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# Consultant approach to decision making on material of construction for chemical industries

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## ABSTRACT

The chemical plants consists of reactor vessels (HPHT), piping, valves, heat exchangers, evaporative cooling, evaporative and drying, distillation, mass separation, mechanical separation, Flue gas, effluent treatment and disposal. Understanding of Chemical reactions and operating conditions of flow dynamics, temperature and pressure and their impact on pH, electrochemical reactions are essential to decide on the most suitable Material of construction (MOC) for chemical plants. In pharmaceuticals wherein the quality of the medicines is vital and hence the corrosion resistance of alloy shall be very high to avoid any contamination by corrosion products. In fertilizer industry strong acids and strong alkali severely affect the corrosion behavior of alloys. In Agro industries MOC shall be corrosion resistant to nitration, ammonolysis, halogenations, polymerization, oxidation, hydrogenation, diazotization vapour phase catalytic reactions. In Biotechnology, low temperature to high temperature conditions is to be taken into considerations. Most of the chemical plants consists of combination of different type of equipments and process vary in different stages and hence always there is need of combination of alloy of different electrochemical potential which can lead to galvanic corrosion and therefore preventive measures are to be in built in design engineering stage itself. In a mixed gas environments it is the dominant process among possible oxidation, sulphidation, nitridation, carburization which can be assessed based on respective chemical potentials.

Keywords: chemical plants, electrochemical reactions, methodology, MOC

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## INTRODUCTION

Among the chemical industries majority are basic chemicals that are both organic and inorganic in nature involve general chemicals, fertilizers, agrochemicals, pharmaceuticals, chemical process in biotechnology, and leather industry. A raw material going into a chemical process or plant as input to be converted into a product is commonly called a feedstock, or simply feed. Output streams from the plant as a whole are final products and Chemical processes may be run in continuous or batch operation. Consultant look for detailed flow diagram of chemical process and list out the processing equipments such as reactor vessels (HPHT), piping, valves, heat exchangers, evaporative cooling, evaporative and drying, distillation, mass separation, mechanical separation, Flue gas, effluent treatment and disposal.

Most of the chemical plants consists of combination of different type of equipments and process vary in different stages and hence always there is need of combination of alloy of different electrochemical potential which can lead to galvanic corrosion and therefore preventive measures are to be in built in design engineering stage itself. In pharmaceuticals wherein the quality of the medicines is vital and hence the corrosion resistance of alloy shall be very high to avoid any contamination by corrosion products. In fertilizer industry strong acids and strong alkali severely affect the corrosion behavior of alloys. In Agro industries MOC shall be corrosion resistant to nitration, ammonolysis, halogenations, polymerization, oxidation, hydrogenation, diazotization vapor phase catalytic reactions. In Biotechnology, low temperature to high temperature conditions is to be taken into considerations. In this review technical paper consultant approach to understand the corrosion issues in chemical plants to suggest suitable material of construction(MOC) have been compiled.

## AN OVERVIEW OF CHEMICAL PLANTS

## The chemical industry consists of the following:

1. Base chemicals:

Industrial gases, fertilisers, chlor-alkali, and other organic and inorganic chemical (Alkali chemicals -Soda ash,Caustic soda, Liquid Chlorine, Inorganic chemicals - Aluminum fluoride, Calcium carbide, Carbon black, Potassium chlorate, Titanium dioxide, Red phosphorus ) Organic chemicals - Acetic acid, Acetone, Phenol, Methanol ,Ortho Nitro Chlorobenzene (ONCB) , Isobutyl Para Nitrochlorobenzene (PNCB)

2. Specialty chemicals:

Leather chemicals, construction chemicals, personal care ingredients and other specialty chemicals.

3. Pharmaceuticals:

Active Pharmaceutical Ingredients (APIs) and formulations

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#### 4. Agrochemicals:

Insecticides, herbicides, fungicides and other crop protection chemical(Pesticides & insecticides - Dichlorodiphenyltrichloroethane (DDT), Malathion, Parathion, Ethicon, Endosulphan, Phosalone, Phorate, Acephate, Fenvalerate). The process involves agitation, heat & mass transfer and all unit operations. Processes scaled up are nitration, ammonolysis, halogenations, polymerization, oxidation, hydrogenation, diazotization vapour phase catalytic reaction.

#### 5. Biotechnology

Bio-pharma, bio-agri, bio-services and bio-industrial products.

The Vessels in chemical plants<sup>1</sup> are often cylindrical with rounded ends, a shape which can be suited to hold either high pressure or vacuum. Chemical reactions can convert certain kinds of compounds into other compounds in chemical reactors. There can also be units (or subunits) for mixing (including dissolving), separation, heating, cooling, or some combination of these. Separation processes include filtration, settling (sedimentation), extraction or leaching, distillation, recrystallization or precipitation (followed by filtration or settling), reverse osmosis. drvina. and adsorption. Heat exchangers are often used for heating or cooling, including boilina or condensation, often in conjunction with other units such as distillation towers. There may also be storage tanks for storing feedstock, intermediate or final products, or waste. There may be structures holding or supporting sometimes massive units and their associated equipment. There are often stairs, ladders, or other steps for personnel to reach points in the units for sampling, inspection, or maintenance. Fluid systems for carrying liquids and gases include piping and tubing of various diameter sizes, various types of valves for controlling or stopping flow, pumps for moving or pressurizing liquid, and compressors for pressurizing or moving gases. Vessels, piping, tubing, and sometimes other equipment at high or very low temperature are commonly covered with insulation for personnel safety and to maintain temperature inside. Solvents can sometimes be used to dissolve reactants or materials such as solids for extraction or leaching, to provide a suitable medium for certain chemical reactions to run, or so they can otherwise be treated as fluids. The cost of material of construction for these components affects the feasibility of the project execution of plant fabrication and commissioning. In practice it is usual to select materials that corrode slowly at a known rate and to make an allowance for this in specifying the material thickness. However, a significant proportion of corrosion failures occur due to some form of localized corrosion, which results in failure in a much shorter time than would be expected from uniform wastage. Additionally, it is important to take into account that external atmospheric corrosion leads to many instances of loss of containment and tends to be a greater problem than internal corrosion. All these aspects of corrosive behavior need to be addressed both at plant design time and during the life of the plant.

## FACTORS RESPONSIBLE FOR CORROSION

The likely corrosive parameters in chemical industries can be listed broadly as follows:

- Impact of flow of solid suspensions
- Impact of presence of dissolved Oxygen
- Impact of Halogens and halides at high temperature

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- Impact of Mixed gas environment CO<sub>2</sub>, SO<sub>2</sub>, SO<sub>3</sub>, CO, H<sub>2</sub>, N, CH4, H<sub>2</sub>S, CI
- Impact of oxidizing acids
- Impact of reducing acids

Consultant take up assessing the corrosion severity based on the interpretation of various test results. The important test involves electrochemical finger printing of the alloy – electrolyte medium behavior in simulated chemical process conditions. The Experimental parameters for consultancy on MOC for chemical Industries are given below

## A. Potentiodynamic Anodic Polarization studies

The electrochemical technique of potentiodynamic anodic polarization studies yields Passivation tendencies and effects of inhibitors or oxidizers on specimens. With this knowledge, the corrosion characteristics of different metals and alloys can be compared on a rational basis and compatible specimen-environment combinations secured for further long term testing and final decision making. The parameters which are fingerprinting of corrosion behavior of an alloy immersed in a given corrosive aqueous solution are given below:

1. Redox Potential

Redox potential is defined as the specific indicator of the extent to which the oxidizing as well as reducing powers of a substance which has both reducing and oxidizing ingredients, have achieved equilibrium. The Redox potential indicates water's relative state to receive electrons or gain electrons. As the redox potential increases in value and turns positive, its ability to oxidize is enhanced. When it decreases in value and turns negative, its reducing ability is quantitatively enhanced. An increase in the redox potential of a solution indicates addition of additional oxidizers to solution. Thus Redox potential is used as indicator of electrochemical reactivity of substances in environmental conditions for predicting corrosion protection of various substances and systems. Measurement of Redox Potential is determined as potential difference between an inert sensing electrode (Platinum electrode) in contact with the solution and a stable reference electrode (Ag/Agcl or saturated calomel electrode) connected to the solution by a luggin probe.

2. Open circuit potential (OCP)

OCP measures the potential of a specimen working electrode immersed in corrosive solution, while specimen working electrode is not connected to Potentiostat and hence simulates the **in**-service condition of the alloy exposure to corrosive medium in the chemical industry being studied. As per the ASTM it is measured after 55 minutes of exposure to corrosive medium. However it can be standardized as per the given chemical process and its corrosive severity. The more positive (or less negative) value of open circuit potential indicates that the specimen is more nobler i.e. more corrosion resistance

#### 3. Critical Passive current density

The maximum current density at the first peak of the potentiodynamic anodic polarization curve, beyond which sudden fall in current density took place. Lower the critical passive current density the better is the corrosion resistance of alloy. The critical passive current density is the function of metal and the electrolyte composition. The ability of the material to spontaneously passivate in the particular medium, which is inversely related to the critical passive current density.

#### 4. Breakdown Potential (pitting potential):

Potential at which Passivation fails and sudden increase in current density take place. The longer the passive potential region, the better is the corrosion resistance of the alloy immersed in the tested the solution. Higher the breakdown potential and lower the corresponding current density better is the corrosion resistance and is desired by the industry.

5. Maximum Current density in the region from OCP to end of passive region:

The corrosion current density in the passive region. The lower the current density in the passive region the better is the corrosion resistance of alloy

#### 6. Repassivation Potentials

The repassivation potential is determined by carrying out reverse scan of onward potentiodynamic anodic polarization and it is the point of intersection between forward scan curve and the reverse scan curve. Alternatively, it can be chosen as that potential at which the current density reaches its lowest readable value on the reverse portion of the polarization scan. The allow susceptibility to pitting related to formation of hysteresis loop between the forward and reverse scan with reverse scan current density is higher than the current density at forward scan and corrosion potential is equal to or anodic (noble) with respect to the pitting potential. Preformed pits, e.g. crevices, might be expected to grow if the corrosion potential lies between the pitting and repassivation potentials. The alloy would be expected to resist localized corrosion if the corrosion potential lies cathodic (active) with respect the repassivation potential. The pitting potential has been shown to vary with the amount of localized corrosion induced by the applied potential e.g. the chemistry changes within the localized area. The difference between the repassivation potential and the pitting potential has been found at least in some environments to be a measure of the extent of crevice corrosion suffered by the sample. A rule-of-thumb that has been employed reasonably successfully require that the corrosion potential be some value (e.g. 200 mV) more active than the repassivation potential for crevice corrosion not to be expected to be a problem. For a given experimental procedure, the larger the hysteresis, the greater the disruption of surface passivity, the greater the difficulty in restoring passivity, and, usually, the greater the risk of localized corrosion

#### B. Poubaix diagram

Poubaix diagram is the potential verses pH plot showing conditions of solution oxidizing potential and acidity or alkalinity for the various possible phases that are stable in an aqueous electrochemical system. It shows the reactions and reaction products that will present when equilibrium has been achieved. Corrosion is possible in the areas of the diagram where soluble ions of metal/alloy are stable. Metal is possible resistant to corrosion or passive in areas where an oxide is stable. In areas where only reduced form of metal is stable, metal is thermodynamically immune to corrosion. Potential can be located in the area of immunity by cathodic protection. Large number of Pourbax diagram for various metals in different aqueous media is available in the open publications and are considered by the consultant while evaluating the chemical process.

C. Gas composition and Predominance chemical potential in a mixed gas environment

In a mixed gas environments it is the dominant process among possible oxidation, sulphidation, nitridation, carburization which can be assessed based on respective chemical potentials. The relative content of various gases influence the corrosion attack predominance i.e. preferentially as oxidation, or sulphidation or carburization or nitridation. A detailed analysis of the Oxygen potential, Sulphur potential, Carbon activity, nitrogen potential , and comparison with the equilibrium oxygen pressure, equilibrium sulphur pressure, equilibrium carbon activity, equilibrium nitrogen activity from the standard Ellingham diagrams – standard Gibbs free energy verses equilibrium pressure of respective components – oxygen, sulphur, carbon, Nitrogen.

## FERTILISER INDUSTRY

In fertilizer industries environments of Sulphuric acid, Ammonia, Phosphoric acid, KCI/NaCl solution and Nitric acid exists depending on the final product. Applicability of various alloys in Sulphuric acid, Phosphoric acid, Nitric acid can be accessed from the standard nomograms published by NiDi in various technical notes <sup>2,3</sup> Sulphuric acid:

The most commonly used nickel alloys in processes containing dilute sulfuric acid are INCOLOY alloys 25-6MO, 825 and 020, and INCONEL alloy G-3. For aggressive, hot, sulfuric acid environments, INCONEL alloys 625, 622, C-276 and 686 are most often selected.

## Phosphoric Acid

Pure phosphoric acid has no effective oxidizing power and is classified as a non-oxidizing acid, much like dilute sulfuric. Commercial phosphoric acid, however, usually contains impurities such as fluorides and chlorides that markedly increase its corrosivity. Oxidizing compounds, such as ferric salts, may also be present to influence corrosion. The most commonly used nickel alloys in processes containing pure phosphoric acid are INCOLOY alloys 825, 020 and 25-6MO, and INCONEL alloy G-3. For aggressive, hot phosphoric acid environments, especially those contaminated with halides, INCONEL alloys 625, 622, C-276 and 686 are selected.

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## Nitric Acid

Nitric acid is strongly oxidizing and, because of this, alloys with the best resistance are those that form passive oxide films. Thus, alloys with significant chromium contents offer much greater resistance than those with lesser amounts. While nickel alloys offer good resistance to pure nitric acid, they are particularly effective in mixed acid media (e.g. nitric with reducing acids such as sulfuric or phosphoric). When small amounts of chlorides or fluorides are present, Ni-Cr-Mo alloys show superior resistance. When Nitric acid used for Ammonium nitrate and potassium nitrate in fertilizer industry, 304L SS is the preferred material of construction for mixers, evaporators, crystallizers, pumps, piping and tanks. Alloy 800 and SS 329 are used in heat exchangers.

## Alkalies

Corrosion rates in chemical processing media usually decrease as the pH increases. In alkaline solutions, the hydrogen ion is present in very low concentrations. However, many metals pass through a minimum corrosion rate at some pH, usually basic, and then suffer increased corrosion as pH continues to rise. Quite often corrosion by alkalies leads to pitting and other localized attack because they tend to form cathodic films, and attack is concentrated at susceptible anodic areas. Austenitic stainless steels and other low nickel materials may suffer either stress-corrosion cracking or general corrosion in hot concentrated caustic. Resistance to attack by alkalies generally improves with increasing nickel content.

## Salts

When dissolved in water, salts increase their conductivity and thereby are able to carry higher corrosion currents. Therefore, galvanic effects are more pronounced in salt solutions than in pure water. The most commonly used nickel alloys in process environments containing sulfate salts are INCOLOY alloys 25-6MO, 825 and 020 and INCONEL alloys G-3, 625, 622, C-276 and 686. For processes using chloride salts, the most commonly used materials are MONEL alloy 400 (for reducing conditions), INCOLOY alloys 25-6MO, 825 and 020, and INCONEL alloys G-3, 625, 622, C-276 and 686.

## PHARMA INDUSTRY

Material selection in pharma industry<sup>4</sup> is influenced by the conservative approach, and the change in material use is slow to occur and driven primarily by the failure of existing material. This industry demands for extremely low tolerance to corrosion and release of metals into drug products as it deal with health and bound by social commitment. Equipment involved in product contact has been constructed largely from austenitic stainless steel 304L (UNS S30403) and 316L (UNS S31603). The satisfactory performance of these materials in most applications, combined with good material availability at acceptable price levels, produces little incentive to change. Historically, in areas where 316L was not adequate, the high-Ni-Cr-Mo alloy C-276 (UNS N10276) was the alternate choice. In the 1970s and 1980s, numerous alloys intermediate to 316L and C-276 were developed that offered the chemical and corrosion resistance necessary for the pharmaceutical industry. A few of these alloys are popular in the sense of market availability and use, and while alloy development continues, it is at a much slower pace. These alloys can generally be characterized into two families, identified as superaustenitic and duplex stainless steels. Superaustenitic Stainless. Of the superaustenitic stainless alloys, the AL-6XN alloy (UNS N08367) has been the most widely used. This alloy is nominally 25Ni-20Cr-6Mo, with the balance essentially iron.

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This protective layer is susceptible to damage from halogens, but if oxygen is present in the environment, repair of the film is often rapid enough to prevent any significant damage. In the absence of a source to replenish oxygen, such as in a tight crevice, corrosion can accelerate as the available oxygen is consumed and the pH drops as a result of the corrosion process. Another location where depleted oxygen can lead to corrosion of stainless steel is at low points of piping systems without adequate drains. Duplex Stainless Steels. A number of duplex stainless steels exist are Alloy 2205 (UNS S32205) contains 22Cr-5Ni-3Mo and is widely used in industrial and chemical process applications. These duplex alloys can be used in pharmaceutical equipment, to replace 304L and 316L as its pitting and crevice corrosion resistance superior to that of 316L stainless and that is also resistant to chloride-induced stress corrosion cracking because of the austenite ferrite (duplex) microstructure. In pharma industry Rouging is a phenomenon of particular interest as it refers to presence of a surface layer of oxide on stainless equipment or piping typically handling high purity water at temperatures above ambient. This includes stills, steam systems, purified water, and water for injection. The oxides can vary in composition, degree of oxidation, color, texture, and adherence. Although generally shown to be innocuous, the mere presence of these deposits can raise concern. The rouge itself is typically composed primarily of iron oxides or iron hydroxides, but because these are developing on stainless surfaces, they may also contain oxides of chromium, nickel, and molybdenum. There is empirical data indicating that resistance to rouging increases with increasing chromium iron ratios in the passive layer and/or the thickness of the passive layer itself. Because both electro polishing and passivation increase the chromium-iron ratio, application of these processes can increase resistance to rouging. Even with such treatments, the passive layer can break down due to the ionizing effect of high-purity water. The low oxygen content of these waters also slows the rate of repassivation and may cause the layer to linger in intermediate states of oxidation. Repeated cycles of this process result in the entrapment of various oxides in the passive layer, hence the wide range of colors. Rouging has also been observed to result from deposits of corrosion products from upstream equipment. Such deposits can simply be wiped from the surface and reveal an unaffected electro polished surface underneath.

#### MIXED GAS HIGH TEMPERATURE ENVIRONMENTS and AGRO INDUSTRY

A plot of standard free energy for the formation of oxides as a function of temperature is known as Ellingham/Richardson diagrams. It is used to predict the partial pressure of O2 required for any metal to form oxide at any temp. The alloys rely upon the oxidation reaction to develop a protective oxide scale to resist corrosion attack such as sulphidation, carburization, and nitridation corrosion. To be protective, this oxide layer must be chemically, thermodynamically stable. Successful high temperature corrosion resistant alloy is achieved by utilising alloys that are capable of forming adherent scales of either alumina ( $Al_2O_3$ ), chromia ( $Cr_2O_3$ ) or silica ( $SiO_2$ ). Most of the high temperature engineering alloys currently in use are Iron, Nickel or Cobalt based alloys. These alloys acquire corrosion resistance by the formation of oxides of Chromium ( $Cr_2O_3$ ), or Silicon( $SiO_2$ ) or Aluminum( $Al_2O_3$ ).

Alloying requirements for the production of specific oxides scales have been translated into minimum levels of scale forming elements or combination of elements, depending on the base alloy composition and the intended temperature of service. Chromium plays an important role in high temperature oxidation corrosion studies, not as a metal for high temperature service application, but as an important alloying element which helps in providing a protective chromia ( $Cr_2O_3$ ) layer. For the temperature of 600 °C, 5Cr-0.5Mo steel has excellent oxidation corrosion resistance.

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Nickel is generally not alloyed with iron for the purpose of improving high temperature properties of iron. The main purpose of alloying Ni to Fe-Cr alloys is to transform the Fe from a ferritic to an austenitic phase which has a FCC structure and is more stable at high temperatures. Thus a combination of chromium and nickel synergise the oxidation corrosion resistance for Fe-Cr allov, viz: 18Cr - 8Ni – Mo alloy. At 900°C temperature 18Cr -8Ni –Mo steel alloy i.e SS 316 has adequate oxidation corrosion resistance. When the temperature exceeds 900°C, Molybdenum present in SS316 steel will form molybdenum oxide (MoO<sub>3</sub>) which volatilize and result in rapid oxidation of steel and severe corrosion. Further the chromia begins to convert to volatile CrO3 as the temperature exceeds 1000°C. Thus the protective scale formation benefit from Chromium will be lost as the temperature exceeds 1000°C. Hence, SS316 is not adequate for 1200°C temperature environment. Above 950°C, chromium is not suitable to provide corrosion resistance. Instead aluminum provides excellent oxidation resistance by forming Al<sub>2</sub>O<sub>3</sub> scale. When both Al and Cr are present within an alloy, they will compete to form surface scale, and with greater than 4 % Al content, alumina formation is favored. Thus oxidation resistance of Fe-Ni-Cr steel is increased significantly by alloving additional 4 - 5% Aluminum. Further at high temperature like1200°C, adhesion of Al<sub>2</sub>O<sub>3</sub> scale is enhanced by inclusion of rare earth like yttrium, cerium and lanthanum which assist in development of a more resilient scale, which delays oxidation and other high temperature corrosion processes like sulphidation.

Reaction Vessel is a heart of agro Industries to manufacture pesticides & this is very important equipment used for Gas – Liquid reactions such as Hydrogenation, Oxidation, Formulation, Chlorination, Carbonation, reaction/ mixing of different type of chemicals in different conditions, pressure/under vacuum, temperature /cooling or at atmospheric conditions. Depending on the dominance of process, MOC is selected as per above discussions.

#### **BIOPROCESSING PLANTS**

The austenitic stainless steel, together with duplex or high performance alloys as required in bioprocess, offer a unique combination of corrosion resistance, ductility, and fabricability when properly specified, designed, and used. SS can be used with high degree of confidence in bioprocessing operations in which high quality surface finish, cleanliness and maintenance of sanitary conditions are essential. Bioprocessing equipment is exposed to many different compounds, including proteins, lipids, carbohydrates, and salts, that may leave difficult to remove residues. Proteins are complex structures, the most likely foul surfaces and the hardest to remove. Although physicochemical forces cause the proteins to adsorb on SS, they can be removed by chemical cleaning.

In bioprocessing plants, fouling and bacteria growth have to be eliminated by sanitization process. In sanitization, extreme caution is vital as sanitization is done through chlorine or hypochlorite solutions to remove bacteria or other microorganism from process equipments. The residual chlorine can not only destabilize the passive film but also can initiate the chloride related localized corrosion such as pitting and stress corrosion cracking. Hence extreme cleaning out sanitization chemicals is mandatory for resuming the plant operation. After post service cleaning, the equipments shall be repassivated with dilute nitric acid or other oxidizing agents to ensure maximum restoration of original corrosion resistant surface.

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#### CONCLUSIONS

Consultant assess corrosion severity in chemical plants based on the interpretation of various test results of electrochemical finger printing of the alloy – electrolyte medium behavior in simulated chemical process conditions. The alloy offering the optimized corrosion resistance during the life cycle of the plant are recommended after taking into account cost, galvanic corrosion, process flexibility, impact of shut downs and other related activities of process plant.

#### REFERENCES

- 1. Prof.Walter Bogaerts "Materials Engineering for the chemical Process Industries" Publ. CPI Material Engineering 2006-08
- 2. C.M.Schillmoles, "Alloy selection in wet process phosphoric acid plants" NiDi publication Technical series no.10015
- 3. C.M.Schillmoles, : Selection and use of SS and Ni bearing alloys in Nitric acid" NiDi publication Technical series no. 10075.
- 4. Paul K. Whitecraft, "Material issues in the Pharmaceutical Industry" Publ. ASM/5145-05J1a-01-03.pdf/A0004203 2006.