OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.

DISCLAIMER

This document has been produced without formal United Nations editing. The designations employed and the presentation of the material in this document do not imply the expression of any opinion whatsoever on the part of the Secretariat of the United Nations Industrial Development Organization (UNIDO) concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries, or its economic system or degree of development. Designations such as "developed", "industrialized" and "developing" are intended for statistical convenience and do not necessarily express a judgment about the stage reached by a particular country or area in the development process. Mention of firm names or commercial products does not constitute an endorsement by UNIDO.

FAIR USE POLICY

Any part of this publication may be quoted and referenced for educational and research purposes without additional permission from UNIDO. However, those who make use of quoting and referencing this publication are requested to follow the Fair Use Policy of giving due credit to UNIDO.

CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org

06813

Distribution
LIMITED

ID/WG.221/7
9 December 1975

Original: ENGLISH

United Nations Industrial Development Organization

UNIDO/FAI Interregional Meeting on Safety in the Design and Operation of Ammonia Plants

New Delhi, India
20 - 24 January 1976

SPECIAL REFRACTORY MATERIALS FOR USE IN GAS REFORMING[1/]

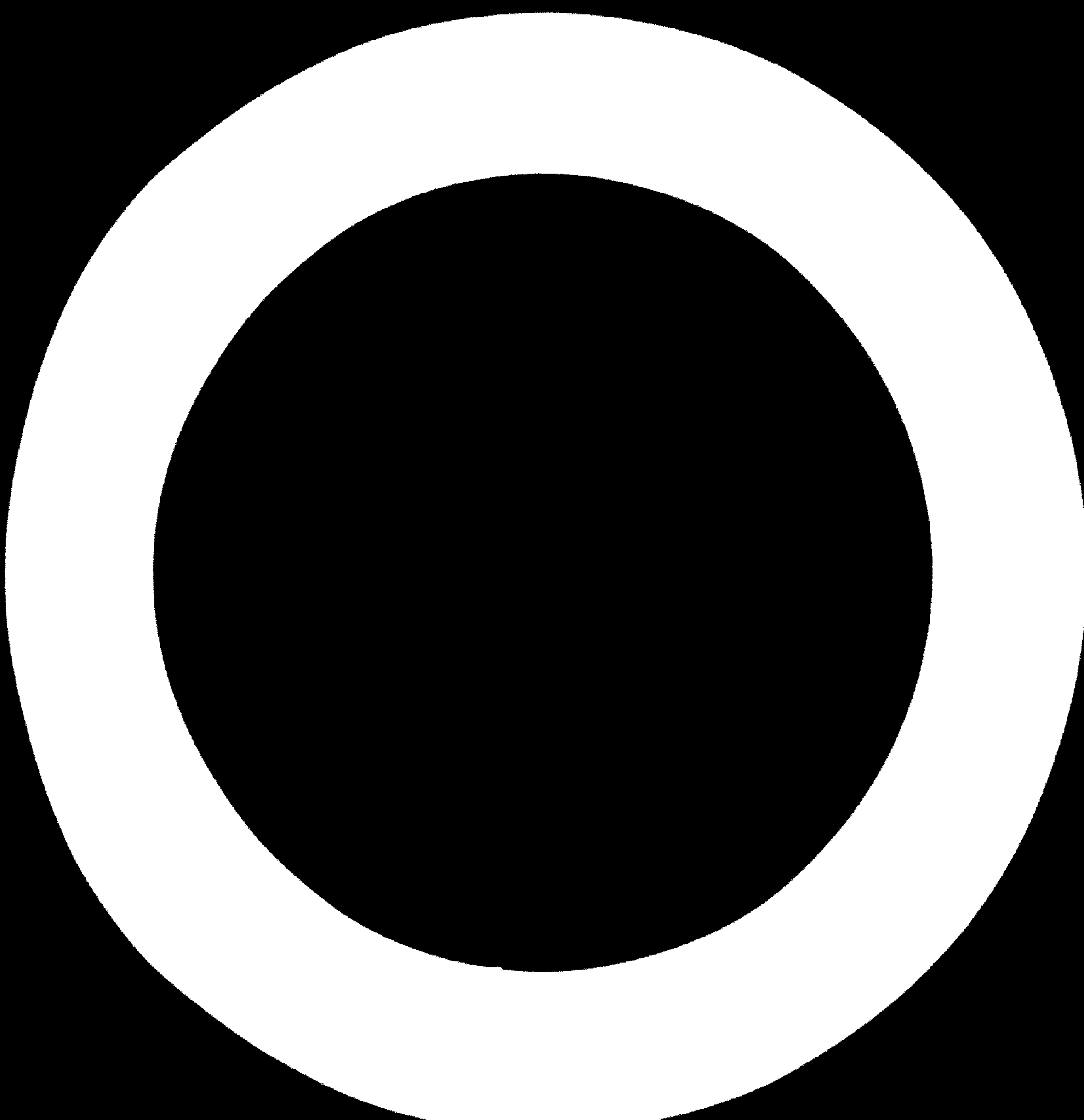
by

R.R. Miner*

* Manager, Technical Services Department, New Products Branch, The Carborundum Company Niagara Falls, N.Y., USA

1/ The views and opinions expressed in this paper are those of the author and do not necessarily reflect the views of the secretariat of UNIDO.
This document has been reproduced without formal editing.

id.75-9045



SPECIAL REFRACTORY MATERIALS FOR USE IN GAS REFORMING

The term special refractories includes products made largely from synthetic raw materials rather than from natural occurring minerals. This discussion will cover the high alumina and alumina-silica (ceramic fiber) portion of the special refractories field, the products used in the ammonia plants.

During the first portion, I would like to review the products that will be involved and the raw materials from which they are made.

1. Alumina Bubble Products

   a. Alumina Bubble Castables.
   b. Alumina Bubble Shapes.

The primary synthetic material here is the alumina bubble. It is made by blowing a stream of molten high purity alumina that is being poured from a furnace (with the molten alumina at about 3700°F) with jet of high velocity air.

FIGURE 1
BLOWING ALUMINA BUBBLES

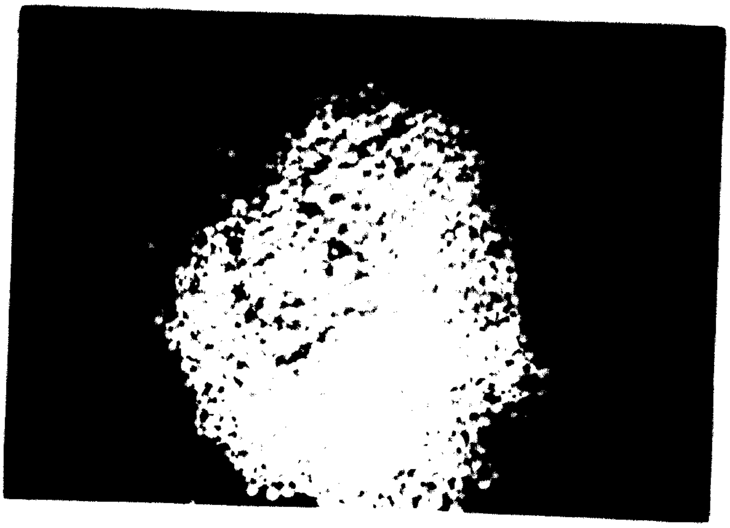


FIGURE 2
ALUMINA BUBBLES

FIGURE 3
ALUMINA BUBBLE CROSS SECTION

The word castable as we use it indicates that the product is bonded with a calcium aluminate hydraulic setting cement. This material is usually installed by casting, gunning, hand packing, or trowelling techniques.

The shapes are generally made by compaction methods, for example, hydraulic pressing and fired to a suitable temperature such as 1600°C. to develop the bond.

Typical data for these products is covered in Figures 4 and 5.

	ALUMINA BUBBLE CASTABLES		ALUMINA BUBBLE SHAPES
Maximum Use Temperature °F Hot Face	3300	3300	3400
Bulk Density, PCF	75	90	91
Porosity, %	68	64	62
Thermal Conductivity 2200°F Mean BTU/Hr/Ft^2/In/°F	4.7	5.2	8.0
Modulus of Rupture, psi			
Cold	380	400	600
1350°C	-	-	200

FIGURE 4

COMPOSITION, %	ALUMINA BUBBLE CASTABLES		ALUMINA BUBBLE SHAPES
Al_2O_3	95.0	94.0	99.0
SiO_2	0.5	0.5	0.7
Fe_2O_3	0.2	0.2	0.1
CaO	4.0	5.0	-
Na_2O	0.3	0.3	0.1

FIGURE 5

2. Dense High Alumina Products

The key materials here are high purity particulates, sintered alumina oxide and/or high purity fused aluminum oxide.

The sintered alumina is formed into spheres about 1" in diameter and fired to high temperature, then crushed to size. The fused material is produced by melting high purity alumina in an arc furnace then cooling and crushing it to size.

FIGURE 6
ARC FURNACE

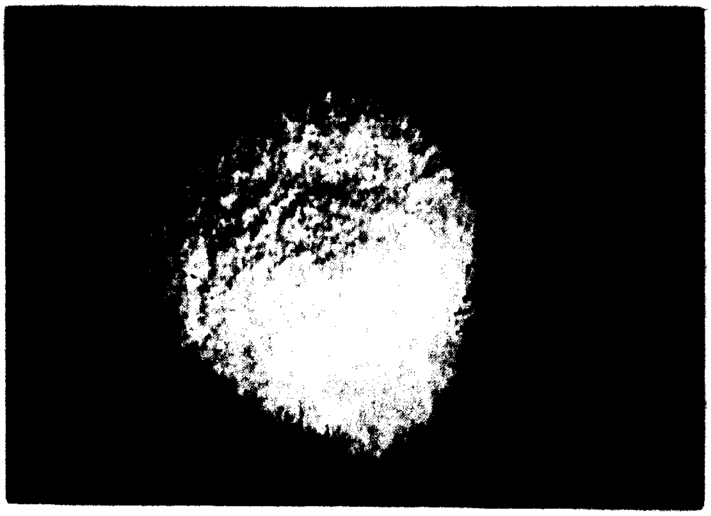


FIGURE 7
FUSED ALUMINA GRAIN

These very high alumina products are required in certain application areas, not only for their refractoriness but also for their resistance to reaction in hydrogen atmospheres. Refractories containing appreciable quantities of silica are degraded under conditions in which the hydrogen reduces the SiO_2 to SiO and H_2O, both of which are lost in service.

The castables, both the bubble and dense alumina varieties, are bonded with high purity calcium aluminate and this bond is not seriously affected by the hydrogen or steam environments. Typical property and composition data for the dense alumina products are found in Figures 8 and 9.

	DENSE ALUMINA	
	Castable	Shapes
Maximum Use Temperature °F Hot Face	3300	3400
Bulk Density, PCF	170	186
Porosity, %	26	20
Thermal Conductivity 2200°F Mean BTU/Hr/Ft^2/In/°F	11	18
Modulus of Rupture, psi		
Cold	1600	2500
1350°C	-	600

FIGURE 8

Composition, %	DENSE ALUMINA	
	Castable	Shapes
Al_2O_3	96.0%	99.2%
SiO_2	0.1	0.5
Fe_2O_3	0.1	0.1
CaO	3.6	-
Na_2O	0.2	-

FIGURE 9

3. Sintered Alumina Balls and Fused Alumina Lumps

Sintered alumina balls or fused alumina lumps are used to support the catalyst bed in the secondary reformer.

The fused alumina, is crushed and graded into lumps about 2" x 3", 1 1/4" x 2" and 1/2" x 1 1/4". The Al_2O_3 content is 99.5% with a packing density of 130 to 140 PCF. The sintered balls are made by forming spheres of high purity calcined alumina and firing at high temperature. An advantage they have in this application is the more predictable packing because of their consistently spherical shape.

4. Ceramic Fiber

As with the bubble alumina, this product, an outstanding high temperature insulation material, is made by blowing a stream of molten alumina-silica with a jet of high pressure air or steam. However, this composition fiberizes instead of forming bubbles as with the high purity alumina melt.

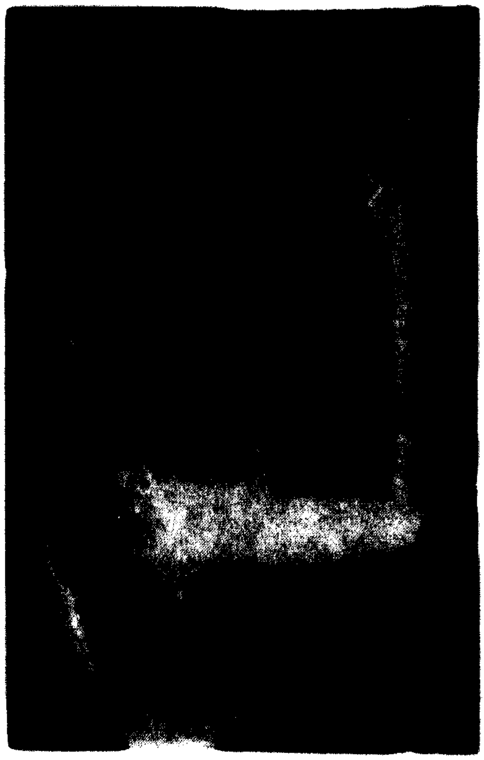


FIGURE 10 -
BLOWING CERAMIC FIBER

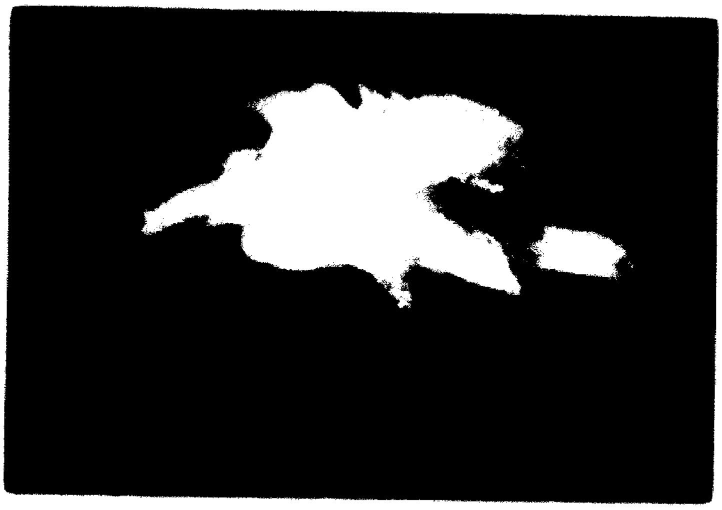


FIGURE 11
CERAMIC FIBER

The two major types of ceramic fiber currently available commercially are considered to be suitable for temperatures as high as 2300°F or 2600°F depending on the silica:alumina ratio.

Typical chemical analyses are shown in Figure 12.

Ceramic Fiber Compositions	2300°F Fiber	2600°F Fiber
Al_2O_3	51.7%	62.3%
SiO_2	47.6	37.2
Fe_2O_3	0.1	Trace
TiO_2	Trace	Trace
Other Fluxes	0.5	0.5

FIGURE 12

5. **Dense Sintered Alumina**

The last product that I will mention is a high alumina sintered material that is used largely for wear or abrasion resistance. It is made primarily from fine grained high purity calcined alumina and fired to 1600°C. Typical properties for this product is shown in Figure 13.

	Sintered Alumina
Maximum Use Temperature	1540°C 2800°F
Bulk Density g/cc	3.75
Porosity, %	0
Thermal Conductivity Mean Temperature 800°F $BTU/Hr/Ft^2/In/°F$	68
Modulus of Rupture Cold 1350°C	 46,000 psi 3,180 psi
Tensile Strength	25,000 psi
Coefficient Thermal Expansion In/In/°C 25°C to 700°C	7.7×10^{-6}

FIGURE 13

Applications I will now review are to be found in the Ammonia Plant Flow Plan as illustrated in Figure 14.

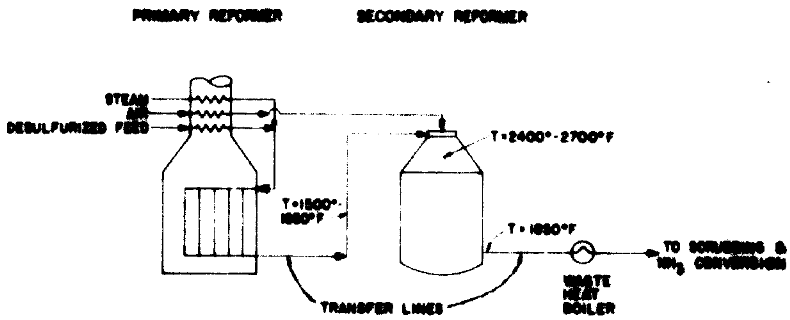


FIGURE 1
AMMONIA PLANT FLOW PLAN

FIGURE 14

In the primary reformer, temperatures range between 1800 - 2100°F and the atmosphere is oxidizing. In the past these units were lined with insulating firebrick. The trend is now to use ceramic fiber linings. In some units, only the arch is ceramic fiber with the walls constructed of firebrick. In others, the entire lining is ceramic fiber.

The high temperature fiber is the one most widely used since high temperature shrinkage is minimized and insurance is provided against run away conditions.

Some of the reasons for using fiber instead of brick are as follows:

Lower Heat Storage Capacity
Lower Thermal Transfer Rate
Lower Heat Input Requirements
Lighter Steel Structural Support

FIGURE 15

The fiber form used here is the blanket or felt. The installation technique calls for the use of refractory metal studs, for example, Inconel 601 or RA 330.

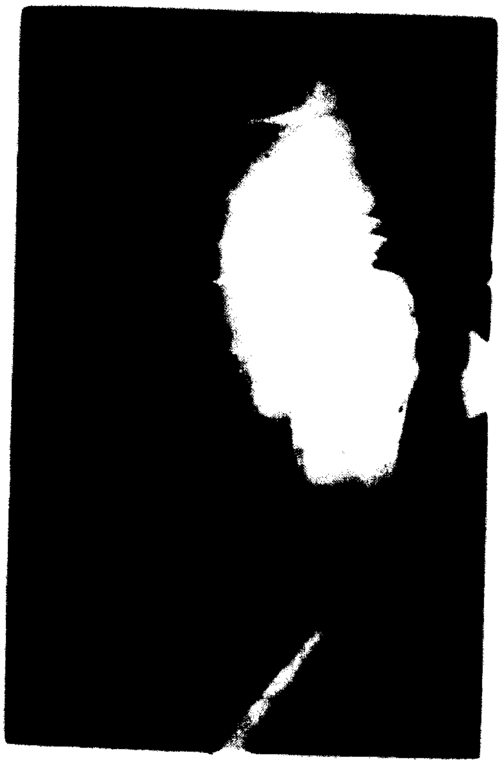


FIGURE 16 - Welding Studs on Wall

FIGURE 17 - Impaling Ceramic Fiber Blanket on Studs.

The blanket or felt is impaled on the studs and a mullite refractory cup is used to lock and hold the fiber in place.

FIGURE 18 - Stud and Ceramic Cuplock.

FIGURE 19 - Completing Fiber Blanket Insulation.

A special ceramic fiber plastic cement is forced into the hole in the refractory to both protect the stud from the environment and help lock the unit in place.

Insulation of the weld joint between the catalyst tubes and the outlet manifold in the primary reformer is of particular interest. Here the pipes are of dissimilar alloys and the internal pressure is high. The two layers of 3/4" blanket typically used are covered with one layer of wet blanket molded into place where it dries hard, effectively insulating and preventing the weld joints of the harp from cracking or rupturing.

FIGURE 20 - Ceramic Fiber Insulating Welds.

In old reformers two to three layers of 1 inch thick ceramic fiber blanket can be installed over the insulating brick to reduce shell temperature to about 175°F, thereby saving considerable fuel.

Figure 21 includes details of two different secondary reformer designs. This pressure vessel operates at 400 to 500 psig with combustion temperature of about 2400°F and an exit gas temperature of approximately 1800°F with partial pressures of hydrogen and steam.

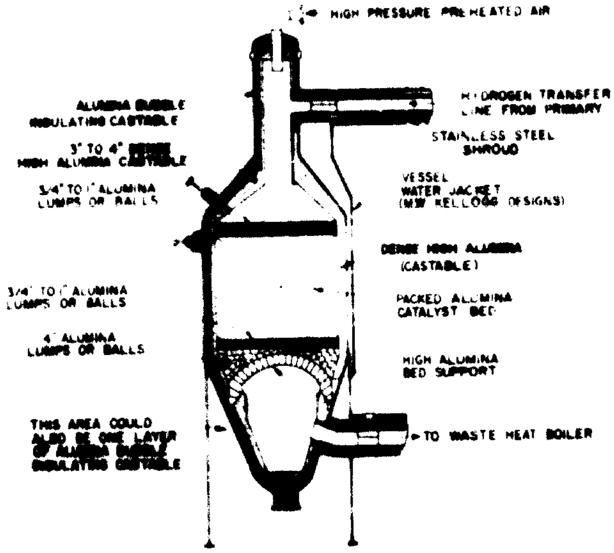


FIGURE 21

SECONDARY REFORMER LINING DESIGNS

The design on the right is typical of the MW Kellogg unit in which a water jacket is utilized to generate steam. The one component lining, dense high alumina castable, is resistant to high temperature hydrogen and steam and provides the balanced heat loss necessary for steam production.

The design on the left used by others incorporates a two component lining to provide shell temperatures consistent with the ASME pressure vessel code requirements for the carbon steel shell material and allowable stresses. The inner portion of the lining is the dense high alumina castable with the alumina bubble insulating castable as the back up or outer material to minimize heat loss.

The high alumina products (very low SiO_2) are selected for this application to resist silica stripping by hydrogen and steam and to resist iron reduction. The high density castable is used as the working lining to resist erosion by the high velocity gases and possible entrained particulate.

The catalyst bed support is a critical area. Here dense high (99%) alumina brick or shapes are used regardless of the specific design involved. This material is selected for its strength at temperature as well as its ability to withstand degradation by hydrogen.

Figure 22 shows a particular design assembled to verify fit.

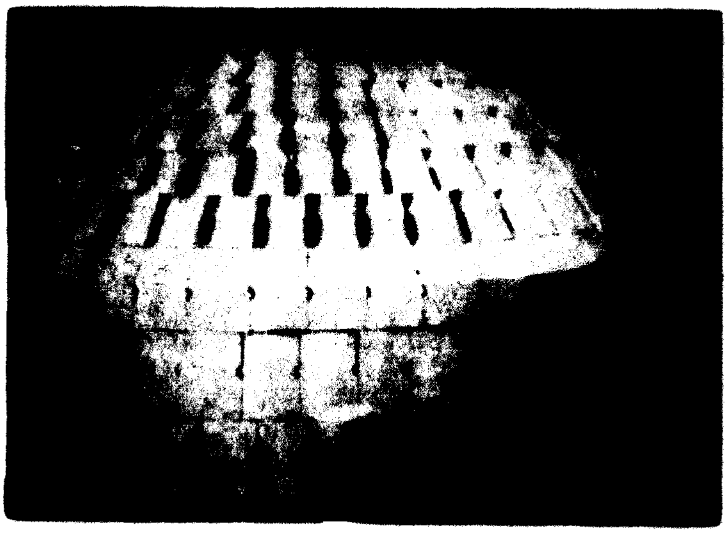


FIGURE 22 - High Alumina Catalyst Support Dome.

The graded calcined alumina balls or fused alumina lumps are placed on the dome and support the catalyst bed. A layer is also placed on top of the catalyst bed to protect the catalyst from the erosion and corrosion of the high temperature, high velocity gases. A section of the dome charge is illustrated in Figure 23.

FIGURE 23 - Cross Section Catalyst Bed.

Next we come to the transfer lines. The first is the primary line which carries the process gas at up to about 1650°F from the primary reformer furnace to the secondary reformer. The secondary lines carry gases from the secondary reformer to the waste heat boiler with temperatures up to 1850°F.

The two basic designs in current use are shown in Figure 24. The top unit is water jacketed.

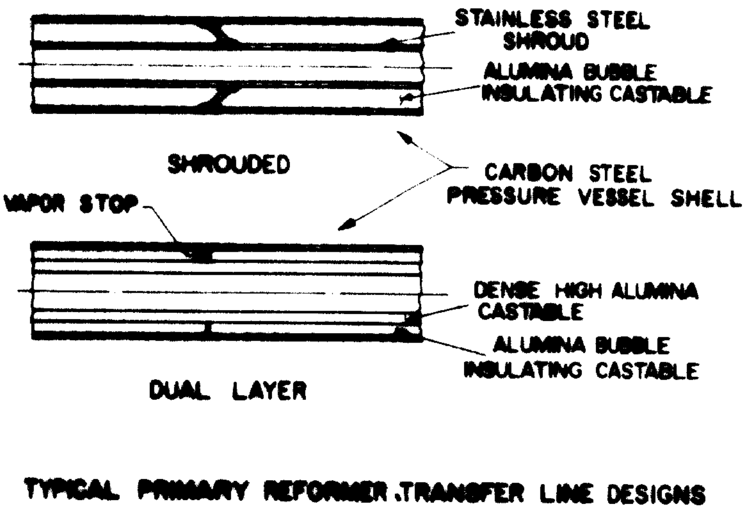


FIGURE 24
PRIMARY REFORMER TRANSFER LINE DESIGNS

In the bottom design, the dense high alumina inner layer is provided to resist erosion by the gases and entrained particulate. We believe, however, that, rather than use this approach, if the entire lining were made from the alumina bubble insulating castable it would perform very satisfactorily since it has good strength and integrity and since the erosiveness of the gas - particulate combination is modest.

The last unit in this system is the waste heat boiler. It both cools the process gas and generates steam. The temperature of the entering gases range up to 1850°F. The high alumina bubble castable is recommended to protect the tube sheet and channel. Although Figure 25 also shows the use of a dense erosion resistant castable we believe that the bubble product again is sufficiently strong to resist the erosive effect of the gas.

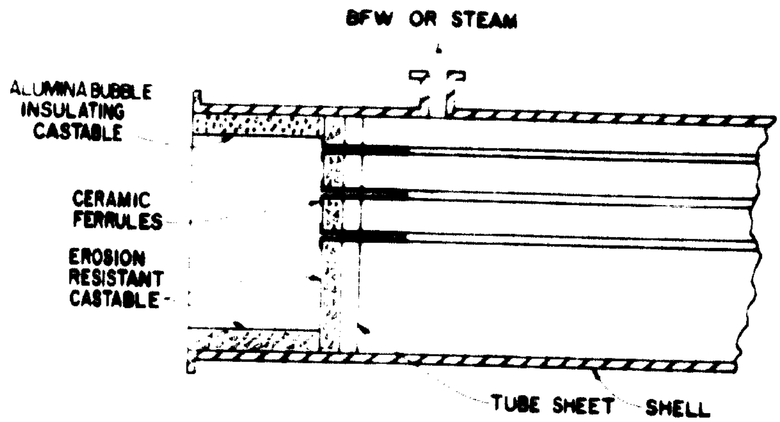


FIGURE 4
FERRULES EMPLOYED WITH VARIOUS CASTABLES TO PROTECT TUBE SHEET AND CHANNEL

FIGURE 25

SINTERED HIGH ALUMINA FERRULES IN TUBE SHEET

Dense sintered high alumina ferrules are used to protect the tube inlets from the very high velocity gases entering the tubes. This material is outstanding in erosion resistance and is also superior in its ability to withstand the degradation that can be caused by hydrogen and water vapor.

One of the problems inherent in the waste heat boiler is the fouling of the tubes by solids. The solids have been largely silica, condensed from the silica stripping of refractories by hydrogen, as well as other oxides that come from deterioration of insulating castables used in the primary and secondary transfer lines. The use of the high alumina products that we have presented minimizes this problem.

In summary, the special refractories that we have reviewed here today have established themselves as important elements in the operation of ammonia plants, on the basis of both increased safety and increased efficiency, at lower cost.

Distribution
LIMITED

ID/WG.221/7
SUMMARY
9 December 1975

Original: ENGLISH

United Nations Industrial Development Organization

UNIDO/FAI Interregional Meeting on Safety in the Design and Operation of Ammonia Plants

New Delhi, India,
20 - 24 January 1976

SPECIAL REFRACTORY MATERIALS FOR USE IN GAS REFORMING 1/

SUMMARY

by

R. M. Miner*

This paper will review the use of a variety of special refractory materials in the ammonia plant that will include the following:

1. Dense, high alumina, fired.
2. Bubble high alumina, fired.
3. Dense sintered alumina.
4. Dense high alumina castable.
5. Bubble high alumina castable.
6. Ceramic fiber blanket.

The characteristics of each product will be discussed as will the reasons for recommending their use in such areas as primary reformer linings, transfer lines and secondary lines. Tube and tube sheet protection will be covered.

Sketches and charts will be provided in the preprint and they will be prepared as 35 mm slides for the oral presentation.

* Manager, Technical Services Department, New Products Branch, Carborundum Company, Niagara Falls, N.Y. 14302, USA

1/ The views and opinions expressed in this paper are those of the author and do not necessarily reflect the views of the secretariat of UNIDO. This document has been reproduced without formal editing.

id.75-8010

76.02.03