CHARACTERISATION OF THERMO-MECHANICAL BEHAVIOUR OF HIGH ALUMINA REFRACTORIES FOR SECONDARY REFORMER APPLICATION

Ranjan Dey, Ravikumar N., Eswaran V. T., Sudip Kumar Paul, Rajagopalan R.
Carborundum Universal Limited, Chennai, India

ABSTRACT

In the secondary reformer, high density, high alumina (99% & more) refractory used in hot face from the burner down to the diffuser cone and to the catalyst dome support. High Alumina hexagonal target tiles are commonly used in the secondary reformer as bed topping media. Refractories are subjected to severe reducing atmosphere, Corrosion, Thermal Gradient and Load Deformation. Therefore the refractory has to be made specially with high purity and careful selection of raw materials and adequate process control.

The high alumina content, low impurity such as silica and high strength of high alumina refractory is ideal for high temperature and steam applications. Processing of high alumina refractories discussed here with various high purity raw material aggregates. Effect of Sintering temperatures vis-à-vis mechanical strength properties studied. Characterization of microstructural properties and thermo-mechanical properties of developed high alumina refractory shared in this paper.

KEYWORDS: Secondary Reformer, High Alumina Refractory, Synthetic Gas, Methanol

INTRODUCTION

The manufacture of Nitrogenous Fertilizers from oil and coal based feedstock is a highly complex, high temperature operation. High refractory of extreme purity, play a very important role in the production of these fertilizers. Although the process of manufacturing nitrogen based fertilizers may differ plant to plant, depending upon the type of feedstock available, the use of high alumina refractories for lining reactors, generators and reformers is common to all processes.

Synthesis gas containing a high percentage of hydrogen concentration is a prime requirement for the product of ammonia, the essential reactant in the manufacture of nitrogenous fertilizers. The high temperature, erosion, corrosion and thermal shock conditions encountered in synthesis gas and ammonia processes, require the use of specially made high purity refractories. High alumina material if containing large amount of amorphous silica and aluminosilicates are not able to perform satisfactorily in secondary reformers, partial oxidation generators and in certain areas of primary reformers. Hydrogen & steam react with silica at elevated temperature and pressure.

Synthesis Gas is generally produced by any of the following processes:

- Partial Oxidation – Any petroleum feedstock from natural gas to heavy fuel oil and even asphalt and coal tar
- Steam Naphtha Reforming – uses straight run naphtha from petroleum. This process is used where natural gas is not available.
- Steam Methane Reforming (SMR) – uses only natural gas

Synthesis gas by Steam Naphtha Reforming

Production of synthesis gas by this process essentially consists of two steps. The feed consisting of hydrocarbons up to naphtha is pretreated by sweetening (desulphurization) and is injected with steam into a primary reformer. The reforming reaction is basically between hydrocarbons and steam to produce oxides of carbon and hydrogen, methane and by products such as ethylene, acetylene etc. The steam hydrocarbon reaction takes place at elevated temperature in the presence of nickel bearing catalysts packed in specially alloy tubes.

The effluent gas from the primary reformer passes through refractory lined transfer tubes (hot hydrogen lines) to a secondary reformer where the residual methane is further converted to hydrogen and carbon monoxide:

$$H_2O + CH_4 \longrightarrow CO + 3H_2 \quad (1)$$

(Steam) (Methane) (Carbon monoxide) (Hydrogen)

The necessary heat for this reaction is supplied by the preheated air in the upper portion of the secondary reformer where the oxygen in the air is completely burnt with the combustible gases. The gases then pass through abed of catalyst where further reaction take place, maximizing the conversion. Fig. 1 shows a typical stem reforming process.

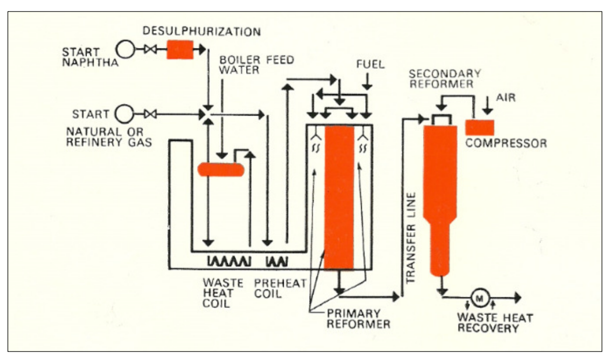

Fig. 1: Typical Steam Reformer Train

A typical Secondary Reformer is shown in Fig. 2 . Reactions which take place in the secondary reformer are such that only materials of high refractory strength can withstand the very androus operating conditions. Burner flame temperature may reach 2500ºC [2] and temperature at the top of the unit may vary between 1200 – 1400ºC and in the atmosphere of hydrogen, steam, carbon monoxide, carbon dioxide and other gases. It is imperative that the refractory construction material should be extremely high in alumina content and very low in impurities like silica and iron. At such elevated temperatures hydrogen reacts with any free silica or silicates to produce gaseous SiO and water:

$$SiO_2 + H_2 = SiO + H_2O \quad (2)$$

These reactions accelerate erosion of the refractories.

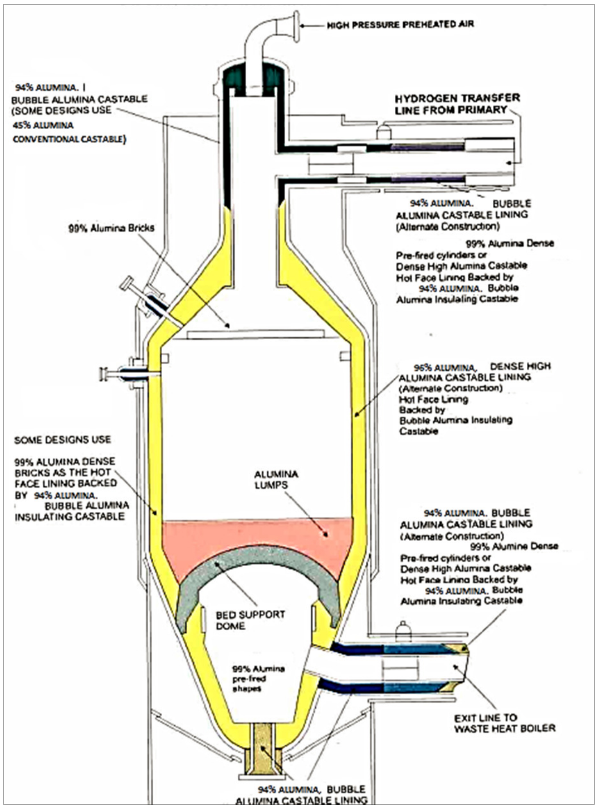

Fig. 2: Typical schematic diagram of Secondary Reformer

Refractory for Catalyst Bed Support

The designs of the catalyst and alumina lump bed supports (Fig. 3 and Fig. 4) depend on number of factors such as pressure drop through the bed, allowable minimum rise of the support, maximum pressure exerted, chemical composition of the process stream, operating temperature and pressures.

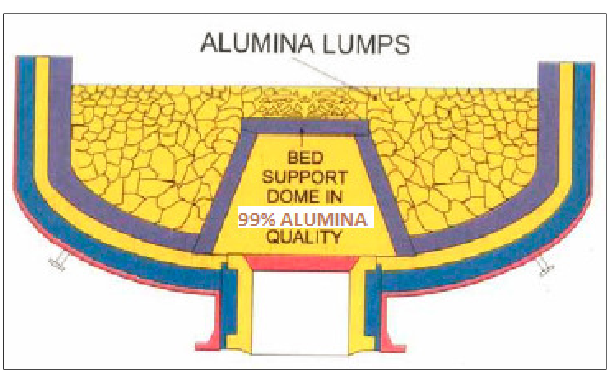

Fig. 3: Catalyst bed support arrangements

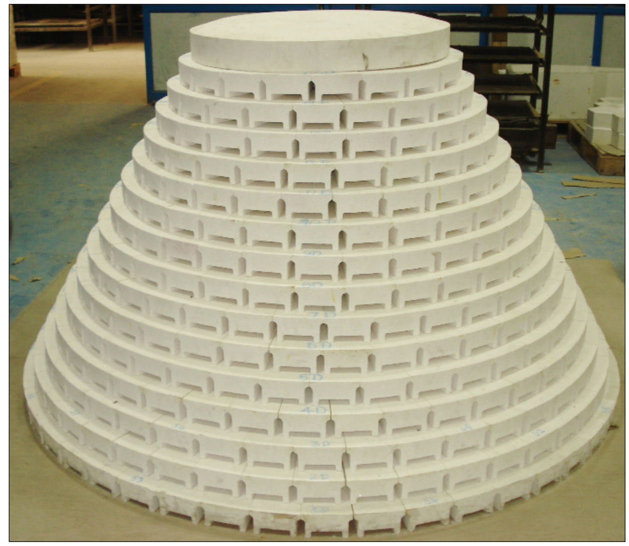

Fig. 4: Pre-despatch assembly of a typical catalyst bed support

Steam Methane Reforming

This is most common method of producing commercial bulk hydrogen. Hydrogen is used in the industrial synthesis of ammonia and other chemicals. At high temperatures (700 – 1100^{o}C) and in presence of nickel based catalyst, steam reacts with methane to yield carbon monoxide and hydrogen.

99.5 % Alumina refractory has become a standard hot face lining for secondary reformer for years, however at times, refractory life is not consistent for combination of reasons e.g. mechanical strength of refractory, operating condition etc. Optimization of raw material and firing temperature have an effect on the properties of refractory and vis-à-vis performance of reformer lining, hence this study on 99.5% alumina refractory based on combination of different high alumina aggregates and sintering temperature was taken up.
Four types of samples were taken for the study. Characterization done to understand thermo-mechanical properties along with Chemical Analysis, Scanning Electron Microscopy [SEM] and XRD Phase Analysis.

EXPERIMENTAL PROCEDURE

Sample Preparation

Four samples A, B, C and D were prepared based on white fused alumina (WFA) & tabular alumina (TA) aggregates as mentioned in Table.1:

Tab. 1: Sample type

Sample #	Target Al_2O_3	Base Aggregates	Firing Temperature
Sample A	99.5 %	WFA + TA	1650^{o}C
Sample B	99.5 %	TA	1650^{o}C
Sample C	99.5 %	WFA	1650^{o}C
Sample D	99.5 %	WFA	1750^{o}C

Samples were prepared with respective aggregates, calcined and reactive alumina and temporary binders and were pressed in brick form with standard dimension as 230X115X75mm. and firing done in shuttle kiln.

CHARACTERIZATION

Tests carried out on these samples: Bulk Density (BD), Apparent Porosity (AP), Cold Crushing Strength (CCS), Modulus of Rupture at ambient (MOR) and at elevated temperature (HMOR), Reversible Thermal Expansion [RTE], Refractoriness under Load (RUL), Hot Load Deformation / Creep under compression, Thermal Shock Resistance [TSR], Reheat Change, Chemical Analysis, Scanning Electron Microscopy [SEM] and XRD phase analysis.

RESULTS AND DISCUSSION

Results

Evaluated properties (mean data) are shown below.

Table 2: Bulk Density (BD), Apparent Porosity (AP)

Sample #	BD (g/cc)	AP (%)
Sample A	3.19	18.2
Sample B	3.16	16.5
Sample C	3.21	17.3
Sample D	3.30	17.2

Table 3: Cold Crushing Strength (CCS), Modulus of Rupture at ambient (MOR) and at 1350°C (HMOR)

Sample #	CCS (MPa)	MOR (MPa)	HMOR (MPa)
Sample A	77	18.6	6.4
Sample B	101	28.6	8.3
Sample C	75	16.8	7.2
Sample D	90	20.2	8.5

Table 4: Reversible Thermal Expansion [RTE]

Sample #	Thermal Expansion Coefficient α(25°C-1400°C) , cm/cm/°C
Sample A	$8.3X10^{-6}$
Sample B	$8.1X10^{-6}$
Sample C	$8.4X10^{-6}$
Sample D	$8.4X10^{-6}$

Refractoriness under Load (RUL) for all the samples exceeded 1750°C.

Table 5: Creep under compression at 1550°C/50 Hrs.

Sample #	5 – 25 Hrs.	5 – 50 Hrs.
Sample A	-0.22	-0.39
Sample B	-0.27	-0.40
Sample C	-0.21	-0.35
Sample D	-0.18	-0.29

Thermal Shock Resistance carried out by air quenching as well as by water quenching method and the result is shown in the Table 6.

Table 6: Thermal Shock Resistance (TSR)

Sample #	Air Quenching (Cycle)	Water Quenching (Cycle)
Sample A	+ 100	22
Sample B	+ 100	25
Sample C	+ 100	+ 30
Sample D	+ 100	+ 30

Reheat Change test carried out at 1750°C with a soaking duration of 6 hrs. This test was repeated 10 times to understand effect temperature cycling, shown in Table 7.

Table 7: Reheat Change (after 1,3,5,8 and 10 cycles)

Sample #	1st	3rd	5th	8th	10th
Sample A	0.06	0.09	0.13	0.19	0.21
Sample B	1.07	1.44	1.67	2.01	2.04
Sample C	0.05	0.09	0.13	0.15	0.16
Sample D	0.02	0.04	0.08	0.10	0.11

Table 8: Chemical Analysis

Sample #	Al_2O_3	SiO_2	Fe_2O_3	$K_2O + Na_2O$
Sample A	99.46	0.12	0.06	0.31
Sample B	99.41	0.11	0.05	0.30
Sample C	99.48	0.12	0.06	0.31
Sample D	99.54	0.11	0.06	0.23

Scanning Electron Microscopy [SEM] carried out on original samples (left top) and after reheat change for 3rd (right top), 5th (left bottom) and 10th cycle (right bottom). Micrographs are shown in Fig. 5, 6, 7 and 8. [Magnification: 1000X]

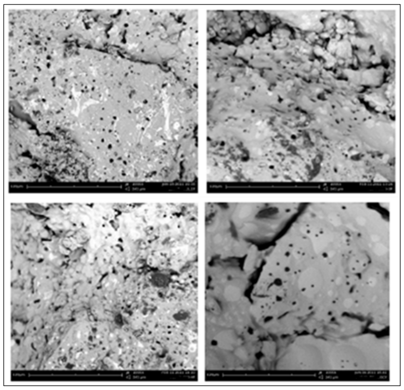

Fig. 5: SEM – Sample A

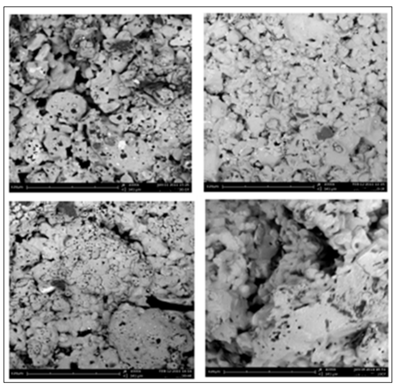

Fig. 6: SEM – Sample B

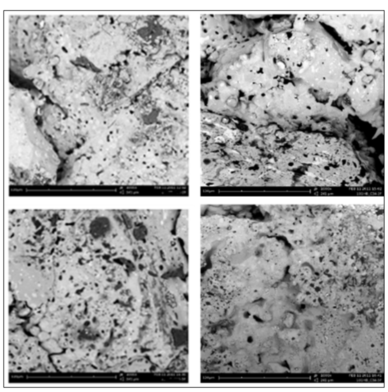

Fig. 7: SEM – Sample C

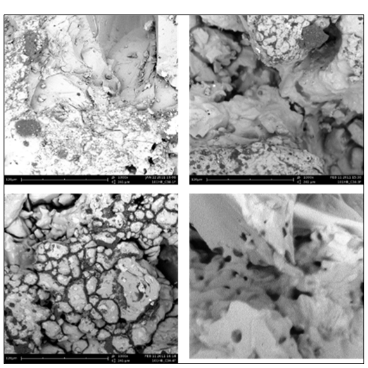

Fig. 8: SEM – Sample D

XRD Phase analysis done for all four samples and α-Al_2O_3 (Corundum) was detected as main component in all.

Discussion

In the secondary reformer, combustion of the process gas hydrocarbon in oxygen causes a temperature rise that provides heat for the reforming reaction. Operating conditions are severe, which places high demands on the individual components of the secondary reformer which includes stable refractory lining for pressure vessel and high-strength target tiles [3] . Selection of refractory is prime importance for long reformer life.

Sample D, WFA based high alumina refractory fired at 1750°C exhibited better density compared to other compositions and adequate mechanical strength. Though TA based composition shows higher strength properties, volume stability is less as determined in TSR.

Being ~99.5% Al_2O_3 compositions, thermal expansion coefficient of all the samples are more or less same and values are above $8X10^{-6}$ cm/cm/°C.

Although reformer hot face may not exceed beyond 1400oC, however considering flame temperature of 2000oC and above, Reheat change test were conducted at 1750oC. WFA based sample D fired at 1750oC showed least changes.

Chemical Analysis shows significant drop of alkali content in sample D, probably due to firing at higher temperature.

SEM micrographs exhibit grain growth for Sample A and very significant grain growth for sample B whereas much less for Sample C and D.

CONCLUSIONS

(1) WFA based 99.5% alumina refractory fired at 1750oC seems to be very suitable for application in hot face lining of secondary reformer considering adequate mechanical strength, lower impurity level, less alkali content, good thermal shock resistance and volume stability.

(2) As 99.5% alumina has high thermal expansion characteristics, Expansion of refractory and mechanical stress generation could be an issue for the reformer lining. Proper design aspects i.e. provision for expansion to be considered as critical design parameter.

(3) High temperature (1750°C) fired refractory has lesser alkali, therefore formation of detrimental β-Al_2O_3 can be avoided under stable operating condition

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MAILING ADDRESS

deyranjan@cumi.murugappa.com