

**AN EXPERIMENTAL INVESTIGATION OF THE REACTION OF HYDROGEN CHLORIDE
WITH LEAD OXIDE UNDER SIMULATED HAZARDOUS WASTE INCINERATION CONDITIONS**

Joel T. Shor
Chemical Technology Division
Oak Ridge National Laboratory*
P.O. Box 2008
Oak Ridge, Tennessee 37831-6495

George C. Frazier
University of Tennessee
Knoxville, Tennessee

Submitted for Presentation at
Western States Section/The Combustion Institute
1996 Spring Meeting
Arizona State University, Tempe, Arizona
March 11-12, 1996

"The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC05-96OR22464. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes."

*Research sponsored by the Office of Technology Development, U.S. Department of Energy.

**AN EXPERIMENTAL INVESTIGATION OF THE REACTION OF HYDROGEN CHLORIDE
WITH LEAD OXIDE UNDER SIMULATED HAZARDOUS WASTE INCINERATION CONDITIONS**

J. T. Shor
Chemical Technology Division
Oak Ridge National Laboratory*
P.O. Box 2008
Oak Ridge, Tennessee 37831-6495

George C. Frazier
University of Tennessee
Knoxville, Tennessee

ABSTRACT

To simulate the behavior of lead during hazardous waste incineration, pellets of sintered lead oxide were treated with hydrogen chloride at concentrations of 2000 and 4000 ppm in air in a laboratory tube furnace. The chemical reaction kinetics and mass transfer properties of the solid-gas and solid-liquid reactions were examined at temperatures between 260 and 680°C. Lead dichloride was found to form and became more volatile at elevated temperatures. At temperatures above 300°C, chemical reaction kinetic limitations were absent and mass transfer resistance in the developing liquid lead oxide, lead dichloride eutectic phases were controlling. Above 590°C, a curious anomaly occurred: The observed global reaction rate appeared to increase slightly while the volatilization of lead dichloride dropped during the initial stages of the reaction. A thick film of a lead oxychloride compound was found which displayed low lead dichloride activity. Below 590°C, a different lead oxychloride compound was identified by x-ray diffraction in which lead dichloride activity was high, and this compound was much more volatile than the oxychloride formed above 590°C.

*Managed by Lockheed Martin Energy Research Corp. for the U.S. Department of Energy under contract DE-AC05-96OR22464.

INTRODUCTION

The incineration of wastes has been growing in the United States during the last 15 years since regulations concerning land disposal of wastes have become more strict. Incineration has the advantages of reducing volume (particularly useful with radioactive materials) and detoxifying waste. At Lockheed Martin Energy Systems in Oak Ridge, Tennessee, where mixed (hazardous and radioactive) waste is incinerated, an air test conducted in 1988 indicated elevated levels of metal emissions, and a development program was then begun to investigate the causes of the emissions.¹ Incinerators were then usually designed to destroy primarily toxic organic materials, and less attention was given to preventing the release of toxic metals via stack gases. This current investigation, an outgrowth of concern in Oak Ridge and elsewhere,² is an effort to elucidate the origin of metal emissions from incinerator kilns. Many approaches to this question have followed thermodynamic lines of reasoning. This current investigation is primarily a study of the kinetics of metal pollutant formation. The focus herein is on the fundamental mechanisms of formation and mass transfer inside a simulated incinerator kiln. The efficiency and function of scrubbing equipment are not considered here except to the extent that it is assumed that particulates in the submicron range are usually difficult to scrub effectively and cheaply.

Much research has been dedicated to the mineral transformations and emissions from coal combustors, and more recently investigations of metal emissions from incinerators have appeared in the literature. A general consensus from these works is that metals, if volatilized in the high-temperature regions of the processes, will nucleate homogeneously and form fine fumes or heterogeneously and preferentially concentrate on the finer fraction of already existing particulates as the combustion or incineration gases are quenched.

Hazardous waste is characterized frequently by the presence of halogenated organic compounds which upon combustion render chlorine in the form of hydrogen chloride.³ The U.S. Environmental Protection Agency (EPA) regulations also recognize the predominant form of chlorine as hydrogen chloride (HCl) and restrict its stack emissions to 1% of the amount entering the scrubber system. Incineration research⁴ has reached a qualitative conclusion that the quantities of certain hazardous metals such as lead, cadmium, and bismuth leaving the combustion chamber rose with increasing chlorine (as chlorinated organic compounds) in the solid feed materials to the incinerator. Also observed were shifts in the particle size distributions toward a smaller average aerodynamic diameter with increasing chlorine-concentration. Volatilities of lead in chlorine-containing feeds were more difficult to predict. In two sets of experiments, under ostensibly the same conditions, lead compounds exited the combustion chamber in proportions of 20 and 80% feed basis.⁵ Laboratory-scale incineration experimentation (which assumed lead emissions to occur as the dichloride) has attracted considerable attention.⁶⁻⁸ Thermodynamic calculations of lead dichloride and tetrachloride formation have not agreed with experimental results in certain instances.⁷

In previous experimentation, little attention was directed to the formation of lead dichloride (PbCl_2) and the subsequent production of fine fume under simulated incineration conditions. PbCl_2 has been assumed to form very rapidly, and techniques have been under development to scrub lead as the dichloride from flue gases. The very natural question arises whether lead dichloride actually

does form from PbO and HCl, as assumed, and, if so, at what rates. If the kinetics of PbCl₂ formation can be determined, can techniques be devised to inhibit or minimize its formation if it is the compound which is indeed leading to stack emissions? This paper addresses those questions, and subsequent theoretical analysis of the experimental results will be presented herein.

METHODS AND MATERIALS

Reagent-grade PbO, in the lithange or tetragonal, massicot allotropic form, was sintered in a special process using nickel molds to produce cylindrical pellets having a surface area of 0.84 m²/g and a porosity of 0.18 as determined by mercury porosimetry. The sample pellets were hung using a platinum wire from an on-line balance which recorded the changes in pellet weight in real time as they were subjected to the HCl atmosphere. The experimental apparatus and arrangement is shown in Fig. 1. HCl gas was mixed with air (or inert gas) and allowed to flow up through a quartz packing (to even the flow and equilibrate the temperature) in a vertical electrical resistance tube furnace which served as the simulated incinerator. The balance chamber was purged with air to prevent corrosion of the mechanism. A filter was used to collect fine particulates which were formed as a result of the hydrochloridation reaction, and two packed bed bubblers were used to scrub the acidic gas which left the apparatus.

At low temperature, in the absence of any product volatilization, the reaction rate could be determined directly from the thermogravimetric weight gain observed during the hydrochloridation. At higher temperature, at which point volatilization and reaction proceeded at significant rates, the global reaction rate was determined by first ending the hydrochloridation flow, and then raising the temperature of the sample to 700°C. At 700°C, it was found from experience that the PbCl₂ formed during the course of the hydrochloridation volatilized over a period of 24 h to completion without appreciable loss of PbO. Because the original and final weights of the pellet were known, the total average extent of reaction could be calculated assuming all lead volatilized was lost as PbCl₂. As a matter of practice, no other forms of volatile lead were ever found. The average quantity of lead volatilizing during a reaction could also be determined in this way.

EXPERIMENTAL FINDINGS

Hydrochloridation of lead oxide pellets was performed at 2000 and 4000 ppm HCl in air at laminar flow conditions ($N_{Re}=5$) at temperatures between 250 and 700°C. The global hydrochloridation rates (during generally a 60-min reaction) are shown in Figs. 2 and 3. These results and the morphological changes in the pellets during the reaction suggest that broadly four different regimes of hydrochloridation behavior may be identified. Between 260 and approximately 320°C, which we call Regime 1, the global reaction rate rose rapidly with respect to temperature. Between 320 and 450°C, which we call Regime 2, the global reaction rate changed little, and few differences were observed in the pellet morphology. Between 450 and 600°C, which we call Regime 3, the

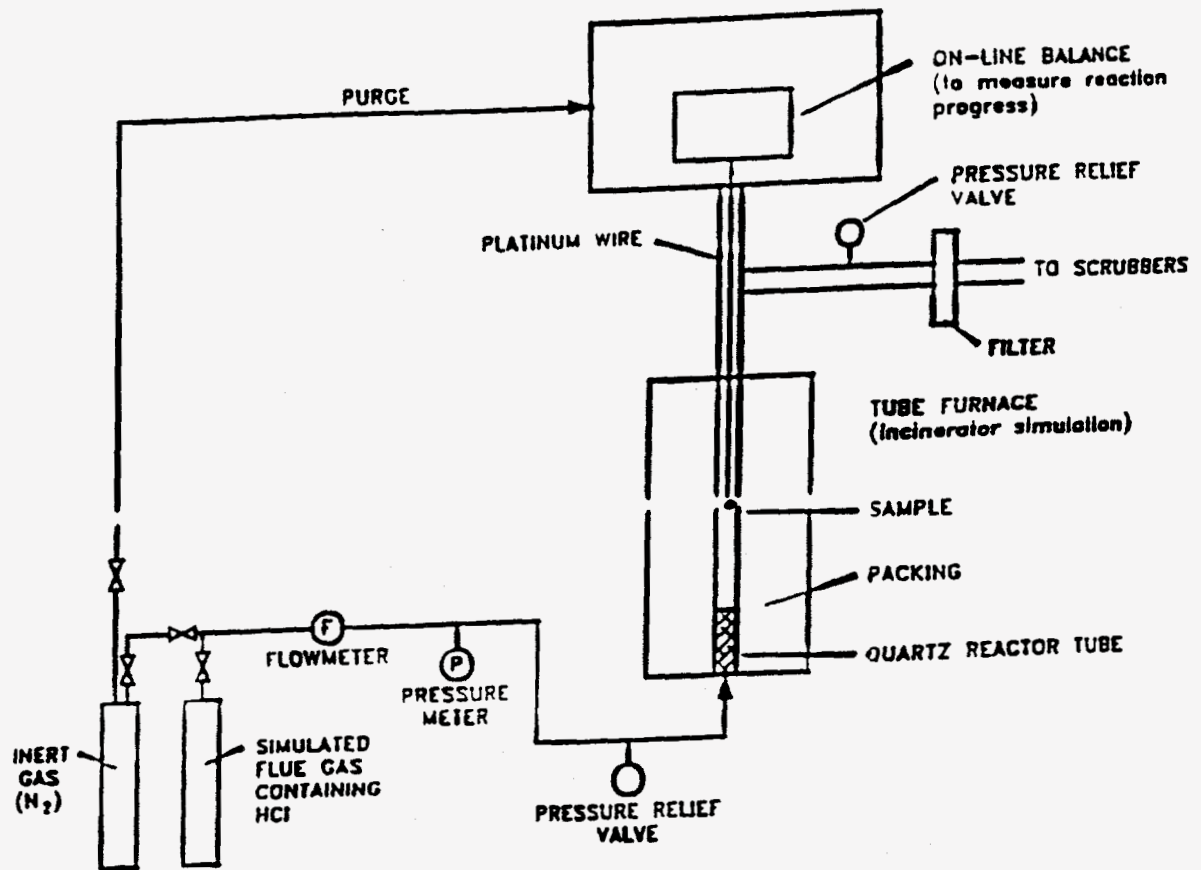


Fig 1. Vertical furnace experimental apparatus with on-line data collection.

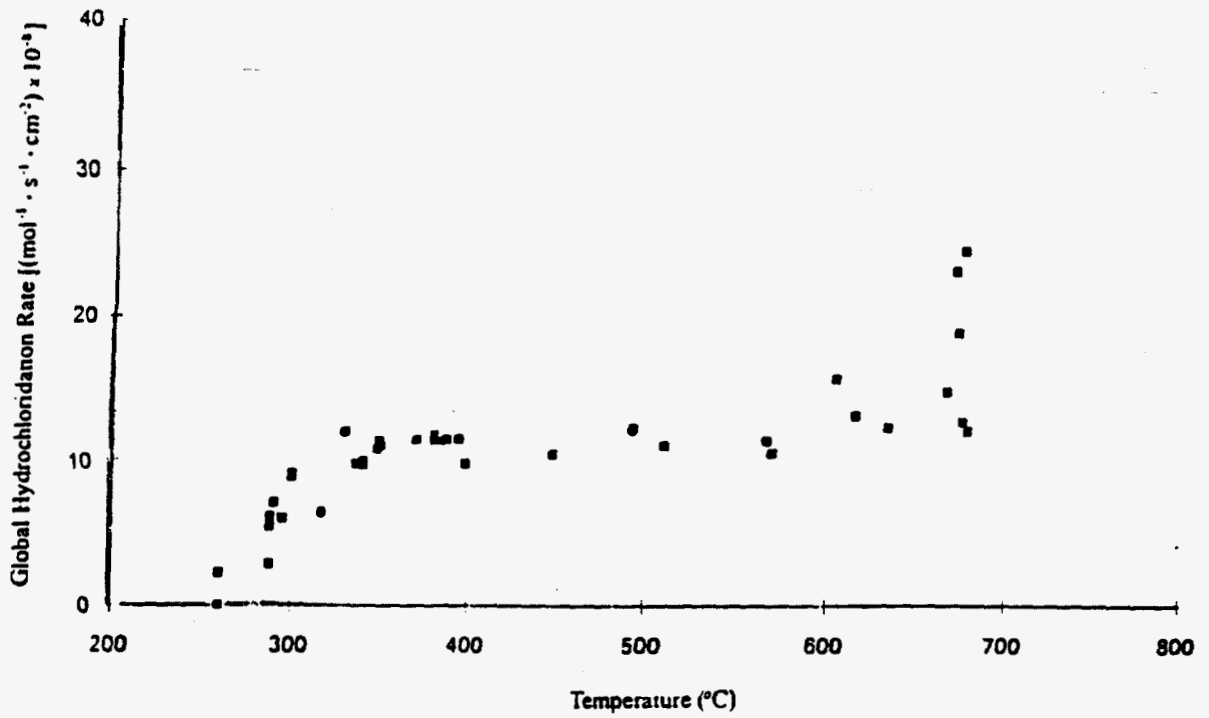


Fig 2. Global hydrochlorination reaction rates vs temperatures, 2000 ppm HCl.

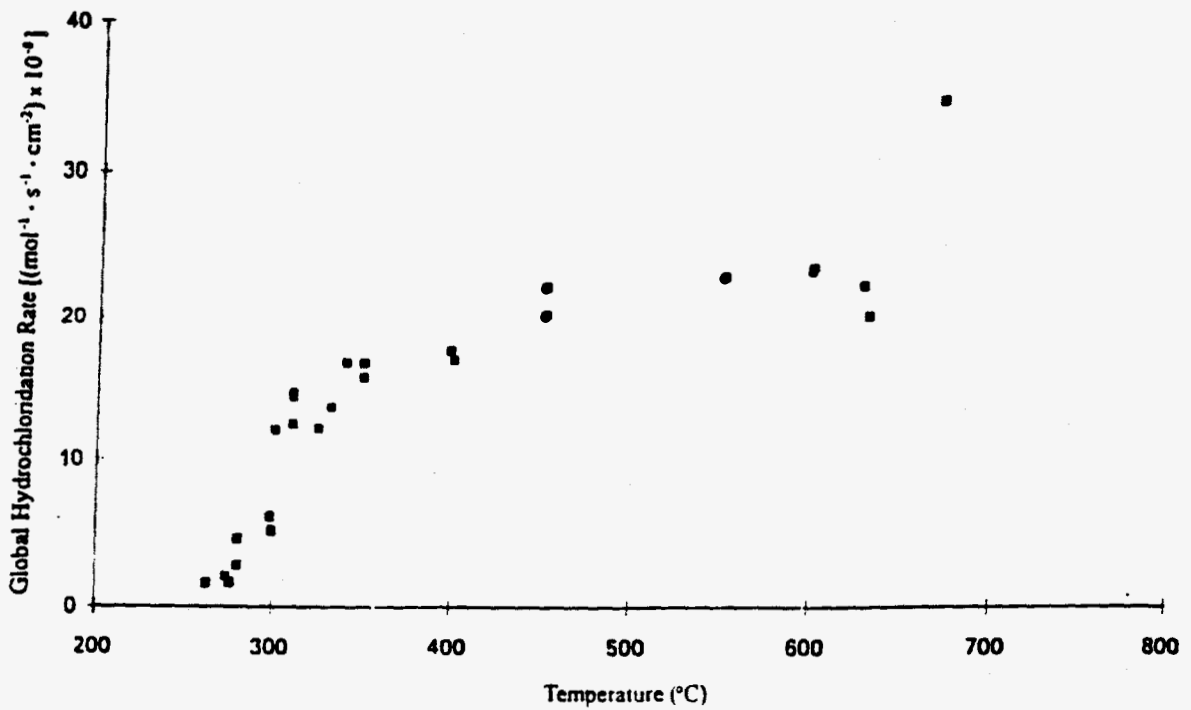


Fig 3. Global hydrochlorination reaction rates vs temperatures, 4000 ppm HCl.

global reaction rate again varied little, but PbCl_2 volatilization became significant, and the pellet morphology changed substantially. From 600 to 690°C, which we call Regime 4, we observed changes in the PbCl_2 volatilization and hydrochloridation reaction rates as well as important physical changes in the pellets.

REGIME 1

Thermograms of total weight gain with respect to time, normalized to the superficial surface area of the pellets, are shown in Figs. 4 and 5. These results were obtained at 2000 ppm HCl and demonstrate the strong tendency of the thermograms obtained in this temperature range to reach a plateau with respect to time. As the temperature is raised, the thermograms became more nearly linear and do not plateau to the same extent with respect to time, as shown in Fig. 6, generated at 300°C. A least-squares fit of the log of the global reaction rates vs the inverse absolute temperature revealed an activation energy of 22 kcal/mol with an R^2 of 0.84.

REGIME 2

In Regime 2, the appearance of the thermograms varied little and generally resembled Fig. 6 quite closely—being fairly linear with respect to time. A slight curvature began to be observed at reaction times in excess of 120 min as is seen in Fig. 7; however, most noteworthy of this regime is a distinct appearance of an ash composed of two layers, as can be seen in Fig. 8, in a sample pellet from which a portion of the ash has been scraped away. An x-ray microdiffraction pattern, Fig. 9 (obtained using a fiber optic wave guide which made possible the observation of the thin layer of the dark ash) revealed the likely presence of Laurionite, PbOHCl , which formed as an intermediate compound to the final formation of PbCl_2 . An intermediate compound may have formed at lower temperatures as well; however, it was not so clearly visible as it was at this temperature and concentration of HCl.

REGIME 3

As the temperature was raised past 450°C, a liquid reaction product formed at the pellet surface, as would be anticipated based on the $\text{PbO} - \text{PbCl}_2$ phase diagram, which indicates a eutectic near this temperature. The thermograms, instead of indicating a linear weight gain with respect to time, now indicated a weight loss which increased in steepness with respect to temperature. Figure 10 shows the typical appearance of a thermogram in this regime. It will be noted that there was a brief period, perhaps 5 minutes, before the sample began to volatilize lead dichloride and lose weight. Polished cross sections of pellets produced in this regime were prepared, and, as seen in Fig. 11, a very thin layer of ash was revealed. Further magnification and x-ray fluorescence analysis of this specimen indicated an ash thickness of 20 microns. X-ray microdiffraction of surface ash formed in this regime revealed the presence of a second lead oxychloride compound, possibly Mendipite, $\text{Pb}_3\text{O}_2\text{Cl}_2$. It can not be stated with certainty since we were observing at ambient temperature a sample prepared at high temperature and which appeared somewhat fused at temperature. Samples of the volatile fume which was formed in this regime were analyzed and found to consist of lead and chlorine in stoichiometric proportions of PbCl_2 .

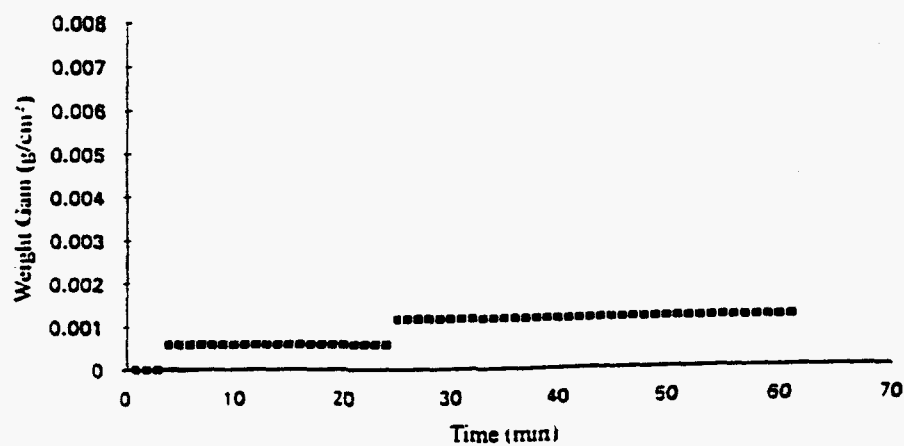


Fig 4. Thermogram of Run 326: T = 260°C, 2000 ppm HCl.

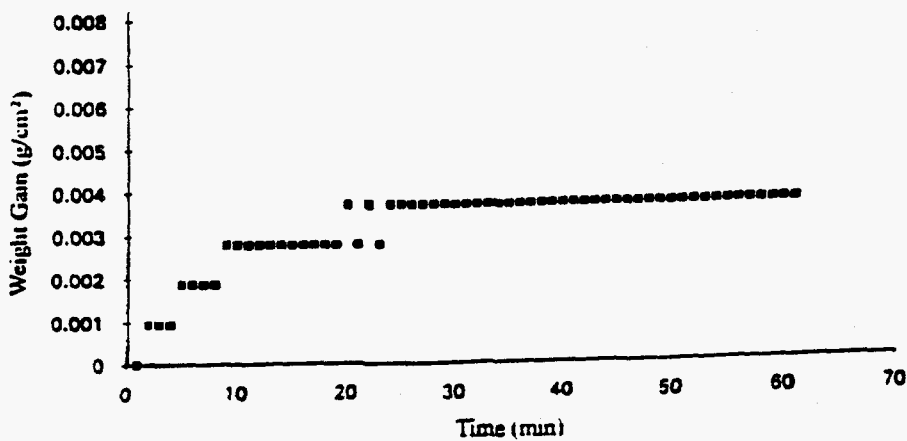


Fig. 5. Thermogram of Run 328: T = 280°C, 2000 ppm HCl.

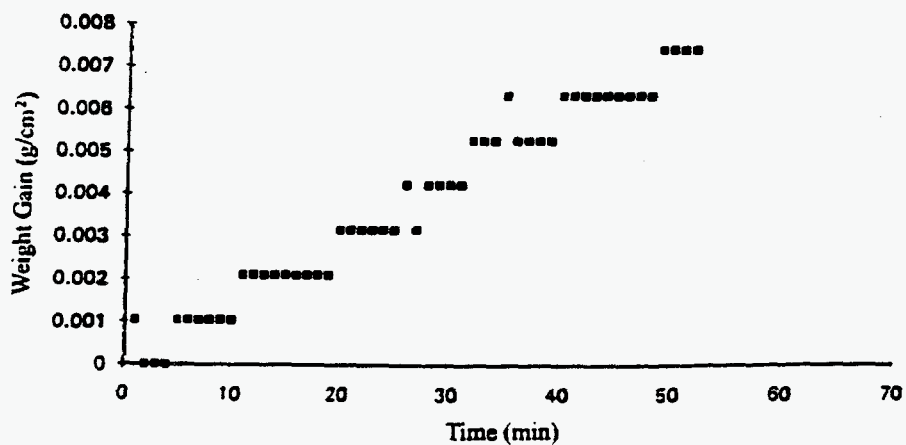


Fig 6. Thermogram of Run 323: T = 300°C, 2000 ppm HCl.

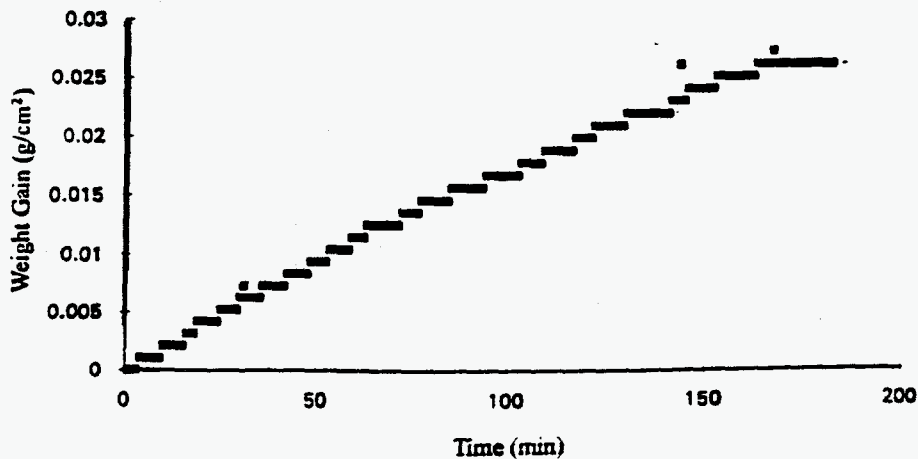


Fig 7. Thermogram of Run 187: T = 370°C, 2000 ppm HCl.

ORNL DWG 96-3509



Fig 8. Photograph of pellet from Run 306: $T = 328^{\circ}\text{C}$, 4000 pm HCl.

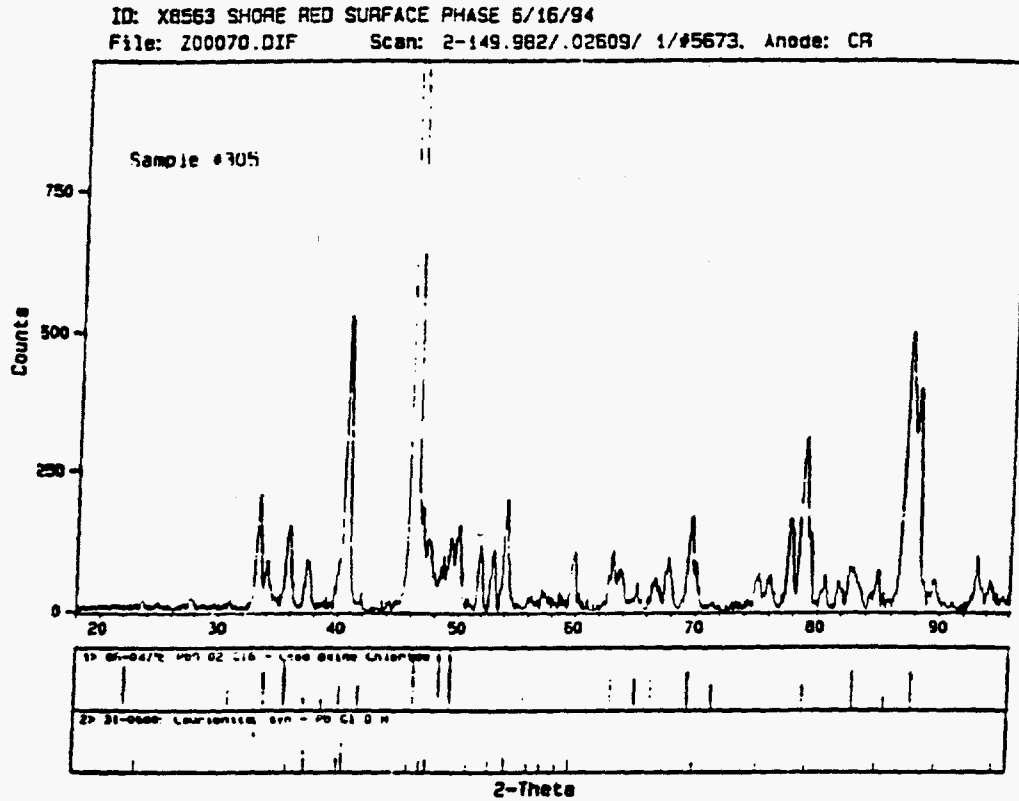


Fig. 9. Powder x-ray microdiffraction pattern of pellet from Run 305: T = 325°C, 72 min, 4000 ppm HCl, grey layer, indicating presence of Laurionite.

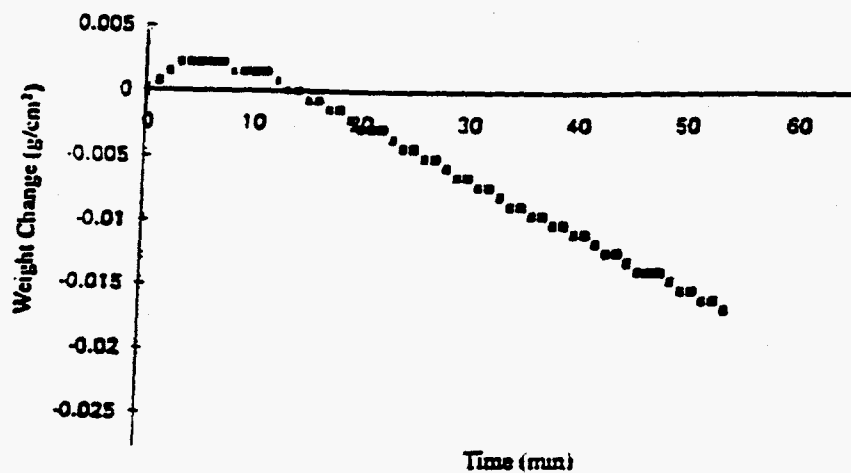


Fig. 10. Thermogram of Run 228: T = 550°C, 2000 ppm HCl.

ORNL DWG 96-3512



Fig. 11. Light micrograph (100x) of cross section of pellet from Run 228: $T = 555^{\circ}\text{C}$, 66 min, 2000 ppm HCl.

REGIME 4

At temperatures above 590°C, the hydrochloridation behavior changed dramatically, as evidenced in the morphology of the pellets and their thermogravimetric behavior. This has interesting implications concerning the incineration of lead-containing wastes. As seen in Fig. 12, the very brief initial rise which we observed at 550°C now rose to a large and substantial initial weight gain. During this initial period, as seen in Fig. 13, a thick ash layer was formed which x-ray fluorescent analysis revealed to contain substantial concentrations of chloride. A third lead-oxychloride compound ($\text{Pb}_2\text{O}_2\text{Cl}$, unnamed) was revealed by x-ray diffraction. Further thermogravimetric analysis of samples in this regime revealed that during the initial weight-gain period of this reaction in Regime 4, the volatilization of PbCl_2 was quite small, and at some times, volatilization was not detectable, as indicated by data in Table 1. As the reaction time was increased at temperatures above 630°C, the extent of PbCl_2 volatilization increased eventually reaching a level similar to that observed in Regime 3. In Regime 4, after approximately 60 minutes, the volatilization rate of PbCl_2 approached that observed in Regime 3; at this point the particle surface was fairly liquid as in Regime 3. In Regime 3, the volatilization rates remained uniformly high and followed approximately the rate of the rise in the vapor-pressure of PbCl_2 until gas phase diffusing resistance likely becomes controlling.

CONCLUSION

At low temperatures in Regime 1, the existence of an activation energy of 22 kcal/mol suggests that we were observing chemical kinetic phenomena. The small differences in the global reaction rates at 2000 and 4000 ppm HCl at temperatures below 300°C may indicate that the reaction is zero order at these conditions and that surface saturation exists. As the temperature was raised between 320 and 600°C, the 4000-ppm concentration of HCl produces a reaction rate almost precisely double that at 2000 ppm. Even the appearance of a distinctly liquid ash layer in Regime 3, occasionally yielding drips, appeared to affect little the global reaction constants through temperatures up to the range of 600°C. This very small rise over a large range of temperatures is consistent with the hypothesis that diffusive resistance is dominant; its energy of activation is generally low. In Regime 4 at temperatures greater than 600°C, the situation became more complex and a very thick layer of ash of a somewhat glassy character was encountered. During the first hour of the reaction, the ash could not be described as liquid because it had very little tendency to drip during that time and because the pellets, when quenched in this state, appeared only slightly deformed from their original appearance, as if the rough edges had been smoothed. This suggests a sintering phenomenon. As the reaction progresses, the concentration of PbCl_2 near the surface of the pellet grew and PbCl_2 began to volatilize at rates similar to those observed in Regime 3 at temperatures of 550°C.

The existence of a temperature regime, Regime 4, in which volatilization of PbCl_2 can be minimized during a period of time has interesting implications for the operation of incinerators. It is generally believed that from the point of view of minimizing metal volatilization, lower temperatures are always preferred.⁹ This investigation suggests that in the case of lead in chloridizing atmospheres, this belief is not always true. Further experimentation on a pilot scale is recommended to confirm the behavior observed in the laboratory setting and reported herein.

Table 1. PbCl₂ volatilization rates during hydrochloridation reaction, determined by difference

Run	T (°C)	Volatilization rate [10 ⁻⁸ × mol/(cm ² · s)]	Reaction time (min)
173	563	3.95	55
174	670	3.96	153
183	570	4.06	107
198	670	2.15	120
199	670	2.25	120
208	630		30
210	494	1.99	124
217	639	^a	62
219	630	^a	61

^aNil.

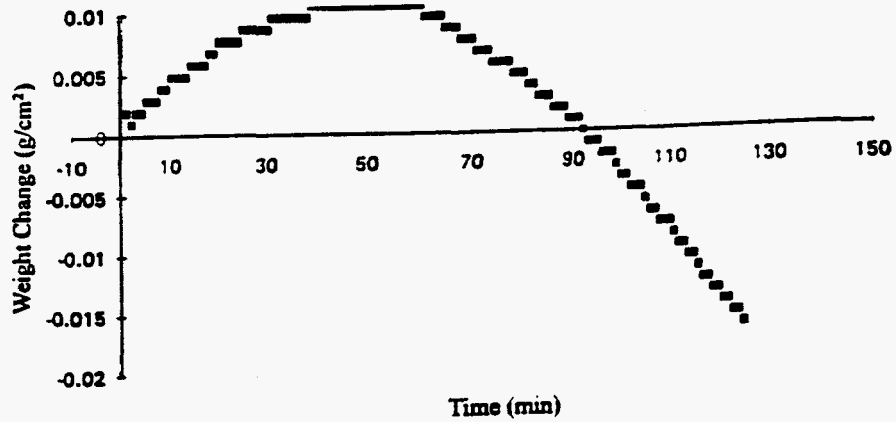


Fig. 12. Thermogram of Run 208: T = 630°C, 2000 ppm HCl.

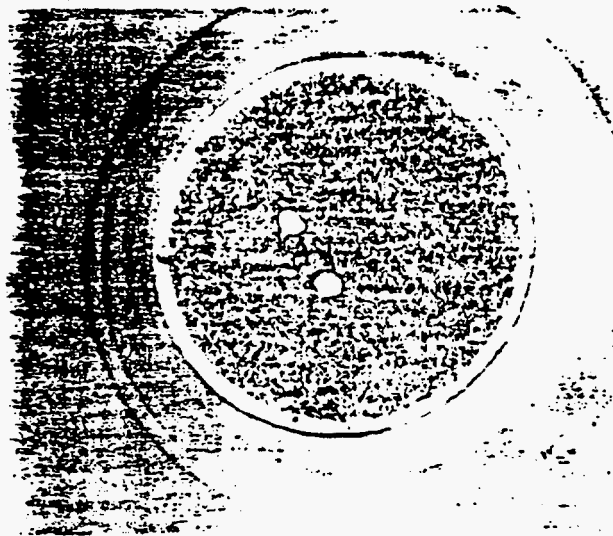


Fig. 13. Polished cross section of pellet from Run 2847: T = at 670°C, 20 min, 2000 ppm HCl.

ACKNOWLEDGMENTS

This research was sponsored by the Office of Technology Development, U.S. Department of Energy, under a contract with the Oak Ridge National Laboratory, which was managed by Martin Marietta Energy Systems, Inc., under Contract DE-AC05-84OR21400 with the U.S. Department of Energy. Gratitude is extended to J. Adcock, J. Begovich, W. Bostick, D. Carpenter, R. Counce, W. Davis, L. Glover, J. Mabon, B. Oliver, S. Singh, and J. Watson, and to Messrs. V. Chua, D. Fielden, P. Hatmaker, F. Holliway, T. Long, and J. Plummer and others too numerous to name, for their generous help without which this project would not have been possible.

LITERATURE CITED

1. ORGDP Report K/SS-521 Technical Evaluation of Lead and Beryllium Emissions for the November 21, 1988 Air Permit Compliance Tests for the K-1435 Toxic Substances Control Act Incinerator, 1989, Martin Marietta Energy Systems, Inc.
2. L. Theodore and J. Reynolds, p. 34 in *Introduction to Hazardous Waste Incineration*, Wiley Interscience, New York, 1987.
3. C. R. Brunner, p. 49 in *Handbook of Hazardous Waste Incinerations*, Tab Books, Blue Ridge Summit, Pennsylvania, 1989.
4. L. R. Waterland, et al., "The Fate of Trace Metals in a Rotary Kiln Incinerator: Tests with Two Different Wet Scrubber Systems," *Proc. Of the Western States Section of the Combustion Institute*, 1991 Fall Meeting, Los Angeles, CA 1991.
5. D. J. Fourier, personal communication to J. Shor, Oak Ridge National Laboratory, Nov. 1991.
6. T. C. Ho, et al., "Metal Capture During Fluidized Bed Incineration of Wastes Contaminated with Lead Chloride," *Combustion Science and Technology*, **85**, 101 (1991).
7. E. Eddings and J. Lightly, "Fundamental Studies of Metal Behavior During Solids Incineration," *Proceedings of the Combustion Institute*, Los Angeles, CA (1991).
8. M. Uberoi and F. Shadman, "Sorbents for Removal of Lead Compounds from Hot Flue Gases," *AICHEJ*, **36**, 2, 307(1990).
9. C. R. Dempsey, and E. I. Oppelt, "Incineration of Hazardous Waste: A Critical Review Update," *Air and Waste*, **43**, 25 (1993).

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.