NATIONAL OPEN UNIVERSITY OF NIGERIA

SCHOOL OF SCIENCE AND TECHNOLOGY

COURSE CODE: CHM 417

COURSE TITLE: INDUSTRIAL CHEMICAL PROCESSES II

COURSE DEVELOPER: EKUTE BETHEL ONYEKA

COURSE GUIDE

CONTENTS **PAGE**

INTRODUCTION

Welcome to the part II of this course entitled “INDUSTRIAL CHEMICAL PROCESSES II”. You may have studied the first part in your third year. This course is meant to expose to certain specific chemical processes involved in the manufacture of chemicals and other products.

A chemical process is any laboratory or industrial activity in which products are chemically reacted with each other to form new products. In the context of this course, a chemical process is an industrial operation in which finished chemical products are created on a large scale. Industrial processes are procedures involving chemical, physical, electrical or mechanical steps to aid in the manufacturing of an item or items, usually on a very large scale. Industrial processes are the key components of the heavy industry.

Imagine how life would have been if there are no chemical processes which yield desirable and useful products. Industrial chemical processes plays a significant role in the economic growth of a nation.

This course has been developed in such a way that you will be able to comprehend every facet of the course. It is a two-unit degree course for students offering Bachelor of Science (B.Sc.) Chemistry.

Do enjoy your journey through this course as we hope that you will find chemistry to be very interesting.

What you will learn in this course

In this course, you will learn how mineral ores are being processed chemically; pyrometallurgical and hydrometallurgical operations in the extraction of metals. You will also learn of how Portland cement is made and the chemistry involved in its manufacture. Fertilizers (inorganic fertilizers to be precise) are essential for effective productivity hence their manufacture is important. This you will also come to learn as you study this course. Heavy inorganic chemicals such as hydrochloric acid, the chlor-alkali chemicals, etc. are the “power house” of most chemical industries. It is therefore imperative that you learn about the chemical processes such as the contact process, the electrolytic cell processes and the Ostwald’s process, etc. in the production of these heavy chemicals as treated in this course.

Objectives

It is expected that on completion of this course, you should be able to:

- discuss the application of electrochemistry in the industry
- differentiate between hydrometallurgy and pyrometallurgy
- explain in details the Baeyer process in the manufacture of aluminium from Bauxite
- identify the methods employed in the manufacture of potassium sulphate
- mention and expantiate on the electrolytic cells employed in the production of the chlor-alkali chemicals

- describe how ammonium nitrate is produced.

Course Materials

We shall be using three different sets of course materials for this course. One is the course guide which gives you a brief detail of what will be considered in this course. The second are the study units which provides you with detailed learning information. Each study unit has a set of learning objectives and self assessment questions in form of tutor marked assignments. This course material consists of three modules and eleven study units. The third is a set of recommended textbooks and relevant websites listed at the end of each study unit.

Study Units

MODULE ONE: MINERAL PROCESSING
Unit 1 Chemical Processing of Minerals
Unit 2 Metallurgy
Unit 3 Hydrometallurgy
Unit 4 Cement and binding minerals
MODULE TWO: THE INORGANIC FERTILIZERS
Unit 1 Synthetic (Inorganic) Fertilizers
Unit 2 Phosphate fertilizers

MODULE 3: ELECTROCHEMISTRY AND THE MANUFACTURE OF SOME HEAVY INORGANIC CHEMICALS
Unit 1 Industrial electrochemistry
Unit 2 Manufacture of some heavy inorganic chemicals: Chlor-alkali
Unit 3 Manufacture of some heavy inorganic chemicals: Sulfuric acid and Sulfates
Unit 4 Manufacture of heavy inorganic chemicals: Nitric acid
Unit 5 Manufacture of Hydrochloric acid: A heavy chemical

Table of Contents

Module One: Mineral Processing

Unit 1: Chemical Processing of Minerals

Unit 2: Metallurgy

Unit 3: Hydrometallurgy

MODULE ONE: MINERAL PROCESSING

Unit 1 Chemical Processing of Minerals
Unit 2 Metallurgy
Unit 3 Hydrometallurgy
Unit 4 Cement and binding minerals

UNIT 1: CHEMICAL PROCESSING OF MINERALS

1.0 INTRODUCTION
2.0 OBJECTIVES
3.0 MAIN CONTENT
    3.1 WHAT IS A MINERAL?
    3.2 CHEMICAL METHODS OF PROCESSING MINERALS
        3.2.1 ELECTROLYTIC METHOD
        3.2.2 HEATING AND ROASTING
        3.2.3 SINTERING
        3.2.4 SMELTING
        3.2.5 REFINING
        3.2.6 ALLOYING
4.0 CONCLUSION
5.0 SUMMARY
6.0 TUTOR MARKED ASSIGNMENT
7.0 REFERENCES

1.0 INTRODUCTION

The processing of minerals is a major division in the science of extractive metallurgy. Extractive metallurgy has been defined as the science and art of extracting metals from their ores. Within an ore body, valuable minerals are surrounded by gangue and it is the primary function of mineral processing, to liberate and concentrate those valuable minerals. Minerals can be extracted or processed either by physical or chemical methods. However, we shall be treating the chemical methods or steps in the processing of minerals.

2.0 OBJECTIVES

At the end of this unit you should be able to:

- Define a mineral
- Mention the physical characteristics of a mineral
- Discuss or explain the chemical methods/steps employed in extracting minerals

3.0 MAIN CONTENT

3.1 WHAT IS MINERAL?

Minerals are solid constituents of all rocks; igneous, sedimentary and metamorphic, and occurs in crystals. A mineral can be defined as any substance that occurs naturally in the earth and is not formed from animal or vegetable matter. It could also be defined as a natural inorganic compound having a particular chemical composition or a range of composition and a regular atomic structure to which the crystalline forms are related.

Minerals are known to possess the following physical properties which include:

i. Color
ii. Form
iii. Luster
iv. Hardness
v. Cleavage
vi. Fracture
vii. Tenacity
viii. Specific gravity

3.2 CHEMICAL METHODS OF PROCESSING MINERALS

Minerals can be processed by several chemical methods. We shall discuss each of these steps and what they involve.

3.2.1 Electrolytic Method

This method is used for the extraction of the highly electropositive metals like potassium, sodium and calcium which occur as chlorides, carbonates and sulphates. In this method, metals are extracted by the passage of electric current through the ores in molten state.

The passage of electric current results in the cation, M^+ migrating to the cathode while the anion X^- moves to the anode. Now what process do you think occurs at the cathode? Well, at the cathode, reduction occurs in which the cationaccepts electrons and are thereby reduced to their respective metals.

For example, consider this:

$$CaCl_2 \rightarrow Ca^{2+} + Cl^-$$

At the cathode

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

3.2.2 HEATING AND ROASTING

The concentrated mineral ore is heated in a controlled amount of air. Heating converts the sulphides and carbonates ores to oxides, prior to the reduction of the oxides to the metal. Impurities are also driven off at this stage. An example is Sphalerite (ZnS) in which arsenic is driven off as impurity.

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

This heating also converts sulphide ore partially into its oxide which is often reduced to metal by further reaction with sulphide ore. For example, Galena (PbS)

$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$$

$$PbS + 2PbO \rightarrow 3Pb + SO_2$$

3.2.3 SINTERING

Sintering involves heating the material unit for partial fusion to occur to form larger more easily handled materials before smelting.

3.2.4 SMELTING

This involves the reduction of roasted sintered ores to molten metal at a high temperature. Fluxes are added to combine with the gangue to form liquid slag which floats on the surface of the molten metal. An example is the extraction of iron which is carried out in a blast furnace inside constructed with steel and lined with firebricks. The extraction process is summarized in the following equations.

$$2C + O_2 \xrightarrow{1400^oC} 2CO$$

$$CaCO_3 \xrightarrow{800^oC} CaO + CO_2$$

$$CaO + SiO_2 \xrightarrow{1000^oC} CaSiO_3 \text{ (slag formation)}$$

$$Fe_2O_3 + 3CO \xrightarrow{600^oC} 2Fe + 3CO_2$$

3.2.5 REFINING

There are different types of refining namely electrolytic refining and zone refining.

Electrolytic Refining:

Here, the metal of interest is purified electrolytically by making the impure metal the anode of an electrolytic cell. Copper for instance is purified electrolytically by making the impure copper anode of an electrolytic cell which contains copper (ii) sulphate solution as electrolyte and a thin strip of pure copper as the cathode. By the appropriate choice of voltage, pure copper is transferred from the anode to the cathode.

Zone Refining:

This method is applied on a very small scale in producing metals and some non metals of extremely high quality. It depends on the principle that an impure molten metal deposits pure crystals on solidifying.

3.2.6 ALLOYING

An alloy is a mixture or solid solution composed of a metal and another element. Alloying is a process in which two metal elements are melted together in a precise combination to form a specific material or alloy. Alloys are often preferred over single element metals, particularly for solder performs, because of their different melting points, specific conductivity attributes or improved thermal expansion values. Alloying is done in either an induction furnace or a casting operation, depending on the alloy. If an induction furnace is used the alloy is poured into bars or ingetsfor future use. After refining a metal, the pure metal can be combined with one or more metals or even non-metals that often enhance its properties. For example steel is stronger than iron, its primary element.

4.0 CONCLUSION

This unit has shown the chemical steps or methods involved in the chemical processing of minerals.

5.0 SUMMARY

Minerals processing is the first step in the solid mineral extractive process. The goal is to produce valuable materials which meetsa specific set of requirements in terms of material composition and physical characteristics. The chemical steps methods of processing minerals includes: the electrolytic method which is applicable to highly electropositive metals, the others are more like steps as one step leads to the other from heating and roasting of the mineral ore to sintering, smelting, refining and alloying.

6.0 TUTOR MARKED ASSIGNMENT

I. Outline the steps involved in the chemical processing of minerals.
II. Mention five physical properties of minerals.
III. What is the difference between sintering and smelting?

7.0 REFERENCES

en.m.wikipedia.org
processengineering.sun.ac.za
Schubert, H., (1975) Aufbereitung fester mineralisherFeststoffsysteme, VEB DentsherVerlagFürGrundstoff industries Leipzig.

UNIT 2: METALLURGY

1.0 INTRODUCTION

Metals make up a major part of the elements in the periodic table. Metals are divided into ferrous and non-ferrous, with the ferrous metals group being Iron, Manganese, Chromium and their alloys. The non-ferrous metals are of four types namely: the heavy metals such as Cu, Pb, Sn and Ni, Light metals (alkaline and alkaline earth metals), the Noble or precious metals such Pt, Ir, Os, Pd, Ru, Rh and Ag; and the rare metals. Metals generally are very important for structural applications, electrical wires, cooking utensils, decorative items and many other purposes. However, metals possess as their main chemical characteristic, the ability to give up electrons and as such almost all metals in nature are found in ores, combines with non-metals such as oxygen, sulfur and the halogens. This therefore, necessitates their separation of these metals from their ores and reduction of the metal ions to free metals and make them available for use in a suitable form. This process is known as **metallurgy.**

2.0 OBJECTIVES

At the end of this unit, you should be able to:

1. Define metallurgy
2. Identify the types of furnaces used or applicable in extracting metals.
3. Discuss the process involved in metallurgy.

3.0 MAIN CONTENT

3.1 Metallurgy. What does it mean?

In the introductory part of this unit, it was mentioned that due to the major chemical property of metals (i.e. the ability of giving up electrons); they exist in ores in combination with non-metals. Therefore, in order to have these metals in a suitable and stable form, metallurgy comes into play. Now, what is metallurgy?

Metallurgy is the branch of chemistry which deals the method of extraction of metals from their ores and preparation of alloys.

The extraction of metals cannot be carried out by any universal method. Why? This is because extraction of metals requires different procedure of extraction which depends upon the nature and properties of the metal. Generally, the noble metals such as Au, Ag etc. are usually extracted by amalgamation or cyanide process. Also, the active metals such as Na, K, Ca, Mg, Al, etc. are usually obtained by electrolysis of their chlorides, oxides or hydroxides while the heavy metals are extracted by the use of roasting and smelting methods.

3.2 Types of Furnaces Used

In metallurgical operations, various types of furnaces are used for heating substances to required temperatures. The following are the types of furnaces employed in metallurgical operations:

- Reverberating furnace: This is used especially for calcinations, roasting and smelting
- Blast Furnace: Used for the smelting of iron, copper and lead ores.
- Bessemer converter: Used in the extraction of copper and in the manufacture of steel.
- Open Hearth Furnace: Used for the manufacture of steel. This furnace is based on the ***regenerative system***of heat economy. The regenerative system in that in which heat is liberated (heat content of the furnace gases) is utilized for preheating the gaseous fuels used in the furnace to save cost.
- Electric Furnace: Used mainly for manufacturing very fine steel.

3.3 STEPS INVOLVED IN METALLURGICAL OPERATIONS

There are basically three major steps involved in metallurgical operations (or metallurgy).These are: Ore pretreatment or Ore dressing, Extraction of crude metal and metal purification. Haven mentioned three steps, lets us now look into what each of these steps involve.

3.3.1 ORE DRESSING

Ore pretreatment is the process of removing gangue or matrix (non-metallic and rocky materials such as quartz, mica, feldspars and other silicates) from a metal ore. This is achieved by the following methods:

a. **Hand Picking**- The gross lumps of rocks may be removed from the ore by simple hand picking and the lumps are then broken away with the hammer. An example of the ore in which this is applicable is Heamatite (an iron ore).

b. **Hydraulic washing or Levigation**: Here, the ore after grinding, is washed with a running stream of water. The lighter gangue particles are thus washed away while the heavier ore particles settle down rapidly. This method is actually based on the difference in the densities of gangue and the mineral particles.

c. **Froath floatation**: This especially suitable for the concentration of low grade ores. The process is based on the different wetting characteristics of the ore and gangue particles with water and oil. The ore is preferentially wetted by oil and the gangue particles by water. Ores like copper pyrites ($CuFeS_2$), galena (PbS) and zinc blende (ZnS) are purified by this method.

d. **Magnetic concentration**: This process is used when the mineral is attracted by a magnet, but not the gangue. It is applicable in the case of ferromagnetic ores such as iron, tinstone associated with wolfram.

e. **Electromagnetic separation**: This method is used for separating ore from magnetic impurities. In this method, the crushed or powdered ore is dropped over a belt moving over two rollers, one of which is magnetic. As the mass passes over the electromagnetic roller, the non- magnetic ore falls off and the magnetic impurities are held and moved round the magnetic roller so long as they are attracted by it. However, when there is no more magnetic force of attraction, the impurities fall down into a separate heap. An example is tinstone ore which is separated from the magnetic impurity, wolframite($FeWO_4$).

3.3.2 EXTRACTION OF CRUDE METAL.

After the ore has been pretreated, the metal is then extracted. This extraction involves the use of the following chemical reaction or processes.

i. **Calcination-** Calcination is the process in which the mineral ore is subjected to the action of heat at high temperature in the absence of air but below its melting point. The process of calcination is carried out in the case of carbonate and hydrated ores. Calcination is usually performed in a reverberatoryfurnace. This process results in the following:

- Removal of moisture
- Removal of volatile impurities
- Expellation of gases may take place
- The mass becomes porous
- Thermal decomposition of the ore takes place

Examples of ores in which calcination is employed are as follows:

$CaCO_3$ (limestone)→$CaO + CO_2$

$MgCO_3.CaCO_3$ (dolomite) →$MgO + CaO + 2CO_2$

$CuCO_3.Cu(OH)_2$ (Malachite) → $2CuO + H_2O + CO_2$

$ZnCO_3$ (Calamine) → $ZnO + CO_2$

ii. **Roasting**- Roasting involves subjecting either the ore alone or with the addition of suitable material to the action of heat in excess of air at temperatures below its melting point. This is usually carried out in a reverberatory or blast furnace. During roasting, volatile impurities like S, As, Sb etc. get oxidized and escape out as volatile gases SO_2, As_2O_3 and Sb_2O_3. Sulphide ores also decompose to their oxides evolving SO_2. Moisture is removed and the mass becomes porous thus making reduction easy.

There are many types of roasting namely:

(a) Oxidizing roasting (b) Blast roasting (c) Reduction roasting (d) Sulphating roasting

(e) Chlorodising roasting.

iii. **Smelting-** This the process in which an ore is melted with a flux and often with a reducing agent and it involves calcination, roasting and reduction. Generally, the process of separation of a metal or its sulphide mixture from its ore in a fused state is called smelting. Smelting is generally carried out in a blast furnace and high temperature is produced by burning coal or by using electric energy.

In smelting, the roasted or calcined ore is mixed with coke and then heated in a furnace. As a result, carbon and carbon monoxide produced by the incomplete combustion of carbon reduce the oxide to the metal. For example, in the extraction of iron heamatite ore (Fe_2O_3) is smelted with coke and limestone (flux). As a result of reduction, iron is obtained in fused of molten state.

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$$

$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO$
$CaCO_3 \rightarrow CaO + CO_2$
$CaO + SiO_2 \rightarrow CaSiO_2$
(flux) (gangue) (slag)

iv. **Reduction:** Extraction of metals from their ore generally means reduction and it can be carried out in a number of ways. We shall consider some of these ways.

(a) Reduction by heating in air: Metals whose sides are unstable towards heat (i.e. the less active metals such as Hg, Pb, Cu, Sb etc.) are extracted by air reduction. For example roasting of cinnabar (a sulphide ore of mercury) yields the mercury metal and not the oxide.

$2HgS + 3O_2 \rightarrow 2HgO + 2SO_2$
$2HgO \rightarrow 2Hg + O_2$
$2HgO + HgS \rightarrow 3Hg + SO_2$

(b) Auto reduction method: This method does not involve any additional reducing method and is similar to the above mentioned way of reduction. In this method sulphide is heated in air until a part is converted into oxide. On further heating in the air, the unchanged sulphide reduces the oxide to metal. E.g.

$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$
$2PbO + PbS \rightarrow 3Pb + SO_2$

(c) Reduction with coke or carbon monoxide: Here, the calcined or roasted ore is mixed with coke and heated in suitable furnace. Carbon and CO (formed by incomplete combustion of carbon) reduce the oxide to the metal. For example, concentrated cassiterite(SnO_2) is reduced to metallic tin by heating with coke in a reverberatory or blast furnace.

$SnO_2 + 2C \rightarrow Sn + 2CO$

Other examples are as shown in the following chemical equations:

$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$
$ZnO + C \rightarrow Zn + CO$

(d) Reduction with hydrogen: Oxides of certain metals such as WO_3, NiO, Co_2O_3, In_2O_3 may be conveniently reduced by means of hydrogen to the corresponding metals as shown below:

$In_2O_3 + 3H_2 \rightarrow 2In + 3H_2O$
$Co_2O_3 + 6H \rightarrow 2Co + 3H_2O$
$NiO + 2H \rightarrow Ni + H_2O$
$WO_3 + 6H \rightarrow 3H_2O + W$

This method is suitable for metals which are heavier than manganese.

(e) Reduction of complex salts: Metals like gold, silver etc. can be precipitated from their complete salt solutions by more electropositive zinc metal.

$2NaAg(CN)_2 + Zn \rightarrow Na_2Zn(CN)_4 + 2Ag$
$2KAu(CN)_2 + Zn \rightarrow K_2Zn(CN)_4 + 2Au$

Metals such as Ti, Zr, Ta etc. are obtained by reducing their complex salts with alkali metals or Aluminum.

$K_2TiF_6 + 4K \rightarrow 6KF + Ti$
$K_2ZrF_6 + 2Al \rightarrow 2AlF_3 + 2K + Zr$

Other reduction methods includes reduction by aluminum for certain metal oxides that cannot be reduced effectively with carbon or carbon monoxide, reduction with water gas, reduction with silicon or calcium carbide and amalgamation.

The next step after extraction is purification of the metals.

3.3.3 PURIFICATION OF METALS

The metals obtained by the methods described above require adequate refining as the metal is not pure. This refining is achieved by a large number of physical and chemical methods. However, the choice of the refining method depends upon the use to which a metal is to be put.

There are several physical methods for refining metals. These are:

1. **Fusion method:** This method is applicable when the metal is associated with adsorbed gases. For instance, dissolved oxygen is removed from silver by this method and also dissolved SO_2 gas from copper metal.

2. **Liquation:** Liquation is employed when the melting point of the metal is lower than that of the impurities. Hence, the material must be heated until one of the metals starts to melt and drain away from the other and can be collected. Zinc is separated from lead by this method.

3. **Distillation:** This is used to refine low boiling point metals such as Hg, Cd and Zn. The process involves heating the impure metal in a retort as a result of which pure metal distils over and collects in the receiver, while non-volatile impurities are left behind. The volatile compounds are further separated by same method to get the pure metal.

   Other physical methods include: fractional crystallization, vacuum arc sublimation method and cage-zone melting technique.

   Pyrometallurgical oxidation is chemical process in which impurities are removed from metals by oxidation. The oxidation may be carried out by either of the following methods discussed below:

(a) **Poling or furnace refining:** Impurities of reducible oxides can be removed from the metals by poling. For instance, blister copper containing traces of cuprous oxide as impurity is refined by melting the impure metal on the hearth of a reverboratory furnace. The melt is stirred with green logs of wood. You may wonder why use green wood? Well, the green wood produces hydrocarbons which reduce the cuprous oxides to copper metal while reducing gases such as SO_2, A_2O_3 etc. are given off. In order to prevent copper metal from re-oxidation by air, a layer of charcoal powder is used to cover the molten copper surface. Another metal refined by poling is tin.

(b) **Cupellation:** This method is used to purify silver containing lead as impurity and depends upon the selective oxidation of lead over silver. The impure silver is smelted in a cupel made of bone ash in a blast of air in reverboratory furnace. The lead is oxidized to lead oxide which is partly blown away from the crucible by blast of air. The remaining part melts and is absorbed by the bone ash cupel. The completion of the purification process is indicated by a flash produced by the pure molten silver in the cupel.

(c)**Electrolytic refining:** This is one of the most convenient and important method of refining and it gives metal of high purity. It is also applicable to many metals such as Cu, Ag, Pb, Ni etc. Here, blocks of impure metals form the anode and thin sheets of metal form the cathode while the electrolyte is a solution of the salts of pure metals. On passing an electric current through the solution, pure metal dissolves from the anode and deposits on the cathode. At the same time, more of the metal ions enter the electrolyte by the oxidation of the anode. The insoluble impurities dissolve in the electrolyte or fall at the bottom and collect as anode mud. For example in the refining of copper, impurities like Fe and Zn dissolve in the electrolyte while Au, Ag and Pt are left behind as anode mud.

4.0 CONCLUSION

In this unit you have learnt in details what is involved in metallurgical operations and the types of furnaces used in this operation.

5.0 SUMMARY

Metallurgy, which is a process of separating a metal from its ore and preparing it for use involves three major steps namely, pretreatment of ore, metal extraction and refining. The first step involves removing gangue from the metal which is achieved by handpicking, hydraulic washing, froath floatation, magnetic concentration or electromagnetic separation. Certain chemical processes such as calcination, roasting, smelting and reduction are employed in the extraction of metals. Finally, the metals are subjected to purification or refining by various physical and chemical methods.

6.0 TUTOR MARKED ASSIGNMENT

1. Differentiate between levigation and froath floatation.
2. What are the results of calcination as a process of metal extraction?
3. What is the difference between flux and gangue?
4. With an appropriate example, describe what cupellation involves.

7.0 REFERENCES

www.sciencedaily.com/.../metallurgy.htm
Sharma, B.K (2011). Industrial Chemistry (Including Chemical Engineering)
(16th edition).KRISHNA Prakashan Media (P) Ltd. Pp 1615-1623

UNIT 3: HYDROMETALLURGY

1.0 INTRODUCTION In the preceeding unit, we considered the metallurgical processes which are usually called pyrometallurgy (pyro means at high temperatures). Pyrometallurgy has been employed in producing metals from their ores since ancient times and requires large quantities of energy. This poses two serious problems namely atmospheric pollution (mainly by sulphurdioxide) and relatively high costs that make treatment of low grade ore economically unfeasible. Toward the end of the 19th century, a different process known as hydrometallurgy was introduced. Hydrometallurgy is now used to produce several metals, including gold and silver, as well as salt of other metals. This process now competes with pyrometallurgy in the production of copper, zinc and nickel.

2.0 OBJECTIVES

At the end of this unit you should be able to

- differentiate between pyrometallurgy and hydrometallurgy
- identify the advantages of hydrometallurgy
- explain the various process involved in hydrometallurgy

3.0 MAIN CONTENT

3.1 HYDROMETALLURGY

Hydrometallurgy (hydro meaning water) has been employed to extract metals from their ores by the use of aqueous chemical solutions at moderate temperatures. Hydrometallurgical processes usually require less energy and produces less air pollution and are well suited especially to low-grade ores and oresthat contain several metals with similar properties. The first two uses of this process were for the extraction of gold from low-grade ores and for the production of aluminum oxide, or aluminum from bauxite and aluminum bearing ore.

3.2 PROCESSES OF HYDROMETALLURGY.

Hydrometallurgy involves two distinct steps. First is the selective leaching of a given metal ion from the solution by selective precipitation as an ionic compound. To get a clearer understanding of these processes, consider these examples:

Gold is sometimes found in ores in the elemental state but occurs usually in relatively small concentration. To extract or obtain the gold metal, a process called cyanidation is employed. In this case the crushed ore is treated with an aqueous cyanide solution in the presence of air thereby forming the complex ion, $Au(CN)_2^-$ as shown in the equation below:

$$4Au_{(s)} + 8CN^-_{(aq)} + O_2 + 2H_2O_{(l)} \rightarrow 4Au(CN)_2^-{}_{(aq)} + 4OH^-_{(aq)}$$

Pure gold is then recovered by the reaction of $Au(CN)_2^-$with zinc powder to reduce Au^+ to Au

$$2Au(CN)_2^-{}_{(aq)} + Zn_{(l)} \rightarrow 2Au_{(s)} + 2Zn(CN)_2^-{}_{(aq)}$$

Consider also the Bayer process for the extraction of alumina from bauxite. The ore is leached with sodium hydroxide to dissolve the amphoteric aluminum oxide.

$$Al_2O_{3(s)} + 2OH^-_{(aq)} \rightarrow 2AlO_2^-{}_{(aq)} + H_2O_{(l)}$$

This process leaves behind solid impurities such as SiO_2, Fe_2O_3 and TiO_2 which are not appreciably soluble in basic solution. After the solid impurities are removed, the pH of the solution is lowered by addition of carbon dioxide. The pure aluminum oxide reforms and is then electrolyzed to produce aluminum metal.

There are different kinds of leaching agents used. A leaching agent can simply be water if the metal containing compound is a water soluble chloride or sulfate. However, most commonly, the metal is present in a water-insoluble substance that must be dissolved. In such cases, leaching agents used are usually aqueous solutions containing acids, bases, oxidizing agents, salts or some combination of these. The leaching or dissolving process often involves the formation of complex ions. For example, an ore containing water-insoluble lead sulfate is treated with an aqueous sodium chloride solution and then a soluble complex ion, $PbCl_4^{2-}$ is formed thus:

$$PbSO_{4(s)} + 4Na^+_{(aq)}4Cl^-_{(aq)} \rightarrow 4Na^+_{(aq)} + PbCl_4^{2-}{}_{(aq)} + SO_4^{2-}{}_{(aq)}$$

Similarly, the cyanidation process for the recovery of gold results in the formation of a complex ion. The gold, since it is present in the ore as particles of metal, it must first be oxidized by oxygen to produce Au^+ which then reacts with CN^- to form soluble $Au(CN)_2^-$ species. Thus, in this case, the leaching process involves a combination of oxidation and complexation.

Recovering the metal ions from the leaching solution involves forming an insoluble solid containing the metal ion to be recovered. This step may involve addition of an anion to form an insoluble salt, reduction to the solid metal (chemically or electrolytically), or a combination of reduction and precipitation of salt. Examples are as shown below:

Method	Examples
Precipitate of a salt	$Cu^{2+}_{(aq)} + S^{2-}_{(aq)} \rightarrow CuS_{(s)}$ $Au^+_{(aq)} + Fe^{2+}_{(aq)} \rightarrow Au_{(s)} + Fe^{3+}_{(aq)}$
Reduction (a) Chemical	$Cu^{2+}_{(aq)} + Fe_{(s)} \rightarrow Cu + Fe^{2+}_{(aq)}$ $Ni^{2+}_{(aq)} + H_{2(g)} \rightarrow Ni_{(s)} + 2H^+_{(aq)}$

(b) Electrolytic	$Al^{3+}_{(aq)} + 3e^- \rightarrow Al_{(s)}$ $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$
Reduction plus precipitation	$2Cu^{2+}_{(aq)} + 2Cl^-_{(aq)} + H_2SO_{3(aq)} + H_2O_{(l)} \rightarrow 2CuCl_{(s)} + 3H^+_{(aq)} + HSO_4^-{}_{(aq)}$

3.3 ADVANTAGES OF HYDROMETALLURGY

In comparison of hydrometallurgy and its traditional counterpart (pyrometallurgy), hydrometallurgy is seen to have these advantages:

(1) Leaching agent can be pumped directly into ore deposits in the earth.
(2) Economically suitable for low grade ores.
(3) The process generates little or no pollution.

4.0 CONCLUSION

In this unit, it was shown that hydrometallurgy is a much more better process for extracting and preparing metals for a suitable use as it is cost effective and applicable for low grade ores.

5.0 SUMMARY

You have learnt from this unit that hydrometallurgy is a process through which metals are extracted from their ores by the use of aqueous chemical solutions at moderate temperatures. Hydrometallurgy involves basically two steps namely: leaching in which the ores dissolved in solution to obtain the metal ion and recovery of the metal ion from the selection through various methods which involves precipitation of metal salt, reduction of metal into the solid metal either chemically or electrically, and a combination of reduction and precipitation.

6.0 TUTOR MARKED ASSIGNMENTS

- How would you explain hydrometallurgy?
- What is/are the advantage(s) of hydrometallurgy?
- Explain briefly the Bayer Process.

7.0 REFERENCES

Fleming, C. A. (1992).Hydrometallurgy of precious metals recovery.*Journal of Hydrometallurgy*.Vol 30,Issues 1-3.pp 127-162

FathiHabashi (2005). A short history of hydrometallurgy.*Journal of Hydrometallurgy*.Volume 79, Issues 1-2,pp 15-22

FathiHabashi (2009).”Recent Trends in Extractive Metallurgy”.*Journal of Mining and Metallurgy*. Section B: Metallurgy. Volume 45, pp 1-13

UNIT FOUR: CEMENT AND BINDING MINERALS

1.0 INTRODUCTION

Cement is the general term given to the powdered materials which initially have plastic flow when mixed with water or other liquid, but has the property of setting to a hard solid structure in several hours with varying degree of strength and bonding properties. The use of cement can be traced to the Greaks, Romans and Egyptians who used volcanic stuff such as pozzolanic cement, a volcanic tufa obtained near puzzuoli in Italy. This is a type of natural cement which may be regarded as a mixture of burnt silicates and lime. James Parker in the 1780s developed a natural cement made by burning septaria (nodules that are found in certain clay deposits and that contain both clay minerals and calcium carbonate). The burnt nodules were ground to a fine powder. This product called the “Roman cement” when made into a mortar with sand, sets in 5 – 15 minutes. Despite the popularity of this cement, it was largely replaced by Portland cement in the 1850s. Portland cement was discovered by Joseph Aspidin, a bricklayer and later the production was refined by William Aspidin and Isaac Charles Johnson.

2.0 OBJECTIVES

At the end of this unit, you should able to:

- identify the mineral constituents of cement
- recall the types of cement
- describe the various types of cement and differentiate between the types.
- understandthe chemistry involved in the use and production of cement.

3.0 MAIN CONTENT

3.1 MINERAL COMPOSITION OF CEMENT

A cement is a binder, a substance that sets and hardens and can bind other materials together. On the basis of the use of cement in construction, it can be characterized as being either hydraulic or non-hydraulic depending on the ability of the cement to be used in the presence of water.

Non- hydraulic cement will not set in wet conditions or underwater, it sets as the cement dries and reacts with carbondioxide in the air. It is prone to chemical attack after setting. Hydraulic cement allows setting in wet condition or underwater and further protects the hardened material from chemical attract. Considering the quality, durability and setting time, you will agree with me that hydraulic cements are more viable. Hence, we shall base our consideration mainly on hydraulic cements. Now what minerals contributes to the binding ability of cements? The minerals which constitutes hydraulic cements such as Portland cement are mainly Belite ($2CaO. S_iO_2$); Alite ($3CaO.S_iO_2$); Celite ($3CaO.Al_2O_3$) and Brownmillerite ($4CaO, Al_2O_3$ Fe_2O_3). The silicates are responsible for the mechanical properties of the cement while the Celite (tricalcium aluminate) and the brownmillerite (tetracalciumaluminoferite) are essential to allow the formation of the liquid phase during the kilnsintering .

3.2 CLASSES OF CEMENTS

Over the years, three classes of cement have been developed commercially: natural cements (non-hydraulic), aluminous and Portland cements (both classes are hydraulic). It is true that we have established the fact that our discussion will be based mainly on hydraulic cements, however, the chemistry involved in the production of natural cements is worthy of note.

3.2.1. NATURAL CEMENTS

Hydraulic lines and slaked line are examples of natural cements how are natural cements manufactured? What is the chemistry ruling the action of these non-hydraulic cements?

Manufacture:

First carbon dioxide is removed from pure limestone (calcium carbonate) by heating for about 10 hours, at atmospheric pressure and temperatures above 825^0C ($1,517^0$F). This process is known as calcination and produces quick lime (calcium oxide) which slakes rapidly in water with the evolution of significant amount of heat. Calcium hydroxide (slaked lime) is thus formed and it does not set under water. Once the water in excess from the slaked lime is completely evaporated, carbonation starts (hardening of slaked lime in the presence of carbon dioxide that is naturally present in the air). Carbonation results in the formation of calcium carbonate. The calcined product of a limestone which has a high calcium content is called fat lime. Calcined products having relatively low content of silica (10 to 20%) and alumina are usually called hydraulic limes. The processes discussed above can be summed up as shown in the equations below:

$CaCo_3 \rightarrow CaO + CO_2$ (Calcination)

$CaO + H_2O \rightarrow Ca(OH)_2$ (Slaking)

$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$ (Carbonation)

This whole process is called the lime cycle.

3.2.2. ALUMINOUS CEMENT

Aluminous cement is essentially a calcium aluminates cement and can be prepared by heating a mixture of limestone and bauxite at 1550 – 1600^0C. This cement is made from alumina rich rocks such as bauxite and limestone or lime. Aluminous cement like Portland cement is a rapid hardening hydraulic cement. Burning of the raw mix is done till sintering or fusion sets in at 1450–1650^0C. The constituents of this cement are tricalcium aluminates ($3CaO. Al_2O_3$, abbreviated C_3A), dicalcium silicate ($2CaO. SiO2$, C_2S) and dicalcium silicate aluminates (2CaO. Al_2O3. SiO2, C_2AS). The main mineral ingredient of aluminous cements is monocalcium aluminate, CaO. Al_2O3. This predetermines the rapid hardening capacity of these cements.

Dicalcium silicate is a slowly hardening mineral, helenite and magnesium spinel are inert admixtures deteriorating the properties of high alumina cement. Therefore, it is of great importance to manufacture aluminous cement from available raw materials free of MgO and SiO_2 for aluminum oxide (Al_2O_3) not to combine into inert materials.

There are basically two ways of manufacturing Aluminous cement namely: (1) by burning the raw mix till sintering sets in or (2) by burning it to fusion.

Alumina cement liberates a great amount of heat and when the temperature of hardening cement rises above 20^0C, monocalcium aluminate and water combine into dicalciumheptahydratehydroaluminate with scaly crystals.

$$2(CaO.Al_2O_3) + 10H_2O \rightarrow 2CaO.\ Al_2O_3.\ 7H_2O + 2Al(OH)_3$$

These crystals then recrystalises into tricalciumhexahydratehydroaluminate with cubic crystals since in these conditions $2(CaO.Al_2O_3).7H_2O$ is unstable. Alumina cements are chemically composed of aluminium oxide, CaO, SiO_2 and Fe_2O_3 with percentages of 35-55%, 35-45%, 5-10% and 1-15% respectively

3.2.3 Portland cement

Portland cement is by far the most common type of cement in general use around the world. This cement is known to be chemically composed of Al_2O_3 (4-7%), CaO (64-67%), S_iO_2 (19-24%) and Fe_2O_3 (2-6%). The chemistry ruling the action of Portland cement like its hydraulic counterpart is hydration.

Portland cement is made by heating limestone (calcium carbonate) with small quantities of other materials such as clay to 1450^0C in a kiln, in a process known as calcination whereby a molecule of carbondioxide is liberated from the calcium carbonate to form calcium oxide or quicklime, which is then blended with the other materials that have been included in the mix. The resulting hard substance, called “clinker”, is then ground with a small amount of gypsum into a powder to make the cement.

This cement is a basic ingredient of concrete and mortar. Its most common use is in the production of concrete. Concrete is a composite material consisting of aggregate (gravel and sand), cement and water.

There are various types of Portland cement depending on the rate of setting, heat evolution and strength characteristics. Five types of Portland cement are recognized which contain varying amounts of the clinker compounds C_2S, C_2S, C_4AF and MgO. These are:

1. **Regular Portland cements:** They are usual products for general concrete construction and harden to full strength in about 28-30 days. They contain 40-60% C_2S, 10-30% C_2AS and 7-13% C_3A. White cements, oil wall cement and quick setting cements belong to this class.
2. **Modified Portland cements:** These are sulfate resisting cements which are used where moderate heat of hydration is required. The heat evolved from these cements in expected not to exceed 70 and 80 cal/gm after one week and four weeks respectively. These cements are characterized by higher C_2S/C_3S ratio.
3. **High early strength (HES) Portland cements:** These cements contain higher percentage of C_3S and C_3A with finer grinding to increase hydration rate. This high proportion of C_3S causes a quicker hardening than regular Portland cement and thus attains a strength of regular Portland cement in just three days. Roads constructed from HES cement can be put into service much sooner than those constructed from regular cements.

4. **Low heat Portland cement:** These cements contain a lower percentage of C_3S and C_3A and thus decrease the heat evolution.It is expected that the heat evolved should not exceed 60 and 70 cal/gm after 7 and 28 days respectively. These cements are designed for massive structure work.
5. **Sulfate resisting Portland cement:** These are good for sea water contact and resist sulfates better than the other four types. They are lower in C_2A (< 4%) and higher in C_4AF.

NOTE:

Dicalcium silicate	is abbreviated	C_2S
Tricalcium silicate	“ “	C_3S
Tricalcium aluminate	“ “	C_3A
Dicalcium silicate aluminate	“ “	C_2A
Tetracalciumaluminoferrite	“ “	C_4AF

4.0 CONCLUSION

This unit has considered cement, its characterization on various basis, the mineral constituents and also the manufacture of the types of cements identified.

5.0 SUMMARY

- Cement is a binder, that is a substance that sets and hardens and can bind other materials together.
- The main minerals present in cement are belite, alite,brownmillerite and celite.
- On the basis of cement, ability to be used in the presence of water, cements can be characterized as hydraulic and non-hydraulic.
- The process by which natural cements are made is known as the lime cycle.
- There are two ways of manufacturing aluminous cement which are: by burning the cement raw mix till sintering sets in and by burning it to fusion.
- HES Portland cements are better than regular Portland cements in that its high proportion of alite enhances to quicker hardening.

6.0 TUTOR MARKED ASSIGNMENT

1. What do you understand by the following:
    - i. a kiln
    - ii. Calcination
    - iii. Carbonation
    - iv. Hydration?
2. Outline the types of Portland cements and discuss each type.
3. What is the difference between fat lime and hydraulic lime?

7.0 REFERENCES

Robert, G. B. (2004). “The History of Calcareous Cements” on Hewlett, Peter C., ed. Lea’s Chemistry of cement and concrete.ed. Amsterdam: Elsevier Butter worth- Heinemann 1-24.

Cements basic molecular structure finally decoded (MII. 2009)

Sharma, B. K. (2011). Industrial Chemistry (including Chemical Engineering) 16th ed. KRISHNA PRAKASHAN MEDIA (P) Ltd. PP 658-671.

MODULE TWO: THE INORGANIC FERTILIZERS

Unit 1 Synthetic (Inorganic) Fertilizers
Unit 2 Phosphate fertilizers

UNIT ONE: SYNTHETIC (INORGANIC) FERTILIZERS

1.0 INTRODUCTION
2.0 OBJECTIVES
3.0 MAIN CONTENT
3.1 FERTILIZERS
3.2 CLASSIFICATION OF FERTILIZERS
3.3 THE INORGANIC FERILIZERS.
3.3.1 NITROGENEOUS FERTILIZERS
    3.3.1.1 AMMONIUM NITRATE
    3.3.1.2 AMMONIUM SULPHATE
    3.3.1.3 UREA
3.3.2 POTASSIUM FERTILIZERS
4.0 CONCLUSION
5.0 SUMMARY
6.0 TUTOR MARKED ASSIGNMENT
7.0 REFERENCES

1.0 INTRODUCTION

Living things (plants and animal alike) require food for their growth and development. The growth and harvest of food and fiber crops is essential to the survival and well-being of humankind. World population is on the increase and as such there is the challenge to increase crop production. In order to meet this challenge, several means has been employed amongst which are the introduction of irrigation, improvement of plant strains and introduction of or increase in fertilizer usage.

For effective productivity of plants, certain elements have been considered essential. The primary and secondary nutrient element are collectively known as major plant nutrients while the nutrients which are used by field crops in very small quantities are known as micronutrients or minor plant nutrients. Amongst these nutrients Nitrogen, Phosphorus and potassium are the most important element and are therefore used in the production of fertilizers.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

i. identify the conditions for a compound to serve as a fertilizer
ii. mention some classes of inorganic fertilizers
iii. discuss how some nitrogenous fertilizers are manufactured

3.0 MAIN CONTENT

3.1 FERTILIZERS

Fertilizers are those substances which must be added to the soil in order to remove the deficiency of essential elements required for plant growth. Why the addition of fertilizers? When the soil is repeatedly cultivated, there comes a stage where the soil becomes less productive hence the need for certain elements in the form of their compounds to be added to the soil to enhance its productivity. The need of fertilizing a land can be summarized as follows:

i. To supplement what has been eaten up by the plants.
ii. To supply them an additional tonic and good food, so that they may grow more healthy and produce a better yield.
iii. To maintain the pH of the soil in the vicinity of 7-8 and thereby facilitate optimum growth and health.

Not every compound containing nitrogen or phosphorus etc. can be used as a fertilizer. For a compound to be used as a fertilizer, it should have the requisites:

i. The element present in the compound must be easily available to the plant.
ii. The substance must be soluble in water.
iii. It should be stable, so that it may be made available to the plant for a long time.
iv. It should not be costly.
v. It should maintain the pH of the soil in the vicinity of 7-8.
vi. It should not be poisonous to the plant.

3.2 CLASSIFICATION OF INORGANIC FERTILIZERS

Inorganic fertilizers are classified on the basis of the role they play in soil chemistry, the numbers and types of nutrient elements they contain, their physicochemical properties used in particular, their solubility in sol water, their physiological effect on the effect on the soil to which the fertilizer has been applied and also the method used for manufacturing them.

We shall consider just a few of these classifications. First fertilizers are classified as direct or indirect fertilizers according to their agrochemical nature. Direct fertilizers are those which contain the nutrient elements in the form of compounds which are directly assimilated by plants. According to the nutrient elements present in them, direct fertilizers are further classified as phosphatic, nitrogenous, potash etc. Indirect fertilizers are those substances which are added to the sol in order to improve the chemical, mechanical or biological properties. Examples of indirect fertilizers include ground dolomite and limestone which are used to decrease soil acidity, and gypsum used to improve the properties of the soil with a high salt content.

Fertilizers are also classified as water soluble or soluble in soil acids according to their solubility in the moisture in the soil. Nitrogenous and potash fertilizers are soluble in water and are readily assimilated by plants but are quickly washed out of the soil by surface water. Most phosphates are the fertilizers soluble in soil acids. They are dissolved much slower, but are retained in the soil much longer.

Fertilizers can be divided as physiologically acid, physiologically alkaline or physiologically neutral, according to their physiological effect on the soil to which they are added. The physiologically neutral fertilizers do not change the pH of the soil.

On the basis of their form or physical properties, fertilizers are divided into powder form or granulated form. Granulated fertilizers are less hygroscopic and do not cake during storage. They are not subjected to weathering after being introduced into the soil and are retained by the soil for a longer time.

3.3 THE INORGANIC FERILIZERS

Inorganic fertilizers can be natural and also synthetic (i.e. artificial). The natural inorganic fertilizers are chile saltpeter ($NaNO_3$), rock phosphates and potassium salts. These fertilizers are not sufficient to make the soil productive, hence the need for making of fertilizers artificially. Therefore, inorganic fertilizers are also known as synthetic or artificial fertilizers. These kind of fertilizers are manufactured and contain nutrients that can be readily absorbed by plants. Artificial fertilizers may be studied under three groups according to the nature of the element. We shall be considering two of these groups in this unit.

3.3.1 NITROGENEOUS FERTILIZERS

The important nitrogenous fertilizers are nitrates of sodium, calcium and potassium, ammonium sulphate, calcium cyan amides, ammonium nitrate and urea. These fertilizers are added to the soil in order to remove the deficiency of nitrogen in the soil. Now let’s consider some of these nitrogenous fertilizers and how they are produced.

3.3.1.1 AMMONIUM NITRATE

This is the most important nitrogenous fertilizer. Ammonium nitrate contains 32-35% nitrogen, half in ammonium form and half in nitrate form with the ammonium form being fairly resistant to leaching. It is a white crystalline salt, very soluble in water and highly hygroscopic in nature. It has the tendency to absorb moisture from air and it forms cake.

What raw materials are required for the production of ammonium nitrate? The raw materials are ammonia and nitric acid. The nitric acid is practically made by oxidizing ammonia and absorbing the resulting nitrogen oxides in water. Haven known the raw materials, how is it produced? There are three important methods of production ammonium nitrate. These are: (i) Crystallization (ii) Flaking (iii) Prilling.

Of these three, prilling is the latest and most important method. Four basic operations are involved in the ammonium nitrate prilling plant. These are:

a. Neutralization: Heated ammonia vapour and 60-80% nitric acid are introduced at the base of the neutralizer tower operating under a pressure of 3-5 atmospheres and through which neutralized solution is recycled. The reaction in the tower is shown:

$$HNO_3 + NH_3 \rightarrow NH_4NO_3; \quad \Delta H = -20.6 \text{ kcals}$$

b. Evaporation: The solution obtained from the neutralizer contains about 83% NH_4NO_3. This solution is allowed to pass through a heater supplied with steam for the neutralizer. The heated solution from the heater is passed to a vacuum evaporator when its concentration is increased to about 95%, 83% solution (if left) is drawn off at this point and used in making solution.

c. Prilling: The concentrated solution is now sprayed into prilling tower (the tower is quite high, about 185ft). The following solution in the tower is cooled by an ascending current of air. The solution is sprayed through spray nozzles in such manner that the liquid breaks up into drops of uniform and adequate size. The prills solidify sufficiently as they reach the bottom of the tower and must be handled carefully until they are dried.
d. Drying and Finishing: Drying the prills of ammonium nitrate is quite difficult because it is delinquent in nature. There are various methods of drying. One method is the Bamag process in which nitric acid and ammonia gas are pumped into a melt of ammonium nitrate at about 150^0C which is then cooled and converted into solid NH_4NO_3.

Another method is the Stengel process. In this process, super heated ammonia vapour (145^0C) and concentrated nitric acid preheated to 170^0C are allowed to react in a packed tower and the reaction mixture is then passed into a cyclone designed to separate steam and solution quickly. Air is blown through the melt as a result of which water is removed from the melt to a greater extent and a melt containing 0.25% moisture is produced directly. The melt can be used directly, prilled in short tower or passed into a cooled steel belt to give a thin layer of solid nitrate which is subsequently broken up to give granular crystals.

3.3.1.2 AMMONIUM SULPHATE

Ammonium sulphate contains 21% nitrogen and can be obtained as by product or may be manufactured synthetically. It is obtained as by product of steel industry in which ammonia (another by product) from coke oven is absorbed in sulphuric acid.

Waste streams from various chemical and metallurgical industries are another source of ammonium sulphate. For example the production of pigments and synthetic flames produces by product solutions containing ammonium sulphate.

Synthetically, ammonium sulphate is made with manufactured ammonia. Saturates and crystallizers are also employed in the synthetic manufacture of ammonium sulphate. The heat of reaction of anhydrous ammonia are concentrated sulphuric acid obtained by Contact process in very high. Hence water evaporated from the crystallizer must be returned either by means of a condenser or by addition of water. The ammonium sulphate is dried thoroughly to prevent caking. Free sulphuric acid is removed either by washing on a centrifuge or filter or by neutralizing with weak ammonia solution.

3.3.1.3 UREA

Urea occupies the third place among the world’s solid nitrogenous fertilizer, but it is the highest in nutrient concentration. This is so because if pure, it contains nearly 45-47% nitrogen. Urea has certain properties which makes it use unfavourable. One is its tendency to hydrolyse and lose ammonia. This property is desirable in some respects as this must occur before plants can use the nitrogen efficiency, but if the urea is applied to the surface of the soil, ammonia produced by hydrolysis can be lost to the atmosphere before it has to combine with soil constituents. Another property is the slower conversion of urea to nitrate in the soil as compared with ammonia, ammonium nitrate or ammonium sulphate.

In producing urea, two raw materials are needed namely CO_2 and ammonia. Urea can be manufactured by passing liquid CO_2 and liquid NH_3 in a silver special autoclave when ammonium carbonate is formed. The latter is heated at $130\text{-}135^0$under about 35 atmospheric pressure to get urea.

$$2NH_3 + CO_2 \rightarrow NH_2COONH_4$$

$$NH_2COONH_4 \rightarrow NH_2CONH_2 + H_2O$$

Ammonium carbonate Urea

In its use as a fertilizer, urea is first hydrolysed by soil on water to NH_3 and CO_2. Then nitrosification of NH_3 takes place by the agency of nitrosomonas and nitrosococcus bacteria and nutrients are formed. Nitrification of nitrites is brought about by nitrobacter bacteria to form nitrates by the plants in the soil.

$$CO(NH_2)_2 + H_2O \rightarrow CO_2 + 2NH_3$$

$$2NH_3 + 3O_2 \xrightarrow{\text{bacteria}} 2NO_2.2H_2O + 2H^+ + \text{Energy}$$

$$2NO_2^- + O_2 \xrightarrow{\text{bacteria}} 2NO_3^- + \text{Energy}$$

3.3.2 POTASSIUM FERTILIZERS

Potassium containing fertilizers are KNO_3, KCl and K_2SO_4. Potassium is most conveniently expressed as K_2O (potash). Of these three mentioned, potassium chloride is the most common potassium fertilizer having potash in chloride form. It is obtained by the evaporation of dead sea by solar energy. During the process of evaporation, the concentration increases from 1.2 in the to 23% in liquor which crystallization in the pan. After refining about 97% pure KCl can be obtained. Potassium chloride contains about 63.17% potash and potassium content of about 52.44%, it is also cheaper than all the potassium fertilizer and so it is extensively used by farmers and cultivators and applied to a wide range of soils and crops except for tobacco and potato in which large doses of KCl affects the quantity of the product negatively (i.e. lowers the quantity). In these cases, K_2SO_4 is generally applied when large amount of potash are needed.

Potash sulphate (K_2SO_4) another potassium fertilizer contains 54% of potash when pure but contains 48-52% of potash of commercial. It is readily soluble in water and becomes available to crops almost immediately. Potassium sulphate can be prepared by any of these methods shown below:

1. The action of sulphuric acid on potassium chloride

$$2KCl + H_2SO_4 \rightarrow K_2SO_4 + 2HCl$$

2. By reaction of burkeite ($Na_2CO_3.2NaSO_4$) with KCl
3. By the reaction of potassium chloride and sulphur.
4. From langbemite, $K_2SO_4.2MgSO_4$, by ion exchange to remove magnesia. It is produced by dissolving langbemite in water and adding concentrated solution of $KCl.K_2SO_4$ is more soluble than $MgCl_2$ and is separated by fractional crystallization.

4.0 CONCLUSION

So far, we have discussed extensively the inorganic fertilizers which are often made synthetically and the methods of producing each of them. Classification of these fertilizers on different basis was also highlighted.

5.0 SUMMARY

- A fertilizer is any substance which is added to the soil in order to remove the deficiency of essential elements required for plant growth.
- Fertilizing a land is necessary to supplement nutrients that has been used up by plants.
- Solubility, availability and inexpensiveness of a substance makes it viable as a fertilizer. These are not the only requisites for a substance to serve as a fertilizer.
- On the basis of their agrochemical nature, fertilizers are classified as direct or indirect.

- Direct fertilizers are those which contain nutrient elements in the form of compounds which are directly assimilated by plants.
- Indirect fertilizers are those substances which are added to the soil in order to improve its chemical, mechanical or biological properties.
- Inorganic fertilizers can be made synthetically though they can be natural. This is so because the natural inorganic fertilizers are not sufficient to make the soil productive.
- Ammonium nitrate is the most important nitrogenous fertilizer and it contains 32-35% nitrogen. Three important methods are employed in producing ammonium nitrate namely: crystallization, flaking and prilling.
- Potassium chloride, the most common potassium fertilizer is obtained by the evaporation of dead sea brine by solar energy. It is also cheaper than all other potassium fertilizers.

6.0TUTOR MARKED ASSIGNMENTS

1. What does fertilizing a land stand to accomplish?
2. How are inorganic fertilizers classified?
3. Differentiate between granulated and powdered fertilizers.
4. Discuss the operations in the prilling of ammonium nitrate.

7.0 REFERENCES

m.wisegeek.com

Sharma, B. K. (2011). Industrial Chemistry (including Chemical Engineering) 16th ed. KRISHNA PRAKASHAN MEDIA (P) Ltd.

www.ctahr.hawaii.edu/oc/.../pnm12.pdf

www.basicsofgardening.com

UNIT TWO: PHOSPHATE FERTILIZERS

1.0 Introduction

Phosphorus intake is essential to the metabolism of both plants. It is an essential plant nutrient which is available in a native material (phosphate rock), though in low quantity. In order to enhance availability of phosphorus to plants, phosphate fertilizers are manufactured commercially. This unit will consider the manufacture of some phosphate fertilizers.

2.0 Objectives

At the end of this unit, you should be able to:

- describe how phosphoric acid is produced
- identify the various classes of phosphate
- explain how some phosphate fertilizers are manufactured

3.0 MAIN CONTENT

3.1 PHOSPHORIC ACID: PRODUCTION AND ITS PLACE IN THE MANUFACTURE OF PHOSPHATE FERTILIZERS

Phosphoric acid plays a vital role in the manufacture of phosphorus fertilizers as it is the stage in the production of most commercial phosphate fertilizers. It is by either of two processes: a dry or wet process.

In the dry process, rock phosphate is treated in an electric furnace. This treatment produces a very pure and more expensive phosphoric acid (it is usually called white or furnace acid) used primarily in the food and chemical industry. Fertilizers that use white phosphoric acid as the P source are generally more expensive because of the costly treatment process.

The wet process involves the treatment of rock phosphate with sulphuric acid. phosphoric acid by the wet process is produced through the following steps namely: (a) dissolution of phosphate rock in sulphuric acid (b) acidulated slurry is held until calcium sulphate crystals grow to adequate size, (c) calcium sulphate crystals are separated from the acid by filtration and (d) concentration of the acid to the desired level.

The phosphoric acid produced by either of these processes (wet or dry) is frequently heated, driving off water and producing a superphosphoric acid.

3.2 CLASSIFICATION OF PHOSPHORUS FERTILIZERS

Various phosphate fertilizers have different solubility in soil solutions and are therefore assimilated by plants differently. Accordingly to their solubility, they are classified as water soluble, available or insoluble. Simple and double (triple) superphosphates belong to the water soluble fertilizers. Precipitate, calcined phosphate fused phosphates and basic slag are the examples of available or insoluble fertilizers. These insoluble fertilizers contain non-readily available phosphorus salts which are soluble only in strong acids.

3.3 MANUFACTURE OF PHOSHATE FERTILIZERS

As earlier mentioned, manufacture of most commercial fertilizers begins with the production of phosphoric acid. The various steps used in the manufacture of various phosphate fertilizers are shown in the generalized diagram below:

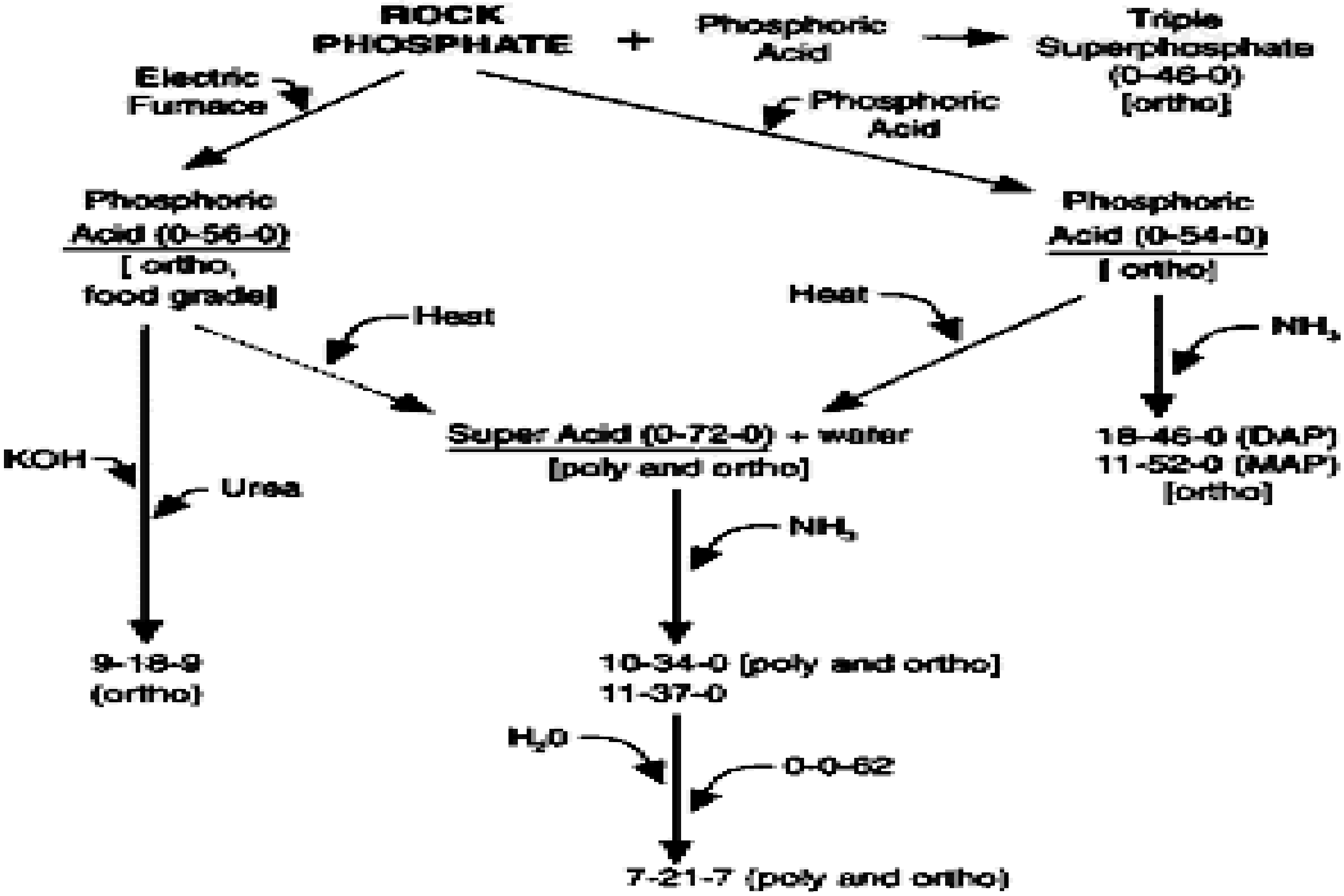

Fig 1: The process used in the manufacture of various phosphate fertilizers.

Let us briefly discuss the manufacture of some phosphate fertilizers.

3.3.1 NORMAL SUPER PHOSPHATE

Raw materials required for the manufacture of normal superphosphate are: a fairly high grade of phosphate that contains 20%, 33.5% or more available phosphorus pent-oxide (P_2O_5) and strong sulphuric acid. But what is a superphosphate? Soluble calcium phosphate prepared by treating rock phosphate with sulphuric acid is called superphosphate.

$Ca_3(PO_4)_2 + 2H_2SO_4 + 2H_2O \rightarrow Ca(H_2PO_4)_2 + 2CaSO_4.2H_2O$

Normal superphosphate is manufactured by mixing equal quantities of powdered phosphate rock and chamber acid into a cast iron mixer provided with a stirring mechanism. The mass is stirred for about 5 minutes and then allowed to remain for a day. The reaction is exothermic and as such temperature rises to about 100-110^{0}C. A mixture of fumes consisting of HF, SiF and CO_2 are evolved. These gases make the material porous. As the reaction continues the mixture stiffens and ultimately set to a solid mass. Successive charges from the mixer are introduced to the pits until it is full and then allowed to stand for some days. When it has become perfectly dry, ii is dug out of the pit and meanwhile the second pit is filled. The gases from the mixture and pits are washed in two successive towers. The resulting hydrofluoric acid solution is then neutrallised either by sodium carbonate or sodium fluoride and finally treated with washed sand to form hydroflousilicic acid. The latter is further neutrallised with sodium carbonate to form sodium silicoflouride (Ni_2SiF_6) or with magnesium to form magnesium silicoflouride ($MgSiF_6$). The product is used without further treatment other than breaking it up to the desired size. The main reaction is:

$$Ca_{10}(PO_4)_6F_2 + 7H_2SO_4 + 3H_2O \rightarrow 3CaH_4(PO_4)_2.3H_2O + 7CaSO_4 + 2HF$$

3.3.2 AMMONIUM PHOSPHATE

(a) **Monoammonium phosphate** is prepared by the action of sulphuric acid on a mixture of calcium phosphate and ammonium sulphate. It is formed along with a slurry of $CaSO_4$. The phosphate is separated from the slurry and crystallized to get fine crystals of monoammonium phosphate containing about 12% nitrogen and 50% P_2O_5

$$Ca_3(PO_4)_2 + (NH)_4SO_4 + 2H_2SO_4 \rightarrow 2NH_4H_2PO_4 + 3CaSO_4$$

Ammonium phosphate is readily soluble in water and so becomes available to crops readily. It is best suited for all crops and soils and is also slightly acidic in nature

(b) **Diammonium phosphate** another form of ammonium phosphate is prepared by a continuous process in which anhydrous ammonia gas and almost pure phosphoric acid are passed into saturated mother liquor containing monoammonium phosphate. The temperature is kept at about 60-70^{0}C and pH of about 6.0. The heat of reaction vapourises water from the liquor and crystals of pure ammonium phosphate are formed. These are centifused, washed and dried.

$$NH_4H_2PO_4 + NH_3 \rightarrow (NH_4)_2HPO_4$$

Other phosphates include calcium metaphosphate, bonemeal (suitable for acidic soils and long duration crops like sugar cane and fruit crop) and thermal phosphates (P_2O_5 content varies from 19-24%).

4.0 CONCLUSION

This unit has treated the general steps involved in the manufacture of phosphate fertilizers andalso the manufacture of some phosphates.

5.0 SUMMARY

- Phosphoric acid is essential in the production of phosphate fertilizers. It can be produced by either of these processes namely: the wet or the dry process.
- The wet process consists of four steps of which treatment of phosphate rock with sulphuric acid is involved. Acid produced by this process contains a variety of impurities which gives the acid its colour though these do not pose a problem in the production of dry fertilizers.
- A superphosphate is soluble calcium phosphate prepared by treating rock phosphate with sulphuric acid.

- The use to which phosphate compounds are put depends largely on their solubilities or availability to the plants. On this basis, phosphate products may be classified as: water soluble, water insoluble and citrate soluble products.
- Monoammoniumphosphate(MAP), a form of ammonium phosphate is prepared by the action of sulphuric acid on a mixture of calcium phosphate and ammonium sulphate.

6.0 TUTOR MARKED ASSIGNMENTS

1. How are phosphate products classified?
2. Describe the two processes by which phosphoric acid is produced.
3. Explain what is involved in the manufacture of normal superphosphate.

7.0 REFERENCES

Houston, E. C., Yates, L.D., Haunschild, R.L. (1955). Fertilizer Manufacture, Diammonium Phosphate Fertilizer From Wet Phosphoric Acid. *Journal of Agricultural Food Chemistry*, 3(1), pp 43-48
http://www.extension.umn.edu/agriculture/nutrient-management/phosphorus/understanding-phosphorus-fertilizers/
guichon-valves.com
Sharma, B. K. (2011). Industrial Chemistry (including Chemical Engineering) 16th ed. KRISHNA PRAKASHAN MEDIA (P) Ltd.
www.sunkarresources.com

MODULE 3: ELECTROCHEMISTRY AND THE MANUFACTURE OF SOME HEAVY INORGANIC CHEMICALS

UNIT ONE: Industrial electrochemistry

1.0 Introduction

The relationship between chemistry and electricity has been for a very long time going by Alessandro Volta's discovery in 1793. He discovered that electricity could be produced by placing two dissimilar metals on opposite sides of a moistened paper. Nicholson and Carlisle in 1800, showed that an electric current could decompose water into oxygen and hydrogen. They actually used Volta's primitive battery as a source of electricity. This chemistry-electricity relationship has become so important that the use of electricity as a means of bringing about chemical change has continued to play a central role in the development of chemistry. In the chemical industries, temperatures higher than 1500^oC can only be achieved on commercial scale by making use of electricity. Chemical industries not only generate power through electrical motors, but they also use electricity to give rise to elevated temperatures and to cause chemical change. Chemical reactions which take place as a result of the impact of electrical energy are called electrochemical reactions. This is the basis of electrochemistry in the industry.

2.0 Objectives

At the end of this unit, you should be able to:

- ✓ define electrochemistry
- ✓ mention the advantages of electrochemical methods
- ✓ identify the requirements of materials used as in industrial electrochemistry
- ✓ give a brief explanation of electrochemical terminologies
- ✓ discuss some applications of electrochemistry in the industry

3.0 Main content

3.1 Electrochemistry

It has been established that electricity causes chemical changes to occur. We therefore, define electrochemistry as the study of chemical reactions which take place at the interface of an electrode usually a semi-conductor, and an ionic conductor, the electrolyte. These reactions involve electric charges moving between the electrodes and the electrolyte. We can also define it as a science that deals with the relation of electricity to chemical changes and with the inter-conversion of chemical and electrical energy.

Over the years, electrochemical processes effected by direct electric current has been preferably used in the chemical industries than the usual chemical methods. This is due to it following advantages:

(i) Simplicity of the technological process

(ii) Raw materials and energy are utilized more completely

(iii) Several valuable products are obtained simultaneously

(iv) Highly pure products are formed.

Electrochemical methods, however, does have a disadvantage which is that there is a large consumption of electric power.

3.2 Basic Electrochemical Terms

For a clearer understanding of electrochemistry, you must know some of the terminologies used and what they mean or stand for. You may have across these terms in your study of chemistry but let's just consider them as it applies to this course.

(i) Electrolysis: This refers to the decomposition of a substance by an electric current. This actually is the main stay of electrochemical industries. "The father of electrochemistry" Micheal Faraday stipulated two laws from his studies to govern electrolysis. These laws are stated thus:

(a) The weights of substances formed at an electrode during electrolysis are directly proportional to the quantity of electricity that passes through the electrolyte.

(b) The weights of different substances formed by the passage of the same quantity of electricity are proportional to the equivalent weight of each substance.

Note: The equivalent weight of a substance is defined as the molar mass, divided by the number of electrons required to oxidize or reduce each unit of the substance. For example, one mole of V^{3+} corresponds to three equivalents of this species and will thus require three (3) Faradays of charge to deposit it as metallic vanadium.One mole of electric charge, 1F = 96,500 coulombs.

The industrial application of electrolysis will be discussed later in this unit and the units to follow.

(ii) Electrode: An electrode is an electrical conductor used to make contact with a non-metallic part of a circuit. It is a conductor through which electricity enters or leaves an electrolyte. For a material to serve as an electrode, it must have these important requirements:

- It should have high electrical conductivity
- It should be stable to corrosion during passage of current or interruptions.
- It should provide a high current efficiency of the needed product.
- It should possess adequate mechanical strength and processibility during the manufacture of desired shapes and sizes
- It should be available and have reasonable cost

(iii) Anode: This is the positively charged electrode and it attracts electrons or anions. Oxidation occurs at the anode.

(iv) Cathode: This is the negatively charged electrode which attracts cations or positive charge. The cathode is the site of reduction.

(v) Electrolyte: An electrolyte is a substance that ionizes when dissolved in suitable ionizing solvents such as water. This includes most soluble salts, acids and bases. Some gases, such as HCl, under conditions of high temperature or low pressure can also function as electrolytes.

3.3 Industrial applications of electrochemistry

Here we shall be considering the use/ role of electrolysis in the industry. Electrolysis has been used widely to produce substances such as aluminum, sodium, fluorine etc. Metals can be obtained from aqueous solution of their salts or from melts by electrolysis. However not all electrolytic processes results in metal deposition. Considering electrolysis of aqueous solutions, it can be with or without metal deposition. Let us briefly explain these electrolytic processes.

1.Electrolysis of aqueous solutions with metal deposition: There are two important methods of recovering metals from aqueous solutions of their salts by electrolysis. The first method consists in electrolysis of solutions obtained after leaching of the corresponding metal from ores or concentrates with the use of insoluble anodes. This method is applicable to metals such as Zn, Cu, Pb, Cd, Mn, Cr,and Fe. The second method consists in the electrorefining of metals. Here, the crude metal to be refined acts as anode and pure metal is deposited at the cathode. During electrorefining of crude metal, noble metals such as gold, silver and platinum are recovered as by-products.

2. Electrolysis of aqueous solutions without metal deposition: This is applicable to aqueous alkali solutions during electrolysis of aqueous alkali solutions. During of alkali metal chlorides, caustic alkalis and hydrogen are formed at the cathode, and chlorine gas is evolved at the anode.

3. Electrolysis of Melts: This process in used to produce substances which cannot be produced by the electrolysis of aqueous solutions. Zirconium, Thorium, some rare and rare earth metals can be obtained from melts by electrolysis. Aluminium also is produced from a molten mixture of cryolite and alumina by electrolysis. This will be discussed in details later. There are certain metals which cannot be obtained at a solid cathode by electrolysis, though most metals are obtained at the solid cathode. In such a situation, the electrolysis of the melt with the liquid cathode is used. An alloy of the metal of interest with the liquid cathode is used as the cathode, and the metal is then distilled in vacuum from the liquid cathode having a higher boiling point or the metal of the liquid cathode having a lower boiling point is distilled off in vacuum.

Now, haven discussed these electrolytic processes, let us see some of the applications of industrial electrochemistry. Electrochemistry has been found useful in the production of certain heavy inorganic chemicals. We shall consider these in the next unit. So, we will concern ourselves with the production of some metals by electrolysis.

3.3.1. Production of Aluminum

Aluminum was first obtained by heating aluminum chloride with a potassium mercury amalgam. However, the entire world's production of aluminum is obtained by the electrolysis of a solution of alumina in fused cryolite (Na_3AlF_6) based on the discovery made by Hall and Heroult.

The manufacture of aluminum consists of three steps. The first is the purification of bauxite. The second step is the electrolytic reduction of pure bauxite or alumina in a bath of fused cryolite (Na_3AlF_6) which acts as a flux. The third step is the purification of aluminum formed as a result of electrolytic reduction of pure bauxite.

Step 1: Purification of Bauxite

Bauxite is often associated with Fe_2O_3, S_iO_2 and T_iO_2. The impurities are removed by either of these three methods namely: (1) Baeyer's process (2) Serpeck's process and (3) Hall's process. The Baeyer's process is the most popular hence we will discuss what it involves.

The Baeyer's process: Bauxite mineral particularly that containing excess of iron oxide as impurity (red bauxite) is first crushed in jaw crushers and them wet ground to 100 mesh. It is then mixed with concentrated solution of caustic soda, (41%) of specific gravity 1.45 in steam jacketed autoclave digesters and digested for about 2hours under 4.5 atmospheric pressure at a temperature of about 150-160^oC. As a result, aluminum oxide passes into solution as sodium aluminates and partly as colloidal alumina, while oxides of iron, titanium and silica remain unaffected.

$$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$$

The slurry is washed in a series of counter current thickeners and the impurities are removed by filtration using rotary filters. The filtrate containing sodium aluminate is hydrolyzed to precipitate aluminum hydroxide by cooling. The precipitated slurry is fed to another set of counter current thickeners, where all the aluminum is removed.

$NaAlO_2 + 2H_2O \rightarrow Al(OH)_3 + NaOH$

The precipitate of Al $(OH)_3$ is washed with water and then calcined in tubular rotary kilns with fire bricks at about 1200 – 1300^0C, whereby alumina is obtained. The resulting alumina, which contains about 99.5% Al_2O_3 is cooled and slipped to the reduction plant. The dilute caustic soda solution from the second set of thickeners is concentrated in a multiple effect evaporator system and recycled to be used again.

$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$

*The Serpecks process is used only when the bauxite mineral contains excess of silica as impurity.

Step 2: Electrolytic. Reduction of Alumina

Electrolysing pure alumina in a flux of molten cryolite and CaF_2 yields aluminum. Pure alumina is dissolved in fused cryolite and electrolysed in electrolytic cells. Each cell is open at the top and first lined with fire bricks and then with gas carbon, coke or anthracite coal. This lining of carbon or coke is built in the form of a layer and acts as cathode. A number of carbon rods made of petroleum coke, attached to copper clamps and dipped in the fused electrolyte serves as the anodes.

The molten bath which contains 5-10% Al_2O_3 in 90-95% flux containing 64% cryolite and 36% CaF_2 is made by putting solid ingredients of the flux in the cell and then melting the flux by strucking an arc between the lining and carbon rods as a result cryolite undergoes melting. The anodes are then raised and a calculated amount of pure alumina is spread over the frozen surface. Some coke is also thrown in to cover the surface of the electrolyte. The ensuing reaction is a combination of oxygen liberated from alumina, with the carbon of the anodes, which are consumed with the formation of CO and CO_2. These gases are allowed to escape through the outlets and aluminum is deposited at the cathode along the bottom of the bath, from where it is tapped off.

Step 3: Electrolytic refining or purification of Aluminium

This is carried out by Hoope's process. The molten aluminium from the electrolytic reduction cell is carried to refinery furnace which consists of three fused layers of different specific gravities. The layers are:

- The bottom layer of copper, aluminum and silicon which acts as anode.
- The middle layer consisting of cryolite and barium fluoride and acts as the electrolyte
- The upper layer of pure molten aluminum which acts as the cathode.

When an electric current is passed, aluminum from the middle layer passes into the top layer and an equivalent amount from the base layer passes into the middle layer. The aluminium copper alloy on the bottom of the cell can be replenished with low purity alumina. The high purity (99.9% pure) aluminum floats to the top and is drained off under CO-CO_2 atmosphere.

3.3.2. Production of Magnesium

Magnesium, a silvery white metal which gets dull easily on exposure to air is extracted or produced by either of the following processes:

i. The electrolysis of fused anhydrous carnalite, KCl, $MgCl_2.6\ H_2O$
ii. The electrolysis of fused anhydrous $MgCl_2$ containing fused $CaCl_2$ and NaCl.
iii. Carbothermal process (Reduction of MgO by carbon or calcium carbide)

iv. Pidgeon or Silico Thermal process (Reduction of MgO with silicon).

From these four processes, it is evident that magnesium is either obtained from $MgCl_2$ or MgO. The cheapest and the best method of manufacturing magnesium is by the electrolytic process. Magnesium is obtained by the electrolysis of fused $MgCl_2$. The dehydrated magnesium chloride obtained from sea water is fused with anhydrous $CaCl_2$ and sodium chloride so that the mixture contains 25% $MgCl_2$, 15% $CaCl_2$ and 60% NaCl. The presence of sodium chloride decreases the melting point and increases the conductivity. The electrolysis in carried out at 710^oC, which is greater than the melting point of magnesium (651^oC).

Two types of cells have been used in the manufacture of magnesium by the electrolysis of fused $MgCl_2$. Let's describe these.

One of the cell is known as Dow electrolytic cell. The cells are large rectangular ceramic covered steel tanks, 5 feet wide, 11 feet long at 6 feet deep and hold about 10 tonnes of fused magnesium choride and salts. The internal parts of the cell act as the cathode and graphite rods suspended vertically in the top of the cell act as anodes. The temperature of the cell is maintained at about 710^oC by the electric current and by external heat supplied by gas fired outside furnaces. The molten magnesium liberated at the cathode rises up to the bath surface and tapped off from time to time. The chlorine liberated as a byproduct is separately reacted with hydrogen to form HCl. Magnesium obtained by this method is 99% pure. It is further refined by subliming at 600^0C under a pressure of 1mmHg.

The other type of cell is a close top smaller cell made of steel. It consists of a centrally placed graphite electrode surrounded by a perforated porcelain tube. The inner surface of the steel cell acts as the cathode and vertical graphite rod as the anode. The bottom and lower sides of the cell are lined with ceramic material. A large number of such cells are joined in series. As a result of the passage of electricity, electrolysis takes place and Cl_2 is liberated at the anode. The magnesium metal floats on the surface of the bath and protected from oxidation by circulating coal gas. The chlorine gas is collected from the top and molten metal is also collected from the top.

Manufacture of magnesium electrolysis of MgO

Magnesium can also be prepared commercially by the electrolysis of magnesium oxide obtained from the calcination of the ore, magnesite.

$$MgCO3 \rightarrow MgO + CO2.$$

Magnesia (MgO) is dissolved in a mixture of fused fluorides of magnesium, barium and sodium in a steel tank at about 900 – 950^0C. The steel tank acts as the electrolytic cell in which cast iron cathodes project into the electrolyte from below and the carbon anodes are suspended from above. On passing an electric current, molten electrolyte forms a solid crust at the surface of the molten mass and the molten magnesium, being lighter, rises up and collects below the crust. The magnesium is thus protected from being oxidized.

4.0 Conclusion

In this unit, we discussed the advantages of electrochemistry, its place in the industry and also its use in the manufacture of some metals

5.0 Summary

- Electrochemistry is the science that deals with the relation of electricity to chemical change and with the interconversion of chemical and electrical energy.

- Electrochemical methods have certain advantages over the usual chemical methods. However, it does have a disadvantage which is that there is a large consumption of electric power.
- The equivalent weight of a substance is defined as the molar mass, divided by the number of electrons required to oxidize or reduce each unit of the substance.
- A material which is to serve as an electrode must among other requirements must have high electrical conductivity and should be stable to corrosion during passage of current or interruptions.
- There are two possibilities when aqueous solutions are electrolyzed which are: a metal will be deposited and no metal deposition.
- The manufacture of aluminum consists of three steps. First, the purification of bauxite; second is electrolytic reduction of pure bauxite and the third step is the purification of the aluminum formed.
- The Baeyer's process, Serpeck's process and Hall's process are employed in the purification of bauxite .
- The electrolytic refining of aluminum is carried out by the Hoope's process.
- Magnesium metal can be obtained by the electrolysis of either magnesium chloride or magnesia .

6.0 Tutor Marked Assignment

1. List the advantages of electrochemical methods.
2. Discuss the Baeyer's process for the purification of bauxite.
3. Explain the two methods of recovering metals from aqueous solutions of their salts.
4. Describe the cells used in the electrolytic manufacture of magnesium from magnesium chloride.

7.0 References/further reading

Christopher, M.A. Brett and Ana M.O. Brett. Electrochemistry: Principles, Methods and Applications. Oxford University Press.

Morris Grotheer, Richard Alkire and Richard Varjian (2006).Industrial Electrolysis and Electrochemical Engineering.The Electrochemical Society Interface pp 52- 54.

http: //www.trentu.ca/chemistry/oldham/echem.html

http://i.word.com/idictionary/electrochemistry

http://chemwiki.ucdavis.edu/Analytical-chemistry/Electrochemistry/Basics-of-Electrochemistry.

Sharma, B. K. (2011). Industrial Chemistry (including Chemical Engineering) 16th ed. KRISHNA PRAKASHAN MEDIA (P) Ltd.

UNIT 2: MANUFACTURE OF SOME HEAVY INORGANIC CHEMICALS: CHLOR-ALKALI

1.0 Introduction
2.0 Objective
3.0 Main content
3.1 The chlor –alkali processes
3.2 The chlor –akali electrolytic processes
    3.2.1 The mercury cell process
    3.2.2 The diaphragm electrolytic cell process
    3.2.3 The membrane cell process
3.3 Manufacture of sodium carbonate
4.0 Conclusion
5.0 Summary
6.0 Tutor marked assignments

7.0 References

1.0 INTRODUCTION

The chlor–alkali industry is the industry that produces chlorine and alkali, sodium hydroxide (caustic soda), sodium carbonate (soda ash) and its derivatives and compounds based on calcium oxide (lime). These are heavy inorganic chemicals. This is so because they are manufactured and used on a large scale. The basic raw material for the manufacture of the chlor–alkali chemicals is salt (common salt). In this unit, we shall be considering the general or basic processes involved in the manufacture of the chlor-alkali compounds.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- state the basic principle in the electrolysis of sodium chloride solution
- list or mention the processes involved in the production of chlorine and caustic soda.
- explain the cell processes applied in the chlor–alkali industry
- differentiate between the cell processes
- discuss how soda ash is manufactured.

3.0 MAIN CONTENT

3.1 THE CHLOR–ALKALI PROCESSES

Caustic soda and chlorine are produced almost entirely as co-products by the electrolysis of brine. There are three basic processes for the electrolysis production of chlorine with the nature of the cathode reaction dependent on the specific process. Each process represents a different method of keeping the chlorine produced at the anode separate from the caustic soda and hydrogen produced at the cathode. The three processes are the diaphragm cell process, the mercury cell process, and the membrane cell process.

The basic principle in the electrolysis of a sodium chloride solution is as follows:

i. At the anode, chloride ions are oxidized and chlorine (Cl_2) is formed.

ii. At the cathode:

- In the mercury process, a sodium /mercury amalgam is formed ad hydrogen and hydroxide ions are formed by the reaction of the sodium in the amalgam with water in the denuder.
- In the membrane and diaphragm cells, water decomposes to form hydrogen and hydroxide ions at the cathode.

For all the processes, the dissolving of salt is

$$NaCl \rightarrow Na^+ + Cl^-$$

The anode reaction for all the processes is:

$$2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^-$$

The cathode reaction is:

$$2Na^+_{(aq)} + 2H_2O + 2e^- \rightarrow H_{2(g)} + 2Na^+_{(aq)} + 2OH^-_{(aq)}$$

The overall reaction is:

$$2Na^+_{(aq)} + 2Cl_{(aq)} + 2H_2O \rightarrow 2Na^+_{(aq)} + 2OH^-_{(aq)} + Cl_{2(g)} + H_{2(g)}$$

Haven laid a basis for a discussion of the three processes, let’s discuss what is involved in each of the electrolysis cell processes.

3.2 The chlor – alkali electrolytic processes

It was mentioned earlier that there are three electrolytic cell processes involved in the production of chlorine, caustic soda along with hydrogen. We shall now consider them one after the other and possibly compare them.

3.2.1 The mercury cell process:

The mercury cell process which has been in use in Europe since 1892 involve two “cells” (the electrolyser ad the decomposer or denuder). In the primary electrolyser (or brine cell),purified and saturated brine containing approximately 25% sodium chloride flows through an elongated trough that is slightly inclined from the horizontal. At the bottom of this trough, a shallow film of mercury flows along the brine cell concurrently with the brine. Closely spaced above the cathode assembly is suspended.

With the passage of electric current through the cell, the brine passing through the narrow space between the electrodes decomposes thereby liberating chlorine gas at the anode and metallic sodium at the cathode. The chlorine gas is accumulated above the anode assembly and discharged to the purification process.

As the sodium metal is liberated at the surface of the mercury cathode, it immediately forms an amalgam. The liquid amalgam flows from the electrolytic cell to a separate reactor, called the decomposer, where it reacts with water in the presence of a graphite catalyst to form sodium hydroxide and hydrogen gas. The sodium – free mercury is fed back into the electrolyser and re –used.

An overall summary of the reactions that take place in mercury cell is as shown below:

Reaction in the electrolyser:

$$2Na^+ + 2Cl^- + 2Hg \rightarrow \underset{\text{amalgam}}{2Na\text{-}Hg} + Cl_{2(g)}$$

Reaction in the decomposer:

$$2Na\text{-}Hg + 2H_2O \rightarrow 2Na^+ + 2OH^- + H_{2(g)} + 2Hg$$

The mercury cell process has an advantage over diaphragm and membrane cell which is that it produces a chlorine gas with nearly no oxygen, and a 50% caustic soda solution. However, this process gives rise to environmental releases of mercury. The cells also operate at a higher voltage than diaphragm and membrane cells and as such more energy is used.

3.2.2 The diaphragm electrolytic cell process

The diaphragm cell was the first commercial process used to produce chlorine and caustic soda from brine. It differs from the mercury cell process in that all reactions take place within one cell and the cell effluent contains both salt and caustic soda. A diaphragm is employed to separate the chlorine liberated at the anode, and the hydrogen and caustic soda produced directly at the cathode. Without the diaphragm to isolate them, the hydrogen and chlorine would react to form sodium hypochlorite ($NaClO$), which in turn reacts further to produce sodium chlorate ($NaClO_3$).

The diaphragm is usually made of asbestos and separates the feed brine (anolyte) from the caustic–containing catholyte. Purified brine which enters the anode compartment percolates into the cathode chamber through the diaphragm.

How is the diaphragm electrolytic cell used in the manufacture of caustic soda and chlorine?

First of all the brine is purified as commercial sodium chloride usually contains impurities such as calcium, magnesium and iron compounds. These impunities are removed by adding lime and soda ash which precipitates the impurities as insoluble carbonates and hydroxides. The clear brine is neutralized with hydrochloric acid ad the purified brine is allowed to settle.

Next, the brine is electrolyzed in the diaphragm cells. During electrolysis, sodium ions move to the cathode, where H^+ ions ad OH^- ions are also formed as a result of reduction of water. The chloride ions on the other hand move towards the anode where they are liberated as chlorine gas. The reaction is as shown below:

$$NaCl \rightarrow Na^+ + Cl^-$$
$$H_2O \rightarrow H^+ + OH^-$$

At the cathode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$
$$Na^+ + OH^- \rightarrow NaOH_{(aq)}$$

At the anode:

$$Cl^- - e^- \rightarrow Cl$$
$$Cl + Cl \rightarrow Cl_{2\,(g)}$$

The caustic soda solution obtained from the cell contains about 10-15% caustic soda and some unconverted NaCl. Therefore to separate the two, the weak caustic soda is first concentrated to 50% in a double or triple effect evaporator ad the NaCl which is less soluble particularly in the presence of caustic soda is thus separated and used again to make more brine.

Are there advantages associated with the use of diaphragm cells? Of course the diaphragm cells have the advantage of:

1. operating at a lower voltage than mercury cells,
2. operating with pure brine than required by membrane cells.

3.2.3 The membrane cell process

The membrane electrolytic process is the most promising and fast developing technique for the production of chlor-alkali. However , the replacement of existing mercury and diaphragm cells with membrane cells is taking place at a much slower rate because of the long lifetime of the former and the high capital costs of replacement.

In this process, the anode and cathode are separated by a water impermeable ion-conducting membrane. The brine solution flows through the anode compartment where chloride ions are oxidized to chlorine gas. The sodium ions migrate through the membrane to the cathode compartment which contains flowing caustic soda solution. The demineralized water added to the catholyte circuit is hydrolyzed, releasing hydrogen gas and hydroxide ions. The sodium and hydroxide ions combine to produce caustic soda which is typically brought to a concentration of 32-35% by recirculating the solution before it is discharged from the cell.

The membrane prevents the migration of chloride ions from the anode compartment to the cathode compartment; therefore, the caustic soda solution produced does not contain sodium chloride as in the diaphragm cell process. If the caustic soda is required to reach a concentration of 50%, the caustic liquor produced has to be concentrated by evaporation using steam.

The membranes used in the chlor-alkali industry are commonly made of perfluorinated polymers. The cathodes material used in the membrane cells is either stainless steel or nickel. The cathodes are often coated with a catalyst that is more stable than the substrate and that increases surface area and reduces over-voltage. The anodes used are metals.

In comparison with the other processes, membrane cells have the advantage of producing a very pure caustic soda solution and of using less electricity. The membrane process does not use highly toxic materials like mercury and asbestos.

.The membrane processes have the following disadvantages:

1. The caustic soda produced may need to be evaporated to be evaporated to increase concentration
2. For certain applications, the chlorine gas produced needs to be processed to remove oxygen.
3. The brine entering the membrane cell must be of very high purity, hence it often requires costly additional purification steps prior to electrolysis.

A schematic presentation of a membrane cell process is shown in fig 1 below.

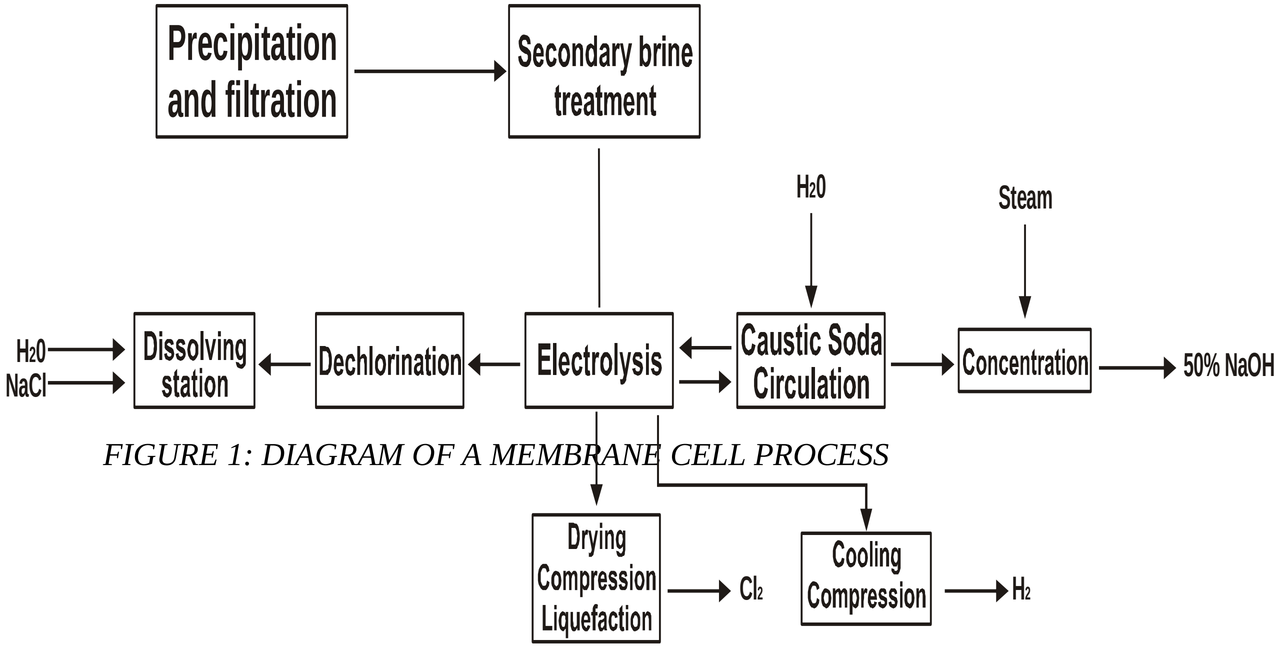

FIGURE 1: DIAGRAM OF A MEMBRANE CELL PROCESS

3.3 Manufacture of sodium carbonate

Sodium carbonate is either found naturally or is manufactured from common salt (NaCl) and limestone. There are two main sources of sodium carbonate:

1. From salt and calcium carbonate through the ammonia soda (Solvay) process.
2. Form sodium carbonate and hydrogen carbonate ores (trona and nacholite)

On industrial scale, sodium carbonate is prepared by the Solvay process. This process involves different stages which are as follows:

Stage 1: Ammoniation of purified brine:

In this stage, saturated or concentrated brine is allowed to flow down an ammoniating tower. This tower is fitted with mushroom shaped baffles. These baffles control the flow of brine and ensure proper mixing ad saturation of ammonia. Ammonia gas is absorbed in concentrated brine to give a solution containing both sodium chloride and ammonia.

Stage 2: Carbonation of ammoniated brine

Here, ammoniated brine is allowed to trickle down a carbonating tower known as the Solvay tower. The tower is also fitted with baffle plates. Brine is mixed with carbon dioxide gas, produced by heating limestone in a separate chamber called “kiln”.

$$CaCO_3 \rightarrow CaO + CO_2$$

The baffle plates ensure the flow of solution and breaks up carbon dioxide into small bubbles to produce good conditions for reaction.

What chemical reactions takes place in the Solvay tower?

1. CO_2 reacts with ammonia to form ammonium carbonate.

$$2NH_3 + CO_2 + H_2O \longrightarrow (NH_4)_2CO_3$$

2. Ammonium carbonate further reacts with CO_{2n} to form ammonium bicarbonate.

$$(NH4)_2CO_3 + CO_2 + H_2O \longrightarrow 2NH_4HCO_3$$

3. Ammonium bicarbonate then react with NaCl to form sodium bicarbonate.

$$NH_4HCO_3 + NaClNaHCO_3 + NH_4Cl$$

These reactions are exothermic in nature, therefore the solubility of NaHCO3 increases. To counteract this, lower part of the Solvay tower is cooled and the precipitate of $NaHCO_3$ is separated by vacuum filtration and washed to remove ammonium salts.

Stage 3: Conversion of $NaHCO_3$ to Na_2CO_3

In this stage, dry sodium bicarbonate is heated in a rotary furnace called “Calciner’ to give anhydrous sodium carbonate. The carbon dioxide is re-circulated to the carbonation tower.

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$$

Stage 4: Ammonia recovery or regeneration process

When limestone is heated, CaO is obtained along with CO_2. CaO is then treated with water to form quicklime, $Ca(OH)_2$. Quicklime is then heated with NH_4Cl to form NH_3 and a by-product, calcium chloride. Ammonia thus produced is used again in this process.

$$CaO + H_2O \rightarrow Ca(OH)_2$$

$$2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2NH_3 + 2H_2O.$$

4.0 Conclusion

So far, we have discussed in details how the chlor–alkali compounds are manufactured industrially.

5.0 Summary

- The chlor-alkali chemicals includes chlorine, soda ash and caustic soda.
- In the manufacture of chlorine, caustic soda along with hydrogen are produced concurrently.
- Three electrolytic cells are generally in use in the chlor-alkali industry. These are: the mercury cell: the diaphragm cell and the membrane cell.
- The membrane electrolytic cell is more advantageous than the other cells in that it uses less electricity ad produces very pure caustic soda solution. It does not use highly toxic materials like mercury ad asbestos.
- The Solvay process is the process employed in the industrial preparation of sodium carbonate.
- The baffles in the ammoniating and carbonating towers are used to ensure flow of solution in each of the towers.

6.0 Tutor Marked Assignments

1. What is the basic principle involved in the electrolysis of brine?
2. Differentiate between the three electrolytic cells used in the chlor-alkali industry.
3. Show with chemical equations, how sodium carbonate is produced on an industrial scale.

7.0 References

Kirk–Othmer.(1991). Alkali and chlorine products, chlorine ad sodium hydroxide.Encyclopedia of Chemical Technology, 4th edition, Vol. 1, 938-1025.John Wiley & Sons Inc.

VCH Verlagsgesellschaft mbh,D-6940 Weinhein. Chlorine.Ullmann's Encyclopedia of Industrical Chemistry, Vol. A6, 399-481.

James, A. K. (1997). Riegel's Handbook of Industrial Chemistry. 9th edition.409-425.

www.citycollegiate.com /sblock2.htm

www.eurochlor.org/the–chlorine-universe/thechlor-alkali-industry-in-europe.aspx.

UNIT THREE: MANUFACTURE OF SOME HEAVY INORGANIC CHEMICALS: SULFURIC ACID AND SULFATE.

6.0 Tutor Marked Assignments
7.0 References

1.0 Introduction

Sulfuric acid is another heavy inorganic chemical which is produced and used in a large scale. It has long been the chemical that is manufactured in the largest quantities on a world scale. Sulfuric acid is manufactured from elemental sulfur. This element is obtained by mining sulfide- containing ores or in very pure form from underground deposits by the Frasch process. However, the large-scale consumption of petroleum and natural gas has changed the situation. This is so since sulfur occurs as an impurity on most fossil fuels and must be removed before the fuels are processed. Thus, these fuels have become the main source of sulphur. Sulphuric acid is a good catalyst for many reactions and is also used to produce sulfates, such as ammonium sulfate, sodium sulfate and aluminum sulfate. We shall consider how sulfuric acid is produced and also the manufacture of some sulfates.

2.0 Objectives

At the end of this unit, you should be able to:

- list the steps involved in the preparation of sulfuric acid
- explain in details the contact process
- explain or write briefly on the manufacture of sulfates like aluminum sulfate.

3.0 Main Content

3.1 Manufacture OfSulphuric Acid

There are two major processes used in the production of sulphuric acid. These are the lead- chamber process and the contact process. The lead- chamber process is the older of the two processes. However, all over the world, sulphuric acid is now produced by the contact process. Let’s just talk about the Lead-chamber process briefly.

The lead-chamber process yields an aqueous sulphuric acid containing 62% to 78% sulphuric acid. The main principle behind the process, is that moist $S0_2$ (sulphur dioxide) in presence of nitrogenous oxides (active catalyst) is oxidized to sulphur trioxide (SO_3) with the oxygen present in air. Sulphur trioxide is made to react with water to produce sulphuric acid. The reaction is as shown below:

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{\text{catalyst}} 2SO_{3(g)}$$

$$SO_{3(g)} + H_2O_{(l)} \longrightarrow H_2S0_{4(l)}$$

The Contact Process

Preparation of sulphuric acid by contact process is based on the catalytic oxidation of SO_2 to $S0_3$. The following steps are involved in the preparation of sulphuric acid.

1. Preparation of $S0_2$
2. Purification of SO_2
3. Oxidation of SO_2
4. Absorption of SO_3
5. Dilution Oleum.

What does each of these steps involve? Let’s see

1. Preparation of SO_2

Sulphur dioxide is obtained by burning sulphur,

$$S_{(s)} + O_{2(g)} \longrightarrow SO_{2\,(g)}$$

by roasting pyrite (iron sulphide) or other metal sulphides

$$4FeS_{(g)} + 7O_{2(g)} \longrightarrow 2Fe_2O_{3(s)} + 4SO_{2(g)}$$

or by burning hydrogen sulphide,

$$H_2S_{(g)} + O_{2(g)} \longrightarrow SO_{2(g)} + H_2O_{(g)}$$

2. Purification of SO_2

SO_2 contains a number of impurities such as dust particles, arsenous oxides, vapors, etc. These impurities must be removed to avoid catalyst poisoning. How is this achieved?

SO_2 is first passed through the dust chamber where steam is spread over the gas to remove dust particles, which settle down. $Fe(OH)_3$ is also sprayed over to remove oxides of Arsenic. SO_2 is then passed through a washing tower after cooling. The gas is sprayed by water to remove any other soluble impurities. The gas is now dried by passing through dying tower where concentrated H_2SO_4 (dehydrating agent) is sprayed. H_2SO_4 removes moisture from $S0_2$.

To ensure that the gas is free from Arsenic oxide (As_2O_3), a poison for the catalyst, it is passed through a test box where a strong beam of light is thrown against the gas. If there is no scattering of light in the box, it is an indication that the gas is free of As_2O_3.

3. Oxidation of SO_2 to SO_3

This takes place in the contact tower where the catalyst, vanadium (v) oxide, V_2O_5 is filled in different pipes. Here, SO_2 reacts with air (O_2) to produce SO_3. Under this condition, 98% SO_2 is converted into SO_3.

4. Absorption of SO_3 in H_2SO_4

SO_3 is not directly passed in water, because a dense fog of minute particles of H_2SO_4 is produced. Therefore, it is dissolved in concentrated H_2SO_4 to form pyrosulphuric acid (oleum).

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7 \text{ (Oleum)}$$

5. Dilution of Oleum

Oleum is now diluted with water to form H_2SO_4 of required concentration.

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

Pure sulphuric acid is produced by this process.

3.2 Manufacture of Sulfates

As earlier mentioned, sulphuric acid is used in the production of sulphtates such as aluminum sulphate, ammonium sulphate, sodium sulphate, etc. The manufacture of ammonium sulphate has been discussed under the unit “Inorganic Fertilizers”. Here we will consider the manufacture of aluminum sulphate.

Aluminum sulphate, $Al_2(SO_4)_3$ is commonly applied in the pulp and paper industry and in the purification of water. Alum is manufactured in a simple two- step process from aluminum trihydrate and sulphuric acid according to the following reaction:

$$2Al(OH)_3 + 3H_2SO_4 + 8H_2O \rightarrow Al_2(SO_4)_3.14H_2O$$

Step 1: Reacting the Raw Materials.

The aluminum trihydrate is transported and stored in one tonne bags. Each bag is carried by hoist to the feed hopper, where it is opened and conveyed to the reaction tank. The reaction water, trihydrate and sulphuric acid batch is stirred for a period of time with water vapour exiting through the stack.

Step 2: Making the Final Product

After the reaction period, either liquid or solid alum is made. If liquid, the concentrated batch is run into the dilution tank filled with dilution water where it cools over time. The liquid alum is then filtered with pumped to storage.

If solid is made, the concentrated alum is run into the casting pans where it sets, aided by fan cooling. The pans are forklifted to storage racks and from there, they are taken to the crushing plant and dropped into a hopper. The pieces are broken further by a large kibbler followed by a small kibbler and then screened. The screened alum is rotary crushed and further screened to either return to the rotary crusher or be bagged as ground product. Dust is continually collected through an extraction system and is sold as product.

4.0 CONCLUSION

This unit dealt with the manufacture of sulphuric acid by two major methods and also the use of sulphuric acid in the manufacture of aluminum sulphate.

5.0 SUMMARY

- Sulphuric acid is processed by two major processes namely: the lead- chamber process and the Contact process.
- For a purer H_2SO_4 ,the contact process is widely used.
- Nitrogenous oxides are used as catalyst in the lead-chamber process while vanadium (v) oxide is used as catalyst in the contact process.
- To ensure SO_2 is free from catalyst poison (arsenic oxide), ferric hydroxide is passed to remove the poison.
- The catalyst,V_2O_5 is used to increase the rate of reaction in the contact tower.

6.0 TUTOR MARKED ASSIGNMENT

1. What is the difference between the lead-chamber process and the contact process for the manufacture of sulphuric acid?
2. Mention and explain the steps involved in the contact process.

7.0 REFERENCES

www.citycollegiate.com/Sulphuric acid_ acid Ixa.htm
www.inclusive-science-engineering.com
en.wikipedia.org/wiki/contact-process
nzc.org.nz/chem processes/production/1F.pdf

UNIT FOUR: MANUFACTURE OF HEAVY INORGARNIC CHEMICALS: NITRIC ACID

1.0 Introduction

Nitric acid also known as aqua fortis and spirit of inter, is a highly corrosive mineral acid. It is the most important and useful oxyacid of nitrogen. Nitric acid is of great commercial importance in the manufacture of various fertilizers, explosives, fibres, dyestuffs and plastics. A growing and very important use of nitric acid is the replacement of sulfuric acid in the acidulation of phosphate rock. Pure nitric acid is usually colorless but the impure form tend to acquire a yellow cast due to decomposition into oxides of nitrogen and water. Nitric acid is completely miscible with water. This solution has a boiling temperature of 120.5^oC at 1atm. Commercially available nitric acid is an azeotrope with water at a concentration of 68% HNO_3, which is the ordinary concentrated nitric acid. This unit is meant to discuss the various ways of manufacturing this highly important heavy chemical and to highlight its uses.

2.0 Objectives

After the consideration of this unit, you should be able to:

- identify the various methods of manufacturing nitric acid.
- explain what each method involves
- differentiate between each of the methods.

3.0 Main Content

3.1 Manufacture of Nitric Acid

Nitric acid is manufactured on an industrial scale by three methods. These are:

1. From Chile saltpetre or nitrate
2. Brikland and Eyde process or the arc process
3. From oxidation of ammonia or the Ostwald's process

We shall now discuss each of these methods and what it involves.

3.1.1. Manufacture of nitric acid from Chile Saltpetre

This has been the method of preparation of nitric acid from early days. Nitric acid has been prepared from sodium nitrate extracted from Chile saltepetre (this contains 35-60% $NaNO_3$, some KNO_3 and NaCl) or nitre (potassium nitrate). The chilesaltpetre is lexiviated with water and then crystallized to get crystals containing about 95% $NaNO_3$ and some KNO_3.

How in practicality is nitric acid prepared from $NaNO_3$? Well, a mixture of about equal weight of sodium nitrate and 93% sulphuric acid is heated in a cast iron retort fitted with an outlet pipe near the bottom to take out the solution of $NaHSO_4$. The reactants are heated to about 200^0C by the hot gases rising from the furnace which is heated by coal fire. The vapours of nitric acid are cooled and condensed in water cooled silica pipes, and the acid is collected in the stone ware receiver.

The uncondensed vapours are scrubbed with water in an absorption tower packed with stone ware balls and through which cold water is made to circulate. The dilute nitric acid collected in the receiver is recirculated till it becomes concentrated. The residue (sodium bisulphate) in the retort is removed through the outlet pipe at the bottom of the retort. The reaction that takes place in this method is as shown:

$NaNO_3 + H_2SO_4NaH\overset{\longrightarrow}{SO4 + HN}O_3$

3.1.2 The Arc process for manufacturing nitric acid.

In the arc process, carbon dioxide and moisture are first removed from air and the dry air is then passed through a chamber containing an electric arc stuck between two copper electrodes connected with an A.C dynamo. Cold water is circulated continuously through these electrodes. A powerful electromagnet place at right angles to the copper electrodes spreads the arc in form of a disc. The chamber is also provided with inside suction pumps by means of which air is drawn in through the holes of the refractory fire work and then forced rapidly across the flame. At the temperature of the flame which is 2000^{o}C, the oxygen and nitrogen in the air combine to form nitric oxide. The exit gases leaving the chamber at about 1000^{o}C are allowed to pass through the fire tube boilers in which steam is produced. The gases are then allowed to pass through oxidation chambers. In the oxidation chambers, the nitric oxide is further oxidized into nitrogen peroxide. The exit gases from the oxidation towers are then passed through a series of absorption towers filled with broken quartz through which cold water or dilute nitric acid is continuously sprayed from the top. The gases enter the first absorption tower at the base and leave at the top. The third tower is fed with cold water and the dilute nitric acid collected at the base is re-circulated to the top of the proceeding tower. In this way, about 50% HNO_3 is obtained at the base of the first tower.

In the last absorption tower, the residual gases leaving it contain traces of oxides of nitrogen. These gases are allowed to pass through two wooden towers in which a dilute solution of sodium carbonate is sprayed. The solution at the base of the sodium carbonate tower is evaporated and crystals of sodium nitrate collected.

The reaction is as follows:

$$N_2 + O_2 \longrightarrow 2NO$$

$$2NO + O_2 \longrightarrow 2NO_2$$

$$4NO2 + 2H_2O + O_2 \longrightarrow 4HNO_3$$

3.1.3 The Ostwald's Process

This is the modern method of manufacturing nitric acid and about 90% of nitric acid is now prepared by this method. The process entails four fundamental steps. These are:

1. Oxidation of NH_3 to NO
2. Oxidation of NO to NO_2
3. Absorption of NO_2 in water
4. Concentration of HNO_3

The necessary raw materials for the manufacture of nitric acid by Ostwald's process are anhydrous ammonia (obtained from synthetic Haber process), filtered air, water and platinum rhodium gauze as catalyst.

How is nitric acid obtained by this process? Let us briefly describe the process.

A mixture of compressed dry air and anhydrous ammonia in the ratio of 89:11 parts is fed to a catalyst chamber. The mixture readily passes through a platinum rhodium gauze cylinder which is suspended vertically and closed at the bottom with a silica lid. This cylinder acts as a catalyst, which is electrically heated initially to 700^{0}C to start the reaction. The heat of reaction maintains this temperature and ammonia is rapidly oxidized to nitric oxide.

The product gases from the chamber, containing 10-12% nitric oxide are passed through heat recovery units, a quench unit for rapid cooling and then into the oxidizer absorber system. When cooled to about 200^0C, the nitric oxide undergoes further oxidation by air into nitrogen dioxide. The oxidation takes place in the oxidation towers which are vertical iron cylinders lined with acid proof stone.
The NO_2 is further cooled to about 50^0C and absorbed in absorption towers filled with broken quartz over which cold water is continuously sprayed. The product obtained from the absorption towers contains 57-60% HNO_3 solution which can then be concentrated.

3.2 Uses of Nitric Acid

Nitric acid is used in the manufacture of:

- fertilizer (e.g ammonium nitrate)
- explosive (e.g. nitroglycerine, cellulose polynitrate, etc)
- fibres
- plastics
- dye stuffs

It is also used in the purification of gold and silver.
Nitric acid serves as an oxidizing agent and is also used as a laboratory reagent.

4.0 CONCLUSION

From our discussion, I am sure that you will be able to identify the methods employed in the manufacture of nitric acid and also explain each of the methods.

5.0 SUMMARY

- The Ostwald's process for the manufacture of nitric acid is the latest and most viable method. It involves four major steps.
- The production of nitric acid from the oxidation of ammonia is based on three reactions:

  Catalytic oxidation of ammonia to nitric oxide

  $$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$$

  Oxidation of nitric oxide to nitrogen dioxide

  $$2NO + O_2 \rightleftarrows 2NO_2$$

  Absorption of NO_2 with water to form dilute nitric acid.

  $$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$
- The arc process is not a favorable method due to its high power requirements.
- To maintain a continuous current of gases in the first absorption tower used in the arc process, a centrifugal fan which is provided with the tower is used.

6.0 TUTOR MARKED ASSIGMENT

1. What methods are used in the manufacture of nitric acid?
2. Describe the Birkland and Eyde process for the manufacture of nitric acid.

7.0 REFERENCES

en.wikipedia.org/niki/Ostwald-process
resources.schoolscience.co.uk/Johnson Matthey/page 8/html
www.citycollegiate.com/nitirc acid.htm.

UNIT FIVE: MANUFACTURE OF HYDROCHLORIC ACID; A HEAVY CHEMICAL

1.0 Introduction
2.0 Objectives
3.0 Main Content
3.1 Hydrochloric Acid
3.2 Manufacture of Hydrochloric Acid
4.0 Conclusion
5.0 Summary

6.0 Tutor marked assignment
7.0 References

1.0 Introduction

The chemical compound hydrochloric acid is the aqueous (water-based) solution of hydrogen chloride gas. Hydrochloric acid or muriatic acid is a strong acid, the major component of gastric acid and of wide industrial use. It is a highly corrosive liquid. Muriatic acid was first discovered by the alchemist Jabir ibnHayyan around 800AD by mixing common salt with sulphuric acid. During the industrial revolution in Europe, there was an increased demand for soda and as such the new industrial soda process (Leblanc process) which enabled cheap large-scale production was used. In this process, salt is converted to soda ash, using sulphuric acid, limestone ad coal releasing hydrogen chloride as a by-product. This by-product was absorbed in water, thereby producing hydrochloric acid on an industrial scale. However, with the replacement of Leblanc's process with Solvay process which does not produce hydrochloric acid as by-product, it is now produced by other production methods. This therefore is the basis of our discussion in this unit.

2.0 Objectives

It is expected that at the end of this unit, you should be able to:

- identify the various ways of manufacturing HCl
- show chemically how hydrochloric acid
- state the uses of hydrochloric acid

3.0 Main Content

3.1 Hydrochloric Acid

Hydrochloric acid is a versatile chemical used in a verity of chemical processes, including hydrometallurgical processing (e.g. production of alumina and titanium dioxide), chlorine dioxide synthesis, hydrogen production, activation of petroleum wells, etc. HCl is used by masons to clean finished brick work. It is also a preferred acid for catalyzing organic process. Muriatic acid is also used in some household cleaning products.

Hydrochloric acid is a highly acidic, corrosive and non-flammable liquid; the typical concentration is in the range of 30% HCl by weight (commonly called concentrated hydrochloric acid), but solutions of up to 38% (commonly called fuming hydrochloric acid) and there are also lower concentrations of this acid.

3.2 Manufacture of Hydrochloric Acid

Muriatic acid can be manufactured by several different processes, although over 90% of the HCL produced in the U.S. is a by-product of the chlorination reaction. This in organic acid is produced by any of the following processes:

1. Synthesis from elements
   $H_2 + Cl_2HCl \longrightarrow$
2. Reaction of metallic chlorides, particularly sodium chloride (NaCl) with sulphuric acid or a hydrogen sulphate:
   $NaCl + H_2SO_4NaHSO_4 \rightarrow HCl$

$NaCl + NaHSO4 \longrightarrow Na_2SO_4 + HCl$

$2NaCl + H_2SO_4Na_2SO_4 + \rightarrow 2HCl$

3. As a by-product of chlorination, e.g. in the production of dichloromethane, trichloroethylene, perchloroethylene or vinyl chloride:

   $C_2H_4 + Cl_2C_2H_4Cl_2 \rightarrow$

   $C_2H_4Cl_2C_2H_3Cl + H\rightarrow Cl$

4. By thermal decomposition of the hydrated heavy-metal chlorides from spent pickle liquor in metal treatment.

   $2FeCl_3 + 6H_2OFe_2O_3 + 3H_2O \rightarrow + 6HCl$

5. From incineration of chlorinated organic waste:

   $C_4H_6Cl_2 + 5O_24CO_2 + 2H_2\rightarrow O + 2HCl$

Production of HCl from the chlorination process.

In the chlorination process, an HCl-containing gas stream is produced. This gas stream proceeds to an absorption column, where concentrated liquid HCl is produced by the absorption of HClvapours into a weak solution of hydrochloric acid. The HCl-free chlorination gases are removed for further processing. The liquid acid is then either sold or used elsewhere in the plant. The final gas stream is sent to a scrubber to remove the remaining HCl prior to venting.

A simplified diagram of the steps used for the production of by product HCl from the chlorination process is shown Fig 1:

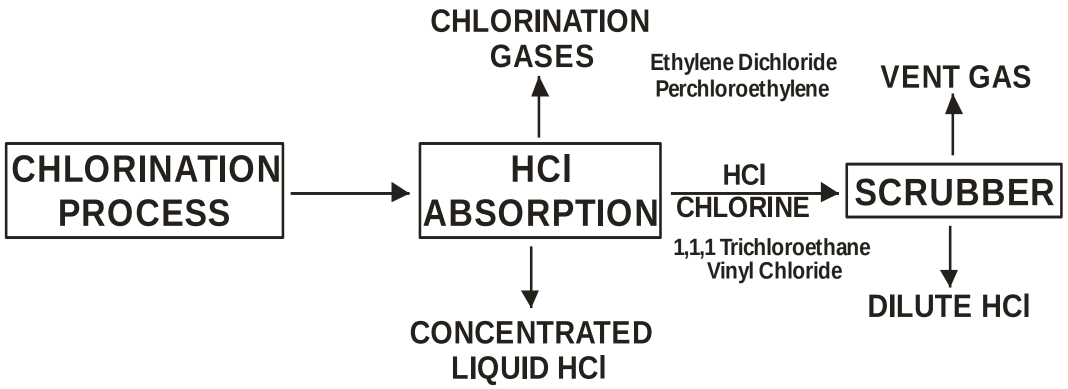

Fig1: HCl production from chlorination process.

4.0 CONCLUSION

This unit has actually shown how hydrochloric acid can be produced and its uses were also highlighted.

5.0 SUMMARY

Hydrochloric acid is a strong inorganic acid that is used in many industrial processes. It can be used in the production of in organic compounds. For instance, water treatment chemicals like iron (iii) chloride and poly aluminum chloride (PAC) are produced with HCl and they are used as flocculation ad coagulation agents in waste water treatment, drinking water production and paper production.

Muriatic acid may be produced by various processes but basically from the chlorination process as a by-product.

6.0 TUTOR MARKED ASSIGMENT

1. Show schematically how HCl can be produced from the chlorination process.
2. What processes are employed in the manufacture of HCl?

7.0 REFERENCES

Encyclopedia of chemical technology, Third edition, volume 12, John Wiley and Sons, New York, 1978.
Ullmann's Encyclopedia of Industrial Chemistry, Volume A, VCH publishers, New York, 1989.
www.solvaychemicals.com