

**ASIA-PACIFIC MEETING OF GLASS AND ALLIED INDUSTRIES
&
ICG STEERING COMMITTEE MEETING -2013
KOLKATA**



**GLASS FRITS FOR GLAZED CERAMIC TILES
AND OTHER APPLICATIONS**

**SUDIPTA SAHA
H&R JOHNSON (INDIA)**

H & R JOHNSON IS ALWAYS IN THE PICTURE.



Glossed vitrified floor tiles



Engineered & laminated wooden flooring



Sanitaryware, Taps & Accessories



Custom made designer modular kitchens



Marbonite Stonefree



Engineered marble & quartz



Wall tiles with stone textures and effects



Specialized tiles for various applications



Digitally printed ceramic wall and floor tiles

JOHNSON

Marbonite
Freedom over fabric. Marble, stonefree

ENDURA
Complete Natural Tiling Solutions



H & R JOHNSON
We are everywhere.

CustomerCare: 022-30647484 Toll Free No.: 1800-22-7484 (toll-free 24x7)
E-mail: customercare@hrjohnsonindia.com Website: www.hrjindia.com

- Established in 1958, H & R Johnson (India) is the market leader in the field of ceramic tiles in India
- Only company in India to offer end-to-end solutions of Tiles, Sanitary-ware, Bath Fittings and Kitchens
- HRJ's sales volume for the year 2012-13 is 42.47 million m² of tiles

H & R Johnson (India) has a vast portfolio of Strong brands comprising **Johnson, Marbonite, Marbonite GVT , Endura & Johnson Ceramics International, Johnson Cristal**

JOHNSON
TILE | BATH | KITCHEN offers glazed floor and wall tiles, laminate and engineered wood floorings, kitchen, sanitary ware, bathroom accessories and bath fittings

The offering of **JOHNSON Marbonite** Preferred over Italian Marble, worldwide | **JOHNSON Marbonite** Preferred over Italian Marble, worldwide |  include a complete range of vitrified glazed and unglazed tiles

JOHNSON CRISTAL
ENGINEERED MARBLE & QUARTZ offers engineered marble and quartz inspired by the beauty of natural marble

 **ENDURA**
Industrial Products & Natural Resources brand offers industrial & specialised tiles, and industrial products & natural raw materials

Awards & Recognitions...

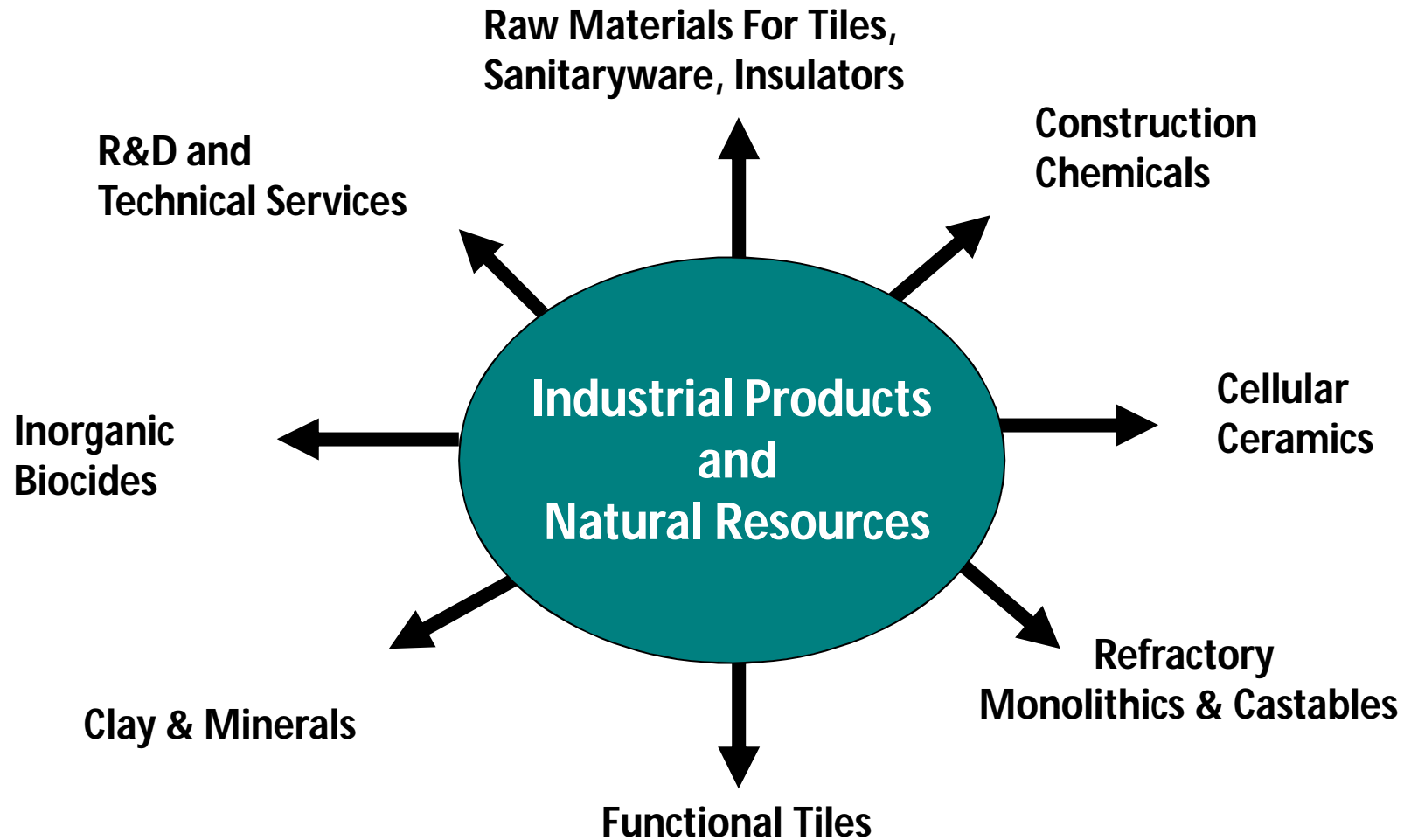
- **Ranked as 6th largest tile company in the world (CERAMIC WORLD REVIEW – 2012)**
- **Only tile company having its R&D Centre recognised by DSIR, Ministry of Science & Technology, Govt. of India**
- **POWER BRAND status (2010 & 2011)**
- **READER'S DIGEST MOST TRUSTED BRAND AWARD – 2008, 2010, 2011, 2012**
- **Industry's First Carbon Points CERs – 2009**
- **CERTIFICATE OF MERIT FOR ENERGY CONSERVATION – Bureau of Energy Efficiency, Ministry of Power – 2006**
- **Best Tile Company M-TECH PINNACLE AWARD – 2006**
- **Gas Conservation Award GAIL – 2004-05**

Industrial Products & Natural Resources AND R&D Centre

-An Idea Born Out of Innovation

Knowledge – The Key Driver

- As IPNR is based on innovative quality products, knowledge is the key driver in this initiative
- A number of young scientists / researchers are working under guidance of senior reputed scientists to maintain our technological edge
- This division is also associated with various R&D institutions with specific expertise



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- Our R & D department is recognised by **Department of Scientific & Industrial Research (DSIR), Govt. of India** for its innovative work in research & development.
 - Our manufacturing and R&D are **ISO 9001-2008, EMS ISO14001, OHAS 18001** certified.

Patents

- **Total No. of Patents – 2 patents granted and 4 in process**
- **Publications in Journal of Indian Ceramic Society**

CERAMIC TILES

- Manufacture of ceramic tiles started around 700 BC, and has evolved over the years.
- Today wall, floor and vitrified tiles are manufactured using modern single firing technology.
- Digital printing technology has opened up a wide possibility of designs and textures which were only a dream earlier.



GLAZING

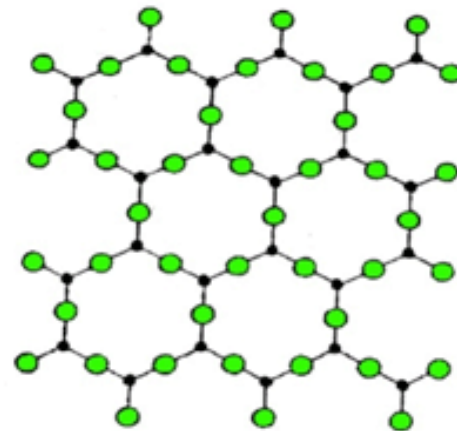
- Glazing is the application of one or more layers of glaze with a total thickness between 250 and 800 microns, covering the surface of the ceramic tile.
- Glazing makes tiles cleanable, glossy, coloured, textured and chemically and mechanically resistant.
- Aesthetics of tiles depends on its fault – free glaze.
- **The key ingredient of glaze are frits.**



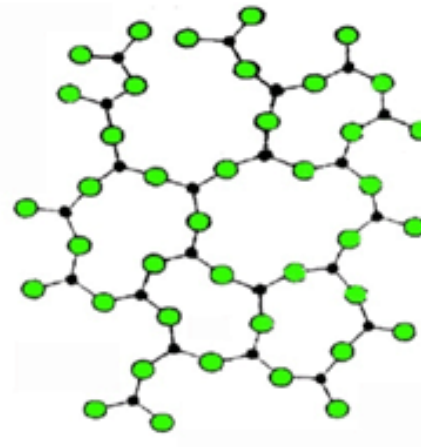
FRITS

- Frits are glassy in nature, obtained by fusing different crystalline materials at high temperatures of 1450 – 1550 °C.
- Fritting is the process of melting to convert soluble fluxes to insoluble oxides.
- A batch composed of natural raw materials and chemicals mixed and melt at high temperatures, and quenched in water to produce a crumbled and brittle glass.
- The process is triggered by low melting compounds and subsequently accelerated by them to melting and dissolve the more refractory materials to make the exact requirement of different categories of tiles.
- Fritting ensures better chemical stability, and ensures that no raw material remains water-soluble.

- Frit is an inorganic product of melting that has been cooled to a solid state without crystallization.
- Solidification to the amorphous state is effected by rapid raising of the viscosity of the melt during cooling.
- When the viscosity is high enough, elements are forced to assume an irregular three-dimensional network.
- The rapid quenching in water freezes the structure of molten batch



Crystalline silica

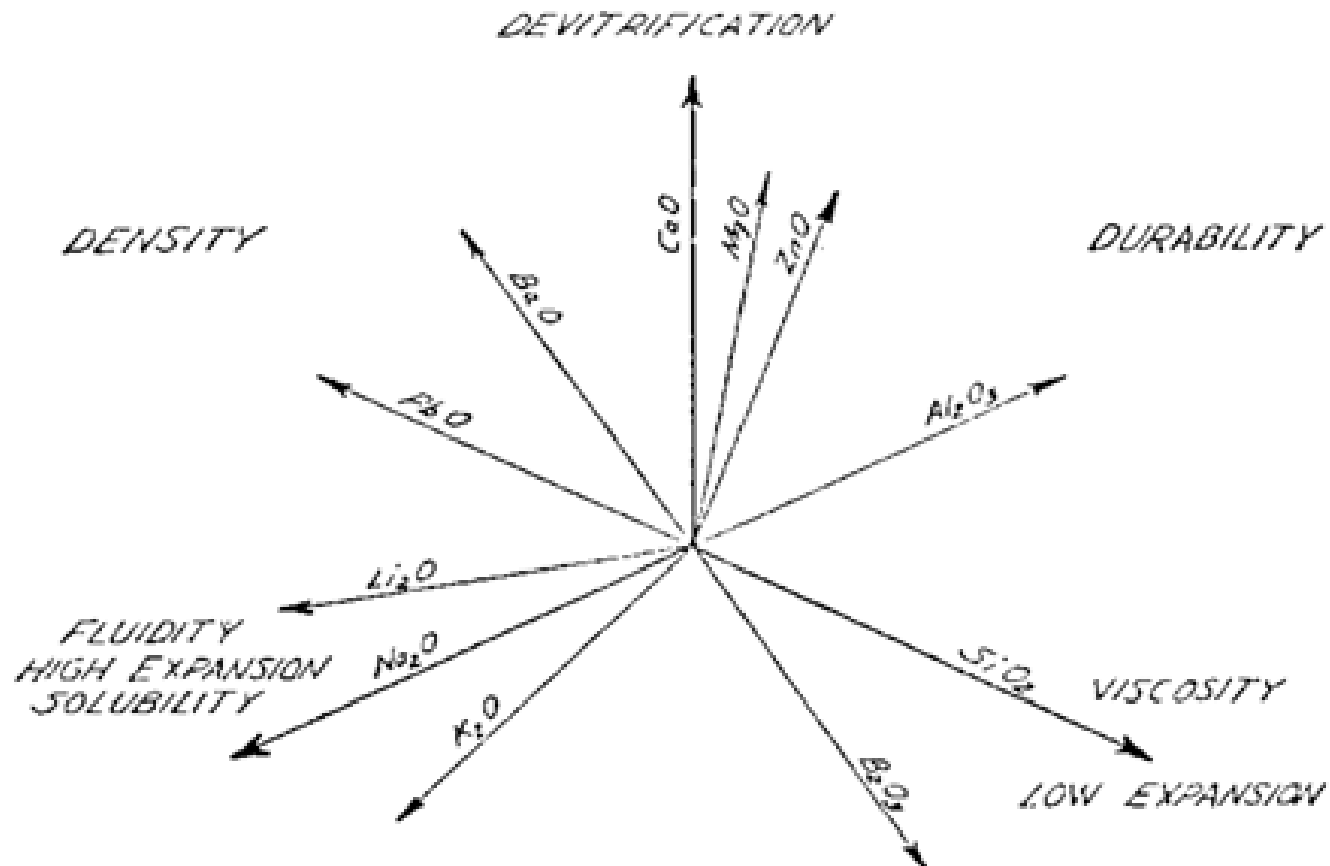


Vitreous silica

Classification of frit ingredients

Vitrifying agents	SiO ₂	B ₂ O ₃			
Fluxes	Na ₂ O	K ₂ O	B ₂ O ₃	Li ₂ O	
Stabilizers	CaO	BaO	MgO	Al ₂ O ₃	ZnO
Opacifiers	ZrO ₂	SnO ₂	TiO ₂		
Devitrificants	ZnO	CaO	BaO	MgO	TiO ₂

Functions of various oxides



Electro-negativity of elements in frits

GROUP 1		GROUP 2		GROUP 3	
Silicon	1.9	Zirconium	1.4	Potassium	0.8
Boron	2.0	Aluminium	1.6	Sodium	0.9
		Titanium	1.6	Barium	0.9
				Calcium	1.0
				Magnesium	1.3

Group 1: having higher electro-negativity. Their oxides form glasses when melted alone.

Group 2: Their oxides do not form glass when melted alone, but they will when melted with elements of Group 1.

Group 3: elements never able to form a glassy structure.

Main criteria for frits are:

- Insoluble in water, so as to ensure homogeneity, viscosity and surface tension during wet grinding.
- Thermal expansion slightly lower than ceramic tile body. Greater the difference in thermal expansion between ceramic tile and glaze, the faster defects will appear.
- A glassy layer under compressive stress makes the tile more resistant to mechanical strain.
- Adequate softening points to ensure release of CO₂ from tile body
- Tile surface must be fault-free (pin-hole, face-hole, crawling, cracks, rippling)

Frits used in ceramic tile industry can be broadly classified based on:

Tile firing temperature

- Single fired Wall tile : 1120 – 1130 °C
- Single fired Floor tile : 1140 – 1155 °C
- Single fired Porcelain tile : 1175 – 1225 °C

Texture

- Transparent
- Opaque
- Matt
- Satin-Matt

Transparent Frits

- Retains glassy nature through the entire firing cycle to ensure good transparency.
- Suitable for better colour tonality especially in dark coloured designs.
- These frits are free from crystallising agents like zircon etc.

Opaque Frits

- Opacity occurs through the partial solubility of zircon in the silicate melt and its crystallisation while cooling.
- The resulting zircon crystals have a significantly higher index of refraction than the glassy matrix and thus effectively scatter light.

Matt Frits

- Matt glazes are produced by forming 'micro crystalline' surfaces that scatter light
- High CaO or ZnO glazes form minute calcium or zinc silicates crystals respectively when cooling
- Mattness depends on shape and dimensions of the crystals formed.

Satin-Matt Frits

- These are matt glazes with a smooth and pleasant feel.
- These contain multiple melt phases that solidify in a non-homogeneous way
- MgO creates multiple phases in the melt that have different fluidity and refractive indexes.

OUR FRIT PLANT

- Our frit plant has 2 continuous smelters with a total capacity of 15000 MT/annum.
- We produce about 40 different types of frits based on market demand.



Batching and melting

- Batching is a fully automatic process. Each raw-material is extracted from its silo and weighed by a hopper, where all components are added.
- The batch is transferred to a mixer for homogeneity of mix.
- The batch is transferred to the tank furnace by a piston according to a fixed speed. This speed regulates the melting or staying time of the frit in tank furnace.
- Pressure and temperature in the tank furnace are controlled.
- Frit is discharged from the exit hole and falls into cold water.

[Our Frit Plant](#)

FUNCTIONAL GLAZE

- **Antimicrobial**
- **Antistatic**
- **Photoluminescent**
- **Metallic**
- **Lustre**

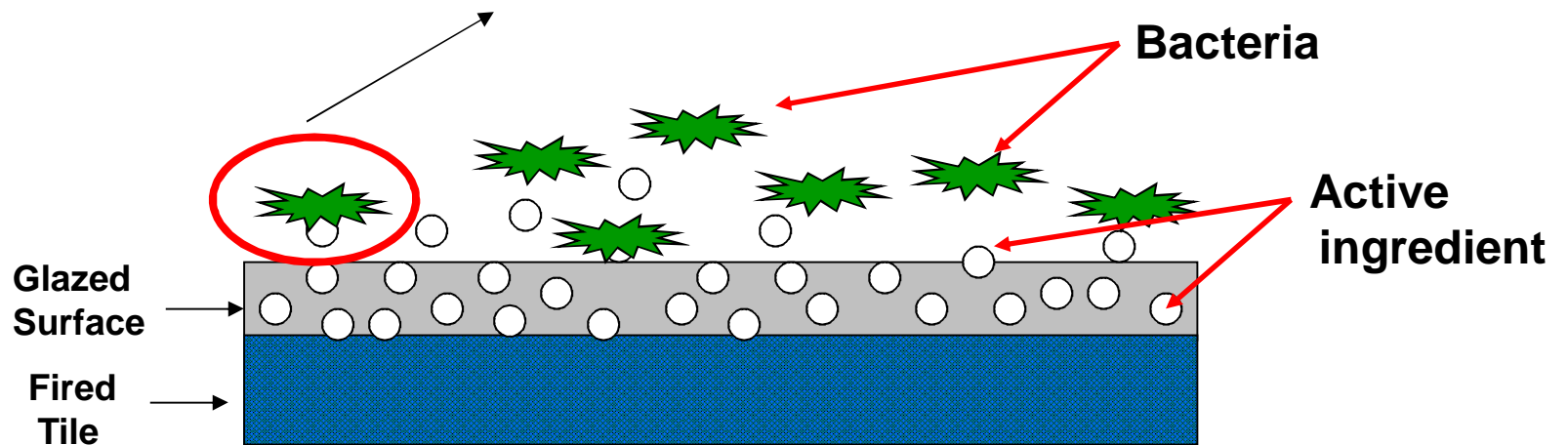
Antimicrobial Glaze

- Antibacterial glaze is prepared by doping antimicrobial Nanocomposite powder developed by our R&D team.
- Based on silver nano-technology, this compound when incorporated in glaze destroys and inhibits the growth of deadly bacteria, fungi, molds etc.
- Johnson Tiles is the only Company manufacturing Anti-microbial **GERMFREE** glazed ceramic tiles in India.
- Tested using international test protocol and certified to exhibit microbial reduction > 99%.

Mechanism

On activation with humidity/moisture these active ingredient get released in a measured rate and punctures the cell wall of bacteria.

Interactions of bacteria and active ingredient (< 40nm)
punctures cell wall –kills bacteria

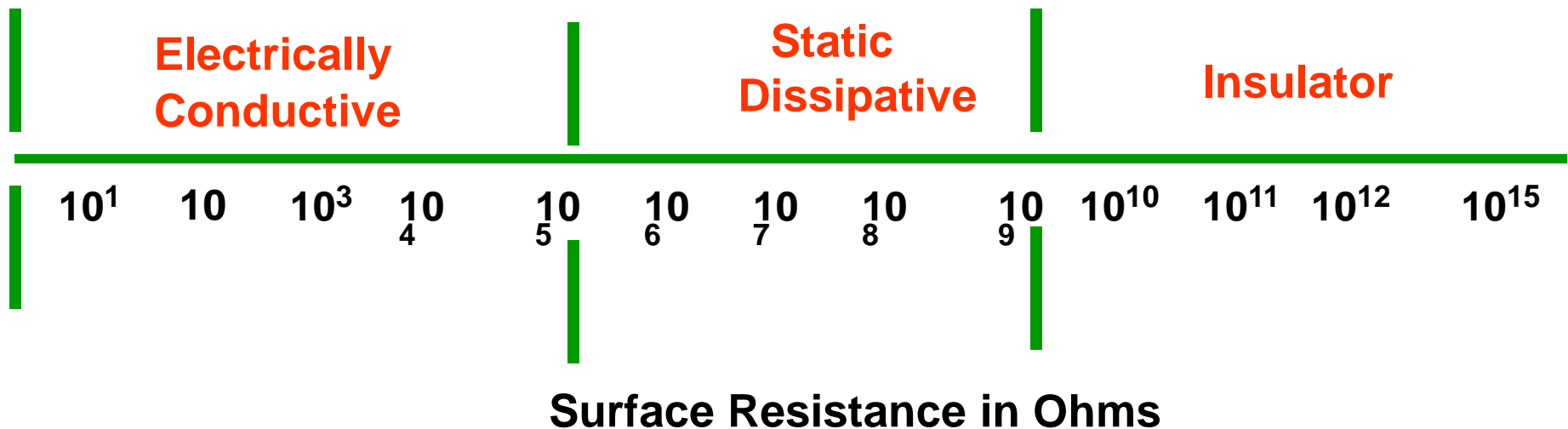
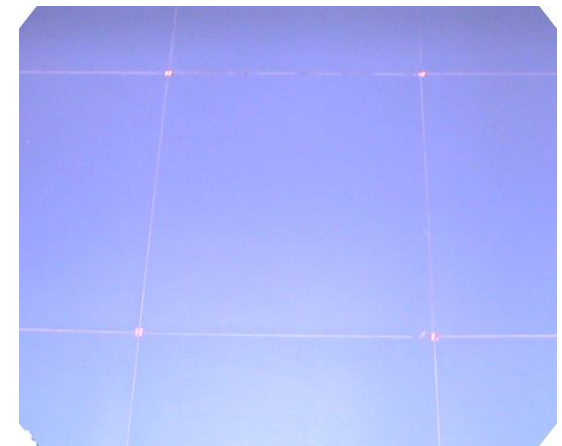


Schematic Diagram of the Tile Surface

Antistatic Glaze



- Electrostatic charges can threaten personal safety or the proper functioning of delicate electronic instruments
- Generally Ceramic Flooring Materials are insulators and do not dissipate the static electricity
- HRJ developed tile with conductive & dissipative glaze.



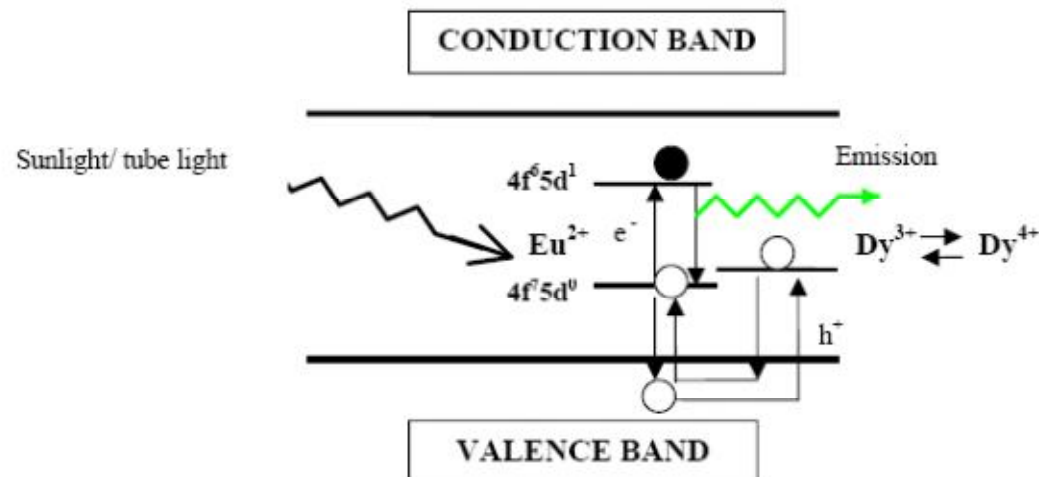
Photoluminescent Glaze

- There is a need for a 'self glow' light source in emergency situations, as in many cases, all power sources can fail
- The lower limit of light perception of the dark adapted human eye is 0.0032 mcd/ m²
- The standard accepted by the escape route markings industry is 0.32 mcd/ m²
- Photo luminescent Exit Path Markings has been Included in the International Building Code 2009



Mechanism

- On exposure to sunlight / tubelight (~ 450nm), the electron in the Eu^{2+} ($4f^7 5d^0$) orbital is excited to Eu^{2+} ($4f^6 5d^1$) releasing a hole (h^+) in the process.
- The released hole migrates through the valence band & is 'trapped' by a Dy^{3+} ion that act as 'hole traps'.
- In the absence of light, the hole is re-excited & liberated to the valence band, which further migrates to Eu^{2+} in the excited state and is captured.
- This recombination gives rise to release of energy i.e. phosphorescence, a bluish green emission (~500nm)



Metallic & Lustre Glaze

- Traditionally, metallic effects were achieved by the application of noble metals (gold, silver, platinum) on a fired tile, followed by low-temperature firing. This process involves very high costs.
- Specially designed frits/glazes produce metallic effect even in single fast-firing process.
- The metallic effect is due to the crystallisation of specific phase, which is formed on the surface of the glaze with a preferred orientation.



Mechanism of metallic glaze

- The metallic effect is due to the crystallisation of an iron phosphate phase, which is formed on the surface of the glaze with a preferred orientation.

Mechanism of lustre

- A reflective lustre effect is due to the crystallisation of a very thin crystalline layer of ceria (CeO_2) at the surface of the glaze. In this case, ceria crystallisation occurs at about 900°C during the heating cycle and no relevant transformation occurs during the cooling step.

FRITS FOR OTHER APPLICATIONS

- **Anti-oxidation coating for carbon based refractories**
- **Nuclear waste containment**
- **Bonding**
- **Insulators**
- **Grinding wheels**

ANTI-OXIDANT COATING

- A fundamental problem of any refractory shape which contains carbon is oxidation.
- Loss of carbon through oxidation limits the service life of the refractory.
- A special frit has been developed to prepare a `Coating Mass' to be applied to carbon based refractories to prevent oxidation.



NUCLEAR WASTE CONTAINMENT FRIT

- Nuclear waste is extremely radioactive and remains in this state for thousands of years. Safe and stable storage of this type of waste is of great concern.
- Modern storage methods include the use of glass vitrification, wherein highly radioactive waste can be stored indefinitely in deep stable formations such as caves and caverns.
- CGCRI, Kolkata has successfully developed a special grade of glass frits /beads approved by NRB, DAE (Mumbai).

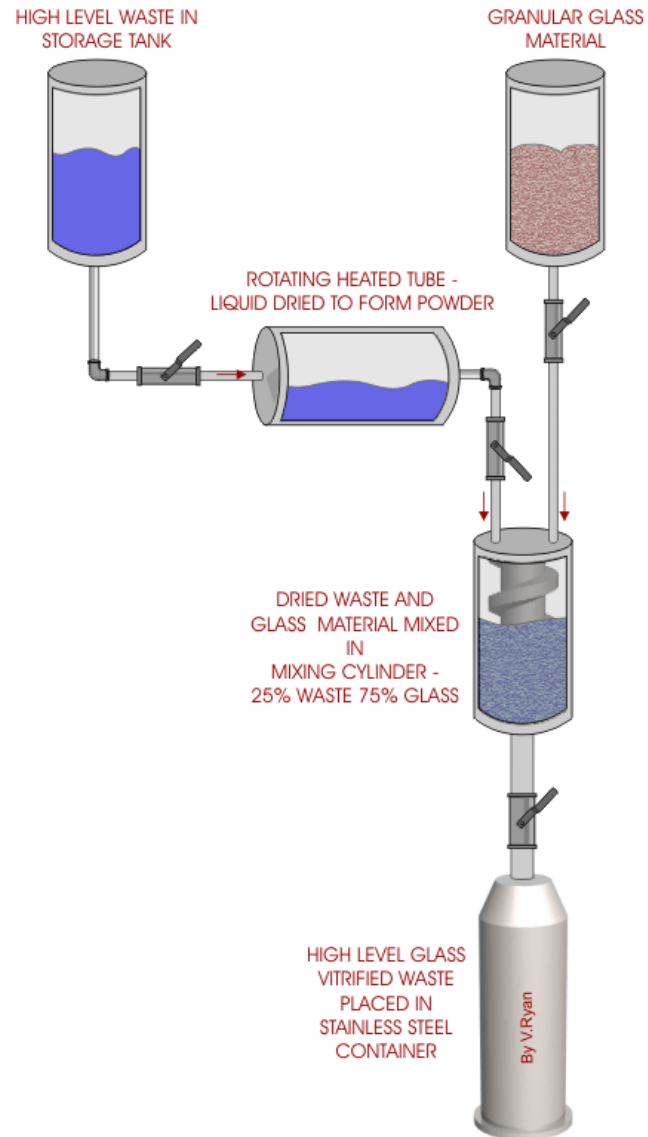


NUCLEAR WASTE CONTAINMENT FRIT

- Technology has been successfully transferred to H&R Johnson (India) to manufacture this special glass frits in the year 2011-12.
- We are the only Organization approved by BARC/CGCRI for manufacturing this glass frit in the country.
- Till date Johnson supplied 29.50 MT glass beads and it is performing perfectly.



NUCLEAR WASTE CONTAINMENT PROCESS



FLOW DIAGRAM TOWARDS COMMERCIALIZATION OF TECHNOLOGY OF MANUFACTURING SPECIAL GLASS BEADS FOR NUCLEAR WASTE IMMOBILIZATION



Demonstration of Frit melting at H R J site




Characterization of glass Frit at CSIR-CGCRI

Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES), Spectro Analytical Instrument

Flame Atomic Absorption Spectrophotometer (FAAS), Perkin Elmer



Bulk Nodulization at H R J's Pen Plant to form spherical shaped glass bead duly certified by CSIR-CGCRI



Finished glass beads ready for dispatch to DAE'S ancillary units



Testing, Evaluation & Inspection of Glass Beads at HR J's Pen Plant



Experimental set up for further testing of Glass Beads at CSIR-CGCRI

ALUMINA INSULATORS

Frits are used to glaze alumina insulators:

- To minimise dirt build-up which may result in the formation of an electrically conducting surface.
- To increase the strength and imperviousness of the surface

Characteristics of frit

- Must have a low thermal coefficient of expansion, similar to that of the alumina substrate to avoid undue stresses which can cause cracking or crazing of the glaze
- Softening temperature must be adequate to allow release of gases evolved from substrate

GRINDING WHEELS

Frits are used in grinding wheels

- To bind the abrasive grains
- To provide strength to the wheel
- To provide a softer matrix to expose the abrasive grains

Characteristics

- Selection of frits depends on the specific purpose of the application, the type of abrasive grain, and the additives used, as well as the firing temperature, which is generally between 680 °C and 1300 °C
- Transparent in nature

THE STEPPING STONE TO YOUR SUCCESS



Industrial Products & Natural Resources
H & R JOHNSON (INDIA)
(A DIVISION OF PRISM CEMENT LIMITED.)