Justyna Jaroszyńska-Wolińska

Chemistry of Construction Materials





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Polish Academy of Sciences Lublin Branch 2016 **Reviewers:**

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Cover: Structure of Alumina Cluster $[(Al_2O_3)_4]^+$

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Historical Perspective

Material and Construction Science can be viewed as beginning at the start of the Stone Age when people began to make tools from stone about two million years ago. This era used natural materials such as stone, wood, clay, skins, etc. and ended about 5000 years ago with the introduction of bronze (an alloy of copper, tin and other elements) in the Far East which metal can be hammered or cast into a variety of shapes, can be made harder by alloying and corrodes only slowly after a surface oxide film forms. The Iron Age began some 3000 years ago and continues today. The use of iron and steel, a stronger and cheaper material, changed drastically daily life. The Age of Advanced Materials began in and has continued throughout the Iron Age in which many new types of materials have been developed including ceramics, semiconductors, polymers, composites, etc.

Progress to new and better construction materials depends on understanding the relationship between:

- Atomic/molecular structure
- Materials chemistry
- Materials processing and
- Materials performance

Such understanding is key to the intelligent design of new materials and has led to remarkable progress in the properties of materials, for example, dramatic increase in the strength to density ratio enabling a wide variety of new products from dental materials to important new construction materials.





1.1. Chemistry of Construction Materials – Paradigm and Scales

The Chemistry of Construction Materials is an important subset of Materials Science so that the methods and disciplines of Materials Science apply, in particular:

- Study of the structure of materials and relation to their properties, i.e. determination of structure property correlations.
- Study of materials processing and synthesis, major determinants of the composition and structure of a material and, thus, of its properties. Its constituent chemical elements must be well known and the way in which they have been processed into the desired form of the material specifically the process control parameters, factors, and responses.
- Study of the performance of a material in a specific application.

This interrelation can be visualised schematically in the Materials Paradigm tetrahedron of the following figure.



Figure 1.1. Paradigm tetrahedron (Simple English Wikipedia)

Chemical and physical structure are critical determinants of the properties of a material, the ways in which it can be used and its performance in an application. Materials science examines the structure of materials from the atomic scale up to the macro scale through characterisation using techniques such as diffraction with x-rays, electrons, or neutrons.

Examples of techniques are:

- Raman Spectroscopy
- Energy Dispersive Spectroscopy (EDS)
- Chromatography
- Thermal analysis
- Electron Microscope analysis, etc. (Atkins P.W., 2001)

In construction materials science and engineering (e.g. quality control) structure is studied at various levels of scale:

Atomic Structure

- This comprises the atoms of the material and how they are arranged to give molecules, crystals, etc.
- Much of the electrical, magnetic and chemical properties of materials arise from this level of structure.
- The dimensional scales involved are in angstroms Å.
- The way in which the atoms and molecules are bonded and arranged is fundamental to studying the properties and behaviour of any material.

Nanostructure

• Deals with objects and structures in the 1–100 nm range. In many materials atoms and/or molecules agglomerate together to form species at the nanoscale leading to many interesting electrical, magnetic, optical and mechanical properties. Materials whose atoms/molecules form nanostructures are called nanomaterials and are the subject of intense research due to the unique properties they exhibit.

Microstructure

- Defined as the structure of a prepared surface or thin foil of material as revealed by a microscope above 25×magnification.
- Deals with objects from 100nm to a few mm.
- The microstructure of a material can strongly influence physical properties such as strength, toughness, ductility, hardness, corrosion resistance, high/low temperature behaviour, wear resistance, etc. Most of the traditional materials such as metals and ceramics are micro–structured. The manufacture of a perfect crystal of a material is physically impossible. For example, a crystalline material will contain defects such as precipitates, grain boundaries, interstitial atoms, vacancies or substitutional atoms. The microstructure of materials reveals these defects so that they can be studied.

Macrostructure

• Macrostructure is the appearance of a material in the scale millimetres to metres. It is the structure of the material as seen with the naked eye.

1.2. Materials – Crystal Structure

A crystal structure is a unique arrangement of atoms, ions or molecules in a crystalline liquid or solid. It describes a highly ordered structure occurring due to the intrinsic nature of its constituents to form symmetric patterns typically through chemical bonding. Crystallography is the science that examines the arrangement of atoms in crystalline solids. Most materials have a crystalline structure. In single crystals, the effects of the crystalline arrangement of atoms are often easy to see macroscopically because the natural shapes of crystals reflect the atomic structure. Generally, materials do not occur as a single crystal, but in poly–crystalline form, i.e. as an aggregate of small crystals with different orientations. The Powder Diffraction method using diffraction patterns of polycrystalline samples with a large number of crystals plays an important role in characterising crystal structure. Some of the important materials that do not exhibit regular crystal structure are:

- Polymers display varying degrees of crystallinity and many are completely non-crystalline. The study of polymers combines elements of chemical and statistical thermodynamics to give thermodynamic, as well as mechanical, descriptions of physical properties.
- Glass, some ceramics, and many natural materials are amorphous, not possessing any long-range order in their atomic arrangements.

Crystal physical properties are often controlled by crystalline defects so that the understanding of both crystal structures and their defects is important in the development of new or enhanced materials and optimisation of their performance in the required application (Kurdowski & Pomadowski, 2001).

1.3. Materials – Bonding Structure

To obtain a full understanding of the material structure and how it relates to material properties, the materials scientist must study how the different atoms, ions and molecules are arranged and chemically bonded to each other.

- A chemical bond is an attraction between atoms that allows the formation of chemical substances that contain two or more atoms. The bond is caused by the electrostatic force of attraction between opposite charges either between electrons and nuclei or as the result of a dipole attraction.
- Since opposite charges attract, the negatively charged electrons orbiting the nucleus and the positively charged protons in the nucleus attract each other. An electron positioned between two nuclei will be attracted to both of them, and the nuclei will be attracted toward electrons in this position this attraction constitutes the chemical bond.

Due to the matter wave nature of electrons and their smaller mass, they must occupy a much larger volume compared to the nuclei. The volume occupied by the electrons keeps the atomic nuclei relatively far apart as compared with the size of the nuclei themselves. This phenomenon limits the distance between nuclei and between atoms in a chemical bond.

The strength of chemical bonds varies widely:

- "strong bonds" covalent or ionic bonds
- "weak bonds" such as dipole–dipole interactions, the London dispersion force and hydrogen bonding.

In general, strong chemical bonding is associated with the sharing or transfer of electrons between the participating atoms. The atoms in molecules, crystals, metals and diatomic gases—most of the physical environment – are held together by chemical bonds which dictate the structure and the bulk properties of matter. All bonds can be explained by quantum theory, but simplification rules allow chemists to predict the strength, directionality and polarity of bonds, e.g.

- The octet rule
- VSEPR theory

More sophisticated theories are:

- Valence bond theory which includes orbital hybridization and resonance.
- The linear combination of atomic orbitals / molecular orbital method which includes ligand field theory.

Electrostatics is used to describe bond polarities and the effects they have on chemical substances.

1.4. Materials – Processing and Synthesis

Synthesis and processing is the creation of a material with the desired micro/nanostructure and, hence, properties and performance. From an engineering standpoint, a material cannot be used in industry if no economical manufacturing method for it has been developed. Thus, the processing of materials is very important industrially and economically. Different materials require different processing/synthesis techniques, e.g. Metallurgy, the branch of materials science for the processing of metals. A wide range of chemical and physical techniques are used to synthesise important classes of materials such as polymers, ceramics, thin films, etc. Currently, new techniques are being developed to synthesise nanomaterials such as graphene and biomaterials.

Materials exhibit many properties. Important properties for construction include:

- Mechanical properties
- Chemical Properties
- Electrical Properties
- Thermal Properties
- Optical Properties
- Magnetic Properties

The properties of a material determine its usability and hence its engineering application.

1.5. Materials – Main Construction Classes

The main classes of construction materials can be broadly classified into:

Ceramics

- These are inorganic, non-metallic solid materials comprising metal, nonmetal or metalloid atoms primarily held in ionic and covalent bonds.
- The crystallinity of ceramics ranges from highly oriented to semicrystalline and often completely amorphous.
- Ceramics are formed by the action of heat and subsequent cooling.
- Ceramics are soft as clay or hard as stone and concrete. Clay is used to produce ceramic pottery but many different ceramic materials are used in domestic, industrial and building products.
- Ceramic materials are typically strong, stiff, brittle, chemically inert and non-conductors of heat and electricity, but properties vary widely.
- Engineering ceramics are used for stiffness and stability under high temperatures, compression and electrical stress, e.g. alumina, silicon carbide, tungsten carbide (Forest J., 1967).

Glass

Glass is an amorphous (non-crystalline) solid broadly defined as including every solid possessing:

- an amorphous atomic-scale structure and
- exhibiting a glass transition when heated towards the liquid state.

The glass-liquid transition (or glass transition for short) is the reversible transition in amorphous materials from a hard and relatively brittle state into a molten or rubber-like state. The most familiar and oldest types of glass are based on the chemical compound silica (silicon dioxide), the primary constituent of sand.

In the amorphous structure of glassy silica (SiO_2) no long-range order is present, although there is local ordering with respect to the tetrahedral arrangement of oxygen (O) atoms around the silicon (Si) atoms.

Typically, bonding in glasses is covalent and ionic–covalent with SiO_2 as a fundamental building block. Most glasses contain a metal oxide fused with silica. Porcelains and many polymer thermoplastics in everyday use are physically glasses also. At the high temperatures used to prepare glass, the material is a viscous liquid. The structure of glass forms into an amorphous state upon cooling.

Metals and metal alloys

A metal is a material (an element, compound or alloy) that is typically hard, opaque, shiny and has good electrical and thermal conductivity. Metals are generally:

- Malleable can be hammered or pressed permanently out of shape without breaking or cracking.
- Fusible able to be fused or melted.
- Ductile able to be drawn out into a thin wire.

About 91 of the 118 elements in the Periodic Table are metals (some elements appear in both metallic and non-metallic forms). The atoms of metallic substances are often closely positioned to neighbouring atoms in one of two common arrangements.

- Body-centred cubic each atom is positioned at the centre of eight others
- Face-centred cubic each atom is positioned in the centre of six others

The arrangement of atoms in these structures forms a crystal. Some metals adopt both structures depending on the temperature.

Atoms of metals readily lose their outer shell electrons resulting in a free flowing cloud of electrons within their otherwise solid structure. This allows metallic substances to easily transmit heat and electricity. Despite this flow of electrons, the metal is a solid because of the electrostatic interactions between each atom and the electron cloud. This type of chemical bond is called a metallic bond.

An alloy is a mixture of two or more elements in which the main component is a metal. Most pure metals are either too soft, brittle or chemically reactive for practical use. Combining different ratios of metals as alloys modifies the properties of pure metals to produce desirable characteristics, e.g. less brittle, harder, resistant to corrosion, more desirable colour and lustre. The alloys of iron (steel, stainless steel, cast iron, tool steel, alloy steel) make up the largest proportion both by quantity and commercial value, e.g. iron alloyed with various proportions of carbon gives low, mid and high carbon steels, addition of chromium, nickel and molybdenum to carbon steels (more than 10%) results in stainless steels. Other significant alloys are of aluminium, copper, titanium, magnesium. Alloys specially designed for highly demanding applications, such as jet engines, may contain more than ten elements (Pauling L., Pauling P., 1983).

Polymers including plastics

A polymer is a large molecule, or macromolecule, composed of many repeated subunits. Polymers, both natural and synthetic, are created via polymerisation of many small molecules, known as monomers. Polymerisation is the process of combining many monomers into a covalently bonded chain or network. During the process, some chemical groups may be lost from each monomer - the distinct piece of each monomer that is incorporated into the polymer is known as a repeat unit or monomer residue. Because of their broad range of properties both synthetic and natural polymers play an essential and very frequent role in everyday life. Polymers range from synthetic plastics, e.g. Polystyrene, to natural biopolymers such as DNA and proteins fundamental to biological structure and function. Their large molecular mass produces unique physical properties, e.g. toughness, viscoelasticity and a tendency to form glasses and semi-crystalline structures rather than crystals. Polymers are the raw materials (the resins) used to make plastics which are a final product created after one or more polymers or additives have been added to a resin during processing which is then shaped into a final form.

Polymers in widespread use include polyethylene, polypropylene, polyvinylchloride (PVC), polystyrene, polyesters, acrylics, polyurethanes, polycarbonates. Plastics are generally classified as "commodity", "specialty" and "engineering" plastics (Malcom, 1983).

Composites

Composites are materials made from two or more constituent macroscopic materials with different physical or chemical properties that, when combined together, produce a composite with characteristics different from the individual components.

The individual components remain separate and distinct within the finished structure. The new material may be better for many reasons, e.g. stronger, lighter or less expensive when compared to traditional materials.

Typical engineered composite materials include:

- composite building materials, such as cements, concrete
- reinforced plastics, such as fibre-reinforced polymer
- metal composites
- ceramic composites (composite ceramic and metal matrices)

Composite materials are widely used for buildings, bridges, boat hulls, water and storage tanks, interior materials such as counter tops, etc.

1.6. Chemistry in Construction

Today, chemistry plays key roles in every area of construction from major civil engineering projects (bridges, dams, airports, roads, etc.) to residential house construction. Virtually every component of construction involves the use of chemistry from vinyl drainage pipes in the ground below the foundation to roofing materials.

Chemistry is used to make pipework, walls and wall coverings, windows, doors, frames, roofing, carpeting, paints, sealants, floorings, insulation and adhesive materials. Chemistry also plays an important role, not only in construction, but also in preserving buildings and engineering structures (e.g.bridges) from damage caused by time and nature and protecting from fire. The average new house contains tens of thousands of euros of chemistry–based products. Chemistry is used to make building materials that are fire and rust retardant.

Chemistry is used to supply energy–saving materials like home insulation and thermal windows. Stronger materials better protect us from high winds and earthquakes. More flexible materials contribute to design, function and comfort. Modern glues and adhesives make plywood and particle board materials for home construction. Chemistry enables special steels that produce their own protective anti–corrosion coat for outdoor applications, e.g. bridge girders. Chemistry has produced much longer lasting paints, long–lifetime roof tiles, thermal protection on windows, bullet–resistant glass, solar panels and wall, floor and roof insulation for ecologically friendly homes and offices. Brick and stone no longer confine architects and builders. The building and construction industry, through the use of advanced materials technologies such as plastic insulation, composite materials, metals and glass, identifies new and creative design solutions for the way we live today.

2. Matter – Review of Atomic Structure



The Concept of Matter (models of the Atom) (Simple English Wikipedia)

The early philosophers ~ 600 BC classified matter into primary substances known as elements, which, according to Aristotle, comprised air, earth, water and fire. All other matter was seen as combinations of elements.

Democritus ca. 460–371 BC developed the idea of atoms. He pounded up materials in his mortar and pestle until he had reduced them to smaller and smaller particles which he called atoms.

"The atomists hold that splitting stops when it reaches indivisible particles and does not go on infinitely." – Leucippus of Miletus

This model said that there is a lower limit to the division of matter beyond which we cannot go. Atoms were impenetrably hard, they could not be divided. In Greek, the prefix "a" means "not" and the word "tomos" means cut. Atom comes from atomos, a Greek word meaning uncuttable. The concept of the atom was further and further developed in the following stages.

2.1. Atomic Model – the 'Hooked Billiard Ball'

John Dalton (1766–1844) postulated:

- 1. Elements are made up of minute, discrete, indivisible, and indestructible particles called atoms
- 2. Atoms of the same element have the same properties, such as weight. Atoms of different elements have different properties, including a different weight
- **3.** Atoms of an element are not changed into different types of atoms by chemical reactions (based on the *Law of Conservation of Mass*)
- 4. Compounds are formed when atoms of more than one element combine (based on the Law *of Constant Composition*)

Dalton found evidence of what he called "hooks" linking together atoms into different materials in his quantitative chemical measurements thus making the foundation of the modern atomic theory of matter. We now know the "hooks" to be electronic bonds.

2.2. Subatomic Particles – the Electron

However, around 1896 it was found that atoms are not indivisible or indestructible but are composed of sub-atomic particles.

Joseph John Thomson (1856–1940) discovered the electron while studying the nature of electric discharge in a high–vacuum cathode–ray tube. He interpreted the deflection of the cathode rays by electrically charged plates and magnets as evidence of "*bodies much smaller than atoms*". The name *electron* was introduced for this charge in 1894 by Irish physicist George Stoney.

J.J. Thomson's cathode ray experiments determined that the ray was made of tiny negatively charged particles–electrons. Measurements led him to conclude that these electrons were smaller than a hydrogen atom. If electrons are smaller than atoms, they must be pieces of atoms. If atoms have pieces, they must be breakable. Thomson also found that atoms of different elements all produced these same electrons.

In 1904 Thomson suggested a model of the atom as a sphere of positive matter inside which electrons are positioned by electrostatic forces – The Plum Pudding model.

2.3. Atomic Model – the Nuclear Atom

Ernest Rutherford (1871–1937) showed that the Plum Pudding model was wrong and proposed the *nuclear* structure of the atom. This followed his experiments on the scattering of alpha particles (helium nuclei) from very thin gold foil (1911).

Rutherford's observations were that about 98% of the alpha particles went through the gold foil as if it were not even there. About 2% of the alpha particles went through the foil but were deflected. About 0.01% of the alpha particles bounced off the foil.

"...it was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you had fired a 15–inch shell at a piece of tissue paper and it came back and hit you..."

- Rutherford, 1936

His conclusions were:

- Most of the alpha particles pass through the gold foil. The alpha particles did not hit anything. Therefore, the atom must be mostly empty space.
- A very few were deflected straight back. In these cases the alpha particles must be deflected by a very small, dense positive nucleus.

This led to Rutherford's Nuclear Model: The atom contains a tiny dense centre called the nucleus with volume about 1/10 trillionth the volume of the atom. The nucleus is essentially the entire mass of the atom. The nucleus is positively charged and contains positively charged particles in the nucleus called protons. The amount of positive charge of the nucleus balances the negative charge of the electrons. The electrons move around in the empty space of the atom surrounding the nucleus. But, experiments showed that atoms were much heavier than the mass of the protons in the nucleus. Since electrons are only 1/1836 of a proton mass they cannot account for the missing mass. Where does the rest of the mass come from?

2.4. Subatomic Particles

James Chadwick (1891–1974) established that the atomic nucleus contains additional particles with masses comparable to protons but with no electric charge – the neutron. Chadwick discovered the neutron in 1932. Table 2.1 shows the first three subatomic particles discovered:

| Particle | symbol | charge | mass, kg |
|----------|----------------|--------|---------------------------|
| Electron | e | _ | 19.1095×10 ⁻³¹ |
| Proton | \mathbf{p}^+ | + | 1.6726×10 ⁻²⁷ |
| Neutron | Ν | 0 | 1.6749×10 ⁻²⁷ |

Table 2.1. Subatomic Particles.

Elements are characterised by:

- An Atomic Number, Z, which is the number of protons in the nucleus which equals the number of electrons in the neutral atom. Z is unique for each element and constitutes the chemical identifier of the element, e.g. Hydrogen Z = 1, Gold Z = 79, etc.
- A Mass Number, A, which is the number of protons plus neutrons in the nucleus. Protons and neutrons are collectively termed nucleons.

Z and A are shown in symbols for nuclei (example is element Bromine) as ${}_{35}\text{Br}^{80}$ where the mass number is 80 and the atomic number is 35.

An isotope is an atom that has the same number of protons (atomic number) as other atoms of the same element but has a different number of neutrons and, therefore, a different Mass Number, A: *Example*: ${}_{35}\text{Br}^{80}$ and ${}_{35}\text{Br}^{81}$

A sub-atomic particle that makes up protons and neutrons is a Quark. Each proton and each neutron is composed of three Quarks. There are 6 types of Quark: Up, Down, Top, Bottom, Charm and Strange.

Atomic Scales

The nucleus is only about 10^{-15} m in diameter. The electrons move outside the nucleus at an average distance of about 10^{-10} m, therefore the radius of the atom is about 100,000 times larger than the radius of the nucleus. For comparison, a 10cm size nucleus would give a 10km diameter atom. Characteristic sizes of subatomic particles are: Neutrons and Protons $\approx 10^{-15}$ m, Electrons $\approx 10^{-18}$ m, Quarks $\approx 10^{-19}$ m.

2.5. Quantum Atomic Model 1: Electronic Shell Structure

Niels Bohr (1913) understood that the Rutherford model alone was not enough to describe the atom. Because the electrons are circling the nucleus, classical mechanics says that they must be continuously losing energy. But this would mean that their orbits would quickly decay and they would spiral down into the nucleus and the atom would collapse. Bohr's conclusion was that classical mechanics cannot describe the electronic structure of the atom and a new model was needed called a **Quantum Theory** model. The Bohr model of the atom was a first step in developing this.

The Bohr model stated that electrons can only occupy certain orbits or 'shells' in an atom. Each orbit represents a specific energy for the electrons in it. Only a limited number of orbits with certain energies are allowed. In other words, the orbits are quantized. The energy of the electron in an orbit is proportional to its distance from the nucleus. The further the electron is from the nucleus, the higher its energy. An electron can only change orbits by either gaining or losing energy:

- If it gains energy it moves to a higher shell, i.e. a shell further away from the nucleus;
- If it loses energy it moves to a lower shell, i.e. a shell closer to the nucleus

The energy absorbed or emitted when the electron moves from one orbit to another is equal to the difference between the energies of the shells.

A quantum or packet of light called a photon is absorbed by the electron when it jumps to a higher energy orbit and is emitted when the electron falls into a lower energy orbit. The energy of the light emitted or absorbed is exactly equal to the difference between the energies of the orbits. This enabled Bohr to interpret the lines that had been observed in the emission spectra of gases as formed by the transitions of electrons between various energy–levels inside the gas atoms.

The Quantum Model explains the Light Emission of Atoms, namely that each element emits its own light spectrum characteristic of its own unique electron structure. The Bohr atomic model explains this. Every electron dropping from a high to a low energy shell must emit a photon of fixed energy being the difference in energies between the shells. Because $\mathbf{E} = \mathbf{h} \mathbf{f}$ ($\mathbf{h} = \text{Planck's constant}$), \mathbf{f} , the frequency (thus the wavelength) is fixed to give the colour of the line in the spectrum. The colour of light emitted reflects the energy released in the fall of the electron between shells.

2.6. Quantum Atomic Model 2: Matter Both Wave and Particle

From classical mechanics we know that matter has kinetic energy $E = \frac{1}{2}mv^2$ and momentum p = mv (m = mass, v = velocity). In 1924, the French physicist, Louis de Broglie, proposed that, like light, particles of matter have both a particle nature and a wave nature connected through the de Broglie relations:

 $p = h/\lambda$

E = h f

where λ is the particle wavelength and f is the particle frequency.

This concept is called "the wave–particle duality of matter" and unites the physics of energy (wave) and matter (particle). It only becomes important at atomic or smaller dimensions. This theory was experimentally confirmed in 1927 when electrons fired at a crystal were shown to behave like waves.

2.7. Quantum Atomic Model 3: Particles Described by Wave Functions

In 1926, Austrian physicist Erwin Schrodinger published his quantum theory of "wave mechanics". In Newtonian mechanics a particle can be exactly described by its position X-Y-Z and momentum p = m v but, in wave mechanics, the position of a particle, e.g. an electron, in space and its movement

are described by two wave functions – a space wave function and a momentum wave function. The Schrodinger equation describes the quantum state of a physical system such as an atom:

 $\hat{H} \Psi = E \Psi$

Where Ψ = wave function of the particle, **E** = energy of the state Ψ , $\hat{\mathbf{H}}$ = the Hamiltonian operator corresponding to the total energy of the system. The important outcome of this equation is that its solution predicts the electronic structure of atoms as described by **orbitals** and **quantum numbers**.

2.8. Quantum Atomic Model 4: The Uncertainty Principle

In Newtonian mechanics a particle can be exactly described by its position X-Y-Z and momentum p = m v but, in 1927, German physicist Werner Heisenberg stated his Uncertainty Principle that because of the wavelike nature of particles it is impossible to exactly know both the location and the momentum of the particle. The more exact the location, the less you know of the momentum and vice versa. The wave function, Ψ , describes only the probability that a particle in a state described by a set of wave functions will have a specific position or momentum. It is not possible to determine the exact location of an electron in an atom, only the *probability* of finding an electron at a given position, the larger is the electron density at that position.

2.9. Quantum Atomic Model 5: Energy Levels and Orbitals

From Schrodinger and Heisenberg we have:

- The structure of an atom is described by Schrodinger's equation and Heisenberg's Uncertainty Principle
- Which predict that electrons move not in exact circular orbits, but in 'fuzzy' orbitals. We cannot tell exactly how an electron moves, but can only say what is the probability of finding it at some distance from the nucleus. The electron wave functions can form standing waves these are the **orbitals** of electrons in the atomic structure. Orbitals describe the region in space in which an electron is most likely to be found, i.e. the volume of high electron density. They each have a characteristic shape and energy. Schrodinger's solution of his equation says that only certain electronic probability density orbitals in atoms are allowed identified by **quantum numbers.** These are the only possible quantum states of an individual electron around an atom.

2.10. Quantum Atomic Model 6: Quantum Numbers

Three Quantum numbers $(\mathbf{n}, \mathbf{l}, \mathbf{m}_{\mathbf{l}})$ describe an orbital – their values are quantised, i.e. discrete and not continuous. Each orbital is defined by a different set of the three quantum numbers and contains a maximum of two electrons. These two electrons are differentiated by the 4th quantum number, \mathbf{m}_{s} , specifying electron spin within the orbital. Each orbital describes a specific distribution of electron probability density in space. Each orbital has a characteristic energy and shape. Orbitals are named in the form: nl^{x} (x = number of electrons in orbital). For example, the orbital $1s^{2}$ has two electrons and is the lowest energy level or shell in the atom (n = 1) and has an azimuthal quantum number of l = 0 (denoted by the letter 's').

Principal Quantum Number, n

The Principal Quantum Number, n, indicates the main energy level or electronic shell occupied by the electron. The allowed values of n are integers ranging from 1 to "n" ($1 \le n$), where "n" is the shell containing the outermost electron of the atom. For example, in cesium (Cs), the outermost valence electron is in the shell with energy level 6, so an electron in cesium can have an n value from 1 to 6. As n increases:

- the orbital becomes larger,
- the electron spends more time farther from the nucleus,
- the electron's energy increases,
- the electron is less tightly bound to the nucleus.

Angular Momentum Quantum Number, *l*

The Angular Momentum (Azimuthal) Quantum Number describes the sub-shell within the main n shell. It defines the shape of the orbital. The allowed values of l are integers ranging from 0 to n-1 ($0 \le l \le n-1$). The values of l are designated not by numbers but by letters: 0=s orbital, 1=p orbital, 2=d orbital, 3=f orbital. These letters are derived from the characteristics of their spectroscopic lines: sharp, principal, diffuse, and fundamental, further values of l being named in alphabetical order, g, h, i, etc. (omitting j).

Magnetic Quantum Number, m_l

The Magnetic Quantum Number, m_l , describes the electron's angular momentum orientation (hence the orbital orientation) in space. m_l defines the specific orbital occupied by the electron within the sub-shell. The allowed values of m_l are integers ranging from -l to +l including 0 ($-l \le m_l \le +l$).

Thus, the s sub-shell (ℓ =0) contains only one orbital, and therefore the m₁ of an electron in an s sub-shell will always be 0. The p sub-shell (ℓ =1) contains three orbitals so the m₁ of an electron in a p sub-shell will be -1, 0, or 1. The d sub-shell (ℓ =2) contains five orbitals, with m₁ values of -2, -1, 0, 1 and 2.

Spin Quantum Number, m_s

The Spin Quantum Number describes the spin of the electron within the orbital. It indicates the two opposite directions in which the electron can spin. Because an orbital never contains more than two electrons, the allowed values of m_s are either $-\frac{1}{2}$ or $+\frac{1}{2}$ corresponding to "spin anti–clockwise" and "spin clockwise".

Quantum Numbers – Rules and Values

An atomic electron orbital is uniquely identified by the values of the three quantum numbers, n, l and m_1 and each set of the three quantum numbers corresponds to exactly one orbital. The quantum number allowed value rules are summarized in the below Table 2.2 for the first 5 atomic electron shells, n=1 to 5.

Each cell in the table represents a sub-shell and shows the orbitals allowed in that sub-shell labelled with their m_l value. Thus, the n=1 shell has one sub-shell, l = 0, containing only one orbital, $m_l = 0$, while the n=5 shell has 5 sub-shells, l = 0 to 4, containing a total of 25 orbitals.

| | l=0 | l=1 | l=2 | l=3 | l=4 |
|-----|------|-----------|-------------------|---------------------------|-----------------------------------|
| n=1 | m1=0 | | | | |
| n=2 | 0 | -1, 0, +1 | | | |
| n=3 | 0 | -1, 0, +1 | -2, -1, 0, +1, +2 | | |
| n=4 | 0 | -1, 0, +1 | -2, -1, 0, +1, +2 | -3, -2, -1, 0, +1, +2, +3 | |
| n=5 | 0 | -1, 0, +1 | -2, -1, 0, +1, +2 | -3, -2, -1, 0, +1, +2, +3 | -4, -3, -2, -1, 0, +1, +2, +3, +4 |

| Sub-shell | s (<i>l</i> = 0) | p (<i>l</i> = 1) | d (<i>l</i> = 2) | f (<i>l</i> = 3) | g (<i>l</i> = 4) |
|-------------------------------------|----------------------|-----------------------------|----------------------|------------------------------|-----------------------------------|
| Orbitals (m _l values) | 0 | -1, 0, +1 | -2, -1, 0, +1, +2 | -3, -2, -1, 0, +1, +2, +3 | -4, -3, -2, -1, 0, +1, +2, +3, +4 |
| No. of orbitals $(2l+1)$ | 1 | 3 | 5 | 7 | 9 |

From the quantum number allowed value rules, it is seen that the number of

orbitals in each sub–shell = (2l + 1) as shown in Table 2.3. Table 2.3. The number of orbitals in each sub–shell = (2l + 1)

The shapes of electron orbitals are not exact because a particular electron, regardless of which orbital it occupies, can at any moment be found at any distance from the nucleus and in any direction due to the Uncertainty Principle. However, the electron is much more likely to be found in certain regions of the atom than in others so that a *boundary surface* can be drawn inside which the electron has a high probability to be found somewhere, and all regions outside the surface have low probability of finding the electron.

Orbital shapes are multiple and increasingly complex with increasing quantum numbers. All are symmetrical about a centre point containing the nucleus. At this point the probability of finding the electron drops to zero as the electron cannot be inside the nucleus of the atom – this point is called a node.



Figure 2.1. s-, p-, d- and f-orbital shapes (Fundamentals of Chemistry)

s-orbitals ($\ell = 0$): All s-orbitals have quantum numbers ℓ and $m_l = 0$. Thus, every atomic shell, n, contains one s-sub-shell ($\ell = 0$) containing one s-orbital ($m_l = 0$). All s-orbitals are spherically symmetric (see above figure).

As n increases, the orbital becomes larger, the electron spends more time further from the nucleus, the electron's energy increases and the electron is less tightly bound to the nucleus.

p – **orbitals** (l = 1): Because l = 1, p – orbitals are present in all shells except the n = 1 shell (see allowed values rule). Because l = 1 then $m_l = -1$, 0 or +1 so that each atomic shell (except n = 1) contains one p–sub – shell containing 3 p – orbitals, p_x , p_y , p_z . The orbitals are double – lobe shaped so that the electron density is distributed over opposite sides of the nucleus (see above figure).

Placing Electrons in Orbitals

The term 'electron configuration' refers to the arrangement of the electrons of an atom, i.e. the way electrons can be distributed in the orbitals. Two rules govern atomic electron distribution, the Pauli Exclusion Principle and the Madelung Rule.

In 1924, Austrian physicist, Wolfgang Pauli, formulated the Pauli Exclusion Principle which states that no two electrons can exist in the same quantum state, i.e. no two electrons in an atom can have the same set of four quantum numbers n, l, m_l and m_s . Since m_s is not needed to specify an orbital and can take either of two values this implies that an orbital can hold a maximum of two electrons but they must have opposite spins, $-\frac{1}{2}$ and $+\frac{1}{2}$.

The Madelung Rule governs the order of electron placing. A maximum of two electrons are put into orbitals in order of increasing orbital energy: the lowest–energy orbitals are filled before electrons are placed in higher–energy orbitals. This principle is expressed in the **Madelung Rule**:

- Orbitals are filled in order of increasing n + 1
- Where two orbitals have the same value of n + 1, they are filled in order of increasing n, i.e. lowest n first

The Rule is an approximation which cannot fully account for all the very complex electron interactions within an atom so there are exceptions to the Rule among the heavier elements with many electrons.

The Pauli Exclusion Principle and the Madelung Rule gives the following order for filling the orbitals: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p.

2.11. From Electron Configuration to the Periodic Table of the Elements

The link between material properties and atomic and molecular structure is a central theme in chemistry. The Periodic Table formalises the connections between the properties of the elements and their electron configurations. The Periodic Table of the chemical elements is a tabular display of the chemical elements providing a useful framework to classify, systematise, and compare all of the many different forms of chemical behavior. Although there were previous versions, its invention is generally credited to Russian chemist Dmitri Mendeleev in 1869, who intended the table to illustrate recurring ("periodic") trends in the properties of the elements. It contains 118 elements to date, 94 are found naturally on Earth, and the rest are synthetic elements produced artificially in particle accelerators.

To construct the Table elements are listed in order of increasing atomic number. The list is then divided into sections according to the value of principal quantum number, n, of the valence shell, i.e. the shell with the highest value of n in the atom. The valence shell electrons are on average furthest from the nucleus and are most often involved in chemical reactions.

The sections are then assembled as a table of rows with the n=1 row at the top and descending rows being in order of increasing n. The Table is then divided into blocks. Each block indicates the value of the azimuthal quantum number, l, of the last sub – shell that received an electron in building up the electron configuration. Thus, the table is divided into *s*-, *p*-, *d*- and *f*-*blocks*. The resulting Periodic Table 2.4 is schematically shown below:

Table 2.4. Electron Configuration mapped into the Periodic Table of the Elements



The Periodic Table displays the symbols and names of the elements along with information about the structure of their atoms.

Classifying the Elements

The Periodic Table can be divided into Groups, Periods and Blocks.

A Group is a vertical column in the Table. All elements in a group have the same number of valence electrons and Groups are the most important method of classifying the elements. Generally elements in a Group have very similar properties and exhibit a clear trend in properties down the group.

Examples are the alkali metals (Group 1), alkaline earth metals (Group 2), halogens (Group 17) and noble gases (Group 18).

A Period is a horizontal row in the Table as shown schematically below. All elements in a Period have the same number of shells (same n). The elements in a period are generally not alike in properties which typically change greatly across a row. However, in the d–block "transition metals" and the f–block "lanthanides" and actinides" this is not always true and here there are similarities and trends in properties like in Groups. The first element in a Period is always an extremely active solid. The last element in a Period is always an inactive, noble gas (Ball P., 2003).

The Table can also be classified into blocks. A Block is defined by the value of quantum number l of the sub-shell in which the "last" electron resides. Thus, the table is divided into *s*-, *p*-, *d*- and *f*-blocks. The s-block contains the alkali metals, the alkaline earth metals, hydrogen and helium. The p-block contains some metals, the metalloids and the non-metals. The d-block contains the transition metals. The f-block contains the rare earth metals. The elements can be grouped into three broad classes based on their general properties. The three classes of elements are Metals, Nonmetals, and Metalloids (also called semimetals). Across a period, the properties of elements become less metallic and more non-metallic (Scerri E., 2007) (Pauling L., 1989) (Pauling L., Pauling P., 1983).



3. Atomic Bonding in Solids

3.1. Some Atomic Quantities and Simple Calculations

Unified atomic mass unit or Dalton (Da) is the unit used to express mass on the atomic scale. 1 Da is defined as $1/12^{th}$ of the atomic mass of the most common isotope of carbon atom, the ${}^{12}C$ atom. The ${}^{12}C$ atom has 6 protons (Z=6) and six neutrons (N=6). The atomic mass of the ${}^{12}C$ atom is by definition 12 Da. Therefore, by definition, 1 Da \approx mass of a nucleon (proton/neutron). $M_{proton} \approx M_{neutron} \approx 1 \text{ Da} \approx 1.66 \text{ x } 10^{-27} \text{ kg}.$

The **Mole** (mol) is the unit of measurement for the amount of substance. A simple analogy to compare a dozen eggs with a mole of atoms. It is defined as the amount of any substance that contains the same number of elementary entities (atoms, molecules, ions, etc.) equal to the number of atoms in 12 grams of the isotope carbon – 12 (¹²C). The number of entities in 1 mol is the Avogadro constant, $N_A \approx 6.022 \times 10^{23}$ entities per mole. From the Da and mol definitions, **Mole** is the number of entities that have a mass in grams equal to the atomic mass in Da of the entity (e.g. atom). For example, a mole of ¹²C has mass of 12 grams. 1 Da/atom = 1 gram/mol; Atomic mass of iron = 55.85 Da/atom = 55.85 g/mol.

Some simple calculations: Calculate the number of atoms per cm^3 , n, for material of density d (g/cm³) and atomic mass M (g/mol):

 $n = N_A \times d \; / \; M$

Graphite (carbon):

d = 2.3 g/cm³, M = 12 g/mol \Rightarrow n = 11.5 × 10²² atoms/cm³. **Diamond** (carbon):

d = 3.5 g/cm³, M = 12 g/mol \Rightarrow n = 17.5 × 10²² atoms/cm³. Water (H₂O):

 $d = 1 \text{ g/cm}^3$, $M = 18 \text{ g/mol} \Rightarrow n = 3.3 \times 10^{22} \text{ molecules/cm}^3$.

For material with $n = 6 \times 10^{22}$ atoms/cm³ we can calculate the mean distance between atoms $L = (1/n)^{1/3} = 0.25$ nm. Thus, we see that the scale of atomic structures in solids is a fraction of 1 nm, namely a few Angstroms, Å.
3.2. Bond Formation

An atomic chemical bond is an attraction between atoms which forms chemical substances, i.e. materials with a definite chemical composition, containing two or more atoms which can be elements (diamond) or compounds (water).

Bonding is caused by the electrostatic force of attraction between opposite charges, either between electrons and nuclei or by dipole attraction. The Potential energy vs. Separation plot for two atoms of the below figure shows a Potential Energy minimum. Such a minimum implies a stable system of two bound atoms in typical potential well.





The cause of the Repulsion between atoms brought close together is relatively simple. It is related to the Pauli principle (no two electrons can exist in the same quantum state, i.e. have same set of quantum numbers). When the electronic clouds surrounding the atoms start to overlap, the energy of the system increases abruptly thus giving rise to repulsion. The nature of the attractive part, dominating at large distances, is complex and depends on the particular type of bonding, ionic, covalent, etc.

As seen from the above figure, a potential energy (U) well gives rise to a bonding force:

F = - dU/dr

For a system of two atoms (diatomic molecule), force depends only on the distance between the two atoms r_{12} .

The energy unit convenient for description of atomic bonding is the electron volt (eV) which is the energy, E, lost or gained by an electron when it is taken through a potential difference of one volt. To determine this energy value in Joules we can use:

 $E = q \times V$

For the electron, the charge, $q=1.6 \times 10^{-19}$ Coulombs so that for a potential difference V=1 volt, 1 eV=1.6 x 10^{-19} J. The electron volt is a more convenient unit of energy than the Joule in the atomic context.

The electronic structure of atoms largely defines the nature of their chemical interaction between each other. Thus, filled outer/valence shells result in a stable configuration as in noble inert gases, He, Ne, Ar, Kr, Xe, Rn. Atoms with incomplete outer shells strive to reach this noble gas configuration by sharing or transferring electrons among each other for maximal stability – strong "primary" bonding results from this electron sharing or transfer.

Electronegativity is a measure of how willing atoms are to accept electrons. Subshells with one electron, e.g. Group IA, have low electronegativity. Subshells with one missing electron, e.g. Group VIIA, have high electronegativity. Elements with filled Subshells, e.g. Group 0, tend to be chemically inert. Electronegativity increases from left to right in the Periodic Table. Metals are electropositive in that they readily give up their few valence electrons to become positively charged ions (Forest J., 1967).

3.3. Types of Bonding

Primary bonds are typically between atoms to create molecules, e.g. Na^+Cl^- , and between atoms and/or molecules to create bulk matter, e.g. metallic bonding of Cu atoms to form copper crystal, ionic bonding of Na^+Cl^- to form common salt crystal.

Secondary bonds are typically between molecules to form bulk matter, e.g. Primary covalently bonded H_2O molecules undergo Secondary hydrogen bonding to form liquid water.

In Primary bonding, electrons are transferred or shared between atoms. Primary bonding is strong bonding with typical bond energies 100-1000 kJ/mol or 1-10 eV/atom. The types of primary bonding are:

• Ionic: This bond type is due to the strong Coulomb interaction between negative atoms (have an extra electron each) and positive atoms (lost an electron). Example – common salt Na⁺Cl⁻ molecule.

- Covalent: In this bond electrons are shared between the molecules • in order to fill the shell and saturate the valency. Example – hydrogen H_2 molecule.
- Metallic: In this bond all the atoms are ionized through losing electrons ٠ from the valence band. These free electrons form an electron sea which binds the charged nuclei in place.

In Secondary Bonding no electrons are transferred or shared. Bonding is due to the interaction of atomic/molecular dipoles. They are a weak bond with typical bond energies < 100 kJ/mol or < 1 eV/atom.

The types of secondary bonding are:

- Permanent dipole bonds between polar molecules such as H₂O, HCl
- Polar molecule-induced dipole bonds where a polar molecule induces • a dipole in a nearby non-polar atom/molecule and the two dipoles then bond
- Fluctuating Induced Dipole where constantly changing electrostatic • charge distributions generate dipoles which then interact to bond. *Examples* are inert gases, H₂, Cl₂
- We will now look at these bonding types in more detail. •

Primary Bonding–Ionic

Ionic Bonding is typical for elements that are situated at the ends of the Periodic Table. Atoms from the left of the table (metals) give up their valence electrons to the (non-metallic) atoms from the right of the table which get electrons to fill their outer shell and acquire stable or noble gas electron configuration. Electron transfer thus means mutual ionization. The atom giving up electron(s) becomes a positively charged ion (cation) while the atom accepting electron(s) becomes a negatively charged ion (anion). The ions are attracted by strong Coulomb interaction where oppositely charged ions attract each other to create atomic bonding. An ionic bond is non-directional, ions may be attracted to one another in any direction.

As an example, let us look at the formation of common salt, NaCl:

Na has 11 electrons, 1 more than needed for a full outer shell (Neon)

11 Protons Na
$$1s^2 2 s^2 2p^6 3s^1$$

11 Protons Na⁺ $1s^2 2 s^2 2p^6$

donate
$$e^- =>$$

Cl has 17 electrons, 1 less than needed for a full outer shell (Argon).

17 Protons Cl 1s² 2 s² 2p⁶ 3s² 3p⁵ receives
17 Protons Cl⁻ 1s² 2 s² 2p⁶ 3s² 3p⁶
$$e^- => 18 e^-$$

This electron transfer from Sodium to Chlorine reduces the energy of the total system of atoms, i.e. electron transfer is energetically favourable. As a consequence of the electron transfer, the Na atom shrinks and the Cl atom expands. The strong electrostatic attraction between the positively charged Na+ ions and the negatively charged Cl– atoms along with Na+ to Na+ and Cl– to Cl– repulsion results in the final NaCl crystal structure arranged so that each Na⁺ ion is surrounded by Cl– ions and each Na+ ion is surrounded by Cl– ions. Any mechanical force that tries to disturb the electrical balance in an ionic crystal meets strong resistance: ionic materials are strong but brittle. The potential energy, U, vs. interatomic distance, r, curve of the below figure shows how the ionic bond is formed:



Figure 3.2. Potential energy U vs. Interatomic distance r

The attraction between atoms is the Coulomb interaction between charges of opposite sign:

Energy: $U_A = A/r$

The force of repulsion between the bonding atoms is due to the overlap of their electron clouds at close distances (Pauli principle):

Energy: $U_R = B/r^n$

So that the total net energy of the bond is net energy:

 $U = U_A + U_R = A/r + B/r^n$

This relation gives a Potential Energy vs. Inter-atomic Distance curve containing an energy well which, in turn, gives an optimum or most probable inter-atomic distance for equilibrium between two ionically bound atoms as shown in the figure.

Primary Bonding – Covalent

In covalent bonding electrons are shared between the molecules to saturate the valency. Covalent bonding is the cooperative sharing of valence electrons to fill shells. Electrons are not transferred, as in ionic bonding, but are localized between the neighbouring ions and form a highly directional bond between them. The ions repel each other, but are attracted to the electrons that spend most of the time in between the ions. The formation of covalent bonds is described by orbital overlap, highly directional bonds directed to the extent of greatest orbital overlap of the electron clouds. An atom can have at most (8-N') covalent bonds where N'= number of valence electrons.

Examples:

- The Cl₂ molecule: $Z_{Cl}=17 (1s^2 2s^2 2p^6 3s^2 3p^5)$; N' = 7, (8–N') = 1 \rightarrow can form only one covalent bond generating the chlorine gas molecule
- The Carbon atom: $Z_C = 6 (1s^2 2s^2 2p^2)$: N' = 4, (8–N') = 4 \rightarrow can form up to four covalent bonds generating different carbon materials such as diamond and graphite

Due to its directionality, the potential energy of a system of covalently interacting atoms depends not only on the distances between atoms but also on angles between bonds.

Primary Bonding – Metallic

In metallic bonding valence electrons are detached from atoms and spread in an 'electron sea' that "glues" the positive ions together. A metallic bond is non-directional and atoms pack closely. The bonds do not break when atoms are rearranged which means that metals can undergo large plastic deformation making them ductile (can be stretched into thin wires) and malleable (can be hammered into this sheets).

Examples of typical metallic bonding are the metals Cu, Al, Au, Ag. Transition metals (Fe, Ni, etc.) form mixed bonds being a combination of metallic and covalent bonds. The result is that transition metals are more brittle (less ductile) than pure metallic bonding materials.

3.4. Secondary Bonding

Secondary Bonding results from the interaction of atomic or molecular dipoles. An electric dipole is a pair of equal positive and negative charges separated by a small distance. Dipoles arise in a molecule where atoms share an electron but the electron spends more time with the highly electronegative atom. Bonding between dipoles happens when the positive end of one dipole is attracted to the negative end of another dipole. Since the effective charges are small compared with those involved in primary bonding, secondary bonding is about one tenth of primary bond strengths. Secondary bonds are weak but very important, e.g. formation of water, with bonding energies $\sim 0.1 \text{ eV}/\text{atom or } \sim 10 \text{ kJ/mol}$.

There are two types of dipole bonding namely Permanent Dipole Bonding and Induced Dipole Bonding:

Permanent dipole bonds:

These exist in **polar molecules** due to the permanent asymmetrical arrangement of positively and negatively charged regions within the molecule (e.g. HCl, H_2O). Permanent dipole bonds between adjacent polar molecules are the strongest among secondary bonds.

Hydrogen bonding is the most common type of bonding between permanent molecular dipoles. Hydrogen is electropositive (wants to give an electron). Bonding between a Hydrogen atom and a more electronegative atom, A, will bind the Hydrogen electron more strongly to the other atom thus creating a molecule A^-H^+ with a permanent dipole (a partially exposed proton) that can interact with other dipoles nearby to form a chemical bond.

An example is the hydrogen bond in water, H_2O . The Oxygen atom binds electrons from both Hydrogen atoms more tightly than Hydrogen can. This creates a molecular dipole. The H end of the molecule is positively charged and can bond to the negative side of another H_2O molecule (the O side of the H_2O dipole). "Hydrogen bond" is, thus, a secondary bond formed between two permanent dipoles in adjacent molecules. Hydrogen bonding is one of the major forces responsible for the attraction between chains in polymers.

Induced dipole bonds:

These are often called Van der Waals forces / bonding. They can be categorised into two types. Firstly, permanently polar molecules can induce dipoles in adjacent non-polar molecules and a bond is formed due to the attraction between the permanent and induced dipoles.

Secondly, even in electrically symmetric molecules/atoms, an electric dipole can be created by fluctuations in electron density distribution. The fluctuating electric field in atom A is felt by the electrons of an adjacent atom B and induces a dipole moment in this atom. This bond, due to fluctuating induced dipoles, is the weakest. *Examples* of this type of bonding are the inert gases, H₂ and Cl₂.

The melting temperature of a material is a measure of the atomic and molecular bond strengths binding the material together. Thus, materials with primary bonding tend to have high melting temperatures, e.g. MgO (ionic) at 2800°C, diamond (covalent) at >3550°C and iron Fe (metallic) at 1538°. Materials with secondary bonding have far lower melting temperatures, e.g. chlorine Cl_2 (van der Waals) at -101°C and water H_2O (hydrogen) at 0°C.

3.5. Bonding in Real Materials

We can classify materials according to the way the atoms are bound together. Some important material classes are:

- **Metals:** Metal bonding is through valence electrons being detached from atoms and spread in an 'electron sea' that "glues" the ions together. Metals are strong, ductile, conduct electricity and heat well, are shiny if polished.
- Semiconductors: Semiconductor bonding is covalent or ionic plus covalent mixed primary bonding. Their electrical properties depend strongly on minute proportions of contaminants. *Examples* are Si, Ge, GaAs.
- **Ceramics:** Ceramics are ionic and covalent mixed primary bonding. They are usually combinations of metals or semiconductors with oxygen, nitrogen or carbon (oxides, nitrides, and carbides). Hard, brittle, insulators. *Examples* are glass, porcelain.
- **Polymers:** Polymers are bound by covalent forces and also by weak van der Waals forces and are usually based on C and H. They decompose at moderate temperatures (100–400 C), and are lightweight. *Examples* are plastics and rubber.

In many materials more than one type of bonding is involved, e.g. ionic and covalent in ceramics, covalent and secondary in polymers, covalent and ionic in semiconductors.

4. How Atoms Arrange Themselves to Form Solids

There are four Primary States of Matter, solid, liquid, gas and plasma.

Gases comprise atoms or molecules that do not bond to one another over a range of pressure, temperature and volume. Gas atoms/molecules have no particular order (disordered) and have no fixed shape or volume unless confined to a container when they take its shape and volume. Gases are not rigid and are highly compressible.

Liquids comprise atoms or molecules held firmly but not rigidly together by inter–molecular bonds. Liquid atoms/molecules are disordered. Liquids have no fixed shape but do have a fixed volume. They are not rigid and only slightly compressible at high pressures.

Solids consist of atoms or molecules executing thermal motion about an equilibrium position fixed at a point in space. Solids have stronger bonds between molecules and atoms than liquids and require more energy to break the bonds. Solid atoms/molecules are generally ordered ranging from strong and long range to weak and short range. Solids have fixed shape and volume and are rigid and only very slightly compressible under very high pressures (Forest J., 1967).

4.1. Types of Solids – Degree of Crystallinity

Crystallinity refers to the degree of structural order in a solid. An ordered region is a spatial volume in which atoms or molecules have a regular geometric arrangement or periodicity. In crystalline material atoms/molecules self–organise in a periodic way so that the atoms or molecules are arranged in a definite, repeating pattern in three dimensions. The reason for atoms/molecules assembling into ordered structures is that such structures, i.e. crystal arrangements, minimises the energy of the system and, thus, are energetically preferred.

Each of the three types of solids, crystalline (single crystal), polycrystalline and amorphous, is characterised by the size of the ordered region within the material.

Single Crystals

Single crystals have a high degree of order, or regular geometric periodicity, throughout the *entire volume of the material*. A single crystal has an atomic structure that repeats periodically across its whole volume. Even at infinite length scales, each atom is related to every other equivalent atom in the structure by translational symmetry.

Polycrystalline

Polycrystal is a material made up of an aggregate of many small single crystals called **crystallites** or **grains.** Polycrystalline material has a high degree of order over many atomic or molecular dimensions within the grains but not over the entire material/system. These ordered, single crystal regions, the grains, vary in size and differ in crystallographic orientation with respect to one another. Where the grains meet there is atomic mismatch so that the atomic order varies from one grain to the next – these regions where the grains meet are called **grain boundaries**. The grains are usually 100 nm–100 microns in diameter; Polycrystals with grains that are <10 nm in diameter are called nanocrystalline.

Amorphous

Amorphous (Non-crystalline) solids are disordered and have no systematic atomic arrangement. They are composed of randomly orientated atoms, ions or molecules that do not form defined patterns or lattice structures. Amorphous materials have order only within a few atomic or molecular dimensions. Amorphous materials do not have any long-range order, but they have varying degrees of short-range order. *Examples* of amorphous materials include amorphous silicon, plastics and glasses. Amorphous silicon is used in solar cells and thin film transistors.

4.2. Crystal Structures – Crystallography

Crystallography is the branch of science that deals with the geometric description of crystals and their internal arrangement. The symmetry of a crystal has a profound influence on its properties. Crystal structures are classified into different types or **crystal systems** according to the symmetries they possess. A crystal's structure and symmetry determine many of its properties such as cleavage (tendency to split along certain planes), electronic band structure, strength, stiffness and optical properties.

Symmetry

An object or function is symmetrical if a spatial transformation of it looks identical to the original. A 'symmetry operation' is an operation that leaves the crystal and its environment invariant, i.e. it is an operation performed on an object or pattern which brings it to a position which is absolutely indistinguishable from the old position.

In crystals two symmetry operations are particularly important. Firstly is Rotational symmetry – rotation by a specific angle (e.g. 60° , 90° , 120° , 180°) which brings it to a position indistinguishable from the old position.

In rotational symmetry the Axis of symmetry is a line about which the structure is rotated and the number of 'folds' is the number of times of rotation through the given angle which restores the structure, i.e. brings it back to its *original* position not just to a position indistinguishable from the old position.

The second symmetry operation of importance is Mirror symmetry. This is reflection across a plane which brings it to a position indistinguishable from the old position.

Hard Sphere Model and the Lattice

The Hard Sphere Model of crystals assumes that atoms are hard spheres with well–defined diameters that touch. We can select an atom or group of atoms that are repeated throughout the structure to form the entire crystal. This is called the **Basis.** We can then replace each basis in the crystal by a representative virtual point. The entire array of these virtual points is the crystal **Lattice**. Lattice points do not necessarily lie at the centre of atoms but are virtual points anywhere in space which represent the basis. The crystal lattice plus the basis constitute the entire crystal structure – Lattice + Basis = Crystal.

4.3. The Unit Cell.

The lattice points can define the key and distinguishing unit of the crystal called the **unit cell** which is the simplest repeating structural unit of the crystal. Translational repetition of the unit cell reproduces the whole crystal. The Unit cell is the simplest portion of the crystal which is repeated and shows the full symmetry of the crystal.

The lattice concept allows us to define seven unique Crystal Systems according to their possession of required symmetries (they may have other symmetries as well but these do not determine system classification). The seven unique Crystal Systems are defined by a required set of rotation and reflection (mirror) symmetries as shown in the following Table:

| Crystal System | Required Symmetries |
|----------------|--|
| Triclinic | None |
| Monoclinic | 1 twofold axis of rotation or 1 mirror plane |
| Orthorhombic | 3 twofold axes of rotation or 1 twofold axis of rotation and two mirror planes |
| Tetragonal | 1 fourfold axis of rotation |
| Trigonal | 1 threefold axis of rotation |
| Hexagonal | 1 sixfold axis of rotation around centre axis |
| Cubic | 4 threefold axes of rotation along cube diagonals |

Table 4.1. The Crystal Systems - their Symmetry

The crystal systems are also characterised by the geometry of the crystal lattice. We define the geometry of the lattice by lattice parameters comprising lengths of the 3 sides (a, b, c) and angles between the sides (α , β , γ) as per the following diagram:



Figure 4.1. Lattice parameters (The LibreTexts libraries)

Thus, the seven crystal systems are characterised by the lattice parameters as shown in the following figure:



Figure 4.2. 7 Crystal systems characterised by lattice parameters (InTechOpen)



Such parameters are reflected in the crystal shapes:

Figure 4.3. Three crystals of Cubic Pyrite FeS₂ (Pinterest)

4.4. Polymorphism and Allotropy

Some materials may exist in more than one crystal structure, this is called **polymorphism**. If the material is an elemental solid, it is called **allotropy**. An example of allotropy is carbon, which occurs in three crystalline forms – diamond, graphite and large, hollow fullerenes. Two kinds of fullerenes are buckminsterfullerene and carbon nanotube.

4.5. Solid Earth Materials

Earth's Molten Stage – During the early formation of the Earth it was molten and the heavier elements, such as iron and nickel, sank to the deep interior of the Earth. This left a thin layer of lighter materials on the surface called the **crust**. The majority of the Earth's mass lies below the crust. Eight elements make up 98.6% by weight of the solid materials of the Earth's crust, namely Oxygen 46.6%, Silicon 27.7%, Aluminum 8.1%, Iron 5.0%, Calcium 3.6%, Sodium 2.8%, Potassium 2.6%, Magnesium 2.1%.

Minerals and Rocks

The eight elements together with minor (by weight) other elements making up the solid materials of the Earth's crust combine to form minerals and rocks. A **mineral** is a solid inorganic material of the Earth that has both a known chemical composition and a crystalline structure that is unique to that mineral. A **rock** is a solid aggregate of one or more minerals that have been cohesively brought together by a rock–forming process. Elements are chemically combined to form minerals. Minerals are physically combined to form rocks. Minerals can be classified into silicates and non–silicates.

Minerals – Silicates

Silicates are made of silicon and oxygen and are the largest and most important class of rock–forming minerals constituting approximately 92% of the Earth's crust. Sand and Portland Cement are silicates. The basic structural unit or building block of all silicate minerals is the silicon tetrahedron in which one silicon atom is surrounded by and bonded to (i.e. coordinated with) four oxygen atoms, each at the corner of a regular tetrahedron:



Figure 4.4. Structure of Silicate Block (SiO₄)^{4–} (Geology Cafe)

These SiO_4 tetrahedral units can share oxygen atoms and be linked in a variety of ways, which results in different structures:



Figure 4.5. The topology of $(SiO_4)^{4-}$ based structures (Geology Cafe)

The topology of these structures forms the basis for silicate classification. Silicates can be structured as:

- Isolated tetrahedrons Isolated silicon–oxygen tetrahedral (shown above and in A below) do not share oxygens. This structure occurs in the mineral olivine.
- Chain silicates Single chains of tetrahedral (shown above and in B below) are formed by each silicon ion bonding exclusively to two oxygens and also sharing two other oxygens with other silicon ions. This structure occurs in augite. Double chains of tetrahedral (shown above and in C below) are formed by silicon ions sharing either two or three oxygens. This structure occurs in hornblende.
- Sheet silicates The sheet structure (shown in D below), in which each silicon shares three oxygens, occurs in the micas resulting in layers that pull off easily because of cleavage between the sheets.
- Framework silicates 3–dimensional network of (SiO₄)^{4–} building blocks in which all oxygen atoms are shared between two SiO₄^{4–} tetrahedrons, e.g. quartz.

Silicates can chemically combine with other elements:

Ferromagnesian Silicates – These compounds are made of iron, magnesium and silicates. They have higher density and darker color than other silicates due to the presence of iron and magnesium, e.g. augite, hornblende, biotite.

Non–ferromagnesian Silicates – These are silicates that do not contain either iron or magnesium. They have lower density and lighter color than the ferromagnesian silicates, e.g. mica, orthoclase, quartz.



Figure 4.6. Structure of Silicates (Geology Cafe)

Minerals – Non–silicates

Non–silicates make up \sim 8% of the Earth's crust. Principal non–silicate minerals are:

- Carbonates a salt of carbonic acid characterized by the presence of the carbonate ion $\text{CO}_3^{2^-}$
- Sulphates a polyatomic anion with the empirical formula $SO_4^{2^-}$
- Oxides a chemical compound that contains at least one oxygen atom and one other element in its chemical formula
- Sulphides an inorganic anion of sulphur with the chemical formula S^{2-}
- Halides a binary compound, of which one part is a halogen atom and the other part is an element or radical
- Native elements elements that occur in nature in uncombined form with a distinct mineral structure, e.g. gold, carbon, silver, tin, copper, iron.

5. Chemistry of Ceramics

Ceramics are inorganic, non-metallic solid compound materials composed of more than one element (e.g. Al_2O_3) comprising metal, non-metal or metalloid atoms primarily held in ionic and covalent bonds. Usually they are metal oxides (compounds of metallic elements, especially Si, and oxygen), but many (especially advanced ceramics) are compounds of metallic elements and carbon, nitrogen or sulphur.

In atomic structure they are crystalline (ranging from highly oriented to semi–crystalline) although they also may contain a combination of glassy and crystalline phases. Most ceramics are polycrystalline materials with abrupt changes in crystal orientation or composition across each grain in the structure.

Ceramics are formed by the action of heat and subsequent cooling. *Examples* of Ceramics are:

- Carbides such as silicon carbide, SiC and tungsten carbide, WC
- Oxides, such as aluminium oxide (alumina), Al₂O₃; zirconium oxide (zirconia), ZrO₂; quartz silicon dioxide, SiO₂
- Nitrides, such as silicon nitride, Si₃N₄.
- Other ceramic materials, including many minerals, have complex and even variable compositions, e.g. the ceramic mineral feldspar, one of the components of granite, has the formula KAlSi₃O₈

The term *ceramic* is, thus, used to describe a broad range of materials that are soft as clay or hard as stone and concrete. Clay is used to produce ceramic pottery but many different ceramic materials are used in domestic, industrial and building products. This class of materials is so broad that it is often easier to define ceramics as all solid materials, except metals and their alloys, made by the high–temperature processing of inorganic raw materials.

Glass–Ceramics is a class of materials that is considered a type of ceramic. However, glasses and ceramics differ in that ceramics have a crystalline structure while glasses contain impurities that prevent crystallisation and are amorphous. Ceramics tend to have high, well–defined melting points, while glasses tend to soften over a range of temperatures before becoming liquids. Most ceramics are opaque to visible light while glasses tend to be translucent. But, some materials are intermediate between ceramic and glass and, thus, fall into the glass–ceramic classification. Glass–ceramics have a structure that consists of many tiny crystalline regions within a noncrystalline matrix. This structure gives them some properties of ceramics and some of glasses. Fabrication of a glass–ceramic involves use of conventional techniques for preparing a glass. The glass product is then heated to 750–1150 °C until a portion of the structure is transformed into a fine–grained crystalline material. Glass–ceramics are at least 50% crystalline after they have been heated. In some cases, the final product is more than 95% crystalline.

Examples of glass-ceramics are:

- MgO, Al₂O₃, SiO₂ all insulators with high mechanical strength at high temperatures, e.g. spark plugs
- CaSiO₃, CaMgSi₂O₆, CaAl₂Si₂O₈ wear resistant building materials
- Li₂Si₂O₅ resistant to thermal shock

Some materials, e.g. SiO_2 , can take the form of either crystalline ceramic as quartz or of amorphous glass. Glass–ceramics are more resistant to thermal shock (used in cookware), expand less when heated than most glasses (used in windows, for stoves, as radiant glass–ceramic cooker top surfaces) and slightly better at conducting heat than conventional glasses (as more crystallographic).

Some materials are stronger at high temperatures than glasses thus, for example, glass–ceramic $MgO-Al_2O_3-SiO_2$ is used to make electrical insulators that have to operate at high temperatures, e.g. spark plug insulators.

5.1. Bonding + Structure = Properties

Two characteristics of ceramics are responsible for their wide range of properties:

- Chemical Bonding
- Crystal Structure

Chemical Bonding

Underlying many of the properties found in ceramics are the strong primary bonds that hold the atoms together and form the ceramic material. The primary chemical bonds in ceramics are of two types:

Ionic = transfer of bonding electrons from electropositive atoms (cations) to electronegative atoms (anions).

Covalent = orbital sharing of valence electrons between the constituent atoms or ions.

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Ceramic bonds are mixed, ionic and covalent, with a proportion that depends on the particular ceramic. The degree of ionic character of the ceramic chemical bonding is given by the difference in electronegativity between the cations (+) and anions (-), i.e. the difference in potential to accept or donate electrons. The larger the electronegativity difference between anion and cation, the more nearly ionic is the bonding, i.e. the more likely electrons are transferred to form positively charged cations and negatively charged anions. Conversely, small differences in electronegativity lead to a sharing of electrons, as in covalent bonds. Very ionic crystals usually involve cations which are alkalis or alkaline–earths (first two columns of the Periodic Table) and oxygen or halogens as anions. It is the primary bonds in ceramics that make them among the strongest, hardest and most refractory materials known.

Crystal Structure

Covalent bonds are highly directional in nature, often determining the types of crystal structure possible. The greater the number of electrons being shared, the greater is the force of attraction, i.e. the stronger the covalent bond. Ionic bonds are entirely non-directional. This non-directional nature allows for closest **hard-sphere packing** of the ions into a variety of crystal structures subject to two building criteria:

- 1. Achieve closest packing
- 2. Maintain electrostatic charge neutrality

Achieving Closest Packing:

A long-term stable material is in a state of potential energy minimum. The condition for minimum energy implies maximum attraction and minimum repulsion. This requires contact, i.e. configurations where anions have the highest number of cation neighbours and vice-versa. The **coordination number** (**CN**) of an atom in a crystal is the number of its near neighbours in contact.

The parameter determining contact is the relative size of the anions and cations, i.e. ratio of cation to anion radii, r_C/r_A . A Table, calculated by applying the geometry of spheres, gives the coordination number CN as a function of r_C/r_A . For example, in the NaCl structure, $r_C = r_{Na} = 0.102$ nm and $r_A = r_{Cl} = 0.181$ nm, so $r_C/r_A = 0.56$. The following Table implies that the NaCl coordination number is 6. If we indeed observe the crystal structure of salt we see that in sodium chloride each sodium ion has 6 chloride ions as nearest neighbours (at a distance of 276 picometres) at the corners of an octahedron and each chloride ion has 6 sodium atoms (also at a distance of 276 pm) at the corners of an octahedron. Thus, we have an octahedral structure with Coordination Number = 6.

| Radius Ratio | CN | Coordination |
|--------------|----|--|
| 1.0 | 12 | Cubic closest packed (CCP) Hexagonal closet packed (HCCP) |
| 1.0-0.732 | 8 | Cubic |
| 0.732–1.414 | 6 | Octahedral |
| 0.414–0.225 | 4 | Tetragonal |
| 0.225–0.155 | 3 | Triangular |
| < 0.155 | 2 | Linear |

Table 5.1. The coordination number CN as a function of r_C/r_A

Anions are usually larger and close–packed, as in the face–centred cubic (fcc) or hexagonal close–packed (hcp) crystal structures found in metals. Cations are usually smaller, occupying interstices, or spaces, in the crystal lattice between the anions.

Maintaining Electrostatic Charge Neutrality

The second limitation on the types of crystal structure adopted by ionically bonded atoms is based on a law of physics, namely that the crystal must remain electrically neutral. This law of electroneutrality results in the formation of very specific stoichiometries, i.e. specific ratios of cations to anions that maintain a net balance between positive and negative charge. Anions typically pack around cations, and cations around anions in order to eliminate local charge imbalance. This phenomenon is referred to as coordination and, again, is characterised by the coordination number. This charge balance dictates the chemical formula of the ceramic material.

The structure for ceramics with **general formula AX** is called 'rock salt' structure as common table salt (sodium chloride, NaCl) has this structure. An example of such ceramic is Cesium Chloride. Each ion is surrounded by eight immediate neighbours of the opposite charge, i.e. the central Cs⁺ cation is surrounded by eight Cl⁻ anions. This extremely efficient packing allows for local neutralization of charge and makes for stable bonding. Oxides that crystallize in this structure tend to have relatively high melting points. Magnesia MgO, for example, is a common constituent in refractory (materials retaining strength at high temperatures) ceramics.

The structure for ceramics with **general formula** AX_2 is called fluorite, after the mineral calcium fluoride (CaF₂). In this structure the anions are bonded to only four cations. Oxides with this structure are known for the ease with which oxygen vacancies can be formed. In zirconia (zirconium dioxide, ZrO₂),

for example, vacancies can be formed by **doping**, i.e. inserting ions of a different element into the composition to create oxygen–ion conductivity for electrical applications. The fluorite structure has much empty space, especially at the centre of the unit cell. Thus, urania (uranium dioxide, UO_2) is used as a fuel element in nuclear reactors as the empty space accommodates fission products to reduce unwanted swelling.

The structure for ceramics with **general formula ABX**₃ is called perovskite. In most cases the perovskite structure is cubic, that is all sides of the unit cell are the same. However, in barium titanate (BaTiO₃) the central Ti^{4+} cation can be induced to move off–centre, giving a non–cubic symmetry and creating an electrostatic dipole, i.e. alignment of positive and negative charges toward opposite ends of the structure. This dipole is responsible for the ferroelectric properties of barium titanate, in which neighbouring dipoles line up in the same direction. The enormous dielectric constants achievable with perovskite materials are the basis of many ceramic capacitor devices to store electric charge.

The non-cubic variations found in perovskite ceramics introduce the concept of anisotropy, i.e., an ionic arrangement that is not identical in all directions. In severely anisotropic materials there can be great variation of properties. These cases are illustrated by yttrium barium copper oxide (YBCO; chemical formula YBa₂Cu₃O₇). Its structure consists of three cubes, with yttrium or barium at the centre, copper at the corners, and oxygen at the middle of each edge with the exception of the middle cube which has oxygen vacancies at the outer edges. YBCO is a superconducting ceramic, i.e. loses all resistance to electric current at extremely low temperatures. The critical feature in this structure is the presence of two sheets of copper–oxygen ions, located above and below the oxygen vacancies, along which superconduction takes place. Transport of electrons perpendicular to these sheets is not favoured, making the YBCO structure severely anisotropic. One of the challenges in fabricating crystalline YBCO ceramics capable of passing large currents is to align all the grains in such a manner that their copper–oxygen sheets.

Crystal Structure in Silicate Ceramics

Oxygen and Silicon are the most abundant elements in the Earth's crust and their combinations, known by the generic name silicates, occur universally in rocks, soils, clays and sand.

The bond is weakly ionic, with Si⁴⁺ as the cation and O²⁻ as the anion, $r_{Si}=0.04$ nm, $r_{O}=0.14$ nm, so $r_{C}/r_{A}=0.286$. Our Table above gives silicates a coordination number of 4 and a tetrahedral coordination as shown in the following molecular schematic:



Figure 5.1. Three–dimensional schematic of a pure fragment of the regular silica structure. (InTechOpen)*

*(The structure is defined by several parameters; the Si–O bond length (d), the tetrahedral angle (φ), the inter–tetrahedral bond angle (α), and the bond torsion angles (δ 1, δ 2). G. S. Henderson, D. R. Baker, (eds, . Synchrotron, Earth. Radiation, Environmental, Sciences. Material, Short. Applications, Series. 3. Course, Association. Mineralogical, Canada. of, (2002)159–178. Henderson G. S., The Geochemical News, 113 113 October (2002), 13.)

The tetrahedron is charged: $Si^{4+} + 4O^{2-} \Longrightarrow (SiO_4)^{4-}$.

Many minerals are known that have the chemical composition SiO_2 . Silica minerals include quartz, tridymite, cristobalite, coesite, stishovite, etc. All silica minerals have structures consisting entirely of SiO_4 tetrahedra that share all of their oxygen atoms with adjacent tetrahedra. These minerals are not merely varieties of quartz but different minerals with different structures, different symmetry, different physical properties, etc., but all with the same composition (SiO₂). Minerals that have the same chemical composition but a different crystal structure are called polymorphs. The strong Si–O bonds lead to high melting temperatures (e.g. 1710°C) for these materials.

Silica polymorphs differ as to how the tetrahedra are arranged. In silica every oxygen atom is shared by adjacent tetrahedra. Silica can be crystalline (e.g., quartz) or amorphous, as in glass. Soda glasses melt at lower temperature than amorphous SiO₂ because the addition of Na₂O (soda) breaks the tetrahedral network. A lower melting point makes it easy to form glass to make, for instance, bottles. Bonding of adjacent SiO₄^{4–} ions is accomplished by the sharing of common corners, edges or faces. The presence in silicate compounds of cations such as Ca²⁺, Mg²⁺, & Al³⁺ maintain charge neutrality and ionically bond SiO₄^{4–} tetrahedra to each another.

5. Chemistry of ceramics

In layered silicates (e.g., clays, mica, talc) SiO_4 tetrahedra are connected together to form 2–D planes. These form units of $(Si_2O_5)^{2-}$. A net negative charge is associated with each $(Si_2O_5)^{2-}$ unit. Such units are bonded together to form a 'negative plane'. Such negative charge must be balanced by adjacent plane/s rich in positively charged cations to achieve electrostatic neutrality.

Faciliating the formation of layered silicate is the inclusion into the silica of cations K (potassium) and Al (aluminium) to form mica $KAl_3Si_3O_{10}(OH)_2$. Varying the cations changes the layer spacing. An example of a Layered Silicate is Kaolinite clay. This structure alternates each $(Si_2O_5)^{2-}$ layer with an $Al_2(OH)_4^{2+}$ layer. The layers meet and mix anions at the Anion Mid–plane. Adjacent sheets of this type are loosely bound to one another by Van der Waal's forces. Another example of a Layered Silicate is the clay Hectorite. It has a sheet–like structure with tetrahedra and octahedra centred on Al, Si or Mg and separated by cations Cs⁺ or K⁺.

5.2. Imperfections in Ceramics

Imperfections in Ceramics include Point defects and Impurities. Their formation is strongly affected by the condition of **charge neutrality** as creation of unbalanced charges requires large energy. Frenkel and Schottky **point defects** are charge neutral. The introduction of **impurity** atoms into the lattice is most probable where neutrality is maintained, thus:

- Electronegative impurities will replace a lattice anion
- Electropositive impurities will replace a lattice cation

The introduction of impurities is more likely when the impurity ionic radius is similar since this minimizes the energy required for lattice distortion. Point Defects will appear if the charge of the impurities is not balanced.

Point Defects can be either:

- Vacancies exist in ceramics for both cations and anions
- **Interstitials** exist for cations but are not normally observed for anions because anions are large relative to the interstitial sites

A *Frenkel–point defect* is a combination of defects, namely a vacancy plus an interstitial involving a pair of cations. Placing large anions in an interstitial position requires a lot of energy in lattice distortion so is not usually seen.

A *Schottky–point defect* is a pair of nearby cation and anion vacancies (Moffatt W.G., Pearsall G.W., Wulff J., 1968).



(Moffatt W.G., Pearsall G.W., Wulff J., 1968)

Impurities must maintain electro–neutrality (charge balance) in the crystal lattice. Impurities can be of two types: Substitutional cation impurity and Substitutional anion impurity.



(Moffatt W.G., Pearsall G.W., Wulff J., 1968)

5.3. Properties of Ceramics

Ceramic crystal structures and the chemical ingredients making up ceramics result in typical ceramic–like properties of: High mechanical strength; Low density compared with metals; Brittleness; Low chemical reactivity, do not react with most liquids, gases, alkalis and acids; Chemical durability against attack by oxygen, water, acids, bases, salts and organic solvents; Hardness, giving resistance against wear/abrasion; Low thermal conductivity, i.e. resistance to heat; Low thermal expansion; Low electrical conductivity as, unlike metals, there are no free electrons, all are tightly bound to ions; Refractoriness (high melting point). **Brittleness** – Unlike most metals, nearly all ceramics are brittle at room temperature, i.e. when subjected to tension they fail suddenly with little or no plastic deformation prior to fracture. Ceramics resist compression, but are much weaker to tensile stress especially applied as bending. High resistance to tensile stress requires that the stress be relieved by movement / slippage of planes in the crystal relative to each other. In ionic solids slippage is very difficult as too much energy is needed to move one anion past another anion (like charges repel) and the strong force of attraction between ions of opposite charge in the planes of the ions makes it difficult for one plane to slip past another. Exceptions to ceramic brittleness are some composite ceramics which contain whiskers, fibres or particulates that interfere with crack propagation. These can deliver toughness similar to metals.

5.4. Manufacture of Ceramics

Manufacture of Ceramics comprises two technologies: **Fabrication of the ceramic compound**, i.e. the crystal raw material and **Fabrication of specific solid parts** and pieces from the raw material, e.g. bricks, pottery, engineering parts.

Fabrication of a ceramic compound generally requires three components: Heat; Chemical reaction between selected elements and/or compounds as reagents; Cooling to achieve crystalline solid ceramic.

The element/compound reagents are carefully selected for their chemistry to produce the required reaction product (the ceramic). The reagents typically include low cost naturally occurring minerals, e.g. silica sand, clays. An example is the fabrication of the important grinding and cutting tool material Silicon Carbide SiC. The reagents are silica sand and graphite carbon. These are furnace heated to $1600-2500^{\circ}$ C and the reaction SiO₂ + C \rightarrow SiC + O₂ produces the ceramic.

Fabrication of specific solid parts is done from ceramic compounds in powder form. This is because ceramics cannot be easily shaped or reworked after formation as the materials are generally too hard and brittle. The shape of the piece must be defined using a mould before the powder raw material is 'fired' to produce the solid piece. Instead, ceramics are usually made from powders, which are moulded, consolidated and densified by sintering. Sintering is a process whereby powder particles bond and coalesce under heat, leading to shrinkage and reduction in porosity.

5.5. Applications of Ceramics

The following Table shows a general classification of ceramics by application/use.

Bonded Clay Ceramics are made from natural clays and mixtures of clays and added crystalline ceramics. Uses for these include whitewares, structural clay products, refractory ceramics, e.g. firebricks for furnaces and ovens.

Abrasive ceramics are either natural (e.g. garnet) or synthetic (e.g. silicon carbide, diamond, fused alumina, etc.). These are used for grinding, cutting, polishing, lapping or pressure blasting of materials.

Cements are used universally in construction to produce concrete roads, bridges, buildings, dams, etc.

Advanced Ceramics can be classified into:

- *Structural:* Wear parts, bio–ceramics, cutting tools, engine components (e.g. Alumina rotor and gears), armour
- *Electrical:* Capacitors, insulators, integrated circuit packages, piezo-electrics, magnets and superconductors
- Coatings: Engine components, cutting tools, and industrial wear parts.
- *Chemical and environmental:* Filters, membranes, catalysts, and catalyst supports.

| Uses of Ceramic Materials | | | | | |
|---------------------------|--|-------------|--------------|---|--|
| Clay products | Refractories | Abrasives | Cements | Advanced ceramics | |
| - whiteware | bricks for high Temperature (furnaces) | - sandpaper | - composites | engine rotors valves bearings | |
| - structural | | - cutting | - structural | - sensors | |
| | | - polishing | | | |

Table 5.2. Applications of Ceramics.

6. Chemistry of Glass

Glass is a state or form of matter with no fixed chemical formula. It is a product of fusion of very hot, molten materials that have cooled into a rigid condition without crystallising. The rigid condition is that of a super cooled liquid of infinite viscosity. Metals and metal alloys are almost always crystalline, but the existence of **metallic glasses** by ultra–fast cooling of metallic alloys shows that the glass–forming process applies to a huge range of materials. For example, hard candies / sweets made from molten sugar are in the glass state.

Thus, glass can be defined as an **amorphous** (non-crystalline) solid possessing an amorphous atomic-scale structure having no definite melting point but exhibiting a glass-liquid transition when heated towards the liquid state.

The glass-liquid transition (glass transition for short) is the reversible transition in amorphous materials from a hard and brittle state into a molten or rubber-like state. At high temperatures (used to prepare glass) the material is a viscous liquid. When glass is cooled from the hot molten state:

- It gradually increases in viscosity over a wide temperature range without crystallisation
- Until the atoms are locked into a random, disordered state before they can form crystals which process creates a super cooled liquid of infinite viscosity

The rate of cooling of molten material is controlled to prevent crystallisation and high strain. Glass is more like a liquid, but, at room temperature, it is so viscous that it behaves like a solid. At room temperature glass has the amorphous structure of a frozen liquid. At higher temperatures glass gradually becomes softer and more like a liquid, which allows glass to be poured, blown, pressed and moulded into a huge variety of shapes.

Typically, bonding in glasses is covalent and ionic–covalent, often with SiO_2 as a fundamental building block. The most widely used and oldest types of glass are based on the chemical compound silica (silicon dioxide), the primary constituent of sand. Most glasses contain a metal oxide fused with silica. Porcelains and many polymer thermoplastics in everyday use are glasses also.

6.1. Constituents of Manufactured Glass

The making of glass involves three basic types of ingredients: formers, fluxes and stabilisers. The glass former is the key component in the structure

of a glassy material. The former used in most glasses is silica (SiO₂). Pure silica is difficult to melt because of its extremely high melting point $(1,723 \,^{\circ} C)$ but **fluxes** are added to lower the melting temperature to 800–900 $\,^{\circ}C$. Standard fluxes are soda (Na₂O), potash (K₂O) and lithia (Li₂O). Frequently the flux is added as a carbonate (e.g. Na₂CO₃), the CO₂ being driven off during heating. But, glasses containing only silica and a flux have poor durability against corrosion and are often water–soluble. To make glasses stronger and more durable **stabilisers** are added. The most common stabiliser is lime (CaO) but others are magnesia (MgO), baria (BaO), and litharge (PbO). The most common glass is based on **silica** as the glass former, **soda** as the flux and **lime** as the stabilizer.

The main raw materials used in manufacturing glass are: Silica from quartz, white sand and flint; Sodium Carbonate Na_2CO_3 used in Soft Glass; Potassium Carbonate K_2CO_3 used in Hard Glass; Calcium from limestone, chalk and lime CaCO₃; Zinc Oxide ZnO used in heat and shock proof glass; lead from lead (II) oxide PbO (litharge) and lead (II, IV) Oxide Pb₂O₄ (red lead) for lead glass; borates from Sodium Borate $Na_2B_4O_7$ (Borax) and Boric Acid H_3BO_3 used in heat and shock proof glass.

Each of the raw materials has a specific function / role in the fabrication of the specific glass and in its properties when formed. Major ingredients form the glass network. To modify the network's properties of hardness, brittleness, colour, etc., other ingredients are added in varying proportions depending upon the type of glass and its use; an example of the constituents of one type of glass is shown below:



Figure 6.1. Constituents of Manufactured Glass (Simple English Wikipedia)

Components of glass can be categorised as:

- Network Formation of the glass materials generated by Glass Formers. These are the major components of the glass structure forming a stable glass network. Key network compounds are SiO₂, B₂O₃, P₂O₅, GeO₂, V₂O₅, As₂O₃, Sb₂O₅.
- Network Modifiers These are additives as **fluxes** to soften and promote melting. Key flux compounds formed in glass networks are Na₂O, K₂O, LiO, Al₂O₃, B₂O₃, Cs₂O.
- Network Modifiers These are additives as **stabilisers** to impart durability / chemical resistance. Key stabiliser compounds formed in glass network are CaO, MgO, Al₂O₃, PbO, SrO, BaO, ZnO, ZrO.
- Colourers These are additives imparting colour: key elements are V, Cr, Mn, Fe, Co, Ni.
- Fining Agents These are additives to remove small bubbles: Key elements are F, Cl, As, Sn, Sb, Pb.

6.2. Manufacture of Glass

Fabrication of Glass can be divided into the major steps of Preparation of the raw material ingredients; Melting; Forming and shaping; Annealing and tempering; Finishing.

Preparation – The correct raw materials for the specific type of glass are separately ground into fine powder, sieved and mixed in the correct proportions.

Melting – The mix is melted and fused in a furnace at \sim 1800°C into a viscous liquid. Typical chemical reactions are:

$$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2 \uparrow$$

 $Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2 \uparrow$

After removal of CO_2 , decolourisers such as MnO_2 are added to remove traces of ferrous compounds and carbon. Heating continues until the clear molten mass is free from bubbles. The mass then cooled to ~800°C ready for forming and shaping. At this stage it is still a viscous liquid.

Forming and Shaping – The viscous liquid mass obtained from melting is poured into moulds. Different types of articles and shapes are made by blowing, pressing, drawing or squeezing between rollers. Glass sheet is made by continuously drawing up and squeezing the molten melt between rollers. High quality glass sheet is made by floating molten glass on molten tin Sn.

Annealing and Tempering – These are heat treatment techniques to improve the durability of glass against mechanical shock, heat and surface scratches. Annealing removes internal stress caused by uneven cooling.

Glass articles are allowed to cool gradually to room temperature by passing them through different heat chambers at descending temperatures. Tempering suppresses growth of cracks from surface scratches by putting the surface only of the glass into compression to squeeze any crack closed. This is achieved by cooling the surface but not the interior with the result that surface crack growth is suppressed.

Finishing is the last step in glass manufacturing and involves the following steps: cleaning, grinding, polishing, cutting and sand blasting.

6.3. Classification of Glass

Glass is classified according to its composition or special use specification. Glasses classified by composition include:

- Soda–lime / Soda ash / Soft glass
- Potash–lime / Hard glass
- Lead / Flint glass
- Borosilicate glass
- Alumino–silicate glass
- 96% silica glass
- 99.5% silica glass / Vitreosil
- Optical glass

Specialty use glasses are glasses specified for particular engineering, industrial or product needs, e.g. safety glass, fibre glass, coloured glass, wired glass, etc.

6.4. Types of Glass-Soda-lime or Soft Glass

About 90% of all glass is soda–lime. This is obtained from furnace melt and fusion at \sim 800–900°C of a mix of:

- Silica from sand as the former of the glass network. Silica comprises ~70% of the glass.
- **Soda ash** (sodium carbonate Na₂CO₃) to form sodium oxide Na₂O in the melt to act as a **flux** to lower the temperature at which the silica melts. Soda ash comprises ~15% of the glass. This soda ash flux hugely reduces the cost and difficulty of melting silica at 1723°C. But, glasses containing only silica and a flux have poor durability and are often water–soluble.
- **Limestone** (calcium carbonate CaCO₃) to form lime (calcium oxide CaO) in the melt to act as a **stabiliser** for the silica. Limestone comprises ~9% of the glass.
- Small amounts of additives.

Soda–lime glass Flux

Soda–lime glass has a much lower melting temperature than pure silica, i.e. \sim 850°C vs. 1723°C and has slightly higher elasticity. These changes arise because the silica and soda ash flux react to form sodium silicates of the general formula Na₂[SiO₂]_x[SiO₃]:

 $Na_2CO_3 \rightarrow Na_2O + CO_2$

 $Na_2O + SiO_2 \rightarrow Na_2SiO_3$

These silicates have much lower melting points than pure silica.

Soda-lime glass Stabiliser

Glasses containing only silica and a flux have poor durability to corrosion and are often water–soluble. The addition of limestone $CaCO_3$ to the melt enables the formation of Ca+Si compounds which are water insoluble and durable.

 $SiO_2 + CaCO_3 \rightarrow CaSiO_3 + CO_2$

 $SiO_2 + 2CaCO_3 \rightarrow Ca_2SiO_4 + 2CO_2$

Soda-lime glass is divided technically into glass used for windows, called flat glass, and glass for containers, called container glass. The two types differ in the application, production method (float process for windows, blowing and pressing for containers) and chemical composition.

Flat glass has higher magnesium oxide and sodium oxide content than container glass, and lower silica, calcium oxide, and aluminium oxide content. The lower content of highly water–soluble ions (sodium and magnesium) in container glass gives higher chemical durability against water as required for storage of beverages and food.

Key soda-lime glass properties are:

- Low cost
- Reasonably hard
- Poor thermal shock resistance
- Chemically stable Resistant to water but not to some acids, e.g. Hydrofluoric HF and Phosphoric H₃PO₄
- Alkalines will etch soda-lime glass
- Very workable as melts easily and can be hot worked and re-softened several times to finish an article ideal for glass recycling
- Suitable for manufacturing a wide array of glass products electric light bulbs, windowpanes, bottles, cheap table ware, test tubes, reagent bottles, art objects, etc.

6.5. Types of Glass-Potash-lime or Hard Glass

Potash–lime or Hard Glass is obtained from furnace melt and fusion at \sim 800–900°C of a mix of:

- Silica from sand as the former of the glass network comprising ~60–75% of the glass
- **Potash** (potassium carbonate K₂CO₃) to form potassium oxide K₂O in the melt to act as a **flux** to lower the temperature at which the silica melts and comprising ~12–18% of the glass. Similar to soda ash, this flux hugely reduces the cost and difficulty of melting silica at 1723°C.
- **Limestone** (calcium carbonate CaCO₃) to form lime (calcium oxide CaO) in the melt to act as a **stabiliser** for the silica and comprises ~5–12% of the glass
- Small amounts of additives

Potash-lime glass properties include: more dense than soda-lime glass; harder and more brilliant, thus better for decorative techniques such as facet cutting and engraving; high melting point; passes from molten to rigid state more quickly and, thus, is less workable; chemically more stable than soda-lime glass, namely less attacked by acids, alkaline and solvents; more expensive than soda-lime glass. Potash-lime glass is widely used for chemical apparatus, combustion tubes, glassware used for heating operations and art objects.

Types of Glass–Lead Glass

Lead glass contains a high proportion of lead oxide and has extraordinary visual clarity, light transmission and brilliance. In this glass type lead replaces the calcium content of a typical potash glass. Lead (II) oxide PbO is fluxed with silica and K_2CO_3 in various concentrations depending upon the application as shown in the following Table:

| Use | PbO (wt%) |
|---------------------------------------|-----------|
| Household "crystal" leaded glass | 24–38 |
| Ceramic glazes and vitreous enamels | 16–35 |
| High refractive index optical glasses | 45-80 |
| Radiation shielding | > 65 |
| High electrical resistance | 20–22 |
| Glass solders and sealants | 56–77 |

Table 6.1. Various concentrations PbO depending upon the applications.

The addition of PbO to glass raises its refractive index and lowers its working temperature and viscosity.

The high atomic number of lead raises the density of the glass as lead has a high atomic weight of 207 vs. 40 for calcium. The density of soda glass is ≤ 2.4 g/cm³ versus the density of lead crystal up to 5.9 g/cm³. Since high density equates to high refractive index, the attractive optical properties of lead glass result from its **high refractive index**-soda-lime glass refractive index n=1.5, lead glass up to 1.8.

High refractive index gives increased dispersion (degree of light separation into its spectrum). Crystal cutting techniques exploit these properties to create a brilliant, sparkling effect as each cut facet reflects and transmits light through the object. The high refractive index is also used for optical lens making since a given focal length can be achieved with a thinner lens.

The viscosity of lead glass is roughly 100 times less than that of ordinary soda glasses across working temperature ranges (up to $1,100^{\circ}$ C). Thus, lead glass is more easily workable, e.g. for glass solders, and free from trapped air bubbles to produce glass without flaws. The high ionic radius of the Pb²⁺ ion renders it highly immobile in the glass matrix and hinders the movement of other ions. Thus, lead glasses have high electrical resistance, two orders of magnitude higher than soda–lime glass, so they are frequently used in light fixtures. Uses of lead glasses include high quality table ware (cut glass, 'crystal' glass), optical lenses, cathode ray tubes, electrical insulators and radiation shields.

Types of Glass–Borosilicate Glass

Borosilicate glass has silica and boron trioxide as the main glass–forming constituents. It possesses very low coefficients of thermal expansion $(\sim 3 \times 10^{-6})^{\circ}$ C at 20°C about one–third of soda glass) making these glasses resistant to thermal shock and breakage. They are also highly resistant to chemical attack. The composition of low expansion borosilicate glass is ~80% silica, 13% boric oxide B₂O₃, 4% sodium oxide Na₂O and 2–3% aluminium oxide Al₂O₃. They are more difficult to make than traditional glass due to the high melting temperature required. But, they exhibit superior durability, chemical and heat resistance. They are industrially used for pipelines of corrosive liquids, gauge glasses, superior laboratory apparatus, kitchen wares, chemical plants, television tubes, electrical insulators, some types of windows, etc. Virtually all modern laboratory glassware is borosilicate glass used due to its chemical and thermal resistance and good optical clarity.

Types of Glass – Aluminosilicate Glass

Aluminosilicate is a naturally occurring mineral with formula Al_2SiO_5 . A small, but important, type of glass, aluminosilicate glass, is fused from a melt of ~20% aluminium oxide, calcium oxide, magnesium oxide and boric oxide in relatively small amounts, but only very small amounts of soda or potash. Typical approximate composition is SiO₂ (55%), Al₂O₃ (23%), MgO (9%), B₂O₃ (7%), CaO (5%), Na₂O or K₂O (1%).

This glass is able to withstand exceptionally high temperatures without softening and thermal shock. It is used in combustion tubes, gauge glasses for high–pressure steam boilers, halogen–tungsten lamps capable of operating at temperatures as high as 750°C, high pressure mercury lamps and chemical combustion tubes.

Types of Glass – 96% Silica Glass

Vycor is the brand name of major glass manufacturer Corning's high silica, high temperature glass. High silica content delivers very high resistance to chemical attack. Vycor is approximately 96% silica and 4% boron trioxide B_2O_3 . Unlike pure fused silica, it can be readily manufactured in a variety of shapes. It is used in applications which demand high temperature resistance 800°C; very high dimensional stability, such as metrology instruments; high thermal shock loads. The glass finds applications in chemical plants, laboratory crucibles, furnace linings and electrical insulators.

Types of Glass – 99.5% Silica Glass or Vitreosil

Vitreosil is short for Vitreous Silica, a transparent fused pure silica with very small amounts of trace element contaminants, e.g. Al at 15 ppm. This glass offers the ultimate in high temperature resistance due to its very low thermal expansion coefficient which equates to high resistance to thermal shock. The glass also has very high chemical attack resistance. It is used in chemical plants, laboratory crucibles, furnace linings, electrical insulators, lamps, etc.

Colouring of Glass

Glass is normally colourless as all electrons are tightly bonded and no electronic excitations in the energy range of the visible light spectrum are possible. Glass may be made to absorb selectively in the visible spectrum (thus becoming coloured) by any one of three processes:

- 1. The addition of ions of **transition metals** to provide electronic excitation possibilities generating visible light. Typical ions added are: Cr++ blue, Cr+++ green, Co++ pink, Mn++ orange, Fe++ blue–green–see below Table:
- 2. Addition of colloidal particles (size 40 to 2000 Å). These small particles, while not impeding light transmission (because of their small size) exhibit selective absorption and complementary reflection. Example: Au particles (at 4–10 g/cm³ concentrations) give colours which vary with particle size: Au 4–10 nm pink, Au 10–75 nm ruby, Au 75–110 nm green, Au 110–170 nm brown.
- 3. Addition of coloured crystals dispersed throughout the glass. *Examples* are scarlet glass from addition of red copper oxide, red from addition of Pb_2CrO_6 , green from addition of Cr_2O_3 .

| Addition of transition metal compounds to glass gives color to the glass. They are outlined below. | | | | | |
|---|---|--|--|--|--|
| YELLOW: Ferric Salts | GREEN Ferrous and Chromium salts | PURPLE: Manese dioxide salt | | | |
| RED: Nickiel and cuprous salts Cu ₂ O | LEMON YELLOW: Cadmium sulphide | FLUORESCENT GREENISH YELLOW: Uranium oxide | | | |
| BLUE: Cobalt Salts, CuO | GREENISH BLUE COLOR: Copper Sulphate | BROWN: Iron | | | |
| OPAQUE MILKY WHITE: Cryolite of Calcium phosphate | RUBY: Auric Chloride | | | | |

Table 6.2. Coloured glass

6.6. Properties of Glass

The strong covalent bonds that exist between the atoms of inorganic glasses plus the lack of crystal structure give glass unusual characteristics, typically chemically stable, poor conductor of heat and electricity, inherently transparent, inherently strong.

Chemical Stability – All glasses are immune to oxidation decay because their atoms are fully oxidized. Glass composed of 100 percent silica tetrahedra is extraordinarily inert. It resists the action of most acids (not hydrofluoric acid HF, used to etch glass), but is attacked by strong alkalis.

Conductivity – The ability of a material to conduct electricity is dependent upon the presence of electrons in the conduction band. These are separated in glasses by a large band gap of up to 10eV from the valence band. Because electrons in glass are tightly bonded, glass is very poor conductor of electricity and an excellent insulator. Glass is also a poor conductor of heat. Thus, hot common glass may crack when cold water is poured onto it because the surface exposed to the cold water will shrink while the dimensions of the interior remain unaffected.

Strength – Glass is harder than many types of steel and is also very elastic. Glass has no crystal structure so the phenomenon of slip cannot take place. This, together with the strong bonding between atoms, gives glass a very high compressive strength and a theoretical tensile strength of about 10^7 kN/m², significantly higher than that of steel. But, since the molecular structures in glass are unable to move, the presence of minute cracks or imperfections in glass permits stress concentrations to localize and exceed the bond strength between atoms so that common glass will crack. Thus, in practice, the tensile strength of glass is less than the theoretical tensile strength by a factor of x 100–1000 so that glass is brittle.

Architectural glass is glass that is used as a building material. Most typically it is used as a transparent glazing material in the building envelope, especially windows in the external walls. Glass is also used for internal partitions and as architectural features. Used in buildings, glass is typically of a safety type, e.g. reinforced, toughened and laminated glasses.

7. Chemistry of Metals and Metal Alloys

In chemistry, a metal is an element that readily forms positive ions (cations) and has metallic bonds. Metals can be described as a crystal lattice of positive ions surrounded by a cloud of delocalized electrons – see below schematic:



Swarm of delocalised electrons

Figure 7.1. Metallic bonding (Civil Engineering Home)

The ~91 **metals** (some elements appear in both metallic and non-metallic forms) are one of the three groups of elements distinguished by their ionization and bonding properties along with the **metalloids** and **non-metals**. On the Periodic Table , a diagonal line drawn from boron (B) to polonium (Po) separates the metals from the non-metals. Most elements on this line are metalloids, sometimes called semi-metals. Elements to the lower left are metals; elements to the upper right are non-metals.

A modern definition of metals is that they are elements or compounds that have overlapping conduction bands and valence bands in their electronic structure. This definition opens up 'metals' to man–made metallic polymers and other organic metals employed in high–tech devices.

Metals tend to be lustrous, ductile, malleable and good thermal and electrical conductors while non-metals are generally brittle (if solid), lack lustre and are insulators. Differences between metals and non-metals include:

• **Malleability** – A malleable metal can easily be deformed, especially by hammering or rolling, without cracking. *Examples* of malleable metals are are gold and aluminium. Malleability occurs as a result of the metallic bonding. The attractive forces between the metal atoms are strong but not rigid. When a force is applied, the layers of metal can slide over one another.
• **Ductility** – The ability of metal to be drawn into a wire or thread without breaking. *Examples* of ductile metals are gold and copper.

Metals are usually crystalline solids with a simple crystal structure with close packing of atoms and a high degree of symmetry. Typically, metal atoms contain less than half the maximum number of electrons in their outermost valence shell. Thus, metals tend not to form compounds with each other, but they combine readily with nonmetals (e.g. oxygen and sulphur) which, generally, have more than half the maximum number of valence electrons. Metals differ widely in their chemical reactivity. The most reactive metals include lithium, potassium radium while low reactivity metals are gold, silver, palladium and platinum.

7.1. Metals – Crystalline Structure

The atoms of metallic substances are closely positioned to neighbouring atoms in one of three primary crystalline arrangements:

- Body-centred cubic (BCC) each atom is positioned at the centre of eight others
- Face-centred cubic (FCC) each atom is positioned in the centre of six others
- Hexagonal close packed (HCP)

The arrangement of atoms in these structures forms a crystal. Some metals adopt more than one structure depending on the temperature.

Body–Centred Cubic (BCC) Structure

The body–centred cubic unit cell has atoms at each of the eight corners of a cube plus one atom in the centre of the cube. Each of the corner atoms is the corner of another cube so the corner atoms are shared among eight unit cells. The BCC unit cell has a coordination number of 8. The BCC unit cell contains a net total of two atoms – one in the centre and eight eighths from corner atoms – see below schematic:



Figure 7.2. Body–Centred Cubic Structure (NDT Resource Center)

BCC does not allow the atoms to pack together as closely as the FCC or HCP arrangements. BCC is often the high temperature form of metals that are close–packed at lower temperatures. The volume of atoms in a cell per total volume of a cell is called the **packing factor** – the BCC unit cell has a packing factor of 0.68. Metals with a BCC structure include lithium, sodium, potassium, chromium, barium, vanadium, alpha–iron, tungsten. BCC metals are usually harder and less malleable than close–packed metals such as gold. When the metal is deformed, the planes of atoms must slip over each other and this is more difficult in the BCC structure.

Face Centred Cubic (FCC) Structure

The FCC structure has atoms located at each corner and at the centres of all the cubic faces. Each corner atom is the corner of another cube so the corner atoms are shared among eight unit cells. Additionally, each of its six face centred atoms is shared with an adjacent atom. Since 12 of its atoms are shared, the FCC unit cell has a coordination number of 12. The FCC unit cell consists of a net total of four atoms: eight eighths from corner atoms plus six halves of the face atoms – see below schematic:



Figure 7.3. Face–Centred Cubic Structure (NDT Resource Center)

In the FCC and HCP structures the atoms can pack closer together than in the BCC structure. The atoms from one layer nest themselves in the empty space between the atoms of the adjacent layer. The packing factor (the volume of atoms in a cell per the total volume of a cell) is 0.74 for FCC crystals. Metals that have the FCC structure include aluminium, copper, gold, iridium, lead, nickel, platinum and silver.

Hexagonal Close Packed (HCP) Structure

The hexagonal structure of alternating layers is shifted so its atoms are aligned to the gaps of the preceding layer. The atoms from one layer nest themselves in the empty space between the atoms of the adjacent layer as in the FCC structure. However, instead of being a cubic structure, the pattern is hexagonal. The HCP structure has three layers of atoms. In the top and bottom layers, there are six atoms in the shape of a hexagon and a seventh atom in the middle of the hexagon. The middle layer has three atoms – see below schematic:



Figure 7.4. Hexagonal Close Packed Structure (NDT Resource Center)

There are six atoms in the HCP unit cell. 12 atoms in the corners of the top and bottom layers each contribute 1/6 atom to the unit cell plus two atoms in the centre of the hexagon of the top and bottom layers each contribute $\frac{1}{2}$ atom plus a further three atoms in the middle layer each contribute 1 atom = 6 complete atoms. The Coordination number of the HCP unit cell is 12–six nearest neighbours in the same close packed layer, three in the layer above and three in the layer below. The packing factor is 0.74, the same as for the FCC unit cell. The HCP structure is very common for elemental metals including beryllium, cadmium, magnesium, titanium, zinc, zirconium.

7.2. Metallic Bonding

Metals are strong because their atoms in the crystal lattice are held together by a strong bonding force. The bond is formed between the metal atoms by allowing their outer valence electrons to be shared by all surrounding atoms. Electrons wander freely through the metallic lattice, called delocalised electrons. This results in a crystal lattice of positive ions (cations) surrounded by a cloud of delocalised valence electrons.

Despite this flow of electrons, the metal is a solid because of the electrostatic interactions between each atom and the electron cloud. This type of chemical bond is called a **metallic bond**. Metallic bonds are one of the 3 main types of intermolecular forces, along with ionic bonds and covalent bonds. Because these valence electrons are shared by all atoms, they are not associated with any atom in particular, very different from ionic or covalent bonds where electrons are shared by only one or two atoms.

The metallic bond is therefore strong and uniform. Even if, when forming alloys, the added elements are non-metals, alloys still have metallic properties as shown in the below Table:

| Chemical Properties | | | |
|---|---|--|--|
| Metals | Nonmetals | | |
| Usually have 1–3 electrons in their outer shell Lose their valence electrons easily to become cations Form oxides that are basic Are good reducing agents Have lower electronegativities | Usually have 4–8 electrons in their outer shell Gain or share valence electrons easily to become anions Form oxides that are acidic Are good oxidizing agents Have higher electronegativities | | |
| Physical Properties | | | |
| Metals | Nonmetals | | |
| Good electrical conductors and heat conductors Malleable – easily deformed, e.g. into thin sheets Ductile – can be stretched into wire Possess metallic lustre Opaque as thin sheet Solid at room temperature (except Hg) | Poor conductors of heat and electricity Brittle – if a solid Nonductile Do not possess metallic lustre Transparent as a thin sheet Solids, liquids or gases at room temperature | | |

Table 7.1. Chemical Properties and Physical Properties

Explaining Properties of Metals

Why do metals have high melting points?

The strong electrostatic attraction between the positive lattice cations and negative delocalised electrons holds the metallic lattice together making it hard to loosen the bonds

Why are metals strong, malleable and ductile?

The layers of atoms in metal are hard to pull apart because of the electrons holding them together. This means that metals are tough. Individual atoms are not bonded to any other specific atoms so that atoms slip easily past one another which makes them ductile and malleable.

Why are metals good conductors of electricity and heat?

Delocalised (free) electrons can move rapidly in response to electric fields and transmit heat through thermal motion.

Why are metals hard?

Strong electrostatic forces between cations and electrons make it difficult to separate particles from one another.

Why are metals lustrous (shiny)?

When light energy hits the delocalised electrons they absorb the energy and jump into a higher energy level. The electron quickly falls back to its original energy level by releasing a photon and, thus, emitting light.

Sources of Metals

Most metals are obtained from ores. Ores are mixtures of minerals containing metals and gangue (sand, clay and unwanted materials). To obtain the desired metal, minerals must be separated from the gangue via a technology called metalurgy. The metallurgy process typically comprises – see schematic example below:

- Mining of the ores from the ground by large scale heavy machinery operations
- Separation ore is crushed and treated to separate mineral from gangue
- Reduction the mineral is reduced from metal oxides or metal sulphides to obtain the crude metal by, typically, chemical process or electrolysis
- Refine/purification Further treatment of the crude, relatively impure metal to produce purer metal by distillation, chemical purification or electrorefining.

Metals

Extraction of Metals from Ores. Example: The Extraction of Iron

• Stage 1: Reaction of <u>coke</u> with <u>oxygen</u>

 $\mathrm{C}(\mathrm{s}) + \mathrm{O}_2(\mathrm{g}) \to \mathrm{CO}_2(\mathrm{g})$

• Stage 2: Reduction of <u>carbon dioxide</u> with <u>coke</u>

 $CO_2(g) + C(s) \rightarrow 2CO(g)$

• Stage 2: Reduction of <u>iron ores</u> with <u>carbon monoxide</u> to produce molten iron

 $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(l) + 3CO_2(g)$



Hemalite: Plty black (Fe₂O₃)



Pyrites: Lustrous cube (FeS₂)



Magnetite: Octahedral black (Fe₃O₄)



Siderite: Bladed crystal (FeCO₃)

Extraction of Metals: Iron from many types of ores (Geology Cafe)

7.3. Metal Alloys

Most pure metals are too soft, too brittle, too chemically reactive, etc. for practical use. Most metals are not used in their pure form but are changed by adding elements to modify their properties for specific applications. The addition of some proportion of a second or more elements to the pure metal to form an **alloy** drastically changes some of its properties producing desirable characteristics, e.g. less brittle, harder, resistance to corrosion, more desirable colour and lustre. Example: Iron is not hard enough by itself to be used so Steel is made by mixing iron with about 2% carbon.

The addition of small quantities of other elements to iron (e.g. carbon, manganese or silicon) greatly increases its mechanical strength because the different atom sizes of the other elements interrupts the iron atoms in the lattice and prevents them from sliding over each other easily.

Alloys are defined as:

- A metallic material
- Homogeneous (uniform) on a macroscopic (large) scale
- Consisting of two or more elements
- Combined so that they cannot be readily separated by mechanical means

A metallic alloy typically consists of a metal or a metalloid base element, comprising the largest percentage of the material, plus one or several added elements. The alloy mix is designed to achieve improved mechanical, physical or chemical properties. The added elements can be metals or non-metals but the alloy retains the characteristics of a metal.

Alloys are made by melting the two or more components together, mixing them and allowing the mix to cool to the solid state. Alloys are classified as substitutional or interstitial alloys depending on the atomic arrangement forming the alloy. A substitutional alloy is where the additive replaces pure metal atoms in the lattice. An interstitial alloy is where the additive sits within the pure metal lattice.

When a molten metal is mixed with another substance, there are two mechanisms that cause an alloy to form:

- Atom exchange
- The interstitial mechanism

The relative size of the atom of each element in the mix plays a primary role in determining which mechanism will occur. When the atoms are similar in size, the atom exchange method usually happens. Some of the atoms in the metal crystals are substituted with atoms of the other constituent. This is called a *substitutional alloy. Examples* of substitutional alloys include bronze and brass in which some of the copper atoms are substituted with either tin or zinc atoms. With the interstitial mechanism, one atom is usually much smaller than the other so cannot successfully replace an atom in the crystals of the base metal. The smaller atoms become trapped in the spaces between the atoms in the crystal matrix, called the *interstices*. This is referred to as an *interstitial alloy*. Steel is an example of an interstitial alloy, because the very small carbon atoms fit into interstices of the iron matrix.

Stainless steel is an example of a combination of interstitial and substitutional alloys, because the carbon atoms fit into the interstices but some of the iron atoms are replaced with nickel and chromium atoms – see below schematic:





Examples of metal alloys are: Bronze (Cu+Sn), Brass (Cu +Zn), Solder (Pb+Sn), Steel (Fe+C), Stainless Steel (Fe+C+Cr+Ni), German Silver (Cu+Zn+Ni).

7.4. Important Metals in Construction: Fe + alloys

Iron (Fe) and its alloys are the most important and widely used metals in construction. Two iron alloys are critical to today's construction technology, Steel and Stainless steel.

Steel – Pure iron is too soft to be used for structures but the addition of small quantities of other elements (carbon, manganese, silicon) greatly increases its mechanical strength because the different atom sizes of other elements in the iron lattice interrupts the orderly arrangement of atoms in the lattice and prevents them from sliding over each other easily. The alloying elements block slip planes. Steels are alloys of iron and other elements, primarily carbon, widely used in construction and other applications because of their high tensile strengths and low cost. Carbon and other elements act as hardening agents that prevent the movement of dislocations that occur in the iron crystal lattice. The carbon content of steel is between 0.002% and 2.1% by weight depending on the other alloying elements such as manganese, chromium, nickel, tungsten, etc. Whereas pure iron is a soft metal that rusts easily, steel is hard, tough and corrosion–resistant. Steel is one of the world's most vital materials. Important chemical elements used to alloy in **structural steels** are:

- **Carbon** (C): Next to iron, carbon is by far the most important chemical element in steel. Increasing carbon content produces steel with higher strength and lower ductility. Structural steels have carbon contents between 0.15 to 0.30%. Greater than 0.3% results in too low ductility and less than 0.15% results in too low strength.
- Manganese (Mn): Manganese appears in structural steel grades in amounts from 0.50 to 1.70%. Mn has effects similar to those of carbon, and the steel producer uses these two elements in combination to obtain a steel with the desired properties.
- Aluminium (Al): Aluminium is one of the most important deoxidizers in steel, and also helps form a more fine-grained crystalline microstructure.
- **Molybdenum** (**Mo**): Molybdenum has effects similar to manganese and vanadium, and is often used in combination. Mo particularly increases the strength of the steel at higher temperatures and also improves corrosion resistance. Typical amounts of Mo are 0.08 to 0.65%.
- Nickel (Ni): Improves corrosion resistance and enhances the lowtemperature behaviour by improving the fracture toughness. Ni is used in structural steels in amounts typically between 0.25 to 1.50%.

Stainless Steel – Stainless Steel (SS) is a generic term for a large family of corrosion resistant alloys containing at least 10.5% chromium (European standard EN10088) and may contain other alloying elements. Fe–Cr alloys show

tremendous increase in corrosion resistance compared to pure iron. There are more than one hundred chromium–containing metallic alloys each developed for a particular need. The most important characteristic common to all SS alloys is that they contain sufficient chromium to make them corrosion resistant, oxidation resistant and/ or heat resistant.

SS is 'stainless' due to the fact that, in the presence of oxygen, the steel develops a thin, hard, adherent film of chromium oxide Cr_2O_3 . Even if the surface is scratched, the protective film is rebuilt through passivation. For passivation to occur there needs to be a minimum chromium content of 10% to 12% by weight. SS has been used for decades in major architectural structures (e.g. Chrysler Building, New York City). SS is found in roofing, structural applications, handrails and balustrades, architectural cladding and drainage components. Using SS as reinforcing bars in concrete structures such as highways buildings and bridges is better than carbon steels as they are resistant to corrosion from road salts and the concrete itself.

7.5. Important Metals in Construction: Al

Important Aluminum properties for construction applications are its high strength to weight ratio, resistance to corrosion and harsh weather, high thermal and electrical conductivity, nonmagnetic, easy formability (malleable and ductile) and machinability into sheets, tubes and castings.

Aluminum is used in windows, doors, wire, outdoor signage and street lights, build of cars, trucks, bicycles and marine vessels, Heating, Ventilation and Air Conditioning (HVAC) ducts, roofs, walls and handles.

7.6. Important Metals in Construction: Cu + alloys

Copper is a ductile, malleable metal, resistant to corrosion from water and soil. Cu is mostly used as a pure metal but, when a higher hardness is required, it is combined with other elements to make an alloy (5% of total use) such as brass (Cu + Zn) and bronze (Cu + Sn).

Major applications of Cu are in electrical wires (60%), roofing and plumbing (20%) and industrial machinery (15%). Cu tubing is easily bonded by soldering making it ideal for piping and tubing. Cu tubing is used to construct pipes in buildings for hot and cold water pipes, refrigerant lines in HVAC systems and heat pumps. Cu has been used since ancient times as a durable, corrosion resistant and weatherproof architectural material.

Important construction properties of Cu are low thermal movement, light weight, lightning protection and recyclability. Cu is used for construction in roofs, flashings, rain gutters, downspouts, domes, spires, doors, wall cladding, bathroom fixtures and counter tops.

8. Chemistry of Polymers

Polymers are materials consisting of *polymer molecules*. Polymer molecules are large molecules built up by repetitive covalent bonding of chemical units derived from smaller molecules called **monomers**. The fundamental repeat unit of a polymer is a chemical unit called a '**mer**'. The **mer** is not necessarily the same as the **monomer**, which is the small molecule from which the mer is derived and the polymer is synthesized – the mer and monomer may or may not be the same. Polymers are formed by linking mers derived from monomers through chemical reaction in a process called **polymerisation**.

Some polymer molecules, called macromolecules, contain hundreds or thousands of mers usually in the form of a chain. A polymer material is not made up of a single, unique molecule but is of a general structure, e.g. n * mer, which generates a chain of mers, e.g.

 $nA \rightarrow - (A - A - A)_{n/3}$

where A = mer, n = number of mers

Since n can be many numbers, a polymer material can contain many different molecules, e.g. many different chain lengths, but all of the same general structure. Polymers generally do not have a single defined structure or molecular weight but a distribution of chain lengths and weights.

When all mers are the same, the molecule is called a homopolymer

Note the simple repeating unit structure (mer) of a homopolymer.

When there is more than one type of mer present, i.e. made up of different monomers, the molecule is a **copolymer**

 $nA + nB \rightarrow - (A-B)_n$

The copolymer can take different forms as per the below schematic:



(DoITPoMS)

Thus, medical vials made of a *random co-polymer* of ethene and propene can give a flexible and clear material. But, an electric cable covering, in the form of a *block co-polymer* of the same materials, give a dark, a very tough material with rubber–like properties. Co-polymers are very useful as they have the properties of all the constituent polymers. They can be designed and manufactured for specific purposes. For example, poly(phenylethene) (polystyrene) is brittle, but when it is co-polymerized with buta–1,3–diene, the additive gives the polymer resilience and strength. Known as High Impact Polystyrene (HIPS), the co-polymer can now receive impacts without damage (Tang C.Y., Tai W.H., Lee W.B., 1995), (Florjańczyk Z., Penczek S., 2002).

Polymers may be **natural**, such as leather, rubber, cellulose, DNA, or **synthetic**, such as nylon, polyethylene. Living organisms are mainly composed of polymerised amino acids (proteins), nucleic acids (RNA and DNA) and other biopolymers.





(Simple English Wikipedia)

Our brains are mostly a complex polymer material in salt water.

8.1. Hydrocarbon Polymers

Most polymers are organic and formed from **hydrocarbon molecules** as monomers. Each C atom has four electrons that participate in bonding, each H atom has one bonding electron. Important hydrocarbon molecule monomers are:

8. Chemistry of Polymers

• Saturated hydrocarbon compounds in which all C bonds are single. *Examples* of saturated hydrocarbon molecules:









Methane, CH₄

Ethane, $C_2 H_6$





Propane, C₃H₈

| Family | Characteristic Unit | Representative Compound | Name |
|--------------------------|---------------------|----------------------------|----------------|
| Alcohols | R-0-H | H H-C-OH H | Methyl ether |
| Ethers | R-0-R | H H H-C-O-C-H H H | Dimethyl ether |
| Acids | R-C | H-C-O-C | Acetic acid |
| Aldehydes | R H C=0 | H_C=O | Formaldehyde |
| Aromatic hydrocarbons | æ | OH | Phenol |

- Unsaturated hydrocarbon compounds in which C bonds are double or triple sharing two or three electron pairs. Unsaturated molecules are more reactive. *Examples* of unsaturated hydrocarbon monomers are Ethylene C_2H_4 and Ethyne (Acetylene) C_2H_2 .
- Many other organic groups can be involved in hydrocarbon polymer molecules see below table. In the table, R = a Radical, namely an organic group of atoms with an unpaired electron (active site) that remains as a unit and maintains its identity during chemical reactions (e.g. CH₃, C₂H₅, C₆H₅), (Pauling L., Pauling P., 1983).

8.2. Hydrocarbon Polymers – Basic Structure

Most polymers consist of:

- Long and flexible chains with a string of C atoms as a backbone;
- Side-bonding of C atoms to H atoms or Radicals, e.g. gas ethylene to solid polyethylene;
- Double bonds are possible in both chain and side bonds.

Mer units that have 2 active bonds to connect with other mers are called bifunctional, e.g. Polyethylene. Mer units that have 3 active bonds to connect with other mers are called trifunctional. They form three dimensional molecular network structures, e.g. Phenol–formaldeyde (Malcom, 1983).

8.3. Hydrocarbon Polymers – Fabrication

Polymers are manufactured by two methods:

• In addition polymerisation, the polymer has the same empirical formula as the monomer, e.g. polymerisation of chloroethene (vinyl chloride) to form poly(chloroethene) PVC:

8. Chemistry of Polymers

| Monomer | Formula | Polymer | Trival name | Structure | |
|-----------------------------------|----------------------------------|---|-----------------------------------|--|--|
| Ethene | $H_2C = CH_2$ | LDPE Low density poly (ethane) | Low density polythene | - CH ₂ - CH ₂ - CH ₂ - CH ₂ - | |
| Chloroethene | $H_2C = CHCl$ | Poly (chloroethene) | Polyvinyl chlorine PVC | CI CI I I – CH ₂ – CH – CH ₂ – CH – | |
| Propene | $H_2C = CH - CH_3$ | Poly (propene) | Polypropylene | $\begin{array}{ccc} \mathrm{CH}_3 & \mathrm{CH}_3 \\ \mathrm{I} & \mathrm{I} \\ - \mathrm{CH}_2 - \mathrm{CH} - \mathrm{CH}_2 - \mathrm{CH} - \end{array}$ | |
| Propenonitrile | $H_2C = CH - CN$ | Poly (propenonitrile) | Polyacrylonitrile | CN CN I I – CH ₂ – CH – CH ₂ – CH – | |
| Methyl 2– methylpropeno ate | CO_2CH_3 $ $ $H_2C = C - CH_3$ | Poly (methyl 2– methylpropeno ate) | Polymethyl methacrylate | $\begin{array}{c} & \text{CO}_2 \text{ CH}_3 & \text{CO}_2 \text{CH}_3 \\ \text{I} & \text{I} \\ - \text{ CH}_2 - \text{ C} - \text{ CH}_2 - \text{ CH} - \\ \text{I} & \text{I} \\ \text{CH}_3 & \text{CH}_3 \end{array}$ | |
| Phenylethene | H ₂ C=CH | Poly (phenylethene) | Polystyrene | - CH ₂ -HC-CH ₂ -HC- | |
| Tetrafluoroeth ene | $F_2C = CF_2$ | Poly (tetrafluoroethe ne) PTFE | Polytetrafluoro– ethylene PTFE | $-CF_2-CF_2-CF_2-CF_2-$ | |

Table 8.2. *Examples* of polymers from addition polymerisation

• In **condensation polymerisation**, polymerisation of one or more monomers is accompanied by the elimination of small molecules such as water or ammonia, e.g. producing polyamide 6,6, from two monomers:

| Polymer | Monomer | Formula | |
|-----------------------------|--|---|--|
| Polyesters | HO-(CH ₂)x-COH | $-\left[(CH_2)_x - C - O\right]_n$ | |
| Polyamides | $H_{H^{-}(CH_2)_x} - N_{H^{-}(CH_2)_y} - N_{H^{-}(CH_2)_y} - C_{-}^{O}(CH_2)_y - C_{-$ | $\begin{bmatrix} NH_{CH_2})_{x} & NH_{C}^{O} & O_{CH_2} \\ H_{C}^{O} & O_{C}^{O} \\ H_{C}^{O} \\ H_{C}^{O} & O_{C}^{O} \\ H_{C}^{O} & O_{C}^{O} \\ H_{C}^{O} \\ H_{$ | |
| Phenol–methanal plastics | OH CH ₂ O | | |
| Polyurethanes | HO-R ¹ -OH O=C=N-R ² -N=O | $\begin{bmatrix} 0 & 0 \\ \parallel & \parallel \\ R^{1}O-C-NH-R^{2}-NH-C-O \end{bmatrix}_{n}$ | |

Table 8.3. *Examples* of polymers from condensation polymerisation.

Fabrication of polymers generally requires the formation of an active mer, i.e. a mer with an unpaired electron, using either a Catalyst, e.g. organometallic compound, or an initiator being a catalytic radical (R.) where the (dot .) denotes an unpaired electron active site. The process often also requires the use of heat and/or pressure to link the monomer material into polymer chains. Thus, steps in polymerization can be:

1. Initiation reaction:



2. Rapid propagation ~ 1000 mer units in 1–10 ms:



3. Termination when two active chain ends meet each other or active chain end meet with initiator or other species with single active bond:



Polymer Additives

Various materials are added to polymers to improve mechanical properties, processing, durability, etc.

- **Fillers** Added to improve tensile strength, abrasion resistance, toughness and decrease cost. *Examples* of fillers are carbon black, silica gel, wood flour, glass, limestone, talc.
- **Plasticisers** Added to reduce the glass transition temperature T_g below room temperature. The presence of plasticizer transforms a brittle polymer to a ductile one. Commonly added to PVC.
- Stabilisers Antioxidants, UV protection
- **Lubricants** Added to allow easier processing of polymer through dies, e.g. sodium stearate
- Colorants Dyes and pigments
- Flame Retardants Substances containing chlorine, fluorine and boron
- Antimicrobials Used to control build–up of bacteria, fungi and algae on the surface of plastic products. A wide range of chemical and natural compounds used, e.g. naturally occurring silver ions used in cell phones or organic acids in food–related products.
- **Antistatics** Used to minimise static electricity, the additive is mixed with the resin or applied to the product surface of the product such as sensitive electronic parts.
- **Fibres** Used to increase strength and stiffness, the additive is most commonly carbon and glass, e.g. glass–reinforced plastic (fibreglass).

8.4. The Polymer Molecule Characteristics

The major characteristics at the molecular level that define the physical and chemical nature of any particular polymer include:

- mer composition major determinant of polymer chemistry
- Size molecular weight, molecule chain length
- Molecule shape what spatial arrangements the atoms in a molecule may adopt and convert between, especially by rotation about individual single bonds
- Molecule structure linkages between individual molecules in the bulk material
- Isomerism compounds with the same composition but different atomic arrangements
- Crystallinity extent and type of crystallisation in bulk polymer materials

The following table shows the relationships between the above characteristics:



Molecular Size

The molecular weight (MW) directly relates to the length of the polymer chain. MW is controlled by the polymer synthesis process, i.e. the relative rates of the initiation, propagation and termination steps of polymerization. For example, high propagation rate + low termination rate = long chain polymer = high MW.

Formation of macromolecules during polymerisation results in a distribution of chain lengths and molecular weights, i.e. no single chain length and MW. This means that the MW of polymer molecules can only be stated as an average. Two MW averages are used:

• Number-average MW (most frequent chain)

 $M_n = \Sigma x_i M_i$

• Weight-average MW (average MW across all chains)

 $M_{w} = \Sigma w_{i} M_{i}$

Where:

 $\label{eq:constraint} \begin{array}{l} i = ith \ chain \ length \ in \ the \ polymer \ with \ MW = M_i \\ x_i = number \ of \ chains \ i \ / \ total \ number \ of \ chains \end{array}$

 $w_i = (MW \text{ of chain } i / \text{ total } MW)$

The below figure shows in red a typical distribution of the MW of a polymer molecule as a function of Chain Length ('Amount of polymer') (Figovski O., Beilin D., 2014).



The average MW per chain (averaged across all chains) is the weight-average shown as M_w . The most frequent chain is the number – average shown as M_n :

$$M_w > M_n$$

as the dynamics of polymerisation favour smaller, lower MW chains.

The properties of polymers strongly depend on molecular weight. Thus, melting/softening temperatures increase with molecular weight. At room temperature:

- short chain polymers (molar weight ~ 100 g/mol) are liquids or gases;
- intermediate length polymers (~ 1000 g/mol) are waxy solids;
- solid polymers (sometimes called high polymers) have molecular weights of 10^4 – 10^7 g/mol.

Molecular Shape

Most polymers consist of long, flexible chains with a string of C atoms as a backbone. Thus, the angle between the singly bonded carbon atoms is important and this is $\sim 109^{\circ}$ so that carbon atoms form a zigzag pattern in a polymer molecule.



While maintaining the 109° angle between bonds, polymer chains can rotate around single C–C bonds (double and triple bonds are very rigid). Molecular chains may, thus, bend, coil and kink. Neighboring chains may intertwine and entangle. Random kinks and coils lead to entanglement, like in the spaghetti structure. The large elastic extensions of rubber polymers correspond to the unraveling of these coiled chains. Mechanical / thermal characteristics depend on the ability of chain segments to rotate.

Molecular Structure

The characteristics of polymer materials depend not only on molecular weight and shape, but also on molecular structure.

Linear polymers rely upon Van der Waals bonding between chains as per below figure A. *Examples* are polyethylene, nylon.



Branched polymers: As per above figure B in which chain packing efficiency is reduced compared to linear polymers giving lower density materials.

Cross–linked polymers: Chains are connected by covalent bonds (Figure A below) often achieved by adding atoms or molecules that form covalent links between chains. Many rubbers have this structure.

Network polymers: 3D networks made from trifunctional mers (Figure B below). *Examples*: epoxies–phenolformaldehyde.



A - Cross-linked polymer

B - Network polymer

Isomers

Isomers are compounds with the same composition but with different atomic arrangements. The polymer material properties may depend on the isomeric state, e.g. boiling temperature of normal butane is -0.5° C, of isobutene is -12.3° C. Two types of isomerism in polymers are possible:

- Stereoisomerism
- Geometrical isomerism

Stereoisomerism: Atoms are linked together in the same order but can have different spatial arrangements:

Isotactic configuration: all side R groups are on the same side of the chain.



Syndiotactic configuration: side groups R are on alternate sides of the chain.



Atactic configuration: random orientations of groups R along the chain.



Geometrical isomerism: Consider two carbon atoms bonded by a double bond in a chain. An H atom or radical R bonded to these two atoms can be on the same side of the chain (cis structure) or on opposite sides of the chain (trans structure) (Figovski O., Beilin D., 2014).

Geometrical isomerism.



Crystallisation

The atomic arrangement in polymer crystals is more complex than in metals or ceramics. The unit cells are typically large and complex. Polymer molecules are often partially crystalline (semicrystalline) with crystalline regions dispersed within amorphous material.

The degree of polymer crystallinity is determined by:

- **Rate of cooling during solidification:** Time is necessary for chains to move and align into a crystal structure.
- **Mer complexity:** Crystallisation less likely in complex structures; simple polymers, e.g. polyethylene, crystallise easily.
- **Chain configuration:** Linear polymers crystallise easily, branches inhibit crystallisation, network polymers are almost completely amorphous, crosslinked polymers can be both crystalline and amorphous.

The higher the degree of crystallinity in a polymer, the higher the density and strength and the higher the resistance to dissolution and softening by heating.

Classification of Polymers

Synthetic polymers can be classified on the basis of the molecular forces holding the bulk material together.

8. Chemistry of Polymers

Fibres are thin threads produced by extruding a molten polymer through a die in which there are small holes. Fibres produced in this way include the polyamides (such as nylon), the polyesters (such as terylene) and poly (propene). Having been extruded and stretched, the polymer molecules become aligned in the direction of the fibre. Any tendency to return to a random orientation is prevented by the strong intermolecular forces between the molecules. Fibres are twisted into threads and can then be woven into cloth or imbedded in a plastic to give it much greater strength.

<u>**Plastic</u>** is a material consisting of any of a wide range of synthetic or semisynthetic organics, typically organic polymers, that are malleable and can be moulded into solid objects of diverse shapes. Plasticity is the general property of all materials that are able to irreversibly deform without breaking.</u>

There are two types of plastic polymer classes depending on the response to temperature increase:

Thermoplastic Polymers:

- These materials soften and liquefy when heated, harden when cooled (reversible).
- Their molecular structure is typically linear or branched polymers with secondary bonding holding the molecules together.
- They are easy to fabricate/reshape by application of heat and pressure.

Examples are polyethylene, polystyrene, poly(vinylchloride).

Thermosetting Polymers:

- These materials become permanently hard during their formation and do not soften upon heating.
- Their molecular structure is network polymers with a large density of covalent crosslinks between molecular chains (typically 10–50% of repeat units are crosslinked). They are harder and stronger than thermoplastics and have better dimensional and thermal stability.

Examples are vulcanized rubber, epoxies, phenolics, polyester resins

Elastomers (rubbers) are moderately cross–linked polymers which can be stretched and rapidly recover their original dimension. Essentially an elastomer is a viscoelastic polymer having both viscosity and elasticity and very weak inter–molecular forces. The term 'Elastomer' is derived from *elastic polymer* and is often used interchangeably with the term *rubber*. Elastomers are amorphous polymers which are relatively soft and deformable at ambient temperatures.

The long polymer chains covalently cross–links at points during curing to form the bulk material. The elasticity is derived from the ability of the long chains to reconfigure themselves to distribute an applied stress. The covalent cross– linkages ensure that the elastomer will return to its original configuration when the stress is removed.



8.5. Some Polymer Applications

Some Polymer Applications include by material:

- **Thermoset epoxies**: Adhesive, for example bonding old concrete to new concrete, welding cracked concrete, bonding diverse materials; Patching voids; Durable overlays and coatings
- **Polyester**: Floor coatings; Protective coatings; Adhesive bonder or sealer; Binder for fiberglass or artificial wood; Sealer for Epoxy injection; Anchoring for drilled holes; Binder for polymer mortar;
- **Polyvinyl chloride, PVC:** Pipes; Raincoats; Window frames and mouldings; Electrical cables; Floor tiles;
- Polyethylene: Sheet plastic, membranes, liners, pipes, electrical conduit.

9. Chemistry of Composites

Composite Materials (Composites) are engineered or naturally occurring materials made from two or more constituent materials with significantly different physical and/or chemical properties which materials remain separate and distinct within the finished composite structure but, typically, chemically bond at their interface.

The purpose is that by combining two or more distinct materials, one can engineer a new material with the desired combination of properties (e.g. light, strong, corrosion resistant). The idea that a better combination of properties can be achieved is called the **principle of combined action**.

9.1. Constituents of Composites

Typical composites have just two materials/phases:

- Matrix material
- Dispersed material

The matrix phase (also called the *continuous* phase) surrounds and binds together pieces of other material dispersed throughout the matrix. This dispersed phase is sometimes called *reinforcement* if it is a phase added to increase strength. Alternatively, it is called a *filler* if it is added for other purposes, e.g. to bulk up the matrix at low cost without affecting the properties of the composite. Thus, the main constituents of composites are the matrix and reinforcement/filler materials. The matrix forms the volume of the composite material within which the reinforcement is embedded. The matrix joins all parts of the composite while the reinforcements strengthen the composite. For the composite to operate effectively, the phases must chemically bond where they join at the interface, i.e. the phases must stick together.

9.2. Some Definitions

Strain: When external forces are applied to objects made of elastic materials they produce changes in the shape and size of the object. A material that has been stretched is said to be under a **Strain**. Strain is the relative change in shape or size of an object due to externally applied forces, e.g. the % increase (extension) in length due to stretching:

Strain = Extension / Length

Because strain is a relative change %, it is dimensionless.

Stress: The externally applied force produces **Stress** which is the internal force per unit area (unit = Pa) associated with the strain:

Stress = Force / Area $(N/m^2 = Pa)$

Stiffness is the rigidity of a *specific object*, i.e. a measure of the resistance offered by an elastic body to deformation in response to an applied force. Stiffness is defined as the ratio of stress to strain.

Elastic Modulus is the rigidity of a *material* rather than the object but for purposes of this monograph is the same as stiffness.

In materials science, the **Strength** of a material is its ability to withstand an applied load without failure or plastic deformation.

9.3. The Matrix Phase

The matrix phase of composites is typically polymer, metal or ceramic. The functions of the matrix are to:

- Bind the reinforcement (e.g. fibres or particles) together
- Mechanically support the reinforcements
- Transfer mechanical load to the reinforcements
- Protect the reinforcements from surface damage due to abrasion or chemicals

High bonding strength between the matrix and the dispersed materials is critical. When a load is applied, the matrix shares the load with the dispersed phase, in some cases deforming so that the stress is mainly borne by the reinforcing material.

Composites are generally named according to the matrix and not the dispersed phase:

- Polymer Matrix Composites (PMC)
- Metal Matrix Composites (MMC)
- Ceramic Matrix Composites (CMC)



Polymers have low strength and stiffness. Metals have intermediate strength and stiffness but are very malleable and ductile. Ceramics have high strength and stiffness but are brittle. Composites based on these matrix materials can address these polymer, metal and ceramic performance issues. In polymer and metal matrix composites, if a strong bond is formed between the dispersed material and the matrix, the matrix transmits loads to the reinforcement through shear loading at the interface giving increased strength and stiffness. In ceramics a low interfacial bond strength between matrix and the reinforcement can enable slippage thus reducing brittleness in the composite material relative to the matrix ceramic.

9.4. The Dispersed Phase

The dispersed material is incorporated into the matrix to achieve the desired properties of the composite. The function of the dispersed material is to reinforce the matrix, i.e. enhance some property, often mechanical strength and stiffness. In most cases the reinforcement material is harder, stronger and stiffer than the matrix. Reinforcing agents are typically of the following shapes: fibres, particles, flakes, textile materials, e.g. sheets.



Figure 9.1. Classification of Composites based on Dispersed Phase

9.5. The Dispersed Phase – Particle Reinforced

Particle reinforcement of matrix material in composites can take the form of spherical, flakes/platelets or any other regular or irregular geometry. The particles are typically harder and stiffer than the matrix and can be of macro–, micro– or even nano–scopic scale. The degree of improvement in mechanical behaviour depends on the interface bonding between matrix and dispersed particles. Particulate composites tend to be much weaker and less stiff than fibre composites (see post) but are much less expensive. The distribution of particles in the matrix is random so that strength and other properties of the composite material are usually isotropic.

Dispersed particles are used to:

- Increase the modulus of the matrix
- Support higher tensile, compressive and shear stresses
- Decrease the permeability of the matrix
- Decrease the ductility of the matrix
- Produce low cost composites

Particles improve the fracture strength of the composite over that of the matrix by preventing or impeding **crack propagation** through the matrix by:

- Physically blocking and stopping cracks
- Diverting and splitting cracks so as to make their progress difficult

Particles also improve the stiffness and strength of the composite over that of the matrix by carrying a proportion of the load.

Examples of particle reinforcement are:

- Silica-epoxy composites for electronic moulding
- Refractory carbides (WC or TiC) to reinforce cobalt or nickel metals for ultra-high performance machine tool cutting tips. These are *Examples* of a **cermet**, a combination of metal + ceramic. The **brittle** carbide provides the wear resistant cutting edge but, by itself, would shatter on impact with the metal being cut. The **ductile** metal matrix adds flexibility to avoid shattering.
- Concrete aggregate-gravel and sand-reinforced cement
- SiC or Al₂O₃ particle reinforced Al matrix
- Carbon black: spherical particles of carbon produced by combustion of oil or gas with a limited supply of oxygen. This dispersed phase is used as a stiffer reinforcing phase in rubber matrix for manufacture of tyres

giving greatly improving wear resistance. The carbon black particles must be in the range 20–50 nm, evenly distributed in amounts up to 30% and well bonded to the matrix.

9.6. The Dispersed Phase – Fibre Reinforced

A fibre has a length which is much greater than its diameter – the length (L) to diameter (D) ratio is known as the Aspect Ratio (L/D). As a general rule, the smaller the diameter of the fibre, the higher its strength in the composite but it is generally more expensive. Matrix materials reinforced with fibres are known as Fibre–Reinforced Composites (FRC). The dispersed fibres can be in multiple different geometries, e.g. unidirectional, woven, chopped and mat.

Fibres increase the elastic modulus, i.e. stiffness, of the matrix material. The elastic modulus measures an object's or material's resistance to being deformed elastically (i.e. non-permanently) when a force is applied to it. Strong covalent bonding with the matrix along the fibre's length gives the composite material a very high modulus in this direction because to break or extend the fibre the bonds must be broken or moved. The mechanical properties of FRC depend upon:

- Fibre properties
- Degree to which an applied load is transmitted to the fibres by the matrix
- Good interfacial bond between fibre and matrix is necessary

Typical materials for fibre reinforcement are:

- Glass most widely used filament.
- Carbon high elastic modulus.
- Boron very high elastic modulus.
- Polymers, e.g. Kevlar
- Ceramics, e.g. SiC, Al₂O_{3.}
- Metals, e.g. steel.

9.7. The Dispersed Phase – Structural Reinforcement

A structural composite is of two types:

- Laminar composite
- Sandwich panel

A laminar composite is a composite material that consists of two or more layers of different materials bonded together.

A **sandwich-structured composite** is a special class of composite fabricated by attaching two thin but stiff skins to a lightweight but thick core in a sandwich configuration. The core material is normally low strength material, but its higher thickness provides the sandwich composite with high bending stiffness with overall low density. Sandwich composites are typically open – and closed – cell structured foams, e.g. Polystyrene and honeycombs, which are commonly used as core materials. The thick core material is then sandwiched between skin materials such as glass or carbon fibre-reinforced thermoplastics or thermoset polymers (unsaturated polyesters, epoxies...). The core is typically bonded to the skins with an adhesive.

9.8. Properties of Composites

Composites possess a huge range of desirable properties depending upon their composition and construction:

- High Specific Strength (ability to withstand an applied stress without failure) (strength/density)
- High Specific Modulus (modulus/density)
- Resistance to fatigue (weakness in metal or other materials caused by repeated variations of stress)
- Resistance to creep (the tendency of a solid material to slowly move or deform permanently under the influence of stress)
- Low, variable coefficient of thermal expansion
- High temperature capability
- Wear resistance
- Corrosion resistance
- Variable electrical conductivity very low to very high
- Variable thermal conductivity very low to extremely high

Such Properties Give Composites Major Engineering and Technological Advantages:

- Customised mechanical, thermal and electrical properties
- Unique combinations of properties not available to single material systems
- Lightweight but high strength
- Improved lifetime against fatigue and corrosion
- Great design flexibility
- Easily formed into complex shapes
- Can be low cost, but not generally

Such advantages enable multiple applications of composites in aerospace, transportation, construction, marine goods, sporting goods, etc. High – performance but costly continuous – carbon – fibre composites are used where high strength and stiffness plus light weight are required.

Much lower cost fibreglass composites are used in less demanding applications where weight is not so critical.

9.9. Specific Composites – Polymer Matrix Composites PMC

In PMCs polymer resin is the matrix. PMCs are the most widely used composite type used in the largest quantities. The three main PMC types are:

- Glass fibre–reinforced polymer composites
- Carbon fibre-reinforced polymer composites
- Aramid fibre-reinforced polymer composites



Glass fibre

Carbon fiber



Figure 9.2. Polymer Matrix Composites (PMC) (SubsTech)

9.10. Glass-fibre Reinforced PMCs

Glass fibre is made from silica (sand), sodium carbonate and calcium carbonate plus other compounds in the molten state. The raw materials are furnace heated to ~1700 K to the liquid state. They are then extruded from the furnace through metal (platinum/rhodium alloy) holes to produce filaments. A high speed winder, revolving faster than the extruded molten glass, "draws", i.e. pulls, the extruded glass under tension into very fine filaments. The filaments are coated with a protective lubricant and wound on a drum like a spool of a thread. The Glass Fibre in PMCs typically forms 20–40% by weight of the composite. It is generally in one of three forms Monofilament, Braided or Chop Fibre.

The glass fibres in glass reinforced PMCs can be either aligned or unaligned with each other:

- If the fibres are **unaligned** (random orientation), the filler and matrix can be blended together as powders or slurries, shaped or moulded and the matrix hardened and bonded to the filler by heat or by chemical reaction. The shaping may be by injection moulding or casting of the unhardened composite. Filaments can also be processed into non-woven mats of fibres, randomly orientated in two dimensions.
- If the fibres are **aligned**, the fibres may be used as monofilaments giving alignment in one dimension or twisted into yarns and then woven or knitted into two or three–dimensional fabrics giving alignment in two or three dimension. The fabrics or mats are placed in moulds, impregnated with matrix material and processed. Again, the matrix is hardened and bonded to the filler by heat or by chemical reaction.

In fibreglass, the matrix is usually a polyester resin although epoxy and acrylic polymers are also used. *Examples* of matrix polymers used with glass fibre reinforcement are Polypropylene (PP), Polycarbonate (PC), Polyethylene Terephthalate (PET), Polybutylene Terephthalate (PBT), Nylon.

9.11. Carbon-fibre Reinforced PMCs

Carbon fibres are made by heating filaments of organic precursor such as polyacrylonitrile (PAN) at ~500 K in air to form oxidized PAN. Oxidized PAN is then placed in a furnace with an inert atmosphere, e.g. argon, and heated to ~2000 K, a process known as pyrolysis (heating of a substance in the absence of air). The product is graphene comprising chains of carbon atoms bonded side–to–side forming narrow sheets of carbon atoms, one atom thick. For carbon fibre, the sheets merge to form a single circular filament.

Carbon fibres are used to form carbon reinforced PMCs as a filler in a continuous matrix of a polymer, often an epoxy resin. Layers of carbon fibre cloth are laid down in the shape required, usually in a mould which is then filled with epoxy resin and heated. Carbon fibres have, even at high temperature high specific modulus, high specific strength and good physical and mechanical properties. However, they are expensive to manufacture as composites and are only used when their properties of lightness plus strength are critical, e.g. aircraft structural components (Neville A.M., 2011).

9.12. Aramid – fibre Reinforced PMCs

An aramid is a polymeric aromatic amide. Kevlar[®] is a very widely used aramid and is very difficult to handle as the only effective solvent is concentrated sulphuric acid. Kevlar[®] is made from lightweight atoms but is very strong and flexible, weight for weight five times as strong as steel. Its strength comes from the way the polymer chains are aligned, the flat molecules being held together by hydrogen bonds. These sheets of molecules can stack up along the fibre axis. Aramid fibres, already strong, are used as the filler in aramid reinforced PMCs with a phenolic resin or epoxy resin as a matrix. They are particularly useful where energy has to be absorbed and dissipated or abrasion resisted. They are used widely in aviation, e.g. helicopter rotor blades, in sport for, e.g. tennis racquets, in boats, in protective clothing for fire resistance and body armour and in vehicle brakes.

9.13. Applications of PMCs

Applications of PMCs include:

- Aerospace: wings, fuselages, landing gear, rotor blades, satellite structure
- Automobile: body panels and frames, bumpers, suspension, drive shafts, tyres
- Marine: boat hulls, decks, masts, propeller shafts
- Chemical plants: process pipes, tanks, pressure vessels, oil field structures
- Recreational goods: tennis, etc. racquets, golf clubs, fishing rods, bicycles, skis, canoes, swimming pools
- Construction: bridge decks, repair of concrete decks, bridges, columns, concrete reinforcement bars
- Biomedical: teeth, bone replacements, artificial limbs
- Electrical: panels, switch gear, insulators, moulding compounds, wind turbine blades.

9.14. Specific Composites – Metal Matrix Composites MMC

An MMC has at least two constituent parts: a metal and a different metal or another material such as a ceramic or organic compound. Matrix materials are typically: Al, Mg, Ti, Cu, Ni. Dispersed reinforcements include: C, SiC, B, Al_2O_3 either as particles or fibres. The matrix metal is more ductile than the reinforcement so that addition of the reinforcement improves specific strength/stiffness, abrasion resistance, creep resistance and dimensional stability.

There are multiple manufacturing methods involving solid, liquid and vapour states.

Advantages over PMCs include much higher operating temperatures, nonflammability and high resistance to organic fluids. Disadvantages are expensive and higher density (means higher weight).

Applications include engine components, aerospace structures and turbine engines.

9.15. Specific Composites – Ceramic Matrix Composites CMC

CMCs consist of ceramic fibres embedded in a ceramic matrix. Matrix and fibres can consist of any ceramic material including carbon/carbon fibres. CMCs were developed to overcome the low crack resistance of conventional technical ceramics such as alumina, silicon carbide, aluminium nitride, silicon nitride and zirconia. These materials fracture easily under mechanical or thermomechanical loads because of cracks started by small defects or scratches.

To increase the crack resistance, long multi–strand ceramic fibres are embedded into the matrix. Carbon (C), silicon carbide (SiC), alumina (Al_2O_3) and mullite $(Al_2O_3-SiO_2)$ dispersed fibres are most commonly used for CMCs. The matrix materials are usually the same, i.e. C, SiC, alumina and mullite.

The advantages of CMCs are high strength and modulus, very high service temperature and reduced weight. The disadvantage is that the materials are very brittle.

Applications typically involve high temperature and severe stress such as in automobile engines, aircraft gas turbine engines, etc.

10. Cement and Concrete

Concrete is the single most widely used man-made material in the world. The amount of concrete used worldwide is twice that of steel, wood, plastics and aluminium combined. Concrete's use in the modern world is exceeded only by that of naturally occurring water.

Concrete has been used in construction for millennia. The basic ingredients – sand and gravel (aggregate), a cement binder and water – were mixed in Egyptian times ~2,500 BC. Romans from ~300 BC were masters of the material, using it to create such wonders as the Pantheon in Rome, topped with a 43.3m diameter concrete dome now over 2,000 years old but still the world's largest non–reinforced concrete dome. With the loss of Roman concrete expertise as the Empire fell into decline, concrete's secrets didn't re–emerge until modern concrete was born in 1824 with the discovery of Portland cement.

Concrete is widely used for making architectural structures, foundations, brick/block walls, pavements, bridges/overpasses, roads, runways, parking structures, dams, pools/reservoirs, pipes, footings for gates, fences/poles, even boats. Concrete is used in large quantities almost everywhere mankind has a need for infrastructure – 4,000 million tonnes in 2013 global production. Concrete is the basis of a huge global commercial industry. Globally, the ready–mix concrete industry (only one segment of the total concrete market) exceeded \$100 billion revenue in 2015. Given the size of the concrete industry and how concrete is used to shape the infrastructure of the modern world, it is difficult to overstate the role this material plays today.

Advantages of Concrete: Concrete has many advantages that make it the most popular construction material. These include:

- Economical and energy efficient
- Versatile can be used in many different applications and modes
- Long life and relatively low maintenance requirements (does not need a coating) conferring major economic benefits
- Strong and durable not as likely to rot, rust, corrode, or decay as other building materials
- Pliable with the ability to be moulded or cast into almost any desired shape building of the moulds and casting can occur on the work–site thus reducing costs
- Non-combustible material, fire-safe and able to withstand high temperatures
- Resistant to wind, water, rodents, and insects

- Very low coefficient of thermal expansion
- High compressive strength. By definition, the compressive strength of a material is the value of uniaxial compressive stress (units = MPa) at which the material fails completely usually obtained experimentally by means of a compressive test.

Disadvantages of Concrete:

- Low tensile strength, typically only ~10% of compressive strength
- Low shear strength, typically ~20% of compressive strength
- Low ductility brittle, low strength–to–weight ratio
- Susceptibility to cracking as shrinks with age
- Some volume instability from shrinkage
- Can be attacked by bacterial corrosion, sea water, chemicals (chlorides, sulphates, etc.) depending on the type of concrete

Despite its disadvantages, concrete remains the material of choice for many applications. The low tensile and shear strengths can be hugely enhanced by reinforcement of a concrete matrix with materials strong in tension, e.g. Steel (Flaga K., Mierzwa J., 1992).

10.1. What is Concrete?

Concrete is a **composite material** composed of:

- Coarse granular *dispersed* material (the **aggregate** or filler)
- Embedded in a hard *matrix* material (the **cement paste** or binder) that fills the space between the aggregate particles and glues them together

Thus, Concrete = Filler + Binder = Aggregate + Cement Paste.

The dispersed Aggregate is fine or coarse:

- Fine aggregate = Sand
- Coarse aggregate = Gravel fragments of crushed rocks, e.g. sandstone, limestone, basalt, of varying size from granular gravel (2 to 4 mm), pebble gravel (4 to 64 mm) upwards

The Cement Paste *matrix/binder* is a mix of components being Cement + Water + Additives. The mixing of these ingredients causes a chemical reaction to occur in the mixture which eventually sets hard. Accordingly, the concrete composite material is generated by the combination: Cement Paste + Aggregate = Concrete

According to the type of cement paste binder used, there are many different kinds of concrete. Portland cement concrete is the most widely used. The composition of Portland Cement Concrete can be presented as follows (cement paste + sand aggregate is called **mortar**):



Typical distribution of ingredients in concrete by volume are:

- Cement Paste = 25–45% cement + 55–75% water + 2–8% air.
- **Aggregate** = 35–45% fine + 55–65% coarse.
- **Concrete** = 60-75% aggregate + 25-40% cement paste.
- **Mortar** = Air + water + cement + additive + fine aggregate (sand) is typically 50–65% of concrete.

10.2. Components of Concrete – Cement

A cement is a binder, a substance that sets and hardens and can bind other materials together. Cement is a manufactured and not natural material. Precursor compounds from which cement is produced and the naturally occurring minerals from which they are mined are shown in the below Table:

Table 10.1. Precursor compounds from which cement is produced and the naturally occurring minerals from which they are mined

| Precursor Compounds | Lime CaO | Silica SiO ₂ | Alumina Al ₂ O ₃ | Iron Oxide Fe ₂ O ₃ | Gypsum CaSO ₄ *2H ₂ O |
|-----------------------------------|-------------|----------------------------|---|--|--|
| Raw Materials of Precursors | Limestone | Sand | Clay | Iron ore | Gypsum |
| | Shale | Clay | Shale | Clay | |
| | Marl | Shale | Slag | Mill scale | |
| | | Marl | | | |
In the production of Portland Cement the following is the relative percentage of precursor compounds:

60% - CaO - Limestone or calcareous rock. $20\% - SiO_2 - Clay or argillaceous rock$ $10\% - Al_2O_3 - Clay or Ore$ $5\% - Fe_2O_3 - Clay or Ore$ $5\% - CaSO_4*2H_2O - Gypsum$

Modern cement was born in ~1820 with the discovery of 'Portland Cement' which is now the most widely used **key ingredient** binding the composite concrete components together.

Cement Manufacturing Process

There are both wet and dry methods for the manufacture of cement. In both methods raw materials are **homogenised** by crushing, grinding and blending. Approximately 80% of the ground materials pass through a #200 (74 μ m opening) sieve. The raw materials are burnt in a kiln to form new compounds and produce "Clinker". Gypsum is then added to regulate the setting of the concrete:

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Clinker + Gypsum = Cement
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The manufacturing process can be either wet or dry: Wet process:

- The mix of homogenized constituents plus 30–40% water is heated up to 1550° C in a revolving inclined kiln
- Oxides of silica, calcium and aluminum combine to form cement clinker
- This is mixed with calcium sulphate (gypsum) to control the rate of concrete setting
- The resulting mix is crushed into powder in ball mills before storing in silos or bags

Dry process:

• The homogenized mix is fed into a kiln and burned in a dry state. The other steps same are as for the wet process. The dry process achieves large savings in fuel but generates dust.

The main reaction in the roasting kiln is the formation of calcium silicates from calcium carbonate $CaCO_3$ (limestone) and clay silicates. At ~1000°C the two raw materials break down into their component oxides, CaO and SiO₂.



(Materials Science and Technology)

As temperature rises further these combine into di- and tri-calcium silicate.

Lesser quantities of iron and aluminium in the clay also react with calcium giving minor components of Portland cement.

The final product from the roasting kiln is clinker comprising:

- C₃S tricalcium silicate
- C₂S dicalcium silicate

C₃A tricalcium aluminate

C₄AF tetracalcium aluminoferrite

In which formulae the Cement Chemist Shorthand is used:

| C = CaO | $H = H_2O$ |
|---------------|--|
| $S = SiO_2$ | $\underline{\mathbf{S}} = \mathbf{SO}_3$ |
| $A = Al_2O_3$ | $F = Fe_2O_3$ |

The constituents of cement after clinker is inter–ground with gypsum vary depending upon the design and type of the cement. Approximately 75% is composed of calcium silicates while the rest is made up of Al_2O_3 , Fe_2O_3 and $CaSO_4$ the percentage weights of each component depending upon the type of cement. The more detailed composition is shown in the below Table 10.2.

| Cement Compound | Weight Percentage | Chemical Formula |
|------------------------------|-------------------|--|
| Tricalcium silicate | 35–65 % | Ca ₃ SiO ₅ or 3CaO SiO ₂ |
| Dicalcium silicate | 15–40 % | Ca ₂ SiO ₄ or 2CaO SiO ₂ |
| Tricalcium aluminate | 0–15 % | Ca ₃ Al ₂ O ₆ or 3CaO Al ₂ O ₃ |
| Tetracalcium aluminoferrite | 6–20 % | $\begin{array}{c} Ca_4Al_2Fe_2O_{10} \text{ or} \\ 4CaO\ Al_2O_3\ Fe_2O_3 \end{array}$ |
| Calcium Sulphate (Gypsum) | 2-3 % | CaSO ₄ ⁻ 2H ₂ O |

Table 10.2. Components of Cement.

Types of Portland Cement

The relative proportions of the cement compounds are controlled by:

- Changing the proportions of raw materials in the feed
- Changing the temperature in the kiln
- Altering the duration in the kiln
- Adjusting the amount of gypsum added to the clinker

Using these process control parameters a range of different cement types can be manufactured each with its specific properties:

- **Type 10 Standard Portland cement –** Used for general purposes, air entrained: 50% C₃S; 24% C₂S; 11%C₃A; 8% C₄AF
- **Type 20 Modified Portland cement** Used when sulphate resistance and/or generation of moderate heat of hydration are required, air entrained: 42% C₃S; 33% C₂S; 5% C₃A; 13% C₄AF
- Type 30 High early strength Portland cement Used for early strength and cold weather operations, air entrained: 60% C₃S; 13% C₂S; 9% C₃A; 8% C₄AF
- Type 40 Low heat Portland cement Used where low heat of hydration is required, air entrained: 26% C₃S; 50% C₂S; 5% C₃A; 12% C₄AF
- **Type 50 High sulphate–resistant concrete** Used where sulphate concentration is very high, also used for marine and sewer structures, air entrained: 40% C₃S; 40 % C₂S; 3.5 % C₃A; 9% C₄AF

Air entrainment is the intentional creation of tiny air bubbles in concrete by adding to the mix an air entraining agent (surfactant). The air bubbles are created during mixing of the concrete and most survive in hardened concrete. Air entrainment increases durability of the hardened concrete and workability of the concrete while in a plastic state.

10.3. Components of Concrete – Water

Water is the key ingredient. When mixed with cement it forms a paste that binds the aggregate together. Water causes the hardening of concrete through a process called **hydration**. Hydration is a chemical reaction in which the major compounds in cement form chemical bonds with water molecules and become hydrates or hydration products.

The water needs to be pure to prevent side reactions which may weaken the concrete or interfere with the hydration process. Any drinkable water can be used for concrete making. Water containing more than 2000 ppm of dissolved salts may harm the concrete. Limits for specific salts are: Chloride ions not more than 1000 ppm, Sulphate ions not more than 3000 ppm, Bicarbonate ions not more than 400 ppm.

The water to cement ratio is the most critical factor in the production of "perfect" concrete. Too much water reduces concrete strength. Too little makes the concrete 'unworkable' (too stiff). Concrete needs to be workable, i.e. "plastic", so that it may be compacted, moulded and shaped into different forms (walls, domes, columns, etc.). Because concrete must be both strong and workable, a careful balance of the cement to water ratio is required:

- Low water to cement ratio leads to high strength but low workability
- High water to cement ratio leads to low strength but good workability

There is a Water to Cement Ratio Law, namely "For a given set of materials the strength of the concrete (so long as we have a plastic mix) depends solely on the relative quantity of water as compared with the cement, regardless of mix or size and grading of aggregate".

An empirical formula known as Abram's Rule relates compressive strength of the concrete, f_c , and the water to cement ratio, w/c. The formula includes two constants, A and B, which depend upon the specific type of concrete. For 28 day set concrete, A is approximately 100 MPa, B is usually taken to be 4.





 f_c = compressive strength w/c = water/cement ratio A = a constant of value ~100

 $B = a \text{ constant of value } \sim 4$

Concrete does not need to dry out to harden as is commonly thought. The cement needs moisture to hydrate and set. When concrete dries it actually stops getting stronger. Concrete with too little water may be dry but is not fully reacted so that the properties will be poorer than that of a wet concrete. The reactions of water with the cement may continue for many years.

The hydration reaction itself consumes a specific amount of water but concrete is actually mixed with more water than is needed for the hydration reactions in order to give concrete sufficient workability as only flowing concrete achieves proper filling of moulds/forms. Water not consumed in the hydration reaction will remain in the microstructure pore space. Pores make the concrete weaker due to the lack of strength–forming calcium silicate hydrate bonds. Some pores will remain no matter how well the concrete has been compacted. The empty space (porosity) is determined by the water to cement ratio. Most concrete is made with a water to cement mass ratio ranging from 0.35 to 0.6. The negative effects of too much water in the concrete mix are:

- Reduced strength
- Increased shrinkage and creep
- Increased permeability
- Reduced abrasion resistance
- Reduced Freeze Thaw resistance to cracking

10.4. Components of Concrete – Additives

Additives/Admixtures are materials as powders or liquids other than cement, water, aggregates and reinforcing fibres. They are added to plastic (nonhardened) concrete as an ingredient immediately before or during mixing in order to change one or more properties of either plastic or set/hardened concrete. They often constitute < 5% by mass of the cement added during concrete mixing. Additives change the properties of both plastic concrete and hardened concrete.

Additives change **Plastic** concrete properties:

- Decrease water content
- Increase workability
- Retard or accelerate setting time
- Reduce segregation of concrete components
- Reduce change in fluidity of the concrete
- Improve the ability to pump, fill moulds and finish, e.g. smooth or roughen, concrete
- Modify the rate and/or capacity for bleeding, i.e. tendency of water to be expelled and gather on surfaces of plastic concrete

Additives change Hardened concrete properties:

- Improve impact and abrasion resistance
- Inhibit corrosion of embedded metals, e.g. reinforcing bar
- Reduce plastic concrete shrinkage and cracking
- Reduce long term drying shrinkage
- Produce coloured concrete
- Produce cellular concrete (lightweight foam concrete building material)

Additives can be classified in two ways:

- By type of additive:
 - Chemical additives such as setting accelerators, setting retarders, water-reducing, air-entraining
 - o Mineral additives conferring strength and durability
- By function, i.e. concrete property: Function *Examples* are workability, control of concrete setting, strength, durability, special properties, e.g. colour, corrosion inhibitors, water repellents.

Chemical Additives

<u>Accelerators</u> speed up hydration (hardening) of concrete, so reducing concrete setting time or improving development of early strength (used in cold– weather concreting). Typical materials are CaCl₂ (25% strength gain in three days from < 2% addition by weight of cement), Ca(NO₃)₂ and NaNO₃. Chlorinated additives, despite their advantages, may increase corrosion of steel reinforcement.

<u>**Retarders**</u> slow hydration and, thus, the setting of concrete so are used in large or difficult concrete pours and in hot weather to keep concrete workable during placement and compaction. Typical retarders are sugar, sucrose, sodium gluconate, glucose, citric acid and tartaric acid.

The operation of Accelerators and Retarders depends upon the following considerations:

- Setting of cement paste requires crystallisation of the hydration products after adding water to cement powder but crystallisation only occurs when the concentrations of ions (calcium, aluminate, silicates, etc.) dissolved into the cement paste from the cement powder mixed in water reach critical state.
- The time to critical state depends upon the solubility of cement powder compounds in water to produce critical concentrations of crystallisation ions in the cement paste solution. The solubility of crystallisation ions is sensitive to the presence of other ions in the solution so, we can change the solubility, i.e. the rate of crystallisation ion production from the cement powder in water, by introducing other ions. This is the principle behind retarding and accelerating admixtures. Retarding additives are chemicals that slow down the dissolution of crystallisation ions from the cement powder into the cement paste. Accelerating additives are chemicals that increase the dissolution of crystallisation ions from the cement powder into the cement paste.

<u>Water-reducing additives</u> are used to reduce the water required in concrete mixes by 5–30%. They are added to improve the workability of concrete despite less water in the mix, thus increasing strength. Additives are surface–active chemicals, i.e. Surfactants, which separate the cement particles by increasing the electrostatic charge on the particle surface thus releasing water trapped in particle clusters. More water is then available to lubricate the concrete mix. Thus, water reducing additives reduce the water required to attain a given workability thus reducing the water/concrete ratio to give high concrete strength, low permeability and improved durability (Neville A.M., 2011).

Normal range water reducers are Lignosulphates, hydroxylated carboxylic acids and carbohydrates which reduce 5–10% of water at normal dosages. What are called **Super–plasticisers** are Sulphonated melamine/naphthalene formaldehyde condensates. These reduce water requirement by 15–30%. Super–plasticisers are long–chain molecules with a large number of polar groups attached to the main hydrocarbon chain. Once adsorbed on a cement particle, a strong negative charge is introduced onto the particle surface. The surface tension of the surrounding water is, thus, greatly reduced to release trapped water.

<u>Air-entraining additives</u> trap air bubbles thus reducing concrete damage during freezing and thawing cycles. They allow dispersal and stabilisation of microscopic air bubbles (diameters ranging from 20 to 2000 μ m) generated in concrete). They are used to improve the frost resistance of concrete (i.e. resistance to stresses arising from the freezing of water in concrete) (Kurdowski W., 2014).

Such additives are based on foaming agents, namely materials that facilitate formation of foam, i.e. air bubbles, such as a surfactant which reduces the surface tension of a liquid thus reducing the work needed to create foam.

Examples of air-entraining additives are Vinsol resin; Sulphonated lignin compounds; Petroleum acid compounds; Alkyd benzene compounds. But the use of these reduces concrete strength as each 1% of air may decrease compressive strength by up to 5%.

<u>Pigment additives</u> are used to change the colour of concrete for aesthetics.

<u>Shrinkage Reducing</u> admixtures are used to minimize drying shrinkage cracking in concrete.

Corrosion inhibitors minimise the corrosion of steel bars in concrete.

<u>Bonding agents</u>, typically a polymer, are used to create a bond between old and new concrete.

<u>**Pumping aids**</u> improve concrete fluidity and, thus, ease of pumping concrete through tubing to the point of delivery at the construction site.

Mineral Additives

Mineral additives to the concrete mix are used to replace part of the cement or sand components. When used to replace sand, the mineral additives are called 'supplementary cementing materials'. Mineral additives are added in large quantities compared to chemical additives, typically > 10% of the cement weight. Industrial by–products are the primary source of mineral additives, for example furnace slags. Mineral additives are categorised into:

- Cementitious possessing the property of a cement, i.e. a binder, a substance that sets and hardens and can bind other materials together;
- Non-cementitious by itself has no binding ability but used together with other materials can create binding.

Cementatious Materials

Cementatious mineral additives possess independent cementing (binding) properties. Two main types are used: Ground–granulated Blast Furnace Slag and High Calcium Fly–Ash.

Ground-granulated blast-furnace slag (GGBS or GGBFS)

GGBS is obtained by quenching molten iron slag by–product from a blast furnace in water or steam to produce a glassy, granular product that is dried and ground into a fine powder. The main components are CaO (30-50%), SiO₂ (28–38%), Al₂O₃ (8–24%), MgO (1–18%). GGBS is used as a direct replacement for Portland cement, on a one–to–one basis by weight. Typically 40 to 50% is used. Concrete containing slag offers better chemical resistance due to improved watertightness since the concrete texture becomes dense. Thus, GGBS:

- Reduces the risk of damage from alkali–silica reaction (ASR) which occurs over time in concrete between the highly alkaline cement paste and the amorphous silica in many common aggregates
- Provides higher resistance to chlorides (from, e.g. marine environments, road salting) reducing the risk of reinforcement corrosion
- Provides higher resistance to attacks by sulphates and other chemicals

GGBS is used to make durable concrete structures extending the lifespan of buildings from fifty to a hundred years.

High calcium (> 10% CaO) Fly Ash

Fly ash is a by-product of the combustion of pulverized coal in electric generation plants. A dust collection system removes the fly ash as a fine particulate residue from the combustion gases. This class of fly ash has both pozzolanic properties (*see post*) and some cementitious (binding) properties.

Thus, unlike pure pozzolans, such as Low Calcium Fly Ash, it strengthens the concrete through both the pozzolanic reaction (*see post*) and direct cementitious chemical bonding. SiO_2 , Al_2O_3 , CaO are the major constituents.

Non–Cementatious Materials

Non-cementatious mineral additives are called Pozzolans. These are siliceous or (siliceous + aluminous) materials which in themselves possess little or no cementitious value, i.e. no binding properties, but will, in finely divided form and in the presence of water, chemically react with $Ca(OH)_2$ at ordinary temperatures to form compounds possessing cementitious properties. The main pozzolans used in cement are:

- Low calcium (< 10% CaO) Fly Ash
- Silica Fume
- It is appropriate here to recall the cement chemist shorthand: C = CaO;
 S = SiO₂; A = Al₂O₃; H = H₂O; <u>S</u> = SO₃; F = Fe₂O₃

The binding together of concrete components is based on the formation of C-S-H = Calcium Silicate Hydrate (*see hydration post*) within the plastic concrete mix. Conventional Portland cement concrete achieves this through hydration reactions such as:

 $C_3S+H \rightarrow C-S-H+CH+Heat$ (CH = Calcium Hydroxide, i.e. Lime)

But, when low-calcium fly ash and/or silica fume are added to cement the 'pozzolanic reaction' occurs:

 $S+CH+H \rightarrow C-S-H$

The Pozzolans react with the calcium hydroxide (lime) generated by hydrating cement to form additional bonding C–S–H. The Pozzolanic reaction creates additional C–S–H by converting the less dense (weaker) CH phase and larger pores into denser (stronger) C–S–H and smaller pores. Thus, a weak phase is converted into a stronger phase which imparts greater concrete strength. The conversion of CH to C–S–H also improves concrete durability as the permeability of the concrete is reduced due to denser microstructure. This gives improved resistance to acidic chemicals and alkali–aggregate reactions.

Low Calcium (< 10%) Fly Ash – Is a Pozzolan by–product of coal from electrical power plants consisting of complex compounds of silica, ferric oxide and alumina. This takes part in the pozzolanic reaction increasing the strength and durability of concrete. An important characteristic of fly ash is the spherical form of the particles which improves concrete flowability.

Silica Fume (also known as micro–silica) – Is a Pozzolan by–product of electric arc furnaces in the production of silicon and ferrosilicon alloys. It comprises non–crystalline silica. Particulate size ranges from 0.5 to $0.01\mu m$ so that, compared with normal Portland cement and typical fly ashes, silica fume is two orders of magnitude finer. With such a small size, the pozzolanic reaction

can occur very fast thus increasing compressive strength at both early and late stages by 40–60% and the durability of the concrete.

10.5. Components of Concrete – Aggregates

Aggregates are chemically inert, solid bodies held together by the cement. They come in various shapes, sizes and materials ranging from fine particles of sand to large, coarse rocks or metal or ceramic pieces. Aggregate is the second most influential ingredient in concrete. Because cement is the most expensive ingredient in concrete, 60 to 75% of concrete volume is aggregate filler keeping the cost of the concrete low. Fine Aggregate is typically 35–45% of the total aggregate and the mortar which includes the fine aggregate (Air, water, cement, fly ash, sand) is typically 50–65% of the total volume of a mixture. In any concrete mix both fine and coarse aggregate fractions are present:

- Fine: Sand or Crushed Stone (< 5mm)
- Coarse: Gravel or Crushed Stone (5–50 mm)

Aggregates have multiple characteristics which must be factored into the selection of materials and design of the target concrete. Selection of aggregate is determined by the desired characteristics of the concrete. Thus, the density of concrete is determined by the density of the aggregate. Soft, porous aggregates give weak concrete with low wear resistance; hard aggregates give strong concrete with high resistance to abrasion.

The compressive strength of aggregates should be higher than the designed concrete strength of 40–120 MPa. Voids represent the amount of air space between the aggregate particles. Coarse aggregates contain 30–50% of voids, fine aggregate 35–40%. Voids need to be minimised to reduce the quantity of cement needed in a mix and to reduce weakness resulting from voids.

Moisture content represents the amount of water in aggregates both absorbed and surface moisture. Coarse aggregates contain very little absorbed water while fine aggregates contain 3–5% of absorbed water and 4–5% surface moisture. These water quantities need to be factored into the concrete mix design.

Aggregates should be clean, hard and strong. Aggregates must be:

- Washed to remove any dust, silt, clay, organic matter and impurities that would interfere with the bonding reaction with the cement paste, then
- Graded into various sizes/classes by passing the material through a series of sieves with different size openings.

The aggregate should be well-graded so as to improve the packing efficiency thus reducing voids (weakness) and so minimising the amount of cement paste needed. The aggregate should also be well-graded so as to make the concrete more workable.

Although typically chemically inert, aggregate has a major influence on concrete properties:

- weight, stiffness/modulus of elasticity, i.e. dimensional stability under load,
- mechanical durability, e.g. abrasion resistance,
- resistance to chemical attack, e.g. alkali-aggregate reaction,
- strength of concrete this is hugely affected by the bond between the cement and the aggregate.

The Cement–Aggregate bond is generated by some combination of the mechanical interlocking or 'keying' between cement hydration products and the aggregate surface, determined especially its shape and texture, and the chemical bond from reactions between cement paste hydration products and the aggregate. Such bond is a critical factor in concrete strength but the nature of the bonding not fully understood.

Bonding strength depends upon multiple factors, in particular the aggregate type and gradation, aggregate shape and texture, the concrete mixing process, the presence and type of any mineral additives and any surface treatment of the aggregate prior to mixing, e.g. washing or chemical treatment.

| Aggregate Class | Examples of aggregates used | Uses |
|-------------------|---|---|
| ultra–lightweight | vermiculite ceramic spheres, perlite | lightweight concrete which can be sawed or nailed, also for its insulating properties |
| lightweight | expanded clay shale or slate crushed brick | used primarily for making lightweight concrete for structures, also used for its insulating properties. |
| normal weight | crushed limestone, sand, river gravel crushed recycled concrete | used for normal concrete projects |
| Heavy weight | steel or iron shot steel or iron pellets | used for making high density concrete for shielding against nuclear radiation |

Table 10.3. Classes of aggregates are shown in the following Table.

10.6. Hydration

Hydration is the general term used to describe the chemical reaction that takes place between cement powder and water. It is a surface reaction that commences immediately water touches the cement grain. Only a small amount of water is needed for hydration, but additional water is needed for plastic concrete workability.

All four of the principal cement compounds active in hydration react simultaneously but not at the same rate. The hydration process is:

- Exothermic
- Consumes the cement grains, i.e. they become smaller as hydration progresses, but large grains may never completely hydrate
- Produces **hydration products** which are the key binding agents throughout the concrete
- Hydration reactions will continue as long as moisture, un-reacted cement and some heat is present, sometimes for years

When cement is mixed with water it is first plastic and then slowly forms through hydration into a hard rock–like material. This curing process is called setting and comprises three main phases:

- **Dissolving** in water of the cement's soluble compounds
- **Hydration** to form the initial colloidal phase state to produce a **plastic** mass
- **Crystallisation** of hydration products to deliver **hardening** of the plastic mass

The curing process comprises an initial set, in which the paste loses its fluidity and within a few hours a noticeable hardening occurs, and a final set in which the build up of hydration products causes a hardening process responsible for the strength of concrete over at least days, even months or years. Gypsum retards and controls the setting process. Hot water used in mixing will accelerate the setting the process.

Chemistry of Hydration

Cement comprises four principal compounds active in hydration as shown in the below Table:

| C ₃ S | Tricalcium silicate | 3CaO'SiO ₂ |
|-------------------|-----------------------------|--|
| C_2S | Dicalcium silicate | 2CaO'SiO ₂ |
| C ₃ A | Tricalcium aluminate | 3CaO, Al ₂ O ₃ |
| C ₄ AF | Tetracalcium aluminoferrite | 4CaO Al ₂ O ₃ , Fe ₂ O ₃ |

 C_3S and C_2S are ~75% by weight of Portland cement and are the only cement compounds contributing to concrete strength. They react with water to form new crystalline concrete binding compounds of C–S–H Calcium Silicate Hydrate and CH Calcium Hydroxide, i.e. Lime.

The aluminium compounds C_3A , C_4AF also react with water but do not contribute to strength, only speed of setting by generating heat. When water is added to cement, each compound undergoes hydration and contributes to the final concrete product as part of the setting stage. However, only the calcium silicates contribute to concrete strength.

Tricalcium silicate is responsible for most of the early strength (first 7 days). Dicalcium silicate reacts more slowly and contributes to strength later.

The chemical equation for the hydration of tricalcium silicate is given by:

Tricalcium silicate+Water \rightarrow Calcium silicate hydrate+Calcium hydroxide + heat

2 Ca₃SiO₅ + 6 H₂O \rightarrow 3 CaO₂SiO₂ 3H₂O + 3 Ca(OH)₂ + 173.6kJ Or, in shorthand: C₃S + H \rightarrow C–S–H + 3CH

The chemical equation for the hydration of dicalcium silicate is given by:

Dicalcium silicate + Water \rightarrow Calcium silicate hydrate + Calcium hydroxide + heat

2 Ca₂SiO₄ + 4 H₂O \rightarrow 3 CaO.2SiO₂.3H₂O + Ca(OH)₂ + 58.6 kJ Or, in shorthand: C₂S + H \rightarrow C–S–H + CH

The resulting **calcium silicate hydrates C–S–H** form an extended **network of bonds** which harden the cement paste/mortar and bind together with the solid aggregate to form concrete.

A typical concrete setting characteristic is as follows:

Heat is generated by **cement hydration** due to the breaking and making of chemical bonds during hydration. The heat generated is shown in the below plot as a function of time:

Stage I hydrolysis of cement compounds occurs rapidly with a emperature increase of several degrees.

- **Stage II** is the 'dormancy' period in which the generation of heat slows dramatically lasting 1–3 hours. During Stage II the concrete is in a plastic state allowing transport, moulding and placing. At the end of this stage initial setting begins.
- **Stages III and IV** the concrete starts to harden and heat generation increases due primarily to the hydration of tricalcium silicate.
- **Stage V** is reached after 36 hours when slow formation of hydrate products occurs and continues as long as water and unhydrated silicates are present.



Figure 10.2. The heat generated is shown as a function of time (Materials Science and Technology)

11. Chemistry of Water

11.1. Water – The Molecule

Water is a POLAR COVALENT molecule comprising two Hydrogen atoms bonded to one Oxygen atom with the chemical formula H_2O . The oxygen atom is bound to each hydrogen atom by a single covalent bond thus helping to fill the outer electron shell of the O atom.



Figure 11.1. Chemical formula of water H₂O (Simple English Wikipedia, Water (molecule))

The water molecule is, of course, electrostatically neutral, but the bonding is not symmetrical, i.e. electrons are not equally shared between the O and H atoms. Electrons spend more time near the oxygen and less near the hydrogen atoms. This leaves the water molecule with a positive (H end) and a negative (O end). These charged ends ensure that the water molecule is POLAR, i.e. possesses a dipole moment.



Figure 11.2. Water molecule with a dipole moment (Simple English Wikipedia, Water (molecule))

Water – Hydrogen Bonding

Water molecules form Hydrogen bonds. The negative O end of one water molecule is attracted to the positive end of another water or other molecule. Thus, in any volume of ice or liquid water each H_2O molecule is bonded to its nearest neighbour. A single hydrogen bond is weak but many hydrogen bonds are strong. The hydrogen bond can form not just between water molecules but between a water molecule and a non-water molecule providing the non-water molecule is also polar covalently bonded, for example between Water and Ammonia (NH₃).

Water - Physical States

Water is found in three physical states – solid, liquid and gas. In the form of ice, the water molecules are held in a fixed matrix pattern but are vibrating. In the form of liquid, the molecules are packed close together in a random arrangement and are free to move. As gas or steam vapour, the molecules are widely separated and move at great speed.



Figure 11.3. The diagram shows the inter-molecular hydrogen bonding of water in its three states (Simple English Wikipedia, Water (molecule))

Ice molecules are bonded into a hexagonal crystal structure. Liquid water molecules are bonded but randomly. Steam molecules are not bonded but move independently. The water molecules in ice are bonded in a hexagonal crystal lattice. As more molecules freeze a 6–pointed crystal snowflake is created always with 6 sides. Because of its structure, ice is slightly less dense than liquid water (984 vs. 1,000 kg/m³). This results in ice forming at the water surface and floating on the liquid water (icebergs).

11.2. Unique Properties of Water

The nature of the polar covalent bond creating the water molecule and its ability to form hydrogen bonds with other molecules are the chemical basis for the unique properties of water.

Life as we know it would not exist without these properties: high cohesion, high adhesion, capillary action, high specific heat capacity, high heat of vaporisation, low viscosity, lower density in the solid (ice) state than as a liquid, universal solvent, transparent, ionisation properties.

Cohesion is the attraction between particles of the same substance. Cohesion in water is the attraction of water to itself, i.e. one water molecule to another. Water clings to polar water molecules through hydrogen bonding. Cohesion is responsible for surface tension (a measure of the force necessary to stretch or break the surface of a liquid). Surface tension is generated by the hydrogen bonding between adjacent water molecules on the surface and the molecules below them.

Adhesion is the force of attraction between unlike molecules. Water interacts with other polar compounds but is repelled by non–polar compounds. Water is adhesive to any substance with which it can form hydrogen bonds.

Capillary Action – The cohesive and adhesive forces of water generate capillary action. Capillary action is the ability of a liquid to flow in narrow spaces without the assistance of, even in opposition to, external forces like gravity. Due to the combination of forces, water molecules will pull other molecules along a wettable narrow space like a glass tube and porous materials such as paper.



Figure 11.4. The cohesive and adhesive forces (Simple English Wikipedia)

Capillary action occurs because of intermolecular forces between the liquid and surrounding solid surfaces. If the diameter of the tube is sufficiently small, then the combination of surface tension (caused by cohesion within the liquid) and adhesive forces between the liquid and the tube wall act to lift the liquid. Capillary action is essential to plant life. Minerals dissolved from soil are carried from roots to all parts of plants.

Specific Heat Capacity is the amount of heat energy (Joules) that must be absorbed or lost to change the temperature of 1kg of a substance 1° C. Water has a very high heat capacity = 4,185.5 J/kg.K, higher than any other common substance. This is because a lot of heat energy is required to break the hydrogen bonds of water so that not much is left to raise the water temperature.

Due to its high specific heat capacity, water resists temperature change both for heating and cooling. Thus, water acts as a thermal buffer, i.e. water can absorb or release large amounts of heat energy with little change in its actual temperature. In consequence, water plays a very important role in temperature regulation on both large and small scales. The oceans act as a thermal regulator for Earth by resisting temperature change and so create a hospitable environment for life.

Heat of Vaporisation – Latent Heat of Vaporisation is the amount of heat energy required for 1 kg of water to be converted from liquid to gas. Water has a high heat of vaporisation = 2260 kJ/kg because hydrogen bonds must be broken before water molecules can escape from the liquid phase and this requires high energy. Evaporation results in loss of heat energy from the liquid surface – Evaporative Cooling – and, because water's vaporisation heat is high, its cooling action is large. Through sweating (animals) and transpiration (plants), this cooling mechanism is critical to thermal management of life.

Water also moderates the global climate by the oceans absorbing solar radiation and dissipating the heat by evaporation of surface water.

Viscosity – Liquid water has a very low viscosity = 8.9×10^{-4} Pa.s. Compare this to motor oil = 0.065-0.319 Pa.s. Viscosity is a measure of the resistance of a fluid being deformed by stress. It describes a fluid's internal resistance to flow. The less viscous the fluid is, the greater its ease of movement (fluidity). The low viscosity of water enables it to act as a lubricant. In the biological context, water is the major component of blood plasma, mucus and other lubricating fluids. It enables blood to function as an efficient medium of transport of gases and nutrients throughout the body.

Density – Water is unique in the way its density varies with temperature. Most substances increase in density with falling temperature because the molecules move more slowly and get closer together. However, in case of water, density increases as it is cooled to 4°C, but it then decreases as the temperature is reduced further. The hydrogen bonds relax and form an ice crystal lattice where the molecules are further apart than in liquid water. Thus, while the mass of water remains constant, the volume expands as it solidifies giving reduced density:

- Density of liquid water = $1,000 \text{ kg/m}^3$
- Density of ice = 984 kg/m^3

Thus, water freezes from the top down. Oceans and lakes don't freeze solid because ice floats so that living organisms can still live in the water underneath the ice during winter.

'Universal' Solvent – A liquid that is a completely homogeneous mixture of two or more substances is called a solution, e.g. a sugar cube in a glass of water will dissolve to form a uniform mixture of sugar and water. The dissolving agent is the solvent and the substance that is dissolved is the solute. In an aqueous solution, water is the solvent. Water is not a universal solvent, but it is a very good and versatile solvent because of the polarity of water molecules. The polar water molecule acts an effective solvent as it can form hydrogen bonds attracting ions and other polar molecules.

Thus, water clings to ions and polar molecules causing them to be soluble which means that it can dissolve many ionic compounds, e.g. salt, sugars, amino acids, which are, therefore, hydrophilic, i.e. attracted to water. However, water tends to exclude non-polar molecules, e.g. Polymers, which are, therefore, hydrophobic, i.e. repelled by water.

The small size of the water molecule allows it to penetrate and saturate volumes of other materials to enable dissolution and enhancing its action as a solvent. Thus, for example, water molecules penetrate the NaCl (common salt) crystal lattice and detach Cl^- and Na^+ ions because each Cl^- ion attracts the slightly positive H atom end of the water molecule and each Na^+ ion attracts the slightly negative O end of the water molecule.

Transparency – The fact that water is transparent means low absorption allowing light in the **visible spectrum** to pass through it. Aquatic plants can thus receive sunlight. Furthermore, visible light can pass through the human eyeball to receptor cells in the back enabling human vision.

pH – The pH scale expresses the concentration of hydrogen ions (H⁺) in a solution. It is a logarithmic scale ranging from 0–14 so that one pH unit represents a ten–fold change in H⁺ concentration.

 $pH = -log [H^+]$

7 on the scale is neutral, < 7 is acidic, > 7 is alkaline / basic.

Because of the strength of the polar covalent bond binding the O and H atoms in the water molecule, only one water molecule in 550 million naturally dissociates into an acidic hydrogen ion H^+ and a basic hydroxide ion OH^- .

 $H_2O \leftrightarrows H^+ + OH^-$

Thus, water at 25°C contains only 1/10,000,000 mole of H+ ions = 10^{-7} moles/litre So that pure water is neutral with a pH = 7.

11.3. Water Treatment and Purification

Water treatment is the process of removing undesirable chemicals, biological contaminants, suspended and dissolved solids and gases from contaminated water. Purifying water reduces or eliminates concentrations of suspended particles, parasites, bacteria, algae, viruses, fungi and dissolved organic and inorganic materials.

Categories of Contaminants are Microbiological (Bacteria, Virus, Protozoa, Helminths), Chemical (Organic, Inorganic, pH) and Physical (Turbidity, Colour, Odour, Taste).

Chemical water treatments include:

- Treatment of wastewater (WW) polluted by human use to make it fit for return to the environment, typically some watercourse such as river, sea, lake;
- Treatment of drinking water (DW) to render it fit for human consumption;
- Treatment of 'hard' water to remove dissolved inorganics causing deposits.

11.4. Water Treatment – Disinfection

Water treatment is a major civil engineering and construction undertaking, essential wherever there is any significant human population. Critical to the process is disinfection, the killing of bacteria, etc. in water. The two principal types of disinfection are:

- Physical disinfection techniques these include membrane filtration, boiling and irradiation with ultraviolet light
- Chemical disinfection techniques include adding halogen or halogen compounds, ozone or potassium permanganate to water. These are the most widely used water disinfection techniques.
- The halogens added to water for disinfection include chlorine, bromine and iodine. Bromine is not recommended for drinking water disinfection due to its bad taste and short lifetime, but it may be used for swimming pool water. Iodine is sometimes used for drinking water disinfection, but causes a bad aftertaste. Chlorination of water is a cheap, effective, relatively harmless and by far the most widely used water disinfection method.

11.5. Water Treatment – Chlorination

Water chlorination is the process of adding chlorine (Cl_2) gas or a hypochlorite compound in aqueous solution to kill bacteria, viruses, and protozoans in water to prevent the spread of waterborne diseases such as cholera, dysentery, typhoid, etc.

Hypochlorite is an ion composed of chlorine and oxygen ClO⁻ whose acid is **Hypochlorous Acid HOCl**, the germ killer. Unfortunately HOCl cannot be isolated in a pure form but can be effectively used through its salts, the hypochlorites. The ClO⁻ ion can be made to combine with counter ions to form **hypochlorites**, e.g. sodium hypochlorite (household bleach) and calcium hypochlorite (bleaching powder, swimming pool "chlorine").

Hypochlorites can be formed by a reaction between chlorine gas and metal hydroxides at close to room temperature (further oxidation will occur at higher temperatures leading to the formation of unwanted chlorates). This process is widely used for the industrial production of sodium hypochlorite NaClO and calcium hypochlorite Ca(ClO)₂:

 $Cl_2 + 2 \text{ NaOH} \rightarrow NaCl + NaClO + H_2O_2$

 $Cl_2 + Ca(OH)_2 \rightarrow CaCl_2 + Ca(ClO)_2 + H_2O$

Hypochlorites are frequently unstable in their pure forms and so are normally handled as aqueous solutions. Their primary applications are as bleaching, disinfection and water treatment agents but they are also used in chemistry for chlorination and oxidation reactions.

Addition of both Cl₂ gas and hypochlorites to water results in the formation of **hypochlorous acid HOCl**:

When dissolved in water, Cl_2 converts to an equilibrium mixture of chlorine, HOCl and hydrochloric acid (HCl):

 $Cl_2 + H_2O \leftrightarrows HOCl + HCl$

When sodium hypochlorite or calcium hypochlorite, is added to water, HOCl is formed.

In commercial NaOCl solutions, the following species are in equilibrium.

HOCI \leftrightarrows H⁺ + OCl⁻

 $\mathbf{HOCl} + \mathbf{Cl}^- + \mathbf{H}^+ \leftrightarrows \mathbf{Cl}_2 + \mathbf{H}_2\mathbf{O}$

These chemical equations use an equilibrium sign \leftrightarrows because the chemical equation can progress in either direction depending on the pH of the water.

The cell walls around bacteria have a net negative charge, thus repelling other negatively charged particles in the water. HOCl, being neutral, can make contact with and breach the cell wall and invade bacterial cells. It disintegrates the lipids that compose the cell wall and reacts with enzymes and proteins inside the cell causing them to lose their complex structure and making them nonfunctional. The microorganisms then either die or are no longer able to multiply.

Disadvantages of chlorination – Chlorine can react with naturally occurring organic compounds found in the water supply to produce compounds known as disinfection by–products (DBPs). The most common DBPs are trihalomethanes (THMs). THMs are chemical compounds in which three of the four hydrogen atoms of methane CH_4 are replaced by halogen atoms, e.g. Chloroform $CHCl_3$. THMs are carcinogenic in large quantities. The formation of THMs may be minimized by effective removal of as many organics from the water as possible prior to chlorine addition. Although chlorine is effective in killing bacteria, it has limited effectiveness against protozoa that form cysts in water. Despite these limited disadvantages, chlorination is overwhelmingly the preferred technique for water disinfection.

11.6. Water Treatment – Ozonation

Ozone (O_3) is a highly effective, relatively harmless disinfection method but is expensive and therefore less popular than chlorine. It is a very strong, broad spectrum disinfectant widely used in Europe. It inactivates harmful protozoa that form cysts and works well against almost all other pathogens. Ozone is made by passing oxygen through ultraviolet light or a "cold" electrical discharge plasma. Because of its short lifetime to use ozone as a disinfectant it must be created on– site and added to the water by bubble contact.

Advantages of ozone include:

- The production of fewer dangerous by-products
- The absence of taste and odour problems (in contrast to chlorination)
- No residual disinfectant left in the water

Ozone is an unstable molecule and readily reacts as a powerful oxidant producing free radicals that react with organic and inorganic molecules in water. When bubbled through water, ozone decomposes and the free radicals hydroperoxyl (HO₂) and hydroxyl (OH) are formed.

 $O_3 + H_2O + e^- \rightarrow O_2 + 2 OH^ O_3 + HO_2^- \rightarrow O_3^- + HO_2$ These have great oxidizing capacity and react directly with materials in water solution. The actual disinfection occurs as the oxidation reactions damage and destroy critical components of microorganisms.

Because of its high oxidation potential, ozone penetrates and oxidises the bacterial cell wall. Once ozone has entered the cell, it oxidises all essential components (enzymes, proteins, DNA, RNA). When the cellular membrane is damaged during this process, the cell falls apart, a process called lysis.

In addition, the oxidising properties can also reduce the concentration of iron, manganese, sulphur and reduce or eliminate taste and odour problems. Ozone oxidises iron, manganese, and sulphur to form insoluble metal oxides or elemental sulphur which particles are then removed by post–filtration. Organic particles and chemicals are eliminated through either coagulation or chemical oxidation.

11.7. Water Treatment – Aeration

Anoxic waters are areas of sea water, fresh water or groundwater that are depleted of dissolved oxygen. The US Geological Survey defines anoxic waters as those with dissolved oxygen concentration of less than 0.5 milligrams per litre. The anoxic condition causes water to contain quantities of reduced metals such as iron, arsenic and manganese harmful to water quality.

Aeration is the process by which air is circulated through, mixed with or dissolved in a liquid or substance. It is widely applied to anoxic water by vigorous agitation in the open air, typically by fountain or cascade. Exposure to atmospheric O_2 causes oxidation of reduced forms of dissolved metals and their precipitation out, thus removing them from the water. Thus, ferrous iron, which is quite soluble in water, is oxidised by reaction with dissolved O_2 in aerated water to ferric iron:

$$\begin{split} & Fe(II) + O_2 \leftrightarrows Fe(III) + HO_2 \bullet \\ & Fe(II) + HO_2 \bullet \leftrightarrows Fe(III) + H_2O_2 \\ & Fe(II) + H_2O_2 \leftrightarrows Fe(III) + HO \bullet + H_2O \\ & Fe(II) + HO \bullet \leftrightarrows Fe(III) + H_2O \end{split}$$

Fe(III) is insoluble in water and precipitates out. Similarly, Mn(II) is oxidised to Mn(III) and precipitates out. However, the highly toxic contaminant Arsenic As is not effectively oxidised by aeration alone and requires other techniques for reduction to safe levels.

11.8. Water Treatment – Softening

Hard water is water that contains cations with a charge of +2, especially Ca²⁺ and Mg²⁺. These ions engage in reactions that leave insoluble mineral deposits. Such deposits can make hard water unsuitable for many uses so that methods have been developed to "soften" hard water, i.e. remove the calcium and magnesium ions.

Mineral deposits are formed by ionic reactions resulting in the formation of an insoluble precipitate. Thus, when hard water is heated, Ca^{2+} ions react with bicarbonate (HCO₃⁻) ions to form insoluble calcium carbonate (CaCO₃).

 $Ca^{2+}(aq) + 2 HCO_3^{-}(aq) \rightarrow CaCO_3(s) + H_2O + CO_2$

The presence of metal cations in hard water causes a variety of problems:

Limescale formation – Such ions in hard water precipitate out and deposit leading to the build up of limescale which can foul plumbing; promote galvanic corrosion; interfere with sewage systems; coat heating elements thus reducing heating efficiency by insulation.

Soap scum – In hard water areas the rinse water from soap contains calcium or magnesium ions which form insoluble salts leaving a coating of insoluble stearates on washing surfaces. For large–scale municipal operations, a process known as the "lime–soda process" is used to remove Ca^{2+} and Mg^{2+} from the water supply.

The water is treated with a combination of slaked lime, $Ca(OH)_2$, and soda ash, Na_2CO_3 . Calcium ions precipitate as $CaCO_3$ and magnesium ions precipitate as $Mg(OH)_2$. These solids can be collected, thus removing the scale–forming cations from the water supply. To see an example of this process in detail, consider the reaction for the precipitation of $Mg(OH)_2$. The $Ca(OH)_2$ of slaked lime is moderately soluble in water. It dissociates to give one Ca^{2+} ion and two OH^- ions for each unit of $Ca(OH)_2$ that dissolves. The OH^- ions react with Mg^{2+} ions in the water to form the insoluble precipitate later removed:

$$Mg^{2+}(aq) + 2 OH^{-}(aq) \rightarrow Mg(OH)_{2}(s)$$

The Ca^{2+} ions are unaffected by this reaction and are removed by a separate reaction with CO_3^{2-} ions from the soda ash.

12. Corrosion

Definition – Corrosion is defined as the deterioration or destruction of a material, usually a metal, because of chemical or electrochemical interaction with its environment. Corrosion is a universal phenomenon degrading not just metals but also plastics, rubber, ceramics, concrete, wood, etc. Corrosion in metals occurs because of the tendency for most metals to return to their natural state, e.g. iron in the presence of moist air will revert to its natural state, iron oxide. Corrosion is:

- A natural phenomenon that occurs over time
- An electrochemical reaction (in metals)
- Happens at different rates with different metals and in different environments.

The consequences of corrosion are many and varied and include:

- Degradation of safe, reliable and efficient operation of equipment or structures
- Failures of many kinds including catastrophic collapse of a part or main structure
- The need for expensive maintenance and replacements even though the amount of material corroded is quite small
- Creation of major safety issues especially in life-critical areas such as aviation
- Reduced strength and performance
- Downtime of equipment and plant for prevention, repair and maintenance
- Escape of fluids, e.g. from corroded tanks
- Loss of aesthetic appearance, e.g. rust
- Reduced value of goods

12.1. Metal Corrosion

Metal corrosion is a spontaneous process of the formation of a compound of the metal by reaction between the metallic surface and surrounding chemicals in its environment. Any spontaneous reaction must result in a reduction in the **Free Energy** of the system. All metals except the noble metals have free energies greater than their compounds, so they easily tend to give up energy to become compounds – this is the driving force of corrosion. According to thermodynamics almost all metals have negative free energy $-\Delta G$. This is readily seen in oxidation reactions of metals in presence of water and air:

| $Fe + 3H_2O + 3/2O_2 \rightarrow 2Fe(OH)_3$ | $\Delta G = -197$ kcal |
|--|------------------------|
| $Mg + H_2O + 1/2O_2 \rightarrow Mg(OH)_2$ | $\Delta G = -420$ kcal |
| $2Al + 3H_2O + 3/2O_2 \rightarrow 2Al(OH)_3$ | $\Delta G = -304$ kcal |

Thus, the lowest free energy state of metal is its oxide, the 'natural' state. This means that most (but not all) metals are naturally reactive in the environment making them highly vulnerable to corrosion. Corrosion is a chemical process causing disintegration and loss of the metal most often due to an electrochemical reaction, e.g. rust on iron, green oxide on copper, etching of Zn by HCl. Typical agents are O_2 (e.g. atmospheric corrosion) or H⁺ (chemical corrosion) or both (Banaszkiewicz J., Kamiński M., 1997).

Electrochemistry

The usual cause of corrosion of metals involves electrochemistry. A flow of electricity occurs from one area of the metal to another area through an electrolyte, i.e. any liquid capable of conducting electricity such as seawater, hard water or other moisture or solution on the metal surface. This process creates an electrochemical reaction at the metal surface which both decomposes and removes metal (i.e. corrodes) and changes the removed metal into a compound. For electrochemical corrosion to occur we must have four things:

- Anode = an electrode which repels electrons due to chemical reaction at the site
- Cathode = an electrode which attracts electrons due to chemical reaction at the site
- An electrical connection between anode and cathode for the flow of current
- A conducting environment for ionic movement, i.e. an electrolyte
- These electrochemical reaction components are shown in the following schematic:



12. Corrosion

The metal itself contains anodes and cathodes (areas on the surface that have different electrical potentials) and it is its own electrical connection. Electrolyte is provided in the form of rain, dew, humidity, chemicals, etc.

Redox Reaction

The metal corrosion process involves **Oxidation and Reduction** reactions. The chemical transformation that decomposes and removes metal from the bulk material surface is the oxidation step of an overall oxidation–reduction process (called a redox reaction). **Oxidation** is the process of losing electrons; **Reduction** is the process of gaining electrons.

Oxidation-Reduction



An example of a redox reaction is:

 $Fe + Cl_2 \rightarrow Fe^{2+} + 2 Cl^- \rightarrow FeCl_2$

3 Steps to Metal Corrosion

Corrosion is a 3-step process comprising 3 chemical reactions:

STEP 1: Anode Reaction

The anode metal corrodes, i.e. decomposes and is removed from the bulk as metal ions which go into solution in the electrolyte, i.e.

$$M \rightarrow M^{n+} + ne^{-}$$
 where $M = a$ metal

This is an Oxidation reaction, i.e. the anodic metal atoms lose electrons, e.g.

$$Fe \rightarrow Fe^{2+} + 2e^{-}$$
$$Al \rightarrow Al^{3+} + 3e^{-}$$

As these ions go into solution, the metal becomes negatively charged (by the electrons left behind) with respect to the electrolyte. Because the anode area is negative, electrons free towards the cathode site (see below schematic):



STEP 2: Cathode Reaction

The electrons coming from the anode site must be removed by consumption in chemical reaction/s at the cathode. These are all **reduction** reactions with a *depolariser*. Common depolarisers which consume electrons are:

• Oxygen in natural or other neutral or basic environments:

 $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

• Hydrogen in acidic environments:

 $2H^+ + 2e^- \rightarrow H_2(g)$

• Oxygen reduction in acid solutions:

 $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

• Metal (M) ion reduction:

 $M^{n+} + ne^- \rightarrow M(s)$

Examples of these are shown in the above schematic.

STEP 3: Formation of Metal Compounds

The species formed by the reduction reaction at the cathode now react with the metal ions in solution (formed by the oxidation reaction at the anode) to generate a metal compound as the final product. The actual reaction or chain of reactions is highly specific to the particular metal and the electrolyte. In the case of water as electrolyte, typically the final product is an insoluble metal oxide which precipitates out as a deposit at or around the cathode site. In the case of iron this displays as rust. We shall now look at two specific *Examples* of metal corrosion, namely iron in water and zinc in hydrochloric acid.

12.2. Corrosion – Iron + Water

Iron and steel are highly vulnerable to corrosion in the presence of water as an electrolyte. The anode oxidation reaction produces Fe^{++} ions:

 $Fe \rightarrow Fe^{2+} + 2e^{-}$

The cathode reduction reactions with water and oxygen dissolved in water produce hydroxyl radicals OH⁻:

 $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

The iron (II) Fe^{++} ions and hydroxyl radicals OH^- now can combine in two principal ways.

Pathway 1:

$$Fe^{2+}(aq) + 2OH^{-}(aq) \rightarrow Fe(OH)_{2}(s)$$

i.e. production of iron (II) hydroxide (precipitates out as 'green rust') a relatively unstable compound which can further react to produce stable Magnetite:

$$3 \operatorname{Fe}(OH)_2 \rightarrow \operatorname{Fe}_3O_4(s) + H_2 + 2H_2O$$

Pathway 2:

The iron(II) ions can also react with hydrogen ions and oxygen to produce iron(III) ions:

$$4Fe^{2+}(aq) + 4H^{+}(aq) + O_2(aq) \rightarrow 4Fe^{3+}(aq) + 2H_2O(1)$$

The iron(III) ions then react with hydroxide ions to produce insoluble hydrated iron(III) oxides (also known as iron(III) hydroxides):

 $Fe^{3+}(aq) + 3OH^{-}(aq) \rightarrow Fe(OH)_{3}(s)$

The loose porous rust $Fe(OH)_3$ can slowly transform into a crystallized hydrated oxide form written as Fe_2O_3 . H_2O the familiar red-brown "rust".

12.3. Corrosion – Zn + HCl

• STEP 1: Zinc is aggressively corroded by HCl as an electrolyte. The anode oxidation reaction produces Zn⁺⁺ ions:

 $Zn \rightarrow Zn^{2+} + 2e^{-}$

• STEP 2: The cathode reduction reactions with HCl produce hydrogen gas and chlorine ions:

$$\begin{split} HCl &\rightarrow H^+ + Cl^- \\ 2H^+ + 2e^- &\rightarrow H_2(g) \end{split}$$

• STEP 3: The zinc Zn⁺⁺ ions and chlorine ions Cl⁻ now combine as zinc chloride:

 $Zn^{2+} + 2Cl^{-} \rightarrow ZnCl_{2}$

12.4. Metal Passivation

Protection against corrosion is achieved by **Passivation**. Metals that would otherwise corrode may protect themselves spontaneously in air or water by the build up of a stable, tenacious, well adhered layer of metal oxide on the surface of the metal. Once the layer, or film, is formed, it acts as a barrier separating the metal surface from the environment and, thus, protecting the metal from attack. This process is called Passivation. The passivating "Native Oxide" layer generally is only a few nanometres (nm) thick and is generated by chemical reaction between the metal and oxygen and/or water in the natural environment. Passivating layers can also be generated artificially, e.g. anodising of aluminium.

An example of passivation is **Aluminium**. Because of its strong affinity for oxygen, aluminium is almost never found in the elemental state; instead it is found in oxides or silicates. In ambient air, Al reacts with oxygen to form Aluminium Oxide (Alumina):

$$\begin{split} 4\text{Al} &\to 4\text{Al}^{3+} + 12\text{e}^{-} \\ 3\text{O}_2 + 12\text{e}^{-} &\to 6\text{O}^{2-} \\ 4\text{Al}^{3+} + 6\text{O}^{2-} + 12\text{e}^{-} &\to 2\text{Al}_2\text{O}_3 \text{ (s),} \end{split}$$

This 'native oxide' layer over the Al surface grows to ~ 5 nm thickness over some years, is hard, very well adhered and forms an excellent physical and chemical barrier to environmental chemicals, e.g. O₂, H₂O, acids, that would otherwise attack and corrode the metal. Other metals such as zirconium, chromium, copper and the stainless steels also form thin, tenacious passivating oxide films when exposed to the atmosphere or to pure water at room temperature which are very effective in minimizing further corrosion.

Another example is **Copper**. The overall reaction that causes copper to oxidize is the reaction of copper with the oxygen in the atmosphere to form black–brown copper (II) oxide:

$$2 \operatorname{Cu}(s) + \operatorname{O2}(g) \rightarrow 2 \operatorname{CuO}(s)$$

The reaction takes place when water, moisture condensation or rain, in which oxygen is dissolved, is in contact with copper. The copper oxide forms a passivating layer protecting the copper metal from further attack. However, due to the continued presence of O_2 in air and of atmospheric pollutants such as sulphur, carbon and chlorine, the coating will often continue to very slowly react over years to form a range of compounds with different colours, e.g. copper monosulphide (blue), hydrated copper sulphate (green).

12.5. The Standard EMF Series

A driving force is necessary for electrons to flow from the anode to the cathode. The driving force is the difference in **electric potential** between the anodic and cathodic sites of the particular corrosion process. This difference exists because each oxidation or reduction reaction making up the corrosion process has associated with it an electric potential determined by the tendency for the reaction to take place spontaneously. The electric potential is a measure of this tendency and can be experimentally measured to give us a guide to how likely a metal is to corrode in a given environment. Thus, we can associate with each metal a STANDARD ELECTRODE POTENTIAL. This is determined experimentally using a reference called a Standard Hydrogen Electrode. From a voltmeter placed across the two electrodes, we can measure the difference in electric potential between metal M and the standard hydrogen electrode reference. Such experimental determinations enable a table of Standard Electrode Potentials V^0 to be compiled for metals called The Standard EMF Series (Bala B., 2000) as per the following Table:

| | Electrode Reaction | Standard Electrode Potential,V ⁰ (V) |
|---|--|--|
| Not corroded | $Au^{3+} + 3e^- \rightarrow Au$ | +1.420 |
| | $O_2 + 4H^+ + 4e^- \rightarrow H_2O$ | +1.229 |
| Ť | $Pt^{2+} + 2e^- \rightarrow Pt$ | ~+1.2 |
| | $Ag^+ + e^- \rightarrow Ag$ | +0.800 |
| | $\mathrm{Fe}^{3+} + \mathrm{e}^- \rightarrow \mathrm{Fe}^{2+}$ | +0.771 |
| | $O_2 + 2H_2O + 4e^- \rightarrow 4(OH^-)$ | +0.401 |
| | $Cu^{2+} + 2^- \rightarrow Cu$ | +0.340 |
| Increasingly inert | $2\mathrm{H^{+}} + 2\mathrm{e^{-}} \rightarrow \mathrm{H_{2}}$ | 0.000 |
| Increasingly inert (cathodic) Increasingly active (anodic) | $Pb^{2+} + 2e^- \rightarrow Pb$ | -0.126 |
| | $\mathrm{Sn}^{2+} + 2\mathrm{e}^- \rightarrow \mathrm{Sn}$ | -0.136 |
| | $Ni^{2+} + 2e^- \rightarrow Ni$ | -0.250 |
| | $\mathrm{Co}^{2+} + 2\mathrm{e}^{-} \rightarrow \mathrm{Co}$ | -0.277 |
| | $Cd^{2+} + 2e^{-} \rightarrow Cd$ | -0.403 |
| | $\mathrm{Fe}^{2+} + 2\mathrm{e}^- \rightarrow \mathrm{Fe}$ | -0.440 |
| | $Cr^{3+} + 3e^- \rightarrow Cr$ | -0.744 |
| | $Zn^{2+} + 2e^- \rightarrow Zn$ | -0.763 |
| | $Al^{3+} + 3e^- \rightarrow Al$ | -1.662 |
| | $Mg^{2+} + 2e^- \rightarrow Mg$ | -2.363 |
| | $Na^+ + e^- \rightarrow Na$ | -2.714 |
| Highly corroded | $K^+ + e^- \rightarrow K$ | -2.924 |

We can use the EMF Series to find which metal in metal–metal combinations will corrode and which will not. The metal with the smaller V^0 will corrode. Thus, in a Cadmium Cd – Nickel Ni cell, $V^0_{Cd} < V^0_{Ni}$ so that it is the Cd that corrodes.

12.6. Protecting Metal

There are a wide range of methods for protecting against corrosion. The main generic method is **coating** the metal. There are three basic types of coatings: sacrificial, inhibitive and barrier.

Sacrificial coatings protect the steel substrate by containing metallic pigments that are anodic to the steel, i.e. have a lower Standard Electrode Potential to Fe. The most common sacrificial coating is zinc or a zinc rich primer. $V_{Zn}^0 = -0.763 \text{ V}$ while $V_{Fe}^0 = -0.440 \text{ V}$ so that Zinc is a more active metal than steel and will become an anode when in direct contact with the less active steel as per the following schematic:



Preventing the Corrosion of Iron (cathodic protection / sacrifical anode)

Galvanisation is the process of applying a protective zinc coating to steel or iron to prevent rusting. The most common method is hot-dip galvanization in which parts are submerged in a bath of molten zinc. Galvanizing protects in two ways:

- It forms a coating of corrosion-resistant zinc which prevents corrosive substances from reaching the iron;
- The zinc serves as a sacrificial anode so that even if the coating is scratched, the exposed steel will still be protected by the remaining zinc.

Inhibitive coatings contain pigments that passivate the steel and therefore mitigate corrosion. Red lead primer is one of the best of the inhibitive primers but is hardly used any more because of health risks. Pigments that have replaced red lead for inhibitive qualities include barium metaborate, iron oxide and zinc oxide.

Barrier coatings create a barrier to the passage of moisture through the film to the substrate, thus preventing the electrolyte from getting to the steel. Without electrolyte there cannot be corrosion. *Examples* of barrier coating materials are: vinyl, chlorinated rubber, asphalt, bitumen, epoxies, urethanes, polyesters.

A typical coating system consists of a primer, an intermediate coat and one, or more, topcoats. Thus, an example of a coating system for a bridge might be:

- Zinc Rich Primer
- Epoxy Intermediate Coat
- Urethane Topcoat

Each coat is performing different physical and chemical functions which mutually reinforce and give years of protection in harsh environments.

12.7. Metal in Concrete Corrosion

Reinforcing steel is widely used in concrete. The highly alkaline conditions inside concrete provide a passivating environment for the steel. A thin layer of oxides forms on the steel surface which is stable in the alkali rich surround and protects the steel against corrosion. The steel is unlikely to rust as long as the passivating conditions remain.

To minimise corrosion of reinforcing steel it is necessary to have well compacted concrete and a sufficient thickness of concrete cover over the steel (50–75 mm) to provide a physical diffusion barrier reducing the penetration of corroding elements.

For corrosion of reinforcing steel to occur, certain elements must penetrate the concrete and reach the steel either through a crack in the concrete or by diffusion through porous and/or thin concrete. The elements needed for corrosion are Oxygen, Moisture and Atmospheric CO_2 or SO_2 or chloride ions, e.g. from marine environments or de–icing salts. These reduce the alkalinity and destroy the protecting passivation opening up the steel to corrosion attack (Gruner M, 1983), (Jaroszyńska-Wolińska J., Dziadko D., 2011).

Once the steel passivation is removed then the normal steel rusting process will begin and continue as long as there are supplies of H_2O and O_2 from outside. The rust created on the reinforcing bars can increase up to two times the volume of the bar. This generates huge internal stresses within the concrete leading to eventual cracking of the concrete, its delamination (called "spalling") from the structure and even complete destruction of the concrete structure.

13. Analytical Techniques for Construction Materials

13.1. Materials-Analysis-by-Probe Techniques

A range of microscopic and sub-micron probe techniques are available to the materials scientist/engineer to characterise construction materials from the mm down to the ~ 0.1 nm atomic domain. Probes used include (Atkins P.W., 2001):

- Visible light \Rightarrow Optical Microscopy, Raman Spectroscopy
- Electron ⇒ Electron microscopy [Scanning Electron Spectroscopy (SEM), Transmission Electron Spectroscopy (TEM)], Energy Dispersive X–Ray Spectroscopy (EDX), Auger Electron Spectroscopy (AES)
- **X-Ray Photon** \Rightarrow X-Ray Photo-electron Spectroscopy (XPS)
- Ion \Rightarrow Secondary Ion Mass Spectrometry (SIMS)

Essentially, the probe is applied to the sample in order to stimulate from the sample emission of electrons, ions or photons (as a *response*), or bounce back off the sample (as the *modified probe*) – see below schematic. In all cases the emitted or reflected particle/wave will carry information unique to the sample enabling it to be characterized. Either the response or the modified probe is captured and analysed.



Characteristics measured include:

- Imaging topography and morphology Figure 13.1a
- Mapping the surface and sub–surface structure
- Composition elemental Figure 13.1b
- Composition chemical Figure 13.1b
- Crystal structure including defects


Figure 13.1. a) Imaging – topography and morphology; b) Composition – elemental and composition – chemical

13.2. Optical Microscopy

Optical or light microscopy involves passing visible light transmitted through or reflected from a sample through a single or multiple lenses to allow a magnified image of the sample. The resulting image can be detected directly by the eye, imaged on a photographic plate or captured digitally. The system of lenses and imaging equipment, lighting equipment, sample stage and support makes up the basic light microscope. The performance of Optical Microscopes is limited by the physics of light, i.e. *Diffraction*, to ~x1000 magnification and a resolution of 0.2 μ m (~2,000 atoms).

Typical imaging applications in construction materials include:



Figure 13.2. Grain size examination – see optical microscope image with 20 µm size bar below. Changes in microstructure from processing (Simple English Wikipedia)

13.3. Electron Microscopy

Electron Microscopes (EM) are scientific instruments that use a beam of highly energetic electrons to examine objects on the micrometre (10^{-6} m) and below scale. EM are similar to optical (visible light) microscopes in using a beam of electromagnetic radiation (remember: electrons are waves as well as particles) condensed, focused and magnified by lenses to image a specimen.

- However, in the case of EM:
- The radiation is much higher energy, shorter wavelength
- The lenses are electrostatic and electromagnetic rather than glass
- Image collection is by a detector rather than the naked eye.

Each of these interactions can be used as a diagnostic tool to investigate the specimen and will be described below.

Reactions above the specimen always take place and are examined in a **Scanning EM** (SEM).

Reactions below the specimen will only occur if the specimen is sufficiently thin and are examined in a **Transmission EM** (TEM).

Each of these reactions can be used for sample analysis so that the EM diagnostic tool can provide data on:

- Topography = The surface features of the sample or "how it looks", its texture
- Morphology = The size, shape and arrangement of the particles which make up the sample and its surface
- Structure and Crystallography = The arrangement of atoms and molecules in the sample, their degree of order, detection of defects
- Elemental composition = The elements the sample is composed of and their relative ratios
- Chemical composition = The elements and compounds the sample is composed of and their relative ratios.

In all cases, the objective is to form a direct relation between the data and the material properties, e.g. compressive strength of concrete.

Now, we can link each of these electron–beam reactions shown in the above schematic with a data set:

Secondary Electrons

Secondary electrons are generated from the collision between the incoming electron and a loosely bonded outer shell electron of the sample. The outer shell electron is ejected from the sample and collected by a detector. Secondary electrons are low energy so only those generated close to the sample surface escape and are collected. Thus, collection of secondary electrons provides topographic data, i.e. imaging of the surface microstructure – see following SEM micrograph.



Secondary e- topographical image

Backscattered Electrons

Backscattered electrons result from an incident electron in the probe beam colliding with a sample atom and bouncing back – see schematic a) below. Yield of the collected backscattered electrons increases monotonically with the sample's atomic number. As the atomic number of the sample material increases (bigger atoms) more backscattered electrons are produced due to less penetration into the sample by incident electrons resulting in less electron losses inside the sample. This results in image brightness across any sample varying with atomic number from place to place. Thus we have data about the sample microstructure as the variations in image brightness show differences in composition between different parts of the sample with differing atomic numbers – see SEM micrograph b) below. Backscattered electron imaging is, therefore, useful in distinguishing one material from another in a sample as well as being useful for topography imaging.



Figure 13.3. a) Backscattered electron imaging , b) Greyscale Backscatter Image (Simple English Wikipedia, Energy-dispersive X-ray spectroscopy), (Krinsley David H., 1998)

X-Ray Analysis

Each element has a unique atomic structure generating a unique set of peaks on its X-ray emission spectrum – see Figure a) below. These peaks correspond to electrons moving between shells by dropping down from a high energy state to lower – see Figure b) below.



Figure 13.4. a) X-ray emission spectrum; b) Atomic electron shell structure (Simple English Wikipedia, Energy-dispersive X-ray spectroscopy)

In each such transfer the electron must give up energy in the form of a photon equal in energy to the difference between shell energies. This generates a unique emission fingerprinting the atom. The magnitude of the electron transfer energies mean that the photons are in the X–Ray spectral region.

An SEM can use this technique to identify what elements are in a sample. The technique is called EDX (Energy Dispersive X–Ray Spectroscopy). To stimulate the emission of X–rays, the SEM electron beam is focused onto the sample. An incident electron excites an electron in an inner shell of an atom ejecting it from the shell and creating a hole where the atom's electron was. An electron from an outer, higher–energy atomic shell then fills the hole – see below schematic (Simple English Wikipedia, Energy-dispersive X-ray spectroscopy).



The difference in energy between the higher energy shell and the lower energy shell is released in the form of an X-ray. The number and energy of the X-rays emitted are measured by an energy-dispersive spectrometer and produce a spectrum (see above) identifying the particular atom. The X-ray energies are characteristic of the difference in energy between the two shells of the sample atom so that EDX both identifies the sample elemental composition and measures the relative concentrations of different elements.

Auger e

Instead of emitting an X–Ray, the process described in X–Ray analysis can emit from the sample atom an electron called an Auger electron. Again, the SEM electron beam is focused onto the sample. An incident beam electron excites an electron in an inner shell of the sample atom, ejecting it from the shell and creating a hole where the electron was. An electron from an outer, higher– energy atom shell then fills the hole releasing energy. This energy is transferred to an atom shell electron in an outer orbit which is ejected from the atom with a characteristic energy – see schematic of the process below:



The energy of the ejected Auger electron is characteristic of the sample atom, i.e. a fingerprint (Simple English Wikipedia, Energy-dispersive X-ray spectroscopy). The Auger electrons are sorted by energy in an *electron energy analyser* and then collected and counted by an electron detector to produce a spectrum (see spectrum above). This technique is called Auger Emission Spectroscopy (AES).

The Auger process requires the sample atom to have at least 3 electrons so that the elements H and He cannot be detected by this technique but all other elements from Li upwards can be identified. Also, chemical compounds can be identified by comparing the spectra with those of standard samples of known composition. The depths from which the Auger electrons are able to escape from the sample are only ~50 Å so that AES provides highly surface specific composition data about the sample surface region.

Transmitted Electrons

In the case of very thin samples, electrons from the incident beam pass **through** the sample and are made to form an image in a technique called Transmission Electron Microscopy (TEM). For the electrons to pass through the sample, the sample must be very thin, typically $< 80 \,\mu\text{m}$. Thus, long and difficult sample preparation is needed. The electrons passing through the sample are collected by electromagnetic lensing and shone onto a detector, e.g. a fluorescent screen but in modern microscopes a CCD camera. TEMs deliver sample imaging and, in the case of crystalline samples, a *diffraction pattern* from the interaction of the electron wave with the crystal lattice from which crystal parameters and structure can be obtained.



Figure 13.5. Some TEM images

13.4. X–Ray Photoelectron Spectroscopy (XPS)

The XPS technique is based on the photoelectric effect in which materials emit characteristic electrons (called photoelectrons PE) when light shines on them. Because of the quantum nature of light (light travels in packets of energy called photons) not just any light will generate PE. Electrons from an atom are only dislodged by photons with enough energy (threshold energy) to rip the electron out of its atomic shell and free it from the atom (see schematic below).



Photon energy is proportional to the frequency of the light. Low frequency infrared light photons are low energy, high frequency X–Ray photons are high energy. To generate PE from any particular material, the incident photons must have or exceed a threshold frequency specific to the material. Thus, red or infrared light may be too low but blue or ultraviolet light may exceed the photon frequency/energy threshold for successful PE generation. In XPS, X–Rays are used to generate PE because of their high frequency, high energy photon packets. The PE energies fingerprint the atomic shell from which they have been ejected which enables elemental and chemical identification of the sample material.

In XPS, X–Rays irradiate the sample surface hitting the core, inner shell electrons of the atoms. The core electrons are close to the nucleus and have binding energies characteristic of their particular element. They are ejected from the sample as PE with these energies. The electron energy analyser in the system sorts the PE according to energy and the electron detector counts the number of electrons at each energy.

The system can then plot the data: No. of PE (Counts) vs. Energy. Because different elements have different electron binding energies, the energies of the PE provide a unique signature of each element. The plot has characteristic peaks for each element found in the surface region of the sample so that the data spectrum identifies what elements are present.

The below figure is an XPS spectrum of a dirty (see Carbon peak) silicon wafer showing the elements present in the surface region. The insert table shows the elements with the PE shell label, their binding energies and their atomic percentages.





Figure 13.6. XPS spectrum silicon wafer (Simple English Wikipedia, Energy-dispersive X-ray spectroscopy)

Not only does the binding energy of an inner shell electron depend upon the element but also upon the chemical state the particular atom is in. If the atom is bonded to a different atom, e.g. an O atom, the exact binding energy of the core electrons will be slightly different causing a chemical shift in the XPS spectral peak. Thus, XPS can also detect the presence of chemical bonds in a sample, for example, Al metal can be distinguished from Al–oxide.

In XPS a useful PE signal is obtained only from a depth of around 10 to 100 Å on the surface. Tables have been compiled by experimentalists, which assign XPS energy peaks to particular eleme nts and chemical bonds enabling easy identification from your data. In principle XPS detects all elements, but to detect H and He requires special X–Ray sources. In practice, using typical laboratory–scale X–Ray sources, XPS detects all elements with an atomic number Z of 3 (Lithium) and above. The detection limits for most of the elements on

a modern instrument are in the parts per thousand range; detection limits of parts per million (ppm) are possible, but require special conditions, i.e. high concentration at the top surface or very long collection time (overnight). XPS is routinely used to analyze inorganic compounds, metal alloys, semiconductors, polymers, elements, catalysts, glasses, ceramics, paints, woods, adhesives, etc. XPS will also identify the functional groups present on a composite surface. This is useful as the chemical nature of a fibre–polymer, e.g. woven carbon fibre, interface will influence the properties of the composite.

13.5. Secondary Ion Mass Spectrometry (SIMS)

A Primary ion beam is generated, e.g. O^- , O_2^+ , Ar^+ , Cs^+ , Ga^+ , with energies between 1 and 30 keV. The beam is fired at the surface of a sample in high vacuum so that the primary ions are implanted and mix with sample atoms or molecules to depths of 1 to 10 nm. The bombarding primary ion beam causes monatomic and polyatomic particles of sample material, electrons and photons to be ejected from the sample (see below schematic). These Secondary particles carry negative, positive and neutral charges and have kinetic energies from zero to several hundred eV. It is the negative and positive Secondary ions that are analysed.



The Secondary ions are mass analysed using either of two techniques. The first is to sort according to their mass/charge ratio, by passing them through a magnetic field in a *mass spectrometer*. Due to the magnetic field, the ions travel different paths through the mass analyser to a detector due to their different mass/charge ratios and are, therefore, sorted according to mass/charge ratios (see below schematic). A detector records the number of ions (Counts) of each ratio (heavier ions) and (lighter ions).

Alternatively, the Secondary ions are mass analysed according to the time they take to travel a set distance, the heavier the ions are the longer they take. On leaving the sample surface, the Secondary ions are accelerated by an external electric voltage into a "flight tube" and their mass is determined by measuring the exact time at which they reach the detector (i.e. time–of–flight). This SIMS technique is called "Time–of–Flight SIMS" (TOF–SIMS).

Both types of mass analysis produce a spectrum of peaks (No. of Secondary Ions vs. Ion Mass) identifying the microscopic species ejected from the sample (see below SIMS spectrum):



Figure 13.7. SIMS spectrum from a sample identifying Cu, Na, K and organic species

All elements from Hydrogen to Uranium may be detected. Most elements may be detected down to concentrations of 1 ppm or even 1 ppb.

13.6. Infrared Spectroscopy

Molecules can vibrate in various modes including stretching, bending, scissoring, rocking, wagging, twisting (see schematic). Each of these modes has associated with it a characteristic energy particular to the mode and the molecule.



Figure 13.8. Vibrational models of the CO₂ molecule

The characteristic energies of the vibrations of covalent molecules are equivalent to the energies of Infrared photons, specifically Mid–Infrared photons in the wavelength range 2.5–25 μ m equivalent to the energy range 0.5–0.05 eV (see Figure below):



Figure 13.9. Relative energies of molecular actions approximately aligned with their position on the energy, i.e. frequency or wavelength, spectrum

So, if we illuminate covalently bonded molecular materials with Infrared light of the correct frequency (wavelength), we can excite molecular vibrations through absorption of light by the material. Infrared spectroscopy exploits this fact that molecules absorb light at specific frequencies that are characteristic of their structure. These absorptions are resonant frequencies, i.e. the frequency of the absorbed radiation matches the transition energy of the bond or group that vibrates.

In turn, the transition energy of the bond or group is entirely characteristic of the particular molecule and its bonding. Thus, we can illuminate a sample with a spectrum of Infrared light and determine which frequencies are absorbed by the sample which then tells us the atoms and bond types in the material.

A grating spatially separates (disperses) the Infrared illumination into its component frequencies. Each frequency is selected by a moving slit to illuminate the sample. A detector measures the light transmitted through the sample thus detecting any frequencies that are absorbed. A Light Intensity vs. Light Frequency spectrum is acquired. The following is an example of an Infrared spectrum of C_3H_8O Isopropanol showing absorption features characteristic of the molecules bending and stretching vibration modes which immediately allow us to identify the molecular bonds and, hence, the molecule:



13.7. Raman Spectroscopy

Photons incident onto a sample may be **scattered** by the collision in two ways, elastically, i.e. photon energy is conserved (remains the same), called Rayleigh Scattering or inelastically, i.e. photon energy is not conserved but the photon gains or loses energy called Raman Scattering. Incident photons are Raman scattered by interaction with molecules in the sample. The photon delivers its energy to the molecule which is then raised into a very short–lived excited energy state called a *virtual energy state* as opposed to the permanent vibrational states of the molecule (see schematic):



The molecule then relaxes back into a new permanent vibrational energy state different from its original state by emitting a photon of energy equal to the difference between the virtual energy state) and the new permanent energy state. The new permanent energy state may be of either lower or higher energy than the molecule's original permanent state so that the emitted photon may also be either lower or higher energy than the original photon. A lower energy emitted photon is called Stokes scattering. A higher energy emitted photon is called Anti–Stokes scattering (see schematic):



Figure 13.10. Raman scattering, Stokes or Anti-Stokes

In both types of Raman scattering, Stokes or Anti–Stokes, there is a shift in the energy (and, thus, the frequency) of the scattered photon away from the energy/frequency of the original excitation photon. Such shifts depend upon the chemical structure of the molecules responsible for the scattering so that measuring the shift provides a unique chemical fingerprint to identify the composition of the sample material. The below schematic shows the principle of Raman scattering and its low probability of occurrence relative to the elastic Rayleigh scattering of the incident photons, i.e. \sim 1photon in 10⁷ incident photons:



Figure 13.11. Change in energy due to Raman scatter

Raman Spectroscopy System:

Monochromatic (single wavelength) light is applied to the sample by laser. The laser frequency/wavelength is in the Visible spectral region to ensure that the incident photons have enough energy to excite the molecules into virtual vibrational states. The incident light is scattered both Rayleigh (elastic) and Raman (inelastic). However, only a small fraction of the total incident radiation (~1 in 10^7 photons) is Raman scattered inelastically. So, in order to detect the Raman photons, the Rayleigh scattered light must be filtered out. The returned Raman scattered light has a different frequency/wavelength. This difference corresponds to an energy shift which provides a unique chemical fingerprint.





Such equipment delivers Raman spectra allowing identification of molecular species in a sample. The following is a typical Raman spectrum of cholesterol showing both the molecular species and their chemical bonds:



13.8. Methods of Computational Chemistry Applied To Study of Matter

Modern experimental techniques, such as femtosecond laser spectroscopy, nuclear magnetic resonance spectroscopy (NMR) or atomic force microscopy (AFM) are powerful tools to study the structure of matter. Despite the enormous capabilities of these techniques, many important issues remain beyond the reach of experimental methods. This gap, thanks to huge advances in the field of computer technology and algorithms, more efficiently strive to complete the computational methods of quantum chemistry. From a formal point of view, it is difficult to speak about any restrictions for methods ab initio related to the amount of the consideration defined as the number of atoms. The only limitation are practical considerations (economic) time–related (expense) calculations. The molecular size of the system is defined by the number of atoms (M). In order to compare the theoretical results of quantum–chemical calculations with experiment, it is necessary to calculate properties that are available from the experimental measurments. The solution of the Schrödinger equation gives us the energy and wave functions.

Comparison with experiment can be made on the basis of:

- the differences in energy, e.g., the chemical reaction energy, the energy of atomization, bond energy dissosiation or the energy difference between the isomers. The nature of this type require information about the energy at different points of the potential energy surface within the Born–Oppenheimer approximation,
- the molecular properties specific to the electronic state, e.g., dipole moment, polarizability, vibration frequency, magnetic susceptinility. The nature of this type of information on the energy required for one state of the one–electron potential energy surface,
- properties characterizing the transition between two different energy states, for example, excitation energies, ionization potential, electron affinity. The properties of this type require information on energy for different energy states. The properties of this type require information for different energy states. Most of the molecular properties may be considered as a response to certain molecules disorder.

There are several types of disorders:

- external electric field (F),
- external magnetic field (B),
- nuclear magnetic moment (nuclear spin I),
- a change in the geometry.

All properties can be calculated molecular quantum chemistry with more or less accuracy.

Methods of Quantum Chemistry

Modern methods of computational quantum chemistry predict and get detailed energetics for complex processes and chemical reactions, where the use of direct experimental methods is very difficult and complicated. Chemical methods also allow the computer to obtain details of the chemical reactions in a very economical for relatively low investment cost as compared to the costly experiments.

The central object is used to analyze the structure and modeling of chemical reactions is the concept of potential energy surface (PES = Potencial Energy Surface), which was obtained on the basis of the solution non-relativistic Schrödinger equation assuming the correctness of the Born-Oppenheimer approximation. This is substantially due to the large mass difference between electrons and nuclei, nuclei kinetic energy can be neglected in a first approximation, so that the movements of the electron and nuclei can be separated. Consequently therefore, solves the Schrödinger equation for a given configuration of nuclei $R = (R_1...R_n)$ finding only part of the electron $H_{el}\Psi_{el}(\mathbf{r}; \mathbf{R}) = E_{el}(\mathbf{R}) \Psi_{el}(\mathbf{r}; \mathbf{R})$ with the Hamiltonian:

$$\widehat{H}_{el} = -\frac{1}{2} \sum_{i} \nabla_{i}^{2} - \sum_{i} \sum_{A} \frac{Z_{A}}{r_{i}A} + \sum_{i} \sum_{J>i} \frac{1}{r_{i}j} = \sum_{i} \hbar_{i} + \sum_{i} \sum_{J>i} \frac{1}{r_{i}j}$$
(13.1)

In the above equation, the energy $E(R_1,R_2, ..., R_n)$ is parametrically dependent on the configuration, e.g., position nuclei, thus determining the potential energy surface. Complete knowledge of the energy as a function of the position of nuclei is not necessary from a practical point of view to characterize the structure of the molecules or the reaction path. Usually stationary points are sufficient for which the first derivatives of energy with respect to nuclear positions are equal to zero. Focusing on energy stationary points on the potential energy surfaces corresponding energy differences can be directly compared with the experiment. This is illustrated in bellow Figure.



Energetic reaction scheme.

In the above case, the hypothetical reaction profile corresponds to the situation where reagents reacting to pass through the transition state (TS), which leads to a product. Two energy parameters can be marked with this profile and directly compared with experiment. The first is ΔE_{react} , which can be directly correlated with the heat of the reaction (enthalpy), and the second is ΔE_{act} , which you can directly refer to activation energy obtained from the kinetic measurements. Both ΔE_{react} and ΔE_{act} can be estimated quantum–mechanically by a series of calculations. To determine the energy of reaction, optimization of the geometries of reactants and products is requiried, to calculate the differences of their energy. The correctness of the minimization of the geometry works by calculating the frequency (second derivative), which all must be positive

Determination of the structure and energy of the transition state is more complicated. The structure of the transition state corresponds to a situation in which one binding is partially broken and partly formed. In this connection, is the optimization of the complex from a partially frozen geometric parameters until the structure, in which one of the calculated vibration is negative (the imaginary coordinate). Then optimizes the layout until you find the stationary point advancing after the coordinate corresponding to oscillation must not be higher. In the final stage of the calculation of the identity of the transition state are verified through calculation of frequency and check whether the imaginary coordinate corresponds to reaction path. Characteristics of reaction profile strongly depends on the level of theory used in the calculation.

Despite of the Born–Oppenheimer approximation, electron Schrödinger equation cannot be solved in an analytical form and should be used for further approximation. The basis of all quantum chemical methods is the Hartree–Fock approximation. In accordance with this approximation it is assumed that the wave function is expressed as a antysymetryczny product one–electron wave functions (i.e., spin–orbitals) in the form of so–called Slater determinant:

$$\Psi(r_1 r_2 \dots r_n) = |\varphi_1 \varphi_2 \dots \varphi_n| = \frac{1}{\sqrt{n!}} \begin{vmatrix} \varphi_1(r_1) & \varphi_2(r_2) & \dots & \varphi_n(r_1) \\ \varphi_1(r_2) & \varphi_2(r_2) & \dots & \varphi_n(r_2) \\ \vdots & \vdots & \vdots & \vdots \\ \varphi_1(r_n) & \varphi_2(r_n) & \dots & \varphi_n(r_n) \end{vmatrix}, \quad (13.2)$$

where φ_i is called spin– orbital.

This form meets the fundamental properties of the wave function, namely is antisymmetric with respect to the exchange of two electrons and a prohibition of the Pauli exclusion principle. Variational wave function in the form of the determinant Slater leads to the coupled integro–differential equations that gives the optimum form of orbitals as well as orbital energies. The solution of such equations in practice is obtained by the self–consistent approach.

Unfortunately, the Hartree–Fock method usually does not give the energy values comparable to the experimental data essentially for two reasons: first, this method does not take into account the correlation energy (i.e., relative motion of the electrons) as well as not being able to properly describe the situation, when a chemical bond is broken. Therefore, in order to obtain results comparable to experiment, use the methods that take into account electron correlation.

In real applications the correlation energies are usually taken into account by using the MP2 methods (Moller–Plasset Perturbation Theory), DFT (Density Functional Theory) or CCSD (Coupled Clusters Singles and Doubles). As regards the approach multi–reference take them by using CASSCF (Complete Active Space Self–Consistent Field). Conceptually the most simple correlation method is MP2. In this approach, the electron correlation is calculated via perturbation theory.

Conceptually, the DFT methods are based on the electron density, and not on the wave function. In practical applications, however the Kohn–Sham formalism is used based on orbital scheme. In summary one can say that the equation of Kohn–Sham are very similar to the equations Hartree–Fock method, except that it is built–in in the exchange–correlation potential. The most popular functionals are B3LYP and BP86. It should be noted that DFT methods have become very popular due to their low cost, as well as the ease of use in practical calculations, especially when the system contains transition metals. The results of the calculations, however, depend on the choice of the functional. Coupled clusters (CC) methods based on the so – called exponetial cluster ansatz. Assuming you are using methysergide, in which development is achieved by the use of the operator eksponencjalnej the form that works on the Hartree–Fock method. Using single and double excitation CCSD nonlinear equations is obtained, which also solved iteratively. CCSD method is very accurate, but very expensive even for medium – sized chemical systems.

These schemas are single – reference methods based on a single Slater determinant. CASSCF method is multi – reference in which active orbital space is definied. This method is particularly important for the description of the transition states. However, the CASSCF method itself does not give satisfactory results and must be corrected by the calculations taking into account dynamic correlation, using the CASPT2 approach (Complete Active Space with Second–order Perturbation Theory). For more information about the working methods of computational quantum chemistry can be found in the monograph (Piela, 2005).

Example of Quantum Chemical Calculations

As a particular example of quntum chemical caluculations, oxidation of nitrogen oxides is presented in this section. The discussion is on oxygen/ozone (O_2 , O_3), nitrogen oxides (NO, NO₂, NO₃, N₂O₄, N₂O5) and search for transition states for the primary oxidation of nitric oxide with ozone based on different variants and methodology of calculation.

Quantum chemical calculations were carried out calculations using different levels of thoery. For this purpose, the methods DFT – based and *ab initio* methods such as MP2 and CCSD were applied. *Ab initio* methods, in contrast to the DFT, properly describe the dispersion energy, which may be relevant in the consideration of elementary chemical reactions. In addition, the correct description of the structure of ozone required to use the multi – configuration CASSCF method (Borowski P., Andersson K., Malmqvist P.A., Roos B.O., 1992).

The aim of the calculation is energy of reaction, which specifically means the calculation of energy substrates, products and the possible transition states by means of geometry optimization. Designated points of characteristic between start and end points, require vibrational analysis in order to obtain information about the energy profile. In this way the energy profile of the individual reaction will determine both their activation energy leading to the transition state, as well as the final result. Particularly important is location of transitional states and corresponding energy barriers associated with individual reactions. They most likely describe the mechanism of the reaction, because the activation energy can be directly related to the reaction rate constants.

Quantum-Chemical Analysis of Oxidation Process of Ozone -NOx

The mono–nitrogen oxides, nitric oxide (NO) and nitrogen dioxide (NO₂), generically known as NO_x , are well known atmospheric pollutants emitted, in particular, by industrial combustion processes such as the burning of natural gas, coal and oil.

 NO_x reacts with atmospheric moisture, ammonia and other compounds to form nitric acid vapour and related particles which adversely affect the environment as a component of acid rain and adversely affect human health through attack on the lungs and aggravation of heart disease. NO_x also reacts with volatile organic compounds in the presence of heat and sunlight to form ozone. This chemical, again, can damage lung tissue and is transported by wind currents to cause health impacts far from the original sources. Finally, NO_x also readily reacts with common organic chemicals, and even ozone, to form a wide variety of toxic products, such as nitroarenes, nitrosamines and the nitrate radical, which may cause biological mutations.

Thus, mono-nitrogen oxides are among the chemical pollutants having the highest perceived risk for human and environmental health. For example, the Australian National Pollutant Inventory (NPI) has ranked the oxides of nitrogen number 1 out of 90 pollutant substances in priority for reporting purposes, rank 1 being the highest perceived risk (Environmental Science Published for Everybody Round the Earth). The total hazard score takes into account both human health and environmental criteria.

Several technologies have been developed to reduce the production of NO_x at the combustion stage. These include flameless oxidation (FLOX), staged combustion and the Bowin low NO_x technology, which techniques can deliver 50–75% reduction in NO_x production.

Of equal interest to industry are techniques to destroy NO_x at the postcombustion stage, commonly called end-of-pipe removal or abatement techniques. These include selective catalytic reduction (SCR) and selective noncatalytic reduction (SNCR) both of which techniques require substantial investment in equipment and have limitations in efficiency and lifetime.

Accordingly, the problem of removal of the serious pollutant NO_x from industrial flue gases at low concentrations is still environmentally important and is commercially difficult because of the cost of current removal methods and the wide variety of emission sources. These problems motivate development of an energy and chemicals efficient, widely applicable, end–of–pipe exhaust NO_x abatement technology. Ozone produced by industrial plasma systems (ozonisers) appears to offer technically feasible and commercially interesting solutions based on the Gas State conversion of NO_x into industrially useful by–products, such as nitric acid. Key to industrial implementation of such a technology is optimisation of the process so as to make the most efficient use of ozone reactant. This has motivated investigation of the O_3 – NO_x reaction mechanism with the objective of improving current chemical models and investigation of those factors affecting reaction efficiency, which can be defined as the number of moles of NO_x oxidised to a higher oxidation state per mole of ozone consumed (Jaroszyńska-Wolińska J., 2006).

The NO_x - O_3 reaction processes are well known at the molecular level and comprise a small number of reactions in which the mono-nitrogen oxides react with ozone to generate higher oxidation states culminating in N_2O_5 which then can be combined with water to form nitric acid (13.7):

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{13.3}$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{13.4}$$

$$NO_2 + NO_3 \rightarrow N_2O_5 \tag{13.5}$$

$$2NO_2 + O_3 \to N_2O_5 + O_2 \tag{13.6}$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \tag{13.7}$$

However, the detailed mechanisms of equations (13.3) to (13.4) remain obscure so that the object of the present study was to apply quantum chemical models to try to elucidate reactions paths, specifically the presence of any transition states, and in the attempted calculation of the two key energetic factors in chemical reactions, namely the relative energy captured or released by the reaction E_{r} , and the activation energy, E_a , of each reaction.

The following quantum chemical methods were applied: Hartree Fock (HF), Density Functional Theory (DFT) with Becke–3–Lee Yang Parr (B3LYP) exchange correlation potential, Complete Active Space Self–Consistent Field (CASSCF), second order Moller Plesset perturbation theory (MP2) and Coupled Cluster with Singles and Doubles substitutions (CCSD).

Computational Details

Determination of Relative Reaction Energies, Er

Determination of relative reaction energies, defined as

$$E_r = E_{\text{products}} - E_{\text{substrates}}, \tag{13.8}$$

for reactions (13.3) - (13.6) can be accomplished by finding the equilibrium geometries and calculating the total energies of substrates and products namely, the oxygen, ozone, NO, NO₂, NO₃ and N₂O₅ molecules.

The total energies may then be corrected by the zero–point vibration energy (ZPE) for each molecule.

The optimal structures of oxygen, ozone and the NO_x molecules involved in the reactions (13.3) and (13.4) were obtained by geometry optimisation procedure at the MP2 level of theory. Three different basis sets were used, namely 6–311G (d,p), cc–pVDZ and aug–cc–pVDZ.

The same molecules plus NO₃ and N₂O₅ were also optimized at the DFT (Parr & Weitao, 1989), level of theory to enable analysis of reactions (13.3) - (13.6). In particular the B3LYP exchange–correlation potential (Becke A.D., 1993), (Lee C., Yang W., Paar R.G., 1993) was used. This method, called DFT/B3LYP, is known to give accurate molecular geometries and (relative) electronic energies. Note, that in the case of the open–shell molecules (O₂, NO, NO₂, NO₃) the unrestricted DFT procedure has to be adopted. The DFT calculations were carried out using the 6–311G (d,p) basis set (Krishnan R.; Binkley J.S.; Seeger R.; Pople J.A., 1980).

Next, the correlated *ab initio* calculations at the optimal structures were carried out. We have chosen the CASSCF (Roos B.O., 1980), (Roos B.O., Taylor P.R., Siegbahn P.E.M., 1980), (Siegbahn P.E.M, Almlöf J.A, Heiberg A., Roos B.O., 1981) method, a special case of the more general MCSCF (Wahl AC, Das G, 1970) approach. This method is known to account for the major part of the static (or non–dynamic) correlation effects of particular importance in the description of systems containing the lone–pair electrons. However, it does not incorporate the very important dynamic correlation effects and, therefore, the final results may suffer from this deficiency. It should be emphasized that for the CASSCF calculations to be of reasonable quality an adequate choice of the active space (the CAS space) is of particular importance. This is especially true with regard to the description of phenomena involving a few different potential energy surfaces. A balanced and consistent (in a well defined way) inclusion of the configurations into the wave functions of all species of interest is essential to obtain reasonable values of the relative energies.

For example, the active space adequate for treatment of the static correlation in the case of the ozone molecule should consist of at least all *p*-derived orbitals, i.e. 6 orbitals from the σ space and 3 orbitals from the π space (Borowski P., Andersson K., Malmqvist P.A., Roos B.O., 1992). This active space may be referred to as the (6/3) active space. The distribution of 12 electrons among 9 orbitals leads to the CI expansion of the CASSCF wave function into approximately 670 configuration state functions (CSFs). Note that the size of the CI expansion has been reduced not only by the spatial symmetry but also by the spin symmetry of the configurations. However, choice of the active space on the same grounds for the biggest molecule considered here, i.e. N_2O_5 , becomes impractical.

We managed to carry out this kind of calculation, called CASSCF (σ - and π -derived), only for the O₂, O₃, NO, NO₂ and NO₃ molecules.

This means, that CASSCF(σ - and π -derived) relative energies were computed only for reactions (13.3) and (13.4). Thus, we decided to reduce the CI expansion of the MCSCF wave functions by including the excitations only within the π space for all systems. However, it is known (Andersson K., Borowski P., Fowler P.W., Malmqvist P.A., Roos B.O., Sadlej A.J., 1992), (Borowski P., Andersson K., Malmqvist P.A., Roos B.O., 1992) that, at least for the ozone molecule, any restriction of the active space below that of the (6/3) quality leads to substantial worsening of some of the calculated properties. Indeed, the π -derived active space turned out to be too small. The CASSCF calculations were carried out using the smaller 6–31 G(d,p) basis set (Hariharan PC, 1973).

In all of the MP2, DFT and CASSCF calculations the type of the stationary point was determined by frequency calculations. All calculated frequencies turned out to be real indicating that structures corresponding to local minima were found. It is also important to realize that dissociation/association processes may lead to change in the number of the vibrational degrees of freedom when going from substrates to products. Thus, the harmonic frequencies were also used in the calculation of the zero–point energy (ZPE) correction for substrates and products.

All MP2 and DFT calculations were carried out using the parallel version of the PQS (PQS version 3.1, 2013) quantum chemistry package. All CASSCF calculations were carried out using the DALTON (Release 1.2, 2001) quantum chemistry software.

Determination of Activation Energies, E_a

Reactions (13.3) and (13.4) above have been computationally modelled assuming a direct reaction of ozone with NO_x proceeding via formation of transition states followed by breaking of the O–O₂ bond according to the following schemes:

| $NO + O_3 \rightarrow \{ONO_2\}^{\ddagger} \rightarrow NO_2 + O_2$ | (13.9) |
|--|---------|
| $NO_2 + O_3 \rightarrow \{O_2NO_2\}^{\ddagger} \rightarrow NO_3 + O_2$ | (13.10) |

In the present study we applied four different quantum chemical models to characterize the potential energy surface of a system comprising nitrogen oxide reacting with ozone, namely HF, MP2, DFT/B3LYP and CCSD.

Energy was computed as a function of the distance between the N-atom of the nitrogen oxide and the O-atom of ozone. All calculations were carried out using the Gaussian 03 (Frisch M.J., et al., 2004) suite of programs for electronic structure calculations. All calculations were performed using the 6–311 g (d, p) basis set.

To compute the potential energy scans, the distance between the N-atom of nitrogen oxides (NO and NO₂) and the O-atom of ozone was systematically varied between 1.25Å and 2.50Å in increments of 0.05Å. At each point, the geometries were re-optimized using HF, MP2 and B3LYP levels of theory. For calculations using the CCSD quantum chemical method, the structures optimized at MP2 levels of theory were used and only single point calculations were carried out (Jaroszyńska-Wolińska, 2010)

The optimized geometries were verified as local minima by carrying out frequency calculations. The geometries with positive frequency values correspond to minima while the geometries with one negative frequency correspond to transition states. The grids were intensified between 1.40Å and 1.80Å to increments of 0.01Å to better locate any transition states.

Following results from these calculations, reactions (13.3) and (13.4) were again modeled using the MP2 level of theory but at higher energy scan resolution with varying finer increments down to as low as 0.0001Å and with three different basis sets, namely 6-311 G(d,p), cc-pVDZ and aug-cc-pVDZ.

Determination of Relative Reaction Energies, Er

Equilibrium geometries and vibrational frequencies. The geometries of all molecules involved in reactions (13.3) - (13.6) generated by DFT and CASSCF analysis are shown in Figure 13.13:



Figure 13.13. The geometrical parameters of the molecules considered in this work (Jaroszyńska-Wolińska J., 2009)

The values separated by "/" are the theoretical values reported in the following order: DFT/B3LYP/6–311G(d,p)/CASSCF (σ – and π –derived) / 6–31G(d,p).

The experimental values (O2: ref. (Slanger TG, 1988), NO: ref. (Huber HP, Herzberg G, 1979), O3: (Tanaka T, 1970), NO2: (Lide DR, ed. CRC, 1995), NO3: (Stirling A, 1994), N2O5: (McClelland BW, 1983) are given in parentheses (bond lengths in Å, valence angles in degrees).

The equilibrium geometries of the O_3 , NO and NO₂ molecules and transition states for reactions (13.3) and (13.4) were obtained by the optimisation procedure at the MP2 level using three different basis sets (Jaroszyńska–Wolińska, 2010).



Figure 13.14. Structures O₃, NO, NO₂ molecule (Jaroszyńska- Wolińska, 2010)



Transition State for NO₂ + O₃ reaction



The total energies, the ZPE and the harmonic frequencies are reported in Table 13.1. These values were used in the subsequent determination of the relative energies for the reactions (13.3) - (13.6).

Table 13.1. The total energies, ZPE and harmonic frequencies of oxygen, ozone and nitrogen oxide molecules calculated at three MP2, the DFT/B3LYP and the CASSCF(σ - and π -derived) levels of theory (Jaroszyńska- Wolińska, 2010)

| | | | ZPE | Harmon | ic freque | ncies |
|-----------------|-------------------------|-------------------------------|-------------------------------------|--------|---------------------|-------|
| Molecule | Method | Energy [a.u.] | [a.u.] | I | [cm ⁻¹] | |
| | MP2/6-311G(D,P) | -150.0238789 | 0.003306 | 1451 | | |
| | MP2/cc-pVDZ | -149.9731825 | 0.003242 | 1224 | | |
| | MP2/aug-cc-pVDZ | -150.0042898 | 0.003254 | 1226 | | |
| | DFT/B3LYP/6- | | | | | |
| | 311G(d,p) | -150.3647908 | 0.003736 | 1640 | | |
| | CASSCF/6-311G(d,p) | - 149.692351 | | 1545 | | |
| O ₂ | Experimental (Slanger 7 | FG, 1988) | | 1580 | | |
| | MP2/6-311G(D,P) | -129.6194881 | 0.008104 | 3557 | | |
| | MP2/cc-pVDZ | -129.5774376 | 0.008342 | 3661 | | |
| | MP2/aug-cc-pVDZ | -129.60215 | 0.008354 | 3666 | | |
| | DFT/B3LYP | -129.9267022 | 0.00453 | 1988 | | |
| | CASSCF | - 129.351396 | | 1919 | | |
| NO | Experimental (Huber H | P, Herzberg G, 197 | ⁷ 9) ^{<i>a</i>} | 1876 | | |
| | MP2/6-311G(D,P) | -224.9781948 | 0.00958 | 750 | 1171 | 2282 |
| | MP2/cc-pVDZ | -224.9003363 | 0.009554 | 740 | 1161 | 2292 |
| | MP2/aug-cc-pVDZ | -224.9577371 | 0.009495 | 738 | 1148 | 2281 |
| | DFT/B3LYP | -225.4707911 | 0.007262 | 747 | 1190 | 1249 |
| | CASSCF | - 224.475823 | | 690 | 1015 | 1078 |
| O ₃ | Experimental (Barbe A. | , Secroun C., Jouv | e P., 1974) | 716 | 1089 | 1135 |
| | MP2/6-311G(D,P) | -204.6570188 | 0.010512 | 774 | 1388 | 2451 |
| | MP2/cc-pVDZ | -204.589136 | 0.010308 | 767 | 1388 | 2368 |
| | MP2/aug-cc-pVDZ | -204.6342717 | 0.010524 | 760 | 1367 | 2490 |
| | DFT/B3LYP | -205.1327198 | 0.008821 | 766 | 1399 | 1706 |
| | CASSCF | - 204.184820 | | 746 | 1321 | 1663 |
| NO_2 | Experimental (Lide DR | , ed. CRC, 1995) ^a | | 750 | 1318 | 1618 |
| | MP2/6-311G(D,P) | -279.657345 | 0.018601 | 740 | 740 | 764 |
| | MP2/cc-pVDZ | -279.5622366 | 0.018524 | 737 | 737 | 769 |
| | MP2/aug-cc-pVDZ | -279.6310734 | 0.018275 | 727 | 727 | 763 |
| | | | 0.010718 | 258 | 258 | 802 |
| | DFT/B3LYP | -280.2985519 | | 1121 | 1121 | 1135 |
| | | | | 440 | 565 | 683 |
| NO ₃ | CASSCF | - 278.993184 | | 946 | 1291 | 1695 |
| | | | | 52 | 62 | 220 |
| | | | | 344 | 384 | 570 |
| | | | | 683 | 683 | 766 |
| | | | | 812 | 894 | 1305 |
| | DFT/B3LYP | - 485.465713 | | 1403 | 1797 | 1843 |
| N_2O_5 | CASSCF | | | | | |

^aFundamental frequencies

For the DFT and CASSCF methods, the equilibrium bond length of the ground state $({}^{3}\Sigma_{u}^{-})$ oxygen molecule is in good agreement with the experimental value. Apparently, the DFT method seems to slightly overestimate and the CASSCF method to slightly underestimate the attractive forces between atoms, causing the bond length to be shorter/longer respectively than that found experimentally. As a consequence, the harmonic frequency of the stretching mode is higher (1640 cm⁻¹) for DFT and lower (1545 cm⁻¹) for CASSCF than the corresponding experimental value of 1580 cm⁻¹ (Slanger TG, 1988). The agreement is less good for the MP2 method but these calculated frequencies confirm energy minima enabling insight into the reaction mechanism.

Again, for the DFT and CASSCF methods, the bond length observed in the case of the NO molecule in its (open-shell, $^{2}\Pi$) ground state is in good agreement with the experimental value.

However, it is well established that ab initio methods typically overestimate vibrational frequencies and this is clearly seen in the MP2 values.

In the case of DFT and CASSCF for the ozone molecule (in the ${}^{1}A_{1}$ ground state) the theoretically predicted bond lengths behave similarly to oxygen–they are too short at the DFT level and too long at the CASSCF level. However, it should be noted that much better agreement of the CASSCF results with experiment for both oxygen (Borowski P., Füscher M., Malmqvist P.A., Roos B.O., 1995) and ozone (Borowski P., Andersson K., Malmqvist P.A., Roos B.O., 1992) molecules was achieved using ANO–type basis set (Almlöf J.A., Taylor P.R., 1987). Consequently, the harmonic frequencies of two stretching modes (symmetric and anti–symmetric) are higher at the DFT level of theory. They are 1249 cm⁻¹ and 1191 cm⁻¹ at the DFT level and 1078 cm⁻¹ and 1015 cm⁻¹ at the CASSCF level, respectively. These values are to be compared with experimental harmonic frequencies of 1135 cm⁻¹ and 1089 cm⁻¹ (Barbe A., Secroun C., Jouve P., 1974). The theoretical (DFT and CASSCF) valence angle reproduces well the experimental value and the frequency of the symmetric bending mode is well accounted for.

The theoretical geometry of the ground state $(^{2}A_{1})$ nitrogen dioxide molecule is in good agreement with experiment for all methods.

The NO₃ molecule in its ground electronic state $(^{2}A_{2})$ is planar. Experimental investigations (Stirling A, 1994) clearly demonstrate that the molecule belongs to the D_{3v} symmetry point group. Thus, all N–O bond lengths should be the same and the O–N–O valence angles should be equal to 120°.

Apparently, the DFT/B3LYP approach is capable of predicting the proper structure of the molecule, both with regard to the symmetry of the ground state and the lengths of the N–O bonds. However, CASSCF is not.

The structure predicted by the CASSCF method has C_{2v} symmetry (cf. Figure 13.13). In addition, the N–O bonds are substantially shorter than those predicted experimentally. Although all the frequencies turned out to be real, indicating that the local minimum was found, the final result seems to be an artifact of the CASSCF approach.

As can be seen (cf. Figure 13.13), only the DFT/B3LYP geometrical parameters for the N_2O_5 molecule are available. Actually, DFT is a very efficient correlated method used to carry out calculations on molecules containing hundreds of atoms. Molecules as small as those considered in the present work should not present a problem. Indeed, the DFT calculated molecular geometry of N₂O₅ is in good agreement with experimental values for the limited number of geometrical parameters reported. It should be noted that the N2O5 molecule is not planar - the torsion O-N-O-N angle predicted by the DFT/B3LYP approach is equal to approximately 30° (or 150°). Next, CASSCF calculations were carried out for this molecule. However, the CASSCF calculations are more complicated than the DFT calculations on account of the rapid growth of the CI expansion of the MCSCF wave function with increasing size of the active space. As has already been pointed out, the choice of the σ - and π -derived active space turned out to be impractical for this molecule so that it was decided to reduce the size of the active space. The choice of a π -derived only active space for all the molecules led, however, to (i) substantial worsening of the results for other molecules and (ii) arriving at a saddle point (one complex frequency) rather than at a local minimum on the N₂O₅ potential energy surface. Many attempts to extend slightly the active space beyond that of the π -derived quality were made. A physically justifiable choice of the active space can be made on the basis of the MP2 natural orbital occupation numbers: (i) orbitals with occupation numbers above a certain threshold remain inactive, (ii) orbitals with occupation numbers below a certain threshold remain virtual and (iii) the remaining orbitals constitute the active space. However, we failed to find the local minimum of the CASSCF potential energy surface of N_2O_5 for all active spaces chosen in this way that could be handled in our laboratory.

Relative Energies

From Table 20, the MP2, DFT/B3LYP/6–311G(d,p) and the CASSCF (σ - and π -derived)/6–31G(d,p) relative energies and the relative energies corrected for the zero point vibrational energy for the reactions (13.3) – (13.6) are calculated and shown in Table:

| Table 13.2. | The relative energies, Er = Eproducts-Esubstrates, and relative energies corrected for |
|-------------|--|
| | the zero point vibrational energy, Er(ZPE), of the reactions (13.3)-(13.6) calculated at |
| | three MP2, the DFT/B3LYP/6-311G(d,p) and the CASSCF(σ - and π -derived)/6- |
| | 31G(d,p) levels of theory (Jaroszyńska- Wolińska, 2010) |
| | |

| Reaction | Method | E _r [kcal/mol] | E _r (ZPE) [kcal/mol] |
|---|--------------------|---------------------------|------------------------------------|
| (13.3) NO + O ₃ \rightarrow NO ₂ + O ₂ | MP2/6-311G(D,P) 5D | - 52.218 | - 54.644 |
| | MP2/cc-pVDZ | - 53.053 | - 55.780 |
| | MP2/aug-cc-pVDZ | - 49.369 | - 51.924 |
| | DFT/B3LYP | - 62.859 | - 62.379 |
| | CASSCF | - 31.36 | - 30.54 |
| (13.4) $NO_2 + O_3 \rightarrow NO_3 + O_2$ | MP2/6-311G(D,P) 5D | - 28.872 | - 27.733 |
| | MP2/cc-pVDZ | - 28.832 | - 27.637 |
| | MP2/aug-cc-pVDZ | - 33.480 | - 32.533 |
| | DFT/B3LYP | - 37.545 | - 38.567 |
| | CASSCF | - 15.63 | - 14.69 |
| (13.5) $NO_2 + NO_3 \rightarrow N_2O_5$ | DFT/B3LYP | - 21.62 | - 16.90 |
| | CASSCF | | |
| (13.6) $2NO_2 + O_3 \rightarrow N_2O_5 + O_2$ | DFT/B3LYP | - 59.18 | - 55.49 |
| | CASSCF | | |

For all reactions considered in the present work, the energy of products is lower than that of substrates so that, apparently, all reactions are exothermic. The most exothermic reactions appear to be (13.3) and (13.6) and the least exothermic is reaction (13.5).

Following the DFT results only, for reaction (13.3) the number of vibrational degrees of freedom is the same for substrates and products so that E_r and $E_r^{(ZPE)}$ are close. A somewhat larger difference between these quantities is observed in the case of reaction (13.4) in which an extra vibrational degree of freedom appears for the products. However, the two low–energy (degenerate, on account of symmetry) vibrational modes result in the ZPE correction for products being smaller than for substrates so that $E_r^{(ZPE)} > E_r$. Six and seven additional vibrational degrees of freedom are gained in the course of reactions (13.5) and (13.6), respectively so that E_r and $E_r^{(ZPE)}$ values for these reactions differ by as much as 4.5–5 kcal/mol.

Due to the lack of the reliable data for the N_2O_5 molecule the relative CASSCF energies of only the first two reactions were calculated. They are much (more than twice as much) lower than the corresponding DFT/B3LYP energies. However, we are inclined to trust more the DFT/B3LYP energies due to the lack of dynamic correlation in the CASSCF wave function.

Ab initio calculations using Hartree Fock (HF), Density Functional Theory (DFT), Complete Active Space Self-Consistent Field (CASSCF), second order Moller Plesset perturbation theory (MP2) and Coupled Cluster with Singles and Doubles substitutions (CCSD) quantum chemistry models have been made on all of the four reactions in which the mono-nitrogen oxides react with ozone to generate higher oxidation states culminating in N_2O_5 . The relative reaction energies were determined and all reactions were found to be exothermic. Potential energy surfaces of the O₃-NO and O₃-NO₂ reactions were modeled using the HF, MP2, DFT and CASSCF methods and the presence of a transition state was indicated in the HF, MP2 and CASSCF calculations but not in the DFT models. The MP2 level of theory was further applied with three different basis function sets and finer potential energy scan resolution and the activation energies, E_a, determined. For the O₃-NO reaction there was reasonably good correlation with the experimental Arrhenius activation energy of 1.1694 kcal/mol. However, for the O₃-NO₂ reaction the calculated activation energy was a factor of 4 higher than the experimental Arrhenius activation energy of 2.2020 kcal/mol.

13.9. Quantum Chemical Analysis of Properties of an $[(Al_2O_3)_4]^+$ Clusters

Aluminium oxide molecules are very important materials in high temperature applications, translucent ceramics, corrosion resistance ceramics, electronic packaging, and catalysis. The most important of them is aluminium oxide (Al₂O₃) known as Alumina. From a crystalline point of view, Al₂O₃ may exist in many forms, including α , χ , η , δ , κ , θ , γ , and ρ forms. (Archibong E.F., St-Amant A., 1999), (Gianotto, Rawlinson, Cossel, Olson, Appelhans, & Groenewold, 2004), (Mitin, 2011), (Patzer ABC, Chang Ch, Sedlmayr E, Sülze D, 2005), (Rahane, Deshpande, & Kumar, 2011), (Shirai T, Watanabe H, Fuji M, Takahashi M, 2009).

Among these forms, the most stable is regarded as α -Al₂O₃ although differences in surface state exist. In addition, while Al₂O₃ may exist in many metastable polymorphs, generally Al₂O₃ may be considered to exist in two forms; a face–centered cubic (fcc) or hexagonal close–packed (hcp) arrangement of oxygen anions, with differences between polymorphs arising from varying atomic positions within each lattice (Levin & Brandon, 1998).

Although many metastable forms of alumina exist, including γ -Al₂O₃, δ -Al₂O₃, and others, Sierka, Asmis and co-workers proposed new structural polymorphs of the most stable isomers of $[(Al_2O_3)_4]^+$ and $(Al_2O_3)_4$ through a combination of experiment and DFT calculations (Sierka, i inni, 2007)

Specifically, the IR multiple-photon dissociation (MPD) spectrum was collected for $[(Al_2O_3)_4]^+$ and the corresponding DFT-based structure was established based on the initial bulk geometry derived from the corundum crystal structure. The structure that was proposed was based on *n*-memebered rings consisting of six- and four-memebered alternating aluminum and oxygen atoms, and the global minimum was determined to be of an "arrowhead" shape with C_s symmetry, where the final oxygen atom is coordinated to the topmost aluminum vertex of the cube fragment. The proposed structure was further used to simulate vibrational spectra, and distinguish from other structural analogs.

Rahne, et. al. systematically investigated structural and electronic properties of $(Al_2O_3)_n$ clusters with n= 1–10 within the pseudopotential DFT framework using the generalized gradient approximation for the exchange–correlation energy. They concluded that the lowest energy isomers show preference towards 4– and 6–membered Al_2O_2 and Al_3O_3 rings respectively, and that these minima have more structural similarity with the γ –Al₂O₃ phase than the α –Al₂O₃ (corundum) phase. In general, they concluded that isomers with cage structures are highest in energy, and in particular for clusters with n=4, the lowest energy isomer was found to be the one without any symmetry.

The purpose of this section is to further investigate the structural and electronic properties of $[(Al_2O_3)_4]^+$, employing DFT.

This study will address the structure based on available vibrational spectra. In addition conclusions regarding the interpretation of the gas phase $[(Al_2O_3)_4]^+$ structure will be presented.

All calculations were performed using the Gaussian09 suite of programs for electronic structure calculations. A number initial structural guesses were generated, and the corrsponding geometries were then optimized using a number of exchange–correlation functionals including B3LYP, CAM–B3LYP, B3PW91, TPSS, TPSSh, BPV86 and BP86. Frequencies along with their respective IR intensities were then calculated. Although a number of different functionals have been tested, only four, namely BP86, TPSSh, CAM–B3LYP, and B3LYP, produced spectra that were in reasonable agreement with experimental data.

Analysis of Vibrational data

Figure 13.16 shows the comparison between experimental and simulated data based on vibrational frequencies as well as IR intensities computed at the CAM–B3LYP/6–311g (d,p), and B3LYP/6–311g (d,p) levels of theory, respectively. Overall the simulated spectra were in very good agreement with experiment, notably around 1000 cm⁻¹ where the most intense band is present. The simulated spectra also captures the relative intensities of the other bands reasonably well.

Based on the fact that computations reproduce the experimental data very well, a correlation in terms of computed vs. experimental frequencies was established, and thus about 14 peaks were assigned.

Figure 13.16 shows this correlation in terms of vertical lines, Table 13.3 contains the associated frequencies, and the eigenvectors for 9 of the most significant calculated peaks at the CAM–B3LYP/6–311g(d,p) level are collcted in Figure 13.17.

While both functionals produce reasonable agreement with experiment, certain differences may be noticed. CAM–B3LYP produces a shoulder within the most intense band, that correlates to the experimental values of 995 cm^{-1} and 1011 cm^{-1} for the most intense peak and shoulder, respectively.

The second most inense experimental peak produced by CAM–B3LYP also correlates better than B3LYP to the 1027 cm⁻¹ experimental value, although the spectra produced B3LYP has an improved resolution of the 1011 cm⁻¹ experimental band. Additionally, CAM–B3LYP reproduces the experimental peak at 962 cm⁻¹, while B3LYP does not seem to, and improved resolution about the 884 cm⁻¹ and 910 cm⁻¹ experimental values may be attributed to B3LYP.



Figure 13.16. Comparison of experimental IR–MPD spectrum (trace a) with simulated spectrum based on B3LYP/6–311g(d,p) (trace b), and CAM–B3LYP (trace c). The experimental spectrum was reproduced from ref. (Rahane, Deshpande, & Kumar, 2011) with permission.

While both CAM–B3LYP and B3LYP correlate well to the experimental spectra comparably about the 771 cm⁻¹, 779 cm⁻¹, and 831 cm⁻¹ experimental values, neither functional has significant correlation to the 818 cm⁻¹ or lower 664 cm⁻¹ values. However, CAM–B3LYP does to some extent correlate to the lower energy range of the experimental spectra better than B3LYP, specifically in the vicinity of the 624 cm⁻¹ transition. In summary, comparison of the experimental values that correlate most significantly to the scaled eigenvalues produced by the CAM–B3LYP and B3LYP functionals are collected in Table 13.3.

Table 13.3. Frequencies of the most intense experimental IR–MPD bands of [(Al₂O₃)₄]⁺ correlated with computed frequencies subject to single–parameter scaling assuming vibration # 51 as a reference. (Jaroszyńska-Wolińska J., Garabato B.D., Alam J., Reza A., Kozłowski P., 2015)

| EXP (IR-MPD)/cm ⁻¹ | B3LYP/cm ⁻¹ (Eigenvalues) | CAM-B3LYP/cm ⁻¹ (Eigenvalues) |
|-------------------------------|--|---|
| 1027 | 1050 (54) | 1043 (54) |
| 1011 | 1027 (53) | 1038 (53) |
| 995 | 995 (51) | 995 (51) |
| 962 | _ | 962 (50) |
| 938 | 905 (49) | 918 (49) |
| 929 | 881 (48) | 904 (48) |
| 910 | 880 (47) | 873 (47) |
| 884 | 839 (45) | 850 (45) |
| 831 | _ | 803 (43) |
| _ | 768 (42) | _ |
| 818 | _ | 774 (41) |
| 799 | 754 (40) | 748 (40) |
| 771 | 703 (38) | 710 (38) |
| 654 | 603 (35) | 634 (35) |
| 624 | 582 (34) | 601 (34) |


Figure 13.17. Selected eigenvectors of [Al₈O₁₂]⁺ corresponding to computed frequencies employing CAM–B3LYP. (Jaroszyńska-Wolińska J., Garabato B.D., Alam J., Reza A., Kozłowski P., 2015)

The eigenvectors associated with the most intense calculated vibrations at the CAM-B3LYP/6-311g (d,p) level mentioned above, are collected in Figure 13.17. The most intense peak, $992 \text{ cm}^{-1}(51)$, shows displacement amplitudes of medium strength between all Al and O atoms within the structure, with slightly higher amplitudes associated with Al–O bending about both Al₂O₃ end-capping moeities. The second most intense peak, $1033 \text{ cm}^{-1}(54)$, on the other hand has significantly large Al-O stretching amplitudes about one of the capping Al₂O₃ moeities, while the remaining displacement amplitudes were comparatively smaller. The shoulder peak between these two vibrations, 1014 cm⁻¹ (53), has moderately high displacement amplitudes for both Al_2O_3 capping moeities, with smaller displacements within the central complex. The remaining calculated peaks at $918 \text{ cm}^{-1}(49)$, $904 \text{ cm}^{-1}(48)$, $873 \text{ cm}^{-1}(47)$, $774 \text{ cm}^{-1}(41)$, $748 \text{ cm}^{-1}(40)$, and $634 \text{ cm}^{-1}(38)$ all have moderate displacement amplitudes throughout the entire complex, with the exception that they differ generally in the location of about 3 high strength amplitudes. $918 \text{ cm}^{-1}(49)$ shows three high amplitude oxygen displacements, while the remaining amplitudes are moderate to small. The eigenvectors corresponding to 904 cm⁻¹ (48) show a high Al–O stretching amplitude, while the 873 cm⁻¹ (47) peak corresponds to a different high amplitude Al-O stretch, and one high O displacement. The eigenvectors of the 774 cm $^{-1}$ (41) peak are similar to that of 904 cm⁻¹(48), showing two high amplitude Al-O stretches, but with two additional high amplitude O displacements around one capping moeity. The 748 $\text{cm}^{-1}(40)$ peak is similar to 774 $\text{cm}^{-1}(41)$, with high amplitudes for both oxygen atoms mentioned (although the stretch is asymmetric), and similar small displacement amplitudes throught the remaining geometry. Finally the calculated peak at 634 cm⁻¹ (38), resembles the most intense peak, 995 cm⁻¹ (51), with large overall displacement amplitudes, specifically from some of the Oxygens about both capping Al₂O₃ moeities.

Structure and Natural Bond Analysis

The analysis of vibrational data presented in the previous section, and very good agreement with IR–MPD spectrum (Figure 13.16) gives strong confidence that the proposed structural models in the present study are reliable. To characterize the nature of bonding within the cluster, Natural Bond Order (NBO) Analysis was performed for the $[(Al_2O_3)_4]^+$ cation and corresponding neutral species. Let us recall that clusters were optimized in the gas phase at the CAM–B3LYP/BP86 level of theory, and their wave functions were confirmed to be stable.

The addition of a single electron to $[(Al_2O_3)_4]^+$ produced a triplet state rather than a singlet, with the energies of both states very close to each other, as will be analyzed further along with frontier orbitals in section 3.3 of this study. To represent the results of the NBO analysis clearly, a graphical scheme was adopted as shown in Figure 13.18, that shows three bond strength ranges of 4.5–10.0, 10.5–20.0, and >20.5 kcal/mol represented as dashed, solid–thin, and solid–thick lines between corresponding atoms, respectively. The bond strengths represented in this way were determined by summation of significant NBO donating or withdrawing contributions from natural bonding units within the cluster, with a threshold for inclusion of 4.0 kcal/mol. Occupancies of Rydberg states were below the threshold for inclusion. It should be noted that the graphical representation in Figure 13.18 does not include the directionality of interactions between fragments (Jaroszyńska-Wolińska J., Garabato B.D., Alam J., Reza A., Kozłowski P., 2015).



Figure 13.18. Structural models of the [Al₈O₁₂]⁺ doublet (left) and the [Al₈O₁₂] triplet (right), along with corresponding interactions based on NBO analysis. Dotted lines: 4.5– 10.0 kcal/mol; thin–solid lines: 10.5–20.0 kcal/mol; thick–solid lines: > 20.5 kcal/mol (Jaroszyńska-Wolińska J., Garabato B.D., Alam J., Reza A., Kozłowski P., 2015)

Although most interactions within each cluster were determined to be bonding in nature, those between Al atoms, that is Al–Al bonds, were determined to be primarily anti–bonding. Within the neutral cluster having triplet multiplicity, three additional Al–Al anti–bonding interactions were found. On the other hand, most of the Al–O bonds were found to be moderately strong.

Based on NBO analysis, it is difficult to distinguish individual Al_2O_3 monomers within clusters regardless of being cationic or neutral. Although Al_2 moeities may be distinguished within each structural model under consideration, it is apparent from NBO analysis that the more appropriate description of the $[(Al_2O_3)_4]^+$ cluster, is more consistent with $[Al_8O_{12}]^+$, implying that the complex should be viewed as molecule. Likewise. for the neutral а $[(Al_2O_3)_4]$ species, the same observation holds based on NBO analysis, and it should also be viewed as $[Al_8O_{12}]$. In sum, individual Al_2O_3 monomers cannot be identified clearly within the obtained structures, and a molecular rather than a cluser interpretation describing overall bonding should be adopted.

One of the most sigficant differences in geometry between the $[Al_8O_{12}]^+$ doublet, and $[Al_8O_{12}]$ triplet is the distortion of an Al away from the cluster upon addition of an electron, as shown in Figure 13.18. Although this Al–O₃ moeity remains bound to the cluster with relatively high bond strengths, this distortion produces one associated O– Al bond that is significantly weaker. The Al–Al bond to which this is oxygen is weakly bound, is also notably more weakly bound to outer oxygens in the O–Al–Al–O moeity in the triplet neutral geometry. Furthermore, within the geometry having neutral charge, significant Al–Al antibonding may be seen as occuring within the core of the cluster, while this is not observed for the cation.

The other Al–O₃ moeity that caps the core of the molecule, is similar in both cation and neutral geometries, with one slightly stronger Al–O bond attributed to the triplet. The outer oxygens that are generally weakly associated with Al–Al bonds also essentially remain the same between both complexes, with some differences. Notably the triplet species contains the most weakly bound outer oxygen atom, with two ~5 kcal/mol bonds to the most strongly antibonding Al–Al pair. This oxygen in the triplet geometry is then associated with the strongest bonding and antibonding Al–O–Al moeity of both geometries.

Electrostatic Properties

The electrostatic potential (ESP) surfaces of both molecules are shown in Figure 4. The distorted Al atom observed in the optimized neutral geometry, remains attractive for both species, around 0.0466 eV, although generally more so for the cation, with a small localized area on the ESP surface of about 0.2455 eV. The Al atom of the neutral molecule that is weakly bound to the distorted Al–O₃ moeity, remains attractive for both clusters as well, with a value of around -1.15 eV.

However, it may be noticed when comparing both structures that within the Al–Al antibonding moeity that is strongest in the triplet, while both species show one Al atom with attractive ESP character as mentioned, the remaining Al of the doublet cation has significantly more repulsive localized ESP character, around 0.445 eV, when compared to the same relatively neutral region of the neutral molecule. This may be interpreted as the area of positive charge in the cation, that upon addition of an electron is stablized within the triplet by distortion of the Al–O₃ moeity, and antibonding interactions within the inner part of the complex (Lide DR, ed. CRC, 1995).



Figure 13.19. Electrostatic potential surfaces of $[Al_8O_{12}]^+$ doublet (right), and $[Al_8O_{12}]$ triplet (left) (Jaroszyńska-Wolińska J., Garabato B.D., Alam J., Reza A., Kozłowski P., 2015)

14. Innovative Plasma Methods in Surface Engineering

In general there are two plasma types used in industrial processing, namely thermal equilibrium and non–isothermal equilibrium plasmas. Thermal equilibrium plasmas are where the principal microscopic species, ions, electrons and neutrals are in approximate thermal equilibrium while in non–thermal equilibrium plasmas the electrons are very hot (>10,000K) while the ions and neutrals are not far from room temperature.

Thermal equilibrium plasmas are typically hot with temperatures ~10,000 K and are used in industry as plasma torches, jets and arcs for welding, metallurgy, spray coating, etc. Non–isothermal plasmas are generally cool but very chemically reactive due to the fast electrons generating a wealth of chemical reactions through energetic collisions. Non–thermal plasmas are employed in manufacturing processes including surface cleaning (removal of unwanted contaminants), etching (removal of bulk substrate material), activation (changing surface energies) and deposition of functional thin film coatings onto surfaces. They are used in a multiplicity of industry segments from microelectronics to medical.

In particular, non-isothermal plasmas can be used in surface engineering to deposit, at low temperatures, functional coatings which conform and adhere well to a substrate surface. The process leaves the bulk of the substrate unchanged. Such coatings allow the surface to have a different set of properties from those of the bulk material of the substrate and, thus, allow the bulk material to have one set of characteristics, e.g. rigidity, while surface may have another independent set of characteristics, e.g. low friction.

The objective of the work described in this section was to develop a nonisothermal plasma technology able to deposit functional coatings comprising large molecules in a single–step, dry process without the need for long and expensive wet chemistry steps. This would provide industry with a relatively powerful, low cost and fast manufacturing process for the functionalisation of surfaces with new, high molecular weight, even bio–active, species.

Specifically, we describe work done in the development of an atmospheric pressure, non-thermal equilibrium corona plasma jet for depositing polymeric, cross-linked coatings with a high degree of retention of functional chemistry, i.e. without excessive damage to the precursor molecule despite the molecules being cross-linked for coating durability.

is well established Plasma polymerization а route to surface functionalisation (Mattox D.M., Mattox V.H., 2007) and has found applications in diverse areas such as biotechnology (Shyong Siow, Britcher, Kumar, & Griesser, 2006), adhesion (Tsai, Boerio, van Ooij, Kim, & Rau, 1995), electronics (Kumar & Yoshida, 2003) and textiles (Shishoo, 2007). Plasma polymerization was initially developed under vacuum conditions and used standard low pressure plasma technology to polymerise gas vapours and produce polymeric coatings in a technique referred to as plasma enhanced chemical vapour deposition (PECVD). In these early systems the vapour phase precursors were bombarded with aggressive plasma species which produced fragmentation and re-arrangement of the precursor monomers. As a result, a wide variety of random fragments were created which could deposit on to a substrate to produce a thin film layer which contained many of the atoms present in the starting monomer. Various models have been created to explain the reaction mechanisms in such systems (Yasuda, 1981), (Wrobel A., Walkiewicz-Pietzykowska, Klemberg-Sapieha, Nakanishi, Aoki, & Hatanaka, 2003). Although PECVD became well established, the coating functionality remained limited to simple materials such as SiO_x, SiN or TiO₂ and complex chemistry could not be deposited using such systems.

From as early as 1983, (Suhr, 1983) pointed out that the main efforts in organic plasma chemistry have always been directed towards highly selective reactions. Forch et al described "soft plasma assisted modification" as where the molecules to be polymerized do not dissociate completely, but are activated predominantly at particular reaction sites so that the process is very different from traditional plasma polymerization based on a high degree of, even total, monomer fragmentation, and where the product shows little resemblance to the original precursor molecule and deposited (Forch R., Zhang Z., Knoll W., 2005) films show little or no repeating structure and no definable molecular weight distribution.

This description follows Yoshimura and Hozumi (Yoshimura & Hozumi, 1996) who distinguished "polymerization sites" in the monomer molecule from "functional sites" containing the key molecular properties to be replicated in the polymer. They characterised "soft plasma conditions" as where the former sites carry out polymerization with the least damage to the latter. Ideally, the latter should be independent from the former.

Thus, the ideal "soft plasma polymerization" (SPP) is the ability to plasma deposit a solid, cross–linked film with a very high degree of structural retention of the starting precursor so that the deposited coating retains the molecular complexity, functionality and value of the monomer.

The benefits of SPP processes are prospectively highly significant and well canvassed in the literature, opening the door to single–step industrial coating of substrates with, for example, complex and valuable, but sensitive, bio–active macromolecules such as enzymes and nucleic acids for applications such as biosensors, lab–on–a–chip and biomedical devices and many other processes.

A range of plasma types and process control parameters have been identified delivering SPP in varying degrees. Thus, control of substrate temperature (Lopez & Ratner, 1990), reactant pressure and flow rate, absorbed continuous wave power (Krishnamurthy, Kamel, & Mei, 1989) and location of substrates at varying distance from the plasma region (Yasuda, 1981) have all been used to bring greater levels of control to the polymerization process.

Additionally, in the mid 1990s, a significant step forward occurred through the development of pulsed vacuum PECVD systems. These allowed the power coupled to the plasma to be pulsed in a manner that still created the active species in the plasma, but did not contain enough energy to fragment all of the bonds within a monomer. The resulting active species interacted with gas phase monomers and produced a soft polymerization reaction which deposited coatings with complex functional chemistry (Ryan, Hynes, & Badyal, 1996), (Schiller S., Hu J., Jenkins A.T.A., Timmons R.B., Sanchez-Estrada F.S., Knoll W., Forch R., 2002) Various mechanisms have been reported to explain the polymerization mechanism within such systems which can be driven by free radical 1994), (Wrobel A. М., Walkiewicz-Pietzykowska, (Grill, Hatanaka, & Nakanishi, 2001) or ionic polymerization (Guerin, Wickramayaka, Hinshelwood, Monolache, Denes, & Shamamian, 2007), (Beck A.J., Candan S., Short R.D., Goodyear A., Braithwaite N.S.J., 2001). Despite the excellent film control offered by this process, these systems were still limited to vacuum processing and this has hindered commercial exploitation of the technology.

In recent years, Badyal et al have developed a controlled polymerization process at atmospheric pressure. By combining a low energy helium atmospheric pressure glow discharge plasma with a liquid aerosol precursor delivery system, it was possible to produce a series of thin films with soft polymerization and a high degree of retention of monomer functionality (Ward, L.J.; Schofield, W.C.E.; Badyal, J.P.S.; Goodwin, A.J.; Merlin, P.J., 2003), (Ward, L.J.; Schofield, W.C.E.; Badyal, J.P.S.; Goodwin, A.J.; Merlin, P.J., 2003)

This technology was further developed by Dow Corning Corporation under the brand name "APPLD" (Atmospheric Pressure Plasma Liquid Deposition) (Albaugh J.D.; O'Sullivan C.; O'Neill L., 2008), (O'Hare, O'Neill, & Goodwin, 2006). Helium glow discharges were chosen as the preferred plasma option as they provide a non-thermal, homogeneous plasma that can be readily produced under ambient pressure (Massines & Gouda, 1998) Introduction of the liquid as an aerosol was preferred as this was thought to protect the bulk of the liquid precursor from the aggressive plasma species by encapsulating it within a droplet of several microns in diameter, thereby minimising fragmentation of the precursor monomers. This technology has received considerable interest and a number of groups are now actively exploring this area (Twomey, Dowling, O'Neill, & O'Hare, 2007), (Heyse, i inni, 2007), (Tatoulian & Arefi-Khonsari, 2007), (Beck A.J., 2008) as it offers a possible route to deposit functional coatings under ambient conditions in a continuous on–line process.

It has long been thought that the soft polymerisation from such systems has been due to a combination of the protection offered by the aerosol droplet and the low energy cold plasma. (Ward, L.J.; Schofield, W.C.E.; Badyal, J.P.S.; Goodwin, A.J.; Merlin, P.J., 2003) (Ward, L.J.; Schofield, W.C.E.; Badyal, J.P.S.; Goodwin, A.J.; Merlin, P.J., 2003), (O'Hare, O'Neill, & Goodwin, 2006), (Albaugh J.D.; O'Sullivan C.; O'Neill L., 2008), (Heyse, i inni, 2007), (Tatoulian & Arefi-Khonsari, 2007).

In this work, an attempt was made to decouple these two factors by introducing the precursor as a vapour rather than aerosol into a non-thermal plasma. The use of aerosol delivery systems produces a number of complexities related to the stability of the spray, control of droplet size, generation of an even precursor distribution over wide areas, the requirement to accurately dispense low volumes of liquid at a constant rate and rapid build-up of unwanted deposits on reactor surfaces. The introduction of vapours rather than liquids allows for standard PECVD equipment (bubblers, mass flow controllers) to be used to generate an easily controlled, even flux of precursor onto a substrate. In this work, a standard vapour generating bubbler system was combined with helium plasma to produce coatings. 1H, 1H, 2H, 2H-Heptadecafluorodecyl acrylate (HDFDA) was chosen as a precursor monomer as it contains a polymerisable vinyl group and a long perfluoro chain which is easily characterized (see below Figure). This allows data to be readily compared to prior data published for vacuum polymerisation (Coulson S.R., Woodward I.S., Badyal J.P.S., Brewer S.A., Willis C., 2000) and for aerosol assisted (O'Neill & O'Sullivan, 2009) plasma deposition of HDFDA.

Furthermore, fluorocarbon films have attracted significant attention as they offer a convenient route to low surface energy coatings which can modify surface properties such as hydrophobicity, oil repellency (Shishoo, 2007), cell attachment (Barz J., Haupt M., Pusch K., Weimer M., Oehr C., 2006) and chemical inertness (Gengenbach & Griesser, 1998).



Chemical structure of HDFDA

Experimental Part

A plasma jet was constructed containing a dielectric head housing two tungsten needle pointed electrodes to which are applied in parallel an alternating current (AC) voltage as shown schematically in the below Figure:



Figure 14.1. Schematic of 2-pin Electrode Head of a Pin Corona Discharge Coating System

A space around each electrode allows a mixture of process gas and precursor vapour to enter the device. Very Low Frequency electrical power was delivered to both electrodes from a modified PTI 100W power supply at a frequency of c. 19 kHz and a peak-to-peak voltage of c. 23 kV. The resultant helium-vapour mixture exited the system through a 75 mm long x 15 mm diameter fluoropolymer tube in which the corona plasma was struck. Essentially, the configuration was a conventional point-to-plane type corona configuration in which a high voltage was applied to generate plasma from the tip of vertically positioned sharp tungsten needles. In the event, the system was run 'open circuit', i.e. no physical counter-electrode in the form of a conductive plane needed to be placed to oppose the needles as the high electric fields at the pin tips saw the surrounding ambient as the 'ground plane' and discharged freely from the needle tips into the tube in the well known corona discharge. Coatings were deposited onto substrates placed adjacent to the plasma outlet. Unless otherwise stated, all coatings were deposited onto 100 mm double polished p-type silicon wafer substrates. The following photograph shows the Corona discharge:



Generation of pin corona plasma

Fourier Transform Infra–Red (FTIR) data was collected on a Perkin Elmer Spectrum One FTIR. Coatings were deposited directly onto NaCl disks and spectra were collected using 32 scans at 1 cm^{-1} resolution.

Contact angle measurements were obtained using the sessile drop technique using an OCA 20 video capture apparatus from Dataphysics Instruments. Drop volumes of 1.5 μ l were used and images were collected 30 seconds after placing the droplet on the surface. Surface energy was then determined using the method of Owens and Wendt (Owens D.K., 1969).

X-ray photoelectron spectroscopy (XPS) survey spectra were recorded on a VSW spectrometer consisting of a hemispherical analyser and a 3 channeltron detector. All spectra were recorded using an Al K α X-ray source at 150 W, a pass energy of 100 eV, step size of 0.7 eV, dwell time of 0.1 s with each spectrum representing an average of 30 scans. High resolution C 1s spectra were collected on a Kratos Axis Ultra system using monochromated Al K α x-rays with a pass energy of 40 eV.

Film thickness and thickness profile/mapping of the coatings was determined by a Woollam M2000 variable angle ellipsometer.

Electrical characterisation of the device consisted of a Bergoz Instrumentation, France CT–E5.0–B toroidal current transformer which was used to measure the plasma current (I_d) and a North Star PVM–5 high voltage probe which was used to determine the applied voltage (V_{app}).

The Bergoz current transformer toroid was positioned around the fluoropolymer tube and 10 mm along the tube from the needle tips to capture the plasma discharge while the high voltage probe was applied at the output of the power supply. The outputs of both probes were captured on a Tektronix TDS 2024 four channel digital storage oscilloscope with a 200 MHz bandwidth.

Results

HDFDA was introduced into the plasma jet as a vapour from a standard bubbler set up. By controlling the flow of carrier gas and the bubbler temperature, the flow rate of the monomer could be altered. Initial experiments were carried out with a bubbler temperature of 80°C and with various flow rates of helium of 1-15 standard litres per minute (slm). Coatings deposited under such conditions were found to produce a wet coating with minimal curing which can be attributed to insufficient activation and cross-linking. In order to enhance the curing of the precursor, the precursor flow was reduced to produce a higher plasma power per unit monomer, as described in vacuum polymerization systems by Yasuda (Yasuda, 1981). The bubbler temperature was decreased to 56°C and the helium flow was adjusted to 14 slm. This produced a series of cured dry coatings which were deposited for times of 10, 30 and 180 seconds. Gravimetric measurements indicate an average flow rate of 0.07674 g/min or 126 μ L/min of monomer into the device at 56°C. Standard tape adhesion tests were conducted according to ASTM D3359-02 and no evidence of coating delamination was detected on any of the dry, cured plasma samples. This indicates that the coatings exhibit reasonable levels of adhesion.

FTIR analysis was carried out to probe the chemistry of the deposited films and a typical spectrum is shown in the below Figure. The presence of the dominant peaks centred at 1150 and 1200 cm⁻¹ in the spectra of the coatings correspond to the CF₂ and CF₃ groups of the perfluoro chain. As both fluorocarbon peaks are still well resolved, it can be deduced that the fluorocarbon chain has not undergone significant levels of fragmentation and degradation. Further examination of the main peak at 1205 cm⁻¹ clearly shows a systematic increase in peak intensity with time Table 13.4, indicating that thicker coatings are deposited at longer times.

Close inspection of the spectra clearly shows loss of the monomer peaks at 1625, 1635, 1412, 1074 and 984 cm⁻¹ corresponding to loss of the C=C bonds of the acrylate group. However, the peak at 1738 cm⁻¹ due to the carbonyl group of the acrylate is still retained in the coating. This indicates that a controlled polymerization of the precursor has occurred through the vinyl group of the monomer with retention of the functional chemistry of the larger fluorocarbon chain, as seen in pulsed vacuum (Coulson S.R., Woodward I.S., Badyal J.P.S., Brewer S.A., Willis C., 2000) and aerosol assisted atmospheric pressure plasma (O'Neill & O'Sullivan, 2009), (Herbert P.A.F., O'Neill L., Jaroszyńska-Wolińska J., 2009) processes.



FTIR spectrum of HDFDA liquid precursor (bottom) and HDFDA coating deposited for 180 seconds on NaCl disk (top) (Herbert PAF, O'Neill L, Jaroszyńska-Wolińska J, Stallard J, Ramamoorthy CP, Dowling DP, 2011)

Examination of the coating in the region between $2800-3200 \text{ cm}^{-1}$ shows an absence of peaks above 3000 cm^{-1} which could be associated with the symmetrical and asymmetrical bending and stretching of the C–H bonds of the vinyl group. Two distinct features are detected at 2851 and 2921 cm⁻¹ which are characteristic of the asymmetric and symmetric stretches of saturated CH₂ groups.

There is evidence of a weak peak at 2874 cm^{-1} and a broad peak from $2940-2990 \text{ cm}^{-1}$ which may be due to the symmetric and asymmetric stretch of a terminal methyl group. However, the low signal to noise ratio prevents unambiguous assignment of these features. This loss of vinyl derived peaks, coupled to the presence of saturated alkane, fluorocarbon and carbonyl signals, further indicates that the plasma reaction is driven through a controlled polymerisation of the vinyl group with conversion to the alkane.

An additional peak can be detected at 1125 cm^{-1} in the spectra of both these samples and in the spectra of previously published plasma polymerized HDFDA coatings. As of yet, this peak has not been unambiguously assigned, though the authors postulate that this could be a secondary C–O species produced due to oxidation of polymer by plasma.

Contact angle analysis was carried out to probe the surface energy of the coated substrates. As shown in the below Table, the hexadecane contact angle values were largely independent of deposition time. All samples were found to produce significantly higher hexadecane contact angle values than the uncoated wafer (15°). All coated samples were found to be hydrophobic, with water contact angle values in excess of 90°. The water contact values were found to increase with increased deposition time. This may be explained in terms of increasing surface coverage of the substrate with increased processing time.

| Depositio n | XPS Elemental Composition (%) | | | | Contact Angle Analysis | | | FTIR peak | Ellipsome try |
|----------------|----------------------------------|----|----|----|------------------------|-------------------|--|-----------|-------------------|
| Time (sec) | Si | С | 0 | F | Water (°) | Hexadecane (°) | Surface Energy (mJ/m ²) | (a.u.) | thickness (nm) |
| 180 | 0 | 41 | 8 | 51 | 114 | 76 | 11 | 17.52 | - |
| 30 | 2 | 40 | 8 | 50 | 112 | 77 | 11 | 6.28 | 50 |
| 10 | 39 | 20 | 17 | 24 | 97 | 76 | 16 | 1.53 | 10 |

Table 14.1. XPS, contact angle and thickness data for HDFDA on Silicon

XPS analysis was undertaken to determine the elemental content of the coatings. The XPS analysis of the 10 second sample revealed significant levels of silicon. This suggests that the coating is either patchy or else the coating thickness may be below 10 nm which would result in concurrent analysis of the substrate and coating occurring during the analysis. High levels of oxygen were also detected. These may be derived from oxidation of the coating or from the native silicon oxide present on the wafer surface.

The presence of a patchy coating coupled to significant oxidation of the deposit may help to explain the relatively low water contact angle value produced by the 10 second coating.

For the coatings deposited at longer times of 30 and 180 seconds the elemental composition of the coating is very similar to that of the un-reacted monomer (41% C, 53% F and 6% O). The spectra from these samples are almost completely devoid of Si, indicating complete coverage of the substrate with a thick polymer layer. A slight increase in oxygen content was detected in the coatings which can be attributed to some minor oxidation of the deposited material by the plasma. However, the results for these two samples are largely similar to results previously seen in soft plasma polymerization reactions and agree with the FTIR data in suggesting that the functionality of the monomer has been largely retained in the coating.

To further probe this point, curve fitting of the high resolution C 1s XPS spectra was undertaken for the 30 second sample and the results are shown in the below Figure. The spectra clearly reveals two peaks at 292.4 and 294.6 eV which can be attributed to the CF_2 and CF_3 species respectively. A peak at 290 eV can be assigned to the ester functionality, though it is likely that some mono substituted fluoro species also contribute to this feature. Finally, there is a broad feature from 284 to 289 eV which can be assigned to a least two different hydrocarbon features, possibly modified by the presence of electronegative F and O species in close proximity. The intensity of the peak at 290 eV suggests that some oxidation of the fluorocarbon has occurred as a result of the process, though the degree of oxidation cannot be determined accurately due to the presence of overlapping features at this energy. The fluorocarbon peaks were well resolved and the ratio of CF_2 to CF_3 was determined to be 5.8:1. This is lower than the 7:1 expected from the starting monomer and this indicates some degradation of the monomer has occurred, though the peak ratios would suggest that greater than 80% retention of the perfluoro chain has been achieved and this compares favourably with previously reported soft plasma polymerisation processes (Coulson S.R., Woodward I.S., Badyal J.P.S., Brewer S.A., Willis C., 2000).



Figure 14.2. Curve fitting of the C 1s XPS spectrum of HDFDA deposited on Si wafer for 30 seconds (Herbert PAF, O'Neill L, Jaroszyńska-Wolińska J, Stallard J, Ramamoorthy CP, Dowling DP, 2011)

Ellipsometry data was collected from the 10 second and 30 second samples. These coatings were found to have thickness values of 10 and 50 nm respectively, indicating that the deposition rate was in the region of 60–100 nm/min. This is significantly higher than the deposition rates quoted for vacuum plasma coatings produced from HDFDA (Coulson S.R., Woodward I.S., Badyal J.P.S., Brewer S.A., Willis C., 2000) and is similar to the deposition rates seen in aerosol assisted atmospheric pressure plasma deposition of a range of precursors. (Ward, L.J.; Schofield, W.C.E.; Badyal, J.P.S.; Goodwin, A.J.; Merlin, P.J., 2003), (Heyse, i inni, 2007), (O'Neill & O'Sullivan, 2009). Thickness mapping of the coated wafers indicates that the coating occupies a circular region of approximately 3-4 cm in diameter on the wafer surface. Attempts to extract thickness data from the 180 second sample were unsuccessful due to the rough nature of the deposited coating. Examination of the surface using optical and electron microscopy revealed the presence of numerous discrete particles within the coating and the resultant roughness distorted the ellipsometry measurements.

Particle formation due to gas phase nucleation is a well documented issue within such plasma devices. However, extrapolating coating thickness from the peak heights in the FTIR spectrum would suggest that the 180 second coating is approximately 3 times thicker than the 30 second coating.

As the vapour deposited coatings have been shown to have the same functional chemistry retention and deposition rate as seen in aerosol assisted atmospheric pressure plasma coatings, it can be deduced that the key to controlling the reaction mechanism cannot be predominantly dependent upon the presence of the monomer as an aerosol droplet. It seemed likely that the key control parameter is the low power coupled per unit of monomer, resulting in coatings being deposited in the power deficient regime described by Yasuda in vacuum polymerisation systems (Yasuda, 1981). It is therefore logical to conclude that the plasma properties must be a highly significant factor which controls the mechanism of polymerization. Therefore, diagnostics were applied to the plasma to determine the properties of the device.

Temperature within the plasma was monitored using an FLIR SC600 infrared camera. Throughout the experimental range investigated the temperature within the device was maintained below 100°C, as shown in the below Figure.



Figure 14.3. Colour mapped temperature scan of corona discharge inside tube

The temperature within the plasma was also monitored by the simple expedient of placing a graduated glass alcohol thermometer so that the thermometer bulb was 15 mm below the electrodes inside the fluoropolymer tube and fully immersed within the helium gas flow and any corona discharge. A gas baseline temperature of 8°C was recorded after 5 minutes of helium gas flow at 14 L/minute in the absence of plasma. A plasma was then struck and after 10 minutes of discharge the temperature recorded by the thermometer was found to stabilize at 18°C, clearly indicating the non-thermal equilibrium and low power nature of the discharge.

Electrical characterization of the plasma using North Star high voltage and Bergoz Instrumentation current probes connected to the digital oscilloscope showed the following data. Under the conditions selected, the plasma was found to operate at a frequency of c. 19 kHz and voltage of c. 23 kV (peak–peak). The following Figure shows the V_{app} vs. time and I_d vs. time characteristics of the discharge.



Figure 14.4. V_{app} vs. t (light trace) and I_d vs. t (dark trace) Corona Discharge characteristics (Jaroszyńska-Wolińska & Herbert, 2012)

It is seen that the peak–to–peak voltage was about 23 kV and the peak current about 8 mA. The curves show that most of the current is displacement with current about 90 degrees out of phase with voltage. The actual discharge power was calculated as the average over 10 periods of the current–voltage product and was found to be 6.8 W with a $\pm/-6\%$ variation over 5 runs.

Discussion

A low power, non-isothermal equilibrium, atmospheric pressure corona plasma was generated from a single electrode with pin geometry and used to deposit plasma polymerized coatings from HDFDA monomer precursor in the purely gas state.

By introducing the fluorocarbon monomer vapour into such a helium corona, it was possible to deposit a cured polymeric coating which retained the chemical structure of the precursor monomer so that the process can be characterised as soft plasma polymerization (SPP). The coating was hydrophobic and was put down at reasonable deposition rates. Analysis of the coatings clearly shows that the precursor has undergone a controlled polymerization through the vinyl component of the acrylate group with minimal fragmentation of the functional chemistry of the monomer. The resultant coatings produced XPS and FTIR spectra which could previously only be produced by pulsed vacuum plasma or by aerosol assisted plasma processing.

Although there have been reports of plasma polymerisation of siloxanes, fluorocarbons (Janca, Klima, Slavicek, & Zajickova, 1999) and hydrocarbons (Kapicka, i inni, 2000) from corona discharge sources, there have been no reports that soft polymerization could be achieved using gas precursors. It is proposed that the ability of the corona discharge to achieve SPP in this work is due to the low specific energy of the discharge. The empirical work of Warburg (Warburg, 1909) and his school around 1909 and Becker in 1920 (Becker H., 1920) connected key plasma discharge parameters with the efficiency of chemical reactions in the discharge. Becker showed that the governing reaction parameter, R, is proportional to the power input per flow of gas, i.e. to the specific energy in J/cm³. Further studies by Rutscher and Wagner (Rutscher & Wagner, 1993) in 1993 and by Hegemann et al in 2007 (Hegemann, Hossain, Korner, & Balazs, 2007) showed that in non–isothermal plasma chemistry, including, of course, plasma polymerization, the specific energy [J/cm³] is indeed the decisive parameter.

In this work, two very simple models were used to estimate specific energies. Model 1 was based on the following assumptions:

- All discharge energy is coupled uniformly into the gas volume enclosed by the tube;
- The discharge energy is partitioned evenly over all elementary entities (atoms/molecules);
- The gas mix of helium plus HDFDA precursor is modeled as an Ideal Gas at SLC (Standard Laboratory Conditions).

Specific energy was found to be 0.029 J/cm³ or 0.72 kJ/mol or 0.02 eV/entity. These appear to be tiny values from the perspective of molecular bond breaking, viz. the dissociation energies of C–C 348 kJ/mol, C–O 360 kJ/mol, C–H 413 kJ/mol, C–F 488 kJ/mol, O=O 498 kJ/mol and the pi–bond of the C=C bond approximately 264 kJ/mol.

However, if we calculate specific energy on another set of assumptions (Model 2);

- The helium is only an inert background gas and the plasma directly or indirectly, e.g. via helium metastables, eventually imparts all energy to the HDFDA;
- Such energy is partitioned evenly over all HDFDA molecules;
- The HDFDA gas is, again, modeled as an Ideal Gas at SLC;
- we obtain a very different set of values, namely specific energy of 54 J/cm³ or 1327 kJ/mol or 35 eV/entity.

Clearly, both sets of assumptions are wrong and represent two extreme models of plasma energy coupling into the HDFDA monomer molecules. However, it is clear that Model 2, where all of the total discharge energy finds its way into the HDFDA molecules, is far closer to reality than the energy equivalence Model 1 in which every atom and molecule receives about the same energy.

Substantial discharge energy is likely to be both absorbed by the surfaces contacting the plasma (e.g. through quenching of helium metastables) and lost by radiation before reaching a HDFDA molecule. Furthermore, some proportion of the helium atoms is likely to retain absorbed energy throughout their residence time in the plasma and until and including relaxation back to the ground state without transferring it to HDFDA molecules. Thus, it is clear that some unknown part of the specific energy coupled into the process will never reach the HDFDA and will not be available to drive its polymerization. Such deductions from the specific energy value of Model 2 (1327 kJ/mol) could result in a value not inconsistent with the energy needed to dissociate the C=C pi–bond (~264 kJ/mol). What the film analysis data shows is that although the C=C pi–bond is dissociated, the next highest bond dissociation energy, the C–C bond at 348 kJ/mol, is not disrupted by the process, indicating that the upper limit of specific energy available for HDFDA fragmentation from this process must be <348 kJ/mol.

Thus, the particular plasma generated within this process appears to deliver sufficient energy to the plasma region to break the weakest monomer bond, thereby enabling the molecule to react and polymerize, but without providing the energy required to break higher energy bonds, in particular those of functional sites. In short, the monomer is not fragmented and the process delivers soft polymerization.

Conclusions

This work achieved what appeared to be the first reported soft plasma polymerization from gas state precursor using a cool, atmospheric pressure, highly non–isothermal equilibrium corona discharge.

Electrical characterisation of the plasma suggests that the retention of chemical functionality is likely to be very strongly related to the low level of power, specifically the low energy density [J/cm³], coupled into the plasma. It appears that with this type of corona discharge, essentially damage–free polymerization of monomer molecules to deposit a functional coating can be readily achieved by use of precursor in the conventional gas state, i.e. operating in standard PECVD mode, so that the use of precursor in the liquid state as nebulised droplets is not required to achieve SPP as has been suggested (Ward, L.J.; Schofield, W.C.E.; Badyal, J.P.S.; Goodwin, A.J.; Merlin, P.J., 2003), (Ward, L.J.; Schofield, W.C.E.; Badyal, J.P.S.; Goodwin, A.J.; Merlin, P.J., 2003), (O'Hare, O'Neill, & Goodwin, 2006), (Heyse, i inni, 2007), (Tatoulian & Arefi-Khonsari, 2007), (Beck A.J., 2008).

This would appear to reduce the need for costly and complex liquid delivery apparatus in many applications using low power corona plasma to achieve functional coatings.

It is proposed that this corona plasma type is inherently predisposed to deliver low specific energy into the reaction zone and, hence, to SPP, even using gas precursors. Although the discharge is not a large area coating source, it is perfectly applicable to substrates $<1 \text{ m}^2$ seeking a high level of sophisticated functionality via surface coating.

15. References

- 1. Akdogan E.; et al. (2006). A new method for immunosensor preparation: Atmospheric plasma torch. *Surface & Coatings Technology*, 201, 2540–2546.
- 2. Albaugh J.D.; O'Sullivan C.; O'Neill L. (2008). Surf. Coat. Technol. 203, 844.
- 3. Almlöf J.A., Taylor P.R. (1987). J. Chem. Phys. 86, 4070.
- 4. Andersson K., Borowski P., Fowler P.W., Malmqvist P.A., Roos B.O., Sadlej A.J. (1992). Chem. Phys. Lett. *190*, 367.
- 5. Application, P. C. Patent No. PCT/EP2010/001703.
- 6. Archibong E.F., St-Amant A. (1999). On the structure of Al2O3 and photoelectron spectra of Al2O3– and Al2O3. *J. Phys. Chem.*, *103*, 1109–1114.
- 7. Atkins P.W. (2001). Physical Chemistry. Warszawa.
- 8. Bala B. (2000). Korozja materiałów–Teoria i praktyka. Częstochowa.
- 9. Ball P. (2003). The Ingredients. In *A Guided Tour of the Elements*. Oxford University.
- 10. Banaszkiewicz J., Kamiński M. (1997). *Podstawy korozji materiałów*. Warszawa.
- 11. Barbe A., Secroun C., Jouve P. (1974). J. Mol. Spectr. 49, 171.
- 12. Barz J., Haupt M., Pusch K., Weimer M., Oehr C. (2006). Plasma Process. Polym. *3*, 540.
- 13. Baulch D., et al. (1982). Evaluated kinetic and photochemical data for atmospheric chemistry. *Supplement Int. J. Phys. Chem.*, 11, 327–496.
- 14. Beck A.J., Candan S., Short R.D., Goodyear A., Braithwaite N.S.J. (2001). J. Phys. Chem. B. *105*, 5730.
- 15. Beck A.J., S. R. (2008). Surf. Coat. Technol. 203 (5–7), 822–825.
- 16. Becke A.D. (1993). J. Chem. Phys. 98, 5648.
- 17. Becker H. (1920). Wissenschaftliche Veroeffentlichungen SIEMENS-Konzern. 1, 76.
- Bhandari S.S., Kabra M.S., Gupta R., Sharma A. (n.d.). ANTIOXIDANT AN OVERVIEW. Retrieved from http://www.pharmatutor.org/articles/antioxidant–overview
- 19. Borowski P., Andersson K., Malmqvist P.A., Roos B.O. (1992). J. Chem. Phys. 97, 5568.
- 20. Borowski P., Füscher M., Malmqvist P.A., Roos B.O. (1995). Chem. Phys. Lett. 237, 195.
- 21. Cartmell E. (1989). Chemistry for Engineers, An Introductory Course. In *Butterworth's Scientific Publications*.
- 22. Civil Engineering Home. (n.d.). Retrieved from www:engineering.civil.com

| 23. | Coulson S.R., | Woodward I.S., | Badyal J.P.S., | Brewer S.A., | Willis C. | (2000). |
|-----|---------------|----------------|----------------|--------------|-----------|---------|
| | Chem. Mater. | 12, 2031. | | | | |

- Czarnecki L. (2005). Ćwiczenia Laboratoryjne z chemii budowlanej. Warszawa.
- 25. *DoITPoMS*. (n.d.). Retrieved from http://www.doitpoms.ac.uk/tlplib/polymerbasics/printall.php
- 26. Egerton R. F. (2005). Physical principles of electron microscopy: an introduction to TEM, SEM, and AEM. *Springer*, 202.
- 27. Environmental Science Published for Everybody Round the Earth. (n.d.). Retrieved from www: http://klimat.czn.uj.edu.pl/enid/3 Ozon i tlenki azotu/– NOx 3pi.html
- Fanelli F, Fracassi F, d'Agostino R. (2007). Plasma Process Polymer. 4, 430–434.
- 29. Fanelli, F. Et al. (2009). Plasma Process. Polym. (Vol. 6).
- 30. Figovski O., Beilin D. (2014). Advanced Polimer Concretes and Compounds.
- 31. Flaga K., Mierzwa J. (1992). Przegląd budowlany.
- 32. Florjańczyk Z., Penczek S. (2002). Chemia Polimerów. Warszawa.
- 33. Forch R., Zhang Z., Knoll W. (2005). Plasma Process. Polym. 2, 351.
- 34. Forest J. (1967). Silicates Ind., 32, 373-427.
- 35. Frisch M.J., et al. (2004). Gaussian 03, Revision V.05, Inc, Wallingford, CT.
- 36. *Fundamentals of Chemistry*. (n.d.). Retrieved from http://www.chem.uiuc.edu/rogers/text5/Tx53/tx53.html
- 37. Gawlicki M. (2008). Ceramiks. 104.
- 38. Gengenbach, T., & Griesser, H. (1998). Surf. Interface Anal. 26, 498.
- 39. *Geology Cafe*. (n.d.). Retrieved from www: geologycafe.com/images/Silicates.jpg
- Gianotto, A., Rawlinson, J., Cossel, K., Olson, J., Appelhans, A., & Groenewold, G. (2004). Hydration of alumina cluster anions in the gas phase. *J. Am. Chem. Soc.*, 126, 8275–8283.
- 41. Grill, A. (1994). *Cold Plasmas in Material Fabrication*. New York: IEEE Press.
- 42. Gruner M. (1983). Korozja i ochrona betonu.
- Guerin, D., Hinshelwood, D., Monolache, S., Denes, F. S., & Shamamian, V. L. (2007). Analytical Chemistry. 79, 6264–6270.
- 44. Hariharan PC, P. J. (1973). Theor. Chim. Acta. 28, 213.
- 45. Hegemann, D., Hossain, M., Korner, E., & Balazs, D. (2007). J. Plasma Process. Polym. 4, 229.
- Herbert P.A.F., O'Neill L., Jaroszyńska–Wolińska J. (2009). Soft Plasma Polymerization of Gas State Precursors from an Atmospheric Pressure Corona Plasma Discharge. (October, Ed.) *Chemistry of Materials*, 21, 4401–4407.

- 47. Herbert PAF, J.–W. J. (2011). A Direct Comparison between Gas State and Atomised Liquid State Precursor in the deposition of functional Coatings by Pin Corona Plasma. *European Physical Journal–Applied Physics*, 55 (1), 13803–13815.
- 48. Herbert PAF, O. L.-W. (2010). Patent No. PCT/EP2010/001703.
- Herbert PAF, O'Neill L, Jaroszyńska–Wolińska J, Stallard J, Ramamoorthy CP, Dowling DP. (2011). A Comparison between Gas and Atomized Liquid Precursor States in the Deposition of Functional Coatings by Pin Corona Plasma, Plasma Processes and Polymers, Vol. *Plasma Processes and Polymers*, 8 (3), 230–238.
- 50. Heyse, P., Dams, R., Paulussen, S., Houthoofd, K., Janssen, K., Jacobs, P., et al. (2007). Plasma Process. Polym. 2, 145.
- 51. Huber HP, Herzberg G. (1979). Molecular Structure and Molecular Spectra. *IV Constants of Diatomic Molecules, Van Nostrand Reinhold.* Toronto.
- InTechOpen . (n.d.). Retrieved from http://www.intechopen.com/books/crystalline-silicon-properties-anduses/defect-related-luminescence-in-silicon-dioxide-network-a-review
- 53. Janca, J., Klima, M., Slavicek, P., & Zajickova, L. (1999). Surf Coat. Technol. 547, 116–119.
- 54. Jaroszyńska– Wolińska, J. (2010). Journal of Molecular Structure Theochem. 952,74–83.
- 55. Jaroszyńska–Wolińska J. (2009). Badanie reakcji tlenków azotu z ozonem generowanym w plazmie niskotemperaturowej. Warszawa: Instytut Chemii i Techniki Jądrowej.
- 56. Jaroszyńska–Wolińska J. (2006). Energetic of the oxidation of NOx by ozone using a simple molecular model in a computational chemistry scheme. *Journal of Advanced Oxidation Technologies*, 9 (2), 202–207.
- 57. Jaroszyńska–Wolińska J., Dziadko D. (2011). *Chemia w laboratorium budownictwa*. Lublin: Politechnika Lubelska.
- Jaroszyńska–Wolińska J., Garabato B.D., Alam J., Reza A., Kozłowski P. (2015). Structural and electronic properties of an [(Al2O3)4]+ cluster. *Journal* of Molecular Modeling, 21, 170.
- 59. Jaroszyńska–Wolińska, J., & Herbert, P. (2012). Przegląd Elektrochemiczny (Electrical Review). 15–17.
- Kapicka, V., Sicha, M., Klima, M., Brablec, A., Biederman, H., Slavinska, D., et al. (2000). Proceedings of Hakone VII International Symposium on High Pressure, Low Temperature Plasma Chemistry., 506, pp. 506–508. Greifswald, Germany.
- 61. Krinsley David H. (1998). Backscattered scanning electron microscopy and image analysis of sediments and sedimentary rocks. *Cambridge University Press*.
- 62. Krishnamurthy, V., Kamel, I., & Mei, Y. (1989). J. Polym. Sci.:Part A, Polym. Chem. 27, 1211.

- 63. Krishnan R.; Binkley J.S.; Seeger R.; Pople J.A. (1980). J. Chem. Phys. 72, 650.
- 64. Kumar, D., & Yoshida, Y. (2003). Surf. Coat. Technol. 600, 169–170.
- 65. Kurdowski W. (2014). Cement and Concrete Chemistry. *Springer Science, Busines Media*.
- 66. Kurdowski, W., & Pomadowski, H. (2001). Silicates, 66, 85.
- 67. Lawrence S. Brown, Thomas A. Holme. (2009). Chemistry for Engineering students II Edition. *Cengage Learning*.
- 68. Lea F.M. (1971). The Chemistry of Cement and Concrete.
- 69. Lee C., Yang W., Paar R.G. (1993). Phys. Rev. B. 37, 785.
- 70. Levin, I., & Brandon, D. (1998). Metastable Alumina Polymorphs: Crystal Structures and Transition Sequences. J. Am. Ceram. Soc. , 81, 1995–2012.
- 71. Lide DR, ed. CRC. (1995). Handbook of Chemistry and Physics. *CRC Press, Inc., Boca Raton*.
- 72. Lopez, G., & Ratner, B. (1990). ACS Polym. Mater. Sci. Eng. 62, 14.
- 73. Malcom, P. S. (1983). *Wprowadzenie do chemii polimerów*. (M. Włodarczyk, Trans.) Warszawa.
- 74. Massines, F., & Gouda, G. (1998). J. Phys. D: Appl. Phys. 31, 3411.
- 75. *Materials Science and Technology*. (n.d.). Retrieved from Department of Materials Science and Engineering: http://matse1.matse.illinois.edu/concrete/prin.html
- Mattox D.M., Mattox V.H. (2007). Society of Vacuum Coaters. 50 Years of Vacuum Coating Technology and the growth of the Society of Vacuum Coaters. Albuquerque, New Mexico.
- 77. McClelland BW, H. L. (1983). J. Am. Chem. Soc. 105, 3789.
- 78. Mitin, A. (2011). Accurate theoretical IR and Raman spectrum of Al2O2 and Al2O3 molecules, Struct. Chem. 22, 411–418.
- 79. Moffatt W.G., Pearsall G.W., Wulff J. (1968). The Structure and Properties of Materials. *1*, 78.
- 80. *NDT Resource Center*. (n.d.). Retrieved from https://www.ndeed.org/EducationResources/CommunityCollege/Materials/Structure/metallic_ structures.htm
- 81. Neville A.M. (2011). Propertis of Concrete 5 th edn,.
- O'Hare, L.-A., O'Neill, L., & Goodwin, A. (2006). J. Surf. Interface. Anal. 38 (11), 1519.
- 83. O'Neill L., et al. (2007). Plasma Polymerised Primers–Improved Adhesion through Polymer Coatings. *Society of Vacuum Coaters*.
- 84. O'Neill, L., & O'Sullivan, C. (2009). Chem Vap. Dep. 21, 1–3.
- 85. Owens D.K., W. R. (1969). J. Appl. Polym. Sci.
- 86. Parr, R., & Weitao, Y. (1989). *Density–Functional Theory of Atoms and Molecules*. New York: Oxford University Press.

- Patzer ABC, Chang Ch, Sedlmayr E, Sülze D. (2005). A density functional study of small AlxOy (x, y = 1–4) clusters and their thermodynamic properties. *Eur. Phys. J. D.*, *32*, 329–337.
- Pauling L., P. P. (1989). *Chemia ogólna*. Warszawa: Państwowe Wydaw. Nauk.
- 89. Pauling L., Pauling P. (1983). Chemia. Warszawa.
- 90. Piela, L. (2005). *Idee chemii kwantowej*. Warszawa: Wydawnictwo Naukowe PWN.
- 91. *Pinterest*. (n.d.). Retrieved from https://pl.pinterest.com/pin/422775483748311077/
- 92. PQS version 3.1. (2013). Parallel Quantum Solutions. Fayetteville, Arkansas 72703.: Green Acres Road.
- 93. Rahane, A., Deshpande, M., & Kumar, V. (2011). Structural and Electronic Properties of (Al2O3)n Clusters with n = 1–10 from First Principles Calculations. J. Phys. Chem. A., 115, 1811–1821.
- 94. Release 1.2. (2001). Dalton, a molecular electronic structure program.
- 95. Roos B.O. (1980). Int. J. Quantum Chem. 175, 14.
- 96. Roos B.O., Taylor P.R., Siegbahn P.E.M. (1980). Chem. Phys. 48, 157.
- Rutscher, A., & Wagner, H.–E. (1993). Plasma Sources Sci. Technol. 2, 279– 288.
- 98. Ryan, M., Hynes, A., & Badyal, J. (1996). J.P.S. Chem. Mater. 8, 37.
- 99. Scerri E. (2007). The Peridic Table. Oxford University.
- Schiller S., Hu J., Jenkins A.T.A., Timmons R.B., Sanchez–Estrada F.S., Knoll W., Forch R. (2002). J. Chem. Mater. 14, 235.
- 101. Shirai T, Watanabe H, Fuji M, Takahashi M. (2009). Structural Properties and Surface Characteristics on Aluminum Oxide Powders. Annual Report of the Ceramics Research Laboratory Nagoya Institute of Technology, 9, 23–31.
- 102. Shishoo, R. (2007). Plasma Technologies for Textiles. *Woodhead Publishing Ltd.*
- 103. Shyong Siow, K., Britcher, L., Kumar, S., & Griesser, H. (2006). Plasma Methods for the Generation of Chemically Reactive Surfaces for Biomolecule Immobilization and Cell Colonization–A Review. *Plasma Processes and Polymers*, 3, 392.
- 104. Siegbahn P.E.M, Almlöf J.A, Heiberg A., Roos B.O. (1981). J. Chem. Phys. 74, 2384.
- 105. Sierka, M., Döbler, J., Sauer, J., Santambrogio, G., Brümmer, M., Wöste, L., et al. (2007). Unexpected Structures of Aluminum Oxide Clusters in the Gas Phase. *Agnew. Chem. Int. Ed.*, 46, 3372–3375.
- 106. *Simple English Wikipedia*. (n.d.). Retrieved from Materials science: https://en.wikipedia.org/wiki/Materials_science

- 107. Simple English Wikipedia, Energy-dispersive X-ray spectroscopy. (n.d.). Retrieved from https://en.wikipedia.org/wiki/Energy-dispersive_Xray_spectroscopy
- 108. *Simple English Wikipedia, Water (molecule).* (n.d.). Retrieved from https://simple.wikipedia.org/wiki/Water_(molecule)
- 109. Slanger TG, C. P. (1988). J. Phys. Chem. 92, 267.
- 110. Stirling A, P. I. (1994). J. Chem. Phys. 100, 2910.
- 111. SubsTech. (n.d.). Retrieved from www:substech.com
- 112. Suhr, H. (1983). Plasma Chemistry and Plasma Processing. 3(1), 1.
- 113. Tanaka T, M. Y. (1970). Spectr., 33, 538.
- 114. Tang C.Y., Tai W.H., Lee W.B. (1995). Modeling of damage behaviors of high impact polystyrene. *Engineering Fracture Mechanics*.
- 115. Tatoulian, M., & Arefi-Khonsari, F. (2007). Plasma Process. Polym. 4, 360.
- 116. *The LibreTexts libraries*. (n.d.). Retrieved from http://chem.libretexts.org/Textbook_Maps/General_Chemistry_Textbook_Ma ps/Map%3A_Chem1_(Lower)/07%3A_Solids_and_Liquids/7.06%3A_Introd uction_to_Crystals
- 117. Tsai, Y., Boerio, F., van Ooij, W., Kim, D., & Rau, T. (1995). Surf. Interface Anal. 23, 261.
- Twomey, B., Dowling, D., O'Neill, L., & O'Hare, L.–A. (2007). Plasma Process. Polym. 4, 450.
- 119. Wahl AC, Das G. (1970). Adv. Quantum Chem. 261, 5.
- 120. Warburg, E. (1909). Jahrbuch der Radioaktivität. 6, 181.
- Ward, L.J.; Schofield, W.C.E.; Badyal, J.P.S.; Goodwin, A.J.; Merlin, P.J. (2003). Chem. Mater. 15, 1466.
- Ward, L.J.; Schofield, W.C.E.; Badyal, J.P.S.; Goodwin, A.J.; Merlin, P.J. (2003). Langmuir. 19 (6), 2110.
- 123. Wrobel, A. M., Walkiewicz–Pietzykowska, A., Hatanaka, Y., Wickramayaka, S., & Nakanishi, Y. (2001). Chem. Mater. *13*, 1884.
- 124. Wrobel, A., Walkiewicz–Pietzykowska, A., Klemberg–Sapieha, J., Nakanishi, Y., Aoki, T., & Hatanaka, Y. (2003). Chem. Mater. *15*, 1749.
- Yasuda, H. (1981). Journal of Polymer Science: Macromolecule Reviews. 16, 199.
- 126. Yoshimura, K., & Hozumi, K. (1996). J. Photopolym. Sci. Technol. 9 (2), 225.

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