Bureau of Mines Report of Investigations/1986

Steam-Induced Volatilization of Silica From Refractories

By L. Y. Sadler III and E. G. Davis

UNITED STATES DEPARTMENT OF THE INTERIOR

Steam-Induced Volatilization of Silica From Refractories

By L. Y. Sadler III and E. G. Davis

CONTENTS

ILLUSTRATIONS

TABLES

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

atm	atmosphere, standard	mL/h	milliliter per hour
°C	degree Celsius	mm	millimeter
g	gram	mV	millivolt
h	hour	pct	percent
in	inch	psig	pound per square inch, gauge
L/h	liter per hour	std ft^3/h	standard cubic foot per hour
mg	milligram		
mL	milliliter	W	watt

STEAM-INDUCED VOLATILIZATION OF SILICA
FROM REFRACTORIES

By L. Y. Sadler III[1] and E. G. Davis[2]

ABSTRACT

The Bureau of Mines conducted a study to determine the loss in weight of silica (SiO_2) volatilization from low-alumina (Al_2O_3) refractories used as hot face liner materials in such process equipment as coal gasifiers, synthesis gas transfer lines, and ammonia plant secondary reformers. Small specimens of 80- and 40-pct-Al_2O_3 brick and 95-pct-SiO_2 brick were exposed to steam in high-pressure furnaces at pressures of up to 1,000 psig and temperatures up to 1,400° C for periods ranging up to 120 h. Weight losses from the 40-pct-Al_2O_3 brick after 40 h of exposure were highest, 2.75 pct at 1,400° C and 1,000 psig. The rate of weight loss had dropped to near zero after 80 h of exposure at all temperatures. No relationship between total silica content of the specimen and weight loss could be established nor did scanning electron microscopic examination of the specimens before and after exposure identify specific regions (e.g., surface) suffering a disproportionate share of the silica loss. It was concluded that minor silica volatilization is likely to occur, if at all, at temperatures of less than 1,000° C and pressures below 1,000 psig, and that low-alumina refractories should be used as dry-ash coal gasifier hot face linings.

[1]Chemical engineer.
[2]Metallurgist.
Tuscaloosa Research Center, Bureau of Mines, Tuscaloosa, AL.

INTRODUCTION

Prior to about 1979, the literature $(1-2)$[3] had suggested that high-temperature, high-pressure gas streams containing steam could remove silica from refractory linings of reactors and hot gas transfer lines in oil refineries, ammonia production plants, and coal gasification plants. The reaction generally proposed for steam-induced silica volatilization was

$$2SiO_2 + 3H_2O \rightarrow Si_2O(OH)_6 \uparrow \qquad (A)$$
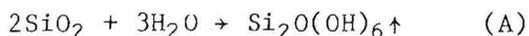
This reaction should be favored by both high temperatures and high partial pressures of steam. Based on these reports, the general consensus prior to the mid-1970's was that only high-alumina refractories should be used as liner materials in high-pressure, high-temperature steam environments $(2-3)$. A comprehensive Bureau of Mines $(4-6)$ evaluation of candidate refractory liner materials for dry ash coal gasifier reactors found that pure steam or atmospheres containing steam at temperatures of up to 1,100° C and pressures of up to 1,000 psig did not cause losses in strength in refractories containing large amounts of silica (up to 55 pct). After exposure to steam environments at 1,100° C (the highest temperature investigated in those studies) and 1,000 psig, a small amount of silica volatilization was detected in low-alumina refractory specimens. The specimens used in these tests were 2.5- by 2.5-cm bars weighing approximately 100 g. Silica losses were detected both by comparing silica analyses performed on the refractory specimens before and after exposure and by analysis of glassy deposits, some up to 1 mm thick, formed on thin alumina plates used to separate specimens of refractory from each other in the sample exposure chamber. The chemical analyses were made on a 1-g sample

taken from the powder resulting from grinding the entire 100-g brick specimen. Subsequent exposures of the same types of refractories to steam and to simulated gasifier atmospheres (40 pct H_2O, 25 pct H_2, 20 pct CO, 10 pct CO_2, 5 pct CH_4) at pressures ranging up to 1,000 psig and somewhat lower temperatures (500° to 1,000° C) failed to produce any evidence of silica volatilization. The studies just described were primarily directed at screening commercially available refractories on the basis of strength changes to identify the best available liner materials for coal gasifier reactors.

Despite these strong indications that steam-induced silica volatilization is not likely to be a problem in coal gasifiers operated at temperatures below 1,100° C, high-alumina refractories, instead of medium- or low-alumina materials, were still being recommended by some designers for gasifiers operating below 1,100° C. In the production of high-alumina refractories, the major raw material is refractory-grade bauxite, which must be imported. Therefore, it is in the national interest to reduce this dependence on imports by utilizing domestic raw materials that are available for the production of low-alumina refractories.

In order to determine the rate of steam-induced silica volatilization as a function of temperature and pressure, the Bureau undertook studies in which small samples of several common refractories were weighed before and after (and in some cases continuously during) exposure to carefully controlled high-temperature, high-pressure steam environments. This report presents the findings of those studies and discusses whether significant volatilization of silica from the hot faces of dry ash coal gasifier reactor refractory lining materials can be expected under temperatures and pressures likely to be encountered in gasifier operation.

---

[3]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

EXPERIMENTAL

Two series of exposures were conducted using high-pressure furnaces in which small specimens (up to 900 mg) of super-duty firebrick (ALAMO[4] and MULFRAX), a silica brick (VISIL), and silica flour were continuously exposed to atmospheres of flowing steam at pressures ranging from 1 atm to 1,000 psig for up to 120 h. In the first exposure series, 50- to 100-mg specimens of finely ground ALAMO brick and silica flour were exposed to steam at pressures of 1,000 psig and temperatures of up to 1,000° C for up to 8 h. In these experiments, the specimen weights were continuously monitored by means of an electrobalance. The temperature was limited to 1,000° C by the furnace design. In the second series, a furnace capable of up to 1,400° C and 1,000 psig operation was used. Specimens (having weights of approximately 900 mg) in these tests were weighed once before and once after exposure.

EQUIPMENT

Low-Temperature Furnace

A diagram of the equipment used in this series is shown in figure 1. An environment of flowing steam at pressures up to 1,000 psig and temperatures up to 1,000° C could be generated with the equipment. The primary system components consisted of the reaction tube, the balance assembly, and the steam generator. The system incorporated some ideas suggested by other investigators (7-9). The reaction tube was made from a 2-in-diam by 24-in-long solid rod of RA-333 alloy (Rolled Alloys Corp) by drilling a 1/2-in-diam hole down to within 8 in of its lower end and then drilling a 1/4-in-diam hole through the remainder of the tube. A 1/4-in-diam hole drilled radially into the tube at about 2 in from the top of

---

[4]Reference to specific products does not imply endorsement by the Bureau of Mines.

the rod provided an exit port through which gases were exhausted.

The lower end of the reaction tube was tapped to 1/4-in NPT. The upper end was machined and threaded to receive a 1-in stainless steel union. The reaction tube was heated in a 1,400-W electrical resistance-type tube furnace (fig. 2) equipped with a proportional controller. Temperatures up to 1,000° C could be maintained to within ±10° C.

The electrobalance assembly (fig. 3) was mounted in a cylindrical pressure vessel rated at 1,250 psig and having a bolted flange closure. The balance had a 1-g capacity (sample + sample holder and hangdown wire) in the configuration in which it was used in this investigation. Samples of up to 100 mg could be weighed. The balance sensitivity could be selected to give zero to full-scale deflections for weight changes ranging from 1 to 100 mg. The balance output was converted into a 0- to 10-mV linear signal and fed to a variable speed strip chart recorder to be recorded as a function of time. Most runs were carried out with the balance sensitivity set so that sample weight changes of as little as 0.25 mg could easily be detected and recorded. Electric feed-through between the balance assembly and the balance control unit was made possible by the use of a multiconductor packing gland.

Steam was produced by a steam generator that consisted of a 12-in long, high-alloy tube made by drilling a 1/2-in-diam hole through the center of a 2-in-diam solid rod. The tube was packed with 3-mm-diam silica gel granules as suggested by other experimenters (9) to minimize pressure surges due to unsteady liquid vaporization. The tube was heated to about 300° C (a temperature above the saturation temperature of water at 1,015 psig) in a 1,400-W, split-tube furnace. Temperature control was maintained automatically using an on-off control that responded to the temperature signal from a sheathed, type J thermocouple mounted

KEY
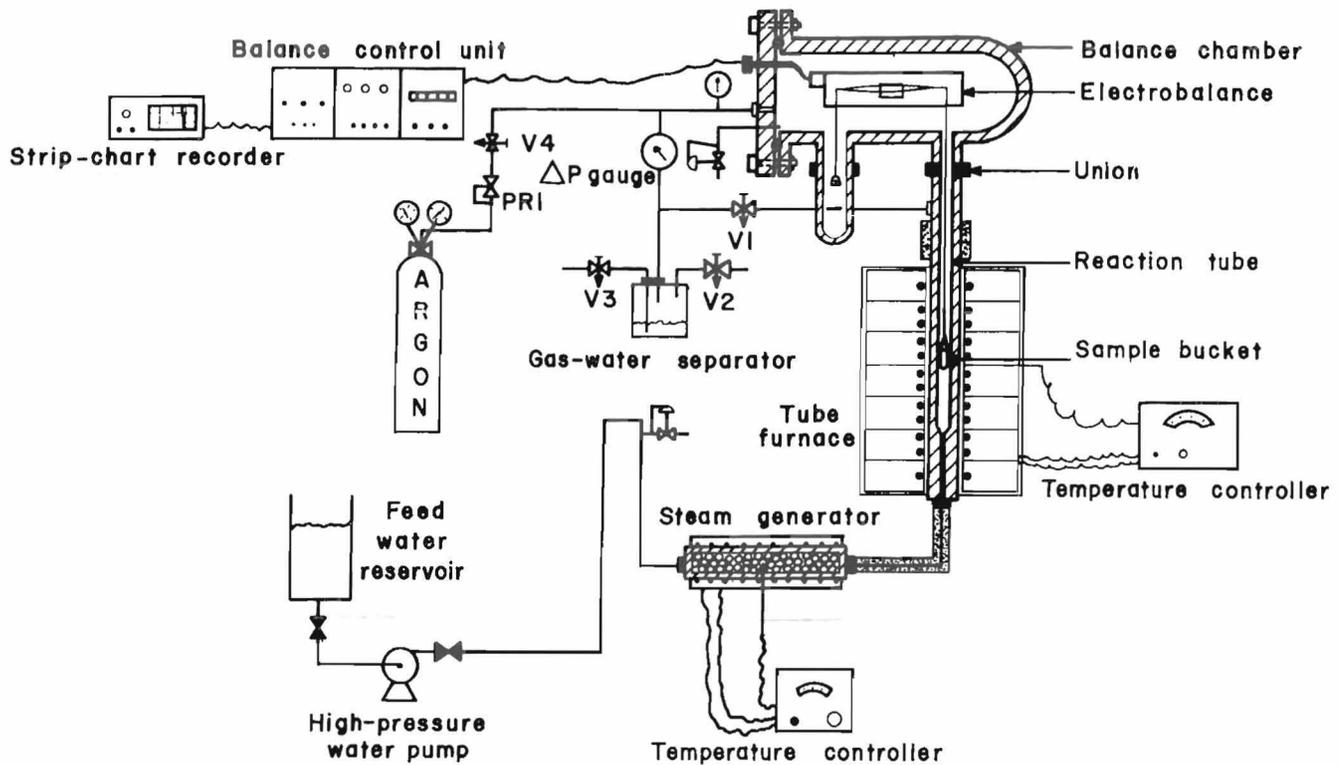
Relief valve

Needle valve

Pressure regulator

Globe valve

Pressure gauge

Differential pressure gauge

FIGURE 1.—High-temperature, high-pressure exposure system.

with a compression fitting in a hole drilled through the tube wall.

High-Temperature Furnace

The equipment in which the exposures in this test series were carried out was the same as described above except that a refractory-lined, internally heated reaction vessel (fig. 4) was used. An environment of flowing steam at pressures of up to 1,000 psig and temperatures up to 1,400° C could be obtained with this equipment.

The reaction vessel was constructed from 8-in-diam 304 stainless steel pipe having a wall thickness of 0.594 in (Schedule 80). The bottom had a crown radius of 6.68 in, while the 3-7/8-in-thick top flange and head were made from 304-type stainless steel. The vessel was made to ASME Code for maximum allowable pressure of 1,250 psi at maximum wall temperature of 600° F. Twelve 1-7/8-in bolts were used to bolt the head to the vessel flange. A 1-in hole was drilled in the head, and a 1-in Schedule 80 304 stainless steel pipe was welded to
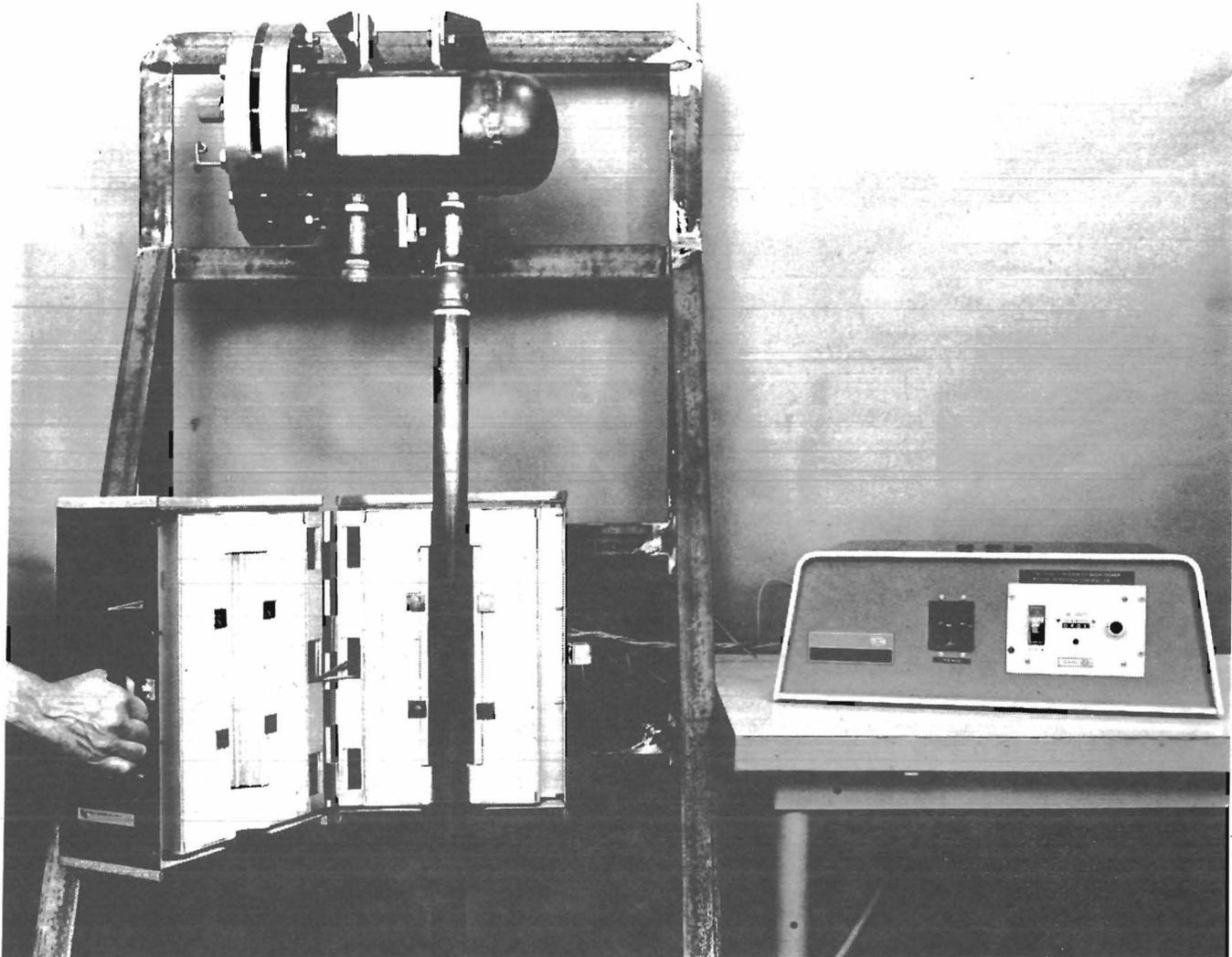
FIGURE 2.—The 1,000° C reaction furnace and pressure vessel assembly.

it to serve as the inert gas inlet port. Four nipples were welded to the side of the vessel to serve as a gas and steam outlet, a thermocouple, an electric power feedthrough, and for attaching a pressure relief disc. One nipple was welded to the hemispherical botton for a steam inlet.

The interior of the vessel was insu-lated with fibrous zirconia, thus forming a 4-in-diam, 8-in-high reaction chamber. Heat was supplied by four 1/16-in-diam molydisilicide heating elements within the reaction chamber. A power input of approximately 1,500 W was required to maintain an internal temperature of 1,400° C.

OPERATION

Low-Temperature Furnace

Prior to the start of an experiment, the balance was first tared with an empty sample cup attached to the hangdown wire. The sample was then loaded into the cup, and the cup was attached to the hangdown wire. The reaction tube was then care-fully raised up around the cup, and the union was tightened securely. The cup and sample were then weighed to establish the sample weight. Argon was admitted to the balance chamber through valve V4 (fig. 1) and pressure regulator 1 (PR_1) until the desired operating pressure was
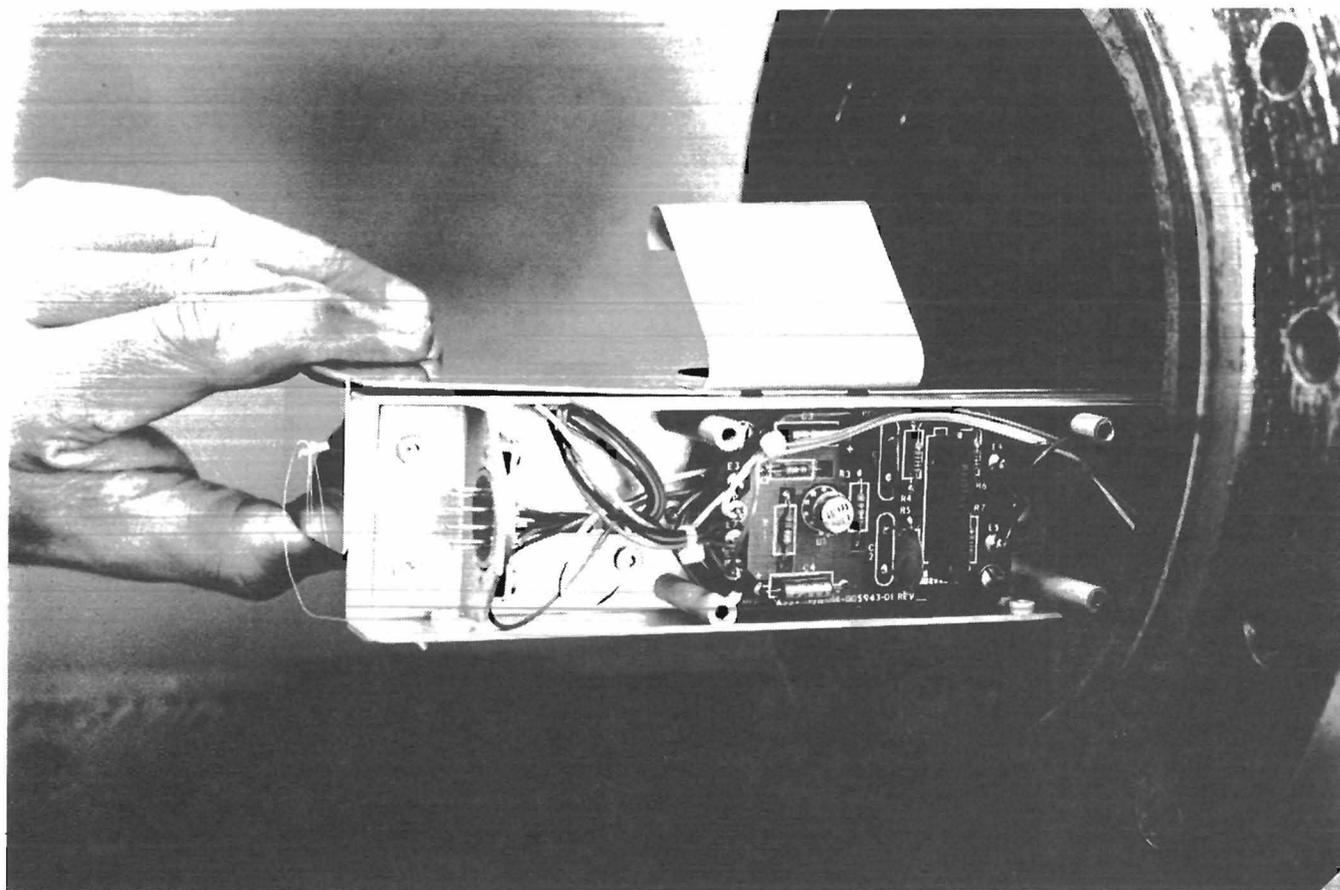
FIGURE 3.—Electrobalance assembly being placed in a cylindrical pressure vessel.

reached. A few milligrams change in apparent sample weight was always observed due to increased gas density at higher pressures and to the effect of pressure on electronic components. Valves V1 and V2 were opened slightly in order to establish a continuous 90-L/h argon purge of the balance chamber. The Δp gauge was used to indicate this purge rate. The temperature of the tube furnace was raised slowly (15° C/min) to, and held at, the run temperature desired.

In runs where steam was to be the reaction gas, the steam generator temperature was raised to, and held at, approximately 300° C. The feedwater was pumped to the steam generator and from there it flowed to the reaction tube. The rate of steam production was usually equivalent to about 10 mL/h of liquid. After passing through the reaction tube, the steam was condensed in the cooler gas lines leaving the reaction tube. The condensate exited, with the argon purge, into the

gas-water separator. Argon was vented continuously from the separator, and usually the water from an entire run was allowed to accumulate in the separator before collection.

A check-out run in which a 65-mg sample of calcite ($CaCO_3$) was decomposed to calcium oxide (CaO), in an argon atmosphere at 1,000 psig, by heating from room temperature up to 1,000° C is shown in figure 5. The recorder showed a residual weight of about 36 mg, while stoichiometry would predict a residual weight of exactly 36.42 mg. This close agreement verifies the sensitivity and accuracy of the techniques and equipment used. A strip chart record for a portion of a typical steam run at 1,000 psig and 1,000° C is shown in figure 6. Oscillations in the record were due to virbrations from external sources, boiling instabilities in the steam generator, and convection currents in the reaction tube, with the latter thought to be the most
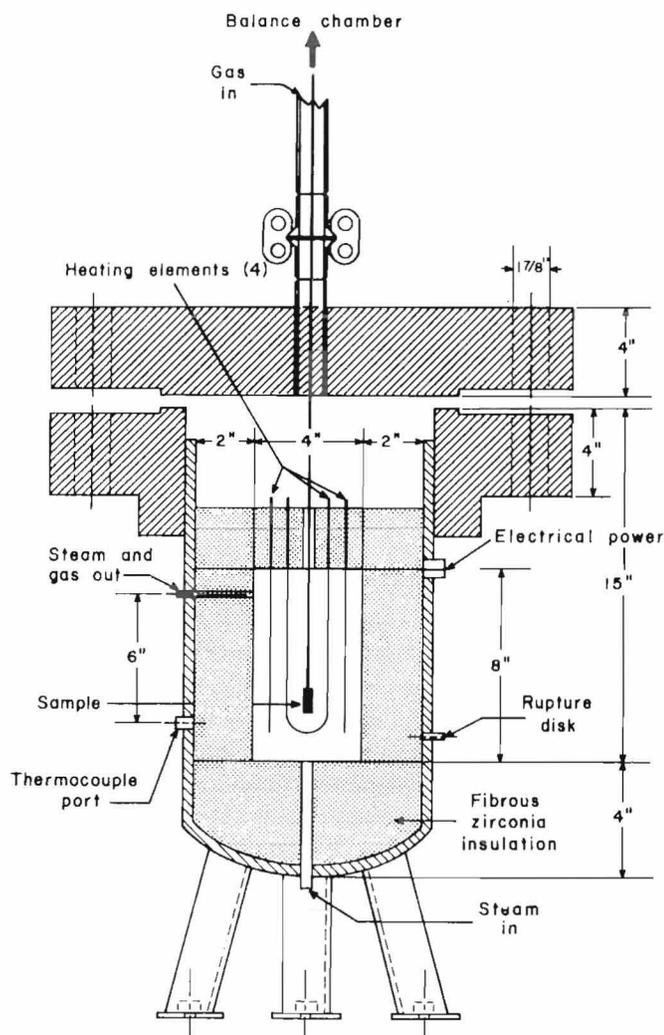
FIGURE 4.—High-temperature reaction furnace.

FIGURE 5.—Decomposition of $CaCO_3$ in argon at 1,000 psig.
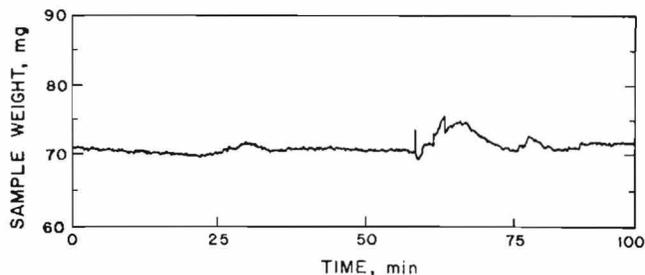
FIGURE 6.—Typical steam run at 1,000° C and 1,000 psig.

important. Oscillations induced by convection currents became more severe at higher temperatures and higher pressures. In a short run at 1,100° C, the oscillations became so severe that the run had to be terminated.

High-Temperature Furance

Cylindrical (approximately 1/2- by 3/8-in) specimens weighing from 500 to 1,000 mg, cut from bricks with a diamond coring bit, were dried in an oven overnight, weighed, and suspended from the end of a platinum wire anchored to a support rod in the balance chamber. The wire passed from the balance chamber, down through the connecting pipe, into the furnace. The wire length was chosen so that the sample was suspended in the center of the
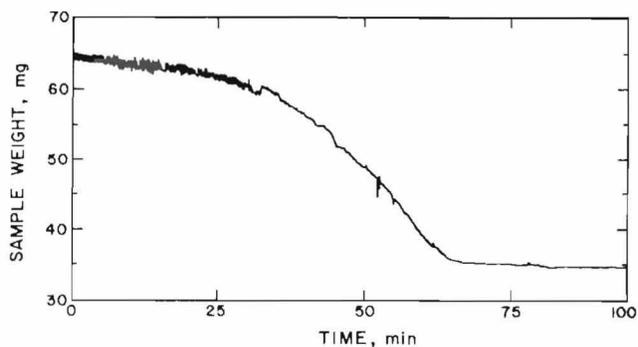
furnace. A single circumferential groove was carved in the specimen, allowing it to be held securely by the end of the support wire wound and tied around the specimen. In some runs, several specimens, each hung from a separate wire, were exposed at the same time. After exposure, the specimens were removed from the furnace, oven dried again overnight, and reweighed. In runs where steam was to be the reactive gas, the stroke was adjusted so that the pump delivered approximately 30 mL/h of water to the steam generator.

MATERIALS

The compositions (as supplied by the manufacturer) of the refractory brick specimens used in the program are given in table 1. For the exposures in the low-temperature furnace, both ALAMO brick ground to minus-325 mesh and silica flour (Supersil, Pennsylvania Glass Sand Co.) were used.

TABLE 1. - Analysis of commercial refractory brick

	Superduty firebrick	High-alumina	Silica
Tradename.............	ALAMO............	MULFRAX 301.	VISIL.
Manufacturer.........	Harbison-Walker..	Carborundum.	Harbison-Walker.
Mineralogy...........	Mullite, quartz cristobalite.	Mullite.....	Cristobalite, amorphous, quartz.
Composition, wt pct:			
SiO_2...............^	52.3	20.6	98.4
Al_2O_3.............	41.9	75.8	.5
TiO_2..............	2.2	Trace	Trace
Fe_2CO_3...........	1.0	.4	.1
CaO................	.2	.1	.1
MgO................	.3	Trace	.1
Alkalis (NaO_2 + K_2O + LiO_2).	1.2	.2	Trace

WEIGHT LOSS STUDIES

LOW-TEMPERATURE FURNACE

Specimens of ground ALAMO brick and silica flour were each exposed for 8 h to steam at 1,000° C at pressures of 100 and 1,000 psig as well as to steam at 750° C and 500 psig. No measurable losses in weight were observed in any of these exposures. A typical trace from the recorder is shown in figure 6. The results indicted that steam-induced silica volatilization from refractories at temperatures below 1,000° C can be expected to be either a very slow process or one that is not likely to occur at all in atmospheres where the steam partial pressure is less than 1,000 psig.

HIGH-TEMPERATURE FURNACE

Table 2 summarizes weight loss data for the specimens exposed in the high-temperature reactor to steam at 1,000 psig. The average values of the weight losses are plotted in figure 7 as a function of exposure time. Although there are some uncertainties in the true mean weight losses at each exposure time, several points can be made. The first is that even at 1,400° C, the weight losses are small--less than 3 pct of the total specimen weight and less than about 6 pct of the total silica in the ALAMO specimens. The second point is that the rates of the weight losses fall to zero

after about 80 h exposure. The third point is that the average initial rate of weight loss is much greater for the 1,400° C exposures than for the 1,100° and 1,000° C exposures, and the utlimate losses also increase rapidly with exposure temperature. For comparison, a total of six specimens of $99+$-pct-Al_2O_3 dense insulators were exposed to 1,400° C, 1,000 psi steam as blanks in several exposures. These alumina specimens registered an average weight gain of 0.3 pct. In othe tests, ALAMO specimens exposed to pure argon at 1,000 psig and 1,400° C for 40 h gained an average of 0.4 pct in weight. Specimens of ALAMO brick were also exposed to air (1 atm) at 1,400° C for 40 h. A weight gain of
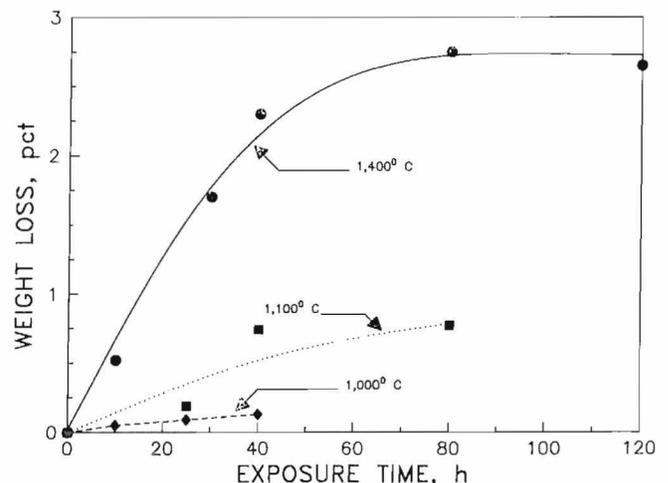

FIGURE 7.—Average weight losses for ALAMO brick.

TABLE 2. – Weight-loss data in
1,000-psig steam

Exposure time, h	Specimen weight loss, pct		
	At 1,000° C	At 1,100° C	At 1,400° C
ALAMO:			
10.........	0.05	ND	[1]0.52
25.........	.09	[1]0.18	ND
30.........	ND	ND	1.70
40.........	[2].13	[1].74	[1]2.27
80.........	ND	[1].77	[2]2.75
120.......	ND	ND	2.65
MULFRAX 301:			
120.......	ND	ND	3.0
VISIL:			
120.......	ND	ND	3.5

ND Not determined.
[1]Average of 3 exposures.
[2]Average of 2 exposures.

0.4 pct was measured. These apparent "weight gains" may have simply been due to inaccuracies in weighing. They could, however, have been due to volatile refractory components from the reactor zirconia (ZrO_2) insulation, the molybdenum disilicide ($MoSi_2$) heating elements, or another source. The latter explanations seem most plausible, since the measured weight changes in these "blank" tests were always weight gains. As an indication of the effect of pressure on steam-induced silica volatilization, two samples of ALAMO refractory were exposed to steam at 1 atm and 1,400° C for 30 h. An average weight gain of 0.25 pct was recorded.

The weight losses for single specimens of the MULFRAX and the VISIL refractories after exposure at 1,400° C for 120 h at 1,000 psig steam pressure were 3.0 and 3.5 pct, respectively. When losses in weight of specimens of all three refractories are compared, no clear correlation with total silica content is apparent. This is not too surprising because these refractories all contained much more silica than was actually lost. Cross sections of the unexposed and exposed (1,400° C, 1,000 psig, 120 h) samples of ALAMO were studied using a scanning electron microscope with energy dispersive spectroscopy in order to determine whether there was a disproportionate depletion of silica at the surface. The results of these investigations were inconclusive, probably because of the very low silica losses.

CONCLUSIONS

Based on results after exposure of 80- and 40-pct-Al_2O_3 and 95-pct-SiO_2 brick to steam at pressures up to 1,000 psig and temperatures as high as 1,400° C for periods ranging up to 120 h, the following conclusions can be made:

1. Steam-induced silica losses from silica-alumina refractories are less than 0.5 pct at temperatures below 1,000° C, even at steam partial pressures of up to 1,000 psig.

2. At temperatures greater than 1,000° C, small losses (<3 pct at 1,400° C) are observed to occur in the first 80 h of exposure if the steam partial pressure is high (1,000 psig).

3. Losses increase with increasing temperature and steam partial pressure.

4. The rate of silica loss drops to zero after about 80 h of exposure even at temperatures as high as 1,400° C.

5. Neither the total silica content (in the refractories containing 20 or more percent silica investigated) nor the crystalline form in which the silica is present were found to have an effect on the rate of steam-induced silica loss.

6. The loss of silica does not appear to come from the exposed face of the refractory, but instead seems to be uniform throughout the specimen.

7. The steam-induced loss of silica from silica-alumina refractories is low enough to permit the use of low-alumina refractories made from domestic raw materials to be used in dry ash coal gasifiers. These refractories are also recommended for other high-steam environments when the small amount of silica lost during plant start-up will not pose a problem in downsteam equipment.

REFERENCES

1. Morey, G. W., and J. M. Hesselgesser. The Solubility of Quartz and Some Other Substances in Superheated Steam at High Pressures. Trans. ASME, v. 73, 1951, pp. 865-875.

2. Raymon, N. S., and L. Y. Sadler III. Refractory Lining Materials for Coal Gasifiers. BuMines IC 8721, 1976, 22 pp.

3. Dial, R. E. Refractories for Coal Gasification and Liquefaction. Am. Ceram. Soc. Bull., v. 54, 1975, pp. 640-643.

4. Sadler, L. Y. III., N. S. Raymon, K. H. Ivey, and H. Heystek. Evaluation of Refractory Liner Materials for Use in Nonslagging, High Btu Coal-Gasifier Reactors. Am. Ceram. Soc. Bull., v. 58, 1979, pp. 705-709, 714.

5. _____. Effects of High Pressure, High Temperature Steam-Containing Environments on Alumina Refractory Concretes.

Am. Ceram. Soc. Bull., v. 60, 1981, pp. 703-706.

6. Sadler, L. Y. III., H. Heystek, N. S. Raymon, and T. A. Clancy. Refractories for Dry Ash Coal Gasifiers. BuMines RI 8913, 1984, 48 pp.

7. Feldkirchner, H. L., and J. L. Johnson. High Pressure Thermobalance. Rev. Sci. Instrum., v. 39, 1968, pp. 1227-1229.

8. Forgac, J., and J. C. Angus. A Pressurized Thermobalance for Use at Extreme Conditions. Ind. and Eng. Chem. Fundam., v. 18, 1979, pp. 416-418.

9. Sears, J. T., E. A. Maxfield, and S. S. Tamhankar. Pressurized Thermobalance for Use in Oxidizing Atmospheres at High Temperatures. Ind. and Eng. Chem. Fundam., v. 21, 1982, pp. 474-478.