

# NEW DATA ON HYDROGEN-SILICA REACTIONS IN REFRACTORIES

Results indicate phosphate-bonded alumina brick and calcium aluminate concretes low in silica are appropriate vessel lining materials for hot hydrogen service.

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The great volumes of hydrogen being generated in petrochemical plants and refineries has brought a new set of problems to the hydrocarbon processing industry. Not the least of these are problems which arise from use of silicate-containing refractories as vessel linings.

In operations such as hydrogen synthesis and steam methane reforming, hydrogen at elevated temperatures reacts with free silica, or silicates in refractory linings and catalyst beds, to produce gaseous SiO and water:



The gaseous products are carried off in the process stream. When temperatures decrease downstream, the reaction reverses and silica is deposited as a solid. The result can be heat-exchanger fouling and product contamination.

The mechanism of the aggressive action of reducing atmospheres on refractories may be very complex (1, 2, 3, 4). It may involve the reduction of silica to silicon, the conversion of quartz to cristobalite, the formation of gaseous SiO, or if water vapor is present, the formation of silica hydrates, such as Si(OH)<sub>4</sub> or Si<sub>2</sub>O(OH)<sub>6</sub> (5, 6, 7).

Recent thermodynamic studies of SiO (8, 9), are not in agreement and serve to emphasize that very careful experimentation is required to attain equilibrium curves for the above equation. A study of the crystalline nature of SiO by Fourier analysis suggests that in some cases SiO may be a stoichiometric mixture of SiO<sub>2</sub> and Si (10). Other refractory oxides such as alumina and zirconia have been reduced to gaseous suboxides by hydrogen at around 3,300° F (11).

The study reported here was conducted in an attempt to learn more about such reactions, and to determine how hydrogen-containing atmospheres affect the strength and stability of various refractories. Samples of ten commonly used refractory brick ranging from 8 to 95% in SiO<sub>2</sub> content were exposed to 100% hydrogen and to 25% to 75% hydrogen in nitrogen at 1,800-2,600° F at atmospheric pressure for 16-200 hr. with and without water vapor present. The changes in weight were measured as a function of time. Effect of high-temperature hydrogen exposure on the compressive strength of one of the refractories was also studied.

## How the tests were made

The ten refractories are identified in Table I. All were standard, commercially available prefired bricks. For the weight tests, rectangular 3/8 x 3/8 x 3/4 in. specimens were cut from the bricks. Compressive strength was measured on 1-in. cubes. Gases were dry cylinder hydrogen and nitrogen, measured by flowmeters.

The apparatus is shown in Figure 1. Furnace temperature was

Table 1. Identification of refractories.

No.	Type	% SiO <sub>2</sub>	Fired to °F	Crystal structure*
1	Silica	95	2,705	CR, TR
2	Semi silica	76	2,642	QTZ, MU
3	High duty	57	2,534	MU, CR
4A	Super Duty (high fire)	52	2,876	MU, CR
4B	Super duty	52	2,534	MU, CR
5	60% Alumina	34	2,534	MU
6	70% Alumina	26	2,534	MU, AL
7	Mullite	24	2,642	MU
8	85% Alumina (phosphate bonded)	10	2,462	AL, MU
9	90% Alumina	8	2,705	AL, MU

\*CR Cristobalite; TR Tridymite; QTZ Quartz; MU Mullite; AL Alumina.

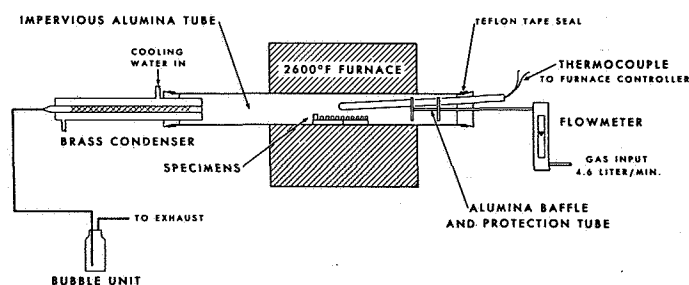


Figure 1. Schematic view of test apparatus.

controlled by a platinum thermocouple at the center of the alumina tube. Maximum temperature differential between the front (coldest) and center (hottest) of the tube was 40° F.

Runs were carried out as follows. A row of ten specimens—one specimen of each refractory—was placed on an alumina tile. A slightly larger specimen of 99% alumina was placed at each end of the row to protect the refractories from erosion by incoming gases or deposition of SiO from the exit gases, and the tile then placed in the cold tube. With pure nitrogen flowing through the tube, the furnace first was brought to a predetermined temperature. Then the desired gas mixture was passed over the specimens at 4.6 liters/min. to give a theoretical moving front of 1.5 in./sec. Repeat runs with various gas velocities were made to get some idea of the effect of velocity on SiO loss. Individual runs lasted from 16 to over 200 hr. Sometimes the incoming gases were first bubbled

through water to provide about a 25-mm partial pressure of water vapor.

At the end of a run, the furnace was shut off, and the specimens were cooled to about 700°F in the test atmosphere. They then were removed from the tube, placed in a desiccator, cooled to room temperature, and weighed.

## Results and discussion

The effects of various temperatures and atmospheres on the weight of the refractories are summarized in Figures 2 through 7. Figure 2 shows the results of a typical 3-day run in pure hydrogen. Longer runs indicated the weight loss curves tend to level off as the silica is removed from the surface of the specimens. All the specimens fit this pattern but some of the individual curves are omitted for simplicity.

The phosphate-bonded 85% alumina, specimen 8, lost about 4.5% initially, but lost very little more with continued exposure. This initial weight change probably is caused by the loss of volatile oxides. Of the two super duty samples, specimen 4A always

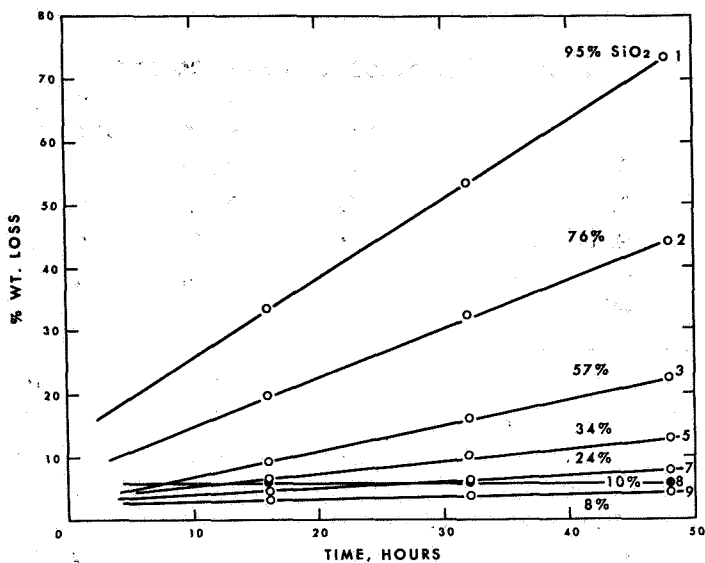


Figure 2. Weight loss of brick at 2,600°F in a 100% hydrogen atmosphere.

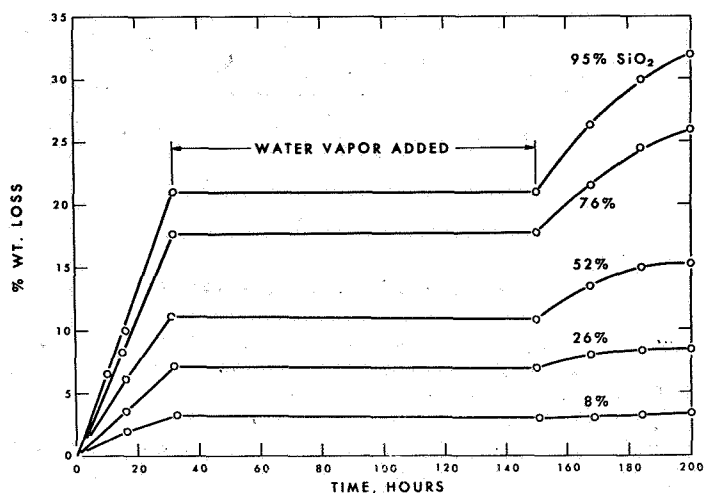


Figure 3. Effect of water vapor on weight loss of brick at 2,500°F in a 75% H<sub>2</sub>-25% N<sub>2</sub> atmosphere. Water vapor (25mm) added after 32 hr. and stopped after 150 hr.

lost less than 4B at a given temperature, probably because it had been fired at a higher temperature.

When water vapor is added to the gas, the equilibrium in Equation 1 is forced to the left and the specimen weight changes very little, Figure 3. When the water vapor is removed, the weight

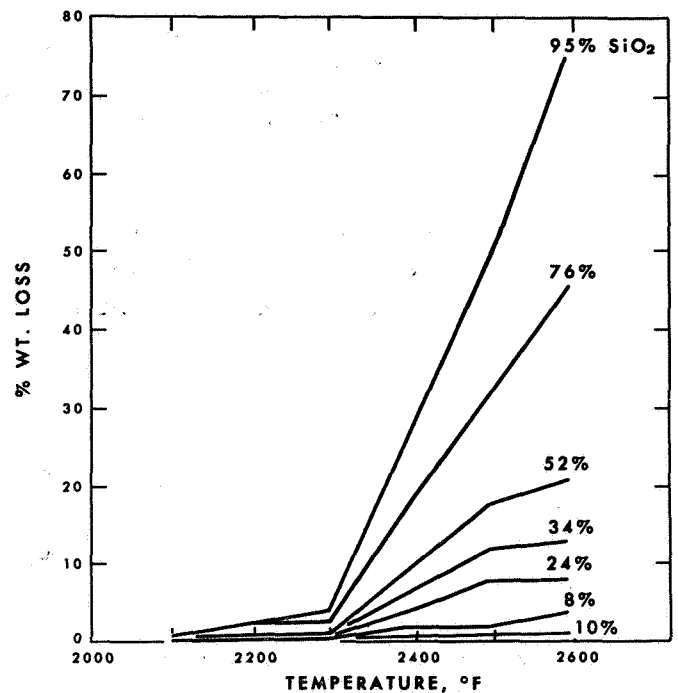


Figure 4. Effect of temperature on weight loss of brick after 50 hr. in hydrogen.

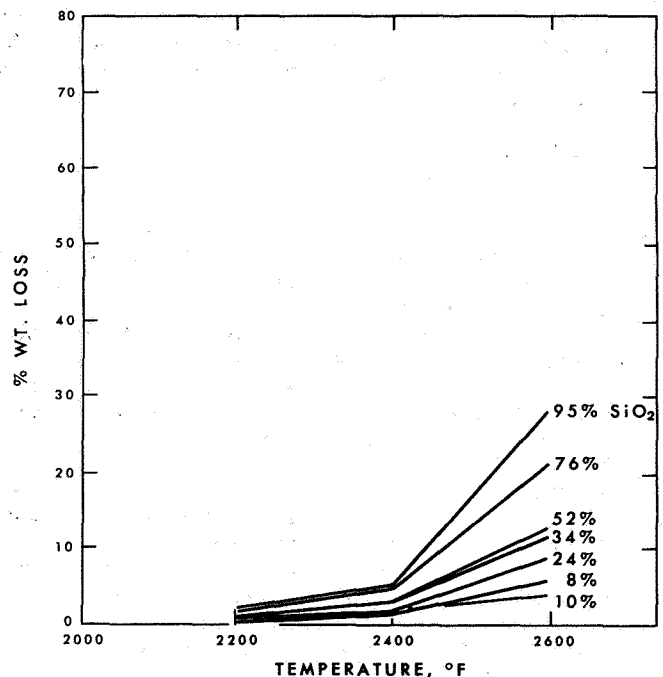


Figure 5. Weight loss of brick after 50 hr. in a 50% H<sub>2</sub>-50% N<sub>2</sub> atmosphere.

loss again increases with exposure time.

Figure 4 shows that 2,100°F is the minimum temperature at which a continuous daily weight loss can be measured, and that the loss does not become significant until 2,300°F. The curve for the 10%-silica phosphate-bonded alumina, which changes very little with temperature, was corrected for the initial 4.5% loss.

Figure 5 shows weight loss at 2,200°F, 2,400°F, and 2,600°F in a 50% H<sub>2</sub>-50% N<sub>2</sub> atmosphere. Refractories which contain free silica (more than 52% SiO<sub>2</sub>) lose less weight in 50% H<sub>2</sub> than they do in 100% H<sub>2</sub>. This result is consistent with the basic reaction. Aluminosilicate- or mullite-bonded refractories with a silica content below 52% lose more weight at 2,600°F in 50% H<sub>2</sub> than in 100% H<sub>2</sub>. The reason for this is not known. The 10% SiO<sub>2</sub> curve has the initial 4.5% weight loss subtracted.

## Weight loss vs. silica content

The change in weight loss with silica content is shown in Figure

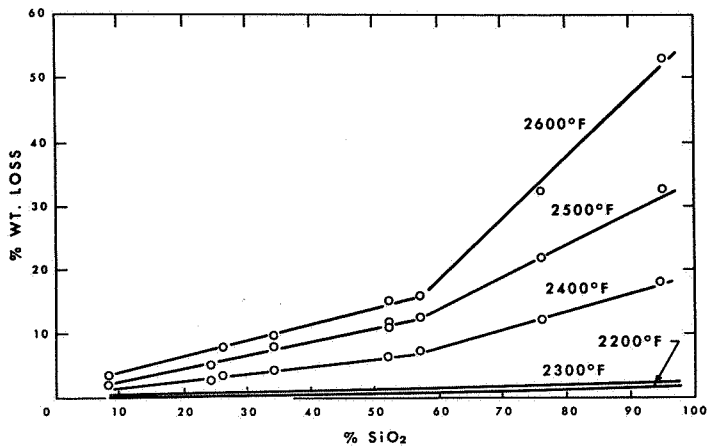


Figure 6. Weight loss of brick after 33 hr. in a 100% hydrogen atmosphere.

6. There is a sharp break at 57% silica in the curves for 2,400° F and higher. The steeper slope from 57% to 95% silica probably reflects the easier removal of the free silica from these specimens. The specimens with less than 57% SiO<sub>2</sub> contain little or no free silica, so the loss of weight must be attributed to a breakdown of the mullite or amorphous aluminosilicate structure.

Atmospheres with 75% hydrogen attack low-silica mullite or aluminosilicate refractories more aggressively at 2,200° F to 2,600° F than pure hydrogen atmospheres do. The results are consistent but the reason is not apparent. The data for 50 hr. at 2,400° F, Figure 7, are typical. Specimens with free silica are attacked less severely. At 50% hydrogen, weight loss is a linear function of SiO<sub>2</sub> content; the 90%-alumina brick loses almost the same weight as in 100% hydrogen.

An unusual feature of the 75% and 50% hydrogen exposures between 2,000° F and 2,500° F is that all the specimens containing mullite became bright blue. Exposure at 1,800° F and 2,600° F in 75% H<sub>2</sub> did not produce this color, and it did not appear after the pure hydrogen runs. A 2,600° F run in 50% H<sub>2</sub> showed a faint blue. X-ray diffraction patterns showed no new crystal structures, so formation of an oxynitride seems unlikely. The color may be due to a change in the mullite structure (12, 13, 14), or to a change in the oxidation state of Ti or Fe.

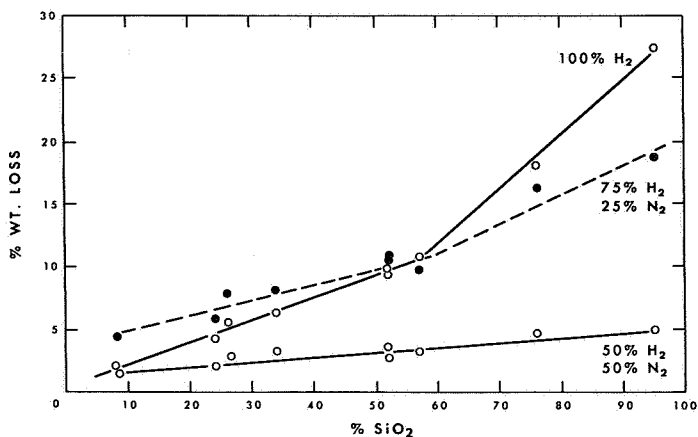


Figure 7. Weight loss of brick after 50 hr. at 2,400° F.

### Effect on compressive strength

Figure 8 shows the decrease in compressive strength of 1 in. cubes of high-fired super-duty brick (specimen 4A) as the weight loss increases. Most of these losses were determined in hydrogen at 2,500° F to 2,600° F. The degree of accuracy is only fair. This loss in strength would be expected because the bonding mediums—mullite or amorphous aluminosilicate—is preferentially attacked in reducing atmospheres. It was not practical to extract more than 10% silica from this specimen because of the time re-

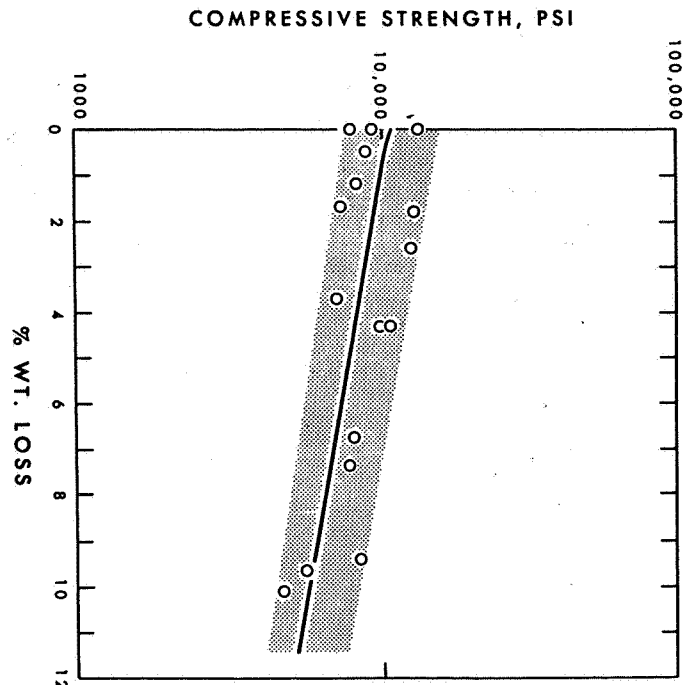


Figure 8. Compressive strength of 1-in. cubes of specimen No. 4A.

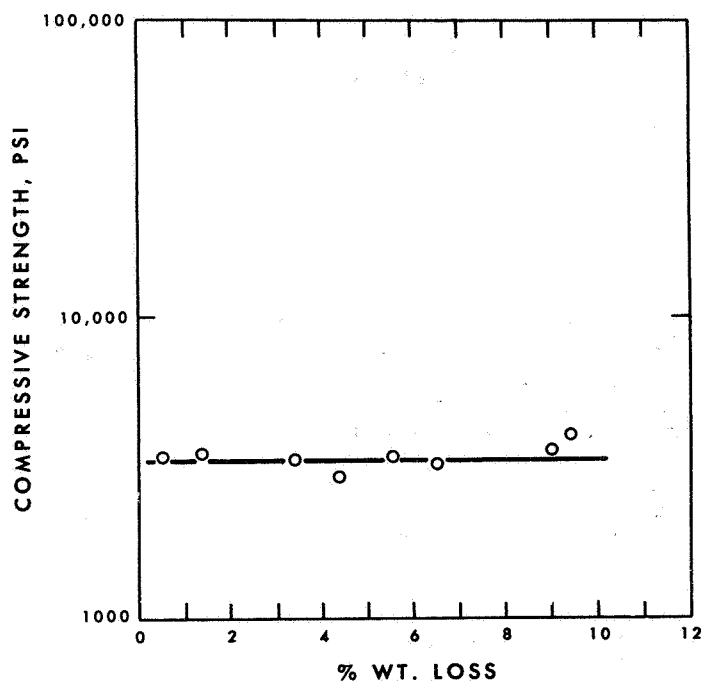


Figure 9. Compressive strength of 1-in. cubes of concrete made of 75% crushed No. 4A brick and 25% calcium aluminate cement. Runs were made in 100% hydrogen atmosphere at 2500-2,600° F.

quired for the gases to pass through the boundary layer.

The compressive strength of refractory concrete made of 75% crushed high-fired super-duty brick and 25% calcium aluminate cement did not change with a weight loss as high as 10%, even though the compressive strength of the concrete was lower than that of brick. Concretes derive their strength from the cement bond; therefore, so long as the aggregate is attacked and not the bond, reducing atmospheres should not lower the strength of refractory concrete.

Additional runs using a variety of cements and aggregates indicated calcium aluminate cements behave alike in reducing atmospheres, regardless of their iron content. For example, exposure to 75% H<sub>2</sub>-25% N<sub>2</sub> at 2,400° F caused almost no weight loss after the initial loss. At 2,600° F in 100% H<sub>2</sub>, however, concretes containing a calcined clay aggregate continued to lose weight.

## Conclusions

This investigation has shown that refractories containing free and/or combined silica lose both weight and strength above 2,100°F in either pure hydrogen or in mixed hydrogen-nitrogen atmospheres. Weight losses generally increase with increases in the free-silica content of the refractory, the hydrogen content of the atmosphere, and the temperature. The presence of water vapor retards such losses but does not stop them completely. Other variables that were not specifically evaluated, but could also be expected to affect weight loss, are the flow rate of the gases and the ratio of the exposed surface to the total volume of the refractory.

Unexpected findings are that refractories with mullite or aluminosilicate bonding turn bright blue on exposure to mixed hydrogen-nitrogen atmospheres at 2,000-2,500°F. These refractories are also attacked to a greater extent in a 75% hydrogen-25% nitrogen atmosphere than they are in pure hydrogen.

The results indicate that silica-containing refractories should not be used for hydrogen service above 2,000°F. Rather, the phosphate bonded 85%-alumina refractories would be appropriate. Or, in extreme cases, 99% alumina may be required. For vessel linings, other alternatives include refractory concretes made of calcium aluminate cement and high-alumina aggregate. For temperatures above 2,400°F, the iron-free calcium aluminate cements are probably preferable.

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## Discussion

**Q.** A very quick examination of the data of weight loss vs. temperature indicates that for materials which contain less than 50% of original silica, when this weight loss is related to the original silica content the percent loss of basic silica is relatively constant, independent of the particular sample you study. This is not true with high silica material at 95 and 76%. There percentage losses at any time or temperature seem to be somewhat higher. One thing that surprises me about the Crowley data is that the plots of the 95% original silica weight loss and the 76% original silica weight loss are straight lines throughout the entire test and you go up to total weight losses of 75-80%. When you lose that much material, out of a sample that was originally 5% non-volatiles, it becomes a material of 25-35% non-volatiles, and I thought the curve would drop off simply because the amount of silica contained in the non-volatile material has gone down considerably. Do you have an explanation?

**CROWLEY:** The curves do drop off with some specimens when run longer. We could not present all of the data available. We

made in the neighborhood of about 800 runs. The curves shown are from actual data. The silica brick, 95%, gets smaller and smaller and the non-volatiles apparently are lost. This is not true of the semi-silica brick which has enough alumina to retain its overall structure, but it becomes honeycombed and after a while it looks like a sponge.

In some cases questions arise: How do you know you're getting a uniform loss and not losing from the front and picking up on the back? Isn't the gas flow through the tubes rather critical? Yes, it is. We did have to set up and determine what minimum flow was necessary to get a constant, uniform weight loss.

**Q.** What is the effect of steam in the gas?

**CROWLEY:** We put the gas through a water vapor system to saturate it. At the point in time where we introduce the water vapor, the weight loss mechanism almost, but not quite, stops. The presence of water vapor in the line retards or inhibits the reaction. When we stop the injection of water, we again get the weight loss.