2.1 GENERAL:

An extensive literature survey has been presented in this chapter reviewing results of studies carried out by other investigators on the following:

1. Corrosion of metal by HCl.
2. Corrosion of metal by H$_2$SO$_4$.
3. Corrosion of metal by H$_3$PO$_4$.
5. Corrosion of metal by Mixed acid.

2.2 Corrosion of metal by HCl:

An ellipsometric study was made on mechanically polished mild steel specimens in 1.0 M HCl at rest potential. The corrosion rates were reduced if the specimens were immersed in the acid and were cathodically polarized before being left at rest potential$^{38}$.

In 96-hours tests with 5-36% HCl, maximum corrosion rates of steel were observed in 30% HCl. Corrosion rates were significantly less in 36% HCl, which was attributed to the formation of a protective chloride film, less soluble in concentrated than in 30% acid$^{39}$.

The corrosion process was examined on steel specimens
(Steel 3) in HCl aqueous solutions (10-36 wt%) for different exposure durations at 10-50°C and at various solution volumes/unit surface of the specimen. The corrosion rate increased exponentially with the temperature and concentration of the acid = 30 wt%. At higher concentrations with longer exposures and smaller volumes of acid, the corrosion rate decreased due to the formation of a protective film (FeCl₂·4H₂O) on the steel surface.

Thin film of FeCl₂·2H₂O and FeCl₂·4H₂O were formed on the steel during exposure to air containing HCl vapour evaporated from HCl solution while stored in a closed vessel.

In industries many process or waste treatments involve HCl-containing atmosphere which might cause severe corrosion of equipment.

Corrosion data in Cl⁻ air mixture for C-steel at 5.25 g Cl/m³ and at 300-550°C showed that initially high rate of corrosion was decreased in 30 hours to a constant rate. The corrosion rate at 400-500°C increased at the higher concentration of Cl, but at 300-350°C, the rate was low and insensitive to Cl concentration.

1 M HCl solution is the most aggressive solution for the SCC of the stainless steel. The most suitable strain rate for studying SCC by the SSR method was 1x10⁻⁶/s.
The corrosion rates for iron in deaerated 1 N solutions of the halogen acids at 25°C were determined by cathodic polarization and substantiated by analytical methods to be $42, 43, 10 \mu$ amp/cm$^2$ for HCl, HBr and HI respectively. The observed cathodic Tafel slopes were also well ordered. $\text{HCl} < \text{HBr} < \text{HI}$. 45

Both increased temperatures and increased acid concentrations increased corrosion rates. The initial addition of small amounts of ferrous salts results either in a decrease in the rate or a plateau in the rate, followed by an increase in rate after a particular concentration is exceeded. HCl is slightly but consistently, less corrosive to base metal when compared on an approximate concentration and temperature basis. 46

The thermal cracking of heavy fractions at the NOVO-Utinsk refinery gives off gas containing HCl and steam. This corrodes heat exchanger tube at 0.7 mm/Yr rate.47

The electrode surface was electropolished in a mixture of HOAc+HClO$_4$ prior to subjecting it to the corrosion potential in 1N HCl for 10 minutes and then changing the electrode potential in the direction of more negative values by 20-30 MV.48

Fe$^{3+}$ and Cu$^{2+}$ ions increase the rate of corrosion both in the presence and absence of an inhibitor. Cl$^-$ ion increases the rate of corrosion in the absence of an inhibitor. 49

To investigate the corrosion of boiler construction materials
resulting from the action of flue gas containing HCl, a series of laboratory experiments was carried out. The increase in corrosion rate with increasing HCl concentration in the flue gas was associated with changes in the scale morphology.

Steel (3 KH 18N NIOT, OKh 23 N23 M3D3J, NiNP-2), and Cr (99.9%) were investigated for corrosion by weight and electrochemically. Cl was passed through H₂O (50 ml/min), the pH of the HCl was 1.5 and SCE was used as reference electrode. The corrosion rate of carbon steel in Cl water was greater than in HCl. But the corrosion behaviour of OKh 23N 28 M3D3T was identical in both the mediums.

2.3 Corrosion of metal by H₂SO₄:

The corrosion of stainless steels was electrochemically examined in 80-95% H₂SO₄ at 30-50°C for 24 hours. The corrosion rate decreased with increasing H₂SO₄ concentration and Ni content in the steel, but the rate did not depend on the temperature. Cyclic potential change occurred in SUS 329J IM H₂SO₄ system between -0.2 and 0.2 V Vs SCE. The cathodic reaction in the active state near -0.2 V was the reduction of H⁺ to H and the cationic reaction in the passive state near 0.2 V was the reduction of H₂SO₄ to S and H₂O. The anodic reaction was metal dissolution in both the active and passive states.

The effects of P concentration in medium C-steel on the
anodic and cathodic polarization curves in 0.1 M \( \text{H}_2\text{SO}_4 \) containing
5x10\(^{-4}\) \% \( \text{As}_2\text{O}_3 \) was determined. With an increase of P concentration
in the steel, the corrosion rate increases considerably, disregarding the presence of the inhibitor \( \text{As}_2\text{O}_3 \). The \( \text{H}^+ \) reduction
is more rapid, but the anodic dissolution is less retarded\(^53\).

Passivity breakdown characteristics of Cr steels were studied by adding chloride ions progressively to \( \text{H}_2\text{SO}_4 \) solutions. Effects of holding time at different potentials on the film growth were also studied by adding a fixed quantity of chloride ions to \( \text{H}_2\text{SO}_4 \) solution after a passive layer formed. Comparative study of corrosion kinetics was made for different models of experimentation\(^54\).

Stainless steel (12 Kh 18 NIOT) shows an increased corrosion (0.32 mm/yr) in 93% \( \text{H}_2\text{SO}_4 \) at 40°-46°C (drying towers).\(^55\)

The passivated electrode undergoes an activation process which is initiated by reaction of the inner layer of passive film with \( \text{H}_2\text{SO}_4 \). The rate of activation is maximum in 2M \( \text{H}_2\text{SO}_4 \) solutions.\(^56\)

The anodic dissolution of hot rolled steel (61299-89-6) was studied potentiodynamically in \( \text{H}_2\text{SO}_4 \) solution of various concentrations. The rate of dissolution increases with increasing acid concentration\(^57\).

The corrosion of cast iron (95508-98-8) pipes in \( \text{H}_2\text{SO}_4 \)
at different concentrations (30-98%) at temperatures (35-100°C) are presented. Corrosion rate indicated no marked difference in the cast iron pipes. Corrosion is severe > 60 cm on the flange ends at extreme of pipes. The inner portions of the pipes are practically unaffected.\textsuperscript{58}

A stable film of liquid $H_2SO_4$ was formed on the surface of Al at a temperature 35-37°K lower than on steel surface. The lowest corrosion rate of steel was monitored at 363°K, when thickness of the acid adsorption film was the minimum\textsuperscript{59}.

A study was made of the influence of P on the passivation kinetics of iron in 1M $H_2SO_4$. In cyclic voltammograms, 2 current peaks were observed in the anodic sweep. The peak current observed in the more anodic potential range (0.6 V Vs saturated calomel), is related partially to the passive current and partially to the oxidation of $Fe^{2+}$ to $Fe^{3+}$. $Fe^{2+}$ is confined in a thick surface layer.\textsuperscript{60}

The corrosion resistance of stainless steel in 5M $H_2SO_4$ decreased with increasing Co content from 2 to 17% and increased with increasing Co content from 17 to 35%.\textsuperscript{61}

The change in hydrogen permeability, corrosion rate, electrode potentials and hardness of boiler steel 16 GNMA(37302-14-0) was determined after hot rolling normalization at 930-50°C and 5-hr annealing at 650°C. A 6N $H_2SO_4$ solution was
selected as the corrosion and hydrogen changing medium. The mobility and permeability of hydrogen was maximum in the annealed steel, and was lower in the quenched non tempered steel, even though the corrosion processes in the quenched steel was higher than in the annealed steel.62

The corrosion rate of C-steel tanks in concentrated $\text{H}_2\text{SO}_4$ is estimated assuming the diffusion of FeSO$_4$. Mechanism and control measures for high localized corrosion rates at welds, inlet and outlet points, and on grooving are also discussed.63

Steel EI-943 (06 Kh N$_2$O MDT) was studied in 40% $\text{H}_2\text{SO}_4$ at 70°C without deaeration. During the initial stage of corrosion in the transition range of potentials, Cu intensely dissolves from the surface with the precipitation of CuSO$_4$.64

The corrosion behaviour of austenitic ferritic stainless steel was studied in boiling $\text{H}_2\text{SO}_4$ as a function of cold working degree by means of electrochemical method, immersion test, and microscopic examination.65

The dissolution kinetics of steel (08 KP) hot rolled low carbon steel sheets in $\text{H}_2\text{SO}_4$ were studied.66

The clean heating surfaces and walls of gas conduits in oil-fired boilers corrode at $\leq 0.05 - 0.07 \text{ mm/yr}$ while not being used. The corrosion of metal ducts and smoke pipes is caused by free $\text{H}_2\text{SO}_4$ (7664-93-9) present in the deposits form
during boiler operation. After shutting down the boiler, the H
SO
solution present in the deposit absorbs H O vapour from the air which increases by \( \leq 30\% \) the weight of the deposit. 67

The mass transfer of H SO to the surface of air preheaters is calculated from condensation and evaporation fluxes in preheaters with normal and 50\% loading. The applications of this calculation to corrosion problem are discussed. 68 A mathematical model is developed for the corrosion of rotating iron disc in H SO. The corrosion reactions takes place at the metal electrolyte interface and are characterized by the interactions among heterogeneous reactions. 69

The highest corrosion rate and H contents of the steel alloys are reported in boiling H SO, the tensile strength does not change in 0.6 - 0.9\% H SO and decreases 2 fold in 1.2\% H SO. At higher temperatures, the corrosion rate decreases for all concentrations and the tensile strength is stable in 0.6 - 0.6\% H SO. 70

The test on sensitized steels were conducted in 92.5\% solution of H SO at 80°C for 500. Corrosion of sensitized steels is indisputable, it is necessary during the upkeep of chemical equipment to pay special attention to the tendency towards such corrosion of the more stressed parts; the base, elbows and welded joints. 71
The anodic behaviour of steel 3 steel was studied over an extended range of $H_2SO_4$ concentration (70-96%) and at 60 - 200°C. The passivation of electrodes at potential $\psi = 0.76$ V is accompanied by a substantial drop in the current density in all solution containing more than 80% $H_2SO_4$. If the maximum permissible corrosion rate is 1 mm/yr, the temperature region of the applicability of anodic protection of C steel is approximately 60°C in 80-5% $H_2SO_4$. On increasing the concentration of $H_2SO_4$ upto 96%, this temperature region is extended to 200°C.\textsuperscript{72}

Measurements made with the galvanostatic polarization technique in 0.001 - 1N $H_2SO_4$ solutions containing 0.1N Na halides showed Cl\textsuperscript{-}, Br\textsuperscript{-} & I\textsuperscript{-} ions to inhibit corrosion in 0.1 N and N $H_2SO_4$ solutions, whereas at lower concentrations Cl\textsuperscript{-} promoted corrosion. The Cl\textsuperscript{-}, Br\textsuperscript{-} and I\textsuperscript{-} ions in 0.1 N and Cl\textsuperscript{-} and Br\textsuperscript{-} ions in N $H_2SO_4$ act by blocking the active sites of the metal surface. The I\textsuperscript{-} ions in N $H_2SO_4$ take part in the dissolution reaction.\textsuperscript{73}

Electrochemical and corrosion measurements were made to show the effects of temperature, concentration and the presence of impurities in acid for gray cast iron in 96 weight% $H_2SO_4$. The low rate of corrosion in hot or boiling acid is due to a passivation effect shifting the corrosion potential towards a more noble potential; passivity arises from the presence of
a difficulty soluble $\text{Fe}_2(\text{SO}_4)_3$ film. At lower temperature, the steep rise in corrosion rate occurs and under optimum conditions can give $\leq 99\%$ protection. Passivity is not possible with dilution to 93\% or the presence of reducing impurities. The corrosion rate can vary by a factor of $10^3$ within a potential range of approximately 250 MV.\textsuperscript{74}

Steel 45 chromized for 10 hr at 1100°C in a powdered mixture of Cr 50, $\text{Al}_2\text{O}_3$ 43, and $\text{NH}_4\text{Cl}$ 7\% with a coating thickness of 28-30μ was not corroded during 30 days in 15\% solution of tartaric acid, or 3\% solution of NaCl, and slight corrosion (55g/m$^2$-hr) was evident after 3 hr in 53\% $\text{H}_2\text{SO}_4$, whereas same nonchromized steel in the latter acid of the same concentration after 24 hr showed a loss of 1000 g/m$^2$. However, the chromized steel after a longer time than 7 days in 53\% $\text{H}_2\text{SO}_4$ exhibited a pitting corrosion with subsequent intensive subsurface corrosion.\textsuperscript{75}

2.4 Corrosion of Metal by $\text{H}_3\text{PO}_4$:

Corrosion of mild steel in $\text{H}_3\text{PO}_4$ can be controlled by anodic protection. The efficiency of protection changes with concentration and temperature. It was established that anodic protection reduces the high corrosion rates.\textsuperscript{76}

Pitting corrosion susceptibility of AISI-304 in $\text{H}_3\text{PO}_4$ and containing different concentrations of NaCl was investigated
at 25-80°C, in different concentrations of the acid. The values of chloride ion concentration required to initiate pitting corrosion decrease in the order 80°C < 50°C < 25°C and those for the 3 acid concentration 80% < 50% < 30%. Anodic polarization of AISI 304 stainless steel was studied in H₃PO₄ with increasing chloride ion concentration.

The highly alloyed austenitic (X2 Ni Cr Mo Cu 25 20 (55178-58-0) and austenitic ferritic (X2 Cr Ni Mo Cu N 25 5 (81508-10-3) steels had good resistance to corrosion by pure H₃PO₄ at room temperature to -80°C. Corrosion increased in the presence of Cl⁻ or F⁻ ions. The latter steel was more sensitive to heat input, owing to the precipitation of intermetallic phases in the ferritic structure, leading to the loss of corrosion resistance.

The polarization resistance method was used to study the corrosion behaviour of stainless steel 08 Kh 17N 15 M 3 T and 06 Kh N 28 MDT) in 85% H₃PO₄ at 100-140°C. With increase in temperature the corrosion rate of the steels increases. Thus the corrosion rate of 08 Kh 17 N15M3T at 80°C, 100°C, 120°C and 140°C was 0.25, 0.60, 2.75 and 7.50 g/m²-h, respectively and of steel 06 Kh N28MDT, it was 0.10, 0.50, 1.28, and 3.42 g/m²-h, respectively.

Anodic polarization curves were determined for 317 and
and 316 stainless steels, and for mild steel coupons in H₃PO₄ solutions. Coupons were made cathodic, and then currents were measured. Moderately concentrated H₃PO₄ is corrosive to mild steel, but concentrated acid reduces corrosivity. Mild steel can be anodically protected in concentrated H₃PO₄. Ionizable iodide compounds are effective inhibitors for mild steel in moderately concentrated H₃PO₄. Moderately concentrated H₃PO₄ can be highly corrosive to stainless steel at elevated temperatures.

The corrosion rates of stainless steels Kh18NIOT, EP 53, EI 448, and EP 54 in 38-73% H₃PO₄ were 0.005-0.028 g/(m²-hr) and increased with increasing acid concentration, in 73% H₃PO₄ at 20°C the corrosion rates were 0.001 g/(m²-hr). The addition of KCl to the H₃PO₄ solutions markedly increased the corrosion rates of the stainless steels, thus the corrosion rates of Kh18NIOT, EP 53, EI 448, EP 54, and EI 943 in 85% H₃PO₄ containing 0.03 wt% Cl⁻ were 360, 158, 13,10 and 0.07 g/(m²-hr). Steel EI 943 (0Kh 23 N17) had a satisfactory corrosion resistance at Cl⁻ concentrations up to 0.16%.

Steel (45) was chromized for 10 hr at 1100°C in a powdered mixture of Cr 50, Al₂O₃ 43, NH₄Cl 7% with a coating thickness of 28-30 µ. In 60% H₃PO₄, the corrosion rate of chromized steel was 0.043 g/(m²-hr), while with nonchromized it was 28, 350 g/(m³-hr).

The corrosion of the Cr and Cr low Ni stainless steels
(Kh17, Kh17 N2, Kh17 N5, and 00Kh 21N16AG 8) in 5, 20, and 50 wt% $H_3PO_4$ at 20-80°C was studied. At 20°C, all steels tested (except Kh 17N5) showed only a slight increase in the corrosion rate with the increase in the concentration of $H_3PO_4$, whereas the corrosion resistance of the Kh 17 N5 steel decreased strongly with increase in $H_3PO_4$. A comparison with the 000Kh 21 N16AG8 and 0Kh 23N28M3D3T steels showed that a decrease in the content of C from 0.06 to 0.03% and of Cr from 23 to 21% as well as a partial substitution of Ni by Mn and N and the total absence of Cu, Mo, and Ti do not affect the corrosion resistance of the steel at a concentration of $H_3PO_4$ of $\leq 50\%$ at temperature $\leq 80^\circ C$.  

Metals corrode to achieve a state of low energy. To block this process, surfaces must be passivated by chemical conversions or by coatings. Rusty ferrous metal surfaces are converted chemically by $H_3PO_4$ and by tannins. $H_3PO_4$ application conditions are noted.  

2.5 Corrosion of Metal by $HNO_3$:

Passivity of mild steel in nitric acid and nitromixtures was studied. It has been found that once the metal was rendered passive in concentrated $HNO_3$, the acid could be diluted to as low concentration as 3N, in which the passivity of metal was retained. Passive metal surface resisted attack up to 75°C.  

A study was made of the applicability of the thermo-
metric or mylius technique to the action of 0.8-15M HNO₃ on mild steel indicating the effect of specimen surface area of volume of the corrosion solution at 26.4-41°C. 86

Defects, for example, undercutting in Kh18N10T steel welds accelerates the corrosion rate in HNO₃ solutions. 87

The corrosion behaviour of stainless steel in boiling nitric acid of 18/8 type steels was studied. 88

The corrosion resistance of AISI 316L(11134-23-9) austenitic stainless steel in boiling HNO₃ was examined. 89

The effect of heat treatment, rolling, rolling direction and filler on the corrosion of austenitic stainless steels in 0.65% HNO₃ were studied by gravimetry (weight loss) and metalloy (intercryst crack depth). 90

The corrosion of iron in 3N HNO₃ at 25°C was studied by thermometry (temperature increased due to corrosion reaction) and weight loss method. 91

The behaviour of 304 stainless steel (12611-86-8) was tested under corrosive conditions (concentrated 69-70% Vol HNO₃ and 105°C) during cold work and sensitization. The rate of corrosion increases with degree of cold work, sensitization, temperature, and duration of treatment. 92

The significant corrosion of heating chambers of evaporators
during dissolution of organic deposits by concentrated HNO₃ was attributed to ignition of the deposits in gaseous phase in the presence of NO₂. ⁹³

The corrosion of stainless steel in HNO₃ at various heat fluxes, with steel surface temperature was studied. Cooler acid, present at the surface under higher heat fluxes, gives slightly smaller corrosion rates than under isothermal conditions. ⁹⁴

During the monitoring experiments, changes in corrosion potential were brought about by addition of chemical species to the 3M HNO₃. ⁹⁵

A commercial SUS 304 stainless steel (11109-50-5) test piece was immersed in aqueous 45 weight% HNO₃ solution at its boiling point containing NH₄NO₃ 0.054 and CuO 0.109 weight% and the solution was continuously supplied at 100 ml/hr. N₂O₃ was blown into the solution at 0.10³ L/hr during the immersion, and test piece showed corrosion rate 0.10 g/(m²-h) Vs 1.53 g/(m²-L) for the same SUS 304 test piece without N₂O₃ gas blowing. ⁹⁶

The corrosion of evaporators during their washing with dilute HNO₃ for dissolving mineral deposits is caused by acidic materials from HNO₃. ⁹⁷

Studies were made on corrosion of different austenitic stainless steels of type 1810 Cr Ni and 2520 Cr Ni by trans-passive nitric acid. ⁹⁸
Corrosion of structural stainless steel 07Kh 16N6 (37245-27-5) in aqueous solution containing 0.5-5 mol HNO₃/L at 20-100°C was studied. The corrosion resistance of the steel was significantly retarded by the presence of activator ions, e.g. 5g Cl⁻/L, in the solution. The highest stability was measured in solution of 3-5 mol HNO₃/L.

Potentiostatic investigations upon a rotating disc electrode were carried out for determining electrochemical and corrosion behaviour of Cr-Ni stainless steels (1Kh18N9T types) in 1-5 M HNO₃ in presence of 0-100g/l Cl⁻. In these solutions specimens passed from the passive into the active state. After a definite period of time, steel, activated by Cl⁻, regained the passive state. The corrosion rate increased with temperature, stirring rate, and the decrease of Ni content in the steel. When HNO₃ concentration, Cl⁻ content or Cr in the steel were increased, the corrosion rate changed, passing through a maximum.

The effect of 0.01-3% Cl⁻ and 0.05-1% F⁻ on the rate of corrosion, K, of steel (1 Kh 18 N 9 T) in 1-100% HNO₃ was studied at 18-25°C by the loss in weight and by the change in corrosion current (\(\Delta C\)) of a steel electrode in 0.1 N \(\text{K}_2\text{SO}_4\) before and after passivation. In 10 and 20% HNO₃, K increased sharply with the concentration of Cl above 0.1%. In 40-95% HNO₃, K changed little with Cl⁻ ion concentration. In 98% HNO₃, K decreased as Cl⁻ ion concentration increased. The addition
of NaCl to 20% HNO₃ lowered the passivation properties and ΔC due to the destruction of the protective film. Addition of NaCl to 70% HNO₃ lowered ΔC to a considerably small degree. In 90% HNO₃, the effect of Cl⁻ on C was insignificant.¹⁰¹

2.6 Corrosion of Metal By Mixed Acid:

The addition of HCl and HNO₃ decreases the corrosion of AISI 304 stainless steel (11109-50-5) by H₂SO₄ at the ratio H₂SO₄:HCl:HNO₃ = 9:6:4. All other ratio studied (90:0:10-90:10:0) showed increase in corrosion, with the maximum at 90:2:8. HCl or HNO₃ added separately to H₂SO₄ decreased corrosion.¹⁰²

The corrosion resistance and electrochemical behaviour of steels (12 Kh 18 N 10T, 0 8 Kh 17N 15 M3T and 00Kh N 2 8 M D T) in a mixture of H₃PO₄ 43.3 and H₂SO₄ 32.7% were studied at 20° and 60°C.¹⁰³

Nitric acid (0.15%) has been found to be a very good inhibitor for steel dissolution in 65% H₂SO₄ by corrosiometric technique.¹⁰⁴

Corrosion of mild steel in mixture of dilute and concentrated acids (HCl, H₂SO₄, HNO₃) has been studied under immersed condition. The data reveals acceleration, mutual reinforcement, break-down of passivity and inhibition depending upon the
nature of the mixture.  

The effects of binary combinations of $\text{HNO}_3$, $\text{H}_2\text{SO}_4$, $\text{HCl}$ and HF on the corrosion of Ni alloys and stainless steels were examined. Unexpectedly high corrosion rates occurred for some alloys in some combinations of acids.  

Corrosion of Al, AD0(37321-70-3) containing Al 99.5, Fe 0.22, Si 0.18, Cu 0.02, Zn 0.05, and Ti 0.03% in the acid mixture containing $\text{HNO}_3$ 89.7, $\text{H}_2\text{SO}_4$ 7.7 and NOxides 0.5% was studied. High corrosion of the material, resulting in loss of grains, was observed on the samples susceptible to the intergranular corrosion.  

Corrosion tests were conducted in 93% $\text{NaCl}$, 10% $\text{H}_2\text{SO}_4$ and 3% $\text{HCl}$. The exoemission were recorded by a secondary electron multiplier in a vacuum of $10^{-3} - 10^{-4}$ pa.  

The corrosion of stainless steel AISI 304 (11109-50-5) in mixtures of $\text{HCl}$ and $\text{HNO}_3$ under different operating conditions was studied. The rate of corrosion increases as the concentration of the reaction between stainless steel and acid mixtures becomes exothermic. The maximum corrosion and maximum rise in temperature are observed for the combination 40:60 $\text{HCl}$:$\text{HNO}_3$. Hexamine was an effective inhibitor.  

The behaviour was studied of the steel 12 Kh 18 NIOT
in solutions containing NO$_3^-$ 0.1-5.0 and Cl$^-\ $0.1-1.0 mol/L at pH 0, 0.5 and 1.0. The solution was acidified with HNO$_3$. The range was determined of the resistance of the steel to generalized and localized activation in acid solutions of NO$_3^-$ and Cl$^-$.\textsuperscript{110}

Corrosion of 304 L (12611-86-8) and 316 L (11134-23-9) stainless steels was studied in 6-12 N HNO$_3$, and 1 N H$_2$SO$_4$ with or without 1 N KCl for pitting. Corrosion rates in H$_2$SO$_4$ and in chloride-modified H$_2$SO$_4$ were higher than for 316 L, but chloride-induced pitting was not observed. The 304 L stainless steel is suitable for HNO$_3$ service.\textsuperscript{111}

The effect of temperature on the corrosion resistance and kinetics of self-dissolving, and on the electrode potentials of low-C steel 08 was studied in aqueous solutions of H$_2$SO$_4$ and HCl over a wide concentration range (0.1 N to concentrated solutions). The dependence log $K$ Vs $f$ (1/T) deviated from the linear for steel corrosion in concentrated H$_2$SO$_4$.\textsuperscript{112}

The corrosion of Kh18N10T and OKh 23N28M3D3T steels was examined in dilute H$_2$SO$_4$ containing HCl 1.2, HCl 1.2 + HNO$_3$ 2%, Na$_2$SO$_3$ 2 and HCl, 1.2 + Na$_2$SO$_3$ 2%. Tests carried out at 60$^\circ$, for 1-100 hr, with or without stirring (180 rpm) were followed by the measurement of corrosion-induced variations in the electrical resistance, the vickers hardness, the stress rupture strength and the elongation. The addition of Cl$^-$ increases the corrosion rate of Kh18N10T in 1% H$_2$SO$_4$, has no effect in
5% $H_2SO_4$, inhibits corrosion in 10% $H_2SO_4$. The dissolution process is substantially accelerated when introducing $Cl^- + NO_3^-, SO_4^{2-}$, and especially $Cl^- & SO_3^{2-}$, corrosion is uniform.\textsuperscript{113}

Electrode potential vs current density curves of A-38 type steel were recorded by the galvanostatic polarization technique in 0.001 to 1N $H_2SO_4$ solutions and in 0.1N HCl. In $\leqslant 0.1N H_2SO_4, Cl^- ions promote corrosion, whereas at higher concentrations they act as inhibitors.\textsuperscript{114}

The corrosion rate of Fe in HCl - $H_2SO_4$ mixtures at 20°C remains almost constant (approximately 2.5g/m$^2$-hr) when the $H_2SO_4$ concentration is changed from 0.0 to 1.0 N; in the presence of 2.0 g $Al_2(SO_4)_3 \cdot 18H_2O$ and 0.5 g thiourea per litre the corrosion rate decreases, from 1.5 to 0.5 g/m$^2$-hr.

The corrosion rate in $H_2SO_4 - HNO_3$ mixtures at 20°C increases from nearly zero at concentration $C = 0.0$ to 160 g/m$^2$-hr at concentration $= 0.7 N$, and then drops again to nearly zero at concentration $C=1.0N$; in the presence of the inhibitor mixture.

The corrosion rate remains insignificant at any $H_2SO_4 : HNO_3$ ratio.\textsuperscript{115}

A study was made of the anodic behaviour of austentic stainless steels, ($03 \text{ Kh 17N 14S and 03 Kh 17N 14MS}$), in $H_2SO_4$ medium, containing $Cl^- (HCl)$. The enhanced corrosion resistance of the investigated steels is related to the screening effect of Mo & Cr oxides, which are formed on the surface during the corrosion process.\textsuperscript{116}
The pickling solution ensuring increased yield of useful products and reduced pickling time contains 10 - 40 weight % HNO₃ in addition to HF 20-40, H₂SO₄ 1-10, HCl 3-15 weight% and the balance H₂O.¹¹⁷

2.7 Scale Formation and Removal by Acids:

The temporary hardness is composed only of CaCO₃ for waters not rich in Mg.¹¹⁸ The mechanism of CaCO₃ precipitation from thermal waters containing various amounts of CO₂ is considered. The effects of gas (CH₄, N, and esp.CO₂) evolution on the CaCO₃ precipitation from these waters are discussed.¹¹⁹

The CaCO₃ deposition characteristics of several different cooling tower waters were investigated for various flow rates and surface temperature of the heated section of heat exchangers. The results of scaling tests are described which indicate the fouling factors possible over a limited range of water chemical and tube surface temperatures¹²⁰.

CaCO₃ scale formation and its avoidance should be investigated by Langelier saturation index graphs. Cooling water control monitoring methods are tabulated, with an indication if automatic and instrumentation are available. A non-chromate, non-phosphate organic inhibitor can be used to avoid pollution from tower breakdown. Methods of scale prevention and corrosion inhibition are discussed.¹²¹
The mechanism is given and explained on the formation of scale when evaporating natural brines and sea water. The component of the scale depends on the temperature and the method of evaporation and on the concentration of $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, and $\text{HCO}_3^-$. When evaporating sea water at $< 80^\circ$, the scale is mainly $\text{CaCO}_3$ but when evaporating at $> 80^\circ$, it is $\text{Mg(OH)}_2$.²²

The deposition mechanism was studied of alkaline scale substances ($\text{CaCO}_3$, $\text{Mg(OH)}_2$) on a heated surface. The explanation of the deposition of alkaline scale in sea water near the boiling temperature showed that $\text{CaCO}_3$ scale deposited initially by thermal decomposition of $\text{HCO}_3^-$, and successively $\text{Mg(OH)}_2$ scale deposited by hydro-decomposition of $\text{CaCO}_3$ scale. The other salts in sea water may not affect directly the deposition of $\text{Mg(OH)}_2$ scale.²³

Tests have shown that the precipitated $\text{CaCO}_3$, obtained by steam boiler water decarbonation with $\text{Ca(OH)}_2$, can be used as an abrasive and as a filler in cosmetic preparations as well as in many other industrial outlets.²⁴

A process is described for removal of scales and rust from a boiler by acid picling while protecting the non-cleaning portion of the boiler from acid attack. An acid solution with colour traces added was circulated at top of the glycol solution for 15 hours.²⁵
CaCO$_3$ was reacted with polyphosphoric acid (70-80% P$_2$O$_5$) at 500° at a molecular ratio 1:2.5 Ca-P. The product contained ortho - 5.8, poly - 23.4, meta - 29.6, and total phosphate 66.4%. When H$_3$PO$_4$ (55% P$_2$O$_5$) was used instead, the product contained ortho - 8.0, poly - 6.5, meta - 42.1, and total phosphate 65.8%. The products had a low solubility in water.\textsuperscript{126}

CaCO$_3$ and H$_3$PO$_4$ are allowed to react to give products which are washed with water, dried, thermally decomposed, mixed with dry CaCO$_3$ and fired. The Ca$_3$(PO$_4$)$_2$ product is useful as dental materials and artificial human bone.\textsuperscript{127}

CaCO$_3$ rock dissolution and the associated increase in surface recession with increasing acid deposition on the rock surface was studied. The interaction of acid rain with the rock has a stoichiometry consistent with the reaction.

$$\text{CaCO}_3(\text{Solid}) + H^+ = \text{Ca}^{2+} + \text{HCO}_3^-.$$

Experimental results are analysed of steam-boiler cleaning by a 2.6% HCl solution with urotropin as the inhibitor, a 14% H$_2$SO$_4$ solution with KI - 1 as the inhibitor, and a 9% H$_2$SO$_4$ solution with KI-1 as the inhibitor with subsequent cleaning with Trilon B.\textsuperscript{129}

The reaction of 20 and 28% HCl and rotating marble cylinders, containing 99.2% CaCO$_3$, was studied at 298 and 313 K.
with respect to producing CaCl₂, for low temperature cement clinker, from waste gases containing CaCO₃. ¹³⁰

The effect of the addition of Na₃PO₄ on the formation of scale and on the corrosion of carbon steel elements in an evaporator fed with Caspian Sea water treated with H₂SO₄ was studied. When the concentration of PO₄³⁻ in the feed water was kept at a level of 5 mg/L, the expenditure of H₂SO₄ was reduced by a factor of 7-10, and no scale formation was observed. ¹³¹

Corrosion and scale formation in potable water systems is inhibited by a mixture of H₃PO₄ 5-650, Na₂HPO₄ 0-285 and ZnSO₄·H₂O 10-450 g/l. ¹³²

The rates and mechanism of CaCO₃ crystal growth were studied by a reproducible seeded growth technique. Precipitation of CaCO₃ in the presence of certain phosphates and phosphonates may play a role in phosphorus exchange between natural waters and sediments. Seeded crystal growth experiments were carried out in solutions with phosphorus containing ions. Both the nucleation and crystal growth rates of CaCO₃ are markedly reduced by low concentration (>10 ppm) of several phosphonate or phosphate ions. The results were interpreted in terms of an adsorption process involving blockage of crystal growth sites on the calcite surface by phosphonate and phosphate ions. ¹³³
A scale problem came up at Petroleos Mexicanos of CaCO₃ in production equipment and pipes due to hard water mixed with the oil which undergoes variations of pressure, temperature, and flow direction. When the flow obstructing CaCO₃ deposits are slight and sporadic, they can be removed by rinsing with HCl. In more frequent and critical cases, injection of scale inhibitors is recommended. Inhibitors act on one of these two steps by either preventing nucleation in reacting with the ions which would precipitate to form highly soluble complexes or by enclosing the crystal nuclei to hinder further crystal growth, which can be accomplished by anhydrous polyphosphates or by organic phosphates, or organic poly-acids which are inhibitors for crystal growth.¹³⁴

Octadecylamino (I) and naphthylamine (II), inhibit the dissolution of CaCO₃ in H₂SO₄. The effects of different factors, particle size of CaCO₃, the initial concentration of H₂SO₄, the temperature, the effect of HNO₃ on this inhibiting action were studied. The inhibitors have no influence on the dissolution of CaCO₃ in the cases where no CaSO₄ film is formed, as in the dissolution in HNO₃, or in its mixtures with H₂SO₄ containing <20% of the latter. Apparently, I and II influence the protecting action of the CaSO₄ film rather than the dissolution itself.¹³⁵

Studies on the effect of MgCl₂, NaNO₂, KCl and KI on separation of CaCO₃ from aqueous solutions containing Ca²⁻ and
HCO\textsuperscript{—} at 50°C indicated that addition of equal concentrations of these electrolytes to natural water differently affects the amount of the solid phase separated. Thus the electrolytes, which tend to stabilize the water structure, decrease the amount of the CaCO\textsubscript{3} solid phase.\textsuperscript{136}

2.8 Concluding Observations:

From the above literature survey it is clear that corrosion of metals in mineral acids and its mixture has been widely studied. Wherever mixture of acids were chosen for studying, one acid was added to inhibit the corrosion of other used acid. Mineral acids are largely for descaling purposes. However, mixture of acids are not used. If demineralized water is fed in the boiler, scale formed consists mainly of CaCO\textsubscript{3} which can be easily removed using HCl. If raw water is fed in boiler, scale formed consists of silica in addition to CaCO\textsubscript{3}, which is very difficult to remove with HCl. Under such circumstances mixture of acids may be useful for descaling purposes. Literature related with scale studies reveals that prevention of scale formation by adding acid and phosphate or other salt has been largely studied, but descaling with mixed acids has not been studied yet. In the present investigation, therefore, corrosion of mild steel by mixtures of mineral acid was studied in detail to choose the acid combinations whose attacking power was least. Such combinations were studied for their descaling effi-
ciency to get the acid combination which may attack the metal to minimum extent and dissolve the scale to maximum extent.