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LUCAS HEIGHTS

HEAVY WATER REACTOR CHEMISTRY STUDIES

PART 2. THE ANALYSIS OF EXHAUSTED HIFAR ION EXCHANGE RESINS

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THE ANALYSIS OF EXHAUSTED HIFAR ION-EXCHANGE RESINS

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ABSTRACT

Four batches of exhausted HIFAR ion-exchange resins have been analysed to obtain information on the nature of impurities in the system, corrosion and radiation degradation of the resins. The life of the ion exchanger was found to be governed by the carbon dioxide in the circuit, the major source of which was the radiation degradation of the resins. Methods for prolonging the life of the HIFAR ion exchanger were considered.

CONTENTS

1. INTRODUCTION

The analysis of exhausted reactor ion-exchange resins can provide valuable information on the nature of impurities in the system, corrosion, and radiation degradation of resins. The results of previous analyses of exhausted ion-exchange resins from HIFAR have already been published (Smythe 1963). Other more detailed studies of later batches of exhausted resin (Batches 11 to 14) are given in this report.

The ion exchanger in HIFAR consists of 1 ft^3 of nuclear grade Amberlite XE-150 mixed-bed resin (manufactured by Rohm and Haas) which is made up of the strongly acidic cation exchange resin Amberlite XE-77 (in the H-form), and the strongly basic anion exchange resin Amberlite XE-78 (in the OH-form); these are mixed so that one equivalent of hydrogen ions is present for each equivalent of hydroxide ions. Before being placed in circuit the resins are deuterated (Winters and Cornett 1960) to convert H- and OH-sites to D- and OD- respectively, thus avoiding unnecessary degradation of the moderator.

The ion exchanger, situated in a bypass system, was operated continuously at a flow rate of 5 gal/min at all power levels above 1 MW until September 1967. The average life of a batch of resin was from 4 to 6 months. The ion exchanger was removed from circuit when a significant rise in the carbon dioxide level of the gas blanket (that is, from the normal level of approximately 200 v.p.m. to approximately 2000 v.p.m.) was observed during an operating period of approximately 28 days, indicating that breakthrough of bicarbonate from the anion resin was occurring. In November 1967, a separate cation column was installed ahead of the mixed bed. This cation column will be operated continuously and the mixed bed intermittently to maintain a pD of 5.8 to 6.0. The mixed-bed ion exchanger was operated intermittently between September and November 1967.

2. METHODS

Details of the analytical methods used are at present being prepared for publication in an A.A.E.C. manual.

After removal from circuit the sealed ion-exchange basket was stored for 3 to 4 months to allow short-lived activity to decay. The heavy water was then drained from the bed and light water passed upwards through the bed until the basket was full. The system was left to equilibrate for a period and then drained. This procedure reduced the tritium hazard in the handling of the resins. The resin was transferred for disposal to a polythene bag in a high activity handling area, mixed quickly, and an appropriate 500 g sample was then taken for analysis. This sample usually had an activity of approximately 150 mR/h associated with it.

The mixed-bed sample was then separated into its anion and cation resin components, each portion being analysed for adsorbed ions, capacity changes due to radiation damage, and in the case of the cation resin, for residual capacity.

3. RESULTS

Table 1 shows the results of chemical analysis of the anion portion of the samples taken from exhausted HIFAR ion-exchange resins (Batches 11, 12, 13 and 14) and the results for the cation portion are shown in Table 2. It was found that in all cases the anion resin was exhausted, while approximately 85 per cent of the cation resin capacity still remained in the H-form. The life of the ion-exchange unit in circuit was also found to be very dependent on the carbon dioxide impurity in the system.

The mixed-bed resin as supplied contains a small percentage of impurities. Amberlite XE-78 is guaranteed by the manufacturers to have at least 80 per cent exchange sites in the OH-form and no greater than 5 per cent as chloride and 15 per cent as carbonate. Amberlite XE-77 is supplied with at least 95 per cent sites in the H-form and less than 5 per cent as sodium. Individual batches of resin vary slightly both in capacity and in impurity levels. In particular the salt-splitting capacity of the cation resin varied noticeably between batches. Analyses of three different batches gave values in the range 1.74 to 1.86 meq/ml. The aluminium content of Batch 14 as supplied was 1.5 per cent, compared with 0.02 per cent for Batch 17. Hence, in order to determine the amount of a particular ion which has actually accumulated in the reactor, or the decrease in capacity on irradiation, an analysis should be done on each batch of resin before it is put into the reactor circuit (blank analysis).

Unfortunately no analyses were carried out on Batches 11, 12 and 13 before their use in the reactor circuit. Detailed calculations based on changes in capacity and concentrations of adsorbed ions have been possible only for Batch 14. The results for Batches 11, 12 and 13 have been used merely to indicate general trends.

With the sampling technique employed it is quite possible that the sample taken may not be representative. This technique needs to be improved before further studies are undertaken. The concentrations of adsorbed impurities, both anionic and cationic, were very similar for all four batches. Hence we are confident that a reasonably representative sample was analysed in each case. This point will be considered again later where anomalies in the results for Batch 13 are discussed (Section 3.2.6).

3.1 Radiation Damage

The irradiation of quaternary ammonium anion exchange resins in the OH-form is known to result in damage to the strongly basic functional groups by two mechanisms:

(i) the destruction of strongly basic groups with the release of soluble aliphatic amines, and

(ii) the conversion of strongly basic groups on the resin to weakly basic groups with the release of an aliphatic alcohol (Hall and Streat 1963).

$$R.CH_2.N\overset{+}{Me_3}\ OH^- \longrightarrow R.CH_2.OH + NMe_3 \qquad .....(1)$$

$$R.CH_2.N\overset{+}{Me_3}\ OH^- \longrightarrow R.CH_2.NMe_2 + MeOH \qquad .....(2)$$

The amine released was shown to be mainly trimethylamine with small concentrations of dimethylamine, methylamine and ammonia. At pH 6 to 7 these amines would be present in solution largely in the protonated form (Me_3NH^+) and thus should be adsorbed on the cation resin.

Decomposition by Reaction 1 results in a decrease in the total capacity, while Reaction 2 leads to the conversion of strong base groups to weak base groups. For Batch 14 the increase in weak base capacity was much greater than the loss in total capacity (see Table 1); that is, degradation by Reaction 2 predominated. This agreed with the results of Hall and Streat (1963) who found that, on irradiation of De-Acidite-FF with ^{60}Co γ-rays, the decrease in strong base capacity was greater than the decrease in total capacity. On the other hand, Reactions 1 and 2 occur at equal rates for the thermal decomposition of Amberlite XE-78 (Baumann 1960).

The amine which should accumulate on Batch 14 cation resin as a result of degradation by Reaction 1, has been calculated from the decrease in total capacity of the anion resin, assuming that all amine released was adsorbed onto the cation resin. It was found that 0.14 meq amine/ml cation resin should have resulted from this cause. However, because of the amine initially present on the cation resin, only 0.095 meq amine/ml resin can actually be attributed to adsorption of amine degradation products of the anion resin during the period in the reactor. Hence, it would appear that in this case, only about 70 per cent of the amine degradation products of the anion resin were adsorbed on the cation resin. The remaining 30 per cent are assumed to have been released into the moderator to be oxidised to nitrate.

Radiation damage to sulphonated polystyrene cation exchange resins results in a decrease in sulphonic acid groups, the formation of weakly acidic phenolic groups, and a decrease in cross-linking (Smith and Groh 1961, Yee and Davies 1964). The loss of sulphonic acid groups is determined from the decrease in salt-splitting capacity and the formation of weakly acidic groups from the difference between the salt-splitting and total capacity. A significant formation of weakly acidic groups in the structure was observed only for Batch 14. In this case a 7 per cent decrease in strongly acidic sulphonic acid groups was accompanied by the formation of weakly acidic groups (5 per cent of the capacity after irradiation). As expected, the cation resin proved more stable to radiation damage than the anion. Because of the absence of blank analysis, the loss of sulphonic acid groups for the other three batches cannot be estimated.

3.2 Anion Resin Analyses

3.2.1 Sulphate

Sulphate ions on the anion resin presumably arise from the radiation decomposition of sulphonic acid groups on the cation resin. The sulphate content of the anion resin in each case represented only 10 to 20 per cent of the apparent loss in sulphonic acid groups from the cation resin. Smith and Groh (1961) found sulphuric acid to be the main decomposition product of Dowex-50W. Other products were sulphonic acid fragments and phenolic compounds. Yee and Davies (1964) identified sulphuric, sulphonic and oxalic acids as the soluble decomposition products of Dowex-50W in a flowing system, with sulphate accounting for 75 per cent of the soluble sulphur in the effluent. No attempt was made in either case to examine the gases released by the degradation.

It is possible that gaseous sulphur compounds (for example SO_2 or H_2S) may be formed as a result of the degradation. Under reactor conditions these would pass into the gas blanket and eventually be removed from circuit by the helium purification unit. The presence of sulphur compounds in the helium has led to poisoning of the recombiner catalyst in a number of reactors. Although this effect has not been observed for the HIFAR recombiner, it is still conceivable that the formation of gaseous sulphur compounds may have contributed to the low

sulphate content of the anion resin.

Benzene sulphonates are adsorbed readily onto strongly basic anion exchange resins (Kunin 1958). Their presence would not be detected in the turbidimetric analysis for sulphate using barium chloride as reagent, because the barium sulphonates are soluble. However, since sulphate appears to be the major product of the cation resin degradation, the presence of sulphonates alone would not account for the very low sulphate figures obtained.

Alumina has a strong affinity for sulphate ions in both acid and neutral solution (Nydahl 1954). Hence it is possible that the sulphate may have been adsorbed onto the protective oxide film on aluminium surfaces, or onto any alumina deposits which may be present in the stainless steel portion of the circuit. This problem requires further investigation.

3.2.2 Chloride

A chloride content of 3 per cent was obtained for each batch. This result was identical with the chloride analysis on the Batch 14 blank. Hence it appeared that the total chloride in the system resulted from the chloride present on the resin as supplied.

3.2.3 Nitrate

Nitrate arises from the radiolysis of nitrogen impurities in the gas space and from the radiolytic decomposition of amine degradation products released into the moderator. Experiments carried out in HIFAR with the ion-exchange unit removed from circuit gave the rate of nitrate formation at the normal nitrogen level of the gas space of 2000 v.p.m. as 137 mg NO_3^-/day (Ryan and Smythe 1966). At this rate, approximately 0.011 meq NO_3^-/ml resin should have accumulated on Batch 14 anion resin during its life in circuit. The practical nitrate content of the resin was found to be 0.037 meq/ml. That is, 0.026 meq NO_3^-/ml may have resulted from the oxidation of amines released into the circuit. The decrease in the total capacity of the resin was 0.08 meq/ml. It appeared that 30 per cent of the amine released by this degradation had passed into the moderator. Complete oxidation of this amine would result in approximately 0.025 meq NO_3^-/ml anion resin. Hence, the total nitrate content of the resin could be accounted for on this basis. In Table 3, the nitrate analysis results for the four batches of resin are compared with the typical nitrate figures expected from the radiolysis rates of nitrogen quoted above. For Batches 11, 12 and 14 the practical figure is greater than the theoretical. This has been accounted for by the release of amine degradation products into the moderator and their subsequent oxidation to nitrate. For Batch 13, the practical figure represented only 30 per cent of the theoretical. During the period when Batch 13 was in service, the experiments to determine the rate of nitric acid formation in the system by radiolysis of nitrogen in the gas blanket were carried out. Hence the application of this rate to obtain estimates of nitrate levels on the resin should be most reliable for this batch. The only other explanation is that the Batch 13 sample may not have been representative. This point will be discussed further in Section 3.2.6.

3.2.4 Carbonate and bicarbonate

Carbonate and bicarbonate ions accounted for 90 to 95 per cent of the capacity of the anion resin in each case. In attempting to assess the contribution of the various sources of carbon dioxide in the system the results for Batch 14 have again been used as the example, since more data are available for this resin. It has been assumed in the calculations that each source would contribute carbonate and bicarbonate ions in the same ratio as that finally present on the resin. For Batch 14, the ratio meq HCO_3^-/meq CO_3^{2-} equalled 1.05.

Carbonate and bicarbonate ions on the resin can arise in the following ways:

(a) The resins as supplied contain a percentage of carbonate. For Batch 14, the carbonate content initially present should account for 11 per cent of the CO_3^{2-} and HCO_3^- on the exhausted irradiated resin.

(b) Air may leak into the system. It is difficult to assess the contribution from this source but it is expected to be negligible in comparison with other sources. Leakage of air into the system is detected by the rise in nitrogen and argon levels of the gas blanket. During normal operation the nitrogen level of the gas blanket remains steady at approximately 2000 v.p.m. A rise through air leakage to the shutdown limit of 20,000 v.p.m. nitrogen, which would rarely occur, would cause an increase of approximately 200 v.p.m. in the carbon dioxide level of the gas space, or 0.01 meq CO_3^{2-}, HCO_3^-/ml resin (1 per cent) if all this carbon dioxide were finally removed on the ion exchanger. In actual fact only a small fraction of this carbon dioxide would be removed on the ion exchanger since clean-up of the gas circuit with the helium purification unit would be carried out soon after the high nitrogen levels were detected.

(c) Leakage could occur from experimental irradiation rigs operated with a carbon dioxide atmosphere or from the graphite reflector space. For a previous experiment, in which the ion-exchange unit was removed from circuit for 14 days (Ryan and Smythe 1966), a rise of 560 v.p.m. in the carbon dioxide level of the gas blanket was attributed to this cause. At the same rate, this would correspond to an increase of 0.25 meq CO_3^{2-} , HCO_3^-/ml resin over the 114-day period Batch 14 was in circuit, or 32 per cent of the total CO_3^{2-} and HCO_3^- . This estimate is necessarily very approximate since conditions prevailing at the time Batch 14 was in circuit may have been quite different. However, it does show that the contribution from this source could be considerable.

(d) $^{14}CO_2$ could be formed as the result of neutron interaction with ^{14}N, $^{14}N(n,p)^{14}C$, followed by oxidation. The significance of this reaction is not yet known but is not expected to be great.

(e) Radiolytic breakdown of the resin structure could occur. Degradation of the resin under irradiation occurs both at functional groups and generally throughout the hydrocarbon skeleton. Degradation of the functional groups of the anion exchanger by Reaction 2 would release methanol into the moderator and this would ultimately decompose to yield carbon dioxide. The increase in the weak base capacity of Batch 14 (0.19 meq/ml resin) would result in 0.25 meq CO_3^{2-}, HCO_3^-/ml resin or 32 per cent of the total carbonate/bicarbonate. Degradation by Reaction 1 results in the release of amines, the majority of which are immediately adsorbed on the cation resin. For Batch 14, approximately 0.025 meq amine/ml resin appeared to have been released into the moderator. Trimethylamine was assumed to be the product of the degradation, the oxidation of which should result in 0.11 meq CO_3^{2-}, HCO_3^-/ml resin, or 14 per cent of the total. That is, degradation of the functional groups of the anion resin accounted for at least 46 per cent of the total carbonate/bicarbonate found on the exhausted resin.

The carbon dioxide released through skeletal degradation of the anion or cation resin cannot be estimated. Nevertheless it has been concluded, on the above grounds, that radiation degradation of the mixed-bed ion exchange resins was probably the major source of carbon dioxide in the system.

Carbonate/bicarbonate adsorbed on the anion resin does not represent the total carbon dioxide which enters the system during the life of a particular ion exchanger. Carbon dioxide is removed during periodic clean-up of the gas circuit with the helium purification unit and through leakage of helium from the system but we have been unable to estimate the carbon dioxide removed through these sources. The build-up of carbon dioxide in the gas blanket and the corresponding increase in dissolved carbon dioxide in the moderator which results from exhaustion of the anion resin should also be considered. For Batch 14 a total increase of approximately 2,250 v.p.m. in the carbon dioxide level of the gas occurred during the approximately 23-day period after exhaustion of the resin, when the carbon dioxide level of the gas blanket rose steadily. This corresponds to an increase of 1.2 mole of carbon dioxide in the gas space and, using data for the solubility of carbon dioxide in water at 45°C and pH 7 (Hodgman 1957), a rise of approximately 0.4 mole of dissolved carbon dioxide in the moderator. Thus a total increase of 1.6 mole of carbon dioxide resulted, compared with the 10.5 mole of carbon dioxide adsorbed on the anion-exchange resin. Hence carbon dioxide removed on the ion-exchange resin represented less than 87 per cent of the total carbon dioxide in circuit. The corresponding percentages for Batches 11, 12, 13 were 85, 75 and 90 respectively.

If the resin is assumed to be completely exhausted for bicarbonate ions when the rise in the carbon dioxide level of the gas blanket commences, calculations show the rate of carbon dioxide formation in the system after exhaustion to be less than the average rate beforehand. In actual fact, the rate of formation after exhaustion should at least equal the rate before exhaustion, and might even be greater than it, since the rate of radiolytic degradation of the resins may increase with dose. Hence it appears that the resin is not completely exhausted for bicarbonate when the carbon dioxide level of the gas blanket begins to rise. Some removal of bicarbonate from solution must still occur. However, breakthrough is such that the low equilibrium concentrations of carbon dioxide in the system can no longer be maintained.

A study of the mechanism of the adsorption of bicarbonate and chloride ions onto Amberlite XE-78 showed that the bicarbonate ions were initally adsorbed onto the resin as carbonate (Ryan and Smythe 1967). Breakthrough of bicarbonate commenced when the resin had been exhausted with carbonate and chloride. Some conversion of carbonate to bicarbonate sites then occurred and the efficient removal of chloride continued for a time. Finally breakthrough of chloride occurred and equilibrium concentrations of carbonate, bicarbonate and chloride were reached on the resin.

A similar mechanism would be expected for the adsorption of dissolved carbon dioxide from the HIFAR moderator. At the pH of the moderator (6 to 7), a proportion of the dissolved carbon dioxide would be present as bicarbonate ions which would be adsorbed as described above. Breakthrough of bicarbonate should occur well before the breakthrough of the other predominant anions (Cl^- , NO_3^- , SO_4^{2-}). However, because of the great differences in flow rate, resin volume and concentration under reactor conditions, the levels of the other anions on the resin at which their breakthrough would be likely to commence under reactor conditions could not be obtained from the laboratory experiments.

3.2.5 Aluminate

The effluent from the irradiated anion resin was also analysed for aluminate to confirm the results of Hatcher and Rae (1961), that Amberlite XE-78 has a very poor capacity for aluminate ions. The aluminium content of the anion resin represented only 0.2 per cent of the aluminium adsorbed on the cation resin.

3.2.6 General comments

When Batch 11, 12 and 14 anion resins were eluted with sodium chloride a yellow coloured effluent was obtained, the colour presumably being due to the presence of resin degradation products. Although Batch 13 had been in circuit for a similar period to Batch 12, its effluent was colourless. The decreases in salt-splitting and total capacity on irradiation were both less than for the other batches examined. It appeared that Batch 13 had received a lower radiation dose for some reason. Alternatively the resin as manufactured may have been more resistant to radiation damage.

The nitrate analyses for Batch 13 tended to indicate that a non-representative sample had been taken (see Section 3.2.3). Studies of the distribution of impurities on a SRP deioniser (Baumann 1965) showed that both nitrate content and degradation of the anion resin decreased along the length of the column. This tends to confirm that the Batch 13 sample was non-representative. However, the cation resin analysis of Batch 13 yielded very similar results to the other samples. Since cationic impurities adsorbed from the moderator are known to concentrate in a band at the inlet to the ion exchanger, the presence of a non-representative sample should be particularly evident from the cation resin analyses (especially the Al, Fe, Mg results). Thus the anomalous nitrate and degradation results for Batch 13 cannot really be explained.

In view of its short in-circuit time of only 114 days, Batch 14 appeared to have suffered greatest radiation damage. The rate of conversion of strong base to weak base groups on the anion resin was highest for Batch 14. A significant formation of weakly acidic phenolic groups in the cation resin occurred only for this batch. In addition, Batch 14 cation resin had a higher activity associated with it (50 mR/h on a 50 ml sample compared with 8 mR/h for a similar volume of Batch 13). Thus it was concluded that Batch 14 had been subjected to a higher dose rate than the other resins examined. It is interesting to note that a significant increase in the activity levels of the gas space and the presence of fission products in circuit were detected during January 1966, just after Batch 14 had been removed from circuit. It is possible that this source had contributed activity to the circuit while Batch 14 was in operation. The activity levels of the gas blanket were slightly higher than normal during the period when Batch 14 was in circuit. However, this increase was very small compared with the high activity of the gas space from January 1966 onwards. No fission products were detected on Batch 14 by spectrographic analysis.

For the anion resin analyses, the total anions accounted for agreed with the salt-splitting capacity to within 2 per cent. That is, the adsorbed resin degradation products occupied a very low percentage of the capacity.

3.3 Cation Resin Analyses

Amine degradation products were the most abundant impurity on the cation resin and occupied approximately 10 per cent of the capacity. The anticipated aluminium and stainless steel corrosion products were present, and also zinc, presumably from corrosion of the zinc/aluminium alloy spacers used at all aluminium to stainless steel joints. The sodium and calcium figures for Batch 14 were identical with those obtained for the blank. However, the magnesium figure was a factor of seven higher than this blank. The ^{24}Mg is produced from the reaction.

$$^{27}Al\ (n,\alpha)\ ^{24}Na \xrightarrow[T_{\frac{1}{2}} = 15h]{\beta} {}^{24}Mg\ .$$

When these analyses were done (6 to 12 months after the removal of the ion exchanger from circuit), any ^{24}Na formed as the result of this process should have decayed to ^{24}Mg. An isotopic analysis for magnesium was attempted to determine whether any enrichment in ^{24}Mg over the natural level had occurred. However, the results were inconclusive and the problem requires further investigation. Trace quantities of Si, Cr, Mn, Pb, Ti, Co, Cd, Mo and B were also detected spectrographically on the cation resin.

With reference to corrosion, the aluminium figures are the most interesting. The blank for Batch 14 was 0.027 meq Al/ml, or 58 per cent of the total aluminium found after irradiation. Thus 0.020 meq Al/ml resin had accumulated on Batch 14 in 114 days. This corresponded to an average dissolution rate of 0.02 g Al/day from the surface oxide films. Without any blank correction the corresponding rates for Batches 11, 12 and 13 were 0.05, 0.04 and 0.03 g Al/day respectively. Thus, there appeared to be very little change in the corrosion characteristics of the circuit from May 6th, 1964 to December 12th, 1965. In comparison, a leaching rate of 40 g Al/day has been reported for the NRU reactor, where colloidal alumina is present in the moderator (Rae 1963).

3.4 The Life of the Mixed Bed

It has already been shown that the life of the mixed-bed ion exchanger is governed by the carbon dioxide impurity in the circuit. In an attempt to prolong the life of the ion exchanger the anion/cation capacity of the mixed bed was increased to 3:1 for Batch 17. Table 4 gives the period in circuit for Batches 11 to 17. For Batches 15, 16 and 17 there was a much higher activity in circuit owing to the presence of fission products. This should result in a higher resin degradation rate and release of carbon dioxide into the circuit. Hence these resins have a shorter life than Batches 11, 12 and 13.

Resin life was not prolonged by increasing the anion/cation ratio. This result confirms the conclusion that radiation damage to the anion resin was the major source of carbon dioxide in the system. By increasing the anion resin volume, a corresponding increase in the release and oxidation of resin degradation products should result. Hence, when degradation is the major source of carbon dioxide in the system, no benefit is obtained from the larger anion resin capacity. If leakage of carbon dioxide from external sources was the major contributor, the life of the mixed bed should be prolonged by increasing the anion/cation ratio.

The ion-exchange resins receive their radiation dose from two sources:

(a) Cationic impurities usually concentrated in a narrow band toward the inlet of the column, and which account for the majority of the activity adsorbed on the resin;

(b) Activity circulating with the heavy water (such as ^{16}N and fission product gases).

The British reactor DIDO operates with a separate cation column before the mixed bed and with intermittent flow through the mixed bed to control the pH at approximately 5.8, thus reducing the dose rate on the mixed bed from both sources. Under these conditions, the life of the mixed-bed ion exchanger is approximately 2 years (Smith 1966).

Batch 19 was prepared with an overall anion/cation ratio of 2:1, but with 0.2 ft^3 cation resin only at the inlet to the column. It was thought that this measure might reduce the radiation dose received by the anion resin from the highly active impurities adsorbed on the cation resin, and thus increase the life of the mixed bed. However, the life of this batch was also four operating periods.

4. CONCLUSION

The major impurity in the circuit has been shown to be carbon dioxide, arising mainly from the radiation decomposition of the ion-exchange resins. That is, the life of the ion exchanger is governed by the activity in circuit. No attempt was made to measure the radiation doses received by the resins. This is extremely difficult for the total bed volume. Hence, we have been unable to compare the radiation damage observed for these resins with circuit activity or with results quoted in the literature for small scale experiments. Valuable semi-quantitative information regarding dose could probably be obtained by incorporating dosimeters at several points in the column. The only means of prolonging the life of the ion exchanger appears to be reduction of the radiation received by the resins, by use of a separate cation column before the mixed bed. As already mentioned, a cation exchanger has recently been installed before the mixed bed so that a longer life of the mixed bed should be obtained from Batch 21 onwards.

The cation resin analyses indicated aluminium and stainless steel dissolution rates of a satisfactorily low level. It will be interesting to compare these results, both from the corrosion and degradation point of view, with those for later batches, where higher activity was present owing to the release of fission products from defective fuel elements. We aim to improve the sampling techniques for these resins in order to eliminate the possibility of an unrepresentative sample.

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TABLE 1

ANALYSIS OF THE ANION PORTION OF EXHAUSTED HIFAR ION-EXCHANGE RESINS

Batch	Days in Reactor	CO_3^{2-} meq/ml	HCO_3^- meq/ml	Cl^- meq/ml	NO_3^- meq/ml	SO_4^{2-} meq/ml	Salt-Splitting Capacity meq/ml	Total Capacity meq/ml	Weak Base Capacity meq/ml
11	139	0.36	0.37	0.027	0.032	0.010	0.82	1.01	0.23
12	167	0.36	0.39	0.023	0.027	0.012	0.81	1.01	0.25
13	168	0.46	0.40	0.022	0.0045	0.007	0.92	1.07	0.22
14	114	0.38	0.40	0.023	0.037	0.009	0.84	1.05	0.30
14 (blanks)		0.13	n.a.	0.025	n.a.	n.a.	1.06	1.13	0.11

n.a. = no analysis

TABLE 2

ANALYSIS OF THE CATION PORTION OF EXHAUSTED HIFAR ION-EXCHANGE RESINS

Batch	Days in Reactor	Al^{3+} (meq/ml)	Ca^{2+} (meq/ml)	Mg^{2+} (meq/ml)	Fe^{3+} (meq/ml)	Ni^{2+} (meq/ml)	Na^+ (meq/ml)	Cu^{2+} (meq/ml)	Zn^{2+} (meq/ml)	Amines (meq/ml)	Salt-Splitting Capacity (meq/ml)	Total Capacity (meq/ml)	Residual Capacity (meq/ml)
11	139	0.079	0.016	0.011	0.0086	0.0055	0.0069	0.0022	0.0015	0.16	1.66	1.68	1.36
12	167	0.071	0.011	0.0079	0.0054	0.0046	0.0069	0.0020	0.0013	0.17	1.74	1.74	1.45
13	168	0.046	0.0092	0.0069	0.0030	0.0007	0.0072	0.0008	n.a.	0.13	1.74	1.76	1.52
14	114	0.047	0.0085	0.0073	0.0034	0.0057	0.0067	0.0038	n.a.	0.16	1.67	1.76	1.41
14 (blank)		0.028	0.0090	0.0016	0.0015	n.a.	0.0070	n.a.	n.a.	0.065	1.80	1.80	

n.a. = no analysis

TABLE 3

COMPARISON OF THE NITRATE ANALYSES OF THE ANION RESIN WITH THE NITRATE EXPECTED FROM RADIOLYSIS OF NITROGEN

Batch	Days at Power	Theoretical NO_3^- on Resin from Radiolysis of N_2 * (meq/ml)	Practical NO_3^- Content of Resin (meq/ml)	Ratio of Practical to Theoretical (per cent)
11	122	0.015	0.032	210
12	130	0.016	0.027	170
13	134	0.016	0.0045	30
14	94	0.011	0.037	340

* Radiolysis of nitrogen produces 137 mg NO_3^-/day for a nitrogen level of 2,000 v.p.m.

TABLE 4

LIFE OF THE ION-EXCHANGE RESINS IN HIFAR

Batch	Period in Circuit	Number of Operating Periods *	Anion/Cation Capacity
11	6/5/64 - 22/9/64	5	1
12	22/9/64 - 8/3/65	6	1
13	8/3/65 - 23/8/65	6	1
14	23/8/65 - 14/12/65	4	1
15	14/12/65 - 6/4/66	4	1
16	6/4/66 - 23/8/66	4	1
17	23/8/66 - 6/12/66	4	3

* Operating period = approximately 24 days.