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ATOMIC ENERGY COMMISSION

DECRUDDING AND CHEMICAL CLEANING OF CARBON STEEL COMPONENTS - AN EVALUATION

by

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Metallurgy Division

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BHABHA ATOMIC RESEARCH CENTRE
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Descriptors

CARBON STEELS

MONEL

HEAT EXCHANGERS

REACTOR COMPONENTS

CORROSION

CORROSION PRODUCTS

CORROSION INHIBITORS

CITRIC ACID

CITRATES

AMMONIUM COMPOUNDS

EDTA

HYDROCHLORIC ACID

ACRIDINES

PH VALUE

MEDIUM TEMPERATURE

SCALING

SOLUTIONS

DESCALING

SURFACE CLEANING

DECONTAMINATION

ABSTRACT

Corrosion and accumulation of corrosion products on the surfaces of structural components and plant equipments can cause severe operational problems during service. An illustration is the heat exchanger systems in nuclear power stations. Development and standardisation of appropriate chemical cleaning and decontamination procedures and their evaluation hence merit serious consideration.

A number of chemical cleaning procedures using formulations based on hydrochloric and citric acid solutions have been examined to study their crud dissolving and derusting ability in addition to the attack on base material. The compositions were chosen (1) along with complexing agents EDTA and ammonium citrate (2) with pH control and (3) with the use of inhibitors acridine, rhodine, hexamine and phenyl-thiourea. The evaluations have been made at 28 and 60°C. Rusted carbon steel coupons having a rust of 10-12 mg/cm^2 on the surface have been used for the purpose of the above evaluations. Data on corrosion rates of monel and cupronickel (70:30) in the descaling solutions have also been presented. Results on the above evaluation studies have been discussed.

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Introduction and Background:

Chemical cleaning of heat-transfer surfaces of industrial equipments is necessitated because of the maintenance problems associated with the formation of undesired scale and corrosion product deposits and occurrence of fouling in heat exchange systems. There have been several attempts to remove the corrosion products from the industrial equipments and the chemical cleaning is one of the methods adopted to have clean surfaces. The choice of the chemical cleaning reagents is based on the following requirements: (i) the chemical solvent should be able to dissolve or disintegrate the deposits so that they can be easily removed (ii) the chemical cleaning composition should be so formulated as to keep the attack on the base metal of the equipment to a minimum or least (iii) the residual chemical, if left over should not cause subsequent corrosion problems during the operation of the process and (iv) it should not be toxic or explosive and should be easy to handle.

The most popularly used chemical for cleaning the carbon steel components is a 10% hydrochloric acid solution in presence of an inhibitor at a temperature of about 40-60°C. However, several instances were noticed on severe corrosion problems subsequently associated with the use of this acid mixture. Localised corrosion effects such as pitting and crevice attack and the effect of hydrogen in the steel during and after the use of inhibited acid are important factors to be considered while adopting this chemical cleaning procedure. It is reported that both Fe^{+++} ions and residual chlorides will contribute to accelerate the corrosive attack on the base material and hence the control of these species after the operation is an important criteria.

In water cooled nuclear reactors, crud is a term referred to the loose corrosion product which circulates and deposits on various components giving rise to problems of activation, hydraulics, heat transfer and reactivity. Stringent water chemistry control is adhered both in PWRs and BWRs in order to keep the crud levels to a minimum. Excess crud levels give rise to increased radio-activity and calls for the removal of these undesired products. Reactor system decontamination is similar to chemical cleaning of normal industrial systems in that the oxides and deposits are removed, and in addition, the radiation levels are brought down considerably.

Organic acids like lactic, oxalic, citric and inorganic acids like phosphoric (H_3PO_4) and sulphamic (NH_2SO_3H) have been used for chemical cleaning of equipments in presence of suitable inhibitors. The inhibitors or restrainers as they are referred, function as adsorbers on the metal surface and hinder the direct attack of the base material. Inhibited citric acid solutions are effective in the concentrations range of 3 to 10 wt.% and at a pH level of 4.5 adjusted by adding ammonia or ammonium citrate and at temperatures ranging from 90° to 100°C. For decontaminating reactors containing both carbon steel and stainless steel, efforts have been made to develop a decontaminant for stainless steel and then inhibit it sufficiently for use on carbon steel. The decontaminant developed has to be effective for both stainless steel and carbon steel in a mixed system and still not corrosive to carbon steel whether or not it is in galvanic contact with stainless steel. In addition it should be effective for removal of the crud formed during the reactor operation. One of the methods, known as alkaline permanganate-ammonium citrate (APAC) method, constitutes treatment in solutions of 10-15% NaOH and 3% $KMnO_4$ at an elevated temperature of 80°-100°C and subsequently rinsing with a 10% ammonium citrate solution (pH 3.5 to 5.1), with or without an inhibitor. The inhibitors added to ammonium citrate include EDTA, phosphoric acid or sulphamic acid, each group of scientists choosing their own formulation. Proprietory brands of chemicals constituting ammonium oxalate/citrate (6% solution) at a temperature 80°-85°C are also used for decontamination of reactor components. Recently a 'Can-Decon', process has been developed in Canada, which has been applied successfully to NPD and Douglass Point reactors to achieve decontamination factors upto about 6. Although decontamination efforts could be successful in these operations, the problem areas are the release of crud during ammonium citrate phase of decontamination and its settling in dead legs which would require further examination of the process. This aspect is beyond the scope of this report.

The present investigation aims at a study of the rust-removing efficiency of different chemical formulations and their assessment. This data would be useful for selecting a composition, to adopt routinely for cleaning of the rusted surface of carbon steel components.

Experimental:

All the chemicals used were either of L.R. or commercially available grades. The experiments were carried out in duplicate. The weighings were done using a Mettler's semi-microbalance to an accuracy of $\pm$ 0.2 microgram.

For derusting studies, duplicate specimens were immersed in a particular chemical formulation for different periods until complete removal of rust is effected. The base metal dissolution is generally expressed as mg/cm^2/hour. For an estimation of crud dissolving capacity, about one gram of the crud is made to react with 200 ml of derusting solution and the dissolved part of the crud is expressed as gm/litre. The crud used in the study is a product obtained due to corrosion of mild steel in aqueous medium.

Results and Discussions:

A. Studies on chemical formulations:

For comparative purposes, it can be said that a base metal dissolution of 0.2 mg/cm^2/hour would be a good limit for operation of the formulation. A crud-dissolving capacity of 1.5 gm/litre is a fair formulation, while above 3.0 gm/litre can be considered as a good one for removal of rust. For decrudding the corroded components, it is desirable to operate at a near neutral pH.

The results on the use of inhibited hydrochloric acid for rust removal has been presented in table-1. Addition of two inhibitors, namely, rhodine and acridine (0.1%) have been studied. It can be seen that for a minimum base metal dissolution, rhodine is effective at about 60°C, while for acridine the temperature of the operation has to be reduced to near room or slightly above room temperature. At 60°C, a base metal dissolution of 6.1 mg/cm^2/hour is on the higher side (for acridine). It has to be noted that while using HCl, residual chlorides may cause subsequent localized corrosion problems and as already mentioned, often an organic acid like citric acid or EDTA has been utilised for removing the crud, and the results of these are presented in table-2. A 3% (w/v) solution of citric acid alone is fairly effective to dissolve the crud, while addition of an inhibitor like acridine protects the metal surface considerably (with a low metal dissolution of 0.20 mg/cm^2/hour). However, this involves low pH operation and subsequent thorough washing has to be done for attaining a neutral pH. A 4% solution of disodium EDTA can also be considered as a fair crud dissolving reagent as it operates at a pH of 5.0.

Various derusting solutions based on citric acid have been formulated to determine their effectiveness and results are summarised in table-3. It is known that citric acid/ammonium citrate combinations are very good complexing agents and are capable of slowly dissolving iron oxides and EDTA salt is capable of dissolving the calcium or other metallic oxides effectively. From table-3, it can be seen that the formulation 3 is a very good composition for effectively removing the rust with minimum base metal dissolution, at temperatures between 50°-60°C. Formulation 6, based on adding phenylthiourea for inhibition also appears to be a very effective formulation; here only a small quantity (such as 10 ppm) would be required to be added. It is noticed that phenylthiourea has a very limited solubility and hence higher concentrations were not found to be very effective for further reduction of base metal dissolution.

In another series of experiments, citric acid-ammonia combinations have been studied and results are summarised in table-4. It is seen that all these combinations are only fairly effective for crud dissolution and lowering the pH of the solution has not shown any remarkable change in crud dissolution. Also, the base metal dissolution was found to be on the higher side.

From the above studies, it can be seen that a formulation containing 5% citric acid, 3% triammonium citrate, 0.2% disodium EDTA either in presence of 0.1% acridine or 0.001% phenylthiourea in the temperature range 55-60°C is very effective for removal of the rust or for the crud dissolution. The base metal dissolution in this formulation has been found to be very low. It can also be stated that a 3% citric acid solution alone or in presence of an inhibitor like acridine is a suitable chemical for routine removal of rust from most of the components.

B. Studies on dissolution of rust from corroded samples:

A few studies have been carried out on the chemical cleaning of the corroded coupons using citric acid and citric acid/ammonium citrate formulation, and the results are summarised in tables 5 and 6. It is seen that more than 98% of the rust could be removed within about 2 hours in 1% citric acid, while in 3% citric acid, the efficiency has been observed to be much better. Complete descaling could be achieved within one hour of the treatment of the coupons. With citric acid/ammonium-citrate formulation a period of four hours was required for complete descaling. Based on these laboratory results, it is possible to extrapolate the descaling procedure to larger size plant equipments.

C. Chemical interaction between descaling solutions and cupro-nickel/monel tubes:

In a heat transport system, in addition to steels, there could be other materials such as monel or cupro-nickels which might come in contact with the descaling chemicals. In such an event, the corrosion rate on these materials also would be required to be assessed. Table-7 summarises some of the corrosion rates obtained from the laboratory exposures in these materials. The dissolution rates were not appreciable in these solutions. However, in citric acid/ammonium-citrate formulation the dissolution rate of about 0.11 mg/cm^2/hour has been observed for monel tubes at a temperature of 60°C.

Summary and Conclusions:

Chemical cleaning of rusted carbon steel surfaces by using a number of chemical formulations have been studied with a view to arrive at the optimum conditions for decrudding and cleaning of heat exchanger systems. It is seen that a formulation containing 5% citric acid, 3% ammonium citrate, 0.2% disodium EDTA either in presence of 0.1% acridine or 0.001% phenylthiourea in the temperature range 55-60°C is very effective for removal of the rust or for the crud dissolution. For routine removal of rust from most of the components a 3% citric acid solution alone or in presence of an inhibitor like acridine is a suitable chemical.

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TABLE - 1: Base metal dissolution and rust removing capacity using HCl solution

S.No.	Medium	Temperature °C	pH	Base metal dissolution $mg/cm^2/hour$	Crud dissolution gm/litre
1.	10% HCl	60	0.2	16.7	3.32
2.	10% HCl + 0.1% rhodine (inhibitor)	60	0.4	1.62	3.46
3.	10% HCl + 0.1% acridine	28	0.4	1.04	1.80
4.	10% HCl + 0.1% acridine	60	0.4	6.1	3.56

TABLE - 2: Inhibited citric acid and EDTA for removal of rust from carbon steel

S.No.	Medium	Temperature °C	pH	Base metal dissolution $mg/cm^2/hour$	Crud dissolution gm/litre
1.	1% Citric acid	60	-	-	0.77
2.	2% Citric acid	60	-	-	0.83
3.	3% Citric acid	60	1.9	0.76	1.3
4.	3% Citric acid + 0.1% acridine	60	2.1	0.20	1.3
5.	2% Citric acid + 0.2% disodium EDTA	60	-	-	0.96
6.	4% disodium EDTA	60	5	2.2	1.1

TABLE - 3 : Citric acid + triammonium citrate combination

S.No.	Medium	Temperature °C	pH	Base metal dissolution mg/cm²/hour	Crud dissolution gm/litre
1.	5% citric acid + 3% tri-ammonium citrate + 0.2% disodium EDTA	28	∽4	1.2	1.06
2.	5% citric acid + 3% tri-ammonium citrate + 0.2% disodium EDTA	60	∽4	2.4	2.6
3.	5% citric acid + 3% tri-ammonium citrate + 0.2% disodium EDTA + 0.1% acridine	60	∽4	0.09	3.2
4.	3% citric acid + 3% tri-ammonium citrate + 0.2% disodium EDTA + 0.1% acridine	45	∽4	0.09	1.8
5.	5% citric acid + 3% tri-ammonium citrate + 0.2% disodium EDTA + 0.1% hexamine	60	∽4	1.0	2.6
6.	5% citric acid + 3% tri-ammonium citrate + 0.2% disodium EDTA + 0.001% (10 ppm) phenylthiourea	60	∽4	0.16	3.1
7.	5% citric acid + 3% tri-ammonium citrate + 0.2% disodium EDTA + 0.01% (100 ppm) phenylthiourea	60	∽4	0.048	3.3

TABLE - 4: <u>Formulations based on citric acid + ammonia combination</u>

S.No.	Medium	Temperature °C	pH	Base metal dissolution $mg/cm^2/hour$	Crud dissolution gm/litre
1.	3% citric acid + 0.2% disodium EDTA + 20 ml/litre of conc. ammonia	60	$\sim$4.1	0.76	2.0
2.	5% citric acid + 0.2% disodium EDTA + 30 ml/litre conc. ammonia	60	$\sim$4.1	1.48	2.5
3.	3% citric acid + 0.1% disodium EDTA + 8 ml/litre of conc. ammonia + 0.2% hexamine	50	$\sim$3	1.04	1.4
4.	3% citric acid + 0.1% disodium EDTA + 8 ml/litre of conc. ammonia + 0.2% hexamine	60	$\sim$3	1.0	1.5
5.	5% citric acid + 0.1% disodium EDTA + 15 ml/litre conc. ammonia + 0.2% hexamine	45	$\sim$3	1.1	1.4
6.	5% citric acid + 0.1% disodium EDTA + 15 ml/litre conc. ammonia + 0.2% hexamine	60	$\sim$3	1.1	1.3

TABLE - 5: <u>Descaling using citric acid solution</u>

Materials used: Rusted carbon steel coupons, having a rust of 10 to 12 mg/cm^2 on the surface; specimen area used $\sim$ 12 cm^2; volume of the derusting solution used, 200 ml.

Exposure time, hrs.	Weight loss, mg/cm^2		Remarks
	1% citric acid 60°C	1% citric acid + 0.1% acridine 60°C	
½	7.0	7.8	
1	9.5	10.0	
2	12.6*	13.6*	* Descaling complete
3	14.3	14.7	
4	-	-	
	3% citric acid 60°C	3% citric acid + 0.1% acridine 60°C	
½	12.2	12.8	
1	14.4*	14.6*	
2	22.3	15.7	
3	-	-	

TABLE - 6: Descaling using citric acid + ammonium citrate

Materials used: Rusted carbon steel coupons, having a rust of 10 to 12 mg/cm^2 on the surface; specimen area used ~ 12 cm^2; volume of derusting solution used 200 ml. Chemical formulations was 5% citric acid, 3% tri-ammonium citrate, 0.2% disodium EDTA and 0.1% acridine.

Exposure time, hrs.	Weight loss, mg/cm^2		Remarks
	28°C	60°C	
1	-	8.7	* Descaling complete
2	6.72	10.2	** Partial descaling
4	7.8	13.9*	
8	9.2**	-	

TABLE - 7: Corrosion rates on monel and cupro-nickel (70:30) in descaling solutions

Medium	Exposure time, hrs.	Weight loss, mg/cm² 28°C	Weight loss, mg/cm² 60°C	Remarks
1. **Monel tubes**				
1% citric acid	1	-	0.06	* Surface remained bright
	2	-	0.09	
	3	-	0.12	
	4	0.03	0.15*	
3% citric acid	1	-	0.03	
	2	0.05	0.05	
	3	0.04	0.09	
	4	0.06	0.11*	
3% citric acid + 0.1% acridine	4	0.07	0.12	
5% citric acid + 3% tri-ammonium citrate + 0.2% disodium EDTA + 0.1% acridine	2	-	0.21	
2. **Cupro-nickel (70:30)**				
2% citric acid	2	-	0.12	
2% citric acid + 0.2% disodium EDTA + 0.1% acridine	1	-	0.03	
	2	-	0.06	