba.sk.

No. 1–2

E. CHMIELEWSKÁ

Chemical composition of the predominant chemicals is based on the polymerized organic matrix with a low content of heavy metals and inorganic salts. Various fabric colours and technical accessories produced by such worldwide known companies as Hoechst, Bezema, Basf etc. were imported into former Czechoslovakia. They all were marked as ecologically friendly products and known best under commercial names, i.e. Cappagen, Depremol, Phoboton, Chemisap etc. [1]–[3].

According to national regulations and hazardous waste catalogue code [1] the above-mentioned chemicals may be classified as in table 1.

2. PROCEDURES OF SAFE DISPOSAL OF WASTE CHEMICALS

The most efficient and inexpensive disposal of waste chemicals from current and past production is either their recycling as originally intended or their recycling in an alternative way.

Therefore, this project dealing with the management of waste chemicals started with the selling of chemical residues to various chemical plants of similar production, which allows reduction of total waste amount by about 1/3. From the economic view-point, waste landfilling is not so expensive as the incineration in specially equipped kilns, therefore we should search for some controlled landfills in the neighbourhood.

In order to reclassify the waste chemicals in such a way as to lower their class of leachability, we have to apply their solidification and stabilization. Numerous solidification additives are currently available on the market. The state-of-the-art solidification processes differ mostly in the proprietary binder preparates, i.e. inorganic binders consist of hydraulic cement, lime, gypsum or pozzolans and organic ones of epoxy, polyester, asphalt, polyolefins, etc. The binding process improves structural integrity and lowers both permeability and waste class categorization. On the other hand, the cost of waste pretreatment rises when this option is taken.

The overfilled landfills in the region force a new scenario for the disposal of waste chemicals. Incineration in hazardous waste incinerators specially designed or in high-temperature facilities such as cement kilns has also been proposed. Cement kilns operate at the temperature ranging from 1400 to 2000 °C and provide optimal destruction of hazardous waste. The residence time of flue gases in a chamber ranges between 6–10 seconds. As a high-caloric fuel substitute, a semi-liquid combustible waste can also be used in rotary kilns. Acid gases and chlorine emitted during incineration are absorbed in the alkaline clinker produced by cement manufacture [4]–[6].

Despite all principal advantages of applying the rotary kilns mentioned and its inexpensiveness, the inland environmental legislation has not permitted us to dispose such a waste in currently operating four cement facilities in Slovakia. The waste disposal consisting in its pyrolytic incineration at the temperature of 1200 °C, finished with cooling of flue gases, scrubbing these gases in an alkaline unit (in order to remove acidic components) and electrostatic removal of fine dust particles was finally selected as an appropriate treatment technology.

3. TECHNOLOGY OF THERMAL TREATMENT

Incineration is applied to thermal treatment of a wide range of specific wastes with primary organic matrices. Information on the physical and chemical characteristics of waste matrix is necessary to assess the matrix impact on waste preparation, handling and feeding, incinerator performance, size and cost, air pollution control (APC) type and residue handling.

Incineration allows treatment of solid and liquid organic contaminants at the temperatures typically higher than 1000 °C and in the presence of oxygen, which facilitates volatilization, combustion and destruction of these compounds.

Combustion processes are slowed down by such air pollutants as toxic metals, e.g. arsenic, lead, mercury, cadmium and chromium, which are not destroyed by combustion and are found in ash.

Alkali metals (sodium and potassium) can cause severe refractory attack and form a sticky low-melting-point submicron particulate which causes APC problems. When PCBs and dioxins are present, higher temperature and longer residence time may be required to destroy them to the levels necessary for meeting regulatory criteria [1].

Waste materials with moisture/water content need some other extra-fuels. In general, as the heating value of the feed increases, the feed capacity and fuel usage of the incinerator will decrease. The form and the structure of waste feed can cause periodic jams in the feed and ash handling systems. Wooden pallets, metal drum closing rings, drum shards, plastics, used clothing and mud can cause blockages if poorly pretreated.

Different incinerator designs are based on different mechanisms which guarantee the temperature of furnace operation and the time necessary for the combustible material exposed to oxygen to undergo a complete combustion. Rotary kiln, circulating fluidized bed and infrared combustion chamber are considered to be three common types of incineration systems for treating wastes. The rotary kiln is a slightly inclined cylinder that rotates about its horizontal axis. Waste is fed into high end of the rotary kiln and passes through a combustion chamber by gravity. In a secondary combustion chamber, the unburned organics are destroyed in the flue gases [6].

In circulating fluidized bed incinerators, the fuel and waste particles are forced by the air of high velocity to circulate and suspend in a combustor loop. Flue gas is separated from heavier particles in a solid separation cyclone. Afterburner is not required. In infrared processing systems, electric resistance heating elements or indirect fuelfired radiant U-tubes are used to generate thermal radiation. Exhaust gases pass through a secondary combustion chamber [5], [6].

4. EXPERIMENTAL

Pilot incineration tests of the representative sample were carried out in order to measure the heat of combustion, to assess the combustion efficiency, and to analyse the chemicals incinerated and flue gases formed before the industrial process started.

E. CHMIELEWSKÁ

4.1. PILOT INCINERATOR

Pilot incinerator of Hoval GG14 type (made in Austria) with pyrolysis drum (process temperature of 500–600 °C) was used for waste chemicals combustion tests. The pyrolysis chamber was equipped with additional thermoreaction unit, where the burner temperature of 1140 °C converted the flue gases into oxides. Due to a sequential heat exchange the temperature fell to 300 °C and flue gas streams passed to the absorption column (alkaline scrubbing). Next, the dust was electrostatically separated from flue gas. A 40 kg dose of waste chemicals was fed each hour into combustion chamber, whose optimal time of operation was 8 h. The dose of mixed waste chemicals was prepared in the same proportions as that prepared for industrial incinerator.

4.2. COMBUSTION HEAT MEASUREMENTS

Combustion heat was determined using the Calorimeter KL-5 according to the following equation:

$$Q = \frac{C(D_t - k) - \sum c}{m} \qquad \left[\mathbf{J} \cdot \mathbf{g}^{-1} \right], \tag{1}$$

where:

C – calorimeter heat value (J·K⁻¹),

 D_t – temperature gradient of combustion (K),

k – temperature correction for surrounding (K),

 Σc – heat generated by combustion of iron wire plus heat generated by chemical reaction of flue gases with water (J),

m – sample weight (g).

4.3. COMBUSTION EFFICIENCY

Combustion efficiency is calculated according to the following equation:

$$Q_{\nu} = Q - Q_{c H_2 O} \left(\frac{W}{100} + \frac{9H}{100} \right) \qquad \left[\mathbf{J} \cdot \mathbf{g}^{-1} \right], \tag{2}$$

where:

 $Q_{c \text{ H}_2\text{O}}$ - condensation heat of water [J·g⁻¹],

W – percentage of water (% w/w)

H – percentage of hydrogen (% w/w).

Elemental analysis of carbon, hydrogen, nitrogen and sulfur was carried out using CHNS-O analyser, model EA 1108, Carlo Erba Milan (Italy).

Water content in samples was determined by titration with the Fischer solution, and ash content – by sample calcination in muffle furnace at 600 °C until the equilib-

rium was reached. The concentrations of metals in samples were determined using atomic absorption spectrometer, model AAS 1100 B Perkin-Elmer (USA), while sulfates were determined chelatometrically, and halogens – by means of isotachophoresis [7].

The composition of flue gases was calculated on the basis of percentage of components analysed in the samples and theoretical flue gas volume as well as theoretical air consumption. The composition of combustion air was as follows: oxygen -21% v/v, nitrogen -79% v/v.

5. RESULTS AND DISCUSSION

The values of combustion heat of individual waste species range between 9576 and 20 691 $J \cdot g^{-1}$ and combustion efficiency – from 7624.8 to 17 311 $J \cdot g^{-1}$.

During the combustion of 1 kg sample of chemicals some contaminants were present in flue gases (table 2). Combustion of 1 kg sample produced 11.18 m³ of dry-flue gases, which consisted of 11% of oxygen. The calculated concentrations of contaminants per 1 m³ of flue gases are presented in table 3.

Table 2

Minimum and maximum values of the relevant specimens during the combustion test

Components of chemicals	% w/w	Components of chemicals	% w/w
Combustible matter	36.90–92.62	Chlorine	0.02–4.35
Ash	0.20–28.0	Combustible sulphur	0–4.02
Water	7.18–62.80	Fluorine	0–0.01

Table 3

Contaminants analysed in flue gases during the combustion of 1 kg sample

Contaminants	mg∙kg ⁻¹	Contaminants	$mg \cdot kg^{-1}$
HCl	2-1584	Hg	0-0.03
SO ₂	0.90-2617	Cd	0-0.01
HF	0.1-3.0	Cr	0.01-0.19
Cu	0.01-0.53	As	0-0.08
Ni	0-0.48	Zn	0-0.02
Pb	0-0.06		

In general, the waste chemicals examined are characterized by the moderate values of combustion heat and water contents, combustible matter in average attains 65% (w/w). Thermal destruction of the above wastes is especially advantageous to high combustible substances.

E. CHMIELEWSKÁ

Contaminants	mg⋅m ⁻³	Contaminants	mg·m ⁻³
HCl	0–158	Hg	0-0.007
SO ₂	0.1-262	Cd	0
HF	0-0.4	Cr	0.002-0.009
Cu	0.001-0.044	As	0-0.009
Ni	0-0.040	Zn	0-0.001
РЬ	0-0.006		

Calculated concentrations of contaminants per 1 m³ of air

With a varying waste composition, pyrolytic pretreatment in an indirectly heated rotary kiln yields homogeneous products. It should be made clear in this context that thermal waste treatment as practiced in waste-incineration plants, with the secondary purpose of using the waste to obtain energy, is an environmentally compatible waste management method. Thermal treatment and energy recovery are laid down in the Act applied to closed cycle of waste management and waste disposal, respectively. However, an important focus of environmental policy in the field of emission abatement is the reduction of atmospheric emissions of climate-relevant substances (CO_x, NO_x, SO_x, HCl, HF, heavy metals, PAHs, dioxins/furans).

6. CONCLUSIONS

The results of the pilot combustion tests allowed the statement that the waste chemicals tested could be efficiently disposed on an industrial scale by their incineration in pyrolytic combustion chamber equipped with alkaline scrubber and a device for electrostatic dust removal. The incinerator (Hoval, Austria) capacity reached 3 t of waste per hour.

The optimal waste dose should be mixed and then fed into incineration kiln. Because of various water contents and various combustion heats of individual chemicals, the waste before being fed into kiln is mixed with such extra-fuels as shavings and sawdust.

REFERENCES

- Waste Management Programme in the Slovak Republic, Ministry of Environment of the Slovak Republic, Bratislava, 1993.
- [2] CHMIELEWSKÁ E., HORVÁTH I., Final research report of the project 0501/2/E/93, Comco Martech Ltd., Bratislava, 1994.
- [3] BREZOVICKÝ J., Expertise for waste chemicals incineration, VÚCHT, Bratislava, 1993.
- [4] ARESTA M., GALATOLA M., Energy from waste, NWT Edizioni NOWATECH, Bari, 1997.

- [5] Assessment of selected technologies for remediation of manufactured gas plant sites, IT Corporation Knoxville, Tennessee, EPRI Electric Power Research Inst., 1991.
- [6] Innovative Treatment Technologies, EPA Office of Solid Waste and Emergency Respon., Washington, DC 204 60, Overview and Guide to Inform. Sources, 1991.
- [7] HORÁKOVÁ M., LISCHKE P., PEKÁRKOVÁ K., GRÜNWALD A., The methods for chemical analyses of water (in Czech), SNTL, Prague, 1981.

GOSPODARKA ODPADKOWYMI CHEMIKALIAMI I USUWANIE ICH PRZEZ SPOPIELANIE

Odpadkowe chemikalia wytwarzane przede wszystkim przez przemysł tekstylny i jako nieprzydatne składowane przez lata są usuwane w wyniku obróbki cieplnej. Ponieważ podstawowymi składnikami takich chemikaliów są pozostałości barwników i pigmenty organiczne, ich usunięcie przez spopielenie ma zasadnicze znaczenie. Wykonano próbne testy, podczas których 40-kilogramową próbkę mieszaniny chemikaliów spalano przez godzinę, aby określić wydajność spalania, zawartość odpadkowych chemikaliów i spalin przed zastosowaniem tej metody na skalę przemysłową. Końcowe, przemysłowe spalanie chemikaliów przeprowadzono w pirolitycznej komorze spalania, którą wyposażono w płuczkę alkaliów i elektrostatyczny odpylacz.

chemikalie odpadkore usumuie chemikalii spopie Lauie tisty probne sparanie premy store

