

# DETERIORATION OF MATERIALS IN A QUARTER-MEGAWATT STRAWBURNER<sup>1</sup>

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An outline is given of the deterioration of refractories and stainless steels during the operation of a large strawburning furnace. The deterioration was caused by high temperatures, which sometimes exceeded 1400°C, and by a corrosive slagged ash. The use of different materials in alleviating these problems is described. Laboratory experiments on the corrosion of metals by straw slag are discussed, including work to determine the influence of chloride on the extent of corrosion.

Les caractéristiques générale de la détérioration des matériaux réfractaires et de l'acier inoxydable pendant l'opération d'un incinérateur à paille sont décrites. La détérioration fut causée par les températures élevées qui dépassaient parfois 1400°C et par l'effet corrosif des résidus de combustion. Certains matériaux sont susceptibles de corriger ces problèmes. Nous discutons des résultats obtenus en laboratoire de l'effet corrosif des cendres de paille sur certains métaux incluant l'influence du chlore.

## Introduction

The energy crisis of the 1970's led to efforts to bring a wide variety of alternate energy sources first to the stage of demonstration and then into commercial production. One such effort was that of Lyndhurst Farms of Canning, N.S., which successfully demonstrated the large scale combustion of straw for drying grain and corn, and for space heating. Over several years the combustor was the subject of a good deal of developmental research sponsored by Agriculture Canada, the National Research Council, and Lyndhurst Farms. During that time a sequence of alterations radically altered its design. The alterations were principally the result of dealing with the deterioration of materials caused by high temperatures and corrosive slags. With the current hiatus in the perception of oil as a scarce commodity, and with laboratory studies having been performed on the attack of straw slags on stainless steels, it seemed an appropriate time to record some of the features of this unique Nova Scotian development.

The calorific value of average straw of moisture content 14% is 14,300 kJ/kg, about one-third that of No. 2 fuel oil (Strehler 1980). In a report to Agriculture Canada (Peill 1980a) it was shown that for agricultural conditions and crop rotations at Lyndhurst Farms it was possible to remove yearly an average of 1.25 tonnes of straw per hectare

without disturbing the organic balance of the land. This straw could be procured, taking into account all costs, for a 1979 price of \$23 per tonne, at a time when No. 2 oil was priced at nearly \$200 per tonne. Thus, providing it could be burned efficiently, straw-fuel in this agricultural milieu provided energy at about one-third the cost of furnace oil. The latter report also described the handling and storage of the straw in large cylindrical bales of 300 to 400 kg, and its combustion in a burner which was capable of being loaded with an entire bale at a time and which provided an energy output of five million kJ per hour (described later in more detail). This energy output was used to dry grain and corn in the summer and fall harvest seasons, and to heat a variety of farm buildings in winter. The report also discussed the economics of this operation, such as capital costs and payback times.

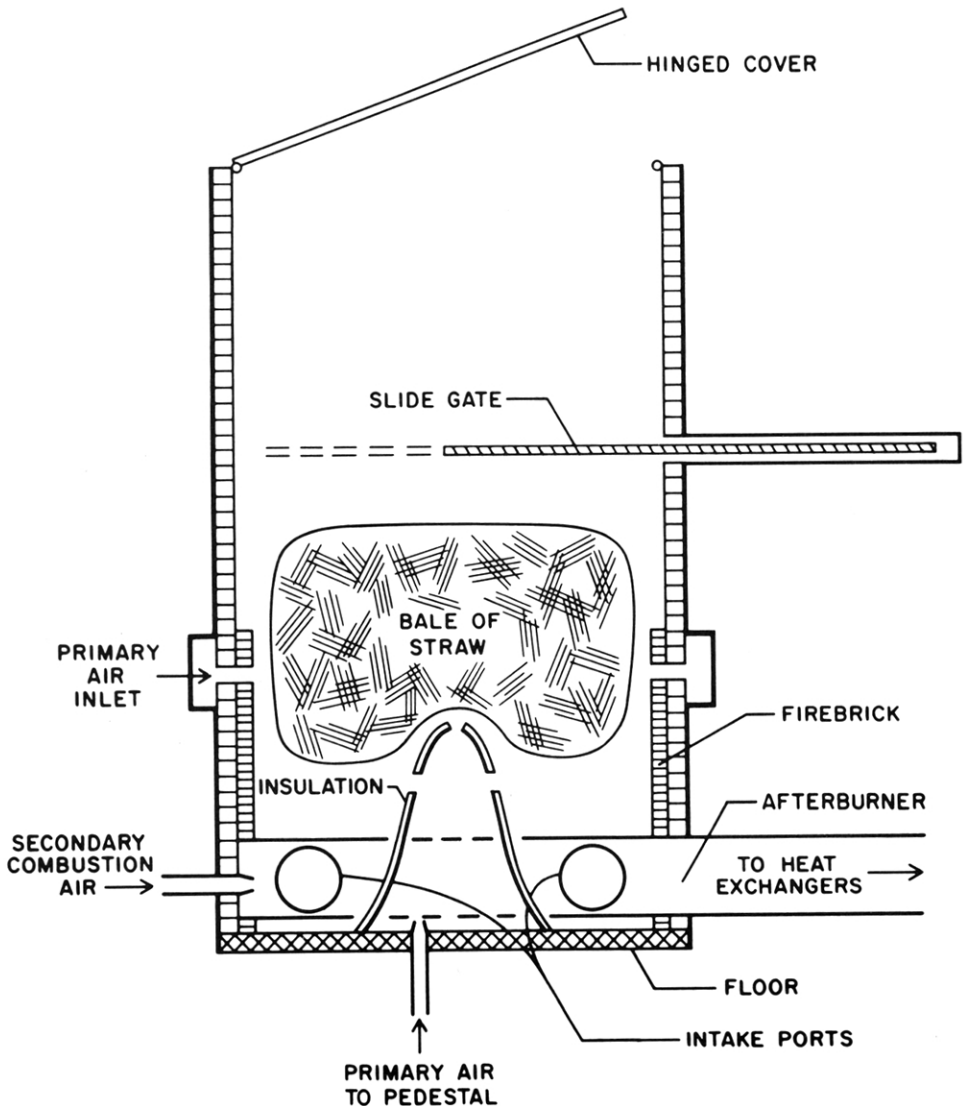


Fig. 1 Schematic drawing of strawburner.

### Field Experience with Strawburner

#### *Description of the Strawburner of 1979 design*

This strawburner was a vertical steel cylinder, about 2.3 m in outside diameter and 4.5 m in height, lined with insulating fireclay firebrick and having a floor of castable refractory. It burned cylindrical bales of straw 2 m in diameter and 340 kg in weight which were introduced through the lidded top. It had two sections (Fig. 1): the bottom section was the burner proper, and the top section could be locked-off by a sliding gate for introducing a new bale of straw while the burner was in operation.

In the burner section this bale sat on an insulated cone-shaped metal pedestal which was about 1 m high and was cemented into the cast refractory floor of the burner. A tunnel-shaped opening was built into the bottom of the cone to accommodate the horizontally oriented exhaust pipe/secondary burner. Primary combustion air was introduced under pressure to the interior of the cone via a pipe set into the floor. The air escaped into the primary combustion chamber through several holes in the walls and tip of the cone, and thus was directed at and into the bale of straw. The cone was fabricated by welding from heavy gauge 0.6 cm stainless steel of the 310 type, and was reinforced by having substantial ribs of the same material welded to its exterior. This reinforcing was necessary because of the stresses imposed when fresh bales were dropped onto the already hot pedestal by retraction of the slide gate. The flow of the combustion air itself helped to cool the underneath of the cone. Primary combustion air also was directed onto the outside of the bale through eight perimeter openings in the wall of the burner.

The exhaust pipe/secondary burner was a heavy gauge stainless steel pipe 35 cm in diameter supported horizontally a few inches above the floor. Four short side-pipes were welded at openings near the ends of the pipe on either side of the superimposed pedestal. These allowed the gases of the primary stage of combustion to be carried into the pipe in a downdraught fashion.

Secondary combustion air was blown axially at one end of the afterburner and the combined primary and secondary combustion gases were emitted from the strawburner at the other end of the afterburner. The hot exhaust gases were used to dry grain and heat water. This was done either directly, or by an appropriate combination of air-air and air-water heat exchangers. The arrangement and sizing of auxiliary equipment such as fans, blowers, dampers, and heat exchangers, as well as data on air flows, are given in a report to the National Research Council by ADI Ltd. (Cocci 1980).

#### *Deterioration of Materials in the Original Burner*

Problems incurred with the type 310 stainless steel pedestal-afterburner assembly ranged from warping to outright melting. Temperatures achieved under some conditions in the combustion chamber exceeded 1300°C (see below) with the result that slag (molten ash) dripped out of the bale, coated the sidewalls, cone and afterburner, and collected as a dense mass on the floor of the chamber. There was an obvious attack of this slag on the sidewall refractories, and suspected attack on the stainless steel components.

Temperature measuring devices had not been installed in the original burner. During the examination by ADI Ltd. (Cocci 1980) an optical pyrometer was sighted through four openings in the steel shell. These were located approximately 0.6, 1.1, 1.6 and 2.2m above the floor of the burner so that a burning bale could be observed through them. Although temperatures varied widely depending upon wetness of the bale and air supply, many observations taken at various times in the burning cycle showed that most temperatures were in the ranges 1025-1175, 1085-1265, 900-1120, and 900-1120°C for the above locations. Because of the meshed nature of the straw,

radiation would approximate black-body conditions, giving reasonable accuracy to these readings. An important observation was that under conditions of exceptional combustion sudden excursions could occur: in one documented case the temperature rose to 1425°C at the third port.

As will be described, in a later modification Pt.-Pt.13%Rh. thermocouples were installed at several locations in the afterburner. It was typical to find that temperatures there dropped to 1000°C when a bale became nearly consumed, and then climbed to and steadied at 1250-1300°C after a new bale was introduced. Again, depending upon particular conditions which seemed to be associated with moisture content, steady temperatures of 1350°C could persist for 10-15 min.

Although the high temperature undoubtedly contributed to the deterioration of materials, it offered two advantages. The first is that total combustion ensured that the flue gases were very clean, and after being cooled by dilution could be used directly to dry grain and corn (with no effect on quality with regard to smell, taste and colour) thereby eliminating the inefficiencies of the air-air heat exchanger. The second was that because the ash was slagged, it did not exit as fly ash but instead collected in the bottom as an easily removed cake having fertilizer value.

#### *Nature of Strawburner Slag*

In order to assess the potential for chemical attack by the slag on the refractories and steel components, chemical analyses were carried out on material collected at the bottom. During the corn-drying season the burner would be operated for 22 h out of the 24, with a shut down period to allow the several inches of slag to be removed. In general, this material was dense, glassy, and of a black to dark-green colour; it was also noticeably soluble in water as compared to most metallurgical slags. In addition, different coloured bands were visible, and these could be identified with the eighteen or so bales of straw combusted.

In order to ascertain whether there were compositional differences between these layers a microprobe analysis was carried out using a JEOL 35 scanning electron microscope with Kevex 7000 energy dispersive X-ray spectrometer. A 0.5 x 0.5 cm section, 10 cm thick, was cut from a piece of slag and mounted and polished (in 5 pieces, each of about 2 cm length). The analyses were made in scanning rather than spot mode, usually at a magnification of 10,000. Mineral standards were used for calibration and ZAF corrections applied. In fact, this slag was found to have a fairly uniform composition, regardless of its banding. The averages of nineteen positions within the 10 cm thickness are shown in Table I. These data are given in weight percentages (along with the average deviation from the mean) as well as mole percentages of the oxides.

There were several points of special interest in these results. When CaO and P<sub>2</sub>O<sub>5</sub> varied they did so in the same way, the mole ratio CaO/P<sub>2</sub>O<sub>5</sub> being nearly three. Possibly this indicates that they occur as Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> in the straw. Chlorine was sought in the slag but never found, in spite of the fact that unburned hay and straw were found to contain chlorine. In a laboratory experiment dry barley straw was burned in an open fire, the black fluffy ash collected and further sintered in air in a platinum dish, and finally melted to a greenish slag using an oxy-propane torch. Its analysis closely resembled that given in Table I, and in addition there were small amounts of embedded crystals of essentially pure KCl. It is possible that the long burnout time associated with the actual strawburner ensured that all the KCl of the straw was either transformed to K<sub>2</sub>O or volatilized.

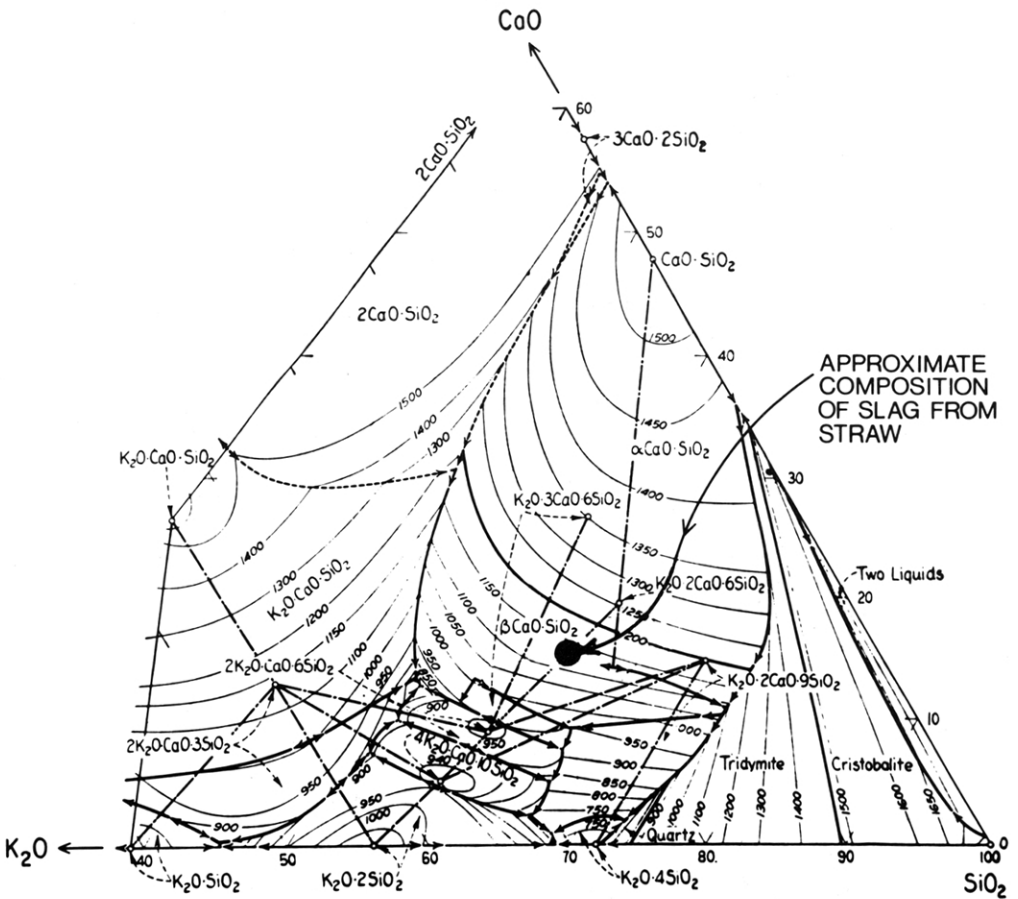
The composition given previously indicates a complex slag. In order to simplify its description we may express the major components in mole fractions and combine them to give  $N_{SiO_2} + 2 N_{P_2O_5} = 0.67$ ;  $N_{CaO} + N_{MgO} + 2 N_{Fe_2O_3} = 0.18$ ;  $N_{K_2O} = 0.15$ . This

**Table I** Composition of strawburner slag.<sup>a</sup>

Component	Weight Percent		Mole Percent
SiO <sub>2</sub>	55.7	(3.7) <sup>b</sup>	62.0
K <sub>2</sub> O	22.0	(0.8)	15.6
CaO	8.7	(1.1)	10.4
P <sub>2</sub> O <sub>5</sub>	7.9	(1.6)	3.7
MgO	3.9	(0.3)	6.5
Fe <sub>2</sub> O <sub>3</sub>	2.4	(1.1)	1.0
MnO	0.6	(0.1)	0.6
Al <sub>2</sub> O <sub>3</sub>	0.3	(0.2)	0.2

<sup>a</sup> Average of 19 determinations.

<sup>b</sup> Figures in brackets are average deviations



**Fig. 2** Approximate location of slag on SiO<sub>2</sub>-CaO-K<sub>2</sub>O phase diagram, in wt.%.

permits placing the composition on the  $\text{SiO}_2 - \text{CaO} - \text{K}_2\text{O}$  phase diagram (Morey 1930) suggesting a liquidus at about  $1125^\circ\text{C}$  (Fig. 2). While this result must be taken as only approximate because of the somewhat arbitrary assignments of  $\text{MgO}$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{P}_2\text{O}_5$ , it does indicate the high temperatures that must be generated in the system in order to fuse the ash completely. (The experimental concentrations of  $\text{P}_2\text{O}_5$  and  $\text{Fe}_2\text{O}_3$  are given double weight in this calculation because the actual slags are expected to contain species having only one atom of P or Fe.)

#### *Deterioration of Refractories*

In the original burner the sidewall refractory was a porous insulating firebrick, rated for  $1260^\circ\text{C}$ , of composition  $\text{SiO}_2 - 58\%$ ,  $\text{Al}_2\text{O}_3 - 37\%$ , with minor quantities of  $\text{K}_2\text{O}$ ,  $\text{TiO}_2$ ,  $\text{FeO}$ ,  $\text{CaO}$ ,  $\text{P}_2\text{O}_5$ . It became severely damaged by the slag. This attack was at least partly simple penetration of the liquid slag into the pores, followed by spalling of this surface layer when the slag hardened and contracted after the burning run ended. In addition, chemical attack was suspected, and to examine this a 1.5 cm thickness of slag adhering to the brick was analysed using the microprobe. Concentration profiles are shown in Fig. 3. The distances from 0 to about 0.8 cm represent a reaction zone where the components of the slag and brick have reacted and interdif-

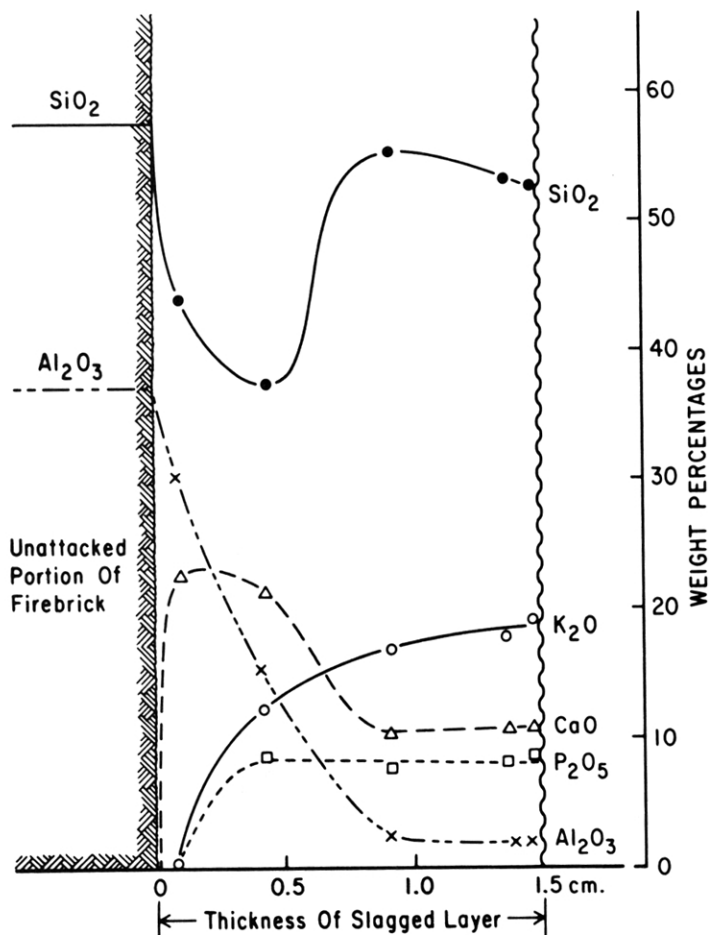


Fig. 3 Reaction zone between slag and refractory firebrick.

fused. The concentration gradients of  $\text{Al}_2\text{O}_3$ ,  $\text{K}_2\text{O}$  and  $\text{P}_2\text{O}_5$  are consistent with this simple picture. The profiles of  $\text{SiO}_2$  and  $\text{CaO}$  are not so simple and suggest a strong tendency toward formation of a compound of  $\text{CaO}$  and  $\text{SiO}_2$ . In any case there is evidence of a chemical reaction between slag and brick which would help explain deterioration of the latter.

Later, Lyndhurst Farms replaced this brick with one that was stronger, less porous, and of higher  $\text{Al}_2\text{O}_3$  content (about 52%  $\text{SiO}_2$ , 43%  $\text{Al}_2\text{O}_3$ ). It was attacked much less severely, and represented a sufficient solution to the problem of attack on the refractory.

#### *Deterioration of the Pedestal - Afterburner*

These components were of type 310 stainless steel, an austenitic stainless steel of nominal composition Cr - 25%; Ni - 20; Si - 1.5 max.; Mn - 2.0 max.; Fe - remainder. Its melting point is about 1450°C. A sample cut from a discarded assembly gave, for 22 microprobe positions, an average analysis of Cr - 25.3; Ni - 18.5; Si - 2; Fe - 54.2. The afterburner in use in 1979 had deteriorated quite badly, and sections of the roof of the pipe had collapsed inward, apparently from melting. Some of this collapsed material was analysed and found to be Cr - 15.5; Ni - 21.3; Si-1; Fe - 61.3. It appeared that material which had been subjected to extreme temperatures had been depleted in chromium.

The Metals Handbook (Bardes 1978) reports that type 310 is preferred to other compositions of the general type where intermittent heating and cooling are encountered, since it forms a more coherent scale. Resistance to further oxidation is conferred by this surface layer of  $\text{Cr}_2\text{O}_3$ . It is claimed to be useful for parts such as firebox sheets, furnace linings and boiler baffles, thermocouple wells, and jet engine burner linings. While for temperatures above 925°C type 310 surpasses some of the other stainless steels (e.g. 316) in rupture strength, it has definite temperature limits as far as strength is concerned, as shown by Table II.

**Table II** Strength of 310 stainless steel.

Temp. (°C)	Tensile Strength (psi.)
Ambient	90,000
425	80,000
650	60,000
870	25,000
1100	7,000

However, because of creep, structures eventually will fail even at temperatures where the tensile strength appears adequate. The available data on rupture time of type 310 does not go beyond 980°C. However, a reasonable extrapolation indicates that a rupture time of 10,000 hours requires an applied stress of no more than 100 psi at about 1150°C, and an applied stress no more than 500 psi at a temperature of 1000°C. It may be supposed that the stress imposed by the dropping of a bale of straw down onto the pedestal-afterburner assembly was responsible for some of the warping observed. In addition, even this grade of stainless steel is limited in its resistance to oxidation at high temperatures, because the protective chromium oxide layer itself fails. It must be assumed that some of the deterioration observed was due to this effect. An important question was whether the slag contributed to accelerating the normal high temperature oxidation. Laboratory experiments, to be discussed

later, showed that when the steel was coated by a layer of slag its oxidation rate was actually decreased; however, uncoated parts oxidized unusually rapidly, and this was presumed to be due to the action of a volatile component of the slag.

#### *Strawburner of 1980 Design*

It became evident that the favourable economics of the strawburner were being eroded by the high cost of replacing the stainless steel pedestal-afterburner. It was concluded that most of the deterioration problems were related to the high temperatures developed, and that one solution would be to control and lower these temperatures by limiting the supply of primary combustion air, some of which was adventitious infiltration. However the advantage provided by the very clean stack gases, and the requirement of a high energy output during the corndrying season, mitigated against this solution. Therefore, two design changes were introduced, as described in detail in a report to the National Research Council (Peill 1980b).

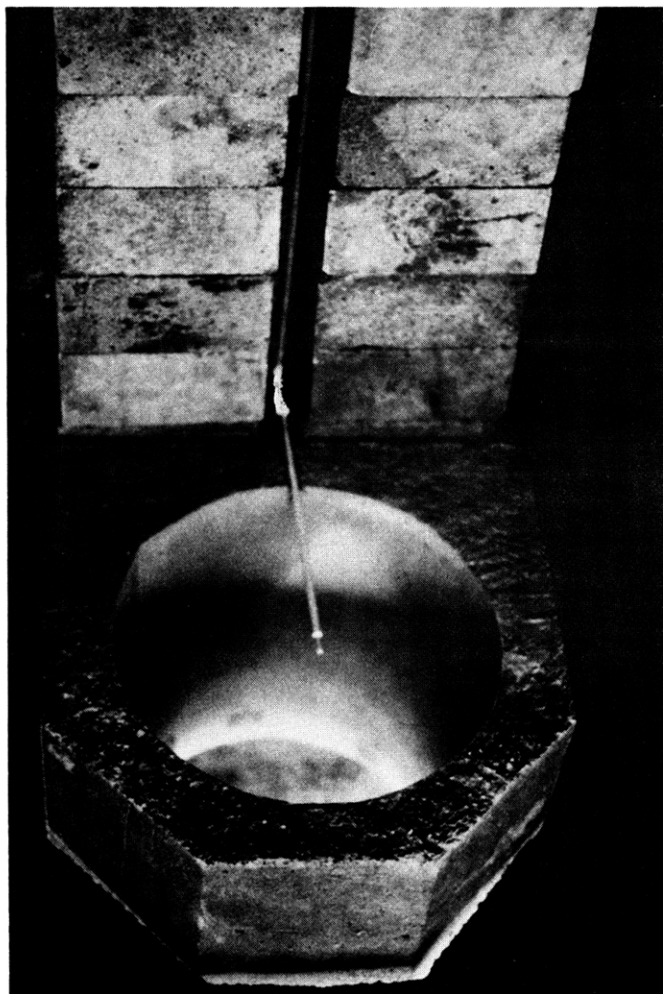


Fig. 4 Castable afterburner segment showing support base of firebrick, and thermocouple installation.



Firstly the cone-shaped pedestal was replaced by a framework fabricated from 5 cm dia. type 316 stainless steel pipe, schedule 80. These pipes also carried the combustion air and it was hoped that the improved heat transfer would keep them sufficiently cool.

The second change was that the afterburner was fabricated from high temperature castable refractory cement. Because of weight, it was cast in four pipe-like sections each 57 cm in length, 40 cm in inside diameter and with wall thickness about 7.5 cm. For experimental purposes four castable cements were used, as supplied by the A. P. Green Firebrick Co.: MC-22, Steelkon GR, Mizzou, and Greencrete ARC. The first three consisted of  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ , with increasing temperature ratings of 1290, 1540 and 1650 C respectively because of increasing  $\text{Al}_2\text{O}_3$  contents. The last was a dense chrome-alumina refractory more abrasion and slag resistant than the others. Figure 4 shows one of these sections being installed on its firebrick base, and the location of one of the three Pt - Pt.13%Rh. thermocouples mentioned earlier.

In general, the cast refractory afterburner was found to be cost-effective. Although temperature cycling caused some cracks to occur they were not serious and did not affect performance significantly. It was concluded that considering economies and ease of fabrication and supply, material of MC-22 or Steelkon grade was the most desirable.

The 316 stainless steel pipe supports for the burning bale were less successful, although the greatest corrosion occurred with mild steel connecting portions used inside the main stainless pipe. It was finally concluded that successful operation of this design required an even better grade of refractory metal of the nickel-chromium type, such as an Inconel. With these modifications the strawburner gave satisfactory performance over several years.

The main fault with this design of burner was that a very large supply of fuel, about  $10^6$  kJ, was introduced at one time. Close control of combustion therefore rested with controlling the air supply, and this was made difficult by accidental infiltration through the lidded top, doors, etc. Later strawburners designed and fabricated by Biomass Combustion Ltd. (associated with Lyndhurst Farms) were of a type where the feed of straw could be controlled also. This change, together with an internal design that eliminated all metal alloys in the combustion chamber, succeeded in overcoming the problems that have been discussed.

For convenience, the nominal compositions of the alloys mentioned in various places in this paper are given in Table III.

**Table III** Composition of alloys, wt.%

Alloy*	Cr	Ni	Mo
304 ss	18-20	8-12	-
316 ss	16-18	10-14	2-3
310 ss	24-26	19-22	-
Inconel	14-16	70-75	-

\* Iron is the main other constituent in all cases.

## Laboratory Experiments

### Introduction

Experiments were conducted to assess the effect of various slags on the rate of corrosion of stainless steels and Inconel 600. These experiments will be described in

more detail in a separate communication; they consisted of holding 6 cm lengths of 0.64 cm dia. rods of the metals upright in  $\text{Al}_2\text{O}_3$  crucibles, with the bottom 2 cm immersed in the molten slags. The rods protruded loosely through holes cut in the lids of the crucibles so that for a given temperature and time sections of the rods were exposed to: slag alone; the atmosphere above the slag, including any volatiles; and just air. These test assemblies were then put in a muffle furnace for various lengths of times at various temperatures. The cooled specimens were examined visually for extent of oxidation, and then selected portions were mounted and polished for analysis using the JEOL 35 SEM/microprobe.

### *Brief Results of Experiments*

Experiments using slag taken from the strawburner, with composition close to that of Table I, were carried out. Type 304 and 316 stainless steels were exposed at  $1150^\circ\text{C}$  for periods up to 24 hr. These alloys are of the composition Cr - 18, Ni - 10%, but differ in that type 316 contains 2.5% Mo. In general, the bottom part of the specimens covered by the slag showed little or no oxidation. The part outside the crucible can be regarded as normal air-oxidation, and the extent of this oxidation increased with time of exposure. Microprobe analysis showed that the corrosion occurred by surface accumulation of a flaking  $\text{Cr}_2\text{O}_3$  layer. The apparently sound metal behind this layer exhibited a diffusion gradient in chromium several hundred microns thick, with nickel having diffused back to occupy alloy positions vacated by the chromium. For all conditions type 316 with 2.5% Mo. showed somewhat less deterioration.

The most striking observation was that the portion of the metal samples above the part wetted by the slag, but within the confines of the lidded crucible, exhibited greatly enhanced deterioration over that found in air. This suggested that a volatile component of the slag was enhancing oxidation. Therefore, further experiments were carried out to investigate the cause of this enhanced oxidation. A suspected agent was chlorine in some form; as noted before, slags made in the laboratory from straw contained embedded crystals of KCl, while slag collected from the strawburner did not. For these experiments, synthetic slags were prepared both free of and containing chloride ion. These slags were of composition in weight percent:  $\text{SiO}_2$  - 39,  $\text{K}_2\text{O}$  - 52, CaO - 8, FeO - 1, with the chloride content obtained by the addition of 1% KCl. Three alloys were tested: types 304 and 316 stainless, and Inconel 600. The temperature used was  $1050^\circ\text{C}$ , with exposure times of up to 48 hr.

One important observation was that under these conditions the Inconel 600 showed little or no sign of deterioration. For the other two alloys the extent and type of attack caused by the actual strawburner slag was duplicated. The most important observation was that there was little difference in the extent of oxidation between the chloride-free and chloride-containing slags. We conclude tentatively that chloride is not responsible for the enhanced oxidation. Possibly potassium itself is the culprit. These high potassium contents are a distinguishing feature of straw ash; in ash from other biomass such as deciduous and coniferous wood the potassium is largely replaced by calcium.

### **Summary**

Examples are given of the types of deterioration of materials of construction used in the combustion of straw at high temperatures. The slagged ash can damage refractories if they are not sufficiently dense or of the correct chemical composition. High temperatures and mechanical stresses can damage even type 310 stainless steels. In addition, the normal high temperature oxidation of stainless steels is enhanced by some component of the slag yet unknown. Inconel 600 has been shown to be superior both in laboratory experiments and actual use. Burner parts, made of

high-alumina castable refractory cement designed for high temperature use, were shown to be useful and cost-effective.

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