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Refractory Lining Materials for Coal Gasifiers

A Literature Review of Reactions Involving High-Temperature Gas and Alkali Metal Vapors

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REFRACTORY LINING MATERIALS FOR COAL GASIFIERS

A Literature Review of Reactions Involving High-Temperature Gas and Alkali Metal Vapors

by

N. S. Raymon[1] and L. Y. Sadler III[2]

ABSTRACT

As part of an interagency agreement with the Energy Research and Development Administration to develop improved refractory materials for use in coal gasification processes, the Bureau of Mines reviewed the literature to determine the effect of steam, H_2, CO, and CH_4 as well as the alkali metal oxides K_2O and Na_2O on refractory materials. Emphasis was given to the performance of high-alumina castable and fired refractories to conditions expected in coal gasification processes. Approximately 85 references were reviewed with 40 cited in the text. The literature was found to contain little data directly applicable to the selection of refractory lining materials suitable for use under the conditions of temperature, pressure, and gas compositions expected in second generation coal gasification reactors.

INTRODUCTION

A large percentage of the U.S. energy supply comes from natural gas. Already domestic production is failing to match the demand for more than 60 billion cubic feet per day of natural gas. Estimates indicate that domestic production of natural gas will amount to only about one-half the demand by 1985. Therefore, it is imperative that a process for producing synthetic natural gas on a large scale from our abundant supplies of coal be developed and utilized rapidly.

Coal gasification equipment must be lined with refractory material to lower the temperature of the outer metal shell to reduce heat losses and prevent metal failure. In addition to atmospheres rich in hydrogen, methane, carbon oxides, and water vapor, highly erosive conditions, resulting from movement of solid coal and slag particles as well as molten slags, are also encountered. These conditions present a special challenge to refractories used in linings and insulation. In recent years, the Bureau of Mines has been engaged in research to develop refractories that will maintain the integrity of the equipment used in coal gasification processes.

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[1] Metallurgist.
[2] Chemical engineer.

As part of an interagency agreement with the Energy Research and Development Administration (ERDA), the Bureau reviewed the literature to determine the role of selected high-temperature gases and alkali metal vapors in producing conditions which may lead to failure of refractory liners in coal gasifiers. Known cases of failure of refractory furnace linings caused by various gases and alkalis at high temperatures also were examined. This report presents the findings of a review of approximately 85 pertinent references, with 41 being cited in the text.

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BACKGROUND

Coal gasification is a highly endothermic process conducted at high temperatures and at pressures ranging from 1 to over 100 atmospheres. Air, enriched air, or pure oxygen is mixed with steam to provide the necessary oxygen and hydrogen to allow the classic gasification reactions to proceed as follows:

$$2C + O_2 \rightarrow 2CO \text{ (exothermic)} \quad (1)$$

$$C + H_2O \rightarrow CO + H_2 \text{ (endothermic)} \quad (2)$$

$$C + CO_2 \rightarrow 2CO \text{ (endothermic)} \quad (3)$$

$$C + 2H_2O \rightarrow CO_2 + 2H_2 \text{ (endothermic)} \quad (4)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \text{ (endothermic)} \quad (5)$$

A typical gas analysis that is generally found in a low-Btu coal gasifier reactor (air used as oxygen source) is given in table 1. Gas concentrations, however, may vary markedly from these values depending on which one of the many gasification processes is used (27, 32).[3] For example, when pure oxygen is used, a "high-Btu" gas is produced by eliminating nitrogen from the raw gasifier product. Other compounds such as alkali metal vapors from coal ash also may be present. A list of the aboveground coal gasification processes and a summary of operating conditions are given in table 2 (26).

[3]Underlined numbers in parentheses refer to items in the list of references preceding the bibliography.

TABLE 1. - Typical low-Btu raw gasifier gas compositions (16), (19)

Component	Volume-percent
CO_2	9.0
N_2	19.0
CO	6.0
H_2	14.0
CH_4	2.0
NH_3	.050
H_2S	.150
C_2H_6	.250
COS	.015
Thiophene	.003
Methyl thiophene	.001
Dimethyl thiophene	.001
Benzene	.034
Toluene	.009
C/Aromatics	.002
SO_2	.001
CS_2	.001
Methyl mercaptan	.006
H_2O	49.477
Total	100.000

TABLE 2. - Coal gasification processes

Process	Reactor bed type	Gasifying medium	Pressure, atmospheres	Temperature, ° C
LOW-BTU GAS				
Commercial:				
Winkler	Entrained	Air-steam	1	800
Lurgi	Fixed	do	20	550
Experimental:				
GE fixed bed	do	do	8	550
Westinghouse	Fluidized	do	10-16	700-1,100
MEDIUM- AND HIGH-BTU GAS				
Commercial:				
Lurgi	Fixed	Oxygen-steam	30-35	250-1,100
Koppers-Totzek	Entrained	do	1	950-1,300
Winkler	Fluidized	do	1	800-1,000
Experimental:				
Hygas (IGT)	do	Hydrogen	75-100	650-1,000
CO_2 acceptor	do	Air-regenerator / Steam gasifier	10-20	850
Synthane	do	Oxygen-steam	40-70	600-1,000
Bigas	Entrained	do	70	[1] 1,500
			1-3	[2] 925
CO gas	Fluidized	Steam	1-3	870-925
UC-Battelle	do	do	6	870-1,000

[1] First stage.
[2] Second stage.

In order to maintain high operating efficiency, primary gasification reactors must be lined with refractory materials to insulate against heat loss. The refractory also acts to reduce metal shell temperatures for protection against high-temperature corrosive attack by process gases, assures that the shell operates at low enough temperatures that its mechanical strength is sufficient to permit an economic thickness of metal to be used and helps prevent erosion of the metal shell by entrained solid particles or by molten slags. Two lining designs have been proven in practice (14). One consists of a layer of low-iron, low-silica dense alumina castable at the hot face with a layer of low-iron, low-silica insulating high-alumina castable backup between the dense castable and the metal vessel shell. The other design utilizes low-iron, low-silica dense alumina shapes in place of the dense castable.

Gasifier conditions present a severe challenge to refractory integrity. The major failure mechanisms either observed or expected in gasifier furnace refractory linings are as follows:

1. Spalling from thermal shock
2. Explosive release of trapped steam
3. Erosion by solid coal and ash particles
4. Molten slag attack
5. Drying and thermal expansion cracking
6. Attack by acids contained in condensed steam near metal shell
7. Attack by H_2, CO, H_2O, CH_4, CO_2, and other gases
8. Alkali metal vapor attack
9. Flame erosion

Some experience has been gained over the years regarding the stability of refractory linings in the secondary reformer of synthetic ammonia plants (39). The conditions in ammonia production are similar to those expected in second-generation coal gasifiers. Synthetic methane has been produced in limited quantities in several foreign countries, notably Germany, South Africa, Turkey, and India, for at least 30 years utilizing certain of the older processes such as Winkler, Koppers-Totzek, and Lurgi.

With this general information available, a detailed literature survey was conducted to determine the effect of steam, H_2, CO, and CH_4 as well as the alkali metal oxides K_2O and Na_2O on refractory materials. Emphasis was given to the performance of high-alumina castables and fired refractories to conditions expected in coal gasification processes. The following sections present the results of the literature review.

HYDROGEN-REFRACTORY REACTIONS

Crowley (5-6), in a two-part investigation, studies H_2-SiO_2 reactions in refractories. He states that the reaction

$$SiO_2 + H_2 \rightarrow H_2O + SiO \quad (6)$$

is responsible for refractory weight loss through (SiO) volatilization followed by redeposition of SiO_2. Samples representing nine refractory compositions having a SiO_2 content of 8 to 95 percent were exposed, after prefiring to 1,350°-1,580° C, to H_2-N_2 gas mixtures (both flowing and stagnant) at 980° to 1,425° C and at pressures up to 300 psig, with and without water vapor present, for times from 16 to 200 hours. Weight losses and, in some cases, compressive strengths were measured. Table 3 lists the refractories investigated.

TABLE 3. - Refractories used by Crowley (5-6) to determine H_2-SiO_2 reactions

Type	SiO_2 percent	Fired to	Minerals present[1]
Silica	95	1,485° C	Cr, Tr
Semisilica	76	1,450° C	Qtz, Mu
High duty	57	1,390° C	Mu, Cr
Super duty (high-fired)	52	1,580° C	Mu, Cr
Super duty	52	1,390° C	Mu, Cr
60 percent alumina	34	1,390° C	Mu
70 percent alumina	26	1,390° C	Mu, Al
Mullite	24	1,450° C	Mu
85 pct alumina (phosphate bonded)	10	1,450° C	Al, Mu
90 pct alumina	8	1,485° C	Al, Mu

[1] Cr = crystobalite; Tr = tridymite; Qtz = quartz; Mu = mullite; Al = alumina.

Crowley concluded that refractories containing free and/or combined SiO_2 lose both weight and strength above 1,150° C in either pure H_2 or in mixed H_2-N_2 atmospheres. Weight losses were found to increase as free SiO_2 content, H_2 concentration, temperature, and gas flow rate increased. The SiO_2-H_2 reaction was found to be as sensitive to changes in gas flow rate as reaction temperature and thus was judged to be mass-transfer controlled. It was found that SiO did not readily diffuse through refractory concrete, and the reaction front can be expected to penetrate only a small distance into the refractory. The minimum temperature required for significant reaction to occur was reported to be about 925° C. The presence of a small amount of water vapor (0.5 psia partial pressure) was found to retard, but not halt, the reaction.

Schwerdtfeger (35) investigated the rate of SiO formation for SiO_2 spheres in contact with H_2, H_2-H_2O, H_2-He, H_2-Ar, and CO-CO_2 gas mixtures at 1,500° C and 1 atmosphere total pressure. He concluded that the rate of formation of SiO by reaction with H_2 was controlled possibly, to some extent, by slow surface reaction but primarily by convective diffusion.

Crowley's work (5) on alumina-phosphate bond in fired phosphate-bonded bricks indicated that these brick were not severely attacked in the H_2 atmosphere, but Crowley (7) and Venable (39) state that field evidence has shown that phosphate-bonded alumina castables cannot be used in ammonia plant secondary reformers. Crowley later reverses himself (9), however, and states that phosphate-bonded high-alumina refractories are effective patching mateials in coal gasification pilot plants.

Mullite and aluminosilicate-bonded refractories were attacked in H_2-N_2 atmospheres at temperatures of 1,100° to 1,370° C to a greater extent than in pure H_2 atmospheres (5). Crowley (5) recommends that refractories containing SiO_2 not be used at temperatures greater than 1,100° C in H_2-containing (rich) atmospheres. Ninety-nine percent alumina fired shapes or iron-free calcium aluminate-bonded refractory castables are recommended for temperatures in excess of 1,315° C.

Ignatova (25) found that with corundum and aluminosilicate refractories held in an atmosphere of H_2 and dissociated ammonia for periods of 50 to 175 hours at 1,200° to 1,700° C, resistance to attack increased with increasing alumina content and density. Changes in phase composition were accompanied by changes in structure and an increase in creep.

Grant (22) showed that on the basis of abrasion tests, silica bricks become embrittled after reheating in H_2 or CO. Enhanced crystallization of calcium silicate in the matrix was ruled out as the major cause of the observed embrittlement. Instead, the H_2 and CO treatments were found to enhance the development of cristobalite from alpha-quartz at 1,400° C and in silica brick at 1,550° C. The embrittlement of silica bricks at temperatures as low as 1,000° C was attributed to the formation of additional cristobalite.

Trostel (38) studied the effect of dry H_2 atmospheres on the "volatilization" of alumina and zirconia. The reaction

$$Al_2O_3(S) + 2H_2(g) \rightleftarrows Al_2O(g) + 2H_2O(g) \qquad (7)$$

is representative of a class of reactions giving volatile aluminum and zirconium suboxides. The stability of alumina and zirconia refractories in H_2 atmospheres was determined by measuring weight losses and compositional changes when heated in dry H_2 using alumina and zirconia rods fired previously to 1,750° C in an oxidizing atmosphere.

For alumina refractories heated in dry hydrogen at 1,100° C, only Na_2O loss was noted. At 1,500° C, loss of SiO_2 in addition to Na_2O was noted. At 1,700° C, MgO, Na_2O, and SiO_2 were lost. At 1,900° C, some Al_2O_3 in addition to Na_2O, SiO_2, and MgO was lost. The work also revealed that during a 2-hour heating period, 50 percent of the Na_2O was lost at 1,500° C. In the same period at 1,900° C, virtually all of the Na_2O, SiO_2, and MgO was lost. Results for oxide impurities in a zirconia refractory were found to be similar. These investigations indicated that the mechanism responsible for the observed weight loss in both refractories is the reduction of oxides to more volatile suboxides and metals.

Trostel (38) concluded the following:

1. Alumina refractories for use in dry H_2 atmospheres up to 1,500° C should have minimum Na_2O and SiO_2 contents.

2. The quantity of Na_2O should be held as low as possible in alumina and zirconia refractories exposed to dry H_2 whenever expected operating temperatures will exceed 600° C.

3. Zirconia refractories exposed to dry H_2 will lose SiO_2 and TiO_2 through volatilization below 1,500° C.

4. CaO used to stabilize ZrO_2 will not volatilize below 2,000° C in dry H_2.

In laboratory investigations of the high-temperature oxidation of metals at 1,320° C, Ahmad (1) found that the volatilization of Na_2O from alumina under high-purity H_2 atmospheres is not by the suboxide formation but by reduction to metallic sodium vapor:

$$Na_2O(s) + H_2(g) \rightarrow 2Na(g) + H_2O(g). \quad (8)$$

From 400° to 500° C, the combination of sodium vapor and H_2 becomes favorable thermodynamically, and a white whiskery deposit occurs.

Ruprecht (34) concluded from his work on the effects of natural gas and H_2 on refractories that H_2 gas passed over fire-clay brick, silica brick, diaspore brick, and magnesia brick at temperatures ranging from 425° to 980° C failed in every case to produce any disintegration. Chrome brick cracked and lost strength when subjected to H_2 at 870° to 980° C.

STEAM REFRACTORY REACTIONS

Huggett (24) investigated the vapor phase transport of SiO_2 in high-pressure steam atmospheres. The investigation was prompted by the fact that 100 pounds of SiO_2 was discovered to have been removed, in a 3-month period, from the refractory liner of the secondary reformer in a British ammonia plant and condensed in downstream equipment operating at lower temperatures. He first used data by Tombs (37) to show that the reaction

$$SiO_2 + H_2 \rightarrow SiO + H_2O; \log K = \frac{22,700}{T} + 7.37 \quad (9)$$

could be responsible for a 180-fold increase in SiO_2 transport at 1,350° C compared with 1,100° C. His calculations prompted relining the reformer with low-SiO_2 alumina bricks but SiO_2 transport was still found. Consequently, the foregoing reaction mechanism was rejected as the dominant one, and steam-induced transport was investigated. In an earlier investigation, Morey (30) measured the "solubility" of SiO_2 in high-pressure steam at 400° and 500° C.

At 400° C, he found the "solubility" to increase from 1 ppm SiO_2 in steam at 35 atmospheres total pressure to 1,550 ppm at 1,000 atmospheres; at 500° C, the "solubility" increased from 4 ppm at 35 atmospheres to 260 ppm at 1,000 atmospheres. Huggett (24) then derived an equation that allowed him to predict the "solubility" of SiO_2 in superheated steam as a function of temperature and steam partial pressure:

$$\log (SiO_2 \text{ ppm}) = \frac{-2,300}{K} = 1.5 \log p \text{ (absolute)} + 0.1. \qquad (10)$$

At 25 psig and 800° C, the "solubility" of SiO_2 in steam was calculated at 5 to 10 ppm. Samples taken from the reformer gas showed that although the vapor was not saturated with "silica vapor," the foregoing analysis could very well explain the observed SiO_2 transport. There was further evidence that the rate of transport is diffusion controlled in the gas phase and dependent on surface contact area.

Budnikov (4) reported that when a fired corundum refractory was exposed to steam at 250° to 370° C and 1,400 to ~4,200 psi, the frequency of occurrence of hydrates on the surface decreased in the following order: boehmite > diaspore > gibbsite. He also reported a strength reduction of ~50 percent for the corundum refractory after ~500 hours exposure to steam at 310° C and 1,420 psi.

A strength reduction of up to 90 percent has been reported by Fuller (17) for a calcium-aluminate-bonded, high-alumina castable after exposure to steam at 200° to 300° C for periods ranging from 100 minutes to 4 hours at pressures below 8,500 psi. (The pressure was not measured, but only estimated from the test conditions.) The principal reactions he observed in samples prefired to 1,010° C prior to exposure, consisted of the hydration of $CaO \cdot Al_2O_3$ and $CaO \cdot 2Al_2O_3$ to form $4CaO \cdot 3Al_2O_3 \cdot 3H_2O$, and, at lower temperatures, the hydration of Al_2O_3 to form boehmite. In contrast, very little reduction in strength was observed for a calcined clay-calcium aluminate-bonded castable and mullite after exposure to steam at 510° C.

Gac (18) investigated the change in properties of a dense high-alumina (94 percent) castable, a dense intermediate-alumina castable (44 to 47 percent), and an insulating low-alumina castable (33 to 36 percent) upon exposure to atmospheres containing 49 volume-percent steam and 51 volume-percent of either CO or N_2. Unfired specimens (dried only at 100° C) were exposed to the test atmosphere at 199° C and 450 psi for up to 18 days. He observed four general chemical reactions: (1) The continued hydration of initially unreacted calcium aluminate cement compounds, (2) the dissolution (leaching) of CaO from the cement bond phases, (3) the hydration of Al_2O_3 to form boehmite, and (4) the dissolution/volatilization of SiO_2. The extent of these reactions depended upon the type of castable (raw materials) used, exposure period, and whether N_2 or CO was present (CO being more reactive than N_2).

All three castables lost weight in the steam-N_2 atmosphere (2 to 4 percent), and gained weight in the steam-CO atmosphere (less than 3 percent). The intermediate-alumina castable containing a mullite aggregate showed the smallest weight changes. In the steam-CO atmosphere, a volume expansion was

observed for all three castables, the expansion being largest for the high-alumina castable and lowest for the intermediate-alumina castable.

Surprisingly, however, no significant reduction in modulus of rupture was observed, except for the high-alumina castable exposed to the steam-CO atmosphere for 12 days or more. Unlike the strength losses reported by Fuller (17) for specimens exposed to steam at higher temperatures (510° C) and pressures (>1,000 psi), the specimens studied by Day (18) gained strength and in the case of the high-alumina castable, the modulus of rupture had nearly doubled after 18 days in the steam-N_2 atmosphere. In a pure steam atmosphere at 450 psi and 237° C, the modulus of rupture of the intermediate-alumina castable increased from 1,000 psi (for samples as-cast and dried at 100° C) to ~2,300 psi after exposure for 15 days and then remained constant up to a maximum exposure time of 48 days (12). During this time, the weight loss reached a maximum of ~4 percent at 15 days, but this was followed by a weight gain such that after 48 days the weight loss was only ~1.3 percent.

Brady (3) concluded that at pressures below 300 atmospheres, $Si_2O(OH)_6$ was the most likely volatile species, which implies that the reaction is

$$2SiO_2\,(\text{quarts}) + 3H_2O\ (g) \rightleftarrows Si_2O(OH)_6\,(g). \qquad (11)$$

Venable (39) gives chemical analyses (table 4) of deposits found in waste heat boilers downstream from the secondary reformer of an ammonia plant. The data tend to substantiate laboratory findings that oxides other than silica are volatilized in hot H_2-steam atmospheres.

TABLE 4. - Deposit analyses[1] of waste-heat boiler tubes, weight percent

Oxide	Boiler 1	Boiler 2
SiO_2	70	42
Al_2O_3	6.7	20
CaO	15	.6
Fe_2O_3	4.4	6
Na_2	.84	21
K_2O	.43	3
TiO_2	Trace	4
NiO	.73	1.8
MgO	.50	.23
Total	[2]98.60	[2]98.63

[1] X-ray diffraction patterns indicate the presence of silica as quartz (SiO_2) and wollastonite ($CaSiO_3$).
[2] Small amounts of other oxides present.

Dial (14) reports that steam removes SiO_2 from a surface layer 1/2-inch thick in dense 80- and 90-percent alumina shapes containing electric furnace mullite in carbon black reactors operating at hot-face temperatures of 1,540° - 1,760° C. The reaction given is

$$SiO_2 + H_2O\ (XS) \xrightarrow{815°\ C} H_xSiO_y\,. \qquad (12)$$

He states that when H_2 and steam are both present, SiO_2-steam reactions, rather than silica-H_2 reactions, are responsible for SiO_2 depletion in the refractory. Dial (13) further states that use of high-alumina castables in ammonia-plant secondary reformers reduces SiO_2 fouling in the waste heat boilers. He (14) also reports that because the thermal conductivity of silicon carbide-base refractories is high, they are not aggressively attacked by H_2-steam atmospheres because hot-face temperatures are kept lower.

Crowley (7) recommends against the use of phosphate-bonded castable refractories as lining material for ammonia-plant secondary reformers because the bond is subject to severe attack in the hot H_2- and steam-rich atmosphere.

CARBON MONOXIDE-REFRACTORY REACTIONS

Berry (2) extensively investigated the reaction,

$$2CO \rightarrow CO_2 + C, \qquad (13)$$

long known to be responsible for disintegration of refractory linings in many furnace atmospheres. Carefully controlled laboratory experiments consisted of measuring weight changes of reagent-grade Fe_2O_3 (well recognized as a catalyst for the carbon deposition reaction in furnace refractories) suspended in a CO-containing gas stream. It was found that reaction (8) proceeded slowly up to 510° C, reaching a maximum at 570° C, and decreasing to practically zero by 730° C.

It was found that iron, magnetite, and normal cementite were not active catalysts for the reaction, but Hagg carbide and another carbide having the structure of cementite were found to be active catalysts. The catalytic effect of these compounds was found to increase or decrease owing to traces of impurities in either the gas phase or catalyst. The amount of carbon formed increased markedly when CO gas contained small amounts of water or H_2. The presence of both water and H_2 increased carbon deposition to an even greater extent than did either water or H_2 alone.

Ammonia in concentrations as low as 0.06 volume-percent in the gas phase suppressed carbon formation as did sulfur compounds. One percent sulfur or ammonium sulfate completely prevented carbon deposition. These effects were attributed to catalyst poisoning by the sulfur and ammonia compounds. The catalyst could be reactivated by addition of metallic zinc, zinc oxide, or an alkali such as potassium carbonate.

Large variations in the amount of carbon deposition were found between CO gases obtained from different sources in the experiments. Variations were even seen as experiments progressed with the same tank of CO. When the CO was passed through a liquid nitrogen trap prior to passage over the iron oxide catalyst, much greater carbon deposition was observed. Six percent of the material found in the trap was later determined to be COS. Further investigations showed that 1 percent COS was sufficient to stop carbon formation completely, and as little as 0.1 percent was sufficient to retard the reactions. Additional investigations showed that SO_2 also retarded the reaction, but methyl

alcohol accelerated it. Ferrous chloride greatly accelerated carbon deposition when it was used to treat specimens of super-duty fire-clay brick.

Patrick (31) investigated the action of zinc and zinc oxide as a catalyst for the decomposition of CO to form CO_2 and C in blast furnace linings after observing that failed linings were greatly enriched in zinc, both as the metal and oxide. He determined experimentally that cyclic melting and freezing of zinc metal impregnated in the refractory was not responsible for the disintegration of refractory blast furnace linings. Neither oxidation nor conversion of the impregnated zinc metal to sulfide cause the refractory to fail. However, ZnO did catalyze the decomposition reaction of CO to form carbon, and the catalytic action increased markedly between 300° and 500° C, although the catalytic activity showed by Zn and ZnO was of an order of magnitude less than the activity shown by iron compounds. The disintegrating effect of deposited carbon in fire brick was attributed to the preferential deposition of carbon at sites where linear disruptive forces could be exerted.

Davis (11) determined that the carbon deposited in fire brick at 450° C was threadlike in appearance.

Shapland (36) investigated the resistance to CO disintegration of five commercial calcium aluminate cements currently used in the formulation of most refractory castables in the United States. After subjecting the cements to flowing CO at 500° C for up to 40 hours, only two were found to have good resistance to CO attack.

Gitzen (21) also investigated the CO resistance of several typical calcium aluminate cements. In this work, he compared castable refractory concretes made from these cements and an aggregate known to be free of catalyzing impurities with a typical fire brick of known high resistance to CO disintegration. The results indicated that the disintegration of calcium aluminate concretes was analogous to that of refractory brick in that low-purity cements and brick had poor resistance to CO attack. The resistance of intermediate-purity cements ranged from poor to good. The high-purity samples had resistance to disintegration comparable to that of super-duty fire-clay brick. Huggett (23) describes the use of a mixture of calcined kaolin and calcium aluminate cement as a satisfactory CO-resistant monolithic lining for an ammonia plant secondary reformer operating at 200 psi and at temperatures up to 1,350° C.

A comparison of the results obtained by Gac and Day (18) for steam-N_2 and steam-CO atmospheres demonstrates the chemical aggressiveness of CO in contact with castable refractories. For identical conditions, the mechanical strength was always lower in the steam-CO atmosphere than in the steam-N_2 atmosphere. Furthermore, boehmite was formed at much larger depths in the castables when CO rather than N_2 was present, increasing from 2-4 to ~20 millimeters for the high-alumina castable for 18-day exposure. CO also seemed to have a greater effect upon the cement bond phases since large quantities of $Ca(HCO_2)_2$ were found on the external surface of samples exposed to the steam-CO atmosphere and the source of CaO for this reaction was the cement-bond phases.

Carbon monoxide can also cause refractory attack by SiO_2 volatilization. Schwerdtfeger (35) concluded that the rate of the CO-SiO_2 reaction was controlled by surface reaction in CO-CO_2 gas mixtures at 1,500° C and 1 atmosphere total pressure.

METHANE-REFRACTORY REACTIONS

Geck (20) investigated the attack of CH_4 gas on several types of refractory brick. Test specimens were exposed to CH_4-N_2 atmospheres at temperatures from 600° to 1,000° C for 1/2 to 6 hours. Examination of the specimens after treatment revealed that forsterite, chrome-magnesite, and magnesite-chrome brick were especially sensitive to methane. Damage proceeded from the outside by spalling of friable layers. Dissociation of carbon from the metastable CH_4 was determined to be the cause of the disintegration of the bricks. Low-iron magnesite, silica, corundum, and fire-clay bricks showed very good methane resistance. The investigator concluded that since magnesium oxide was resistant to methane, increasing the proportion of magnesium oxide in forsterite bricks would increase their resistance to methane.

Currier (10) states that at temperatures between 540° and 1,100° C, most basic refractories are completely disintegrated by atmospheres containing cracked hydrocarbons, and carbon is deposited. Although it takes place more gradually, a similar reaction occurs between CO and fire-clay brick in the range of 400° to 480° C. Ruprecht (34) reports that, because iron catalyzes the decomposition of CH_4 at temperatures as low as 350° C, only essentially iron-free basic bricks can withstand the reaction. Ruprecht (34) states the most pronounced attack was observed with the natural gas that was first "cracked" at a temperature of 760° C or higher and then passed over the refractory at a temperature between 480° and 815° C.

ALKALI-REFRACTORY REACTIONS

When the reaction occurs, the metal vapors oxidize again. Shapland (36) found that castable refractories made with five different commercial high-alumina cements showed poor resistance to attack by potassium carbonate, with all specimens failing after exposure to K_2CO_3 at 950° C for 5 hours.

Vol'fson (40) described sodium oxide-induced failure of 63-percent alumina brick in a chemical incinerator, operating at 1,100° C, over a 2-month period. A laboratory testing program to aid in selecting a more resistant refractory was undertaken in which the sodium oxide resistance of spinel, spinel-magnesia, 45-percent Al_2O_3, 25-percent Al_2O_3, magnesite, dolomite, and chrome-magnesite specimens was determined at 1,100° C. The study revealed that alumina samples were penetrated and embrittled by NaOH and that bloating increased with increasing alumina content. Magnesite brick were also severely impregnated and bloated by the slag as were the dolomite specimens. Chrome-magnesite specimens were somewhat less affected. The spinel-containing refractories did not show any reaction with NaOH, and thus the incinerator was lined with spinel-magnesia and spinel refractory. Examination of this lining after 4 months of service showed almost no damage.

Farris (15) investigated the mechanism of attack and destruction of aluminous refractories ranging in composition from super-duty (42-percent) to 90-percent alumina content in order to determine the refractory constituents (phases) most subject to alkali attack, the rate of attack, the reaction products, and properties that make aluminous refractories resistant to alkali attack. The tests were made by placing granular potassium carbonate in a hole drilled in the refractory specimen followed by heating to 950° C (alkali cup tests), and the results were compared with tests made by heating ground refractory mixed with various alkalis to between 855° and 1,440° C. The most common reaction products were alkali aluminum silicates. The refractory components of the various aluminous refractory compositions were all attacked as follows: The cristobalite and glass were the first to be consumed, followed by a continuous solution of mullite until depletion. There was little attack of alpha-alumina unless excess soda was available or the amount of silica was low and the temperature was above 1,100° C. The more reactive products of high glass and fine crystalline mullite were found most resistant to alkali. They had the ability to react with the alkali and to contain its attack at the surface, thereby limiting its penetration into the interior of the refractory.

Results of the alkali cup test on refractories from 42 to 70 percent alumina revealed that alkali resistance was inversely proportional to the amount of alumina content of the refractory. The 42-percent super-duty product had the highest resistance, followed by the 45-, 60-, and 70-percent alumina products. Of the 70-percent alumina products tested, the coarse-crystalline, high-fired 70-percent alumina brick with low surface area and maximum bond neck size was the most resistant to alkali attack. The attack mechanism of alkali on aluminous refractories consisted of impregnation, bond reaction, and bond depletion. Potassia reacted to form potassium aluminosilicates and sodium oxide formed soda aluminosilicates. Mechanical deterioration due to the expansive nature of the reactions was responsible for failure. For refractories of less than 50 percent Al_2O_3, alkali resistance can be maximized by a low surface area, porosity, and alkali content. For aluminous refractories with greater than 50 percent Al_2O_3, the matrix mullite bond should be mature and have minimum exposed surface area. Similar conclusions were reached by McCune (28) in an investigation of the mechanism of peeling of fire-clay brick in the low-temperature region of a blast furnace where 3 to 10 percent K_2O was the principal contaminant. He concluded that the formation of leucite and kaliophilite was the probable cause of peeling. Since silica is the first constituent to be attacked by K_2O, a high-silica low-alumina dense brick would tend to react with K_2O at a temperature low enough (below 925° C) to seal the surface and prevent subsurface alkali attack.

Rigby (33) studied reactions between alumina-silica specimens and mixtures of sodium carbonate and vanadium pentoxide. Specimens were made by heating mixtures of silica and alumina powder to between 1,500° and 1,700° C, grinding to minus 100 mesh, mixing with sodium carbonate, pressing into cylinders, and heating to progressive temperatures between 800° and 1,600° C. The results indicated that when alumina-silica refractories are attacked by soda, shrinkage on the refractory hot face occurs if the alumina-silica ratio is 1.5 or higher. The higher this ratio, the higher the shrinkage and the lower the

melt-formation temperature. At alumina-silica ratios below 1.0, there is expansion rather than contraction. When vanadium and sodium oxide are present, the sodium vanadate formed acts as a flux and increases the total amount of melt at any given temperature as well as acting as a mineralizer by enhancing the formation of sodium aluminum silicates at temperatures as low as 800° C. Reactions occurred at lower temperatures with vanadium oxide present.

CONCLUSIONS

Refractories are subject to attack by gases and volatile alkali metal oxide vapor at high temperatures and pressures in large coal gasification reaction vessels. However, the literature contains very little data on refractory resistance under these combinations of temperature, pressure, and gas compositions. The available data may be summarized as follows:

1. Both dry H_2 and H_2-steam atmospheres attack SiO_2-containing refractory shapes and castables via SiO_2 volatilization. Dry H_2 was shown to result in production of volatile aluminum suboxides, but the presence of steam retards this attack mechanism of both alumina- and silica-containing refractories.

2. Steam, at elevated temperatures and pressures, will attack calcium aluminate-bonded high-alumina (95-percent) refractories by hydration of both the bond and aggregate phases. These reactions can result in large losses in refractory mechanical strength.

3. Iron-containing refractories are subject to CO and CH_4 attack via carbon deposition. The presence of zinc was found to enhance CO attack but the presence of ammonia, sulfur compounds, and/or water vapor tend to retard CO and CH_4 attack.

4. In general, the rate of gaseous attack on refractories was found to increase with increasing temperature and pressure.

5. The stability of phosphorus compounds in atmospheres rich in steam, H_2, CH_4, and CO remains open to question.

6. Alkali attack on refractories was found to be accelerated by the presence of silica and vanadium compounds and enhanced by high porosity and surface area.

Published information covers steam, CH_4, CO, and H_2 attack, and except for steam-H_2, steam-CO, steam-N_2, N_2-H_2, and CO-CO_2 mixtures, gives very little information on attack by atmospheres consisting of multiple gas mixtures. Although some data describing exposure of refractories to various gases were presented for temperatures above 1,500° C, no information was presented on the effect of reducing gases at pressures above 30 atmospheres (with the exception of steam). Thus, there appears to be a pressing need for determining refractory resistance to reducing gas mixtures as well as alkali attack at elevated pressures (above 30 atmospheres) and at temperatures up to 1,200° C.

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