THE IJES

Evaluation of Environmentally Benign New Chemical Rust Removing Agent – Hydroxy Ethane Diphosphonic Acid (HEDPA)

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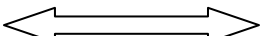Naval Surface Warfare Center, West Bethesda, MD, 20817 USA
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--**Abstract**--
In order to evaluate the adaptability of hydroxyethane diphosphonic acid (HEDPA) as an environmentally benign alternative rust removal agent, the present investigation was undertaken. The effectiveness of HEDPA was studied as a function of acid concentration in the range 2-20 vol. % and at different temperatures in the temperature range 23^oC -$55°C$. The results suggest that the acid HEDPA is very effective to remove the rust and the rate of rust removal depends upon the acid concentration and/or the solution temperature. Once an optimum value is reached, further increase in either the acid concentration and/or the solution temperature has a negative effect on the rust dissolution kinetics. In addition, it was also found that the chemical treatment with concentrated HEDPA solution (concentration range 5 -20 vol. % HEDPA) produces rust free steel samples with very rough surface topography. The chemical processing at higher temperatures ($> 40^oC$-55^oC), and higher HEDPA concentrations (> 5vol. %), produces strong pungent smell and an unpleasant cleaning environment. The most effective HEDPA concentration and temperature for the rust removal appears to be 2-4 vol. % and $< 40^oC$ respectively. The activation energy for the rust dissolution process using 2-4 vol.% HEDPA was in the range 12 +2 kcal/mole. The activation energies for rust dissolution by 5, 10 and 20 vol. % HEDPA were found to be 20, 28 and 32 +2 kcal/mole respectively. The reaction product contains a mixture of various higher order iron phosphates. The soils that were contaminated low concentration (< 0.5 wt. %) of with the reaction products improved the germination of seeds and the plants that were fed with solution containing the chemical reaction by products up to < 0.5 wt.% were healthy and increased in their size. Above 0.5 wt. %, the trends were reversed.

Keywords: Chemical Rust Removal, Reaction Kinetics, Activation Energy, Hydroxyethane Diphosphonic Acid (HEDPA)

1. Introduction

The development of new materials with improved hot water and saltwater corrosion resistance is important. However, it is also equally important to develop procedures and methods to maintain the existing materials that are currently in use. For example, the steels that are used to build large structures, and other industries, suffer from the environmental degradation. Therefore, the advanced technological maintenance processes would have applications in several areas, viz. the electric utility communities, for the removal of deposits from the thermal power plant equipment, the highway administration – rust on the bridges, and in the civilian ship building industry where the removal of corrosion products from ship platforms, onboard tanks, etc. The common classical rust and / or paint removal methods are based on the use of abrasive grits, or the use of high power water jet blasting. These procedures do offer logistical advantages in the removal process, but the operational labor tends to be costly. An alternative approach is to adopt a less labor intensive and an environmentally acceptable procedure that will dissolve the rust with in a reasonable time and produce a cleaned surface.This project was undertaken to demonstrate a cost effective alternative technology for the removal of rust from steel using an environment friendly chemical reagent. The overall program of this investigation is to provide basic scientific information of the chemical interactions at the metal (steel) - chemical reagent interface during rust removal, and to determine the rate of rust removal.

The chemical rust removing reagent that was selected for this study is a commercial reagent and the chemical reagent is phosphoric acid based organic acid "hydroxyethane diphosphonic acid" also referred as (HEDPA). The chemical reagent is a water-soluble liquid with general characteristics similar to water. In this paper for convenience both names hydroxyethane diphosphonic acid and /or HEDPA were used. The chemical structure of the HEDPA is shown in Figure 1. The hydroxyethane diphosphonic acid has two phosphate groups and one extra hydroxyl group, indicating that the iron in Fe^{2+} and/or Fe^{3+} state can compound with free hydroxyl (-OH) group and/or with the (P=O) cation sites and /or with the (P-OH) cation site. Phosphoric acid treatment of steel surfaces has been shown to improve the adherence of subsequently applied paint systems [1]. As the HEDPA is phosphorus based, the likelihood that the coating would serve in a similar fashion to a phosphated surface seemed possible. Therefore this investigation was undertaken to study the use of HEDPA for cleaning rusted steel.
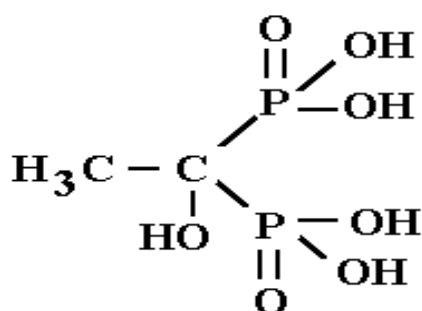
Figure 1. The chemical structure of commercial reagent the hydroxyethane diphosphonic acid [HEDPA].

2. Theoretical

Two generally accepted mechanisms for the dissolution of metal oxides are reported in the literature [2-6]. The first is referred to as the adsorption mechanism [2,3] and the second is referred as electrochemical mechanism [4-6]. Based on the electrochemical considerations, it was suggested in the literature that the overall rate of dissolution of rust can be written as:

$$(d\alpha/dt) = k \{(a_H)^{0.5} (a_{Fe}^{+2})^{0.5} (a_{Fe}^{+3})^{-0.5}\} \qquad (1)$$

Where "α" is the fraction of metal species dissolved, "a" the activity of the acid and metal ion species and "k" the rate constant. For rust removal, the potential for the acid to dissolve iron species is determined by the reaction.

$$Fe^{3+} + e \rightarrow Fe^{2+} \qquad (2)$$

From equations (1) and (2) it can be suggested that by lowering (Fe3+/Fe2+) ratio, the rust removal products can be accelerated. If one assumes the kinetics of rust removal is a chemically controlled process, the rate of rust removal can be expressed as

$$[1- \{1- \alpha\}^{1/3}] = k' t \qquad (3)$$

where k' is the kinetic constant and t is the reaction time. Although the above model can predict the dissolution kinetics of rust particles in HEDPA, it may not be appreciable for predicting the rust dissolution from a large surface of rusted steel plates. In order to account for the effect of large surface area on the reaction kinetics, a new model was developed [7]. The model assumes that the surface species first forms new and active nuclei, which is dissolved by the HEDPA and the reaction proceeds as in a 2-dimensional reaction with the reaction zone covering the entire surface area of the sample. The overall reaction process thus can be represented as

$$\ln[\alpha/(1- \alpha)] = k'' (t – t_i) \qquad (4)$$

where k'' is the rate constant and t_i is the time for the termination of the accelerated rust removal sequence.

3. Experimental

Two types of rusted steel plate samples were collected. The first set of steel samples was rusted naturally due to exposure to the environment along the Severn River in Annapolis, MD. The second set of samples was subjected to accelerated corrosion process according to the following procedure. In this method, the surface of steel samples was cleaned with vinegar. Then table salt was applied to the steel samples. After 24 hours, the samples were cleaned with distilled water and left to rust. After 2 days the samples were ready for rust removal experiment. In order to maintain acceptable experimental reproducibility, the loose powdery rust

was removed from all rusted samples prior to the chemical kinetics experiments. The typical size of the rusted samples was 5 cm long X 2 cm wide X 0.1 cm thick. Each experiment was repeated for five times. The samples were freely suspended from a sensitive single pan balance. The sample was hung such that the steel plate can be introduced into a beaker that was placed on hot plate with magnetic stir capability. Five different HEDPA solutions were prepared by adding as obtained commercial reagent to predetermined amounts of distilled water. All concentrations were produced on volume basis. Approximately 1000ml of the diluted chemical solution (HEDPA) were then introduced into the beaker and the rusted steel samples were introduced into the acid solution. The weight of the sample that was immersed in HEDPA was noted at 5-minute intervals. The weight loss was noted by subtracting the weight of the steel sample noted at a particular time from the original weight of sample. The weight of steel without any visible rust was approximated as the final weight of sample (with 100 % rust removed).

4. Results

Figure 2 shows typical percent weight loss versus time plot obtained for rust removal by HEDPA as a function of solution the reagent concentration at 23°C time. The results indicate that the test samples continuously lost material due to the dissolution of rust and some metal by HEDPA solution. The results also suggest that as the HEDPA concentration is increased, the total time for the rust removal decreases. Similarly, it was also found that an increase in the solution temperature decreases the total time for rust removal. The results shown in Figure 1 also suggest that, once the rust is removed, continued chemical treatment of the steel sample with the HEDPA solution tends to dissolve the bare metal. However, the loss of steel was less than 5 %. Figure 3 shows the typical surface morphology of rusted steel samples that were treated with HEDPA solution as a function of chemical treatment time. Although it is not evident from the figure 3, it was found that a thin layer of the chemical residue was left on the surface of the cleaned steel sample. The XRD analysis of this thin coating suggests that the coating contains mixture of complex iron phosphates.

From the percent (%) material removed versus time plots, the linear slope that represents the average value of the rate of rust removal by the HEDPA solution was determined. Similarly, the rate of fast chemical reaction and the rate of slow chemical reaction process were also determined using the procedure that was suggested by Rao [7] and Rao and Murray [8]. The rate of rust removal rate versus HEDPA solution concentration is given in Table 1. The results suggest that at 23°C, the rate rust removal increases with an increase in reagent concentration. Similarly, the rust removal rate was determined for all samples that were subjected to chemical rust removal at different solution temperatures. Once the rate of rust removal was determined as a function of reaction temperature, the activation energy for the rust removal process was determined using the Arrhenius equation. The actual activation energy values are given in Table 2. The results suggest that the activation energy for the rust dissolution process using 2, 3 and 4 vol.% HEDPA was in the range 11, 12 and 13 $\pm$2 kcal/mole. The activation energies for rust dissolution by 5, 10 and 20 vol. % HEDPA were found to be 20, 28 and 32 $\pm$2 kcal/mole respectively.
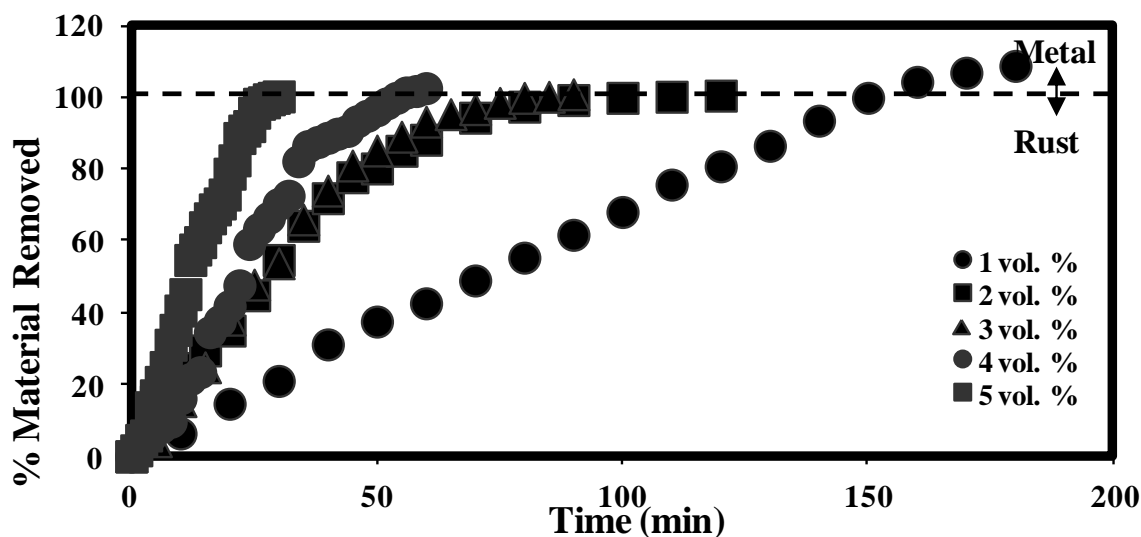

Figure 2. % Material removed versus time plot by hydroxyethane diphosphonic acid (HEDPA) solution for the rust removal process at 23°C.
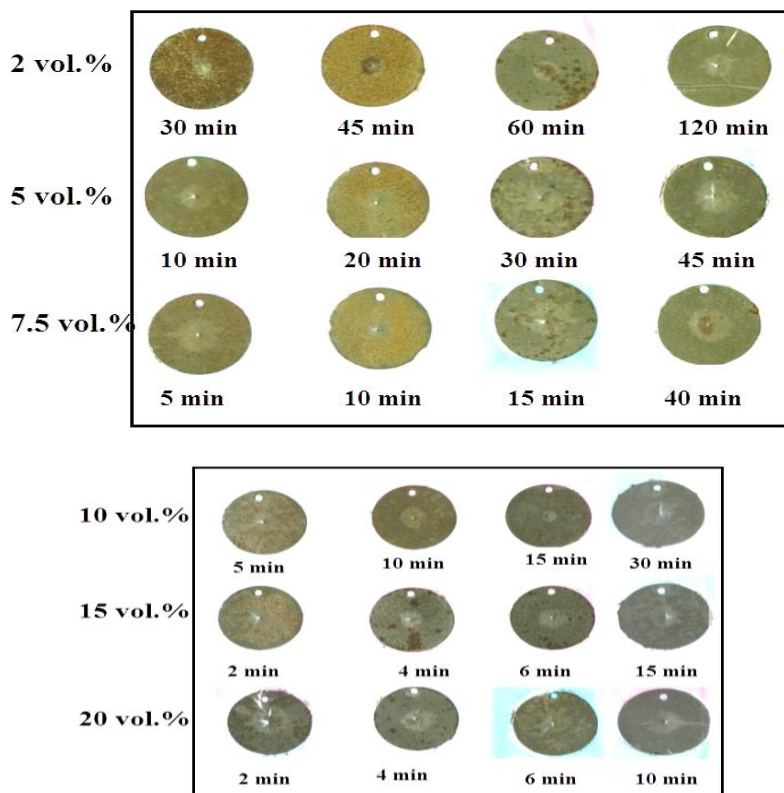
Figure 3. The surface morphology of rusted steel samples that are being treated with hydroxyethane diphosphonic acid (HEDPA) solution at 23°C.

5. Disussion

From the present investigation it is evident that the chemical reagent dissolves the rust and the rest removal kinetics depends upon the concentration and the solution temperature. It is also noticeable from Figure 2 that the steel sample also lost more weight than 100 % rust. This suggests that the reagent also dissolved the metal. If this system has to be used for commercial application, it is important (1) to understand the mechanism of rust removal by hydroxyethane diphosphonic acid reagent and (2) to understand whether the metal dissolution by HEDPA is a continuous process and /or at some stage the metal surface tend to passivate.

Table 1. Experimentally determined rate constants for different stages of chemical reaction process represented as a function of hydroxyethane diphosphonic acid (HEDPA) solution concentration for rust removal at 23°C.

HEDPA Concentration (vol %)	Rate Constant (gm cm^{-2} min^{-1}) X 10^{-3}			
	Overall Process	Stage I	Stage II	Stage III
2	0.31	0.24	0.31	0.08
3	0.43	0.32	0.45	0.06
4	0.49	0.34	0.55	0.08
5	0.57	0.44	0.68	0.06
10	0.76	0.38	0.90	0.17
20	0.80	0.44	1.30	0.18

In order to understand the mechanism of rust removal by HEDPA, it is important to analyze the chemical structure of the HEDPA. From Figure 1, it can be understood that hydroxyethane diphosphonic acid (HEDPA) has two phosphate groups and one extra hydroxyl (-OH) group. This would indicate that the iron from rust may dissolve in the HEDPA solution in either $Fe2^+$ and/or Fe^{3+} state. These Fe ions can compound with free hydroxyl (-OH) group and / or with the (P = O) cation sites and or with (P -OH) cation site. These different variations can produce different iron phosphates.

Table 2. The activation energy for the rust removal process by HEDPA solution

HEDPA Concentration (vol.%)	Activation Energy (kcal / mole)
2	11 ± 2
3	12 ± 2
4	13 ± 2
5	20 ± 2
10	28 ± 2
20	30 ± 2

The progression of metal dissolution after the rust removal was studied by continuing the reaction kinetics for 24 hours. It was noticed that the weight loss continued for approximately one hour. Later the sample started to gain weight. After 12 hours, a pale golden yellow precipitate was observed on the surface. After 18 hours, the precipitate resolved into the HEDPA solution. After 24 hours, a thick orange / yellow precipitate was observed on the sample surface. These samples were analyzed using x-ray diffraction. It was found that the peaks found in the x-ray diffraction patterns correspond to the standard peaks of several different hydrated iron phosphates. The detailed chemistry of the reaction by products will be reported later. he environment benign nature of the chemical reagent was tested using the following procedure. Two separate tests that involve the seed germination and/or the plant growth in presence of the chemical reaction by products were carried out. In the first set of experiments, the soil samples were mixed with 0 – 1 vol. % chemical reagent by products. The alpha-alpha seeds were implanted. In the second set of experiments, small spider plants were fed with solution containing 0 – 1 vol. % chemical reagent. The seed germination and growth and the plant growth was monitored for 5 weeks. Figures 4 show the germination of the seeds and Figure 5 shows the measured growth of the plants germinated from the seeds. The growth of the plant that was fed with chemical reagent by products is shown in Figure 6.
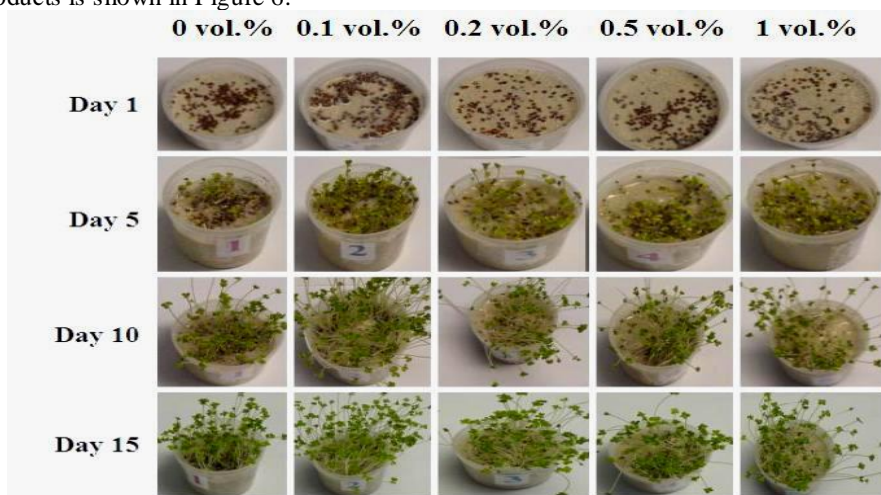

Figure 4. The germination of alpha- alpha seeds and the growth of the seedlings in soil containing 0, 0.1, 0.2, 0.5 and 1.0 vol. % of chemical reaction by products.

The results shown in Figures 4 and 6 suggest that the germination and / or the plant growth is not hindered by the presence of the chemical by products. The addition of the chemical by products either to the soil or as a plant feed improved the plant growth. The results shown in Figure 5 suggest that the addition of 0.1 wt.% chemical reagent has resulted in maximizing the germinated plant growth increased. Above 0.1 wt.%, an increase in the amount of chemical reagent present in the soil has decreased the growth rate of the germinated plants .At the present time we have not conducted any specific testing on the water pollution. However, it was noted that the pH of the HEDPA solution has changed from pH ~ 2 to pH ~ 3.8 after the rust removal process. It is possible that the volume of HEDPA solution used to clean each sample may be too large and the reuse of the agent may bring down the pH. These test results will be reported at a later date.
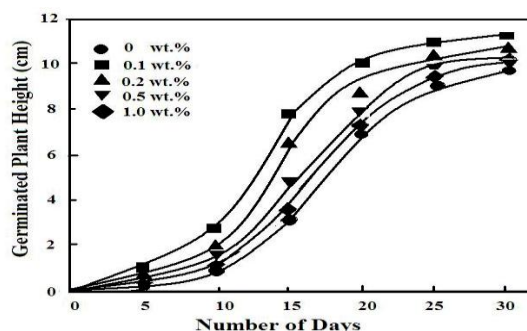

Figure 5. The average height versus the growth time of alpha – alpha seedlings germinated in soil containing 0, 0.1, 0.2, 0.5 and 1.0 vol. % of chemical reaction by products.

6. CONCLUSION

From my kinetics of rust removal investigation, the following conclusions can be derived.

1. The commercial chemical reagent hydroxyethane diphosphonic acid (HEDPA) is very effective in removing the rust.
2. The rate at which rust is dissolved by the chemical reagent increases with an increase in solution concentration and temperature.
3. The activation energy for the rust removal process for 1 and 3 vol % hydroxyl ethane diphosphonic acid [HEDPA] solution is 10 ± 1 and 12 ± 1 kcal /mol respectively.
4. The final reaction product is found to be complex mixture of iron phosphates.
5. The addition of 0.1wt. % chemical reaction by product to the soil has improved the germination and growth of plants. Similarly, the plants fed with 0.1 wt. % chemical by products of the rust removal process have shown an increase in the plant growth.
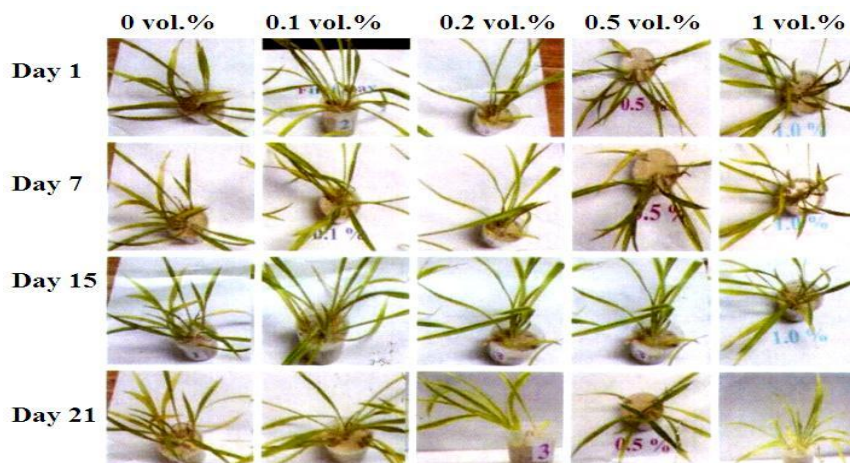

Figure 6.The growth of spider plants that were fed with a solution containing 0, 0.1, 0.2, 0.5 and 1.0 vol. % of chemical reaction by products.

7. Acknowledgements

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