

***Development of green rust converters using natural products to transform rust
on iron and steel heritage and artifacts to protect them from corrosion***

**Dr. Achal Pandya, Head of Department, Conservation Division, Indira Gandhi
National Centre for the Arts, New Delhi 110 001**

**Dr.D.D.N.Singh, Consultant, Indira Gandhi National Centre for the Arts, New Delhi
110 001**

The importance of metals was recognized by human beings about 6000 years B.C. after they discovered their use for different applications. The first metal was Gold, which was discovered as it exists in metallic form in the nature. This was followed by the discovery of Copper, Silver etc. All these metals are known as Noble metals (immune to normal corrosive environments) and they existed abundantly at many places in the form of pure metals. Due to their lustrous appearance, ancient people began collecting and using them for making ornaments and sharp weapons. Since the metals were found as small particles, people discovered the novel technology of hammering to make them into foils. This was followed by melting the tiny particles and casting them in various shapes. Since the furnaces available during the old period were not able to raise the temperature beyond 1000 °C only copper, silver and gold (these metals melt below 1000 °C) could be melted in these furnaces. The discovery of mercury, tin, iron and lead took place between 3500-4500 B.C. By this time people had gathered the knowledge of reduction of metallic ores by using charcoal as reductant at hot temperatures. It took almost 5000 years to discover presently available 85 metals (the 85 metals known

today), out of which 41 were discovered in 19th century. The understanding of processes of metals and their mechanical, magnetic, electronic properties were also followed with their discoveries. This was catalyzed by the discovery of microscopes which helped in giving a better insight of metals.

Now, it is possible to explain different behaviour of metals and alloys by considering their atomic structures and arrangement of crystal structures, inter metallic bonding, crystal defects, etc. Discovery of electron microscope which helped to see the tiny particles by magnifying them several hundred thousand times, further advanced the understanding of the science of metals and alloys.

It is inherent in the nature of human being to amalgamate many things together and observe the outcome of these amalgamations. This tendency led to the development of alloys comprising of various metals at different compositions. Mixing of these metals resulted in a phenomenal improvement in the properties of their alloys. There are now innumerable alloys available and to have their proper identifications, they have been divided in different categories and standards.

The discovery of Iron and its alloys had maximum impact on living standards, cultural and economic revolutions in the world. Due to their excellent mechanical and forming properties, iron and its alloys had been in use to design, cast, roll and erect existing and future heritages. Unfortunately, the iron based metals and alloys are thermodynamically unstable in most of the environments and develop porous, non-protective and unstable oxides on their surfaces. United State (US) Steel Corporation developed corten steel by alloying iron with low content of Cu, P, Ni and Cr with a claim that the corrosion rate of

such steels was drastically reduced when exposed in normal environments. A considerable decrease in rate of corrosion was attributed to the formation of a protective patina / layer on their surface. Studies revealed that this patina/layer comprised of stable oxides of iron such as hematite ($\alpha\text{-Fe}_2\text{O}_3$), maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and goethite ($\alpha\text{-FeOOH}$). These oxides are quite stable and very adherent to steel surface. However, the steel structures erected from corten steel structures and when such steel exposed in an environment having high salinity and relative humidity it exhibits very high rate of their deterioration. This is attributed to the formation of unstable phases of oxides/ rusts such as akaganeite ($\beta\text{-FeOOH}$), feric hydroxide $\text{Fe}(\text{OH})_3$, lepidocrocite ($\gamma\text{-FeOOH}$), ferroxihite ($\delta\text{-FeOOH}$) etc. These loosely bound and porous oxides/ rusts serve as reservoir for moisture and aggressive gases which aggravates further rusting of structures. In majority of the cases, it is reported that the localized type of attacks on steel structures take place, adversely affecting their life. Such type of problems are also encountered in old iron and steel based heritages exposed in normal environments and artifacts retrieved from soil and sea water.

Literature survey reveals that old steel and iron heritages and artifacts excavated from soil and sea water remain covered with unstable phases of rusts. In majority of the cases the post retrieval deterioration is localized type of corrosion on the surface which adversely affects the shape and look of artifacts. The old heritages made from iron and steel, exposed in normal environments form loose rusts on their surface which get washed away by wind and rain. Thus rusting (formation of oxides of iron) on the surface of heritages continues unabatedly resulting in thinning of structures, defacing, loosing mechanical strength, and disappearing of scripts / information written on their surface.

Similar is the case with artifacts retrieved from sea water and soil. Due to low availability of oxygen and high content of chloride in deep sea and soils the rust formed under these conditions are normally akaganeite (β -FeOOH) and magnetite (Fe_3O_4). Once such artifacts are retrieved and exposed to open atmosphere where plenty availability of oxygen and moisture are present, the unstable rusts act as catalyst for the accelerated rate of rusting of artifacts.

Removing rust from the surface of artifacts and heritage either by mechanical methods or chemical processes poses the risk of changing its originality. In order to retain their original shape and develop an aesthetic look on the surface, the following steps are desirable:

- (a) Removal of chloride and other harmful ingredients of the rust on the surface of the metallic heritage and artifacts;
- (b) Transformation of unstable rust into a stable compounds to control cathodic depolarization reaction of corrosion;
- (c) Provide an aesthetic look to the surface of the metallic structures which may be preserved without any further deterioration.

Various methods have been suggested to achieve the above objectives. Unfortunately, none of the techniques provide a satisfactory solution to the problem of post retrieval preservation. Indira Gandhi National Center for Arts, New Delhi has taken up an exhaustive program to develop means, methods and materials to conserve the deteriorating artifacts and heritages made from iron and steels. We plan to bring out a

series of publications on the subject related to transformation of rust by using eco - friendly technologies. The broad areas will include:

- a. Principles and mechanism of formation of unstable and stable rusts on the surface of iron and steels;
- b. Methods and materials available to control the deterioration of metallic heritages and artifacts;
- c. IGNC A approach to preserve rust covered iron and steel heritages and artifacts using environmental friendly naturally occurring substances.

Principles and mechanism of formation of unstable and stable rusts on the surface of iron and steels;

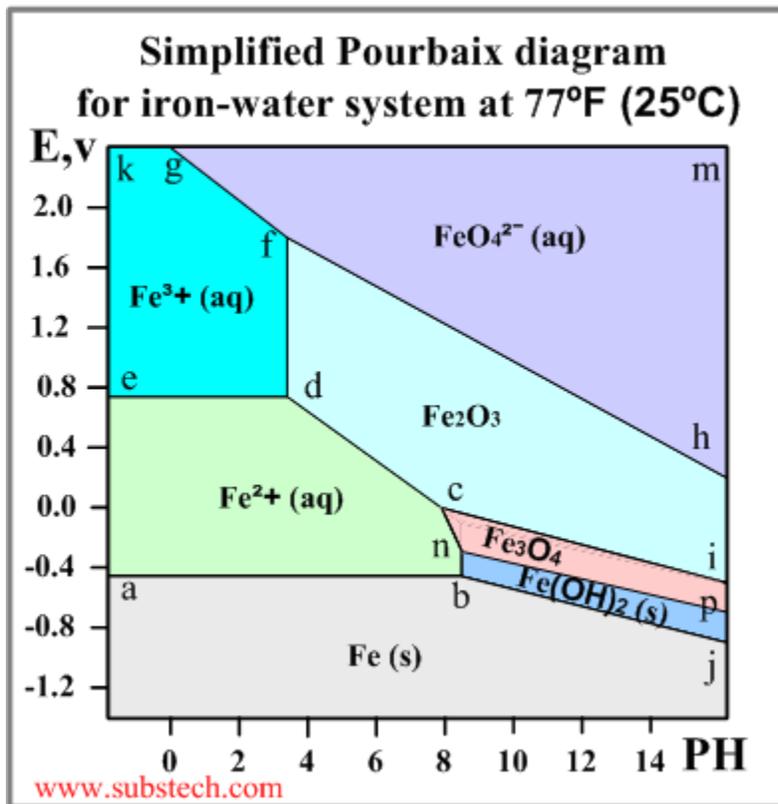


Figure 1: Pourbaix potential- pH diagram for passivation of steel

To understand the deterioration and protection of iron and steel artifacts and structures, it is helpful to understand the potential-pH diagram developed by M.Pourbaix. This diagram for different metals and alloys are drawn based on the thermo dynamical calculation, using Nernst equation given by :

$$E = E^{\circ} - 2.303RT/nF \log \{[C_{\text{red.}}] / [C_{\text{oxid.}}]\}$$

In the above equation, E is the electrode potential of a metal undergoing corrosion at temperature T and concentrations of its reduced and oxidized species respectively are C_{red} and C_{oxid} , E° = standard redox potential of the metal, n= number of electrons involved in the reaction and F is Faraday constant.

Potential - pH diagram for iron is presented in figure 1. In this diagram, the area

k d f c n b a is corrosion zone for iron. Under these conditions of potential and pH, iron metal ionizes in to soluble metal cations and corrosion reactions take place. In majority of cases of iron and steel heritages, the conditions of this zone exist resulting in spontaneous corrosion. The zone FHICD is the passive zone i.e. a stable and adherent oxide forms on the metal surface, considerably reducing the corrosion rate.

It is to be noted that the potential-pH diagram provides an indication on the probabilities of proneness of corrosion of a metal in aqueous environments. These diagrams are constructed considering ideal conditions of a metal in water having very low concentration (10^{-6} mole) of iron cations. The diagram miserably fails to provide any clue

on corrosion of the metal in an environment having chloride, sulphates etc. In practical world where artifacts and heritage structures exist, the conditions are too complex to predict their exact corrosion behavior using pH-potential diagram. The metal surface combines with its surroundings to form unstable compounds such as oxides, sulphates, chlorides etc. However, the diagram provides a definite clue for the proneness of a metal to corrode in an environment. In case an iron based object remains under a condition where the environment is alkaline and oxidizing in nature i.e. meets the condition of FHICD of the figure 1 shown above, it attains a state of passivity due to the formation of a very thin film of maghemite ($\gamma - \text{Fe}_2\text{O}_3$).

Unstable phases of oxides present on the surface of iron and steel artifacts retrieved from the bottom of sea and soil

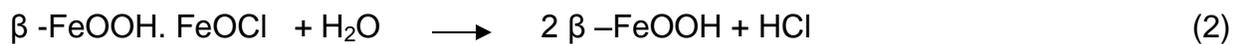
The conditions surrounding the artifacts buried in soil and at the bottom of deep ocean are normally anaerobic and very limited quantity of oxygen is available to take part in cathodic reactions. The initial phases formed on the surface of such objects are porous and unstable phase of magnetite (Fe_3O_4) and akaganeite ($\beta\text{-FeOOH}$). Magnetite (Fe_3O_4) phase of iron oxide is unstable and acts as cathode for further oxidation of the surface of iron and steel artifacts, as follows:



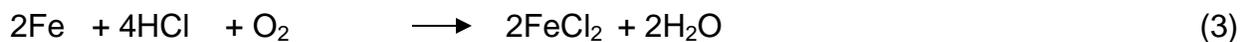
The above equation shows that the magnetite phase (Fe_3O_4) present on the surface of artifacts activates the corrosion of iron if moisture and oxygen are available.

Akaganeite (β -FeOOH) is also an unstable oxide and activates the corrosion of iron. This phase of oxide is also known as β - oxide mono hydrate and consists of mixed crystals of akaganeite and iron oxy chloride (FeOCl) and may be written as:

(β -FeOOH . FeOCl). The crystals of akaganeite- oxy chloride hydrolyze in the presence of moisture and generate hydrochloric acid:



The hydrochloric acid (HCl) formed in the above reaction reacts with iron to form acidic iron chloride.



The iron chloride in the presence of moisture and oxygen hydrolyses to form akagenite-iron oxy chloride and hydrochloric acid:



β - FeOOH .FeOCl again undergoes the reaction 2 above to generate hydrochloric acid. The above reactions 2-4 show that the generation of hydrochloric acid from akaganeite-iron oxy chloride phases present on the surface of retrieved artifacts is an auto catalytic process and continues till the whole content of iron is consumed by the above reaction 3. Thus it is important to transform the akagenite phase present on the surface of artifacts either into a stable phase of iron oxide such as maghemite or make them inactive for the further transformation and generate hydrochloric acid.

Available techniques to stabilize retrieved iron and steel artifacts from further deterioration

As discussed above, the iron and steel artifacts retrieved from deep sea or buried in soil are found invariably covered with akagenite-iron oxy chloride phases. Many techniques based on the principle of removal of chloride from the layer of rust deposited on the surface of retrieved artifacts are proposed. These techniques are partially effective but a complete curing of the artifacts is always doubtful. It is mainly due to the fact that the chloride extraction techniques are effective in dislodging unbound chloride ions embedded in the rust. However, the chlorides present in the form of complexes such as β -FeOOH-FeOCl, do not get dislodged during the chloride extraction process. Such left over chlorides take part in autocatalytic reactions as stated above in (2)-(4), generating hydrochloric acid and attacking the base metal.

IGNCA novel approach

The solution to the above problem is to deactivate the whole molecule β -FeOOH-FeOCl in to a passive film so that the above reactions 2-4 do not take place. During a preliminary and exploratory study, it was noted that the fruit extract of Amla (*E. officinalis*) transformed the chloride laden rust in to a passive compound. The rust generated on steel samples exposed in salt spray chamber was collected and treated with the fruit extract of *E. officinalis*. The photographs taken for the as received rust powder, washed with water and with the extract of fruits of *E. officinalis* are shown in figure 2. The colour of the rust washed with the extract of fruits of *E. officinalis* is completely changed and transformed in to bright black colour.



Figure 2: Photographs of iron oxides, as received and after washing

Raman Spectroscopy of the washed and as received rust powder revealed that:

- a. The as received rust powder from the salt spray chamber showed major peaks of akaganeite (β -FeOOH), lepidocrocite (γ -FeOOH), magnetite (Fe_3O_4), hematite (α - Fe_2O_3) etc.
- b. The water washed rust too exhibited the presence of these peaks in the Raman Spectroscopy, indicating that a simple washing of rust with water did not remove the unstable oxides,
- c. The rust washed with extract of *E.officinalis* (10% v/v) are showing no trace of akaganeite in rust and stable rust i.e. maghemite was found. Some other peaks other than iron oxides were detected by Raman spectroscopy but these peaks

have to be identified. Raman spectroscopy of rust washed with the fruit extract of *E. officinalis* exhibited very interesting observations.

These facts suggested that the unstable oxides of iron including akaganeite (β -FeOOH), FeOCl had been transformed in to an inactive compound i.e. maghemite and hematite

- d. The above findings suggest that the transformed phase was stable and the process may be used to treat the retrieved artifacts to protect them from further deterioration. The shining black colour is an added advantage and may improve the aesthetic look of the artifacts.

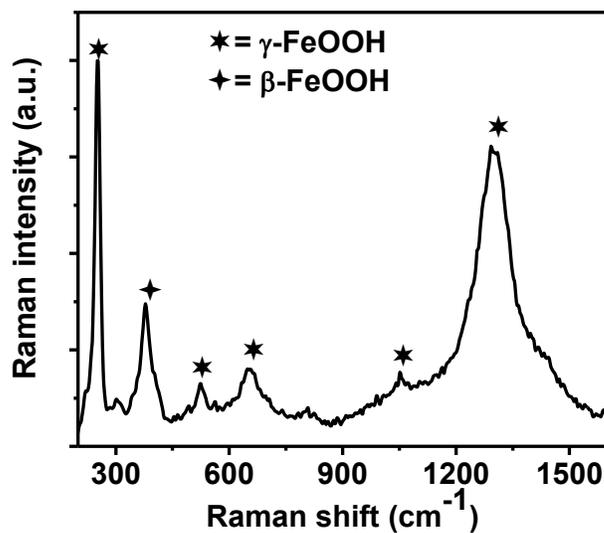


Figure 3: Raman spectra of mild steel rust formed in salts spray chamber after exposure of 17 days

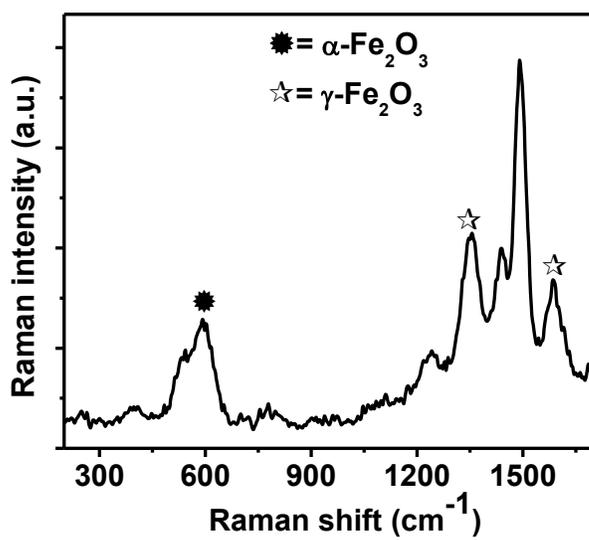


Figure 4: Raman spectra of chloride contaminated rust after washing in water solution of 10 v/v% extract of E.O

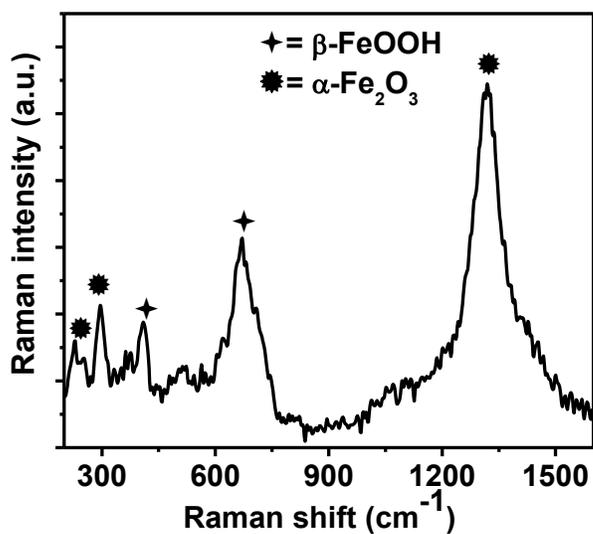


Figure 5: Raman spectra of chloride contaminated rust after washing in distilled water

Table 1: pH of E.O. fruit extract mixed in different proportions in distilled water

S.N	% of Amla solution	pH
1	1	3.61
2	5	3.38
3	10	3.28
4	25	3.23
5	100	2.93

Table 2: pH of extract of E.O. (100 % solution) after blending of different concentrations of chloride contaminated rusts and stirred 2 hours (100 rpm) on magnetic stirrer at 25°C

S.N	% iron oxide in Amla solution (with iron oxide)	pH
1	1	3.11
2	5	3.31
3	10	3.46
4	25	3.58

Table 3: pH of filtrate exposed in different concentration of iron oxide after 48 hours of exposure at 25°C

S.N	% iron oxide in Amla solution (filtrate)	pH
1	1	2.98
2	5	3.28
3	10	3.35
4	25	3.45

Performance tests:

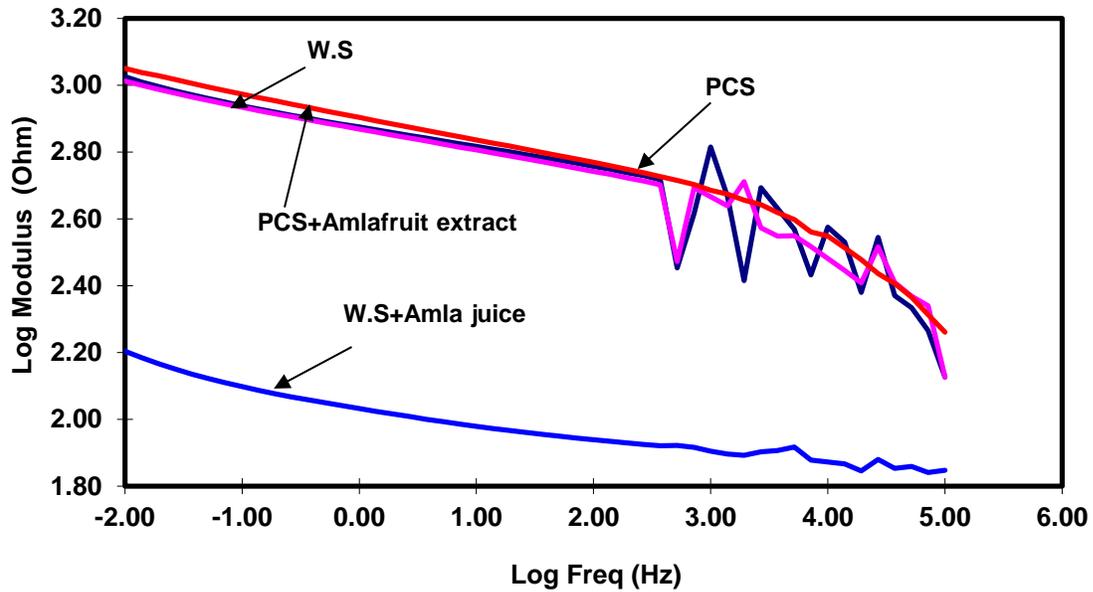


Fig.6: Electrochemical impedance spectra of rusted weathering steel (WS), plain carbon steel (PCS) plates before and after treatment with Amla fruit extract in SAEJ solution, after 24 hours.

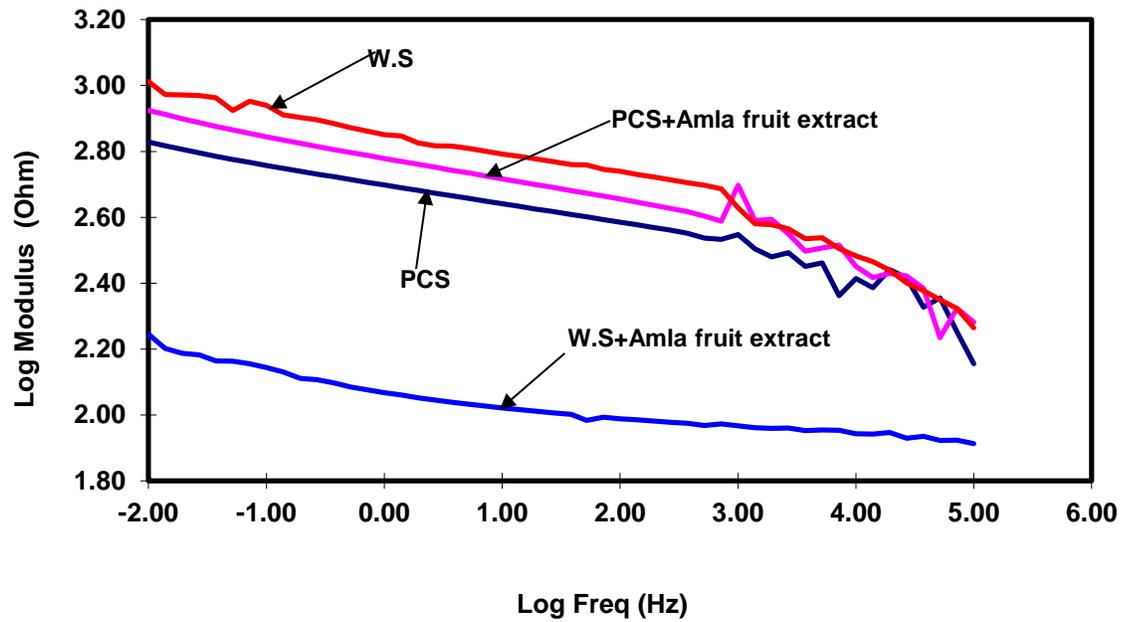


Figure 7: Electrochemical impedance spectra of surfaces of Weathering steel (WS), plain carbon steel (PCS) before and after treatment with fruit extract of Amla conducted in SAEJ solution, after exposure of 48 hours

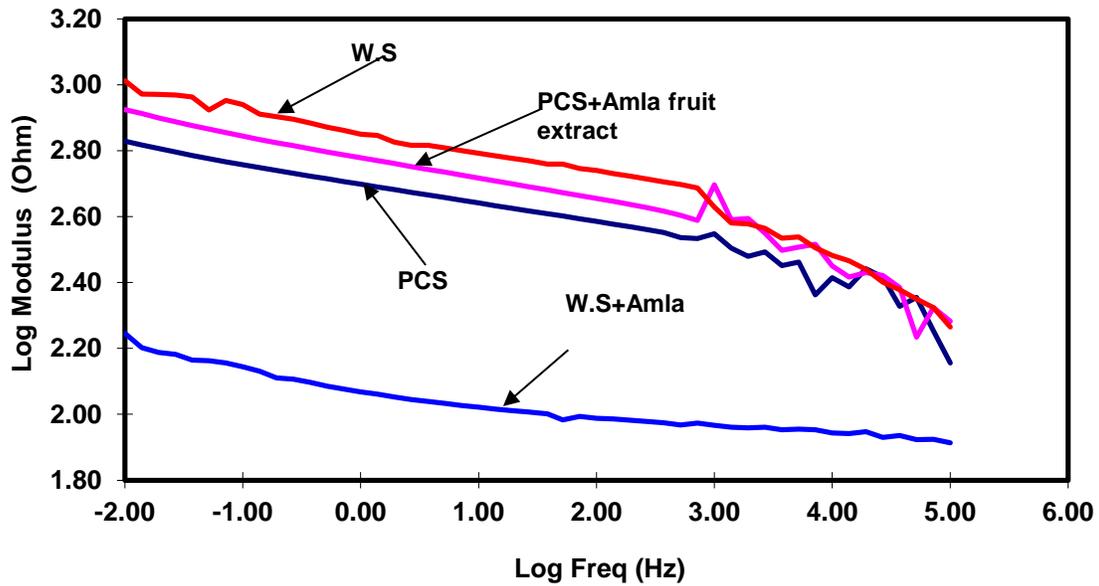


Figure 8: Electrochemical impedance spectra of surfaces of Weathering steel (WS), plain carbon steel (PCS) before and after treatment with fruit extract of Amla conducted in SAEJ solution, after exposure of 144 hours

Further detailed study on this subject is in progress and will be incorporated in the next communication.