

Physical and Mechanical Properties of High Alumina Refractory Materials for shielding Applications of Steam Reformer Reactor

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Abstract

This research studied the physical properties of high alumina refractory materials, which are using as lining material in the primary and secondary reformer for Ammonia production in Kima project of Aswan City, Egypt .The study focused on the effect of materials balance variations of the mixture content, with different chemical recipes on The physical and mechanical properties which are affected by the in-service conditions of the primary and secondary reformer; these physical and mechanical properties are ; the bulk density, the thermal conductivity, permanent linear change (PLC), the cold crushing strength.

Key Words: Primary and secondary Reformer, alumina base refractory materials, ASTM C134,C133, C856, Ammonia production process.

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1. Introduction

Steam reforming of natural gas is the most common method of producing commercial bulk hydrogen at about 95% of the world production [1, 2] of 500 billion m³ in 1998. [3] Hydrogen is used in the industrial synthesis of ammonia and other chemicals.[4] At high temperatures (700 – 1100 °C) and in the presence of a metal-based catalyst (nickel), steam reacts with methane to yield carbon monoxide and hydrogen ,according to the reaction; $CH_4 + H_2O \rightleftharpoons CO + 3 H_2$.

Due to high temperature it is indispensable to use high durable refractory materials to resist and insulate such high temperature and keep the heat balance required to achieve the reaction. The refractory tiles supposed to be mounted in internal wall of the reformer as illustrated in the attached schematic design, **Fig.1[5]**

In this research i used high alumina refractory material, with a different chemical recipes of alumina, silica, iron oxide and titanium dioxide, CaO, Magnesia, Alkalis (Na₂O+K₂O),phosphorous Pentoxide **[6]** .the mixing and dry out of this mixtures was done in accordance to the technology provider of Reformer technology KBR**[6]**

The main criteria used to test the produced refractory product is; the bulk density, permanent linear change (PLC), the cold crushing strength. **[7,8]**

All the activity of the research has been accomplished at the site of the Urea and Ammonia project under construction at ASWAN city in the south of Egypt under the authority of the company of Orascom construction.

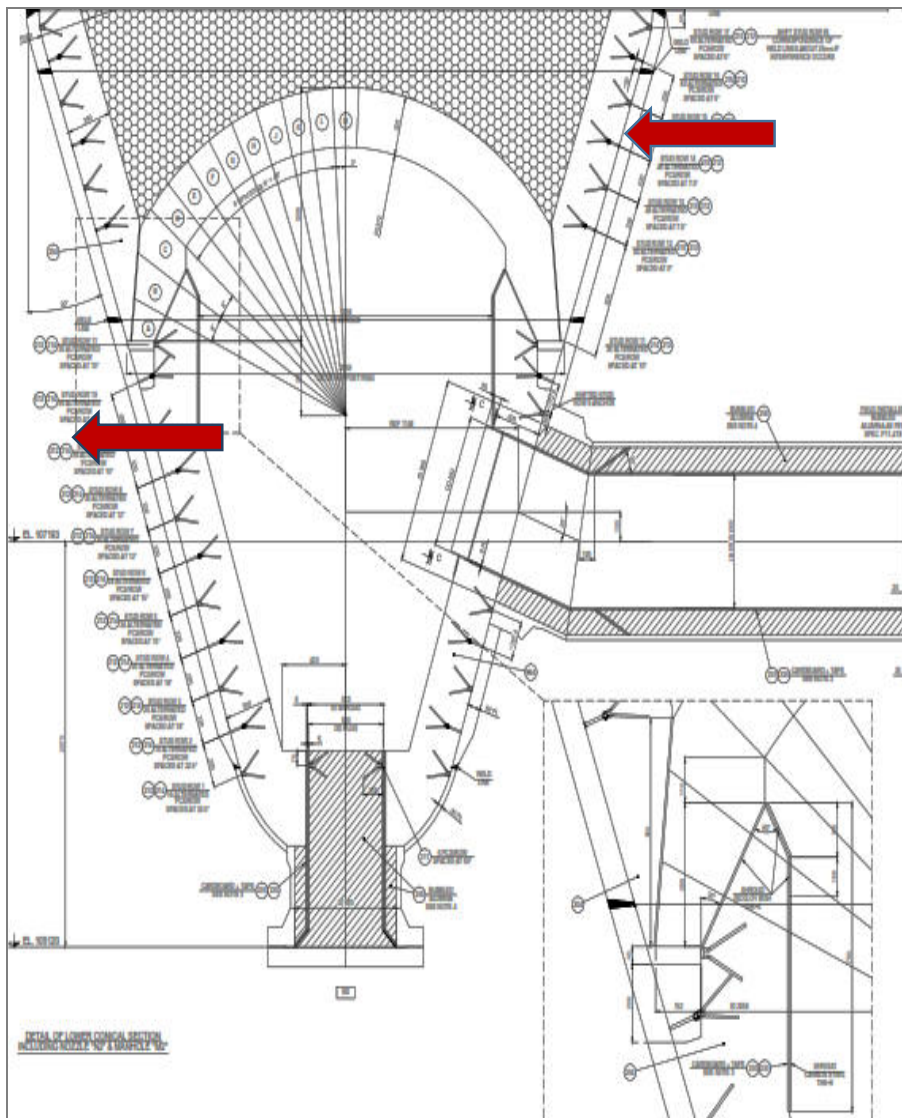


Fig.1. Schematic view of the internal side wall of the reformer illustrating the location of the refractory tile in the direction of the red arrow

2. Experimental Work

The experimental work started with materials preparation with a different recipes, where I selected the alumina from manufacturer with brand name called Al100 and the white sand as source of silica, hematite as source of iron oxide, Anatase form of TiO_2 white pigment, and calcium carbonate as source of CaO , Dolomite as source of Magnesia, Sodium hydroxide as source of Na_2O , potassium hydroxide as source of K_2O , and Apatite as source of the phosphorous pentoxide. The mineral balance weigh will be kept as knowhow and knowledge preservation but the analysis of the balance of the all oxide will be demonstrated to show the variation recipes. The recipes are as follow in table 1, were it has been categorized into four categories; A, B, C, D where category #A has only content of Al_2O_3, SiO_2, Fe_2O_3 and the percentage of Alumina was changed, in Category #B I added content of Calcium oxide and Magnesia, Alkalis, and the content of both alumina and Calcium oxide were changed, in Category #C I added TiO_2 and phosphorous pentoxide, where percentage of Al_2O_3, SiO_2, P_2O_5 were changed, in category # D I discarded the content of P_2O_5 and changed the percentage of both Al_2O_3 and CaO

Table.1: The recipes percentage content by weight

Recipes Categories	Recipe No /Sample ID	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	TiO ₂	CaO	MgO	Alkalis Na ₂ O,K ₂ O	P ₂ O ₅
		%	%	%	%	%	%	%	%
A	A101	99.5	0.1	0.1					
	A102	95	0.2	0.2					
	A103	90	0.4	0.4					
B	A104	94.3	0.1	0.1		5	0.1	0.4	
	A105	93.3	0.1	0.1		6	0.1	0.7	
	A106	92.3	0.1	0.1		7	0.1	0.7	
C	A107	91	5	0.1	0.1	0.1	0.2	0.3	3.2
	A108	88	6	0.1	0.1	0.1	0.2	0.3	5.2
	A109	85	7	0.1	0.1	0.1	0.2	0.3	7.2
D	A110	94.5	0.5	0.1	0.1	4.4	0.1	0.4	
	A111	90.5	0.5	0.1	0.1	8.4	0.1	0.4	
	A112	85.5	0.5	0.1	0.1	13.4	0.1	0.4	

2.1. Materials preparation

All minerals had been grinded and sieved to be less than 500 micron and then dried mixed for 10 minutes, to assure from homogeneity before wet mixing by water addition [16-21]

2.2. Wet mixing



In this step 10 kilograms of each sample ID after dry mixing were poured inside the mechanical vibrator mixer (Fig.2.) for 10 minutes and then adding the total weight of water which representing 12% of the total weight of the sample, the pouring of the water shall be done into two half; one half after mixing 10 minutes and the other half shall be after 10 minutes, the wet mixing continue for 20 minutes [16-21]. there are controlling method to test the quality of mixing; called ball in hand test each sample is taken from the mixer and rounding it like a ball if the mixture was loose and not adhered then the mixer needs more water if the ball in hand was sticky and rounded it means that the water content is optimum, if the ball in hand was fluidized then the water is much more than required, Fig.3. Showed the criteria of the ball in hand test [22, 23]

Fig. 2.Schematic View of Wet Mixer



Fig.3.Schematic View of ball in hand test rejection and acceptance criteria

2.2. Pouring in Cubic Molds

After adjustment and monitoring of the mixing process by ball in hand test, the mixed recipe of each sample from each category A,B,C,D were poured into wooden cubic molds with a dimensions 50X50X230 mm and dimensions 50X50X50mm to use it for the test required after curing and drying.The total number of samples to cover the required tests are 264 specimens.

2.3. Curing and Dry Out

At this stage all molded samples shall be dried and cured in accordance to the specifications of KBR design criteria, where it designed to the fitness for services[6],the regime of dry out and curing is to make ignition and heat up to 135°C with a rate of 15 °C/hr, then hold 8 hours in temperature 135°C, after that heating up to 300°C at rate of 15°C/hr. then holding temperature for 12hr ,then heating up the temperature to 480°C at the rate 15°C/hr and directly go forward to heat up the temperature to 950°C at rate 50°C/hr, then holding the temperature at 950°C for 24hr,after that the temperature shall be descended to 200°C at rate of 25°C/hr.The curing and dry out regime is showed in **Fig.4**.

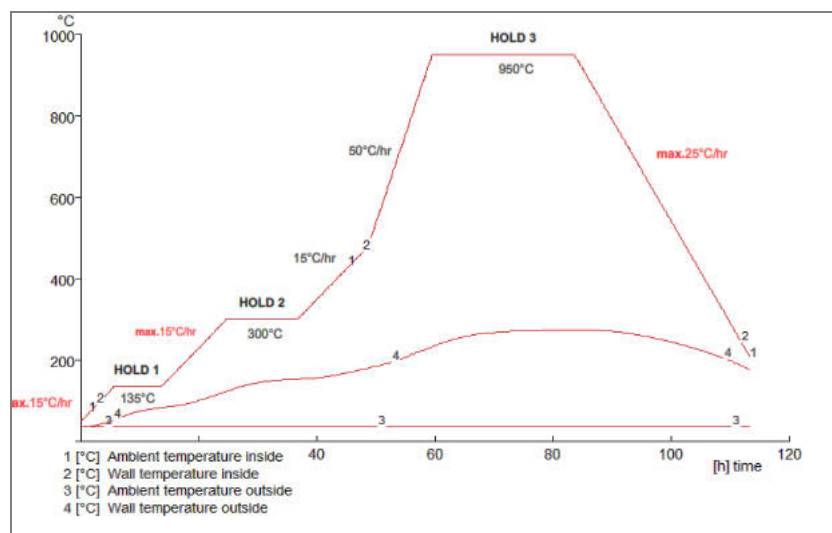


Fig.4.the curing and dry out regime

2.4. Sounding Test

The purpose of this test to sort the samples which have no any defect due to the casting and mixing or any defect regarding to the preparation to judge on the samples in according to variation of its material balance only. This test have been conducted by phased array technique by using apparatus of OMNISX-PA1664PR with 16 piezo electric elements. Test was done for all test samples and selected only the sounded samples and neglect all samples which have defects. The test have been repeated twice to increase the reliability as shown in Fig.5a,b where A scan showed no defect indications and also b scan but in C scan showed some textures indications regarding to sound noise but when repeated due to different calibration and neglecting the noise effect of the device showed completely sounded indications in Fig.5b.

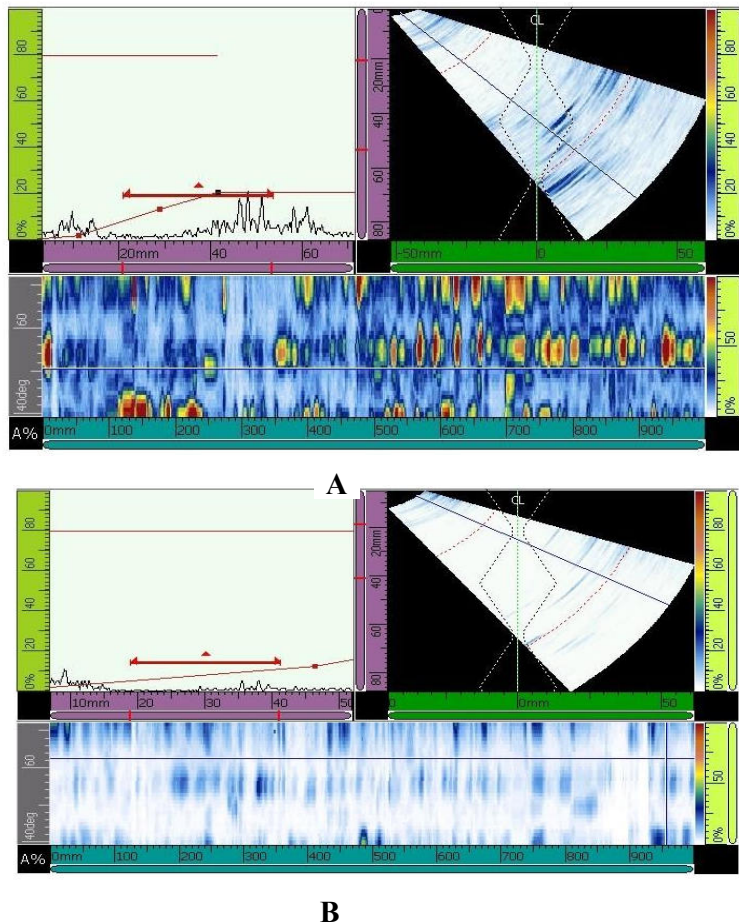


Fig.5. Results of tests by Phased Array method showed soundness of test samples

2.6. Testing Required for Sample Evaluation

The test specimens of each category were tested and evaluated, where thermal conductivity test has been conducted by the device; DFX200 High speed Xenon-pulse delivery source and solid state PIN detector for unmatched sensitivity down to -150°C as shown in Fig.6.A., Also the bulk density was tested in accordance to ASTM C134 by device of XQK Ceramic refractory products apparent porosity bulk density as shown in Fig.6B., also cold crushing strength was tested in accordance to ASTM C133 by apparatus of PERCISION as shown in figure Fig.6C..., the permanent linear change also was tested in accordance to ASTM C113 by universal testing machine with furnace escalated temperature as shown in Fig.6.D



Fig.6. A is apparatus DFX200 High speed Xenon-pulse delivery source and solid state PIN detector for thermal conductivity Measure ,B is apparatus XQK Ceramic refractory products apparent porosity bulk density ,C is apparatus of PERCISION to measure the cold crushing strength ,D is apparatus of universal testing machine to test the permanent linear change

The bulk density test was conducted at temperatures 105°C, 815°C, where each sample from each category were tested, the total tested samples are 24. The cold crushing test was conducted at temperatures 105 °C, 815 °C, 1095 °C, 1370 °C, the overall samples are 48. The permanent liner change test was conducted at temperatures 105 °C, 815 °C, 1095 °C, 1370 °C, 1600 °C, 1820°C the total numbers of these samples are 72 . The thermal conductivity test also was conducted at temperatures 205°C, 425°C, 650°C, 870°C, 1095°C, 1315°C with over all samples up to 72.

3. Results and Discussion

3.1. The Measurement of Bulk Density

The test samples in accordance to the recipes as illustrated in table 1 was tested by device of XQK Ceramic refractory to measure the bulk densities of test samples, the results showed (Fig.7)&Table.2. that the values at measuring temperature 105°C are 3320,3150,3050 Kg/m³ for the samples; A101,A102,A103(category A) with alumina percentage ranging from 99.5%, 95%,90% respectively, and showed sever decrease in the value of bulk density up to 2550 Kg/m³ at the sample A104(Category B) ,where such decreasing appears when added a

considerable amount of calcium carbonate as source of CaO with percentage up to 5%, the increasing of CaO percentage resulting also slight increase in the bulk densities values of Al05,Al06(category)with values;2700 Kg/m³,2600 Kg/m³.at the samples Al07,Al08,Al09(Category C)it was noticed that when added 5,6,7 % respectively of white sand as source of SiO₂ and amount of apatite as source of P₂O₅ % ;3.2.5.2,7.2 respectively and fixed amount of TiO₂ as 0.1% it was noticed that the values of bulk densities are; 2920Kg/m³,2700Kg/m³,2600Kg/m³ respectively but it can considered that such change in the bulk values are considering smooth change form sample Al04 to Al09 but at sample Al10 was noticed that the value was severe decreased to 1750 Kg/m³and the samples Al11,Al12 continue to decrease to values 1550Kg/m³,1300Kg/m³ respectively ,such decrease in bulk densities was due to the absence of P₂O₅ and fixed amount of TiO₂; 0.1% and ascending value of CaO ; 4.4,8.4,13.4% respectively and descending value of Al₂O₃;94.5%,90.5%,85.5% .

Regarding to the temperature 815°C, the results of test samples showed almost agreement of the values of bulk densities at 105°C, except a severe change of the bulk density value of sample Al03, where the value dropped from 3050Kg/m³ to 2050 Kg/m³ such severe drop was noticed at the value of 90% of Al₂O₃.

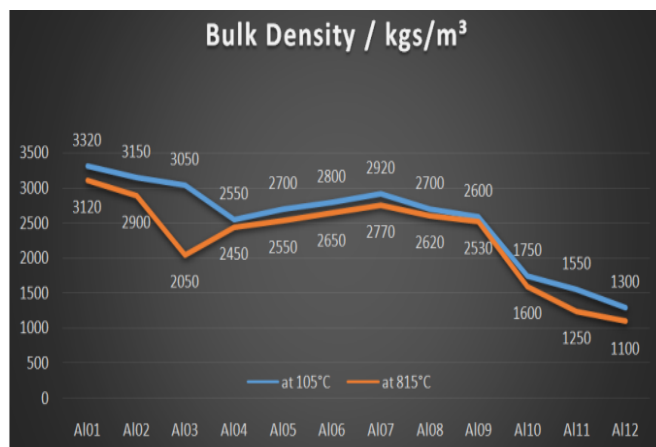


Fig.7: Bulk density of test samples at testing temperature of 105°C,815°C

Table.2: The Results of Bulk Densities

CHARACTERISTICS		Bulk density / kgs/m ³	
	-	@ 105°C	@ 815°C
Category A	Al01	3320	3120
	Al02	3150	2900
	Al03	3050	2050
Category B	Al04	2550	2450
	Al05	2700	2550
	Al06	2800	2650
Category C	Al07	2920	2770
	Al08	2700	2620
	Al09	2600	2530
Category D	Al10	1750	1600
	Al11	1550	1250
	Al12	1300	1100

3.2. Measuring of the Cold Crushing Strength.

The cold crushing strength test was conducted in accordance to ASTM C133 and C856 and used apparatus of PERCISION.the test was conducted at temperatures 105°C, 815 °C, 1095 °C, 1370 °C the results of the test(**table 3&Fig.8**). at 105°C was ranging from 80 to 14 MPa with slightly descending for the samples AL01 to AL12 . the samples Al04,Al05,Al06 showed durable and stable strength at temperatures 815°C,1370°C where they showed strength values almost compatible 47,40-42,37-38 Mpa respectively ,where adding calcium carbonate provide the samples such stability at such materials balance. The cold crushing strength was direct proportional with value of alumina percentage.

Table.3: Results of the cold crushing strength

CHARACTERISTICS		Cold Crushing Strength - ASTM C133 and C865 - MPa			
<u>Category A</u>	-	@ 105°C	at 815°C	@ 1095°C	@ 1370°C
		Al01	80	73	66
	Al02	70	62	54	43
	Al03	66	52	40	32
<u>Category B</u>		@105°C	@ 815°C	@ 1095°C	@ 1370°C
	Al04	58	47	34	47
	Al05	55	42	30	40
	Al06	40	38	25	37
<u>Category C</u>		@ 105 °C	@ 815°C	@ 1095°C	@ 1370°C
	Al07	44	33.5	22	15
	Al08	30.15	28.5	24	18
	Al09	27	20.15	18	13
<u>Category D</u>		@ 105°C	@ 815°C	@ 1095°C	@ 1370°C
	Al10	20	7.5	7.5	11.5
	Al11	18	6	5.78	10
	Al12	14	5	4.55	8

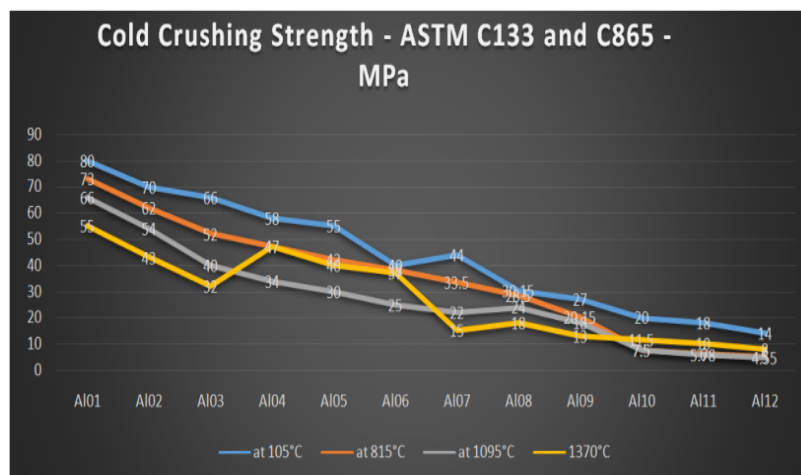


Fig.8.cold crushing strength of test samples at testing temperature of 105 °C,1370°C

3.2. Measuring of the Permanent Linear Change

The test samples were tested by apparatus of universal testing machine at temperatures 105°C, 815 °C, 1095 °C, 1370 °C , 1600°C, 1820°C. The results showed (**Fig.9**).that the PLC percentage at 105°C for sample Al01, Al02,

Al03 are; 0.1%, 0.6%, 0.9% and suddenly decreased to 0% at sample Al04, where the addition of Cao caused this amendment and started again to slightly increased but returned again to value zero %,at the sample Al06 such decrease in the value of PLC was due to increasing the percentage of Cao to 7%.the with the decreasing of alumina percentage. It is noticed that the values of PLC at temperatures 105°C, 815 °C, 1095 °C, 1370 °C , 1600°C are almost agreed for the samples Al01,Al02,Al03, the values were noticed to be increased at samples Al07,Al08,Al09 at temperatures 815 °C, 1095 °C, 1370 °C , 1600°C, where at those samples has doped with considerable amount of SiO₂ P₂O₅ as shown in table 1.the results showed also that the sample Al010 showed lowest PLC at highest temperature 1820°C.

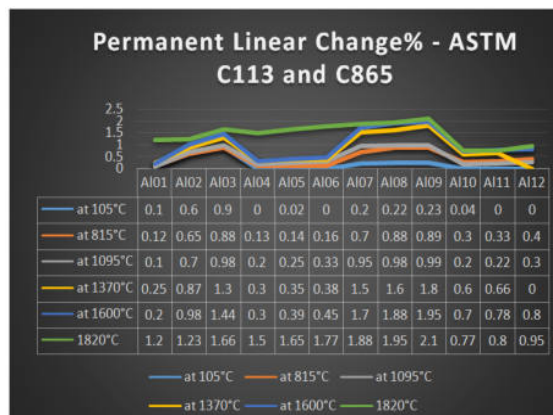


Fig.9: Permanent linear change% at testing temperature of 105°C, 815 °C, 1095 °C, 1370 °C , 1600°C, 1820°C.

3.3. Measuring of the Thermal conductivity

The thermal conductivity was measured for test samples by apparatus DFX200 High speed Xenon, the results showed (Fig.10) that the category A for samples Al01,Al02,Al03 have been almost agreed in the values of its thermal conductivity at temperatures; 205°C,425°C,650°C,870°C,1095°C,1315°C ,where the values ranging from 1.89w.m⁻¹.k⁻¹ to 1.29w.m⁻¹.k⁻¹ for the sample Al01 at temperature 205°C, Al03 at temperature 1095° C respectively. Regarding to the samples Al04, Al05, Al06 (category B) showed disagreement in its value at the test temperatures due to doping of Cao and traces of Alkaline, where they showed sudden increase in thermal conductivity; up to 4.41 w.m⁻¹.k⁻¹ for the sample Al03 at temperature 205°C. Regarding to the sample Al07, Al08, Al09 (category C) their thermal conductivity started again to be decreased to values 2.28w.m⁻¹.k⁻¹, 2.2w.m⁻¹.k⁻¹ .1.98w.m⁻¹.k⁻¹ respectively at temperatures 205 oC, and showed almost stability and agreement of its values at escalated temperatures up to 1315°C where the lowest thermal conductivity recorded for the sample Al09 at temperature of 1315°C with value of thermal conductivity 1.95w.m⁻¹.k⁻¹.Regarding to the samples Al09,Al10,Al11(category D) showed also almost agreement in its thermal conductivity values , where the lowest thermal conductivity values was recorded for the sample Al10 with value up to 0.8 w.m⁻¹.k⁻¹

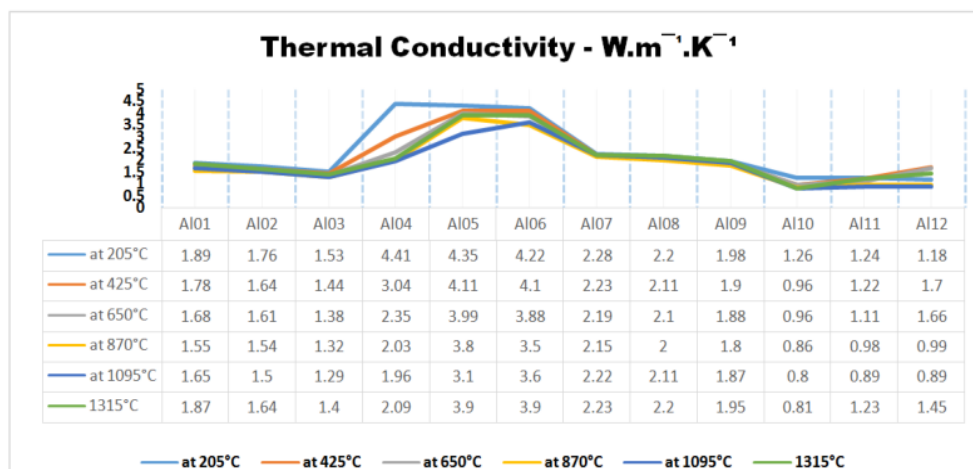


Fig.10. the thermal Conductivity at testing temperature of 205 °C, 425 °C, 650 °C, 870 °C, 1095 °C, 1315 °C

4. Conclusions

- High alumina samples were tested and evaluated to be used as refractory materials for steam reformer reactor ,which it is main process for producing hydrogen required for ammonia production ,this articles provide the fabricator the ability to select the material which suitable for his application which required mechanical durability and low thermal conductivity, the data provided in this article make the fabricator has the wide range application to select material with low thermal conductivity and high mechanical properties .there was clear correlation between high bulk density and the high cold crushing strength where the sample Al01 showed the highest bulk density with value 3320 kgs/m³ and 3120 kgs/m³ at temperatures 105 °C,815°C respectively and maximum cold crushing strength 80Mpa and 73Mpa at the same temperatures respectively where escalated alumina content contributed effectively to show high bulk density and high cold crushing strength .
- Regarding to the permanent linear change which it is important for the fabricator to receive materials with minimum linear change at highest temperatures, the sample Al12 (category C) showed minimum linear change at temperature up to 1820°C with percentage up to 0.95%, where the balancing between alkalis and Cao with percentage up to 13.4% contributed effectively to receive such result.
- Regarding to the thermal conductivity also itis indispensable to get refractory materials with lowest value of thermal conductivity and also category C of sample Al10 showed lowest thermal conductivity at 0.81 w.m⁻¹.k⁻¹at highest temperature at 1315°C.

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