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Project Summary

Laboratory Feasibility Studies for the Fluidized-Bed Combustion of Spent Potlining from Aluminum Reduction

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This study was undertaken with the objective of providing a preliminary assessment of the technical feasibility and environmental acceptability of a fluidized-bed combustion (FBC) process for the disposal of spent potlining waste from the aluminum reduction process. In accomplishing the above, technical efforts were directed to two main areas of laboratory studies: (1) differential thermal analysis experiments to establish the operating temperature range to prevent agglomeration in a FBC process, and (2) fixed-bed combustion experiments to determine cyanide destruction and gaseous emissions expected from a FBC process.

The results from the differential thermal analysis and the fixed-bed combustion experiments indicated that FBC should be limited to temperatures below 760°C due to agglomeration of potlining waste that occurs above that temperature. Analysis of the combustion residues showed that 99.9 to 99.99 percent of cyanide was removed from the potlining and that substantial burning of the carbon in the potlining could be achieved at temperatures as low as 760°C. The results on cyanide removal and carbon combustion are very encouraging and indicate that potential application of a FBC process to the disposal of spent potlining wastes is technically feasible.

A small fraction (0.01-2 percent) of CN^- and a substantial fraction (15-35 percent) of F^- were found in the gaseous effluent from the combustion of potlining. The gaseous emissions, however, can be adequately controlled and should not pose an insurmountable technical barrier in the FBC process. No significant emissions of SO_2 or Na_2O were found during combustion of potlining waste.

Results of the laboratory studies indicate that further investigation of the FBC process, through a pilot-plant scale test program (particularly efforts to prove the operability of a fluidized bed over a range of combustion temperatures to accomplish effective destruction of cyanide in the spent potlining waste), would provide valuable information in this technological area.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Approximately 230,000 tons of spent potlining is generated each year in the production of aluminum metal in the U.S. This discarded carbon potlining material contains significant quantities of aluminum, and sodium metals, aluminum oxides, fluorides of sodium and aluminum, carbides and nitrides of aluminum, and quantities of cyanide which have penetrated the potliners over their 3 to 5 year useful life.

Because of the significant energy, chemical, and environmental implications of the generation and storage of spent potlining, efforts by the aluminum industry have been directed toward developing environmentally sound resource recovery alternatives. In December 1981, The Environmental Committee of the Aluminum Association, Inc. sponsored a workshop on the storage, disposal, and recovery of spent potlining.

Although in July 1980, spent potlining was listed by EPA as a hazardous waste under RCRA, its listing is currently suspended because of relevant court challenges. However, EPA's interest and responsibility in working with concerned groups in addressing the potlining disposal problem remains active.

The scope of this program was to conduct laboratory studies to evaluate the thermal destruction of cyanide in the potlining waste and potential gaseous emissions from FBC of spent potlining. The objective was to assess the technical feasibility and environmental acceptability of the FBC process and provide a basis for recommending and evaluating test plans for follow-up pilot-scale FBC of spent potlining.

Conclusions

The study results have identified agglomeration as a potential problem for a FBC process due to softening or melting of the potlining from the aluminum reduction process during the combustion process. Although the combustion residue (ash) from the potlining could be maintained free flowing without agglomeration at temperatures above 900°C using a kaolin clay as an additive, the potlining itself was observed to agglomerate at temperatures as low as 760°C even with the clay additive. Whether the turbulent mixing obtained in the FBC process could overcome the agglomeration problem appears to be the key technical issue that must be resolved to prove the FBC process for application in spent potlining disposal.

The results from fixed-bed combustion experiments have also indicated that 99.9 to 99.99 percent of the cyanide in the potlining can be removed at 760°C. Small quantities of HCN were found in the gaseous combustion products from fixed-bed combustion tests performed on potlining samples. It is expected that the HCN generated during combustion of potlining waste can be destroyed by providing sufficient gas-phase residence time at combustion temperature in a FBC. No detectable emission of SO_2 was found in the flue gas from combustion of potlining.

A significant evolution of HF has been found from combustion of potlining. Therefore, the flue gas from potlining waste combustion will need to be treated to control HF emission and possibly reclaim the fluoride value.

Results from fixed-bed combustion experiments have indicated that the carbon in potlining waste can be ignited and burned efficiently at temperatures as low as 760°C. The reactivity of the carbon in spent potlining waste appears to be sufficiently high to obtain a high combustion efficiency (>90%) and possibly sustain combustion without an auxiliary fuel in a FBC.

No significant volatilization of Na_2O from possible reactions between potlining and CaO or water vapor was detected at 760°C. Therefore, generation of Na_2O from combustion of potlining and associated slagging and fouling problems are not expected in the FBC process.

Recommendations

Based on the laboratory feasibility studies, a FBC test program should be of value. A major technical issue that could be addressed in such a program would be demonstration of the operation of a fluidized bed over a practical range of temperature to effectively destroy cyanide without bed agglomeration. The target temperature range would be at least 50°C (preferably 100°C) to allow for normal temperature fluctuations and process upsets that can be anticipated in a full-scale FBC unit. The clinkers formed by molten potliner waste are extremely hard, and formation of such clinkers in a fluidized bed by temperature excursions would cause a major shutdown and possibly extensive damage to the refractory in a FBC. If bed agglomeration causes a severe problem in fluidized bed operation, other combustion technologies (e.g., a rotary kiln incinerator) could be considered as an alternative.

Other technical issues that could be addressed in a fluidized-bed test program are:

1. Multiple sampling of the feed and ash during the test program, due to the inhomogeneous nature of potline waste.
2. The use of kaolin clay as an additive to increase combustion temperature to the suggested 600 to 800°C combustion temperature range.
3. Flue gas analysis for HCN and HF emissions to further establish the need for downstream treatment of the flue gas. (The level of HF in the flue gas has an important bearing on possible recovery of fluoride value and waste heat.)
4. Confirmation of cyanide destruction by FBC by leaching tests on the combustion residue.

Results

Laboratory studies were conducted in two parts: (1) differential thermal analyses (DTAs) to establish the operating temperature for the FBC process dictated by ash agglomeration, and (2) fixed-bed combustion experiments to determine cyanide destruction and gaseous emissions at the operating temperature established in the experiments of differential thermal analysis.

Potlining Samples

Potlining samples were supplied by Aluminum Company of America (Alcoa) and Reynolds Metals Company Chemical analyses of the potlining samples are shown in Table 1. Both samples exhibited a strong odor of ammonia, probably produced by hydrolysis reaction between moisture in ambient air and aluminum nitride present The samples contained some coarse (about 1/4-in or 0.635 cm) particles and appeared nonhomogeneous. Therefore, the samples were dumped from the shipping containers, mixed, coned, and split into smaller aliquots by sequential quartering and coning or by using a sample splitter. The head samples prepared in this manner were the 1/32 cut of the Alcoa sample and the 1/128 cut of the Reynolds sample. The head samples were pulverized and stored in sealed containers for use in the DTA studies.

Table 1. *Composition of Potlining Samples*[a]

	Composition, Percent	
	Alcoa	*Reynolds*
C	*28.6*	*42.7*
Al	*14 2*	*4 7*
Si	*4.76*	*0.11*
Fe	*3.23*	*0.27*
Na	*13 9*	*20.0*
F	*18.2*	*17.6*
CN	*0 09*	*0 135*
Al Carbide	*0 46*	*-*
Ash	*68.7*	*57 1*

[a] Analyses provided by Alcoa and Reynolds, except ash analyses performed by Battelle

Differential Thermal Analyses

DTAs were carried out on two potlining samples and the ash samples prepared from the potlining samples. Ash samples were prepared by burning off the combustible matter from the potlining samples in a muffle furnace in ambient air at 750°C to constant residue weight. DTAs were also carried out on mixtures of the potlining ash samples with a reagent-grade calcium oxide or a commercial-grade kaolin clay used as additives. Adding kaolin clay has been shown to be effective in preventing stickiness in fluidized beds containing sodium salts with low melting points. Composition of the clay is given in Table 2. Calcium oxide and a kaolin clay were tested as additives for raising the ash agglomeration temperature.

Table 2. Manufacturer's Data on Kaolin (No. 6 Tile) Clay

Component	*Percent by Weight*
SiO_2	46.9
Al_2O_3	38.2
Fe_2O_3	0.35
TiO_2	1.42
CaO	0.43
MgO	0.58
Na_2O	0.04
Loss on Ignition at 1000°C	13.9

Results from the ash agglomeration tests are presented in Table 3 and summarized below:

- Alcoa potlining ash has higher agglomeration temperature than Reynolds potlining ash.
- Adding CaO has little or no adverse effect on raising ash agglomeration temperature.
- Adding clay significantly increases the ash agglomeration temperature to above 900°C.

Fixed-Bed Combustion Studies

Fixed-bed combustion experiments were performed to determine cyanide destruction and emissions of cyanide and fluoride in the gaseous combustion products. The reactor was a quartz tube, 2 in. ID by 44 in. long (5.08 by 111.76 cm), heated by an electric tubular furnace. The off-gas from the reactor was first cooled in water bath and split into two streams: one stream, directed to an impinger train loaded with 0.1 *N* NaOH solution for collection of HCN and HF, and the other stream, directed to on-line gas analyzers for measurements of CO, CO_2, SO_2, and O_2.

To perform a combustion test, the furnace was preheated to a prescribed temperature. The reactor (loaded with a potlining sample) was inserted into the furnace and quick connections were made on the reactor inlet and outlet ports. Dry combustion air was supplied from a compressed air cylinder. Flue gas compositions were recorded continuously on strip chart recorders. After the test, the combustion residue in the reactor and the liquid collected in the traps were removed to the analytical laboratory for chemical analyses. Parameters investigated in the fixed-bed combustion tests were:

1. Potlining sample quantity: 12 and 75 g.
2. Additives: clay addition at 15 to 87 percent based on ash in the potlining sample, and CaO addition at 87 percent based on ash in the potlining sample.
3. Temperature: 760 to 911°C.
4. Residence Time: 30 and 120 minutes.

A significant finding from the fixed-bed combustion tests was the lower agglomeration temperature of the potlining samples compared with the agglomeration temperatures of the potlining ash samples observed in the prior DTA and ash agglomeration tests. Results of potlining agglomeration observed in the fixed-bed combustion tests are summarized in Table 3. The prior DTA and ash agglomeration tests conducted with clay addition had indicated ash agglomeration temperatures above 900°C for both Alcoa and Reynolds potlining ash samples. The potlining samples in the fixed-bed combustion tests showed agglomeration at temperatures as low as 760°C. One possible cause of agglomeration of potlining is sintering during dehydration of the $Al(OH)_3$ that is formed by hydrolysis of AlN in potlining. For this hypothesis, agglomeration could be avoided in a fluidized bed, since dehydration of $Al(OH)_3$ is commercially practiced in fluidized-bed calciners. However, the probability of the $Al(OH)_3$ sintering process' being the sole cause of agglomeration is remote in view of the complex salts included in the potlining compositions. Therefore, agglomeration of potlining poses a potential problem in a FBC process. Results of the fixed-bed combustion tests on bed agglomeration are, in summary:

1. The Alcoa potlining sample showed greater tendency for agglomeration than the Reynolds potlining sample. (Compare Tests 5 and 9, or Tests 7 and 8.) This behavior of the potlining samples is opposite from that observed with the ash samples in the DTA tests which showed higher agglomeration temperatures for the Alcoa sample compared with the Reynolds sample.
2. Reducing the sample size decreased the apparent extent of agglomeration of potlining. (Compare Tests 4 and 7.) However, even a smaller quantity of test samples showed agglomeration at 760°C (Tests 8 and 9).

Table 3. Summary of Fixed-Bed Combustion Tests on Potlining Samples

	Potlining		*Clay Addition*				
Test	*Type*	*Sample Wt., g*	*Wt., g*	*% of Ash*[a]	*Temperature, °C*	*Residence Time, min*	*Results*
1	*Alcoa*	*75*	*7.5*	*15*	*911*	*30*	*Very severe agglomeration; quartz reactor cracked, apparently caused by fused potlining*
2	*Alcoa*	*75*	*7.5*	*15*	*762*	*120*	*Very severe agglomeration*
3	*Reynolds*	*75*	*7.5*	*17*	*760*	*120*	*Very severe agglomeration*
4	*Reynolds*	*75*	*37.5*	*87*	*762*	*30*	*Very severe agglomeration*
5	*Reynolds*	*12*	*6*	*87*	*760*	*120*	*Slight agglomeration*
6	*Alcoa*	*12*	*4.1*	*50*	*875*	*30*	*Very severe agglomeration*
7	*Reynolds*	*12*	*6*	*87*	*760*	*30*	*Slight agglomeration*
8	*Alcoa*	*12*	*7.2*	*87*	*760*	*30*	*Severe agglomeration*
9	*Alcoa*	*12*	*7.2*	*87*	*760*	*120*	*Severe agglomeration*
10	*Reynolds*	*12*	*6+6(CaO)*	*87+87(CaO)*	*760*	*120*	*Slight agglomeration*
11[b]	*Reynolds*	*12*	*6*	*87*	*760*	*120*	*Slight agglomeration*

[a] *Based on 68.7 percent ash in the Alcoa potlining and 57.1 percent ash in the Reynolds potlining.*
[b] *Combustion air was humidified to approximately 2 percent water vapor concentration.*

Due to the severe agglomeration of the bed that resulted in poor gas/solid contact, the ash residue and impinger train samples that were selected for analysis were chosen from those tests performed during the latter part of the combustion test program in which bed agglomeration was substantially reduced by decreasing the combustion temperature and the amount of potlining sample used. Material balance results describing the fate of cyanide, fluorine, carbon, and sodium during the fixed-bed combustion of potlining were calculated from these sample analysis results.

Tests 5, 7, 8, and 9 were performed to determine cyanide destruction, emissions of cyanide and fluoride in flue gas, and carbon combustion efficiency. Results are:

1. Cyanide was removed from the potlining in the range of 99.9 to 99.99 percent with both Alcoa and Reynolds potlining samples at 760°C and 30 to 120 minutes residence time. Small quantities of cyanide in the range of 0.01 to 2 percent of feed were found in the flue gas. It is expected that a FBC should provide sufficient gas-phase residence time in the bed and in the freeboard to destroy the cyanide evolved as HCN from the potlining.
2. Approximately 20 to 30 percent loss of fluoride from potlining was observed under the conditions employed in the combustion tests. Fluoride collection from the flue gas was measured to be in the range of 0.2 to 8.7 percent. The fluoride unaccounted for was probably lost by reaction with the quartz reactor and other glass surfaces that contacted the flue gas. Nevertheless, the results strongly suggest that a significant fraction of fluoride is generated as HF from potlining during the combustion process. Therefore, flue gas should be treated to control HF emission and possibly recover the fluoride value.
3. Results on carbon balance show approximately 70 to 90 plus percent carbon combustion efficiencies in the combustion tests. The total carbon found in the ash and the flue gas was found to be approximately 25 to 35 percent above the carbon introduced with the potlining, indicating a reasonable closure on the carbon balance. Combustion efficiency in a fluidized bed is expected to be higher due to improved mixing and gas/solid contact in a fluidized bed. Therefore, combustion of potlining in a fluidized bed at temperatures as low as 760°C appears to be feasible.
4. No detectable emission of SO_2 was found in the flue gas from combustion of potlining.

Tests 10 and 11 were performed to determine volatilization of Na_2O by reactions of a potlining sample with CaO and with H_2O vapor. The tests were carried out with the Reynolds potlining sample that has a higher Na content than the Alcoa potlining sample. Test 10 was carried out with CaO addition and dry combustion air. Test 11 was carried out with the combustion air humidified to approximately 2 percent water vapor. Results on sodium balance show essentially no volatilization of Na_2O due either to CaO or H_2O vapor under the conditions employed in the combustion tests.

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The complete report, entitled "Laboratory Feasibility Studies for the Fluidized-Bed Combustion of Spent Potlining from Aluminum Reduction," (Order No. PB 84-168 764; Cost: $10.00, subject to change) will be available only from:

National Technical Information Service
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