RESEARCH ARTICLE OPEN ACCESS

Steel-plant Refractory: A Review

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Abstract:

In the steel industry, competitive pressures such as worldwide demand, high cost of energy, environmental and safety regulations, competing materials, customer demand for high quality, and the high cost of capital have led to a need for changes across the industry. Refractories for all unit processes are selected on the basis of their longevity and the cleanliness of the steel. The various types of refractories influence the safe operation, energy consumption and product quality; therefore, selecting refractories to each application is of great importance. This study discusses the types, characteristics and properties of various refractories suitable for steel plant ladle.

Keywords — **Steel, Ladle, Refractory.**

I. INTRODUCTION

A steelmaking ladle is essentially a bucket which is used to take molten steel from the primary steelmaking furnace to the casting area. Ladles are generally cylindrical, with an open top, small off-centre casting nozzle in the base. They consist of an external steel shell (50-100 mm thick), and many layers of internal refractory lining (up to 400 mm). A refractory-lined steel lid can be used to cover the top of the ladle. When molten steel is contained in a ladle, it loses heat to the refractories in the wall and base. Very little heat is lost through the top surface, due to an insulating slag layer. Natural convection causes the steel to circulate, flowing down near the walls, and rising in the centre of the ladle. Under normal operating conditions, a vertical temperature gradient forms in the ladle.

1.1. WHAT ARE REFRACTORIES USED FOR

Refractories are used by the metallurgy industry in the linings of furnaces, kilns, reactors and other vessels for holding and transporting metal and slag. In non-metallurgical industries, the refractories are mostly installed on fired heaters, hydrogen reformers, ammonia primary and secondary reformers, cracking furnaces, incinerators, utility boilers, catalytic cracking units, coke calciner, sulfur furnaces, air heaters, ducting, stacks, etc. Majority of these listed equipment operate under high pressure, and operating temperature can vary from very low to very high (approximately 900°F to 2900°F). The refractory materials are therefore needed to withstand temperatures over and above these temperatures. Listed below is the sample melting temperatures of key metallurgical elements where refractory application is critical **[1]**.

TABLE.1.1. Melting point chart **[1]**

KEY MATERIALS	MELTING TEMPERATURE(^{O}C)
IRON	1536
NICKEL	1452
COPPER	1081
ALUMINIUM	659
ZINC	415
LEAD	326
TIN	231

Due to the extremely high melting point of common metals like iron, nickel and copper, metallurgists have to raise furnace temperatures to over 2800°F. Furnaces are lined with refractory materials such as magnesia, which has a melting point of 5070 degrees **[1], [2]**.

1.2. REQUIREMENTS OF RIGHT REFRACTORY

The general requirements of a refractory material can be summed up as:

1) Its ability to withstand high temperatures and trap heat within a limited area like a furnace;
2) Its ability to withstand action of molten metal, hot gasses and slag erosion ;
3) Its ability to withstand load at service conditions;
4) Its ability to resist contamination of the material with which it comes into contact;

5) Its ability to maintain sufficient dimensional stability at high temperatures and after/during repeated thermal cycling;
6) Its ability to conserve heat.

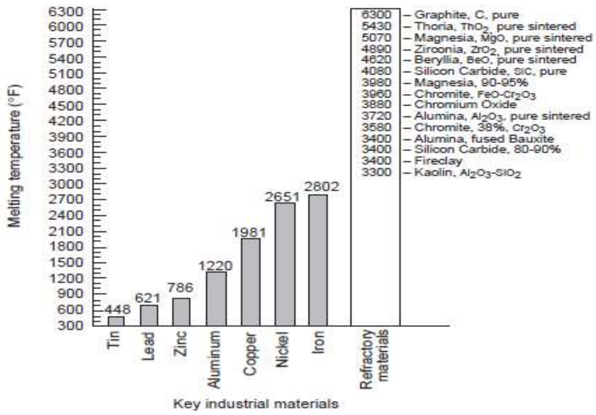

Fig. 1.1. Refractory and industrial materials melting point chart **[1]**

1.3. PROPERTIES OF REFRACTORIES

Some of the important characteristics of refractories are:

1.3.1. **Melting Point:** Melting temperatures (melting points) specify the ability of materials to withstand high temperatures without chemical change and physical damage. The melting point of some elements that constitute refractory composition in the pure state varies from 3100°– 6300°F as indicated in the table below:

TABLE.1.2. Melting point chart of pure compound **[2]**

REFRACTORY ELEMENT	MELTING TEMPERATURES(°C)
Graphite C Pure	3478
Thoria, ThO_2 Pure Sintered	2995
Magnesia, MgO, Pure Sintered	2796
Zirconia, ZrO_2 , Pure Sintered	2696
Lime, CaO	2568
Beryllia, BeO, Pure Sintered	2546
Silicon Carbide, SiC, Pure	2246
Magnesia, 90-95%	2171
Chromite, FeO-Cr_2O_3	2180
Chromium Oxide	2135
Alumina, Al_2O_3 , Pure Sintered	2046
Chromite, 38%, Cr_2O_3	1969
Alumina Fused Bauxite	1869
Silicon Carbide, 80-90%	1869
Fireclay	1869
Titania, TiO	1847
Kaolin, Al_2O_3 -, SiO_2	1813
Silica, SiO_2	1713

The melting point serves as a basis for considering the thermal stability of refractory mixtures and is an important characteristic indicating the maximum temperature of use.

1.3.2. Size and Dimensional Stability: The size and shape of the refractories is an important feature in design since it affects the stability of any structure. Dimensional accuracy and size is extremely important to enable proper fitting of the refractory shape and to minimize the thickness and joints in construction.

1.3.3. **Porosity:** Porosity is a measure of the effective open pore space in the refractory into which the molten metal, slag, fluxes, vapors etc can penetrate and thereby contribute to eventual degradation of the structure. High porosity materials tend to be highly insulating as a result of high volume of air they trap, because air is a very poor thermal conductor. Refractory materials with high porosity are usually not chosen when they will be in contact with molten slag because they cannot be penetrated as easily.

1.3.4. Bulk Density: The bulk density is generally considered in conjunction with apparent porosity. It is a measure of the weight of a given volume of the refractory. For many refractories, the bulk density provides a general indication of the product quality; it is considered that the refractory with higher bulk density (low porosity) will be better in quality. An increase in bulk density increases the volume stability, the heat capacity, as well as the resistance to abrasion and slag penetration.

1.3.5. Cold Crushing Strength: The cold crushing strength, which is considered by some to be doubtful relevance as a useful property, other than it reveals little more than the ability to withstand the rigorous of transport. It can be seen as a useful indicator to the adequacy of firing and abrasion resistance in consonance with other properties such as bulk density and porosity.

1.3.6. **Pyrometric Cone Equivalent (PCE)** Refractories due to their chemical complexity melt progressively over a range of temperature. Hence refractoriness or fusion point is ideally assessed by the cone fusion method. The equivalent standard cone which melts to the same extent as the test cone is known as the pyrometric cone equivalent (PCE).

1.3.7. **Refractoriness under load:** The ability to withstand exposure to elevated temperatures without undergoing appreciable deformation is measured in terms of refractoriness. The refractoriness under load test (RUL test) gives an indication of the temperature at which the bricks will collapse, in service conditions with similar load.

1.3.8. Creep at high temperature: Creep is a time dependent property which determines the deformation in a given time and at a given temperature by a material under stress. Refractory materials must maintain dimensional stability under extreme temperatures (including repeated thermal cycling) and constant corrosion from very hot liquids and gases.

1.3.9. Volume stability, expansion and shrinkage at high temperature: The contraction or expansion of the refractories can take place during service. Such permanent changes in dimensions may be due to:

1) The changes in the allotropic forms which cause a change in specific gravity.
2) A chemical reaction which produces a new material of altered specific gravity.
3) The formation of liquid phase
4) Sintering reactions

1.3.10. Reversible Thermal Expansion: Any material when heated expands, and contracts on cooling. The reversible thermal expansion is a reflection on the phase transformations that occur during heating and cooling.

1.3.11. Thermal Conductivity: Thermal conductivity is defined as the quantity of heat that will flow through a unit area in direction normal to the surface area in a defined time with a known temperature gradient under steady state conditions. The thermal conductivity of a refractory decreases on increasing its porosity **[1].**

Table 1.3. Some Typical Thermal Conductivity values **[10].**

Material		T [°C]	k [W/mK]
Al_2O_3-SiO_2 refractories	Low Al_2O_3	600 – 800	0.80 – 1.00
	High Al_2O_3	700 – 1000	1.20 – 1.25
Siliconcarbide, 90% SiC		1000	1.30 – 1.40
Insulating brick		200 – 700	0.30 – 1.40
Ceramic fibre board		100 – 500	0.30 – 0.80
Steel		50 – 250	0.04 – 1.06

1.4. CLASSIFICATION BASED ON CHEMICAL COMPOSITION

Refractories are typically classified on the basis of their chemical behaviour, i.e. their reaction to the type of slags. Accordingly the refractory materials are of three classes - Acid, Basic & Neutral.

1.4.1. Acid Refractories: Acid refractories are those which are attacked by alkalis (basic slags). These are used in areas where slag and atmosphere are acidic. Examples of acid refractories are:

1) Silica (SiO_2)
2) Zirconia (ZrO_2)

1.4.2. Neutral Refractories: Neutral Refractories are chemically stable to both acids and bases and are used in areas where slag and atmosphere are either acidic or basic. The common examples of these materials are:

1) Carbon graphite (most inert)
2) Chromites (Cr_2O_3)
3) Alumina

Out of these graphite is the least reactive and is extensively used in metallurgical furnaces where the process of oxidation can be controlled.

1.4.3. Basic Refractories: Basic refractories are those which are attacked by acid slags but stable to alkaline slags, dusts and fumes at elevated temperatures. Since they do not react with alkaline slags, these refractories are of considerable importance for furnace linings where the environment is alkaline; for example non-ferrous metallurgical operations. The most important basic raw materials are:

1) Magnesia (MgO) - caustic, sintered and fused magnesia
2) Dolomite (CaO*MgO) - sintered and fused dolomite
3) Chromite -main part of chrome ore

1.5. Classification Based on Method of Manufacture

The refractories can be manufactured in either of the following methods:

1) Dry Press Process
2) Fused Cast
3) Hand Molded
4) Formed (Normal, Fired or chemical bonded)
5) Unformed (Monolithic – Plastics, Ramming mass, Gunning, Cast able, Spraying

1.6. Classification Based on Physical Form

Refractories are classified according to their physical form. These are the shaped and unshaped refractories. The former is commonly known as refractory bricks and the latter as "monolithic" refractories.

1.6.1. Shaped Refractories: Shaped refractories are those which have fixed shaped when delivered to the user. These are what we call bricks. Brick shapes maybe divided into two: standard shapes and special shapes. Standards shapes have dimension that are conformed to by most refractory manufacturers and are generally applicable to kilns and furnaces of the same type. Special shapes are specifically made for particular kilns and furnaces.

1.6.2. Unshaped Refractories: Unshaped refractories are without definite form and are only given shape upon application. It forms joint less lining and are better known as monolithic refractories. These are categorized as Plastic refractories, ramming mixes, castables, gunning mixes, fettling mixes and mortars **[2].**

II. DESCRIPTION OF THE OBJECT AND THE SOLUTION METHOD

The wall of a casting ladle represents a multilayer thermal resistor consisting of:

a) A working refractory lining; whose thickness varies, depending on the stage of operation of the ladle and the properties of its design, from 80 to 400 mm;
b) A buffer fill in the form of a refractory powder (magnesium oxide) layer of thickness from 5 to 20 mm;
c) A reinforcing lining of aluminosilicate composition, usually from normal chamotte brick, the thickness of whose layer is 115 mm for the wall and 130 mm for the bottom;
d) A heat insulator from aluminosilicate fibrous articles of thickness from 10 to 30 mm;
e) A metal jacket of the ladle of thickness from 10 to 40 mm; in the investigated ladle.

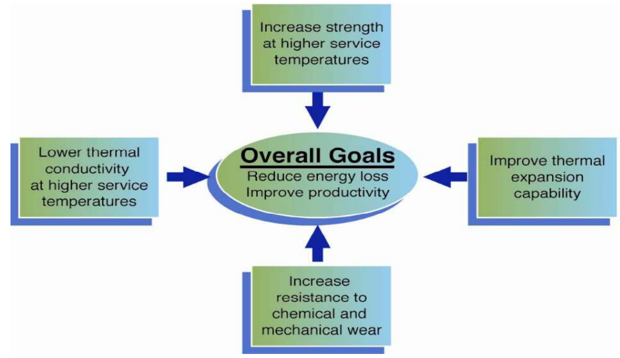

Fig. 2.1. Improving refractory materials for improved energy efficiency

Based on the findings presented, a number of recommendations can be made for the reduction of heat losses. **[3].**

2.1. REFRACTORY SELECTION

In addition to the steelmaking process, it is important to consider the wear mechanisms in a steel ladle, depending upon its location, the physical and chemical properties required for the refractories. For discussion purposes, the ladle will be confined to the working lining; slagline; barrel; and bottom, but with obvious appreciation for the safety lining. The slagline is the region that comes into contact with various slag types and compositions, which can produce aggressive behaviour in terms of chemical corrosion and erosion at the refractory interface. There is also a potential for oxidation, depending upon the refractory type. The main feature of the refractory material should be to offer good slag resistance. The sidewalls undergo thermo-mechanical movement during operation, which can result in the reduction of the structural integrity of the lining. The materials must therefore exhibit optimum physical properties. The bottom tends to suffer from mechanical wear, due to steel impact during metal transfer and the factors associated with it. Ideally, the materials should offer good impact and thermal shock resistance **[4], [11].**

2.2. PARAMETERS AFFECTING REFRACTORY WEAR:

List of the parameters affecting refractory wear in steelmaking is as the following.

1) Chemical corrosion,
2) Hydration,
3) Infiltration of steel and slag,

4) Atmosphere containing too much oxygen,
5) Desulphurization,
6) Mechanical erosion,
7) Mechanical wear, impact,
8) Thermo-mechanical stresses,
9) Thermo-mechanical fatigue,
10) Preheating procedure of refractory,
11) Gas stirring conditions,
12) Arc radiation,
13) Rate of power input to the vessel,
14) Refractory maintenance practice,
15) Operation time,
16) Operation temperature,
17) Refractory design of vessel,
18) Ca Si injection **[5], [7], [9]**.

2.3. BUSINESS ANALYSIS OF TOTAL REFRACTORY COSTS

Refractory materials, design, and maintenance can improve or degrade energy efficiency and melt rate. In addition, the cost of refractory is typically the largest maintenance expense of a melt or hold furnace. Total refractory costs include refractory materials, installation, energy, and downtime. Many attempts have been made by companies to hold down these costs in various ways. The various methods that were compared included: reduction of refractory material costs, reduction of installation costs, reduction of installation time, energy efficient insulation, repair versus total reline, and extension of the life of the refractory **[6].**

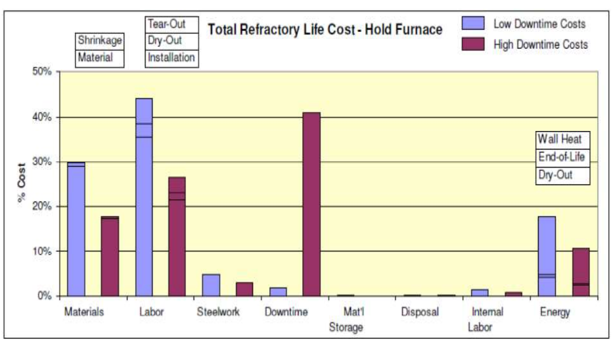

Fig.2.2. Total Refractory Costs – Hold Furnace

2.4. SOME IMPORTANT LADLE REFRACTORIES

2.4.1. Magnesia or Magnesia–Lime Group

This group includes all refractories made from synthetic magnesites and dolomite. These constitute the most important group of refractories for the basic steelmaking processes. All these materials are used primarily as a source of magnesia (MgO).

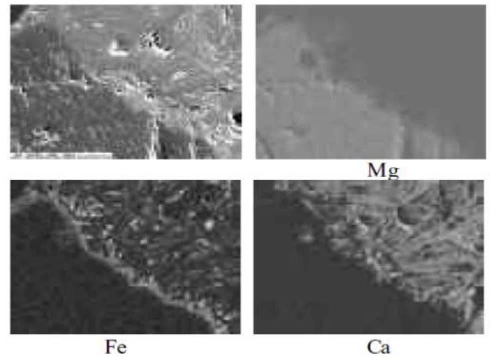

Fig.2.3.MgO grains indirect corrosion **[7]**.

Modern high-purity magnesia is produced in well controlled processes. The principal sources of magnesia are brines (often deep well type) and seawater. Magnesium hydroxide, Mg(OH)2, is precipitated from these sources by reaction with calcined dolomite or limestone. Minimizing the total impurities content in magnesias is quite important because impurities affect refractoriness and performance.

2.4.2. Dolomite

The natural double carbonate dolomite (CaCO3 MgCO3) can be converted to refractory dolomite (CaO+MgO) by high temperature firing. A limited number of dolomite deposits exist in the world with satisfactory uniformity, purity, and calcining behavior to be processed into high purity, refractory dolomite at a reasonable cost. High purity dolomite is greater than 97% CaO + MgO and 0.5–3% impurities. Dolomite has excellent refractoriness and is thermodynamically very stable in contact with steel or steelmaking slags.

2.4.3. Magnesia–Chrome Group

Chrome ores, or chromites, often called chrome enriched spinels, are naturally occurring members of the spinel mineral group. These materials are all characterized by relatively high melting points, good temperature stability. In addition to basic refractory raw materials composed of dead burned magnesia and chrome ore as starting materials, other magnesite chrome combinations are also a part of this series. A magnesite- chrome group of raw materials exists, including co-sintered magnesite-chrome, fused magnesite- chrome and synthetic picrochromite—a combination of magnesite and chromic oxide.

2.4.4. Silicon Carbide

Commercial silicon carbide (SiC) used as a refractory raw material is manufactured by abrasive grain producers in electric furnaces from a mixture of coke and silica sand. The finished material is extremely hard (9.1 MOH's scale) with high thermal conductivity and good strength at elevated temperature as well as very good resistance to thermal shock. The material is serviceable at 1535–1650°C (2800–3000°F) for many applications.

2.4.5. Zircon/Zirconia

Zircon, or zirconium silicate ($ZrO_2 \cdot SiO_2$), is a naturally occurring raw material having excellent refractoriness. Specific gravity (4.5–4.6 g/cm3) is unusually high compared to most refractory materials. Zircon usually is found with other heavy mineral sands, most notably titania minerals. The refractory industry has been a major growth area for zirconia. Zirconia in the natural state occurs in the monoclinic crystal phase.

2.4.6. Clays

Although clays were among the first raw materials used to make refractories, their usage has diminished as demands placed on modern refractories have necessitated better performing materials to replace them. Nevertheless, clays are still an important material in the industry. Clays may be used as binders, plasticizers, or as aggregates for producing refractories.

2.4.7. Bauxitic Kaolins

Several other types of 50–70% alumina raw materials are also used in refractories. Bauxitic kaolins, or bauxite clay combinations, represent another class of natural aluminum silicates used in refractory manufacture.

2.4.8. Sillimanite

Andalusite, sillimanite and kyanite comprise the water-free, natural aluminum silicate varieties of minerals known as the sillimanite group. Andalusite and kyanite are the more common commercial materials. These minerals are normally about 60% alumina, with the balance composed primarily of silica with minor iron and titania impurities.

2.4.9. Bauxite

Bauxite in the crude state is a naturally occurring group of minerals composed primarily of either gibbsite ($Al_2O_3 \cdot 3H_2O$), diaspore, or boehmite [AlO(OH)], and various types of accessory clays. Crude bauxite is converted to the minerals corundum (Al_2O_3) and mullite ($3Al_2O_3 \cdot 2SiO_2$). Important features of bauxites are maximum alumina values (85% or more desired), maximum bulk specific gravity, and minimum impurities such as iron oxide, titania, alkalies (Na_2O,K_2O and Li_2O) and alkaline earths (CaO and MgO).

2.4.10. Processed Alumina Group

Several types of chemically and thermally processed alumina are used in refractories. These include calcined, tabular, and fused alumina all from the Bayer process.

2.4.11. Carbon Group

Modern refractories use various graphite forms in combination with oxides to impart special properties. Graphites are used in refractories in order to reduce the wetting characteristics of the refractory material with respect to slag corrosion and to increase the thermal conductivity which will result in better thermal shock resistance. In oxide-carbon refractories, the carbon content may range anywhere from as low as 4–5% up to as high as 30–35% **[1].**

III. BARRIERS RELATED TO REFRACTORY MATERIALS FOR LADLE FURNACE[4]

Refractories and insulation materials play key roles in the smelting, refining, and melting operations used in the iron and steel industries; it is estimated that 85% of the industries direct energy consumption is in processes affected by refractories. Specific barriers are shown below:

1) Unavailability of advanced refractory materials with improved corrosion/erosion resistance, improved reliability, and reduced maintenance costs.
2) Lack of refractories with resistance to high alkali atmospheres and high levels of stress, which lead to ladle containment issues.
3) Lack of alternate refractory designs which would provide refractory surfaces (using coatings, chemical alteration of refractory surfaces etc.) that are more impervious to wear and corrosive attack.
4) Unavailability of refractory materials with greater thermal compatibility with metallic materials used in ladle.
5) Lack of adequate corrosion resistance for refractories in contact with molten metal, which leads to undesirable equipment lifetimes. This is especially important for refractories used in parts of furnaces, ladles, and tundishes.

6) Unavailability of improved materials for runners (used to flow the molten steel from a BOF or an electric arc furnace to the refining ladles)
7) Lack of utilization of advanced monolithics in ladles due to problems with their explosive tendencies and lack of data on some of the key input properties and parameters for most of the monolithic products that meet the requirement for steel ladle practice .
8) Unavailability of improved impact pads at the bottom of ladles, which experience high wear, thermal shock, and abrasion.
9) Unavailability of thin-walled alumina refractory ladle shrouds that are used to reduce oxygen pick-up during pouring .

IV. CONCLUSIONS

In this work different types of refractory materials are studied for ladle furnace, the above discussed literature results the following conclusion for steel-making ladle:

1) Use advance methods for suppressing the hydration of magnesites.
2) Develop refractory linings combination with improved life and reduced maintenance requirements, to reduce the maintenance shutdowns generally necessary to repair refractory problems. Reducing the frequency of or eliminating these shutdowns would provide significant cost reduction.
3) Manufacture advanced materials (such as refractories with coatings or externally applied coatings) for resisting corrosion/erosion damage.
4) Use of new materials along with improved materials databases for members of the industry to adapt to new materials in their operations.
5) Develop improved refractories for use in various parts of furnaces, heat processing equipment, ladles, and tundishes.
6) Develop improvements in runners, water-cooled pipes and stirrers, which all experience corrosion, wear, and thermal issues that can limit their life and require weekly repair.
7) Research improvements in materials and installation methods for ladle bottoms and impact pads by using ceramic coatings or alternate localized materials.
8) Improve long-lived, economically feasible, prefired refractory crucible linings for induction melting of stainless steel in air-melt operations.
9) Develop improved ceramic/refractory materials for net shape steel casting, eliminating rolling mill operations.

REFERENCES

[1] Steel Plant Refractories, D.H. Hubble, Chief Refractory Engineer, U.S. Steel Corp. (Retired)

[2] Bhatia PDH Course M158, Overview of Refractory Materials. 2011

[3] Heat losses from ladles during teemingby R. C. Urquhart*, M.Eng. (McGilI), Ph.D. (Visitor) R. I. L. Guthriet, B.Sc. (Eng.) (London), A.R.S.M., Ph.D., D.I.C. (Visitor), and D. D. Howatt, B.Sc. (Glas.), Ph.D. (Fellow)

[4] Refractories for Industrial Processing: Opportunities for Improved Energy Efficiency ,James G. Hemrick,* H.Wayne Hayden,Peter Angelini,* Robert E. Moore, and William L. Headrick*Oak Ridge National LaboratoryMetals Manufacture, Process, and Controls Technology, Inc. R. E. Moore and Associates January 2005

[5] Journal of Engineering Physics and Thermophysics, Vol. 84, No. 2, March, 2011 Modeling Of The temperature field of the casting ladle lining,V. Zabolotsky UDC 536.248.1/519.688

[6] Business analysis of total refractory costs,Cynthia K. Belt1 1Fayetteville, AR 72701, USA

[7] Analysis of the wear mechanism of mgo-c slag line bricks for steel ladles Silvia Camelli*, Instituto Argentino de Siderurgia, San Nicolas, Argentina Marcelo Labadie, Siderar, San Nicolas, Argentina

[8] V.M. Fokin, G. P. Boikov, and Yu. V. Vidin, Principles of Applied Thermal Physics [in Russian], Mashinostroenie-1, Moscow (2004).

[9] H. Uong, Basic Formulas and Heat Transfer Data for Engineers [in Russian], Atomizdat, Moscow (1979).

[10]Heat Conservation in Liquid Iron,Dr. E. G. Hoel, C. M. Ecob and D. S. White; Elkem Foundry Products Reviewed 2005-07-10

[11]Dashrath Singh Kathait, Virendra Singh Rana, Arun Negi, Economic Optimization of Ladle Furnace RefractoryLining; Proceedings of 20th IRF International Conference, 1st March 2015, Chennai, India.