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provide important theories and feasible plans for the maintenance of the stability of oasis system. And their potentials were effectively shown up in the practice in Weigan River.

3. Utilization of feedback mechanisms of ecology: we explored regulation modes of MODS in the specific soil development and land covering; and these regulation modes become the research pivots for coupling relations. MODS coupling modeling and MODS development modes hold important theoretical value and practical significance.

4. The theories and methods on MODS coupling relations, especially the simulation and quantity analysis on relations between subsystems and essential elements, need to be further intensively studied.

Achievements in the Project - "The Adsorption of Rare Earth Metal Ions and Ligands on Steel, Aluminum and its Synergistic Mechanism"

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1. Background

Corrosion is a fundamental process that plays an important role in economics and safety, particularly for metals and alloys. Nowadays, corrosion problems have received a considerable amount of attentions. The annual direct cost of metallic corrosion ranges from 2% to 4% of national GDP in industrialized countries, and this cost sounds escalating in the future. Therefore, the research in metallic corrosion & protection is very important. They are not only technical problems, but also the problems of resource protection, energy saving, material saving, environmental protection and so on. Researchers in this field endeavor to avoid all kinds of corrosions. The main strategy to prevent electro chemical corrosion is metal isolation from corrosive agents in the most effective possible manner, including anodic protection, cathodic protection, heat treatment, chemical passivation, conversion coating, surface treatment, electroplating, surface oxidation, inhibitor, and so on.

Inhibitor is the chemical agent that can drastically reduce corrosion rate of metal in corrosive medium, and the concentration of inhibitor is always very low (0.01 ~ 1000 mg/L). Among the above different methods available, the use of inhibitors is usually the most appropriate way to protect metals because of high efficiency, low price, and easy production. The inhibitor science is a new cross-disciplinary subject, namely, it studies the inhibitive effect and mechanism of the inhibitors for metals in different corrosive mediums. With the fast pace of oil chemical engineering and chemical cleaning, the development of inhibitor science was promoted greatly especially in the 1960s. The investigation of new non-toxic and green corrosion inhibitors is more strategic than in the recent past. In the 21st Century, the research in the field of "green" corrosion inhibitors has been addressed toward the goal of using cheap, effective molecules with low or "zero" environmental impact. In order to achieve the above objective, the basic theory of inhibitor is very important especially in the study of the inhibitive mechanism.

Synergism is a combined action of compounds greater in total effect than the summation of the individual effects (1 +1 > 2). Synergism of corrosion inhibitors is either due to the interaction between components of the inhibitor composition or due to interaction between the inhibitor and one of the ions present in the aqueous solution. Synergistic inhibition is an effective means to improve the inhibitive force of inhibitor, to decrease the amount of inhibitor usage, to diversify the application of inhibitor in acidic medium. Synergism plays an important role in not only theoretical research of corrosion inhibitors but also practical work.

Steel and aluminum have been found in wide applications in a broad spectrum of industries because of their low cost, high production and easy availability. China is rich in rare earth salts. Rare earth (RE) ions have low or

none toxicity, and can be considered as economically competitive products. Up to date, there are many papers in the literatures concerning the application of RE ions for the corrosion inhibitors of aluminum alloys. There are also several papers dealing with the use of RE salts as corrosion inhibitors for other metals and alloys such as zinc, bronze, nickel, mild steels or stainless steels. Obviously, most rare earth (RE) salts inhibitors were almost used in neutral or approximate neutral medium. However, the corrosion inhibition of RE salts in strong acidic medium was seldom studied. In our laboratory, much preliminary work was conducted to study the synergism between RE ions and ligands on the corrosion of steel and aluminum in acidic medium. In 2002, the proposal of the project "the adsorption of rare earth metal ion and ligand on steel, aluminum and its synergism" was formally submitted to the National Natural Science Foundation (NSFC).

In 2003, the project (No.: 50261004) was approved formally by NSFC. Prof. Guannan Mu from Yunnan University directed the project. The main goal was to study the adsorption of rare earth metal ion and ligand on steel, aluminum and its synergism. It was hoped to get the synergistic mechanism and direct the exploration of low-toxic and effective complex inhibitors.

2. Innovative Achievements

2.1 Corrosion Behavior of Steel, Aluminum in Mineral Acids

Mineral acids were applied in the most important fields of acid pickling, industrial acid cleaning, acid etching and oil well acidizing et al. Thus, the study of the corrosion behavior of metals in mineral acids is very important. In this project, the corrosion behavior of steel, aluminum in mineral acids (HCL, H_2SO_4, and H3PO4) was studied systematically. The effects such as temperature, acid concentration and corrosion immersion time were investigated. Based on the results, the corrosion kinetic equation was put forward, and the kinetic parameters such as activation energy, pre-exponential factor, corrosion rate constant, and corrosion reaction constant were calculated and discussed. The achievement is more systematical than previous studies and will become an important reference for chemical industry.

2.2 Effects of Rare Earth Ions on the corrosion of steel, aluminum in mineral acids

Most rare earth (RE) salts inhibitors were used in neutral or approximate neutral medium. However, the corrosion inhibition of RE salts in strong acidic medium was seldom studied. In the project, the corrosion inhibition of rare earth ions (La^{3+}, Ce^{3+}, Nd^{3+}, Ce^{4+}, Y^{3+}, and Sm^{3+}) on steel, aluminum in acidic medium was studied systematically. The effects of temperature, acid concentration and corrosion immersion time on rare salts (chlorides, sulfates, nitrates) were also studied. The experimental results showed that rare earth salts had poor inhibitive ability for steel in acidic medium. However, rare earth sulfates and nitrates ($La(NO_3)_3$, $Ce(NO_3)_3$, $Nd(NO_3)_3$, $Ce(SO_4)_2$, etc.) had good inhibitive ability for aluminum in acidic medium. This could be attributed to the obvious synergism between the rare earth ions and sulfate (nitrate).

2.3 Adsorption and Corrosion Inhibition of Ligand on Steel and Aluminum

Nowadays, inhibitive mechanism is not clear. Relationship between adsorption and corrosion inhibition plays an important role in disclosing the inhibitive mechanism. In this project, the adsorption and corrosion inhibition of inorganic ligands (molybdate, tungstate, and nitrate), organic ligands (containing O, S, N, P compounds) on steel, and aluminum were studied. The adsorption model was discussed, and the adsorption thermodynamic and kinetic parameters were calculated and employed for discussing the inhibitive mechanism. The amended Langmuir equation by using the amended factor H was proposed based on the Langmuir adsorption isotherm. The physical meaning of the amended factor was also detailedly discussed. The achievement was innovative and could be used in explaining the experimental phenomena. And this work was published on *Corrosion Science* and *Huaxue Xuebao* respectively. Besides, the adsorption mode (horizontally, vertically, laterally, and decubitally) was also discussed. The adsorption results in the project were more systematical and detailed than the previous studies, and the

major innovative achievement was the inhibitive mechanism proposed by using the thermodynamic and kinetic equations. The achievement is also an important reference in the basic theory of inhibitor science.

2.4 Synergistic Inhibition Effects of Rare Earth Ions and Ligands on Steel, Aluminum

The synergistic inhibition effects of rare earth ions and ligands on metals have only been studied by Mansfeld (USA), Aramiki (Janpan) and our research group. It should be noted that the synergism between rare earth ions and ligands on steel and aluminum in acidic medium was only investigated by our research group. Therefore, the project is of important scientific value in the basic theory of inhibitor field. On the other hand, the project is also difficult to carry out because of the lack literatures and theories. Through tons of hard experiments, a lot of ligands have been found. Namely, there are a lot of synergistic systems in acidic medium for steel and aluminum. In addition, the complex inhibitors (rare earth ion — ligand) have high inhibition efficiency, low-toxicity, none environmental impact, namely, the complex inhibitors can be applied for the chemical industry.

In order to detailedly study the synergism mechanism, atomic force microscope (AFM) was employed to study the steel and aluminum surfaces. In addition, the Fourier transform infrared spectroscopy (FT-IR), ultraviolet and visible spectrophotometer (UV-VIS), X-ray photoelectron spectroscopy (XPS) were also applied to study the inhibitive mechanism in order to add more reliability.

Through the data analysis of a lot of synergistic systems, the synergism mechanism between rare earth ions and ligands was proposed — "bridge theory". The "bridge theory" is that when the rare earth ion and ligand is mixed in medium, the new complex compound (RE ion-ligand) forms. This compound has strong adsorptive ability, and can be easily attached onto the metal surface. The result is that the inhibition increases largely and produces synergistic inhibition effect. The adsorption mode and order (comparing with RE ion, ligand) of the new complex was studied detailedly by using the above analysis instrument (UV-VIS, FT-IR, XPS, and AFM).

3. Conclusions

In this project, a lot of work including references review, data analysis, and experimental work etc. were carried out during the past 5 years. By the end of this project in December 2005, 30 papers including 12 SCI, 2 EI, and 3 international corrosion congress papers had been published. 6 master dissertations were involved in.

The project of "the result of the synergistic effects of rare earth ions and ligands in acids" holds its own peculiarity and adds the "margin" in the inhibitor science field to some extent.

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