SYNOPSIS

Interactions of complexants and complexes with ion exchange resins in dilute chemical decontamination processes

INTRODUCTION

The nuclear power plants face the problem of radiation field build-up on the out-of-core surfaces\(^{(1)}\) of the primary heat transport system as a result of transportation of activated corrosion and fission products from the core by the coolant. The activated corrosion products and the fission products are impregnated into the oxide lattices of the corrosion product layers. The radiation emanating from the $\gamma$-emitting isotopes of the activated corrosion products and fission products give rise to MAN-REM problem in nuclear power reactors\(^{(2)}\). These $\gamma$-emitting activities can be removed from the system surfaces by dissolving the host oxides using chemical formulations called decontamination formulations\(^{(3)}\).

REGENERATIVE TYPE OF DILUTE CHEMICAL DECONTAMINATION PROCESSES:

Several dilute chemical decontamination processes are in vogue to decontaminate the surfaces constituting the primary coolant systems\(^{(4-5)}\). These processes use organic acids to dissolve the oxides and to act as complexants for the dissolved metal ions and redox agents for modifying the oxide layer so as to facilitate the dissolution reaction. The metal ion complexes formed in the oxide dissolution reaction are passed through the cation exchange resin where the metal ions are transferred to the resin phase and the complexant is released (regenerated) back to the solution for further dissolution. Anion exchange resin is used for the removal of complexants and other remaining formulation components and metal ions, on completion of the decontamination operation. An attempt has been made in this work to study the heart of the dilute chemical decontamination processes namely the ion exchangers and their behaviour with complexants and the metal ion complexes. A catalyst loaded anion exchange resin in enhancing the rate of decomposition of organic acids by hydrogen peroxide, has also been studied.
AIM AND SCOPE OF THE STUDY:

Complexones such as EDTA, NTA, HEEDTA, DTPA etc. have good complexing ability and do not pose any serious corrosion problems. These are, therefore, considered to be good decontaminants. When solutions of these complexones are passed through cation exchange resin, the concentration of the complexones decreases in solution because of their pick-up by the cation exchange resin\(^6\). A quantitative relation to estimate the amount of absorption of these complexones on the resin phase does not exist and the variation in absorption with solution composition could not be explained properly. Hence, a detailed study was undertaken to arrive at a quantitative relation which can be used for estimating the amount of absorption of complexones by the cation exchange resin as a function of solution composition.

Metal ions released by the dissolution of corrosion product oxides such as Fe\(^{3+}\), Fe\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\), Cr\(^{3+}\), Co\(^{2+}\) etc. form anionic complexes with complexones and other complexing agents used as decontaminants. The metal ions from the complexes should be transferred to the cation exchange resin in quantity commensurate with the ion exchange capacity of the resin for an efficient functioning of the decontamination process operated in regenerative mode. The complexant and the acid regenerated thus are used for further dissolution of oxides. An attempt has been made to arrive at an optimum value of the stability constant of complexes which would enable efficient transfer of metal ions from the complexes to the cation exchange resin. Studies on the removal of activated corrosion products and fission products by cation and anion exchange resin from the solution containing complexants also can help in understanding their ion exchange removal behaviour. Investigations on the ion exchange behaviour of complexants and metal ion complexes can help in choosing a better complexant as decontaminant. However, the chosen complexants have to be investigated for their ability to disssolve the oxides and their compatibility with materials to which they will be applied. The material compatibility and oxide dissolution aspects of decontaminant formulations consisting of NTA and mixture of NTA and EDTA were investigated at high temperatures.

Collecting the complexants used for decontamination by anion exchange resin poses some problems at the waste disposal stage. Decomposition of the used complexants by an
oxidant is a good option to circumvent this problem. In this work, a catalyst loaded anion exchange resin has been investigated for its catalytic action in decomposing organic acids by hydrogen peroxide. Kinetic investigations with a view to get an insight into the mechanism of the catalysed oxidation reaction were made.

Following are some of the important results and observations made out of this work:

Solubility of EDTA measured as a function of pH (0-3) showed that it decreases as the pH is lowered from 3 and reaching a minimum value at pH 1.6. Thereafter, there is an increase in solubility. The value of solubility at the minimum of the solubility curve was found to be 140 ppm. EDTA was found to be absorbed on strong acid cation exchange resin even at 100 ppm concentration. This observation excludes the possibility that EDTA could precipitate at the high acidity existing in the ion exchange resin. Further experiments carried out on EDTA absorption as a function of pH by both batch and column methods showed that the mono positive and dipositive species of EDTA present in the solution were involved in ion exchange reaction with the cation exchange resin and the quantity of EDTA absorbed by the cation exchange resin (measured as a function of pH and EDTA concentration) was found to tally with the equation derived from the ion exchange laws. Similar behaviour was observed with NTA, HEEDTA and DTPA(7). Studies carried out in heavy water (D₂O) showed that the absorption behaviour of EDTA was different from that observed in light water(H₂O). Large difference existed in the amount of EDTA absorbed per unit volume of cation exchange resin observed in light water medium and heavy water medium. This change caused by the isotopic differences is explained by the differences in the concentrations of mono positive and dipositive species of EDTA in heavy water as compared to light water under the conditions of experiment.

Corrosion product metal ions released to a chemical formulation form complexes with the chelants constituting the formulation. Polarographic investigations of the iron complexes formed in a formulation containing EDTA, Oxalic acid and Citric acid (EOC) showed that Fe²⁺ from Fe²⁺-EDTA could be transferred to the resin easily where as Fe³⁺ from Fe³⁺-EDTA could not be exchanged with the H⁺ ions of the cation exchange resin(8) because of the high stability of the Fe³⁺-EDTA complex(9). Polarographic studies on other iron complexes such as Fe²⁺-Citrate, Fe²⁺-oxalate have also been carried out. Further studies
carried out with other corrosion product metal ions such as Ni$^{2+}$, Cu$^{2+}$, Cr$^{3+}$ showed that regeneration of EDTA is difficult when the solution contains metal ions other than Fe$^{2+}$. It has been established that under such situations NTA is a better reagent.

Ion exchange experiments carried out with coupons exposed to the environment existing in the primary heat transport system of PHWRs showed that most of the activated corrosion product isotopes such as $^{60}$Co, $^{58}$Co and $^{54}$Mn could be removed by strong acid cation exchange resin from EDTA as well as EOC (EDTA, Oxalic acid and Citric acid) formulation. However, $^{125}$Sb could not be removed by cation exchange resin. Similarly, among the fission product isotopes $^{103}$Ru, $^{106}$Ru, $^{95}$Zr and $^{95}$Nb were not efficiently removed by the cation exchange resin. However, formulation equilibrated anion exchange resin$^{(10-11)}$ could efficiently remove these activities. Based on complex equilibria and stability constants of the complexes formed in the formulation, the ion exchange behaviour of the activated corrosion and fission product nuclides have been explained. It is also proved that in mixtures of complexants such as EAC and EOC it is the EDTA which decides the ion exchange behaviour of most of the metal ions. Activated corrosion product isotopes and fission product isotopes dissolved by the complexants have the tendency to redeposit on the metal surfaces. This redeposition process has been found to be linked to the ion exchange removal behaviour of those activities.

Corrosion compatibility studies carried out in oxalic acid and ascorbic acid based formulations and considering other factors like IGA and oxalate formation showed that ascorbic acid based formulations are preferable over that of oxalic acid based formulations. A formulation consisting of EDTA, Ascorbic acid and Citric acid (EAC) was constituted. Experiments carried out under simulated decontamination conditions revealed that the rate at which the formulation is regenerated by ion exchange resin can decide the efficiency of oxide dissolution and it was also found to decide the rate of the reaction of metal with the acid. A relation has been established between the corrosion rate and the ion exchange regeneration rate. The increase in the corrosion rate with increase in the regeneration rate is attributed to the increase in the steady state concentration of the formulation made available by the increased rate of ion exchange regeneration of the formulation. It has also been observed that the unregenerable Fe$^{3+}$-EDTA if formed or added will be reduced by ascorbic acid to regenerable Fe$^{2+}$-EDTA.
NTA is better than EDTA from the point of view of ion exchange regeneration. In addition to its ion exchange behaviour, dissolution of spinel containing chromium, iron and nickel and its compatibility with nuclear reactor coolant structural materials have been evaluated at high temperature (150-180°C). The effect of additives such as dissolved oxygen, hydrazine, and other chelating/reducing agents in influencing the high temperature oxide dissolution and metal corrosion reaction have been studied. NTA or a mixture containing EDTA and NTA can be used as a high temperature decontaminant for decontaminating chromium, nickel and iron containing oxide deposits without the need for either oxidising or reducing agents.

Palladium loaded ion exchange resin was found to catalyse the oxidative decomposition of oxalic and other organic acids by hydrogen peroxide. Kinetic study of the catalysed reaction showed that the reaction is first order with respect to hydrogen peroxide but is independent of oxalic acid concentration. The rate was also found to increase in proportion to the volume of CLIX. Temperature and the influence of metal ions such as Fe²⁺, Cr³⁺ have also been found to influence the reaction. A mechanism involving adsorption on the catalyst surface prior to decomposition has been proposed. Other organic acids such as formic acid and glyoxylic acid were also found to be decomposed to carbon dioxide. On the other hand ascorbic acid, pyruvic acid, EDTA and NTA were found to decompose to smaller organic entities. The possible intermediates formed during the oxidation reaction has been discussed.

The findings from this work are:

i) EDTA is absorbed on the cation exchange resin through ion exchange mechanism and the amount of EDTA absorbed on the cation exchange resin can be given by the relation

\[ \text{EDTA absorbed} = (yK_a + zK_h)[\text{EDTA}](m_{H^+}/m_{H^+}) \]

where 'y' and 'z' are fractions of mono positive and di positive ions.

ii) NTA, HEEDTA and DTPA were also found to behave like EDTA. The order of selectivity was found to be in the order

\[ \text{NTA < EDTA < DTPA < HEEDTA} \]
iii) Pick-up of metal ions by strong acid cation exchange resin is dependent on the stability of the complex formed by the metal ion in the medium. Complexants forming Complexes of intermediate stability are preferable over the complexants forming complexes of high stability. In this context, NTA is considered to be superior to EDTA.

iv) NTA or a mixture consisting of major portion of NTA can be used as high temperature decontaminant for dissolving chromium and nickel containing ferrites without the need for oxidising treatment.

v) A palladium loaded anion exchange resin has been found to catalyse the decomposition of oxalic acid and other organic acids by hydrogen peroxide. Based on the kinetic studies of this oxidative decomposition reaction a probable mechanism for this reaction has been proposed.

ORGANISATION OF THE THESIS:

The whole work is presented in five chapters as described below.

Chapter I, Introduction:

In this introductory chapter, the problems pertaining to activity transport and the methods of decontamination of operating reactor systems are discussed. Relevant literature surveyed in these areas is also presented. The aim and scope of the present work is discussed.

Chapter II: Methods and materials:

The experimental methods, procedure and the materials used have been discussed. Batch experiments, column experiments and experiments carried out in dynamic glass loop have been described in detail. Experiments carried out in a teflon lined autoclave to investigate the high temperature oxide dissolution and material compatibility with complexants have also been described.

Chapter III: Ion exchange behaviour of complexones and metal ion complexes:

The results and observations made in the work pertaining to the ion exchange behaviour of dilute chemical decontaminants normally used at temperatures of 60-90°C and at high
temperatures (140-180°C) and the relevant metal ion complexes are presented in this chapter.

Chapter IV: High temperature decontamination:

In this chapter the high temperature dissolution of Ni$_{0.75}$Cr$_{0.75}$Fe$_{1.5}$O$_4$ using NTA, EDTA etc. have been discussed. Material compatibility and ion exchange behaviour of the complexes formed in the dissolution process also have been discussed.

Chapter V: Studies on Catalyst Loaded Ion exchange Resin:

Results of the studies carried out on the decomposition of oxalic acid and other organic acids by hydrogen peroxide catalysed by Palladium loaded strong base anion exchange resin has been presented.

Chapter VI: Conclusions:

This chapter lists the major findings of the present work. Also, suggestions for further work in this area has been given.

References:


