

2.1. Introduction:

The occurrence of periclase, or magnesia as it is commonly called, in its natural form is rare and is generally produced either by the calcination of magnesium hydroxide or magnesium carbonate, as a mineral contaminated with ferrous oxide. The word periclase is derived from the Greek word peri, which means “around,” and the word klao, which means “to cut,” presumably alluding to the way periclase cleaves. There is a large amount of data concerning the physical properties of magnesia owing to its importance as a refractory oxide. Some of the more useful properties are summarized here.⁽¹¹⁾

2.2. Physical properties of magnesium oxide:

2.2.1. Color/luster:

Colorless to grayish white, also yellow to brown or black due to iron or foreign inclusions. Its luster is vitreous and transparent.

2.2.2. Crystal system/habit isometric:

Usually occurs as anhedral to subhedral crystals in a matrix.

2.2.3. Crystal structure:

Periclase has a cubic face-centered crystal lattice isomorphous with that of sodium chloride and calcium oxide.

2.2.4. Density:

3.55–3.68 g/cm³. X-ray density 3.581 g/cm³.

Hardness 5.5 on the Mohs scale.⁽¹¹⁾

2.2.5 Index of refraction:

The refractive index of periclase (polycrystalline) is 1.7350 at 633 nm.

2.2.6. Thermal conductivity:

The thermal conductivity of magnesia has been determined by a number of workers. The figures for polycrystalline sintered magnesia at lower temperatures and sintered magnesia at a higher temperature range are given in Tables 2.1 and 2.2, respectively.⁽¹¹⁾

Table 2.1: Thermal conductivity of polycrystalline sintered magnesia:

Temperature(C°)	Thermal Conductivity (cal s ⁻¹ cm ⁻² °C ⁻¹ cm)
0	0.10
100	0.083
300	0.067
500	0.031
600	0.026

Table 2.2: Thermal conductivity of sintered magnesia at high temperatures:

Temperature(C°)	Thermal Conductivity (cal s ⁻¹ cm ⁻² °C ⁻¹ cm)
1000	0.015
1200	0.014
1400	0.014
1600	0.016
1700	0.018

2.2.7. Electrical resistance:

The electrical insulating power of magnesia is very high, which makes for an excellent high-temperature electrical insulator. The specific

resistance of crystals of pure periclase is the highest and has been measured as $2.3 \times 10^9 \Omega \cdot \text{cm}$ at 700°C . The relationship between specific resistance ρ of magnesia and temperature T (K) can be expressed by:

$$\rho = Ae^{B/T}$$

2.2.8. Melting point:

Periclase has a very high melting point of 2800°C and a boiling point of 3600°C .

2.2.9. Thermal expansion:

The thermal expansion of periclase is the greatest of all pure refractory oxides and approaches the expansion of metals.

Exact expansion measurements have been carried out on single crystals of periclase and high-purity sintered magnesia.⁽¹¹⁾

2.2.10. Heat capacity:

Values for the specific heat capacity from ambient temperature to 3600K are shown in **Table 2.3**.

Table 2.3: Specific heat capacity for MgO

Temperature(K)	Specific Heat Capacity ($\text{J K}^{-1} \text{mol}^{-1}$)
298.15	37.106
600	47.430
1000	51.208
1800	54.898
2800	58.490
3600	61.214

2.3. Chemical properties of magnesium oxide:

The physical and chemical properties of magnesium oxide are primarily governed by the source of the precursor, that is, derived from magnesite or precipitated from brine or seawater. Other important factors include time and temperature of calcination and the presence of trace impurities. Electron microscope studies have revealed that the precursor particle morphology has a large impact on the morphology of the final MgO particle. It has been shown that when brucite and magnesite crystals are thermally decomposed at low temperatures, pseudomorphs of a size and shape similar to the parent crystal are formed.⁽¹¹⁾

Caustic-calcine magnesias are calcined below 900°C and are characterized by moderate to high chemical reactivities. They are readily soluble in dilute acids and hydrate rapidly in cold water. They also slowly react with atmospheric moisture and carbon dioxide to form the basic carbonate, $5\text{MgO} \cdot 4\text{CO}_2 \cdot x\text{H}_2\text{O}$. Common test methods for determining the reactivity of caustic-calcine magnesias are specific surface area and the caustic magnesias activity test.⁽¹¹⁾

Magnesium oxide has very limited solubility in water. However, an accurate determination is complicated by trace quantities of dissolved carbon dioxide in the water and the purity of the sample, where the presence of lime can introduce error. Another complicating factor is the source of the periclase and what heat treatment it had received. All these factors influence the rate at which equilibrium is reached in solution and hence solubility. Many solubility measurements have been made that have produced a wide variation in results. The most accurate determination to date has produced a result of 8.6 mg/L at 3°C. Caustic-

calcined magnesia readily hydrates to the hydroxide on exposure to moisture.⁽¹¹⁾

2.3.1. Dissolution of magnesium oxide:

The dissolution of magnesium oxide in acidic media has been extensively studied by Segall. Its dissolution rate in pH 1 acid at 30°C has been estimated by them as $1.2 \times 10^{-4} \text{ mol m}^{-2} \text{ s}^{-1}$, which is very close to diffusion control and corresponds to a penetration rate of 10^{-3} - $10^{-4} \text{ cm s}^{-1}$. They speculate that the initial rate is controlled by the speed with which water molecules formed from the surface hydroxyl ions and protons can be transported out through the Helmholtz layer.⁽¹¹⁾

Several pH-dependent rate-controlling processes were found to be present at room temperature:

1- At $\text{pH} < 5$ the rate-controlling step was H^+ attack followed by desorption of Mg^{2+} and OH^- . The rate was proportional to either $-\text{pH}$ or $\text{pMg}-\text{pH}$, and these processes are part of the overall neutralization reaction:



2- At $\text{pH} \approx 5$ the rate-determining step was proton diffusion, the rate being proportional to pH .

3- At $\text{pH} > 7$, the rate-controlling step was OH^- adsorption followed by Mg^{2+} and OH^- desorption. These processes are part of the overall dissolution reaction:



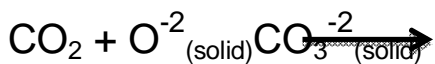
2.3.2. Molecular adsorption on MgO:

Chemisorption on an MgO surface will be primarily an acid/base interaction. Cation sites are Lewis acids and may interact with donor molecules such as H₂O through a combination of electrostatics (ion-dipole attraction) and orbital overlap. Oxide ions also act as basic sites and can interact with acceptors such as H⁺. In fact one of the most common dissociative reactions is the deprotonation of an adsorbate to produce surface hydroxyl groups.⁽¹¹⁾

2.3.3. Chemisorption of various molecules on MgO:

Hydrogen: Experimentally no evidence for interaction with H₂ has been observed at room temperature.

Carbon Dioxide: Lattice oxygen is essentially basic toward acidic molecules such as CO₂, forming surface CO₃⁻² see reaction:



Water and Methanol: The interaction of H₂O with the (100) surface of MgO prepared by polishing and ion-bombarded single-crystal surfaces has been studied using X-ray photoelectron spectroscopy (XPS) both before and after annealing at 900 K. It was observed that at room temperature water did not adsorb on the annealed surfaces. However, ion-bombarded surfaces did display features of OH⁻, presumably due to the creation of surface defect sites allowing water adsorption. At 200 K, both the polished and ion-bombarded surfaces showed evidence of OH⁻ after exposure to H₂O, the ion-bombarded surface being covered with a monolayer of OH⁻. Like H₂O, methanol (CH₃OH) adsorbs only at

defectsites on the (100)surface, undergoing heterolytic dissociation to methoxide (CH_3O^-) and OH^- .⁽¹¹⁾

Carboxylic acids: Both formic and acetic acid dissociate at room temperature and below on (100) terraces giving surface hydroxide and the formate (HCOO^-) and acetate (CH_3COO^-) species.

Hydrogen sulfide: Hydrogen sulfide is similar to water and may adsorb either as a molecule or by proton loss (OH^- formation) through an acid/base type interaction; see reaction:



2.4. Tanning leather:

Processing of skin or hides into stable material – leather is known as tanning. Leather, the primary product from the tanning industry, where the product has got its applications in making footwear, furniture, bags, etc. The global leather industry generated about 18 billion square feet leather in 2003 with an estimated price of US\$40 billion. Most developing countries including India is producing 60 % of world's leather needs. For making the leather, Tanning is considered as a major process which involves more chemical reactions as well as mechanical operations. During the process more chemicals including chromium, acid solvents, etc are involved, these processes release effluent of 30L/kg of processed skin, where tanneries of India are releasing effluent more than 50,000mg/day with huge quantity of organic pollutants. 70% of chrome (III) is usually discharged and leads to heavy metal contamination in water. Release of chromium by tanneries are higher now than mentioned parameters^{(14) (15)}.

Chromium, a major heavy metal exploited in leather industry. In India, it was found to release 30 billions of waste water with 3000-5000mg/L of total solids and chromium in between 100-200mg/L on processing 700,000 tons of skins in about 3000 tanneries. More than 170,000 tons of with 0.04Mt Cr (III) wastes per year are released into environment worldwide. With the enhancement of environment realization and change in manufacture patterns, the world industry is desirous to take cleaner and greener approaches for leather processing.⁽¹⁴⁾

2.4.1. Steps involved in leather processing:

2.4.1.1. Soaking:

Soaking is the first step involved in tanning where the preserved raw skins or salted skins are treated with water to make the skin dirt free and soft. The main purpose of soaking is to remove salt, rehydrate the dry skin and also to remove unwanted materials like blood, soil, dung, etc. The soaking time depends on condition of skins or hides⁽¹⁴⁾.

2.4.1.2. Liming:

The second operation is liming which involves the removal of hair and unwanted materials which are not transferred to leather. It also loosens the epidermis and also remove soluble skin proteins. It uses lime and sodium sulphide as liquor. The hair is loosened due to increase in high pH. The higher pH also cause splitting and swelling of fibre bundles. Dehairing and fleshing is also done in order to remove extra flesh and allow tannins to penetrate easily^{(14) (16)}.

2.4.1.3. Deliming:

Deliming is the process of adjusting pH between 8-9 which enhances the enzyme activity and converts proteins into soluble forms. It uses ammonium sulphate and results in de-swelling of pelts. Deliming decreases the plumping of skin or hide⁽¹⁴⁾.

2.4.1.4. Bating:

Bating makes the grain surface soft and flexible. It prepares skin for tanning. It is an enzymatic operation which removes unwanted proteins

and increases the degree of stretch. It imparts flexibility and softness towards the leather⁽¹⁴⁾.

2.4.1.5. Degreasing:

Degreasing is a process used to remove extra fat and oils which allows the tannin to penetrate easily through the skin. This step can be carried out by emulsion of fats using detergents or surfactants⁽¹⁴⁾.

2.4.1.6. Tanning:

Tanning is the main operation which converts skin or hide to stable material called leather. In this step tannins are allowed to interact with the prepared skin which act on collagen and make it stable⁽¹⁴⁾.

2.4.1.7. Fixing:

Formic acid is mostly used in this process which ensures homogenous tanning of hides in leather processing⁽¹⁴⁾.

2.4.2. Types of tanning:

2.4.2.1. Mineral tanning:

Mineral tanning is a process which uses basic chromium sulphate as tanning agent after the process of pickling. Once the desired level of penetration the pH is again increased to facilitate the process which is termed as basification and the obtained product is called as wet blue⁽¹⁴⁾.

2.4.2.2. Tawing:

Tawing is another practice which uses aluminum salts and alum along with other materials such as flour, egg yolk and other salts. It is an age old traditional process which gives a wet white product. In this method the

skin is tawed in alum and salt solution which increases flexibility, stretchability, etc whereas egg yolk and flour enhances the handling properties. Tawing was conventionally used on goatskins and pigskins⁽¹⁴⁾.

2.4.2.3. Chrome tanning:

Chrome tanning is the most commonly used tanning process. It uses Chromium (III)sulfate which has been considered as the most effective and efficient tanning agent. It forms poly chromium compounds by a process called oxidation which acts as active compounds in tanning that crosslinks the collagen subunits. The leather obtained by chromium contain 4-5 % of chromium and its efficiency is determined by enhanced hydrothermal stability and resistance to shrinkage at high temperature. Although chrome is an effective tanning agent it is having some hazards towards human⁽¹⁴⁾.

2.4.3. Effects of chrome tanning towards human:

Chromium in its +6 oxidation state is referred to as Hexavalent chromium. It is mainly used for coatings, wood preservation, dyeing, etc. The chromate mimics the sulphate in its structure and surface charge which can enter the cell and cause cancer, eye irritation and skin allergies. There is a high risk of getting cancers to the workers exposed to hexavalent chromium for a prolonged time. It has been reported lung cancer among workers in chromium chemical production. Repeated exposure to hexavalent can also damage the respiratory tract and may also cause nasal cancer. Direct eye contact of chromate cause permanent eye damage and eye irritation. Prolonged exposure to skin cause skin allergies, dryness, fissured skin, skin ulcers and swelling [36].

In other way some workers may develop allergic sensitization where exposure to small amount cause serious skin rash. Other effects of chromium include dizziness, growth problems, reproductive disorders, discoloration and erosion of teeth⁽¹⁴⁾.

2.4.4. Nanotechnology in leather processing:

Nanoparticles, because of their small size and their ability to combine with polymers shows its potential for the application in tanning. Introduction of nanoparticles into tanning agents enhances the physical and mechanical properties of leather. In order to this, silver nanoparticles due to its properties against bio-activities they can even impart some functional properties such as anti-microbial, UV-resistance and fungal resistance of leather. Rajiet al (2019) used various tannins mediated silver nanoparticles for tanning process and able to produce a stable leather^{(14) (17)}.

2.5. Aim of research:

There are several processes involved in leather making, one of the process is tanning. In tanning process, higher concentration of chromium is commonly used. Whereas chromium is regarded as one of the toxic heavy metal. The disposal of these chromium effluent into water bodies is known to cause various ill effects.

In this review, I will dealt about various procedures in leather processing especially chrome tanning and health hazards caused by chromium.

The aim of this study is to Prepare the magnesium oxide nanoparticles to increase the effectiveness of chromium used in leather tanning and thus reduce the amount of chromium used.