PROSPECTS OF ENERGY RECOVERY FROM THE INCINERATION OF CHEMICAL PLANT WASTES

by

R. G. Novak, P.E.

and

J. J. Cudahy, P.E.

Hydroscience Associates, Inc.
Tennessee Regional Office

Background

The recovery of energy from industrial wastes has not been widespread, although certain industries such as lunber and pulp and paper have practiced energy recovery from wastes for many years. Although the chemical industry has had considerable experience in recovering energy from selected wastes, it generally has had little experience in recovering energy from a mixture of wastes. This paper will identify the significant problems associated with the recovery of energy (as steam) from a mixture of incinerable chemical wastes and propose a program for their definition, evaluation, and resolution.

Identified Problems

When high pressure steam is generated in boilers that utilize the flue gas energy from the incineration of mixed chemical wastes, a number of potential problems must be considered. The following table itemizes the main areas of concern.

Table I

1. Corrosion
    a. Slagging (alkali and heavy metals)
    b. Acid vapors
    c. Free halogens
    d. Fluctuations between oxidizing and reducing conditions
    e. Condensation of mineral acids
    f. Frequent shutdowns
2. Erosion
3. Turndown capability
4. Reliability of steam supply

What is the best approach to defining and solving these problems? The standard corrosion engineering technique of placing test coupons in the corrosive medium is inadequate. Applicable corrosion testing techniques require lengthy periods of time, and the results must be interpreted by experienced and specialized personnel. Even under these conditions, the interpretations can be controversial.

The identified problems can be placed in sharper perspective by studying similar problem areas in the operation of coal-fired power plants. Table II provides a comparison of some of the basic parameters.

A study of Table II indicates several sharp differences. First, pulverized coal-fired power plants have been around for about 50 years, and an expected life of 20 to 30 years is not uncommon. On the other hand, no history of experience is available that would allow us to make an accurate long-range prediction for the life of a chemical waste incinerator energy recovery unit, since the experience in this area is less than 10 years.

It is common practice for a power plant to be designed for an on-stream time of 93 to 95%. On-stream time in a sophisticated chemical waste incinerator energy recovery system will be about 85-90% due to the cumulative downtime requirements of the waste handling equipment, primary and secondary combustion chambers, the steam generating equipment, and the gas cleaning system.

The capacities of coal-fired power plants can range from about 136,200 kg/hr (300,000 lb/hr) steam up to 4,540,000 kg/hr (10,000,000 lb/hr). In general, steam generation from a chemical incinerator will range from 6,810 to 34,050 kg/hr (15,000 to 75,000 lb/hr). The corresponding flue gas volumes are also shown in Table II.

Particulate grain loading for the coal-fired steam plant is somewhat higher than for a chemical waste incinerator. However, in many cases the composition of the particulate can reveal significant differences between a coal-fired power plant and a chemical incinerator as is shown in Table II.

In general, the particulate from a chemical waste incinerator will be much higher in alkali and heavy metals and generally lower in the relatively inert oxides of Si, Al, and Fe. Although the particulates are expressed in terms of alkali and other metal oxides, they may initially be present as salts, such as chlorides. The partial breakdown to the oxides may occur during incineration to form HCl vapor due to the reaction of the salts with water vapor. The alkali metal oxides and salts have lower melting points than the Si and Al oxides and can form eutectics which further reduce the melting point. The low melting particulates and the HCl that can be evolved from the high temperature oxidation of the metal chlorides can form potentially corrosive coatings that create problems not present in coal firing.

In addition, many chemical wastes will contain organic chlorides which form HCl upon combustion. The effect of various concentrations of HCl on boiler tube corrosion needs to be seriously considered. Very little HCl is present in the flue gas from power plants since coal or fuel oils to not contain significant amounts of chlorinated organic compounds.

Finally, it should be noted that flue gases from chemical incinerators can contain small amounts of free halogens, such as chlorine. Chlorine vapor, a very strong oxidizing agent at elevated temperatures, would add to the corrosivity of the flue gas.

In summary, there are several problems of primary concern in the recovery of energy from chemical waste incinerators that are not significant problems in power generation. These unique problems are listed below:

1. Potentially corrosive and low-melting slag, composed of metal salts and oxides, capable of generating HCl vapor at high temperature by the following general equilibrium reaction:

$$\text{Metal chloride} + H_2O(v) \rightleftharpoons \text{Metal oxide} + 2HCl(v)$$

2. Hydrogen chloride vapor produced from the combustion of chlorinated organics

3. Free chlorine produced due to lack of available hydrogen or the following equilibrium reaction:

$$2HCl + 1/2\ O_2 \rightleftharpoons Cl_2 + H_2O$$

Problems of erosion, flame impingement, and condensation corrosion must also be considered but are similar to problems present in power plant operations.

Recommended Program

The best source of problem identification and definition information, at this point, is the data from operating waste chemical incinerators, although relatively few exist.

Following are areas of primary concern in the evaluation and design of an energy recovery system for a chemical waste incinerator:

1. Attention should be given to the optimum design of the initial section of the boiler to maximize the removal of corrosive slag forming inorganic vapors and particulates prior to contact with the metal portions of the boiler heat transfer surface. The problem becomes complex when economic factors such as additional revision costs versus low boiler capacity are considered, along with the fact

that off-the-shelf units, which may not be readily amenable to design modifications, may be used. Also, the additional space requirements may be a limiting factor in some installations.

2. Heat transfer corrosion rate as a function of heat transfer surface operating temperatures would be very useful design data. Economic and feasibility studies should be conducted to establish the optimum boiler design conditions by balancing the energy level requirements with the useful life of a chemical waste heat boiler operating over a range of duty conditions.

   For example, at the relatively low heat transfer surface temperature of 478°K (400°F), a steam pressure of 1721 kPa (235 psig) can be produced. This pressure level is high enough to satisfy many process energy requirements in the chemical industry while drastically reducing the severity of temperature-related corrosion. High pressure superheated steam, required for the economical generation of electricity, is not needed for most process steam requirements.

3. The effect of boiler feed water quality standards on the corrosion rate and life of a waste heat boiler should be studied. High quality feed water will minimize internal deposits on the steam side of the boiler and reduce metal wall temperatures which should result in reduced corrosion.

4. The corrosivity of HCl vapor on boiler surfaces needs additional study. The corrosive action of HCl appears to be variable and influenced substantially by the presence, composition, and physical state of the ash deposit on the heat transfer surface.

5. The effect of low concentrations of free chlorine on heat transfer surfaces needs further definition. The prime area of concern is for the equilibrium quantities of chlorine formed during the combustion of chlorinated organics.

Operating chemical waste incinerators, both in this country and abroad, provide an excellent source of information to aid in the solution of these problems. Although there are only a small number of chemical waste energy recovery incinerators in operation, their operation should be studied relative to types of materials being incinerated, heat recovery design, maintenance performance, and the general achievement of design objectives. Both successful and troublesome installations should be examined in order to document the actual reasons for success or failure.

Finally, the energy recovery experience in other process industries, such as the pulp and paper industry and the metallurgical industry, should be examined. These industries have been recovering energy from their unique waste materials and may have had to solve one or more of the key problems that were identified above.

TABLE II

COMPARISON OF OPERATING PARAMETERS
FOR A CHEMICAL WASTE INCINERATOR
AND A COAL-FIRED POWER PLANT

Parameter	Coal-Fired Power Plant	Chemical Waste Incinerator
Expected Life	20 years reliable service (can go to 25 years or more)	gerater than 10 years
System Reliability	93-95% (for new boiler) 87% (20 years old boiler)	85-90% expected
Capacity (lb/hr steam)	custom design for process use - 300,000 to 600,000 large power plants - 1,000,000 to 10,000,000	15,000 to 75,000
Flue Gas (ACFM) Volume	150,000 to 5,000,000	20,000 to 100,000
Particulate Concentration (grains/scf)	2-8	1-4
Composition of Particulate	refer to Table III	refer to Table III
Acid Gas Concentrations (ppm)		
HCl	Nil	100 to 10,000
SO_2	up to 3,000	100 to 1,000
Free halogen (ppm Cl_2)	Nil	Nil to 100

Conversion Factor: (lb/hr) = 0.454 (kg/hr)
(ACFM) = 0.0283 (actual m^3/M)
(gr/SCF) = 2.3 (g/m^3)

TABLE III

Constituents of Ash	Illinois Coal Ash Composition (wt %)	Chemical Incineration Ash Composition* (wt %)
SiO_2	37.4	31
Al_2O_3	15.3	6
Fe_2O_3	20.8	4
TiO_2	1.0	--
CaO	5.2	--
MgO	0.9	--
Na_2O	3.8	18
K_2O	2.7	3
SO_3	9.6	15
Chloride	--	11
Not determined	3.3	12

* highly variable