HIGH ALUMINA REFRACTORY MATERIALS FOR GAS REFORMING

High purity alumina bubble castable refractory material does an excellent job of reducing hot spots; high alumina materials can reduce downtime in reforming furnaces.

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The high temperatures, corrosion, erosion, and thermal shock conditions encountered in present synthesis gas and ammonia processes require use of high purity, high quality refractories. "High alumina" materials containing large amounts of amorphous silica and alumina silicates are not able to perform the job needed in secondary reformers, partial oxidation generators, and certain areas of primary reformers.

Specific materials needed to resist these conditions, as well as materials which exhibit low thermal conductivity and the compressibility needed to operate successfully for prolonged periods, are dealt with here under the various process steps.

Hot hydrogen lines

Use of high purity, low silica alumina bubble castable is finding increasing acceptance as insulation of hot pressured hydrogen lines. This type castable is easily placed between the inside stainless steel shroud and outer steel shell in conventional design, with minimum vibration on new lines or through openings cut in old lines. Large voids do not occur in properly prepared insulations. Properties and composition of this type of castable are given in Table 1. This high quality castable satisfactorily resists attack by hydrogen and steam; and therefore, better resists erosion and washout due to loss of bond.

Table 1. Bubble alumina castable.

Maximum usable temperature, ° F	3,300
Dry material, lb./cu.ft.	75
Porosity, %	68
Thermal conductivity @ 2,200° F Mean, BTU/hr./sq.ft./in./° F	4.7
Modulus of rupture, lb./sq.in.	
Cold	300-400
At 1,350° C	300-400
Composition, %	
Al_2O_3	94.6
SiO_2	0.5
Fe_2O_3	0.2
CaO	4.2
Na_2O	0.4
MgO	0.1

It appears that the proper design use of more sophisticated refractory materials can eliminate the cause of the ruptures of hot pressured hydrogen lines. These ruptures can be traced to the buckling of the internal stainless steel protective shrouds currently placed in these lines. Erosion and corrosion of the insulating materials used follows with subsequent rupture of the steel outer shell. Attrition of the present insulating materials can occur even without buckling of the shroud, since at the location of the expansion joint the shroud does not give a positive seal to the atmosphere.

A recommended solution to this problem is the use of dense, fired shapes with lap joints as shown in Figures 1 and 2; or dense castable of high purity alumina as the inner hot face material to replace the stainless steel shroud, Table 2. Bubble alumina castable is recommended for use in the annular space between the dense hot face material and the steel shell.

The use of a stainless steel shroud puts a high expansion material in the hottest position in the system surrounded by lower expansion materials which are at lower temperatures. The use of a ceramic inner core, to replace the stainless steel shroud, will allow for a more stable construction chemically and physically.

The shapes in Figure 1 are made from a high alumina composition containing fused mullite grain. It is a material not containing amorphous silica, and it is really my choice for the material of construction for the lining of hot hydrogen lines. It is a more thermal shock material, more stable dimensionally, and can be formed into larger more intricate shapes than high purity alumina. Of course, the high purity alumina is the " safe" material to use for most operating people.

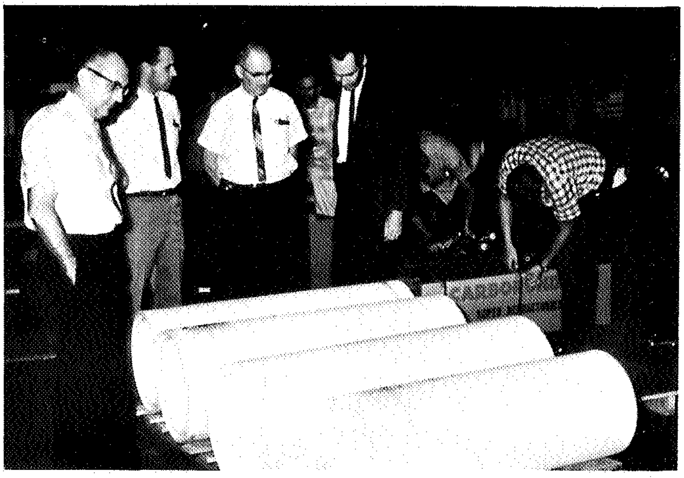

Figure 1. Shapes made from a high alumina composition containing fused mullite grain.

Table 2. Alumina products proposed for inner surface of hot hydrogen lines.

	Dense Castable	Dense Shapes
Maximun usable temperature, ° F	3,300	3,400
Dry material, lb./cu.ft.	170	181
Porosity, %	26	25
Thermal conductivity @ 2200 °F Mean, BTU/hr./sq.ft./in./ °F	11	18
Modulus of rupture, lb./sq.in.		
Cold	1,500-1,800	2,500
At 1,350° C	1,500-1,800	600
Composition, %		
Al_2O_3	96.0	99.2
SiO_2	0.05	0.5
Fe_2O_3	0.1	0.1
CaO	3.6	0.01
Na_2O	0.16	0.2
MgO	0.1	0.01

Synthesis gas generators

Premature failures of materials of construction and costly downtime for rebuilds of partial oxidation and steam reforming synthesis gas generators, primary reformers and secondary reformers can be minimized by use of high alumina refractories and ceramic fiber products. Good construction and good materials may cost more at the beginning but will give safer, longer life and more economical operation in the long run.

Partial oxidation processes for synthesis gas presently use dense alumina shapes for the hot face lining, bubble alumina shapes or castable as the primary insulation, and ceramic fiber paper or blanket as the secondary insulation in front of the insulating firebrick and the steel shell.

The high purity dense and bubble alumina products resist the high temperature (2,600°-2,800° F or higher) and the corrosive atmospheres of these reactors. The ceramic fiber layer provides the following benefits: (1) A sharp temperature drop over a very thin layer of insulation, (2) a slip-plane for relieving stresses as the reactor is heated up and cooled down, and (3) a compressible material which will help prevent spalling as the materials of construction expand upon heating.

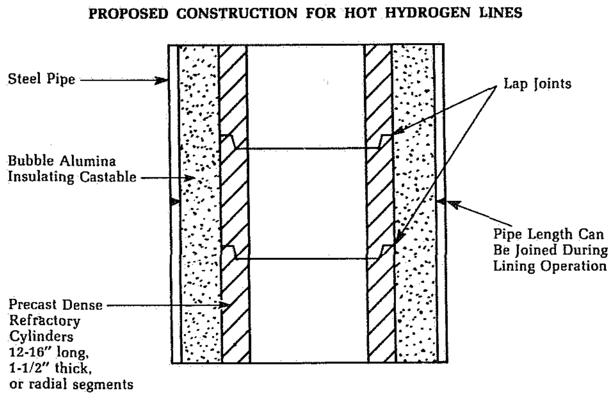

Figure 2. Proposed construction for hot hydrogen lines.

Tables 3 and 4 give data on the type of materials used in the partial oxidation processes. Figures 3a and 3b show cross sectional views of the typical construction of these kinds of reactors.

Primary reformers which use radiant walls for heating the tubes have experienced thermal shock problems with firebrick where the gases from the burners impinge on the walls, Figure 4. The use of high alumina brick containing fused mullite grain will alleviate this problem and give extended life of the furnace.

Table 5 gives data on this type product. Its dimensional stability, high load-bearing capacity at high temperature, and excellent thermal shock resistance make it a good alumina refractory.

Ceramic fiber rope gasketing around primary reformer tubes provides a high temperature resilient packing to reduce heat loss without the danger of spalling of dense refractories around the tubes as they expand on heating. The properties of this material are shown in Table 6.

Another factor to consider is the use of ceramic fiber products in primary reformers next to the shell to reduce heat loss, and possibly to reduce weight by replacing some of the brick thickness with ceramic fiber block, board or blanket. These products are flexible, resilient and chemically stable in many atmospheres.

The problem of falling roofs seems to be common to many primary reformers of many designs. The firebrick expand on use, causing the brick walls and roof to bulge inward until a number of metal anchors break. The roofs then fall down, while the sidewalls continue service for an additional period of time.

It is believed that a new product, a composite board composed of ceramic fiber hot face (properties similar to that shown in Table 4 under paper) and 1,800 °F mineral wool backup, should be considered for roofs and sidewalls of primary reformers. It is suggested that this new product be tried first to patch roofs of primary reformers. When this practice has proven successful, then the entire roof and walls of primary reformers should be lined with this material.

The composite fiber board of 4 in. thickness (1-3/4 in. ceramic fiber and 2-1/4 in. mineral wool) would serve as the entire lining to handle a 2,000 °F furnace temperature and keep the shell at 250 °F. The material will not spall and can withstand reasonable amounts of gas flow and flame impingement. It could also give great savings in weight, easier and less fragile handling and shipping, and lower cost construction.

Table 3. Alumina products used in partial oxidation synthesis gas reactors

	Dense *alumina* shapes	Bubble *alumina* shapes	Bubble *alumina* castable
Maximum usable temperature, °F	3,400	3,400	3,300
Dry material, lb./cu.ft.	181	91	75
Porosity, %	25	62	68
Thermal conductivity @ 2,200°F mean BTU/hr./sq.ft./in./°F	18	8	4.7
Modulus of rupture, lb./sq.in.			
Cold	2,500	600	300-400
At 1,350°C	600	200	—
Composition, %			
Al_2O_3	99.2	98.6	94.6
SiO_2	0.5	1.0	0.5
Fe_2O_3	0.1	0.1	0.2
CaO	0.01	0.01	4.2
Na_2O	0.2	0.05	0.4

Table 4. Ceramic fiber properties

Composition, %	Paper	Blanket
Al_2O_3	51	51
SiO_2	47	47
Other	2	2
Melting Point, °F	3,250	3,250
Recommended maximum use temperature, continuous, °F	2,300	2,300
Thermal Conductivity @ 1,000°F mean BTU/hr./sq.ft./in./°F	0.58	0.80
Density, lb./cu.ft.	12	6
Fiber diameter, micron ave.	2	2

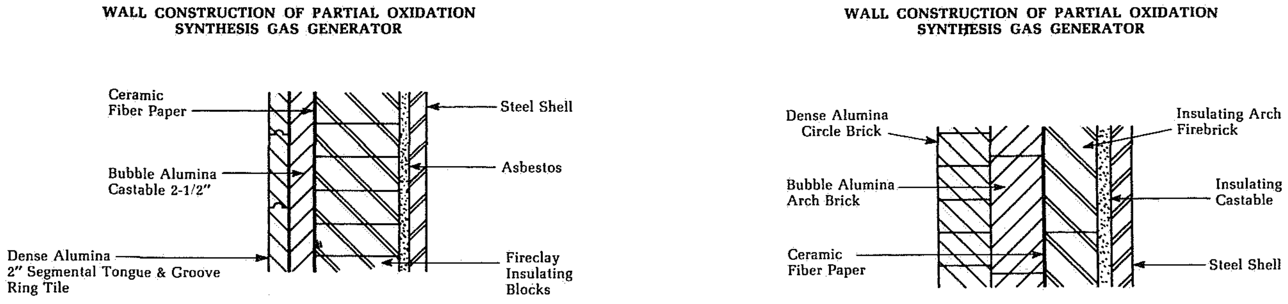

Figure 3a, 3b. Cross sectional views of the wall construction of partial oxidation synthesis gas generator.

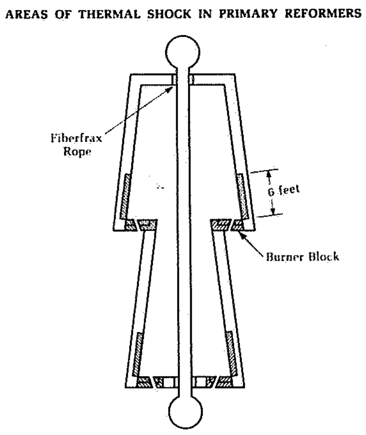

Figure 4. Areas of thermal shock in primary reformers.

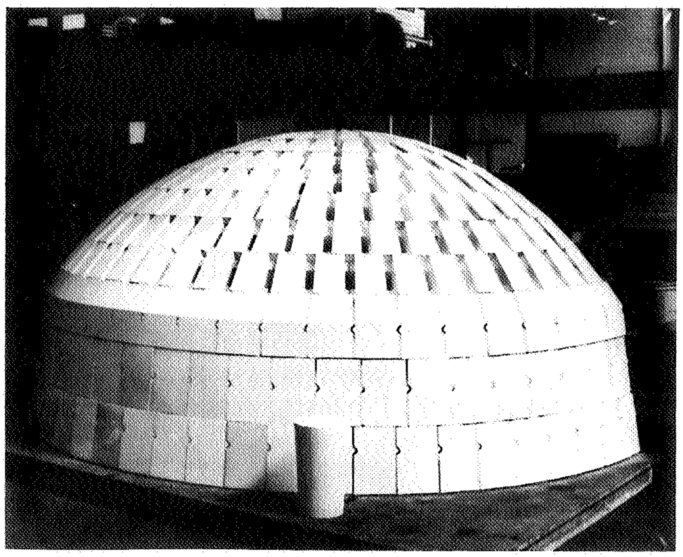

Figure 5. Dome made of high purity alumina.

Table 5. Mullite-containing alumina for thermal shock applications.

Maximum usable temperature, ° F	3,300
Bulk density, lb./cu.ft.	176.5.
Porosity, %	20
Thermal conductivity @ 2,200° F mean, BTU/hr./sq.ft./in./°	14
Modulus of rupture, lb./sq.in.	
Cold	1,970
At 1,350° C	1,903
Compositions, %:	
Al_2O_3	89.8
SiO_2	9.6
Fe_2O_3	0.2
CaO	—
Na_2O	0.2

Table 6. Properties of ceramic fiber rope.

Composition, %	
Al_2O_3	45.2
SiO_2	51.2
Other	3.6
Melting point, ° F	3,250
Recommended maximum use temperatures, continuous, ° F	2,300
Density, lb./cu.ft.	25
Fiber diameter, ave., microns	5

Table 7. Denser bubble alumina castable

Maximum usable temperature, ° F	3,300
Dry material, lb./cu.ft.	90
Porosity, %	64
Thermal conductivity @ 2,200° F mean, BTU/hr./sq.ft./in./° F	5.2
Modulus of rupture, lb./sq.in.	
Cold	400-500
Composition, %	
Al_2O_3	94.1
SiO_2	0.5
Fe_2O_3	0.2
CaO	4.7
Na_2O	0.4
MgO	0.1

Secondary reformers

The secondary reformer provides a hostile application for materials of construction, bed support materials, and catalysts. The high temperatures at the top of the unit of up to 2,600 °F (and higher during upset conditions) and the atmosphere of hydrogen, steam, CO, CO_2 and other gases, demands a number of high quality materials to obtain a resonably long, trouble-free life. In addition to maintaining the integrity of the lining, bed support, and catalyst carrier materials, the silica transport problem must be minimized to preserve good heat transfer in the waste heat boiler.

Linings of some secondary reformers are made with dense, high-alumina castable on metal anchors. This construction results in rather high heat losses. The shell, therefore, must be water jacketed to prevent failure due to overheating. Some companies are using an insulating castable next to the shell over which is placed a dense castable.

Recently, there has developed an interest in the use of bubble alumina castable for the entire thickness of the secondary reformer lining. Possibly, the trowelling of a thin layer of dense castable over the bubble castable to produce a harder surface will be necessary to withstand the placement of the catalyst and the possible erosion by the gas and catalyst during operation.

A compromise between the use of dense and bubble castables, singly and in combination as described above, could be the use of a denser bubble alumina castable as described in Table 7. The denser bubble castable contains more bond than the lighter bubble castable to give it more strength. This castable also could be covered with a thin layer of dense castable, if needed, to form a harder, less porous surface to withstand the placement of catalyst and the possible erosion by the gas and catalyst during operation and yet give less heat loss than the present constructions.

Shrouds in secondary reformers will probably be eliminated in the future, also, by the use of materials such as the high alumina/fused mullite shapes Table 5 as the hot face lining below the catalyst bed. One unit has operated in this manner for two years and is still going strong.

The domes, arches and other means of holding up the catalyst bed while providing for the exit of gases generally are made of shapes of high purity alumina, such as described in Table 2 previously. A dome made of this material is shown in Figure 5. This material withstands the corrosive atmosphere, high temperature and the weight of the catalyst bed. For this purpose the dome construction appears to be the more stable structure according to our experience. Domes of diameters up to 26 ft. have performed well in other processes for a number of years.

The catalyst beds of secondary reformers generally have been supported by layers of dense alumina balls of graded sizes. In the last two years, another product has met growing acceptance as a *media for catalyst support.* This material is fused alumina lumps in the grades sizes of 1/2 by 1-1/4 in., 1-1/4 by 2 in., and 2 by 3 in. These lumps have the advantage of maximum density, very high purity and are without a bond system that might be attacked.

The larger size range of these lumps also are being used on top of some of the catalyst beds to protect the catalyst from the high temperature and erosion of the "fire-ball" and the fast flowing gases. They also help to distribute the gases and minimize channeling of the gases through the bed. Even though there are not good data available on the pressure drop through beds of these lumps, it is believed that the pressure drop is a function of the catalyst bed, not the support bed.

Fused alumina lumps contain over 99.5% Al_2O_3 and only 0.04% SiO_2. The density of 130-140 lb./cu.ft. make it an excellent material for holding down the catalyst bed to prevent movement and attrition of the catalyst particles.

The calcium aluminate based carrier now used to support the nickel catalyst required for gas reforming gradually shrinks and powders during use and fuses under "upset" conditions. These "happenings" can cause the pressure drop through the bed to rise and could even cause plugging of the bed.

Catalyst manufacturers and users of gas reforming catalysts now are actively considering high purity alumina porous cylindrical pellets as a carrier for the nickel catalyst. Such a catalyst carrier will neither shrink and powder at 2,600 °F, nor fuse at temperatures substantially above 3,000 °F. It is possible that less nickel can be used with this high quality material to produce the same catalytic effect through impregnation with soluble nickel compounds. The characteristics of the alumina carrier pellets are given in Table 8.

For *gas inlet* systems and shapes around *ports* and *gas outlets,* where thermal shock may be a problem, the high alumina/fused mullite material discussed for primary reformer walls and burner blocks should be considered, Table 5. This family of high alumina/fused mullite material (up to 21% SiO_2 as fused mullite) has done an excellent job in carbon black reactors with atmospheres similar to those found in gas reformers and even higher temperatures (up to 3,200 °F). Of perhaps greater significance, it withstands the severe thermal shock condition in the quenching chamber of carbon black reactors.

Table 8. New gas reforming catalyst carrier

Composition, %	**Range**	**Specific**
Al_2O_3	99.5-99.8	99.5
SiO_2	0.02-0.1	0.02
Fe_2O_3	0.04-0.06	0.04
Na_2O	0.04-0.45	0.45
Surface area, m^2/g	0.5-5.5	2.6
Porosity, %	15-55	4.5
Pore diameter range, microns	0.1-1.0	0.2-0.8
Average pore diameter, microns	0.3-0.8	0.4
Water absorption, %	4-31	20
Crush Strength,		
5/8 in. x 5/8 in. x 1/4 in.		
Hollow cylinders, lb. ave.	Up to 300	177
Volumetric Bulk Density, lb./cu.ft.	50-70	60

Summary

High quality materials are available for safe, long life operation of gas reforming processes; and even though these materials cost more originally, they are economical in the long run. Which of these materials should be used in a particular situation is best decided by the applications engineering group of the refractory supplier with the help of the engineering group of the customer company specifying as many of the details of atmosphere, temperature, temperature changes, erosion possibilities and other conditions. This cooperative approach of user and supplier produces better answers to your problems faster. Cooperative programs will allow for the elimination of stainless steel shrouds inside these reactors and lines and water cooling outside, while ending up with ceramic lined vessels with greater life and safety.

Discussion

ESCHENBRENNER, G.P., M.W. Kellogg Co.: You made a statement with respect to the necessity of water jackets to keep the shell of shrouded reformers or transfer lines cool. Since most of the comments at the session on reformer piping was on no water jackets I would like to make some statements on why water jackets from a safety point of view are almost a necessity. Very few engineers would put a pressure vessel into service without a relief valve. The design of a process or pressure vessel is generally such that over-pressuring is unlikely to occur. But it does occur and that is why we have relief valves. If we have pressure vessels in the 500 lb./sq.in. pressure range and in hydrogen service at 2,000 to 3,000 °F, whatever construction, design, or fabrication, the chances for failure are there. A water jacket, if well-designed and well-operated, will provide needed safety measures. It will indicate failures of the lining. If they occur you have two indications: very heavy steaming and an increased demand of makeup water. These two indications will permit reasonable shutdown procedures to be undertaken without hazard to life or property. The water jacket is installed for that reason, not to make up for deficiencies of the lining. The pressure vessel itself should be designed based upon normal pressure and temperatures and the water jacket is there solely as a safety device.

When we consider dual layer linings with low density and high density layers, the risk of bypassing gas, particularly hydrogen gas, in the interfaces between the metal and the refractory lining is there because we never get perfect fabrication. For simple straight transfer lines this is a minor problem, but for complex shaped fittings, bends, curved parts, intersections, etc. the refractory lining becomes more complex and is subject to service deterioration.