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MOESSBAUER STUDY OF THE BEHAVIOUR OF SYNTHETIC CORROSION PRODUCTS OF NUCLEAR POWER PLANTS

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Abstract—Iron oxides are the main components of the circulating particles carried by the fluid in the primary circuit of nuclear power stations. The oxidation state of iron is (II, III), as in Fe_3O_4, or (III), as in Fe_2O_3, depending upon the reducing or oxidizing condition of the medium.

Moessbauer Spectroscopy allows the characterization of different forms of iron oxides, as well as iron and other metal mixed oxides. Also with this technique it is possible to detect the gradual changes in the stoichiometry of the phases due to oxidation.

From the results obtained, it is concluded that the change in the oxygen content of the coolant in nuclear power stations will rapidly reflect itself in changes in the stoichiometry of the magnetite-type solids and, if higher levels of oxygen or localized attacks take place, the structure of the particles will suffer more drastic changes to hematite in a short time.

INTRODUCTION

SYNTHETIC corrosion products have been used in simulation studies of the behaviour of the natural ones.[1,2]

Iron oxides are the main components of the circulating particles carried by the fluid in the primary circuit of nuclear power stations. The oxidation state of iron is (II, III), as in Fe_3O_4, or (III), as in Fe_2O_3, depending upon the reducing or oxidizing conditions of the medium.

In the matrix of these oxides other metal ions may be present as a result of the hydrothermal synthesis produced by the fluid at the high temperature prevailing in the system (~250°C).[3] These metals, such as chromium, nickel, cobalt, manganese and others, are also released from the structural materials and give rise to ferrite-type structures.

Moessbauer Spectroscopy permits the study of the states of iron in samples to be analyzed. In a different context Moessbauer Spectroscopy has been used previously in the study of iron oxidation processes.[4] Thus the gradual changes that take place under mild oxidative conditions can be put in evidence. Therefore this spectroscopy will be used in the study of the mentioned iron products. As a first step in our work, we have employed this technique in order to evaluate the method proposed by Fletcher *et al.*[1] for synthesizing corrosion-like products by a wet method.

EXPERIMENTAL

Synthetic cruds of various compositions were prepared according to the following techniques.

Sample 1 was prepared by alkaline hydrolysis of iron sulphate. To a 6% w/w aqueous $FeSO_4 \cdot 7H_2O$ solution, concentrated (40%) NaOH was added dropwise and with mechanical stirring at 22°C under nitrogen. The volume of NaOH was *ca.* one tenth of the initial volume of iron solution. The light green precipitate ($Fe(OH)_2$) was centrifugated and rinsed at least 10 times with deaereated water. The preparation was carried out in a glove-box under purified nitrogen, to prevent contact with air. The solid was dried in an evacuated oven at ~120°C, and finally it was calcinated in a tubular furnace under N_2 at 500°C for 5 h. In this period, reaction (1) takes place:[5]

$$3Fe(OH)_2 \rightarrow Fe_3O_4 + 2H_2O + H_2 \quad (1)$$

Samples 2 *and* 3 were prepared as sample 1, but without resorting to the use of a glove-box. In the presence of air, the extent of oxidation varies from one preparation to another, as discussed below.

Sample 4 was prepared as sample 2, but using the equivalent amount of $FeCl_2 \cdot 4H_2O$, rather than iron sulphate.

For *sample* 5, the composition and treatment was exactly analogous to sample 2, but after calcination at

500°C, the sample was exposed to air at 300°C for 3 min, in an effort to reproduce the possible effect on an accidental oxygen accumulation. The colour of the sample changed from black to red in this short period.

Sample 6 was a mixed oxide sample prepared from a solution containing $FeCl_2 \cdot 4H_2O$ (13.8% w/w), $NiCl_2 \cdot 6H_2O$ (15.3%), $CrCl_3 \cdot 6H_2O$ (0.13%), $MnCl_2 \cdot 4H_2O$ (0.07%) and $CoCl_2 \cdot 6H_2O$ (0.05%). Oxidizing conditions (air) were kept during calcination, and a reddish product ensued.

Sample 7 was similar to sample 6, but was obtained in air-free conditions. Its colour was black.

All samples were analyzed by atomic absorption spectroscopy and flame photometry.

The Moessbauer spectra were measured in a transmission geometry with an ELRON Moessbauer Spectrometer in a constant acceleration mode with an Ar/CO_2 filled Reuter Stokes R.S.G.-61-M2 proportional counter. Spectra were displayed in a multichannel analyzer operated in the time mode. The source used was ^{57}Co in Pd matrix, and the samples, in the form of powder, were weighed out to give an iron content of approximately 8 mg cm^{-2} and were encapsulated between thin acrylic disks. Measurements were carried out with the source and absorbers at room temperature.

Spectra were least-squares fitted[6] employing a pure Lorentzian shape and constraining the corresponding peaks. The quality of the computer fit was checked by a χ^2 test and only those of lower value were accepted.

Counting statistic (N) ranged from 3×10^6 to 9×10^6 counts per channel; the corresponding statistical and percentage statistical errors lay between 1.7×10^3–3×10^3 and 0.06%–0.03% respectively.

RESULTS AND DISCUSSION

The Moessbauer spectra are shown in Figs 1–7. Their parameters are shown in Table 1. The intensity ratios, Table 2, were obtained from the corresponding area ratios.

The Moessbauer parameters (Tables 1 and 2) of sample 1 indicate the presence of a magnetite (see Fig. 1).[7]

Sample 2 parameters (Table 1) indicate the presence of a magnetite and a ferric oxide (Fig. 2).[8,9] The last one could not be distinguished

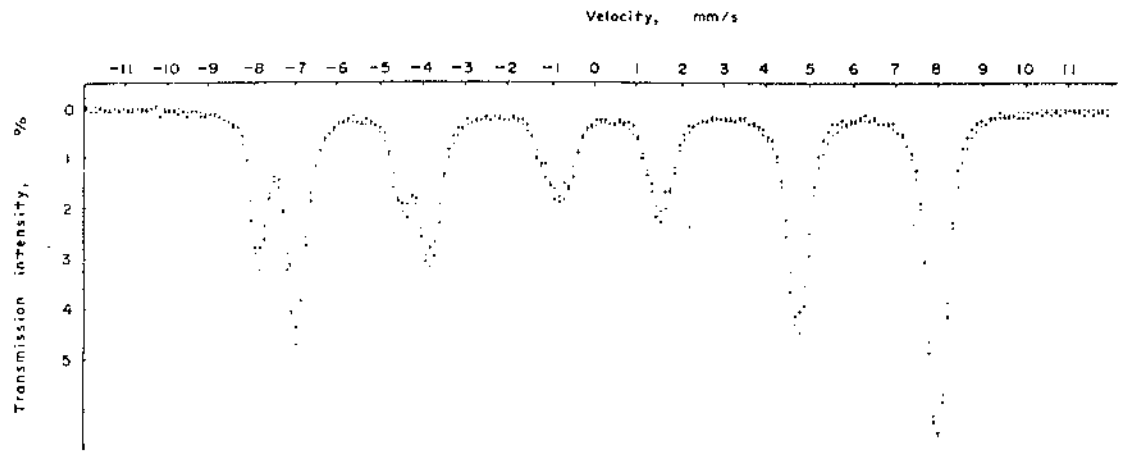

FIG. 1. Moessbauer spectrum of sample 1 at room temperature. ○: experimental points; +: fitted points; ▲: coincident points).

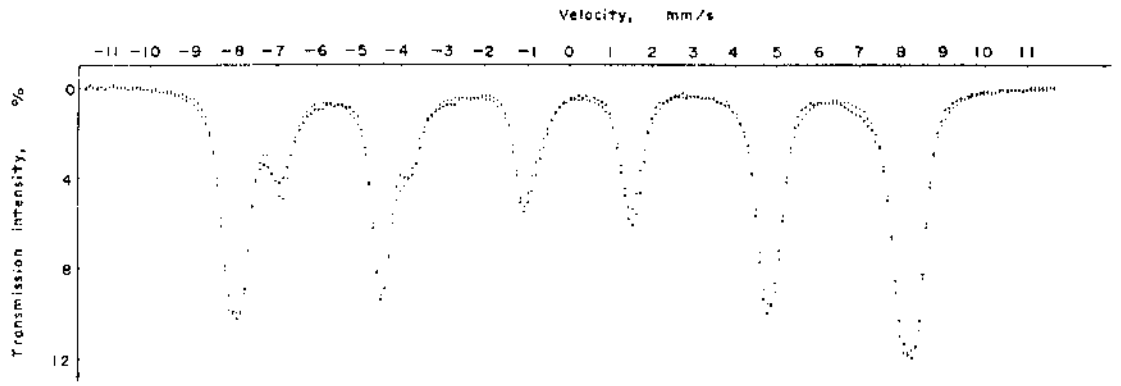

FIG. 2. Moessbauer spectrum of sample 2 at room temperature. For key, see legend to Fig. 1.

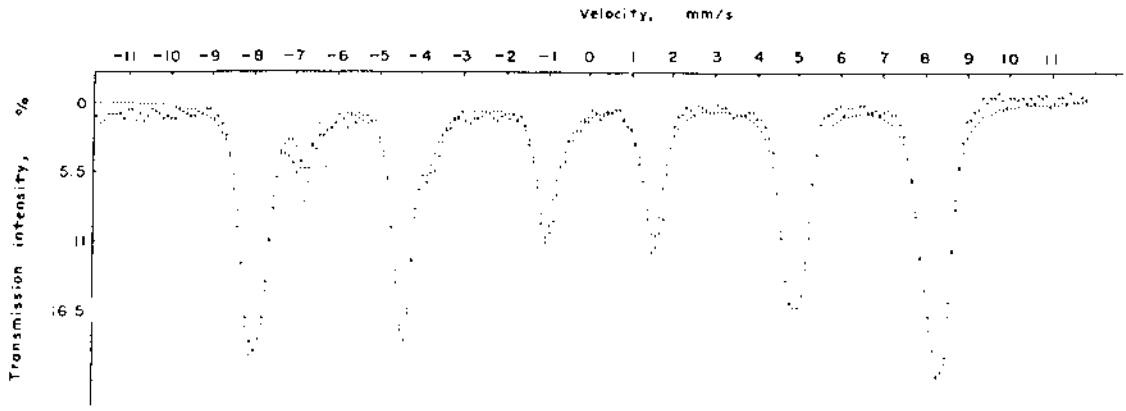

FIG. 3. Moessbauer spectrum of sample 3 at room temperature. For key, see legend to Fig. 1.

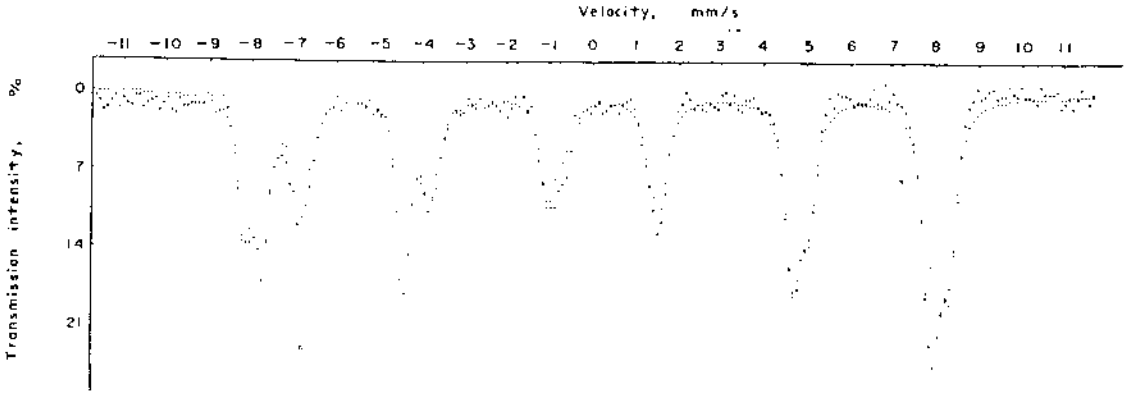

FIG. 4. Moessbauer spectrum of sample 4 at room temperature. For key, see legend to Fig. 1.

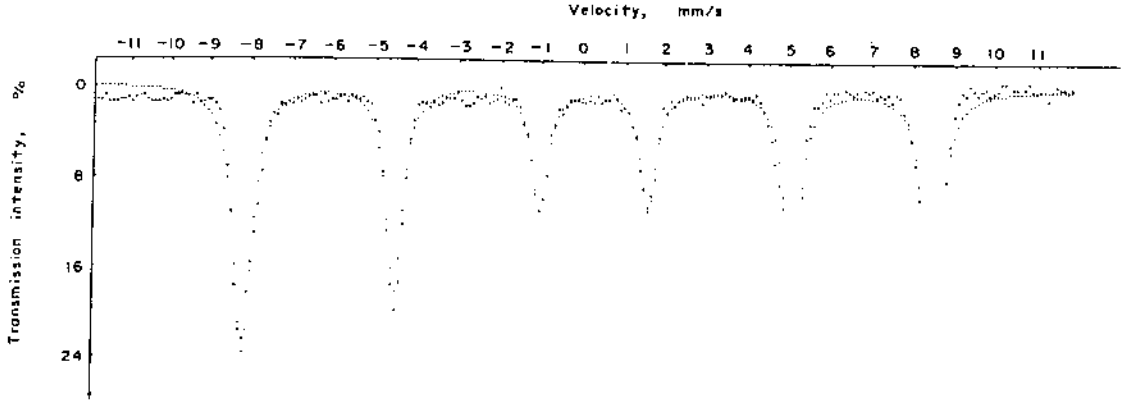

FIG. 5. Moessbauer spectrum of sample 5 at room temperature. For key, see legend to Fig. 1.

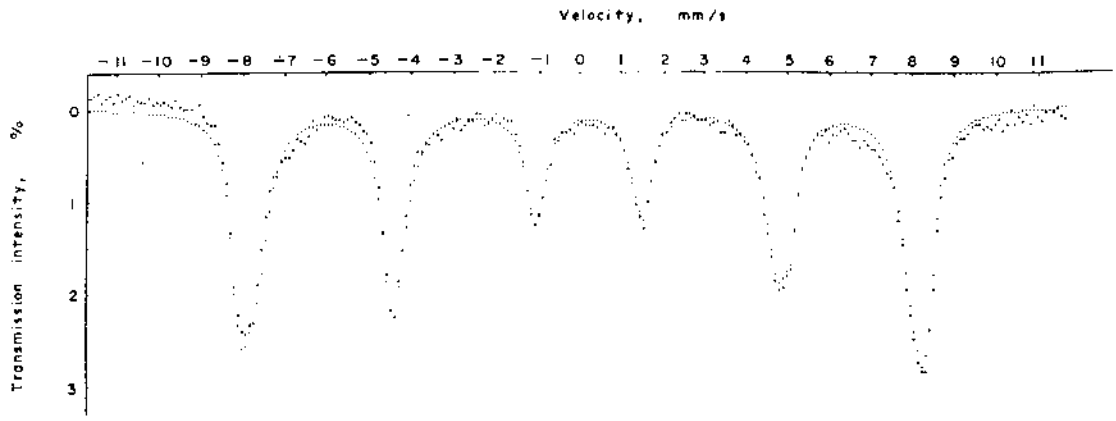

FIG. 6. Moessbauer spectrum of sample 6 at room temperature. For key, see legend to Fig. 1.

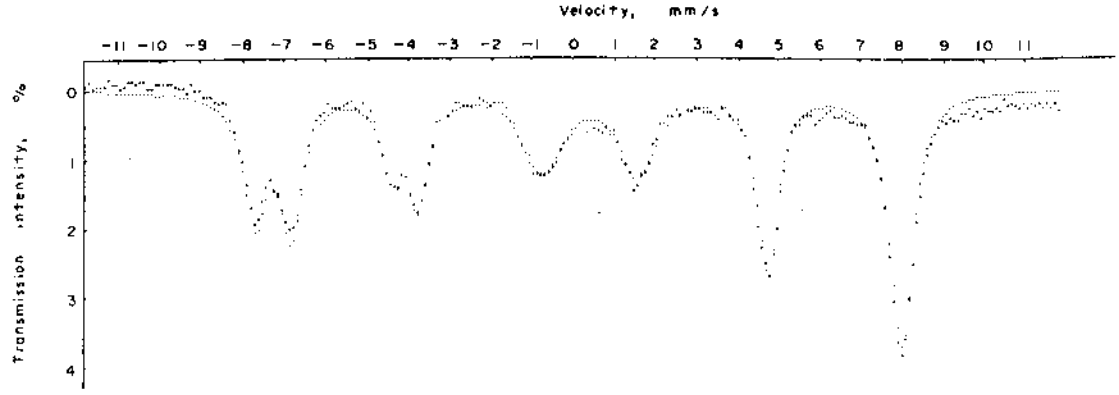

FIG. 7. Moessbauer spectrum of sample 7 at room temperature. For key, see legend to Fig. 1.

between a maghemite and an hematite. The intensity ratio for the magnetite (Table 2) is greater than the one corresponding to a stoichiometric magnetite, pointing out the existence of $Fe_{3-x}O_4$. In a non-stoichiometric $Fe_{3-x}O_4$ there is an excess of non-paired Fe^{3+} giving rise to a sextuplet which overlaps that due to the A-site Fe^{3+} ions; for this reason the relative intensity of the A-pattern is increased.[10]

For sample 3, the Moessbauer parameters (Table 1) are similar to those of sample 2, except for the intensity ratios (Table 2), which show a different number of vacancies (Fig. 3). In this case it could be concluded from the spectrum at liquid nitrogen temperature, that the iron oxide is α-Fe_2O_3.

The parameters and intensity ratios for sample 4 (Tables 1 and 2) show the presence of non-stoichiometric $Fe_{3-x}O_4$ and α-Fe_2O_3 (Fig. 4). The goodness of the fit assures the presence of the α phase iron oxide.

The parameters of sample 5 (Table 1) indicate the presence of α-Fe_2O_3 (Fig. 5). This conclusion is strengthened by the fact that the sextuplet has a line width of the same order as the natural one, excluding the possibility of another overlapping sextet being present.

From the Moessbauer spectrum corresponding to sample 6 (Fig. 6) it can be concluded that the main phase is γ-Fe_2O_3, although small quantities of α-Fe_2O_3 might also be present.

Figure 7 shows a non-stoichiometric magnetite corresponding to sample 7. Parameters are listed in Tables 1 and 2.

The Moessbauer spectra clearly indicate that even small amounts of oxygen do give rise to varying degrees of oxidation, pointed out by the changes in the intensity ratios as well as in the relative proportions of the different phases present (*cf.* spectra 2 and 3).

The replacement of sulphate by chloride in the initial preparation seems to be related to the same

TABLE 1. MOESSBAUER SPECTRA PARAMETERS AT ROOM TEMPERATURE

Sample		H (kg)	Q* (mm s^{-1})	IS† (mm s^{-1})
1		495 ± 1	0.00 ± 0.01	0.12 ± 0.02
		462 ± 1	−0.01 ± 0.01	0.47 ± 0.01
2		489 ± 1	0.05 ± 0.02	0.10 ± 0.02
		467 ± 1	−0.09 ± 0.05	0.56 ± 0.05
3		514 ± 1	0.04 ± 0.02	0.18 ± 0.02
		491 ± 1	0.04 ± 0.02	0.11 ± 0.02
		466 ± 1	−0.13 ± 0.06	0.57 ± 0.05
4		515 ± 1	0.06 ± 0.03	0.19 ± 0.03
		485 ± 1	0.05 ± 0.02	0.09 ± 0.02
		462 ± 0.8	−0.06 ± 0.03	0.53 ± 0.03
		512 ± 0.8	0.10 ± 0.03	0.19 ± 0.04
5		518 ± 1	0.07 ± 0.04	0.18 ± 0.02
6	Hyp. 1	492 ± 1	0.02 ± 0.05	0.16 ± 0.06
		511 ± 2	0.09 ± 0.05	0.19 ± 0.05
		490 ± 1	0.02 ± 0.05	0.16 ± 0.06
		506 ± 1	0.05 ± 0.03	0.17 ± 0.04
	Hyp. 2	517 ± 1	0.07 ± 0.04	0.19 ± 0.04
7		490 ± 1	0.00 ± 0.01	0.13 ± 0.02
		459 ± 1	−0.02 ± 0.01	0.49 ± 0.01

*$Q = \frac{e^2qQ}{8}(1 - 3\cos^2\Theta)$.

†Referred to Pd matrix.

TABLE 2. INTENSITY RATIOS AT ROOM TEMPERATURE

Sample	$(I_A/I_B)_a$	$(I_A/I_B)_b$	(I^i/I^a)	(I^i/I^b)
1	0.48 ± 0.06	—	—	—
2	1.62 ± 0.07	—	0.48 ± 0.06	—
3	1.95 ± 0.09	—	0.80 ± 0.1	—
4	0.88 ± 0.06	—	0.35 ± 0.06	—
6	—	Hyp. 1 3.2 ± 0.2	—	—
		Hyp. 2 5.9 ± 0.2		0.14 ± 0.2
7	0.89 ± 0.07	—	—	—

A = tetrahedral site; B = octahedral site; a = magnetite; b = maghemine; i = present phase different from magnetite.

end-products (*cf.* spectra 3 and 4), but the intensity ratio of the magnetite (Table 2) tends to be that of the stoichiometric one, and the α-Fe_2O_3 proportion decreases. This is probably related to the well-known fact that the nature of the anion is relevant to the mechanism of crystal growth in hydrolyzed Fe(III) solutions.[11] In our case, also, the extent of oxidation seems to be greater when $FeSO_4$ is employed instead of $FeCl_2$.

Rather extensive oxidation can take place without disruption of the basic structure (magnetite), as shown by spectrum 6 in which γ-Fe_2O_3, structurally related to magnetite, is the most important iron-containing substance present. On the other hand, the results on sample 5 are particularly interesting for our purposes, as the spectrum confirms that the short exposure to air at 300°C was enough to produce quantitatively the oxidative lattice transformation from magnetite to hematite:

$$(2) \qquad 2Fe_3O_4 + \tfrac{1}{2}O_2 \rightarrow 3\alpha\text{-}Fe_2O_3.$$

Although water was not present in this case, the relevance of this result to operating conditions of nuclear power plants is immediate, and is in agreement with proposed methods for physico-chemical decontamination[12,13] involving fast transformations from magnetite to hematite and *vice versa*.

It is therefore concluded that changes in the oxygen content of the coolant in nuclear power stations will rapidly reflect itself in changes in the stoichiometry of the magnetite-type solids and, if higher levels of oxygen, or localized attacks take place, the structure of the particles will suffer more drastic changes to hematite in a short time. Moessbauer spectroscopy could therefore yield important information on the coolant chemistry in nuclear power stations.

REFERENCES

1. (a) W. D. FLETCHER, A. KRIEG and P. COHEN, *WCAP* 1961, 1689; (b) W. D. FLETCHER, *WCAP* 1964, 3730.
2. P. COHEN, *Water Coolant Technology of Power Reactors*, Gordon & Breach, New York, 1969.
3. P. H. TEWARI and W. LEE, *J. Colloid interf. Sci.* 1975, **52**, 77.
4. See for instance D. A. CHANNING and M. J. GRAHAM, *Corros. Sci.* 1972, **12**, 271; D. A. CHANNING, S. M. DICKERSON and M. J. GRAHAM, *Corros. Sci.* 1973, **13**, 933.
5. F. J. SHIPKO and D. L. DOUGLAS, *J. phys. Chem.* 1956, **60**, 1519; U. R. EVANS and J. N. WANKLYN, *Nature* 1948, **162**, 27. Following one reviewer's suggestion we are currently engaged in the study of this reaction using Moessbauer Spectroscopy.
6. D. ST. P. BUNBURY, Programme "MANCFIT", Schuster Lab., Univ. of Manchester, 1974.
7. B. J. EVANS and S. S. HAFNER, *J. appl. Phys.* 1969, **40**, 1411.
8. R. J. ARMSTRONG, A. H. MORRISH and G. A. SAWATZKY, *Phys. Lett.* 1966, **23**, 414.

9. O. C. KISTNER and A. W. SUNYAR, *Phys. Rev. Lett.* 1960, **4**, 412.
10. J. M. DANIELS and A. ROSENCWAIG, *J. phys. Chem. Solids* 1969, **30**, 1561.
11. R. J. KNIGHT and R. N. SYLVA, *J. inorg. nucl. Chem.* 1974, **36**, 591.
12. B. MONTFORD, Cycling Decontamination Techniques at Douglas Point Generating Station, Atomic Energy Canada Limited, AECL-4223, 1973.
13. A. J. G. MAROTO, M. A. BLESA, E. DIAZ, R. FERNANDEZ PRINI, F. M. ROUMIGIERE and R. A. SAINZ, Departamento Química de Reactores IN-QR-C3, Comisión Nacional de Energía Atómica, Buenos Aires, Argentina, 1977.