IBAAS 2023
TECHNICAL LECTURE SERIES

SPECIAL HYDRATES/ALUMINA: PROPERTIES AND APPLICATIONS

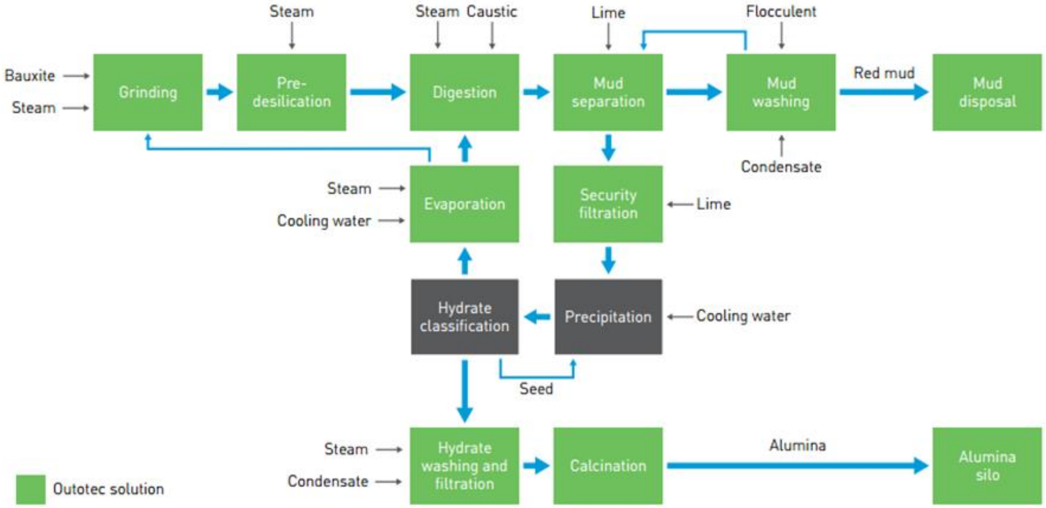
DR. SUCHITA RAI

IBAAS 2023

Contents

INTRODUCTION: The Bayer Process

An Alumina Refinery



Alumina Category

- Metallurgical grade (90%) – for producing aluminium metal
- Nonmetallurgical grade (10%) –for producing special products

Classification of Alumina

Bauxite
↓
Alumina (Bayer Process)

100%

- ~ 90 % → Metallurgical grade alumina
- ~ 10 % → Non- metallurgical grade Aluminium trihydroxide & alumina
  - 100%
  - ~ 60% → Aluminium trihydroxide
    - Chemicals
    - Flame retardants
    - Fillers
  - Activated alumina
    - Absorbants
    - Catalysts
    - Dessicants
  - ~ 40% → Calcined alumina
    - Abrasives
    - Ceramics
    - Refractories

Alumina through Bayer process and some of its applications

Applications of special hydrate/ alumina

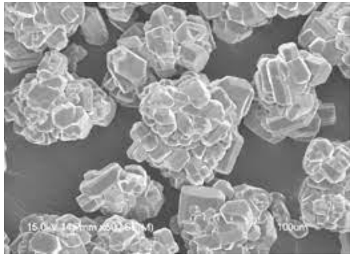
- Aluminium hydroxide: Chemicals, fillers, flame retardants, pharmaceuticals
- Activated alumina: Adsorbents, catalysts, desiccants, de-colourising agents
- Calcined alumina: Abrasives, ceramics, refractories, prod. of tabular and fused alumina
- Tabular alumina: Refractories, electric insulators, ceramic parts
- Fused alumina: Abrasives, ceramics
- High purity alumina: Nuclear ceramics, specialist electronic component

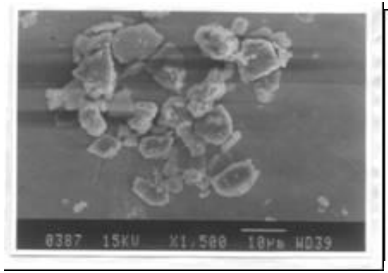
Hydrate ⟶ Alumina

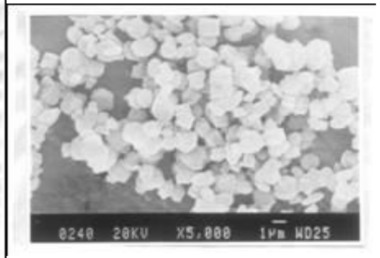
- Production of alumina trihydrate through Bayer Process
- Calcination to obtain free-flowing alumina
- Bayer alumina (0.3-0.6% soda content)
- After suitable treatment, purity can be improved (up to 0.1% soda content)
- High purity for non-Bayer alumina (<0.01% soda and others ≈ ppm)

Characteristics of Aluminium Trihydroxides

	Normal	Fine	Ultrafine/Superfine
$Al(OH)_3$ (%)	99.6-99.7	99.7-99.8	99.5-99.6
Fe_2O_3 (%)	0.01-0.02	0.01	0.01
SiO_2 (%)	0.01-0.02	0.01	0.01
Na_2O(total) (%)	0.2-0.3	0.2	0.3-0.4
d_{50} (µm)	30-70	3-25	0.6-1.5
Whiteness (%)	75-85	85-97	95-98
Source	aluminium hydroxide	grinding of normal aluminium hydroxide	special precipitation technique
Applications	feed stock for the manufacture of aluminium salts, glass, ceramic, catalyst industries	flame retardant fillers in rubber, cables and plastics, foams, carpets. Hydrates having whiteness >92% used in paper, toothpaste, synthetic marble	filler in special paints, pigments, inks, pharmaceuticals, electronics and as fire retardant filler in flexible plastics







ATH as fire retardant fillers

Due to its physical and electronic properties, cost-effectiveness, high versatility, and portability.

More than 50% of flame retardants which are sold worldwide are inorganic hydroxides and ATH is the largest flame retardant used.

During burning of the polymer, ATH releases water vapor, reduces the polymer surface temperature and act as a heat sink.

Polymer-based materials: key components in many important industries: construction, automotive, electronic and aerospace.

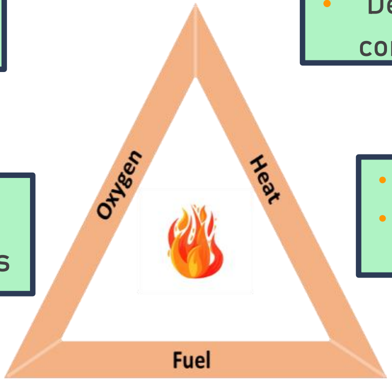
Fire Triangle

The burning of polymer

- Rapid
- Exothermic
- O_2 induced degradation process

Fire

- Initiated by high temperature
- Decomposes the polymer into combustible gaseous species



- Formation of hydrogen radicals
- These combines with O_2 molecules

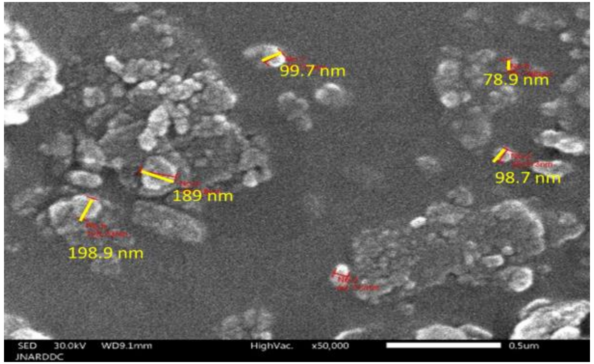
- Creates further free radicals (O▪ and HO▪)
- They react with carbon monoxide exothermically

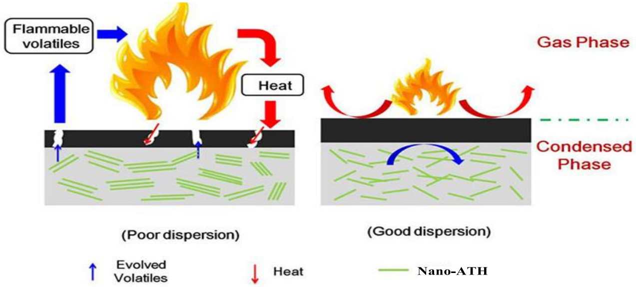
- Propagation of the chain reaction
- Causes additional burning
- reaction is interrupted by flame retardants

The flame-retardant filler:

- Interrupt the free radical formation reaction
- Suppress the formation of chemical species

Nano-ATH





- High loadings of coarse ATH, commercially used in polymers as a fire-retardant filler.

- This causes uneven dispersion and reduce workability and physicomechanical properties.

- Better tensile properties can be achieved by uniform dispersion of nanosize ATH in polymers while maintaining its flame-retardant properties.

High Energy planetary ball Mill

Polymer+Nano-ATH

PP+MAPP

+ATH(nano or micro)

Batch mixing at temperature 190 200^{0}C

Shredded into small size

Injection molding

(micro compounder) or compression molder

Batch mixing of PP, nano or micro ATH and MAPP

Compounded material with nano or micro ATH and MAPP

Micro-injection jet

Compression molded

Onyx grade ATH

Bayer liquor consists of impurities → ATH with less whiteness and Fe_2O_3, SiO_2 in the range of 0.015% is produced → The sintering process, highly energy intensive, is followed to remove organics

Pure and white ATH used in synthetic marble/ onyx → Apart from its flame-retardancy, ATH filler imparts a marble-like translucency to the cast acrylic → 'Synthetic marble': for various consumer applications such as kitchen counters, bathroom panels → Less natural resource (marble) depletion to a great extent. → Onyx grade ATH: Fe_2O_3 ≤0.005%, SiO_2 ≤ 0.008%, Na_2O(total) ≤ 0.25%, d_{50}: 20-30µm, Whiteness: >96% imported

Activated Alumina

Transition phase of aluminium oxide

Principal uses are as drying agents, adsorbents, catalysts and catalyst carriers.

Mainly these are used to absorb moisture, water, vapor, humidity, odor etc.

Highly porous, high surface area materials (about 275-350 m^2/g)

Molecular water is driven out by heating the hydroxides; leaving behind a highly porous structure of aluminium oxide having a high surface area.

Mostly used for drying of gases like oxygen, hydrogen, nitrogen, carbon-dioxide etc.

Obtained by thermal dehydration of aluminum hydroxides at various temperatures in the range of 250- 700°C

The properties of the final 'active' product depends upon the physical and chemical nature of the starting hydroxide and thermal history of dehydration.

Activated Alumina

These activated aluminas are highly customizable.

The product which can be specifically developed for air drying should have optimized characteristics in a sphere size.

Mostly the sphere size ranges in between minus 45 micron, 2-5mm, 2.5 - 5mm and 4 – 8mm.

Polluted water has very much negative effects on public health.

Imported activated alumina by India since last 5 years are mostly- 45-micron size, 6 - 8 mm and 3 - 5 mm beads size.

Activated alumina can be taken as an adsorbent for water purification process and the same can also be used for drying.

Activated alumina product demand

Rising demand for clean water, shrinking water reserves, and the implementation of new water treatment facilities

Government initiatives, such as the launch of various projects for the regular supply and treatment of water, are likely to propel the product 3-12%

Water treatment infrastructure and the increasing demand for oil and gas applications are key drivers for global activated alumina market.

Thermal Dehydration of Alumina hydrates

Trihydroxides

Gibbsite $\xrightarrow{300°C}$ χ-Al_2O_3 (Chi) $\xrightarrow{700°C}$ κ- Al_2O_3 (Kappa) $\xrightarrow{1100°C}$ α-Al_2O_3 (alpha)

Monohydroxides

Boehmite $\xrightarrow{300°C}$ γ-Al_2O_3 $\xrightarrow{800°C}$ δ-Al_2O_3 $\xrightarrow{1000°C}$ θ-Al_2O_3 $\xrightarrow{1100°C}$ α-Al_2O_3

Diaspore $\xrightarrow{500°C}$ α-Al_2O_3

Powdered Activated Alumina

Produced by heating alumina hydrate to a temperature range of 300-750°C

BET Surface area is 200-350 m^2/gm and LOI- 3-12%.

Uses:

-decolorizing agents for organic chemicals

-starting materials for the production of aluminium fluoride

- chromatographic and catalytic applications in organic chemistry

Granular Activated Alumina

Produced by heating precipitated hydrate to 400-600ºC in hot air /flue gas stream.

Properties	F-1	H-151	S-100
Al_2O_3 (%)	92	90	95
Na_2O (%)	0.58	1.6	0.35
SiO_2 (%)	0.12	2.0	0.03
Fe_2O_3 (%)	0.06	0.03	0.05
L.O.I (%)	7	6	5
Loose bulk density (g/cm^3)	0.83	0.82	0.80
Packed bulk density (g/cm^3)	0.85	0.85	0.75
Total pore volume (cm^3/g)	0.40	0.43	0.49
Total porosity (%)	56.3	59.4	60.6
BET surface area (m2/g)	250	360	260

Activated Alumina application in drying and purification of air used in healthcare sector.

Production of Activated Alumina from Boehmite and Gelatinous Aluminium Hydroxide

This is used for catalytic application hence no soda is permissible.

The activation temperature is 500-600^{o}C.

SSA is 185-250 m^2/gm.

Alumina Gels

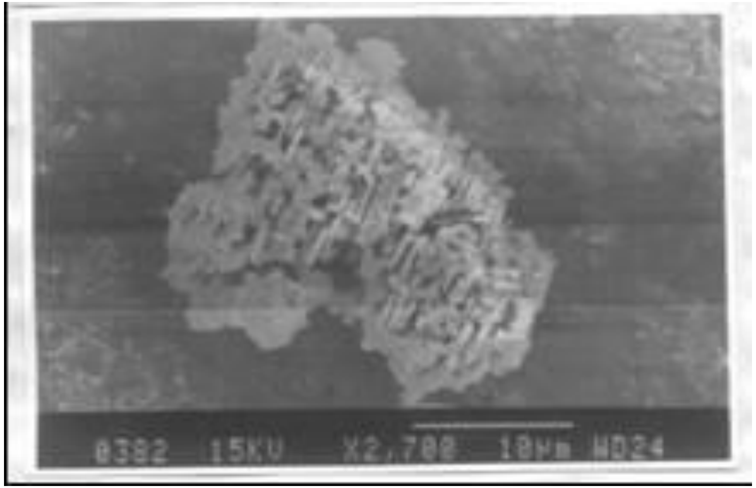
This is produced by neutralisation of aluminium sulfate or ammonium alum using NH_3 or from sodium aluminate by neutralisation with acids, CO_2, $NaHCO_3$ and $Al_2(SO_4)_3$.

The gel in various shapes are activated at 400-600°C.

BET SSA- 300-400 m^2/gm and LOI- 3-4 %.

Speciality Calcined Alumina

- These are prepared from alumina trihydrate by calcining at fairly high temperature 1000°C or more .
- Major utilisation of calcined aluminas are in ceramics (20-30%), refractories (50-60%), abrasives (15-20%) and others (3-4%)



Characteristic Properties of Calcined Alumina

	Normal soda	Intermediate soda	Low soda
Chemical composition			
Al_2O_3 (%)	99.2-99.6	99.5	99.8
Na_2O (%)	0.25-0.40	0.15-0.25	<0.1
Fe_2O_3 (%)	0.025-0.04	0.035	0.04
SiO_2 (%)	0.025-0.035	0.025	0.08
Physico-chemical properties			
α- Al_2O_3 (%)	>90	95-98	>95
Specific surface area (BET) (m2/g)	4-7	0.4-0.7	0.5-0.8
L.O.I. (1100°C)	0.1-0.2	<0.1	0.05-0.15
Applications	abrasives, glass, electrical porcelain, sanitary wares and Tabular, White fused aluminas.	electrical insulators, electroporcelain, high voltage supporting insulators, refractories, electronic ceramics	spark plugs, and sodium vapour lamps

Origin of soda in hydrate during precipitation

Caustic liquor adhering to the surface

Soda adsorbed on the surface and sealed in by crystal growth

Co-precipitation of other salts of sodium along with hydrate

Methods for soda reduction

- Special operating conditions during precipitation
- Leaching out soda from partly or fully calcined Bayer alumina by water or dilute acids
- Use of coarse-grained silica minerals to remove soda from Bayer alumina
- Hydrothermal conversion of Bayer hydroxide (gibbsite) to the oxide-hydroxide boehmite

Tabular Alumina

Tabular Alumina is a highly dense, high-strength form of pure sintered alumina.

It is made by high-temperature sintering of an agglomerated shape of ground, hard calcined alumina.

Derives its name from the large (typically 50-400 microns size), flat corundum crystals that have formed during sintering and constitute the sintered shape.

These large crystal facets can be observed by the naked eye. The high sintering temperature of nearly 1800°C produces a fully shrunk material.

This unique structure makes it distinctly different from other dense, fine crystalline sintered aluminas and from fused aluminas.

The size of crystallites is very important because this is characteristic of tabular alumina.

Typically characterized by the retention of closed spherical porosity (approx. 10%) and the near-complete elimination of open porosity (2-3% residual).

Characteristic Properties of Tabular Alumina

Particulars	Values
Chemical composition	
Al_2O_3 (%)	upto 99.5
SiO_2 (%)	0.04-0.06
Fe_2O_3 (%)	0.03-0.06
Na_2O (%)	0.1-0.3
Physical characteristics	
α- Al_2O_3 (%)	>90
Grain size	50-400 microns
BET surface area	0.1-1 m^2/g
Bulk specific gravity	3.5-3.65 g/cc
Hardness	9 (Moh's scale)

Application of Tabular Alumina

- The strength of grains of tabular alumina is 1-3 times higher than that of corundum.
- It is used as a component of the refractory bricks, concretes and masses in the:

- Iron and steel industry
- In the metallurgy of other metals
- Cement lime industry
- Ceramic industry
- Chemical and petrochemical industry
- Energy production
- Heating element bricks

Fused Alumina

Brown Fused Alumina

Calcined bauxite containing more than 80% Al_2O_3 is used for the production of brown fused alumina

It contains 95-97% Al_2O_3, the impurities being TiO_2, SiO_2, and Fe_2O_3.

To obtain >95% Al_2O_3 from calcined bauxite containing about 85% Al_2O_3, reducing agents such as coke and anthracite are added to reduce Fe_2O_3 and SiO_2 (also partially TiO_2 to the metal).

The abrasives industry is the biggest consumer of brown fused alumina.

White Fused Alumina

It is produced from Bayer calcined alumina in a continuous furnace.

The melt from continuous furnaces is poured into water-cooled cast iron, steel or aluminum molds.

White fused alumina grains are used in both abrasive and refractory applications.

A variation of white fused alumina is pink/red fused alumina formed by the addition of chromium oxide which improves certain abrasive properties.

Properties exhibited by alumina used in ceramics

Properties	Values
Density, g/cm^3	3.97
Poisson's ratio	0.27
Hardness (knoop), (kg/mm^2)	2100
Modulus of rupture, MPa	275-550
Electrical resistivity, (ohms-m)	$>10^{12}$
Thermal conductivity, W/m-K	30
Coefficient of thermal expansion, / °C (Mean value taken over the temperature range 0-1000°C)	8.8×10^{-6}
Melting temperature, °C	2050

Reactive Aluminas

The commercial-scale fabrication of high performance +99% Al_2O_3 technical ceramics suitable ceramics for industrial applications have been developed from Bayer derived low soda aluminas (<0.1% Na_2O)

Sintering it to a high temperature of about 1500°C.

Supergrinding it to fine crystalline alumina (<1 micron).

Methods Of Production For High Purity Alumina

FROM ALUMINIUM SALTS

Thermal decomposition of aluminium salts

Precipitation of aluminium hydroxide from aqueous solution

FROM ALUMINIUM METAL

Direct oxidation with O_2

Reaction with water

FROM DECOMPOSITION OF ORGANO-METALLIC COMPLEXES

Thermal decomposition

Hydrolysis to aluminium hydroxide

From Aluminium Salts

Thermal decomposition of aluminium salts

- Aluminium salts used for thermal decomposition (at 1000°C) are ammonium aluminium alum $(NH_4)_2SO_4.Al_2(SO_4)_3$, aluminium nitrate, aluminium chloride, aluminium salts of organic acids such as aluminium oxalate and acetate. The product after calcination at 1200°C consists of fine (0.1 to 0.25 microns) $\alpha\text{–}Al_2O_3$ particles.

Precipitation of aluminium hydroxide from aqueous solution

- Aqueous solutions of aluminium sulphate and nitrate are neutralized using ammonia, ammonium hydroxide, urea and formamide resulting in precipitation of aluminium hydroxide which is then calcined to form aluminium oxide.

From Aluminium Metal

Direct oxidation with O_2

- Direct oxidation of aluminum metal in air or oxygen atmosphere at 800°C to aluminium oxide is a highly exothermic reaction.
- $2Al + 1.5O_2 \text{------}\rightarrow Al_2O_3 + 400.2\ kcal$

Reaction with water

- This reaction produces hydroxide with the simultaneous evolution of hydrogen.
- $Al + 3H_2O \text{------}\rightarrow Al(OH)_3 + 1.5\ H_2$
- In the process developed by ALCOA, the aluminium powder is reacted with choline ($(CH_3)_3NCH_2CH_2OH$) solution at 50-80°C to yield crystalline aluminium hydroxide which is then calcined to yield alumina.

Decomposition Of Organo-metal Complexes

Aluminium forms compounds with most alcohols which have the general formula $Al(OR)_3$ where R represents the alcohol chain. Decomposition of alkoxides can be achieved either by thermal decomposition (800- 1000°C) in N_2 atmosphere or by hydrolysis with water.

1) Thermal decomposition :

It occurs according to the reaction

$2\ Al(OR)_3 \text{----}\rightarrow Al_2O_3 + 6R' + 3H_2O$

Where R' is an olefin such as ethylene, propylene, butylenes etc.

The product is very fine (0.2 µm) particles of amorphous aluminium oxide.

2) Hydrolysis to aluminium hydroxide:

Hydrolysis of aluminium alkoxides gives the highest purity (99.999%) uniform size alumina.

$Al(OR)_3 + 3H_2O \text{---}\rightarrow Al(OH)_3 + 3ROH$

Chemical Composition of high purity alumina

Characteristic	Calcined	Calcined	Calcined
Crystal phase	>90 % gamma	85 % alpha	Alpha
Purity (%)	99.99	99.99	99.99
Impurity analysis of ceramic grade (ppm)			
Na	20	20	
Pb,Cr &Zn	4	4	
Si	18	18	
Fe & Ca	10	10	
Ga	15	15	
Mg & Ti	5	5	
Mn &V	3	3	
Cu	2	2	
SiO_2			< 50
Fe_2O_3			< 20
CaO			< 10
Na_2O			< 10
Ga_2O_3			< 10
Others			< 10

Characteristic properties of high purity alumina

Characteristic	Calcined	Calcined	Calcined
Ultimate particle size (µm)	0.01	0.15	<0.5
Specific surface area (m^2/g)	115	10	5-50
Agglomerate size (µm)	2	0.6	0.5
Crystal density (g/cm^2)	3.67	3.98	3.98
Apparent bulk density (g/cm^2)	0.12	0.51	----

Application of High Purity Aluminas in High Tech Areas

Analytical instruments :

Typical applications are in HPLC pumps (piston, balls and seats, rotars and stators for injection valves, pump heads etc.), precision dispensers (pistons for pipettes and metering pumps).

Medical instruments :

Used in Opthalmology, Endoscopy, Microtomy, Electro-surgery, components for implantable devices and dental applications.

Electrical and electronic materials :

In active and passive electronic components such as resistors, capacitors, hybrid circuits, cameras, sensors and other critical devices which are used in automotive electronics, satellite and telecommunications, medical equipments and biotechnologies, servers and computers.

Navigation and submarine :

Precision ceramic parts are required for excellent performances of bearings for navigation instruments and insulator for accelerometers for submarines.

Other Industries :

High purity aluminas are used in processed food and beverage industry,

Oil and natural gas exploration industry, chemical and refining industries.

Alumina in transition form are used as paper anti-skid coatings, polymer additives, thickeners, rheology modifiers and wash coats for exhaust gas catalytic converters.

Abrasives and refractory:

It is the basis of the most important polishing agents for industrial and private use. It is used to polish the hard drive in the computer as well.

Transmission of sound :

The high-tech ceramics transit sound better than other metals used in traditional transducers.

Aerospace industry :

in satellites and spacecraft. High alumina rod tubes are used in turbines of jet engines to withstand high temperature and provide wear resistance.

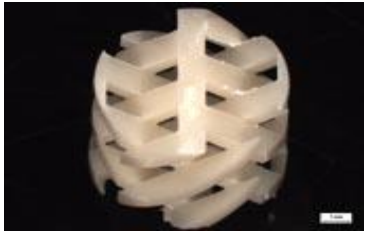
Prices of Special Grade Alumina

Variety	Number of times the special grade is costlier than smelter grade
Activated	5.9-8.2
Catalyst carrier	8.2-26.5
Abrasive grade	2.1-3.6
Refractory	1.5-3.3
Ceramic grade	2.1-3.6
Spark plugs	20
Electronic ceramics	5

Special hydrate/alumina developed at JNARDDC

- Ultrafine hydrate (1-2 microns size).
- Low soda hydrate (Na_2O<0.1%).
- 3 N Alumina (99.9% Al_2O_3)
- Fine hydrate (d_{50}: 10-12 microns) through precipitation process.
- nanosize ATH (50-350nm) for fire retardant fillers
- Onyx grade ATH
- High alpha content alumina (>99%).
- Coarse (d_{50}: 90-100 microns) and fine (d_{50}: 10-12 microns) activated alumina with high specific surface area (250-300m^2/g).
- Coarse (d_{50}: 90-100 microns) and fine (d_{50}: 10-12 microns) boehmite hydrate.
- Coarse (d_{50}: 90-100 microns) and fine size (d_{50}: 10-12 microns) gamma alumina having high surface area (100-110m^2/g).
- Smelter grade alumina from boehmite hydrate

ENGINEERING PRODUCTS



Ceramic valves

Alumina substrates for electronic circuits

High Purity Alumina Ceramic products

Thank You All