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# Colloid Stabilization by Polyelectrolytes. Application to Decontamination Processes of Nuclear Reactors

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*ABSTRACT*

*The redeposition of colloidal magnetite particles can reduce the effectiveness of the chemical decontamination of nuclear reactors. Sodium salts of the following anionic polyelectrolytes were evaluated as particle stabilizers: polyacrylic acid, polymethacrylic acid, poly (methyl vinyl ether/maleic anhydride), sulfonated polymers. A cationic polyelectrolyte, a polyamine, was also evaluated. An active and an inactive oxidized carbon steel sample were treated in the same experimental set-up with the decontaminating reagent and with or without the polyelectrolyte. Activity pick-up by the inactive sample was measured. When no polyelectrolyte was added, 15% of the Co-60 activity was redeposited. With polyelectrolyte addition in the 5–450 mg kg$^{-1}$ range, the Co-60 activity redeposition ranged from 8·5 down to 0·8%. Polyacrylic acid was the most effective reagent. The transfer of the magnetite outer oxide crystals from the active to the inactive surfaces was identified on SEM micrographs.*

*Key words*: Colloid stabilization, polyelectrolytes, decontamination, nuclear reactors, primary heat transport system, magnetite.

## 1 INTRODUCTION

Stability control of colloidal dispersions and suspensions by adsorption of polymers or polyelectrolytes has been studied quite extensively[1,2] and its technical



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applications are steadily increasing. Although polyelectrolytes are widely used in many industrial processes, for example as flocculants in water purification, as stabilizers for food and pharmaceutical emulsions, in paint production and in soil stabilization, in the paper industry, for mineral separation processes, etc., most of the systematic work done on the adsorption of polymers on colloids has involved non-ionic polymers, whereas ionogenic polymers have received relatively little attention.

It is now accepted that stabilization or destabilization of colloids by polyelectrolytes is the result of the following mechanism:[1,2] the first factor which has to be considered is the adsorption of the polyion on the colloidal particles. This process depends on a first approximation on electrostatic factors, that is, whether charges on both partners are alike or not. In the most common case, where the charges are opposite, after adsorption, the absolute value of the particle charge may decrease (low adsorption density), remain equal (intermediate) or increase (high). For the two extreme cases, electrostatic considerations only lead to a destabilization in the first one, and to a stabilization in the last one. In addition to the above factor, the so-called steric factor also influences the stability of the colloidal dispersion. This factor may be visualized as the presence of a coating on the particles, which leads to an increase in the closest approach when two particles interact, and hence to a decrease in the probability of attractive interactions. These interactions depend on very short-range forces, which are the cause of the destabilization. It seems that the relative importance of the steric factor is larger than the electrostatic factor.[1]

The second factor is the relative molecular weight of the adsorbed molecules, since it is well known that rather high molecular weights lead to destabilization, whereas in general low molecular weights ($< 10\,000$) contribute to the stabilization of colloidal systems. A rather simple idea explains this difference: at larger molecular weights, the same molecule may attach itself to two or even more particles, thus contributing to the destabilization.

Another practical and novel application of these principles, which to the best of our knowledge has not been recognized up to date, has been explored in our laboratories and shall be presented in this paper.

Primary heat transport systems (PHTS) of nuclear reactors become contaminated during operation, because of a dynamic interplay between dissolution and precipitation of the oxides formed by corrosion of the alloys constituting these circuits. As radioactive fields increase due to this phenomenon, maintenance operations become increasingly difficult, and eventually, these radioactive oxides have to be removed. The process by which this objective is accomplished, the decontamination, consists mainly of the dissolution of the oxides containing radionuclides. In the case of CANDU (Canadian Deuterium Uranium) pressurized heavy water reactors (PHWR), the predominant alloy of the PHTS is carbon steel and the oxide formed is mainly magnetite ($Fe_3O_4$). For magnetite dissolution, the CAN-DECON® (CANDU-Decontamination) decontamination process was developed. It consists mainly of a dilute (0·1 %) mixture of weak organic acids (oxalic acid, citric acid and ethylenediamminetetraacetic acid, EDTA) in which the oxalic acid seems to be the important one from the point of view of the ability to dissolve $Fe_3O_4$.[3,4]

During the early stages of the development of the CAN-DECON process, it became apparent that activity removal from component surfaces occurs not only by dissolution of the oxide film, but also by removal of the particles from surfaces.

Only sub-micron filters were effective in removing particles from the decontamination solution. It was thus concluded that the particles liberated during decontamination are in the colloid size range.

Even when a decontamination is effective, that is, when most of the radioactivity is removed from the circuit, there are a few locations where an increase rather than the expected drop in radiation field is observed. This increase in radiation field is attributed in part to radioactive particle deposition.

Both activation and fission products are redeposited during decontamination. In the decontamination of the PHTS of a CANDU reactor, approximately 15 % of the Co-60 activity, which constitutes the principal contributor to the high radiation fields, is removed on filters and the remainder is eliminated by ion exchange resins. During the CAN-DECON treatment of circuits also contaminated with fuel debris, activity redeposition can be a problem. The fuel particles and several of the fission products, such as Zr-Nb-95 and Ru isotopes are insoluble in the CAN-DECON reagent, and their removal is exclusively by particle transport.

An experimental program has been initiated to investigate the particle redeposition process and to find ways to reduce it. In the PHTS of the CANDU reactor, Co-60 is associated with magnetite. Therefore, the initial work has been concentrated on magnetite particles.

Polyelectrolytes have been successfully used in conventional boilers to control the deposition of iron oxides,[5-7] therefore we have directed our efforts into exploring their effectiveness in reducing magnetite redeposition during the CAN-DECON decontamination process. Results of this investigation are presented here. The influence of these polyelectrolytes on the dissolution of magnetite has also been studied. These results were presented elsewhere.[8,9]

## 2 EXPERIMENTAL

Preliminary experiments were conducted using commercial magnetite powder with a sub-micron particle size range. Dispersion of this powder in the CAN-DECON reagent solution was promoted by agitation in an ultrasonic bath. The settling rate of the magnetite was measured in 0·1 % decontamination solution with and without dispersant addition. Poor reproducibility of these experiments indicated incomplete dispersion of the magnetite powder, and thus this approach was abandoned.

A procedure that more closely simulates decontamination conditions was subsequently used. In it, the magnetite particles were generated during the CAN-DECON treatment of preoxidized carbon steel samples. Samples covered with a radioactive oxide film, and others covered with a non-radioactive oxide film, were treated concurrently in the same solution. Transfer of activity to both the surface of the carbon steel sample, that was initially inactive, and into the solution was evaluated. Sample pretreatment conditions are listed in Table 1. Figure 1 illustrates the equipment used in the decontamination experiments.

**TABLE 1**
Sample Pretreatment Conditions

| | *Active* | *Inactive* |
|---|---|---|
| Material | Carbon steel | Carbon steel/Incoloy-800 |
| Pretreatment environment | U-2 loop autoclave[a] | Static autoclave |
| Temperature | 300°C | 350°C |
| pH | 10·2 (LiOH) | 10·2 (LiOH) |
| Duration | 6–8 weeks | 6 days |

[a]In-reactor loop of the NRU reactor at Chalk River Nuclear Laboratories.

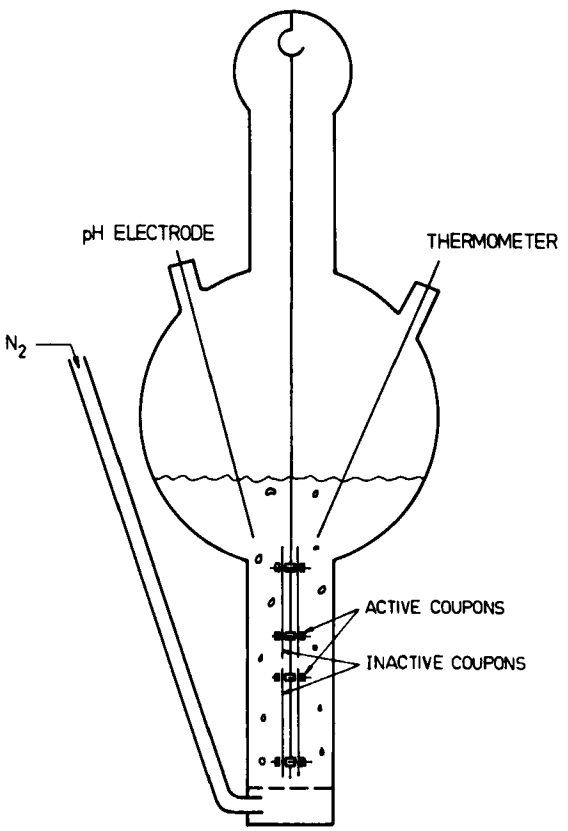



**Fig. 1.** Apparatus used for redeposition studies.

The glass vessel was partially filled with 0·1% decontamination solution, containing or not containing the dispersant. The glass vessel was immersed in a constant temperature bath held just above 85°C, the temperature at which the CAN-DECON process is normally performed. To exclude oxygen from the system and to provide mild agitation, nitrogen was bubbled through the solution. When the solution temperature reached 85°C, an active and an inactive carbon steel

sample were immersed in the reagent for 2·5 h. In selected experiments, a preoxidized, inactive Incoloy-800 sample was also immersed in the decontamination solution (Incoloy-800 is the alloy often used in CANDU steam generators). On completion of the experiment, radionuclide concentrations in solution and on alloy sample surfaces were determined by gamma spectrometry. Alloy samples were also subjected to examination by scanning electron microscopy.

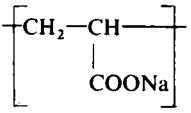
The commercially available polyelectrolytes tested in this program are listed in Table 2. The detailed compositions of some of them were not provided by the manufacturer. Several of the polyelectrolytes tested are normally used as additives to boiler feedwater to reduce particle growth and deposition, and as additives to cooling water to reduce iron oxide deposition. With the exception of one cationic polyelectrolyte, Ucipol GC700, all of the reagents tested were anionic.

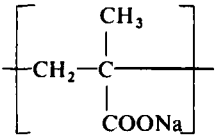
**TABLE 2**
List of Polyelectrolytes Tested

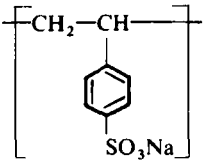
| *Trade name* | *Chemical composition* | *Manufacturer* | *Molecular weight range* |
|---|---|---|---|
| Antiprex A | Sodium salt of polyacrylic acid | Allied Colloids | 2000–4000 |
| Antiprex MNE | Sodium salt of polymethacrylic acid | Allied Colloids | 2000–4000 |
| Versicol E-7 | Sodium salt of homopolymers and copolymers of acrylic acid | Allied Colloids | ~27 000 |
| Versicol E-9 | | | ~76 000 |
| Gantrez AN-119 | Sodium salt of poly (methyl vinyl ether/ maleic acid) | GAF Corp. | Low |
| Gantrez AN-149 | | | Medium |
| Gantrez AN-169 | | | High |
| Betz Sperse Plus | Sodium salt of carboxylated-, sulfonated polymer + surfactant | Betz | N.A.[a] |
| Alchem 7WT-283 | Sodium salt of polyacrylic acid + detergent | Alchem | N.A.[a] |
| Ucipol GC700 | Polyamine | Union chimique et industrielle de l'ouest (France) | N.A.[a] |

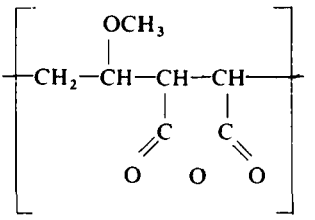
[a]N.A., not available.

The chemical structures of the monomeric units of some of these polyelectrolytes are as follows:

Antiprex A: 

Antiprex MNE: 

Sulphonated polymer: 

Gantrez AN: 

## 3 CALCULATIONS

The per cent activity redeposition ($K$) was evaluated for Co-60 in each experiment by equation (1).

$$K = \sum_{i=1}^{n} A_i \Big/ \left( L + \sum_{i=1}^{n} A_i \right) \times 100 \qquad (1)$$

where $A_i$ = activity deposited on the surface of $i$th alloy sample during decontamination, measured in Becquerels (Bq), $n$ = number of samples in the experiment (two or four) and $L$ = activity in solution (Bq).

$A_i$ was evaluated directly for alloy samples that were inactive initially and was calculated for the active samples, assuming that the specific activity (activity/surface area) of redeposited activity on both types of sample was identical.

Decontamination factors ($DF$) were calculated for initially active samples by

$$DF = \text{Activity before decontamination/activity after decontamination} \qquad (2)$$

The activity after decontamination included redeposited activity.

## 4 RESULTS AND DISCUSSION

### 4.1 General

Tables 3 and 4 illustrate the effect of polymer type and molecular weight on per cent Co-60 activity redeposition at the same polymer concentration. Surprisingly, polymer molecular weight had a relatively minor effect on activity redeposition, even though the molecular weight of the sodium salt of polyacrylic acid tested ranged from 2000 to about 76 000. When no polyelectrolyte was added to the

**TABLE 3**
Effect of Polymer Structure on Co-60 Redeposition

| | *%Co-60 deposited on carbon steel*[a] |
|---|---|
| No polyelectrolyte added | 15 |
| Anionic polyelectrolyte (50 mg $kg^{-1}$) | |
| Sodium salt of: | |
| Polyacrylic acid | 2·4 |
| Polymethacrylic acid | 5·7 |
| Sulfonated polymer | 8·5 |
| Cationic polyelectrolyte (110 mg $kg^{-1}$) | |
| Polyamine | 7·7 |

[a]100% = activity removed from active coupon.

**TABLE 4**
Effect of Polymer Molecular Weight on Co-60 Redeposition

| *Trade name* | *Molecular weight* | *% of Co-60 deposited on carbon steel* |
|---|---|---|
| Sodium polyacrylate (50 mg $kg^{-1}$) | | |
| Antiprex A | 2000–4000 | 2·4 |
| Versicol E-7 | 27 000 | 4·3 |
| Versicol E-9 | 76 000 | 3·3 |
| Poly(methyl vinyl ether/maleic anhydride) (110 mg $kg^{-1}$) | | |
| Gantrez 119 | Low | 2·8 |
| Gantrez 149 | Medium | 2·9 |
| Gantrez 169 | High | 3·1 |

decontamination system, 15% of the activity was redeposited on the carbon steel surfaces. With the addition of polyelectrolyte, a very dramatic improvement was observed. The per cent redeposition ranged from 8·5% at low polymer concentration to 0·8% at high polymer concentration. The effectiveness of the salts of polyelectrolytes ranged as follows:

polyacrylic acid > poly (methyl vinyl ether/maleic anhydride) > polymethacrylic acid > sulfonated polymer ≅ polyamine

Similar trends have been observed when studying the influence of polyelectrolytes on the dissolution and precipitation of iron oxides.[8-10] A simple but convincing explanation may be given by considering that the three phenomena, redeposition, dissolution and precipitation of oxides in the presence of polyelectrolytes depend basically on the adsorption of polyions on the surface of colloidal particles. How easily this occurs depends on the flexibility of the polymeric chain and its charge, as compared with the colloidal particle charge. This last criterion explains why a

cationic polyelectrolyte is quite ineffective as dispersant (see also point 4.3). In the case of anionic polyelectrolytes, the flexibility criterion dominates. In this sense, polyacrylic acid, being a weak polyacid, is the most flexible; the polymethacrylic acid molecule is much more rigid, at the same degree of dissociation, because the $-CH_3$ groups introduce a great restriction on the rotations about C–C bonds. Similar arguments apply to Gantrez AN. In the case of a strong polyacid, like a sulfonated polymer, internal repulsions convert this molecule into a rigid rod, therefore it may attach to the colloidal particle at only one point, contrary to what may happen to a flexible macromolecule.

In several experiments, an inactive, preoxidized Incoloy-800 sample was also included. Co-60 deposition on such a surface was a factor of 20–50 times smaller than on preoxidized carbon steel surfaces.

### 4.2 Sodium salts of polyacrylic acid

Since sodium salts of polyacrylic acid were the most successful in preventing activity redeposition, their effectiveness was evaluated at several concentrations. Activity redeposition as a function of Antiprex A addition levels is illustrated in Fig. 2.

Compared with the case involving no addition of polyelectrolyte, a very large reduction in activity redeposition was obtained even when only 5 mg $kg^{-1}$ Antiprex were added. Increasing this quantity resulted in further small reductions in activity redeposition. The shape of the curve is typical of a saturation phenomenon, as it is the adsorption of a polyelectrolyte on colloidal particles.

The ratio of carbon steel surface area to solution volume was the same in each experiment and was selected to give a final pH within the range of typical CAN-DECON decontaminations. The change in pH of the solution with time is illustrated in Fig. 3 for two runs—one without the addition of polyelectrolyte, the other with the addition of 450 mg $kg^{-1}$ of Antiprex A. The higher initial pH of the polyelectrolyte-containing solution is due to the buffering action of the sodium salt of polyacrylic acid added. The lower final pH in this system indicates a lower

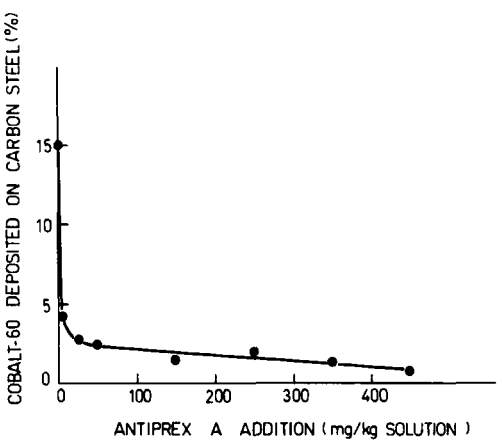



Fig. 2. Co-60 redeposition on carbon steel as a function of Antiprex A (sodium salt of polyacrylic acid) addition levels.

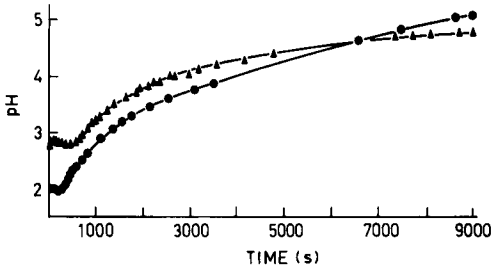



**Fig. 3.** Change of solution pH with time during decontamination with and without polyelectrolyte added. ●, No polyelectrolyte addition; ▲, with 450 mg $kg^{-1}$ Antiprex A added.

dissolution rate of the oxide, a fact that has been described as being due to partial blocking of the oxide surface by the polyelectrolyte.[8,9] This trend is substantiated in the series of runs conducted with various levels of Antiprex A added. These lower dissolution rates, resulting from the addition of polyelectrolyte, were offset by lower activity redeposition, producing little change in *DF*s. This is a very important result from the practical point of view, as *DF*s measure quantitatively the success of a decontamination. Results, including initial and final pH values, are listed in Table 5.

### 4.3 Cationic polyelectrolytes

From an electrostatic point of view, it would be expected that cationic polyelectrolytes do not adsorb on positively charged surfaces, such as magnetite in a low pH environment. Yet, the polyamine did reduce activity redeposition. This result may be interpreted by assuming that other types of interactions, probably van der Waals or London short-range attractive forces, are operative to overcome the long-range electrostatic repulsions. Anyway, as expected, the polyamine ranks last in the effectiveness scale.

### 4.4 Microscopic examination of carbon steel surfaces

The surface morphology of active and inactive carbon steel specimens was dissimilar due to differences in pretreatment duration and hydrodynamic

**TABLE 5**
Effect of Antiprex A Addition on Solution pH and Co-60 Decontamination Factor for Carbon Steel Coupons

| *Antiprex A added* (*mg* $kg^{-1}$) | *Solution pH* | | *Co-60 Decontamination factor* |
|---|---|---|---|
| | *initial* | *final* | |
| None | 2·0 | 5·0 | 6·9 |
| 5 | 2·3 | 5·0 | 7·2 |
| 25 | 2·3 | 5·1 | 7·0 |
| 50 | 2·2 | 4·9 | 7·2 |
| 250 | 2·6 | 4·9 | 7·4 |
| 450 | 2·8 | 4·7 | 5·8 |

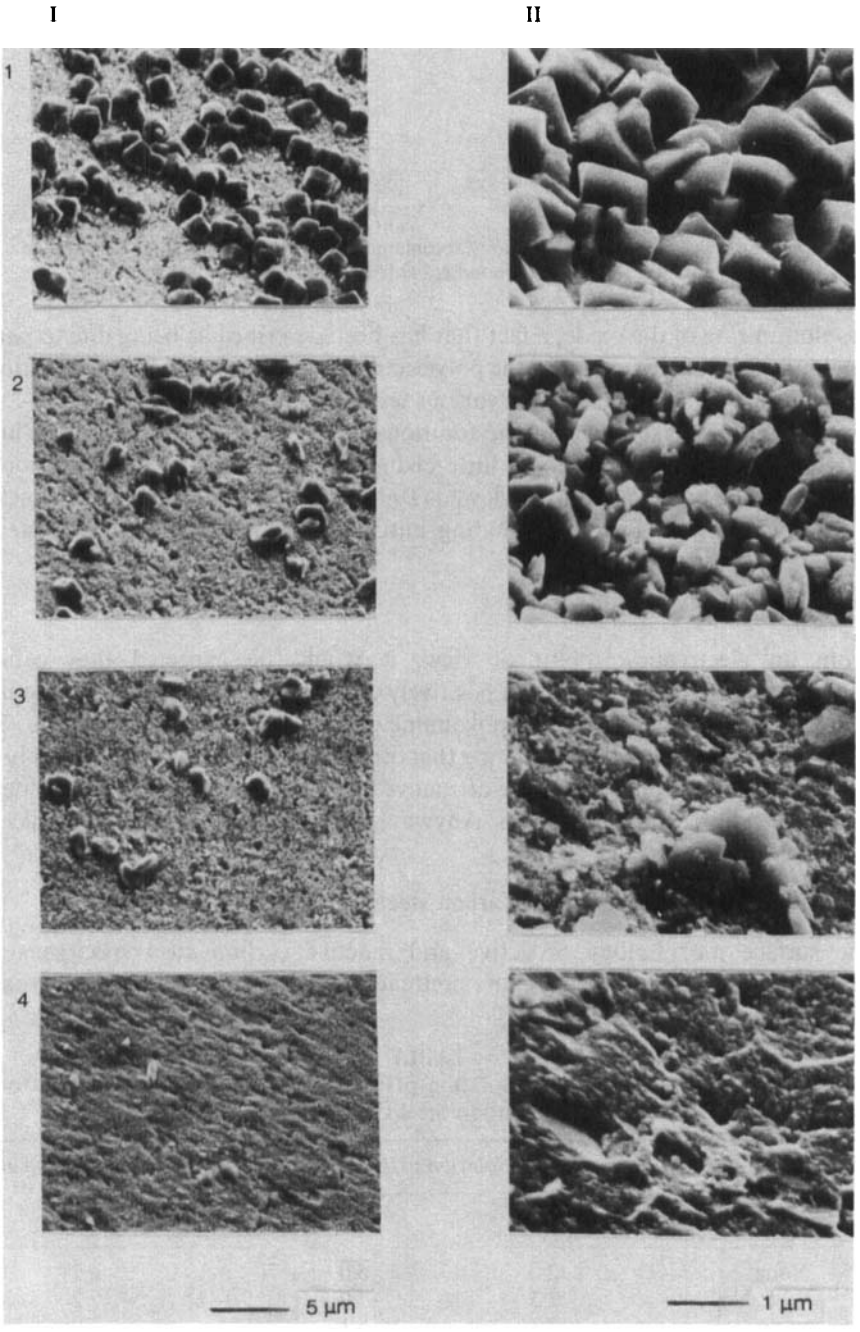



**Fig. 4.** SEM micrographs of carbon steel samples following CAN-DECON treatment. Effect of addition of Antiprex A. I, Initially inactive samples; II, initially active samples; 1, CAN-DECON treatment with no polyelectrolyte added; 2, with 5 mg $kg^{-1}$ Antiprex A added; 3, with 50 mg $kg^{-1}$ added; 4, with 450 mg $kg^{-1}$ added.

conditions (see Table 1). The inactive surfaces did not develop a distinctive outer oxide layer, but were covered by poorly formed crystals approximately 0·1 $\mu$m in diameter. The active specimens were covered by multiple layers of well defined crystals 0·2–2 $\mu$m in diameter. Figure 4 shows SEM micrographs of active and inactive samples taken after the decontamination, with several levels of Antiprex A.

It can be seen that large crystals from the active samples deposited on the inactive carbon steel samples during CAN-DECON treatment without Antiprex A being added. The addition of Antiprex A resulted in reduced redeposition on inactive surfaces. The larger the Antiprex A dosage, the smaller is the redeposition. This observation is consistent with the Co-60 redeposition data in Fig. 2.

CAN-DECON treatment without the addition of dispersant resulted in the incomplete removal of outer oxide from the surface of the active sample. Increased dispersant dosage resulted in improved removal of the outer oxide. At the 450 mg $kg^{-1}$ addition level removal of the outer oxide was complete. Some of the outer oxide crystals were embedded in the inner oxide. In micrograph II-4 of Fig. 4 the imprint of the outer oxide crystals on the inner oxide layer is clearly visible.

### 4.5 Fission product deposition

Besides Co-60, fission products such as Zr-Nb-95, Ru-103 and Ce-144 were present on the contaminated samples.

Material balances were calculated for the radionuclides. However, the glass reaction vessel was not included, since it was too large to be accommodated in the gamma spectrometer. While over 85% of the Co-60 was accounted for, the material balance for fission products was generally poor. More recent experiments indicate that some of the fission products preferentially deposited on the glass surfaces. In an experiment in which polyacrylic acid was added as a dispersant, the fraction of Ru-103 and Nb-95 deposited on the initially inactive carbon steel surface was two orders of magnitude lower than the fraction of Co-60 deposited on the same surface. This result indicates that less than 2% of these fission products were occluded in the magnetite crystals, and thus the redeposition characteristics of over 98% of the fission products are quite independent of magnetite, the major particulate in solution. Since Ru-103 and Nb-95 are insoluble in the decontamination reagent,[11] they must be associated with particles other than magnetite, most likely fuel debris.

## 5 CONCLUSIONS

Summarizing, the following are the main conclusions of the present work:

1. The addition of a low concentration of polyelectrolyte is an effective way to reduce magnetite and Co-60 redeposition during decontamination.
2. The effectiveness of the salts of polyelectrolytes ranged as follows: polyacrylic acid > poly (methyl vinyl ether/maleic anhydride) > polymethacrylic acid > sulfonated polymer $\cong$ polyamine.
3. The decontamination rate was reduced by the blocking action of the polyelectrolytes. Even so, decontamination factors did not change, because the

reduction in surface oxide dissolution was offset by the reduced activity redeposition.
4. Magnetite preferentially deposited on preoxidized carbon steel surfaces, as compared with preoxidized Incoloy-800 surfaces.
5. Deposition of fission products was independent of Co-60 and magnetite deposition. The fission products were preferentially deposited on glass surfaces.

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