

# Reduce, Reuse and Recycling Technology for Refractories in Cement Industries

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**ABSTRACT:** The environmental problems caused by refractories have become an increasingly important issue in recent years. The disposal of spent refractory materials has become a major problem for metals producers. The main issue of refractory disposal is elimination of the hazardous components of refractories, most commonly bauxite, copper, magnesite and chrome-bearing materials in cement industries. The various approaches to pollution prevention involve re-design to eliminate or significant reduction in wastes, recycling or reuse of the materials, and the least valuable approach, abatement. The objectives of this research are to recycle and reuse of used refractory material optimized by porosity, service temperature for low duty process to save the rebuild costs, energy, resources and global environment. Samples from different types of refractory linings were characterized to determine and predict possible metal penetration. Crushing and grinding were used to liberate brass through the formation of strips which could be separated from the crushed refractory by screening. A refractory mix was developed to recycle the remaining crushed refractory size fractions by mixing with virgin refractory materials for manufacturing low duty refractory castables for furnace backup and refractory mortar. An assessment study of spent refractory materials on application is studied.

## 1. INTRODUCTION

In our modern, industrialized society responsibility for active environmental protection is already one of the most important aspects. Not surprisingly environmental awareness has grown immensely in refractory production as it has elsewhere to tough official regulations governing waste disposal provide the legislative background to this increased environmental sensitivity. The solid waste generated from the many production industries will have threading like ground water table contamination by leachate. Hence, the convention methods like secure land filling is questionable with the above criticism. So the technology required to recycle the hazardous materials from the waste. Recycling has become a major buzz word because we are all being made aware of global warming and climate change. The pyrometallurgical industry can greatly contribute to conserving the environment by increasing the recycling of reclaimed refractory bricks generated by its operations.

Increasing the use of recycled refractory materials in their respective monolithic mixes not only helped manufacturers lower their product prices but also helped the industry to shift their focus to recycled alternatives to reduce their respective input and waste disposal costs.

A refractory material is one that retains its strength at high temperatures. ASTM C71 defines refractories as "non-metallic materials having those chemical and physical properties that make them applicable for structures, or as components of systems, that are exposed to environments above 1,000 °F (811 K; 538 °C)". Refractory materials are used in linings for furnaces, kilns, incinerators and reactors. They are also used to make crucibles and moulds for casting glass and metals and for surfacing flame deflector systems for rocket launch structures.

A suitable selection of the refractory lining material for a furnace can only be made with an accurate knowledge of the chemical and physical properties of the refractories and refractory materials, and of the stresses of the materials during service. There are four types of stresses which refractories face during their period of service. These are given below: 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<sub>2</sub>O<sub>3</sub>)
- 3) Alumina

# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 6, June 2016

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

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) Magnesite (MgO) - caustic, sintered and fused magnesite
- 2) Dolomite (CaO\*MgO) - sintered and fused dolomite
- 3) Chromite - main part of chrome ore

Chemical characteristics of the furnace process usually determine the type of refractory required. Theoretically, acid refractories should not be used in contact with basic slags, gases and fumes whereas basic refractories can be best used in alkaline environment. Actually, for various reasons, these rules are often violated.

Table 1.1 Types of refractories based on temperature.

S.No	Type of Refractories	Refractoriness (°C)	Examples
1	Low Heat Duty Refractories	1520 - 1630	Silica Bricks
2	Intermediate Heat Duty Refractories	1630 - 1670	Alumina Bricks
3	High Heat Duty Refractories	1670 - 1730	Chromite Bricks
4	Super Heat Duty Refractories	>1730	Magnesite Bricks

A thermal insulator is a poor conductor of heat and has a low thermal conductivity. Insulation is used in buildings and in manufacturing processes to prevent heat loss or heat gain. Although its primary purpose is an economic one, it also provides more accurate control of process temperatures and protection of personnel. It prevents condensation on cold surfaces and the resulting corrosion. Such materials are porous, containing large number of dormant air cells. Thermal insulation delivers the following benefits:

- Reduces over-all energy consumption
- Offers better process control by maintaining process temperature.
- Prevents corrosion by keeping the exposed surface of a refrigerated system above dew point
- Provides fire protection to equipment
- Absorbs vibration

## II. MATERIALS AND METHODS

Refractory area in cement cooler process is taken in study. We use different kinds of refractory based on process. We have taken following refractory materials from manufacturer and spent refractories from plant to do a research process.

- 72% Al<sub>2</sub>O<sub>3</sub> bauxite based castable
- 80% Al<sub>2</sub>O<sub>3</sub> mullite based castable
- 53% Al<sub>2</sub>O<sub>3</sub> mullite based castable
- 72% Al<sub>2</sub>O<sub>3</sub> bauxite based used refractories
- 80% Al<sub>2</sub>O<sub>3</sub> mullite based used refractories
- 53% Al<sub>2</sub>O<sub>3</sub> mullite based used refractories

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 6, June 2016

Typical datasheets of a high strength castable and gunning material for the cement industry based on Aluminum oxide

Table. 3.1 Chemical composition and properties of different linings

Chemical Analysis (%)	Cooler 1 <sup>st</sup> Grate	Cooler 2 <sup>nd</sup> Grate	Cooler 3 <sup>rd</sup> Grate
Al <sub>2</sub> O <sub>3</sub>	72	80	53
SiO <sub>2</sub>	23	15	41
Fe <sub>2</sub> O <sub>3</sub>	1.5	1.6	1.5
<b>Physical Properties</b>			
Raw material	Bauxite	Mullite (type 1)	Mullite (type 2)
Max service limit (°C)	1700	1450	1300
Material requirement (kg/m <sup>3</sup> )	2600	2200	2100
Water addition (l/100kg)	5.0 – 6.0	4.5 – 5.5	6.0 – 7.0
Bulk density 110°C (g/cm <sup>3</sup> )	2.7	2.6	2.3
Crushing strength 110°C (kg/cm <sup>2</sup> )	800	800	700
Health and safety	Hazardous to health	Hazardous to health	Hazardous to health
Method of Application	Vibration Casting	Vibration Casting	Vibration Casting

Listed below is a selection of the tests and the industry-specific testing suites available to understand the quality of refractories.

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 6, June 2016

### PHYSICAL ANALYSIS:

- Density and porosity
- Pyrometric Cone Equivalent (PCE)
- Particle Size Determination (PSD)
- Cold crushing strength
- Modulus of rupture

### CHEMICAL ANALYSIS:

- XRF (X-Ray Fluorescence)
- XRD (X-Ray Diffraction).

### THERMOMECHANICAL ANALYSIS:

- Thermal conductivity
- Crushing and Grinding
- Refractoriness under Load (RUL)
- Permanent Linear Change (PLC).

### MICROSTRUCTURAL EVALUATION

- SEM/EDA

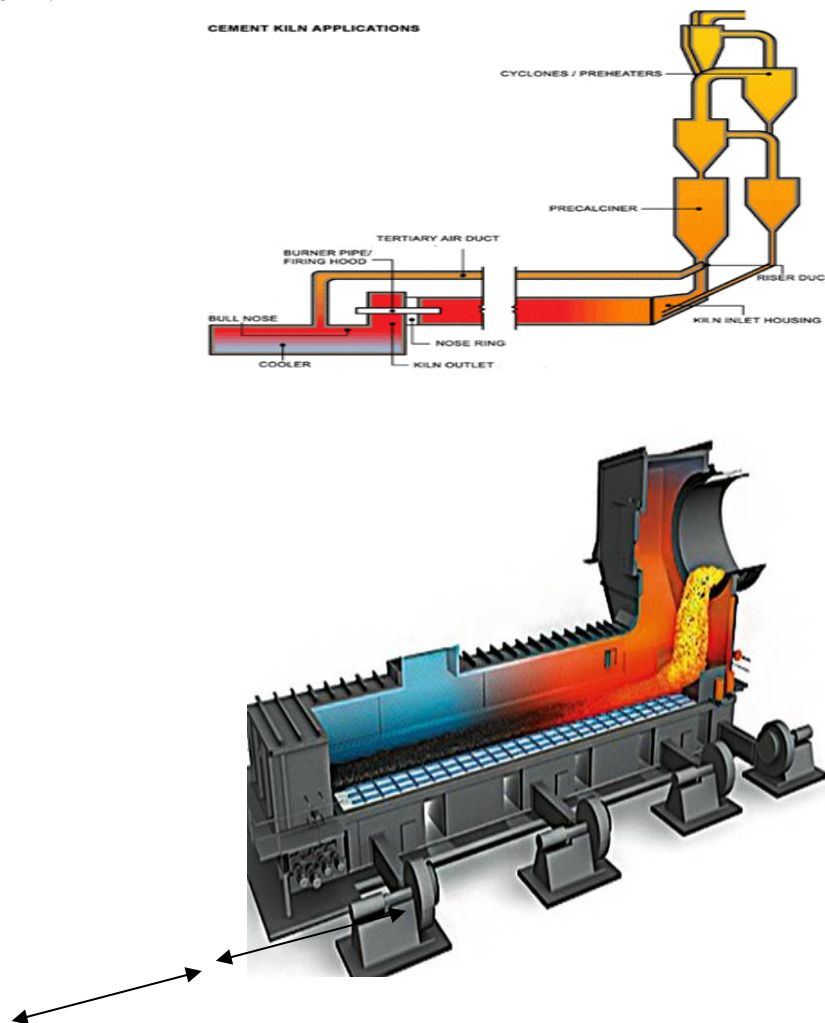


Figure 3.1 Grate Cooler in Cement Industry

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 6, June 2016

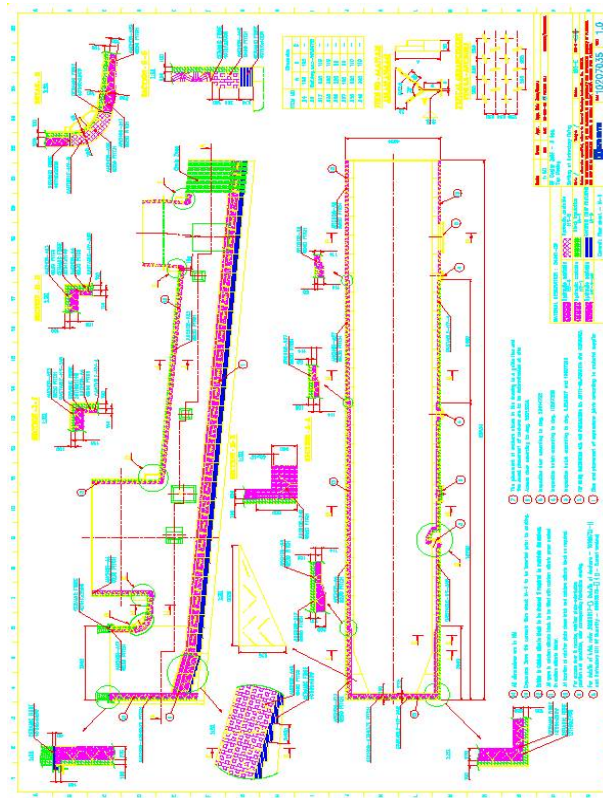


Figure 3.2 Refractory Blueprint for Grate Cooler

The existing old castable blocks are to break off and removed from its surface. Breaking the existing castable with brook machine would reduce the time consumption. Practically hacking castable with jack hammer or breaker would consume a lot of time. Hacked castable would be cleared from the surface and working platform and stored in dump yard for safety precaution.

For a given cooler, several different types of refractory are used at different parts of grate. The old refractories that were hacked from the cooler are a mixture of different types of refractory. Therefore, simply collecting and using them directly as a recycled refractory is undesirable from the standpoint of refractory quality control. For this reason, when old refractories are torn down, they are sorted and categorized in MGO refractory,  $Al_2O_3$  refractory, carbon-containing refractory and carbon-free refractory, etc through color codes of spent refractory.

Cooler 2<sup>nd</sup> grate is highly abrasive area in cement manufacturing process. Lot of analysis should be taken care in choosing of refractories. Clinker enters the cooler at a temperature of around  $1,200^\circ C$ , rapidly spreading its heat into the grate and surrounding refractories. High refractoriness, high abrasion resistance and resistance to thermal shock are necessary, especially at the clinker downfall and bull nose. The cooler walls directly above the grate are also subject to extreme wear. The partition wall, designed to limit the inflow of cool air to the kiln system, must withstand the abrasive effect of clinker dust entering the tertiary air duct as well as the temperature fluctuations resulting from its exposed position. Top quality material selection plays an important role in order to restrict the frequent failures. With the current advances and changing technology, a lot of new demands are imposed on the refractories. Refractory consists of mixtures of coarse and fine refractory grains together with a bonding agent which is normally based on high alumina cement. Installation of the refractory plays an important role in quality and lifetime campaign. This type of castable is relatively cheap and its raw materials are widespread. The refractoriness of high alumina refractories increases with increase in alumina percentage.

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 6, June 2016

By reviewing the manufacturing process and design of site, we preferred to chose mullite based castable for hot face at Cooler 2<sup>nd</sup> Grate.

As per design fig 3.3, the insulation lining is required to be done with Calcium silicate blocks of 100mm with complete area. While the calcium silicate block has large number of pores to avoid the contact of heat and lower the temperature to equipment shell and density of calcium silicate is comparatively lower than high alumina refractories. The crushed spent refractories of approx. 10 to 20mm is now taken and mixed with the use of mixer machine. Water can be added slowly till to get a good mix. Spent high alumina refractory will not be affected in its quality by adding excess water since an insulation requires more porosity. The mixed castable must be packed in fabricated form board fitted at cooler 2<sup>nd</sup> grate. Refractory lining must be packed closely without any gap. It requires to be compressed and tightened with plywood for few hours and left undisturbed. Remove the plywood and keep 5mm ceramic fiber blanket for higher service temperature CERAWOOL 1200°C between hot and cold face lining for expansion purpose. It resists thermal shock and thermal expansion during uneven temperature load. During preheating process, hot face lining tends to expand will be managed by ceramic fiber blanket.

After placing ceramic fiber blanket, hot face required to be lining with high alumina refractory as discussed above. Clean the mixer machine without any dust and set the speed of blades to 37 – 40 rpm for efficient mixing. Add prescribed water as suggested by manufacturer to achieve porosity. Water addition is very important in mixing of castable for quality concern. Dry mix of castable for 2 mins and add appropriate water in regular intervals of time and complete the mix before 6 mins. Now the area is tolined with fresh castable then closed and compressed with plywood and left undisturbed for 24 hours. Around 8 to 10% of old refractories is separated and reused now in second campaign.

Same as like in cooler 2<sup>nd</sup> grate application procedure we need to follow in cooler 3<sup>rd</sup> grate also. According to the process and temperature conditions in 3<sup>rd</sup> grate, low cement alumina castable will be feasible for better lifetime. As per design fig 3.3, the insulation lining is required to be done with Calcium silicate blocks of 100mm at cold face area. The crushed spent refractories of approx. 10 to 20mm is now taken and mixed with the use of mixer machine. Water can be added slowly till to get a good mix. Spent high alumina refractory will not be affected in its quality by adding excess water since an insulation requires more porosity. The mixed castable must be 80mm is now taken and packed in fabricated form board fitted at cooler 3<sup>rd</sup> grate. Refractory lining must be packed closely without any gap. It requires to be compressed and tightened with plywood for few hours and left undisturbed. Remove the plywood and keep 5mm ceramic fiber blanket for higher service temperature CERAWOOL 1200°C between hot and cold face lining for expansion purpose. After placing ceramic fiber blanket, hot face required to be lining with alumina castable. Dry mix of castable for 2 mins and add appropriate water in regular intervals of time and complete the mix before 6 mins. Now the area is tolined with fresh castable then closed and compressed with plywood and left undisturbed for 24 hours.

Comminution processes result in a continuous particle size distribution and hence can be used to process new castables. The fine particles fill up the voids between large size particles. A discrete particle size distribution cannot attain maximum density as the volume of the voids to be filled cannot be completely filled by cement and silica fume (typically -90 microns). The void area or porosity of the castable would increase as a function of the decreasing ratio between the largest diameter particles (DL) and the smallest diameter particles (DS). Highly dense castables are prepared by 'fill out' which essentially implies that certain fillers/modifiers are used to obtain dense packing of particles. Many mathematical models have been developed and three major distribution principles for the particle size distribution of the aggregates are proposed which are

- Andreason distribution (equation 1.1)
- Furnas distribution (equation 1.2)
- Funk-Dinger model (equation 1.3)

for crowded particulate suspensions. All the three principles define particle size distribution in terms of largest particle diameter against cumulative percent finer than (CPFT).

# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 6, June 2016

$$\frac{CFPT}{100\%} = \left( \frac{D}{D_L} \right)^n \quad (1.1)$$

$$\frac{CFPT}{100\%} = \frac{(D)^n - (D_S)^n}{(D_L)^n - (D_S)^n} \quad (1.2)$$

$$\frac{CFPT}{100\%} = \frac{(D)^{\log r} - (D_S)^{\log r}}{(D_L)^{\log r} - (D_S)^{\log r}} \quad (1.3)$$

Where

D - diameter of the particle

DL - diameter of largest particle

DS - diameter of smallest particle

n - distribution modulus

The Funk-Dinger model is a modified Furnas equation, where the distribution modulus  $n = \log r$ ;  $r$  is defined as the ratio between two consecutive sieve opening sizes and is most widely used for a sequence of comminution and sieve analysis operations. The Andreasen distribution does not define the smallest particle diameter and maximum density is attained by adding smaller particles which fill the void area. However, the Furnas distribution introduces the smallest particle size diameter and calculates the maximum allowable porosity for a defined DS/DL ratio. As the DS/DL ratio decreases, the particle size distribution becomes wider thereby filling all possible voids and achieving maximum density attainable by particulate materials. The distribution modulus ( $n$ ) was found to be 0.37 for maximum packing, allowing blend suppliers to calculate particle size distribution for specified porosity levels. This is particularly useful in recycling of spent refractory linings, as the crushed lining is subjected to particle size analysis and the particle size distribution is calculated to process a new castable blend incorporating all of the crushed particles. The rheological factors determining the flow properties of the castable do not conform to the calculated mathematical factors and more often a factor of 0.21 is used in industries. Since the porosity levels increase with this packing factor, industrial particle size distribution generally follows bimodal or multi-modal distributions wherein micron and submicron size additives are added to fill out the pores in the castable, improving the overall performance of the castables.

### III. CURING AND FIRING

The blend or mix of aggregates, binders and admixtures can be either chemically set or hydraulically set. The type of bonding agents used in castables have been increasing and many new types have been developed including non-cement bonds such as hydratable alumina, clay, silica and alumina gels, and chemical bonds such as phosphates and alkali silicates with each binder attributing special properties depending on the application. The present study uses calcium aluminate cement as the binding agent for a proper blend of spent lining and fresh virgin lining aggregate. The binding mechanism of calcium aluminate has been investigated and reported. The principal hydrating phase is calcium monoaluminate-  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  or CA. CA upon addition of water changes to  $\text{C}_3\text{AH}_6$  which is the stable hydratable phase with curing temperatures above 350 C. However, lower temperatures are not favorable as CA would form metastable hydrates which upon further heating would convert back to stable  $\text{C}_3\text{AH}_6$ , but the conversion is accompanied by phase volume shrinkage leading to a weak bond. Dehydration takes place during the curing stage and generally in the temperature range of 210-315o C. The curing time is generally long as the smaller size fractions which are used to attain maximum density delay the dehydration process. Finally, after curing the castables are fired to gain significant strength and wear resistance. The firing temperature is selected as the temperature at which the refractory has maximum modulus of rupture.

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 6, June 2016

The crushed lining material of type II refractory obtained after crushing and screening to remove metal was used for processing of new castables. The particle size distribution of the blend influences the properties and performance of castables. A small crucible mold was designed for castable preparation (Figure 3.5). The top plunger of the mold was designed to moderately ram the castable mix for achieving better densification.

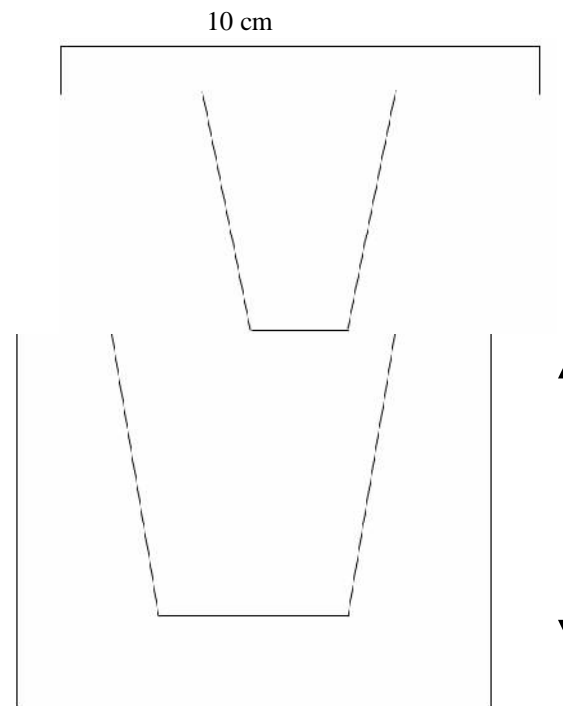


Figure 3.5. Crucible mold design for processing castables from virgin and crushed spent lining.

Virgin refractory castable mix of type I was obtained from industry for a base line comparison with crush refractory lining of type I. The material datasheet for the virgin castable mix is already discussed.

Initial trials were done to understand the particle size distribution of the virgin refractory mix and determine the optimum particle size distribution based on the theoretical model. Sieve analysis of the virgin mix indicated that the castable aggregate distribution was a multi-modal distribution. The initial trial used the virgin refractory mix with 5-6% water and the castable was found to be porous as shown in Figure 3.6. Porosity was due to the fact that the diameter of largest particle was greater than one-third of the wall thickness. Normalization is the process of screening the undesired large diameter particles and extrapolating the remained particle size distribution such that the distribution modal is not disturbed. After the first trial, the refractory mix was normalized such that the maximum particle diameter was restricted to 2.3mm and with the normalized particle size distribution (Figure 3.7), a new castable was prepared (Figure 3.6. b).



# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 6, June 2016



Figure 3.6. a) Porous castable prepared from virgin castable mix b) dense castable prepared from normalized castable mix of type I refractory.

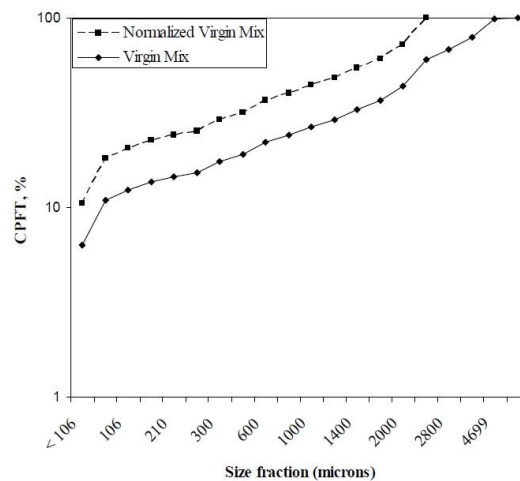


Figure 3.7. Particle size distribution for virgin mix and normalized virgin mix plotted with cumulative percent finer than (CPFT) against size fraction in mm.

To compare the performance of castables prepared from crushed spent lining with the virgin lining material, three different blend compositions were analyzed along with virgin refractory for testing their performance. The different blend compositions tested were listed in Table 3.2. The particle size distribution of the castables followed the normalized virgin mix distribution. The silica fume was added to the crushed lining to achieve increased density. The percentage of silica to be added was selected to keep the total silica content of the entire lining to be in the same chemical composition range as prescribed by the refractory material supplier. Secar 51 grade cement was also selected to keep the total alumina content consistent with the prescribed chemical composition of the refractory supplier.

Table 3.2. Blend compositions for different castables.

Castable	wt.% Virgin	wt.% Spent Lining	wt.% Cement	wt.% Silica
Virgin Raw Materials	100	0	0	0
Bauxite Type I	90	9	0.5	0.5
Bauxite Type II	50	45	2.5	2.5
Bauxite Type III	0	90	5	5

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 6, June 2016

The experimental procedure was set up for testing the processed castables as described below:

- Determine the particle size distribution of the virgin material.
- Screen the large diameter particles such that the largest particle diameter was 2.3mm and normalize the particle size distribution.
- Add calcium aluminate Secar 51 grade cement (5% maximum) as the binding agent.
- Add silica (-90 microns) as described in Table 3.1 to adjust the percentage of fine size fraction and also maintain the chemical composition.
- Cure at 210°C for 12 hours.
- Fire at 1200°C for 6 hours and cool to room temperature.
- Test at 1200°C for 48 hours by adding a mixture of 75% copper and 25% carbon to fill 75% of volume of the crucible (carbon to avoid oxidation of copper).

Figure 4.1. Macro photographs of all four castables

Mixing of virgin castables and blended with spent refractory materials are allowed to cast in mold. Blend compositions of different castables are taken for testing in three different methods Figure 4.1 illustrates the castables before firing, After firing at 1200°C and after testing for 48 hours at 1200°C.

The castable crucibles were fired at 1200°C and then filled with 75% copper and 25% carbon powder to test the ability of each blend to prevent copper penetration and survive for 48 hours at 1200°C. The firing cycle was designed based on the ASTM C 401 standard for regular castables. The macro photographs of the castables 3 and 4 (Figure 4.1) after firing at 1200°C for 6 hours have significant surface growth because of scab formation. The scabs are formed due to the oxidation of copper present in the brass particles of crushed spent lining. However, there was no scab formation in castable Type I which has 9% of the crushed spent lining indicating the possibility of using the castable Type I for low duty applications. The macro photographs of the four castable crucibles after testing for 48 hours (Figure 4.1) have no noticeable change with regard to copper oxidation in the lining, indicating that the entire copper present in the crushed lining was completely oxidized during the firing stage. However, there is noticeable discoloration in castables Type II and III indicating the possibility of copper penetration.

Cross-sectional samples were taken from the bottom of the castable crucibles (Figure 4.2) and analyzed using stereoscope for possible metal penetration (Figure 4.3)



Figure 4.2. Macro photograph of castable Type III indicating the location of all cross-section samples.

The cross-section images from hot face to the cold face. Copper penetration could not be observed from the stereoscope images for the four castables. Hence, the cross-section samples were analyzed for the hot face using optical microscopy to analyse the copper penetration exactly inside the castable.

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 6, June 2016

The walls of the crucibles have also been analyzed along with the cross-sectional samples. The cross-section of the wall of the crucibles did not yield significant results with respect to the metal penetration and hence the cross-section samples were analyzed for metal penetration.

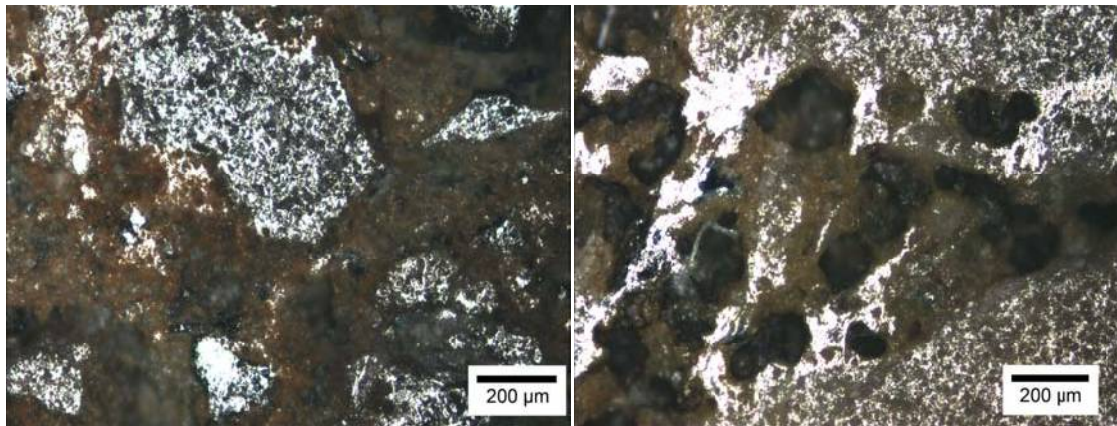


Figure 4.4. Optical micrographs of hot face of four types of castables showing no metal penetration after 48 hours of testing

No metal penetration was found for castable Type 1 and Type 2. The macro-photos also showed no copper oxidation after firing for castable 2 (90% virgin-10% crushed lining). Therefore, the mix Type 2 can be used as a back up layer in the melting furnaces. However, copper penetration of ~11% of the cross-section thickness for castable Type 3 and ~13% for castable Type 4 was observed. Hence, for further studies, the crushed lining can be pre-fired to oxidize the copper or can be chemically leached to remove the copper, and then use the spent lining for preparing castables.

An industrial scale up model was developed to summarize the economic costs and benefits of refractory recycling and provide a method for achieving optimum benefits. The present section discusses the method of developing the economic model to design and scale up the process to industrial operations using METSIM version 15.12 software.

The METSIM software provides models to analyze different comminution techniques, the power draw for each process, and gives comprehensive data on the particle size distribution obtained from each operation. The software has to be backed by preliminary data to design a comminution flow chart. The Bond Work Index ( $W_i$ ) and dimensions of the process equipment are important parameters for designing the flowchart. Bond defined work index as a comminution parameter used to calculate the energy consumed or expended in grinding the feedstock to 80% passing of specified product particle size. The Bond Work Index test is used to evaluate the grindability of feedstock based on the Bond's third theory of comminution given in equation 4.1

$$W = \frac{10W_i}{\sqrt{P}} - \frac{10W_i}{\sqrt{F}} \quad 4.1$$

Where W - work input in kWh/short ton,  
 $W_i$  - work index calculated by Bond Work Index test  
P - 80% passing product particle size and

# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 6, June 2016

F - 80% passing feed particle size

The test is a measure of the grindability of the feedstock. A short description of the standard test procedure

- Crush dry feed to 100% passing 3.3mm mesh.
- Calculate packed density and 700ml constant feed for ball mill bond work index test.
- Sample using splitting techniques to obtain a representative feed from the crushed lining.
- Sieve analysis of the feed to understand the particle size distribution and calculate 80% passing feed particle size.
- Run the mill for 50 revolutions and re-circulate the over-size feed to the mill thereby maintaining constant volume of 700ml.
- Repeat the test process until steady state is attained for at least the last two periods. Steady state is obtained for 250% recirculating load.
- Calculate the net product produced per mill revolution of grindability of product (Gpr).
- Sieve product and 80% passing product particle size is calculated.

The work index is calculated using Bond's formula for Work Index given in equation 4.2

$$W_i = \frac{44.5}{P_1^{0.23} G_{bp}^{0.82} \left[ \frac{10}{P^{0.5}} - \frac{10}{F^{0.5}} \right]}$$

4.2

Where P<sub>1</sub> – micron size at which grindability test was conducted,  
G<sub>bp</sub> – Grindability value,  
P -80% passing product size in microns and  
F- 80% passing feed size in microns

- Lab Mill Feed = 1.709 g/cm<sup>3</sup> equivalent to 1196.3g (700cc) in mill.
- Ideal Potential Product = 341.8 g.
- Average of last 2 periods = 247% circulating load.
- Grindability at 106 microns = 0.745 net grams per revolution.

The test reached steady state in fifth, sixth and seven periods. The graph between the net grams per revolution against number of period was plotted as shown in Figure 4.5.

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 6, June 2016

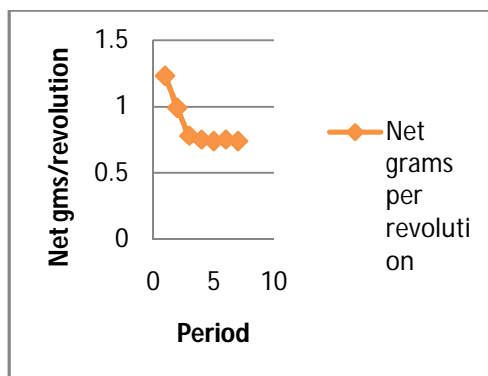


Figure 4.5. The net grams per revolution plotted against period number showing steady state for fifth, sixth and seventh period.

The results for the Bond work index are tabulated in Table 4.1. The feed, product and circulating load size distribution were illustrated in Figure 4.6. The bond work index  $W_i$  was calculated from equation 4.2 and was found to be 21.2 kWh/st.

Table 4.1. The BWI test results for crushed lining

Period	Revolutions of Mill	Grams of Product	Grams in Feed	Net grams Produced	Net grams Per revolution
1	70	164.4	78.2	86.20	1.23
2	269	278.0	11.0	267.0	0.99
3	327	275.2	18.3	256.9	0.78
4	410	323.0	18.0	305.0	0.75
5	432	343.9	21.4	322.5	0.74
6	427	345.7	22.5	323.2	0.75

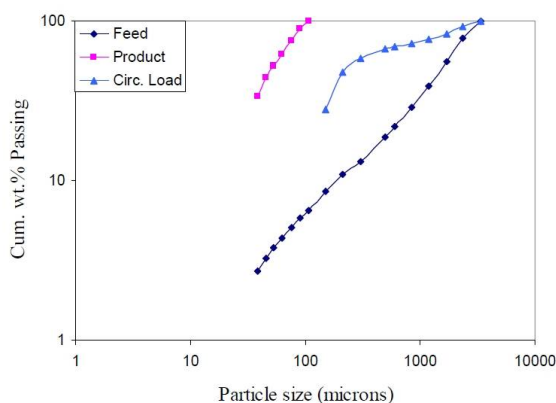


Figure 4.6. The particle size distribution of feed, circulating load and product

# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 6, June 2016

The particle size distribution determines the amount of power drawn by the ball mill. An increase in the 80% passing product decreases the power draw of the process as it requires less grinding action.

## METSIM Design.

METSIM software was used to evaluate the power draw for the comminution operation and optimize the design for using various crushing and grinding equipment. The software calculates particle size distribution for the type of crushing and grinding equipment based on the input parameters such as open side setting, closed side setting and throw of crushing equipment and mill diameter, critical mill speed for ball mill equipment.

## METSIM PROCESS DESIGN

The comminution operations are energy intensive and therefore the energy requirements might inhibit recycling benefits. The energy expended for liberation of copper from the spent lining was considered as a crucial parameter. The other important economic parameters are the cost of liberated copper and the cost to landfill. The cost of landfill for specific refractory type is constant; however, the cost of copper is variable thereby the economics of the recycling process can be evaluated depending on energy consumption and copper scrap cost for the present model. To relate energy consumption to cost benefits, the Bond work index was used to design the energy requirements for crushing and grinding of the large refractory pieces to smaller fractions. The METSIM model was an attempt to optimize the energy consumption for maximum copper yield from lining material with minimal energy and to also obtain particle size distribution which can be used to prepare and process new refractory castables. The preliminary model was used to compare the energy expended to crush the feed into the required product 80% passing size and also a particle size analysis for the two primary crushers - jaw crusher and cone crusher. Preliminary studies were done by modeling flow charts using a jaw crusher (CRJ) and roll crusher (CRR) and ball mill (MLB) and screen (SCK) in sequence. The “cone crusher and ball mill” model was designed similar to the Figure 4.7 except for the replacement of jaw crusher and roll crusher with a cone crusher. The mass flow rate for all the models was taken as 10 metric ton/ hr. The sequence of operations is connected with lines which are called streams.

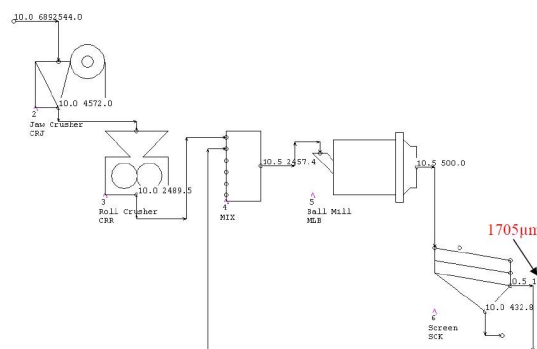


Figure 4.7 METSIM grinding circuit (Jaw crusher model) for calculation of comminution energy for refractory lining showing mass flow rate and P80 for respective streams

In Figure 4.7, there are numbers along the exit of each stream. The numbers represent the mass flow rate 10 tons/hr and P80 of the mass passing through the stream. The oversize material after screening has higher P80 (1705  $\mu\text{m}$ ) because the coarse particles from the ball mill and roll mill are screened and constitute much lower percentage of the entire material. The jaw crusher model has input parameters of 160mm open side setting and 155mm throw. The dry grinding factor for the circuit was taken as 1.3 as defined by the METSIM software and energy expended to crush the feed was calculated for 106  $\mu\text{m}$ , 250  $\mu\text{m}$ , 500  $\mu\text{m}$ , 750  $\mu\text{m}$  and 1000  $\mu\text{m}$  product 80% passing particle sizes. The

# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 6, June 2016

parameters for ball mill are driven by industrial specifications. The details of crusher and ball mill and the model results were tabulated in Table 4.2.

NA – Not Available

To compare the power draw and particle size distribution between a jaw crusher and cone crusher, a similar model was created for a cone crusher. The power draws for screening and mechanical separation were minimal with respect to the power draw of the comminution operation and hence were neglected for energy calculations.

A third model was developed with a double stage jaw crusher excluding the ball mill and roll crusher. The flow chart for the double stage jaw crusher model is illustrated in Figure 4.8.

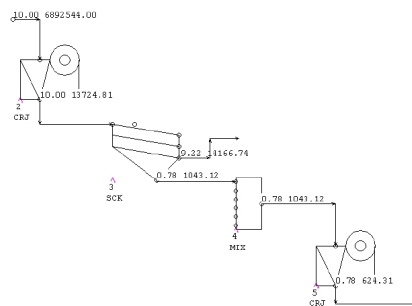


Figure 4.8. Process flow chart developed in METSIM for double stage jaw crusher

The double stage jaw crusher (CRJ) would eliminate the use of ball mill. Since, the ball mill is energy intensive as found from Table 4.2; the double stage jaw crusher would result in significant economic benefits. A double stage jaw crushing operation with screens (SCK) in between the two crushing operations would allow control over the particle size distribution.

The particle size distribution from a double stage (DS) jaw crusher model was compared to the theoretical particle size distribution are illustrated in Figure 4.10. Theoretical particle size distribution and the particle size distribution obtained through METSIM models are different in comparison with the industrial distribution and therefore, fines are incorporated to fit the industrial particle size distribution.

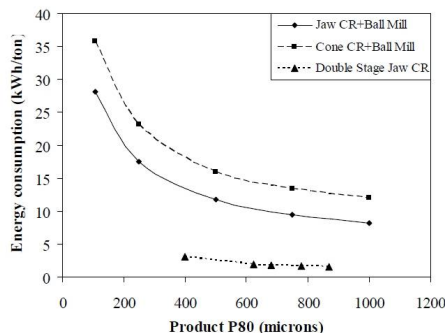


Figure 4.9 Comparison of three models based on the energy expended to crush to a specified product 80% passing

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 6, June 2016

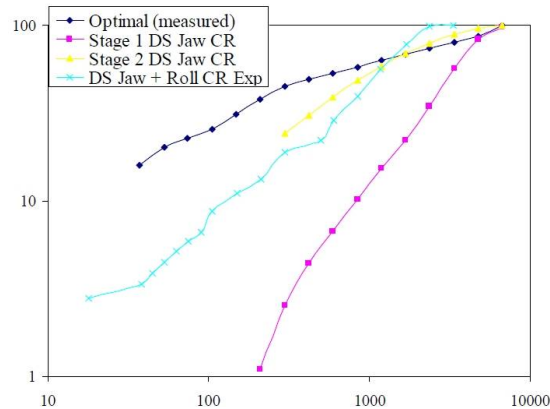


Figure 4.10 Particle size distributions obtained from double stage (DS) jaw crusher model compared with optimal distribution

In the Figure 4.10, the percentage of fines generated in a double stage jaw crusher as per the METSIM model was found to be much higher than the other models developed. The ‘DS Jaw + Roll CR Exp’ was the particle size distribution obtained experimentally which does not comply with the theoretically developed model. Therefore, fines have to be added to the product obtained by crushing and grinding to build a multi-modal distribution suitable for preparing new castables. The industrial multi-modal distribution is quite complex and cannot match fit with the simple theoretical models developed. Hence, based on the industrial design, fines have to be incorporated to achieve good castable properties.

However, a double stage jaw crusher utilizes lower energy than other comminution operations. Hence, it is recommended that double stage jaw crusher liberates the entrapped metal and the crushed lining that is obtained can be added to a fine distribution mix to prepare new castables.

The total cost benefits to recycle all the materials from the spent refractory lining were evaluated. The economics of the model results were evaluated using a cost analysis function. The constants used in the value analysis were the

Cost of brass scrap	-	130/kg (25 % of value of copper)
Cost of landfill	-	1200/mt
Cost of cement	-	45/kg
Cost of fresh refractory mix	-	75/kg
Cost of electricity	-	9/kWh.

The net value was calculated assuming that 3% of secondary brass can be liberated from the spent refractory lining. The costs involved for the entire recycling program are estimated as defined by the net value cost analysis function.

$$\begin{aligned} \text{Net value, INR/ton} = & + (\text{Cost of landfill per metric ton, INR/ton}) \\ & + (\text{Metal recovered, mt/hr}) * (\text{Scrap price, /mt}) \\ & - (\text{Energy consumed, kW/hr}) * (\text{Electricity cost, /kWh}) \\ & - (\text{cost of raw materials, /ton}) = \text{INR12550 / ton} \end{aligned}$$



# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 6, June 2016

The cost benefits of recovering all materials from spent refractory linings are tabulated in Table 4.3. The cost benefits of recovering all materials are beneficial than landfill. The difference can be attributed to the higher prices of raw materials which adds value to recovery of refractory materials from spent linings.

Table 4.3. Cost savings for different recycling alternatives

Parameter	Economic Benefits (INR/ ton)
Landfill all materials	-1200
Recovery of refractory materials	+12550

## IV. CONCLUSION

This Project work involves the reduce and reuse of spent refractories as secondary refractory lining and additives for manufacture of new castables are studied. The conclusions are

- The performance of spent refractory materials at Cooler 2<sup>nd</sup> and 3<sup>rd</sup> grate is to be assessed since 11 months of two years service life has been comparable to virgin refractory materials. Sub-material performance issues associated with the spent refractory applications have been noted and sample is yet to be collected and tested for root cause analysis.
- The assessment studies showed that the reuse of refractory wastes around 12 to 15% of total consumption for a particular period.
- As a part of our activities to achieve zero waste, the use of waste refractories as an insulating materials and results of use as roadbed material and landfilling has been significantly reduced, which poses major environmental problems.
- It is cleared that three types of refractory lining samples have been macro characterized and micro-characterized for preliminary understanding of the spent lining samples. Based on the results, copper was physically wetting the lining as there was no reaction at the interface between copper and the refractory matrix.
- The brass strips were separated after crushing operation by screening. These separated strips rich in copper (~90%) can be directly remelted. Two stage crushing and grinding operation liberates 65% to 90% of copper in lining samples. Variation of metallic content in lining samples can be attributed to the alloy chemistry. Alloying elements that have higher wetting angles with alumina create cracks in the refractory lining facilitating increased metal penetration.
- The crushed lining was blended with the virgin refractory mix obtained from refractory industry and new refractory castables have been processed. The 50% virgin – 50% crushed lining blend can be used as refractory mortar mix, while the 90% virgin – 10% crushed lining blend can be used for back up lining in furnaces and for lining low duty application furnaces.
- A value-based model was developed to understand the economics of recovering refractory materials. The economic benefit of recovering refractory materials and the value of new castables processed from the spent lining is studied.

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 6, June 2016

This Project work involves the reduce and reuse of spent refractories as secondary refractory lining and concludes

- Assessment has to be done periodically for cooler 2<sup>nd</sup> and 3<sup>rd</sup> grate insulation lining and analyse the root cause for failures.
- Sorting the Type I and II samples which constitute ~13% of the total annual percentage of refractory landfilled, would effectively recover ~70% of the total metallic content entrapped in all of the spent refractory linings. Samples from type III refractory can also be sorted based on visual inspection. The sorting procedure with visual inspection can effectively recover ~90% of the entrapped metal.
- To find out optimum grain size, porosity and service temperature to spent refractories used for recycling process.
- Based on the METSIM models, a cone crusher with adjustable open side setting or jaw crusher with roll crusher are to be studied in detail for economical capital investment. Crushing the spent furnace linings to crushed product with intermediate screening steps can maximize metallic yield.
- In recycled refractories by optimum parameters is to be analysed by Scanning Electron Microscopy (SEM), Refractoriness under load (RUL), Cold crushing strength (CCS).

### REFERENCES

- [1]. J. P. Bennett, K.S. Kwong, "Refractory recycling-Concept to reality," Environmental Issues and Waste Management Technologies VII, Ceramic Transactions, Vol. 132, pp 3-15, 2002.
- [2]. J. D. Smith, K. D. Peaslee, A. S. Barnes and H. Fang, "An economic, logistic, and technological approach to refractory recycling," Proceedings of UNITECR'97, pp-17-25, 1997.
- [3]. J. P. Bennett, K. S. Kwong, "Spent refractory recycling/resuse efforts in the steel and aluminum industries," Fourth International symposium, Recycling of metals and engineered materials, TMS, pp 1353-1367, 2000.
- [4]. R.T. Oxnard, "History and trends in refractory recycling: an integral part of waste minimization," 52nd Electric Furnace Conference, proceedings, pp 397-400, 1994.
- [5]. M. D. Crites, "Chrome-free refractories for copper production," thesis-UMR, pp 12-26, 1999.
- [6]. M. D. Crites, M. Karakus, M. E. Schlesinger, M. Somerville and S. Sun, "Interaction of chrome-free refractories with copper smelting and converting slags," Canadian Metallurgical Quarterly, Vol. 39, pp 129-134, 2000.
- [7]. K. S. Kwong and J. P. Bennett, "Recycling practices of spent MgO-C refractories," Journal of Minerals & Materials Characterization & Engineering, Vol. 1, pp 69-78, 2002.
- [8]. A.G.M. Othman, W.M.N Nour, "Recycling of spent magnesite and ZAS bricks for the production of new basic refractories," Ceramics International, Vol. 31, pp 1053-1059, 2005.
- [9]. C.A. R. Gonzalez, W.F. Caley, and R.A.L. Drew, "Copper matte penetration resistance of basic refractories," Metallurgical and Materials Transactions B, Vol. 38B, pp 167-174, 2007.
- [10]. K.S. Kwong, J.P. Bennett, and K.W. Collins, "The recycling of a 70% Al<sub>2</sub>O<sub>3</sub> spent refractory," proceedings of UNITECR, refractories, pp 487-496, 1997.
- [11]. K.S. Kwong, J.P. Bennett, A.E. Wayne, III, "The recycling of spent refractories from a secondary brass producer," Ceramics Transactions, Vol. 87, pp 135-146, 1998. 70
- [12]. Society for Mining, Metallurgy and Exploration, Inc. (SME), "Copper leaching, solvent extraction, and electrowinning technology," Ed. Gerald V. Jergensen pp 89-93, 1999.
- [13]. J. Hur, S. Yim, and M. Schlautman, "Copper leaching from brake wear debris in standard extraction solutions," Journal of Environ. Monit., Vol. 5, pp 837-843, 2003.
- [14]. Mecucci and K. Scott, "Leaching and electrochemical recovery of copper, lead and tin from scrap printed circuit boards," J. Chem. Technol Biotechnol, Vol 77, pp 449-457, 2002.
- [15]. F.R. Valenzuela, J.P. Andrade, J. Sapag, C. Tapia and C. Basualto, "The solvent extraction separation of molybdenum and copper from acid leach residual solution of Chilean molybdenite concentrate," Minerals Engineering, Vol. 8, pp 893-904, 1995.
- [16]. L.J. Bear and J. F. Moresby, "Recovery of copper from refractory furnace-lining bricks by segregation roasting," Proc. Australas Inst. Min. Metall., No. 266, pp 21-27, 1976.
- [17]. W. Hui, G. G. Hua, Q. Y. Feng, "Crushing performance and resource characteristic of printed circuit board scrap," J. Cent. South Univ. Technol., Vol. 12, pp 552-555, 2005.
- [18]. G. C. Lowrison, "Crushing and Grinding: The Size reduction of solid materials," CRC Press, Inc., pp 17-30, 1994.
- [19]. M.G. Nicholas, T.M. Valentine, M.J. Waite, "The wetting of alumina by copper alloyed with titanium and other elements," Journal of Materials Science, Vol. 15, pp 2197-2206, 1980.



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- [20]. C.C. Lin, R. B. Chen, R. K. Shiue, "A wettability study of Cu/Sn/Ti active braze alloys on alumina," Journal of Materials Science, Vol. 36, pp 2145-2150, 2001.
- [21]. Meier, V.Gabriel, PR. Chidambaram, and G.R. Edwards, "Wetting and spreading of manganese and copper-manganese alloys on alumina surfaces," Processing and Fabrication of Advanced Materials III, Ed. V.A. Ravi, T.S. Srinivasan and J.J. Moore, The Minerals, Metals & Materials Society, pp 47-58, 1994.
- [22]. P. D. F.C Bond, "Crushing & Grinding Calculations Part II," British Chemical Engineering, Vol. 6, pp. 543-548, 1961.
- [23]. M. Dekker, Inc., "Refractories Handbook," Ed. Charles A. Schacht, pp259-334, 2004. 71