PERFORMANCE ASSESSMENT OF REFRACTORY SAMPLES IN THE LOS ALAMOS CONTROLLED AIR INCINERATOR

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ABSTRACT

A refractory evaluation project was initiated in 1979 to study the performance of six selected refractory materials within the Los Alamos Controlled Air Incinerator (CAI). Determining refractory resistance to thermal shock, chemical attack, and plutonium uptake was of particular interest. The experimental refractories were subjected to a variety of waste materials, including transuranic (TRU) contaminated wastes, highly chlorinated compounds and alkaline metal salts of perchlorate, chlorate, nitrate and oxylate, over the six year period of this study. Results of this study to date indicate that the use of high alumina, and possibly specialty plastic refractories, is advisable for the lining of incinerators used for the thermal destruction of diverse chemical compounds.

BACKGROUND

The Los Alamos Controlled Air Incinerator was commissioned in the mid-1970s to demonstrate the production-scale volume reduction of transuranic (TRU) combustible solid wastes [1]. The CAI system was selected because the immediate need to solve the TRU waste problem dictated the use of off-the-shelf components wherever possible. In addition, the CAI was chosen over other possible incineration systems due to its flexibility in handling different waste types, ease of combustion rate control and completeness of combustion, and its low generation of particulate emissions. Although originally designed for combustion of solid wastes, the CAI has since been modified, with the addition of a high intensity vortex liquid injection burner, to handle a variety of waste feeds in solid, liquid, and slurry form. At present the Los Alamos system is the only radioactive waste incineration facility in the United States permitted for treating polychlorinated biphenyls (PCBs).

The heart of the CAI process is a commercially available dual-chamber incinerator. The primary chamber is a refractory lined cylinder with an internal diameter of 1.5 meters (4.8 ft) and a length of 1.8 meters (6 ft). The secondary chamber has an i.d. of 1.16 meters (3.8 ft) and is also 1.8 meters (6 ft) long. Combustion gases leave the secondary chamber through a refractory lined crossover duct from which they enter the offgas cleanup system, consisting of a water-spray quench column, a high-energy venturi scrubber for removal of particulates, a packed-column acid gas absorber, offgas condenser, reheater, high efficiency particulate air (HEPA) filters, and an activated carbon bed adsorber. The addition of a gravity ash dropout system (GADOS) allows for semi-continuous ash removal from the incinerator hearth while the unit is in operation. Normal operating temperatures within the primary and secondary chamber are 930°C (1700°F) and 1100°C (2000°F), respectively.

An important objective of the Los Alamos transuranic (TRU), chemical and mixed waste incineration studies is the determination of materials reliability--resistance to chemical attack, thermal stress, and erosion. Of particular interest are the refractory materials within the incinerator chamber and the immediate downstream ductwork. Unfortunately, little published work is available regarding refractory behavior in the demanding environment generated by waste combustion. Accordingly, in August of 1979, a refractory evaluation project was initiated to assess the performance of selected lining materials for the Los Alamos Controlled Air Incinerator with respect to physical degradation, chemical attack, and plutonium uptake. It is hoped that the generation of this refractory data will provide guidance for future design specification and recommendation of the essential lining materials needed to achieve incinerator operation of predictable duration.

Sample Selection and Preparation

Prior to selection and installation of sample refractories for the study, the existing CAI refractory lining was inspected. The "super-duty" fireclay plastic in service appeared to have been adequate for the exposure and operating conditions to which it had been subjected. Feed to the incinerator up to that time had consisted of a combination of combustible materials simulating anticipated Department of Energy (DOE) contractor facility typical waste compositions, as shown in Table I.

TABLE I

Design Basis Incineration Feed

Component	Wt%
Paper and rags	35
Plastics	
Polyethylene	23
Polyvinylchloride (PVC)	12
Rubber	30
Total	100

There were some signs of rough, poorly filled out regions in the existing lining that could offer increased surface area for enhanced chemical attack and physical wear. This was most likely due to poor installation practices rather than actual degradational effects due to incinerator operating conditions [2].

The effective service temperature of a refractory can be significantly lowered by the presence of certain contaminants, e.g. chlorides, sulfates, sulfur containing materials and molten metals [3]. In anticipation of more severe operating conditions in the future, particularly the possibility of higher chloride and alkali content in feed materials, a variety of refractories was considered for testing. With the assistance of Dr. C. E. Semler of the Refractories Research Center, Ohio State University, six refractory materials of varying quality were chosen for comparison studies (Table II). The selected refractories ranged in composition from a "super-duty" fireclay plastic similar to that already in use for the CAI lining to a very high purity alumina castable, and included some high quality specialty refractories of varying composition. Both of the castable samples were also prepared with either 302 or 310 stainless steel fiber inclusions to assess their effect on structural integrity. In addition to the six refractory materials and the stainless steel fiber inclusions, two coating materials, Mulset BF and Tasil 101, were selected for testing in the lower chamber hearth area. All samples appeared both with and without surface coating [4].

TABLE II

Refractory Sample Material Composition

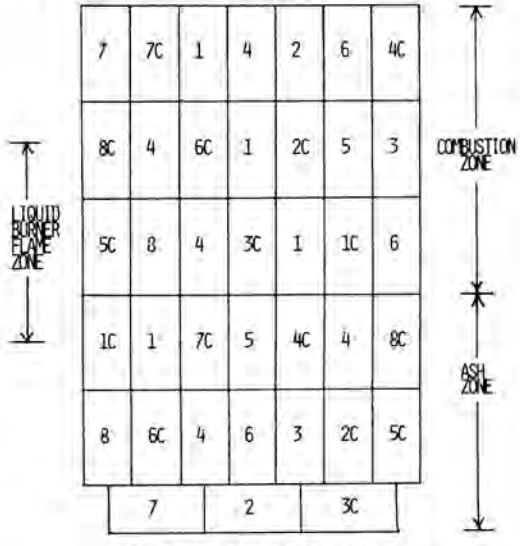
Sample Number	Type	Major Constituents
1	Super-Duty Fireclay Plastic	45% Al_2O_3, 50% SiO_2, 1.5% Fe_2O_3, 2% TiO_2
2	Phosphate-bonded Plastic	87% Al_2O_3, 2.5% SiO_2, 10% Cr_2O_3
3	Plastic	73% Al_2O_3, 22% SiO_2, 2.5% TiO_2, 1.5% Fe_2O_3
4	Dense Fireclay Castable	55% Al_2O_3, 36% SiO_2, 3% CaO, 2% TiO_2
5	Dense Fireclay Castable	Same as #4 with 302 SS Fiber
6	Hydraulic Setting Castable	96.5% Al_2O_3, 2.7% CaO
7	Hydraulic Setting Castable	Same as #6 with 310 SS Fiber
8	Chemical Bond Mullite Plastic	68% Al_2O_3, 26% SiO_2, 1.7% TiO_2, 2.5% P_2O_5

Coating Number	Material	Used on Sample Numbers
1	Mulset BF	1, 3, 4, 5, 6, 8
2	Tasil 101	2, 7

To obtain representative data on refractory performance it was necessary to place the refractory samples within the incinerator so that they became an integral part of the refractory lining. To do so, the existing refractory was removed from the hearth area of the lower chamber. The area was then relined with a 5 cm thickness of insulating board and a dense fireclay was used to pour a flat floor surface, to permit installation of a continuous brick floor for the hearth area.

Samples were prepared as 23 cm by 11.4 cm bricks approximately 12.7 cm thick. Plastics were rammed into molds using an air hammer with a 5 cm by 5 cm ram. Castables were dry-mixed in 136 kg batches in a cement mixer to assure uniformity, then wet-mixed in a Hobart blender and cast into molds on a vibrating table to assure proper filling of the molds. Samples containing the stainless steel fibers were weighed to produce a fiber loading of 64 kg/m^3 based on mixed refractory volume [2], then blended into the wet mix and cast into molds on the vibrating table. Fiber distribution throughout the samples appeared to be good. All samples were pre-fired before installation to achieve dimensional stability and to avoid damage during installation and initial heatup.

For the purpose of sample layout, the hearth was subdivided into two regions, the combustion zone near the feed end of the hearth and an ash zone near the discharge end. Samples were placed randomly within each zone, both with and without surface coating (Fig. 1). The sample bricks were installed using a Mulset refractory mortar. Prior to operational use of the CAI following the sample installation, the temperature was brought up slowly to cure the new refractory and samples in place. This cure consisted of cycles of slow heat-up at a rate of 28°C/hour (50°F/hr) with "soak" periods of 18 hours at 121°C (250°F) and 315°C (600°F), and soaks of 5 hours at 540°C (1000°F) and 870°C (1600°F).



C INDICATES SAMPLE IS COATED

Fig. 1. Lower Chamber Hearth Sample Pattern

Incinerator Operating Conditions

Following completion of their installation in August 1979, and until their removal in November 1985, the samples were subjected to approximately 2000 hours of hot time at temperatures of 870-1100°C (1600-2000°F) and 22 cycles of heat-up and cool-down. As part of incineration studies for various agencies, a wide range of simulated and actual wastes were fed to the CAI during this period. These wastes included simulated fission activation products, pentachlorophenol (PCP)-treated wood, polychlorinated biphenyls (PCBs), ion exchange resins, TRU combustible wastes, and various military smoke and flare compounds (Table III) [5,6,7,8,9,10,11]

TABLE III

Major Composition of Test Program Feed Materials

Test Run	Amount	Major Constituents
FAP-1 & 2	Trace	Cs-137, Co-60, FE-59, I-131, Ru-106
PCB-1	1814 kg	Pentachlorophenol (PCP) treated wood
RS-1	163 kg	Cationic beaded ion exchange resins 95% Hydrocarbons, 5% Sulfur
PCB-1	378 l	PCBs (61% Arochlor 1260, 39% Trichloroenzene)
16-CS1	907 kg	Navy Colored Smoke Compounds: Sugar, $KClO_3$, $Na_2(CO_3)_2$, Organic Dyes
17-CS2	635 kg	Army Colored Smoke Compounds: Sugar, $Na_2(CO_3)_2$, $KClO_3$, $MgCO_3$, ZnO, Al, Hexachloroethane, Organic Dyes
CAI-P-1	1514 l	TRU Contaminated PCBs (1 1/2 g Pu) 33.3% Arochlor 1254, 19.2% Arochlor 1260, 47.5% Trichlorobenzene)
19-CF-1	272 kg	Navy Colored Flare Compounds: Mg, $KClO_4$, $Na_2C_2O_4$, $Ba(ClO_3)_2$, $Ba(NO_3)_2$, Hexachorobenzene

Plutonium Migration Analysis

Before the samples were removed from the CAI, the hearth was monitored by health physics personnel to check for surface alpha activity and was found to have a uniform count of 10^6 cpm/cm^2. Surface swipes indicated that the activity was fixed within the glass-like glaze covering the surface of the hearth. Upon removal, the samples were nondestructively assayed for presence of plutonium by a passive neutron coincidence count of even-numbered Pu isotopes, using a shuffler in the passive mode as a high efficiency coincidence counter. Results of this assay show the presence of 0.2 gm +/- 50% of Pu-239 for the total hearth area.

A carbide drill was used to drill individual samples from the "cold" side of the brick towards the "hot" side where this surface activity was present. Representative depth samples from each brick were leached in a hot HCL/HNO_3 solution for 48 hours and then analyzed via liquid scintillation techniques to determine the presence of Pu for a gross estimate of variance in Pu uptake by the different sample materials. Results are shown in Table IV for samples taken at a depth of 0.16-0.5 cm from the "hot" side surfaces.

TABLE IV

Results of Pu Penetration Analysis

at Depth of 0.16-0.5 cm

Sample Number	Pu Count	Comments
1	24 +/- 12 ng/g	+/- value is 2 std
1C	<17 ng/g	w/in 3 std of background
2	---	Unable to sample
2C	---	Unable to sample
3	<10 ng/g	w/in 3 std of background
3C	8.6 +/- 4.4 ng/g	+/- value is 2 std
4	<13 ng/g	w/in 3 std of background
4C	<17 ng/g	w/in 3 std of background
5	---	Unable to sample
5C	---	Unable to sample
6	<10 ng/g	w/in 3 std of background
6C	<6 ng/g	w/in 3 std of background
7	---	Unable to sample
7C	---	Unable to sample
8	11 +/- 7 ng/g	+/- is 2 std
8C	5 ng/g	w/in 3 std of background

In most cases count rates were within 3 standard deviations of background levels and had to be reported as "less than" values-i.e., quantifiable levels of Pu in the samples could not be determined with any degree of accuracy. Bricks 5, 5C, 7 and 7C were so severely degraded upon removal from the hearth that representative depth samples were impossible to obtain. Bricks 2 and 2C were extremely tough and were unable to be drilled to obtain samples for analysis by this method. The three bricks which did show some evidence of plutonium uptake were all located in adjacent areas of the hearth at the interface of the combustion and ash zone (Fig. 1). As this is the area upon which the flame from the liquid burner impinges, it would be tempting to assume that some correlation exists.

However, samples 1C and 4 also came from this same area of the hearth and showed no significant levels of Pu. Conclusions as to the relative difference in resistance to Pu uptake are further complicated by two factors: 1) A large sample population allowing for statistically significant results was not possible, and 2) the glaze covering the sample surfaces, a result of combustion residues from the incineration of ion exchange resins and alkali metal oxides, could well have served to shield the samples from Pu introduced to the CAI during subsequent incinerator runs.

Evaluation of Degradational Effects

The mortar used to cement the sample bricks within the hearth proved to be very tenacious--samples had to be removed using an air chisel. One brick from each row had to be sacrificed to remove the other samples. It was immediately apparent during the removal of the samples that the castable bricks with the stainless steel fiber inclusions were severely degraded. These samples showed a marked tendency to crumble under the shock of being removed from the hearth. The fibers within the matrix showed evidence of chemical and/or thermal attack and the bricks were very friable. This could result either from the lack of a thermal gradient through the sample under operating conditions or to the presence of higher than anticipated acid condensation (chloride) during cooldown [2,12].

The plastic refractories were less subject to breakage when being removed from the hearth, showing greater resistance to mechanical stress. The moderate alumina refractories exhibited an increased tendency to fracture upon removal from the hearth. At least one of the plastics (phosphate bonded 87% Al_2O_3-19% Cr_2O_3) exhibits greater toughness after experiencing the temperatures and thermal cycling of the CAI than it did prior to installation. The specialty plastic refractories with trace element composition (TiO_2, Cr_2O_3, P_2O_5) appear more resistant to abrasion/erosion than the standard fireclay or lower alumina bricks.

CONCLUSIONS

No significant difference in resistance to plutonium uptake in the different samples can be shown. The presence of the glass-like glaze covering the sample surfaces undoubtedly helped shield the samples from greater Pu penetration. This surface glaze may also have protected the samples from greater chemical attack as well as masking differences in resistance between the coated and uncoated bricks. It is apparent, however, that the higher alumina and plastic refractories withstood the CAI environment, and subsequent physical removal from the hearth, better than the moderate alumina samples. This is in agreement with expectations at the outset of the experiment. High alumina refractories exhibit greater resistance to alkali attack than moderate alumina or fireclay types. In the presence of acid condensation, plastics are more resistant, as a rule, than castables. Plastics also exhibit greater resistance to thermal shock than do castables[2]. The use of stainless steel fiber inclusions within the refractory lining is not recommended for incinerators operating at the temperatures of, or burning mixed chemical wastes similar to, the Los Alamos CAI.

Future Plans

Although the Los Alamos CAI was originally conceived and designed for demonstration of incineration feasibility studies, plans now exist for its use for operational scale incineration of TRU, chemical and mixed wastes generated at Los Alamos. In response to our findings in this study, we have decided to replace the existing hearth with the phosphate-bonded alumina-chrome specialty refractory. This refractory shows excellent resistance to both chemical and thermal attack. In addition, it should provide good protection against abrasion that the introduction of noncombustible feed materials could present to the hearth area. Should the remainder of the CAI refractory lining require upgrade in the future, the use of a high alumina castable would afford increased resistance to chemical attack, without the need of the heavier plastic refractory in areas not as subject to erosional effects. It is hoped that this refractory upgrade will substantially extend the life of the CAI. Future plans include detailed chemical and microstructural analyses of samples to provide more in-depth assessment of the degradational effects of the CAI environment of the various refractory types.

REFERENCES

1. A. S. NEULS, W. E. DRAPER, R. A. KOENIG, J. M. NEWMEYER, and C. L. WARNER, "The Los Alamos Controlled Air Incinerator for Radioactive Waste," LA-9427, Vol. I, Los Alamos National Laboratory (1982).

2. C. E. SEMLER, Ohio State University, Ohio State University, personal communication (Feb. 1979).

3. "Refractory," Environmental Control Products Bulletin No. R-1-173, Environmental Control Products, Inc., Charlotte, NC (1972).

4. L. A. STRETZ, "Preparation and Installation of Refractory Samples in the Controlled Air Incinerator," unpublished report, Los Alamos National Laboratory (1979).

5. J. S. VAVRUSKA and L. C. BORDUIN, "Commercial Incineration Demonstration," LA-UR-2308, Los Alamos National Laboratory (1982).

6. L. A. STRETZ and J. S. VAVRUSKA, "Controlled Air Incineration of Pentachlorophenol-Treated Wood," EPA-600/2-84-089, prepared for USEPA Industrial Environmental Research Laboratory, Cincinnati, Ohio, Los Alamos National Laboratory (1984).

7. J. S. VAVRUSKA, "Research Incineration of Polychlorinated Biphenyls at the Los Alamos National Laboratory," unpublished report, Los Alamos National Laboratory (1983).

8. D. G. VANCE and J. S. VAVRUSKA, "Disposal of Ion Exchange Resins by Combustion in the Los Alamos Controlled Air Incinerator," unpublished report, Los Alamos National Laboratory (1982).

9. Treatment Development Facility, Los Alamos National Laboratory, unpublished data (1983).

10. Treatment Development Facility, Los Alamos National Laboratory, unpublished data (1984).

11. Treatment Development Facility, Los Alamos National Laboratory, unpublished data (1985).

12. J. F. WOOLDRIDGE, "Extending Refractory Life, "Modern Casting, 90 (April 1978).