SKB TECHNICAL REPORT

90-07

Examination of reaction products on the surface of UO_2 fuel exposed to reactor coolant water during power operation

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Studsvik Nuclear

March 1990

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EXAMINATION OF REACTION PRODUCTS ON THE SURFACE OF UO_2 FUEL EXPOSED TO REACTOR COOLANT WATER DURING POWER OPERATION

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Information on SKB technical reports from 1977-1978 (TR 121), 1979 (TR 79-28), 1980 (TR 80-26), 1981 (TR 81-17), 1982 (TR 82-28), 1983 (TR 83-77), 1984 (TR 85-01), 1985 (TR 85-20), 1986 (TR 86-31), 1987 (TR 87-33) and 1988 (TR 88-32) is available through SKB.

STUDSVIK NUCLEAR

STUDSVIK/NF(P)-89/35

1990-03-02

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ABSTRACT

A limited experimental programme has been performed to examine the reaction products on the surfaces of fuel fragments from a BWR fuel rod which had operated in the defective condition for about 100 days.

A yellow crust which was observed mainly on the fuel surfaces directly exposed to the reactor coolant water was identified by XRD as the sub-monohydrate of schoepite, the same material which had been found previously in spent fuel corrosion tests in deionized water.

Other corrosion products with varying morphology and size, also probably UO_3 hydrate(s), were observed on surfaces some distance from the position of clad fracture.

Approved by RS Forsyth

List of contents

1 INTRODUCTION

The SKB/STUDSVIK experimental programme for the study of the corrosion of spent fuel in groundwaters involves both solution analysis of the leachants and examination of the fuel before and after water exposure in order to identify attack sites and reaction products and hence, to define the corrosion mechanisms.

In the course of the programme, the examination of a yellow surface deposit formed on an irradiated PWR fuel specimen subjected to a corrosion test in deionized water at room temperature has been reported [1]. XRD analysis of two specimens of the deposit showed that it was composed of the sub-monohydrate of schoepite, α $UO_3 . xH_2O$ ($x = 0.7-0.9$), sometimes denoted dehydrated schoepite (DS).

Yellow deposits or crusts are also occasionally observed on fuel which has been exposed to reactor coolant water during reactor operation due to through-wall cracking of the Zircaloy clad and subsequent ingress of water or steam.

Such a fuel rod (BWR rod: O2-13544-H8) has recently been subjected to an extensive post-irradiation examination in the Studsvik Hot Cell Laboratory to determine the cause of failure. The primary failure site was located in the upper part of the fuel rod, and subsequent internal degradation process had caused clad fracture about 210 mm from the bottom end. Records of the release of radioactivity to the reactor coolant water showed that the fuel rod had operated in the defective condition for about 100 days.

Post-irradiation examination of the rod was completed about 10 months after reactor shut-down, a period consisting of both water-storage at the reactor station and air-storage in the hot cells. Although this inevitably implied some uncertainty as to the origin of any corrosion products on the fuel surface, it was decided to perform a limited investigation of the yellow material observed near the breached section of the rod.

2 VISUAL INSPECTION

The fuel at both sides of the breach appeared to be covered by the yellow crust. The lower section of the rod, from the fracture position down to the bottom end-plug, had not been involved in the post-irradiation examination and was available for further inspection.

A section of this part of the rod, about 100 mm long, from the fracture downwards, was cut off and then sectioned longitudinally through the clad to give two halves, denoted here A and B, which are shown in Figs. 1 and 2 respectively. The fuel in half A remained essentially in its original position, while the fuel in half B had been disturbed in the cutting operation and consisted largely of loose fragments which had been moved from their original positions.

Inspection of the two halves showed that the yellow material was largely restricted to the surface exposed directly to the reactor coolant water during operation at power, although some was also observed at the lower end of half A. At higher magnification, the material displayed a granular appearance. (Figs. 3a, b and d).

Most of the fuel fragments had a bright lustre and were probably fracture surfaces formed on reactor shut-down. Some surfaces near the clad, however, had a dull appearance and could have been those exposed to the coolant during operation. A narrow band of fuel at about the half-radius position displayed a structure similar to columnar grains (Fig. 3c), formed during operation under oxic conditions.

3 STRUCTURAL ANALYSIS

Samples of the deposit for XRD analysis were taken from two positions denoted GI and GII in Fig. 1. This was effected by taking selected fuel fragments with adherent deposit from these positions, and sampling the deposit by pressing warmed plastic tape against the surface. Small specimens of the material thus removed were then mounted in the normal manner and analyzed in a Guinier-Hägg focussing camera. Good quality diffraction patterns were obtained [2] which showed that both specimens consisted of the sub-monohydrate of schoepite as reported by Dawson et al [3] and which had already been identified in earlier corrosion tests on the laboratory scale [1]. No other phase was detected.

4 SEM EXAMINATION

A rather limited SEM examination was also performed in order to record the appearance of the surface deposits for future comparison with reaction products expected to be found during the spent fuel corrosion programme.

The instrument used, a JEOL-JXA840 analytical SEM, although commissioned for use with radioactive materials, is only provided with local shielding around the spectrometers. It was therefore necessary to reduce the size of the selected fuel fragment in order to attain acceptable working levels of radiation. This was effected in a special device in the hot cell, in which a fuel fragment with adherent surface crust from position GI (see figures 1 and 3a) was fragmented into a number of smaller fragments by the pressure of a steerable tool. A few of these smaller fragments, with volumes up to about 1 mm^3 were then mounted on warm plastic tape and examined in the microscope.

The appearance of the (yellow) deposit crust at about the position sampled for XRD specimen GI is shown in Figs. 4 and 5. Although the morphology of the material is poorly defined, the larger crystals show a resemblance to the material also identified as the sub-monohydrate of schoepite (dehydrated schoepite-DS) by Taylor et al [4] in their work on the corrosion of unirradiated CANDU fuel in steam-water mixtures at 200-225°C.

A small fragment of the surface crust, from an unknown location on the fuel fragment, showed a completely different appearance, and consisted of sub-micron sized granules and platelets about 2 microns in size. Qualitative EDS examination of both this material and that shown in Figs. 4 and 5 showed only the presence of uranium.

It was mentioned earlier in this report that the occurrence of the yellow material appeared to be restricted mainly to the ends of the fuel column directly exposed to the reactor coolant. The sharp local boundary to the deposit is shown clearly in Fig. 3d.

A small fragment from the lower end of the sampled fuel fragment with surface crust was also examined in the scanning electron microscope. At low magnifications it was difficult to distinguish between the surfaces which had been exposed to the reactor coolant and those caused by the specimen size reduction technique. At higher magnifications, however, the inter- and intra-granular fracture typical of the fresh fracture surfaces could be clearly seen. This is shown in Fig. 7 for comparison with the following photographs.

The appearance of a corroded fragment surface is illustrated in Figs. 8 and 9, showing smoothly rounded fuel grain surfaces and an irregular covering of UO_3 hydrates, with varying morphology and size, located on grain faces and at grain boundaries. The fuel grains themselves appear to be evenly covered by a granular material of the order of 100 nm in size. Two of the fuel pores visible in one of the high magnification photographs in Fig. 9 are seen to contain spherical particles, presumably consisting of the fission product metals Mo, Tc, Ru, Rh and Pd, either as the original metallic inclusions or as oxidized/hydrated reaction products.

5 DISCUSSION

The corrosion of UO_2 fuel exposed to reactor coolant water during power operation, where the reactions proceed at fuel surface temperatures appreciably higher than 400°C and in an intensely radiolytic environment, is not strictly relevant to the study of spent fuel corrosion under repository conditions. In the repository case, radioactive decay during pre-deposition storage will reduce fuel temperatures at deposition to about 70-80°C, and temperatures at the time of possible capsule failure will be much lower. Since the relative thermodynamic stabilities of possible reaction products will be significantly different in the two cases, different reaction mechanisms may be favoured.

The chemical constituents of possible groundwaters, granitic or saline, for example, could also markedly affect reaction mechanisms and products.

In spite of these considerations, the results of the limited experimental programme described in this report are useful for comparison with results from laboratory-scale experiments at lower temperatures, particularly those performed in deionized water. The main finding, that the yellow material found on fuel surfaces near the clad breach was the sub-monohydrate of schoepite (or dehydrated schoepite DS) is not, of course, surprising since this would be the most stable hydrate form at temperatures above about 130°C [5]. However, the (only) two specimens examined by XRD showed the absence of the dehydrate form (schoepite itself), which Taylor et al [4] detected in some of their experiments and tentatively attributed to secondary hydration of DS during cooling or handling. The rod examined in the present work had been stored in the reactor pool for about 3 months before shipping to the Studsvik Hot Cell Laboratory.

No attempt was made in this limited programme to positively identify the other corrosion products observed on the fuel surfaces, (Figs. 5, 8 and 9), partly because of shortage of time and partly because of some uncertainty with regard to whether they were formed in-reactor or during subsequent storage. A reasonably assumption, however, is that they were UO_3 hydrate(s).

In corrosion tests on spent fuel exposed to granitic groundwaters, the amounts of reaction or alteration products on the fuel surface are significantly lower than those found after deionized water exposures, since the carbonate ligands in the groundwater retain in solution as complexes some (a few mg/L) of the oxidized and dissolved uranium.

Severe experimental difficulties are involved in selectively sampling for analysis such material from the highly-active fuel matrix. Comparison of the morphologies of observed surface materials with those recorded in reference photographs from this and other work on spent fuel, and well-characterized minerals is expected to furnish useful supplementary evidence for the necessary identification.

6 ACKNOWLEDGEMENTS

The authors take pleasure in thanking Mr. K. Lilja of the Hot Cell Laboratory for preparing the clam-shelled rod halves prior to visual inspection, and to Dr. L.O. Werme, SKB for useful discussions.

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Fig. 1 Fuel/clad half A

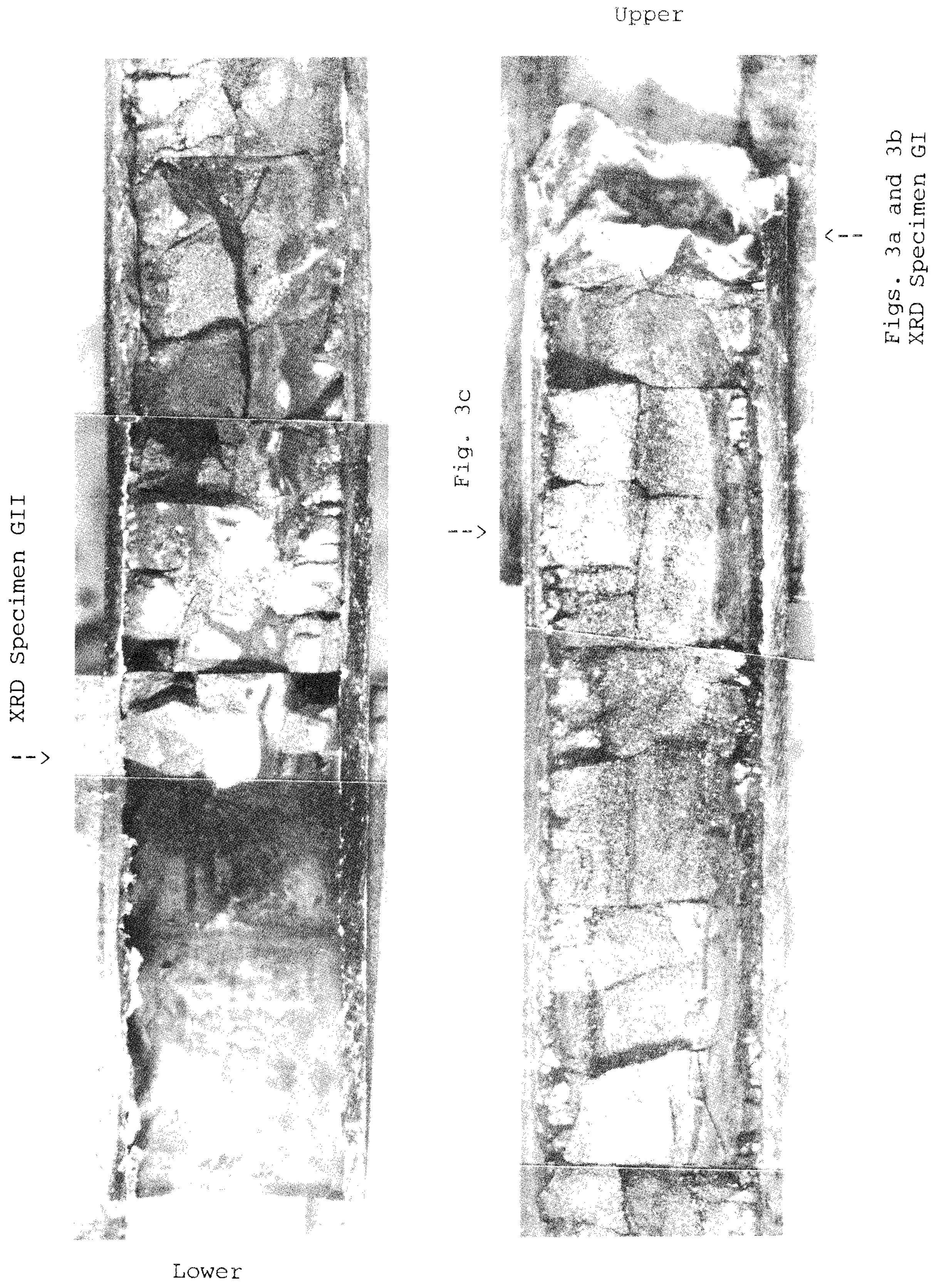
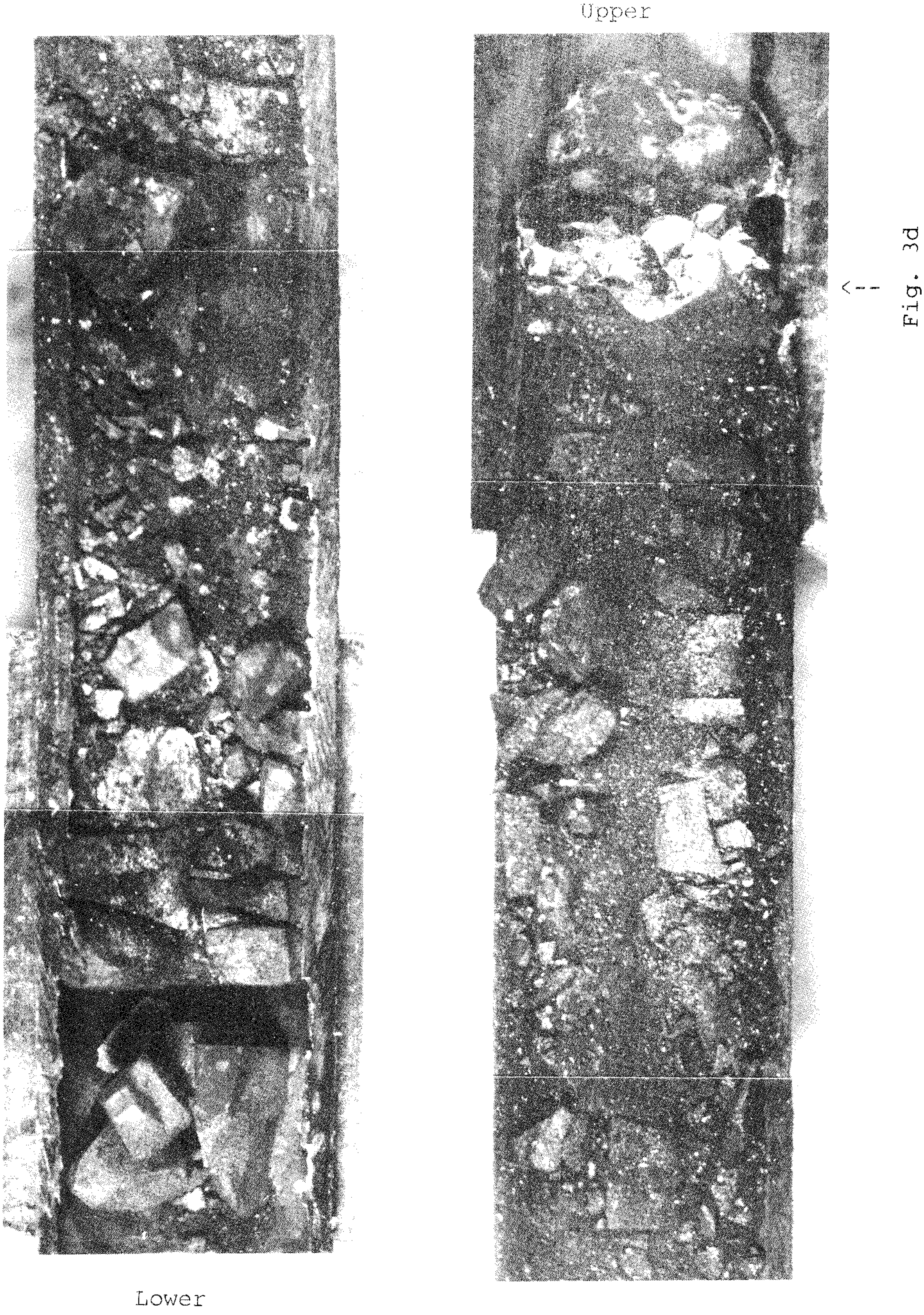
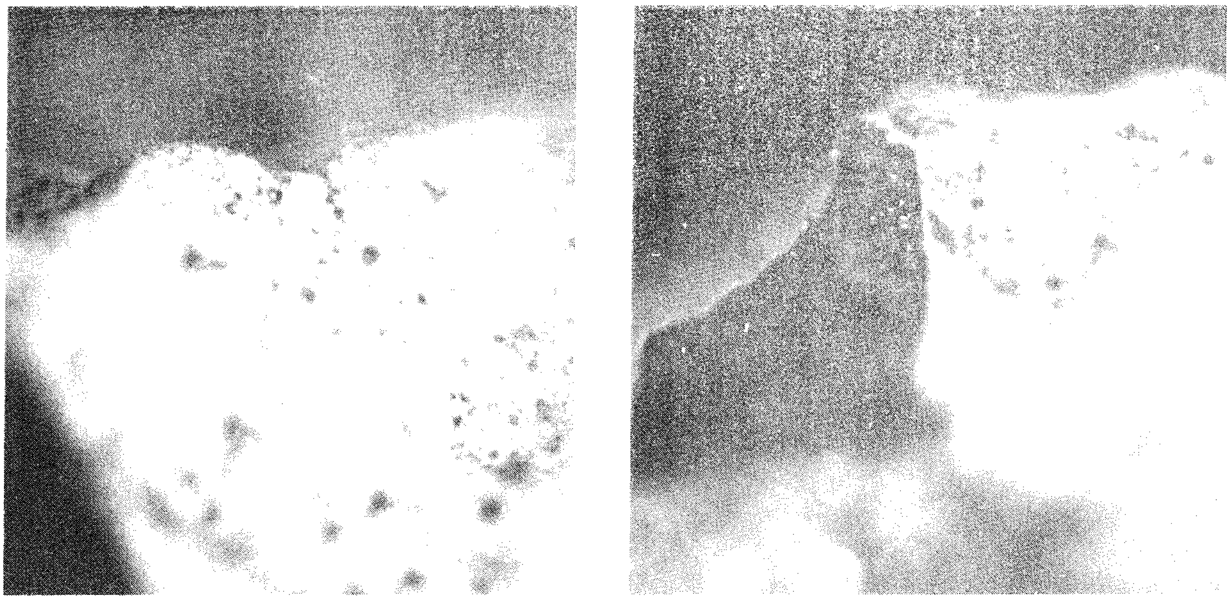


Fig. 2 Fuel/clad half B

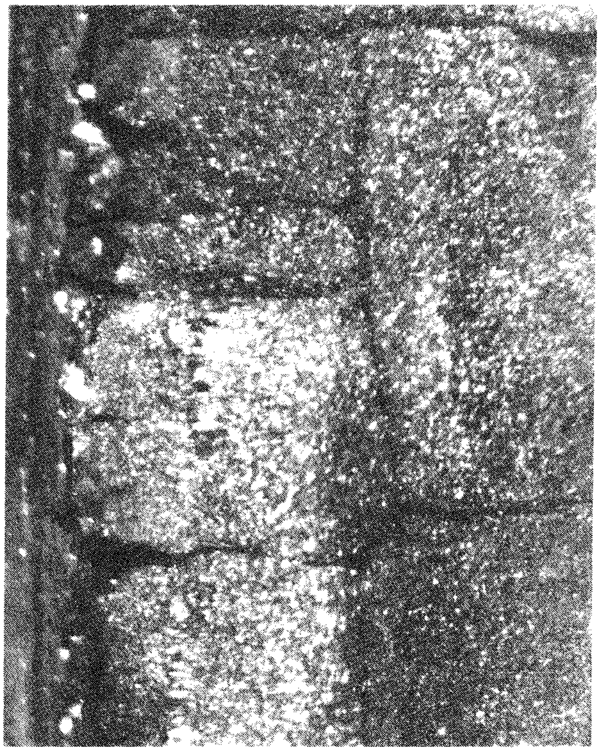




3a) x25

3b) x30

Detail of deposit crust at upper end of clad half A.



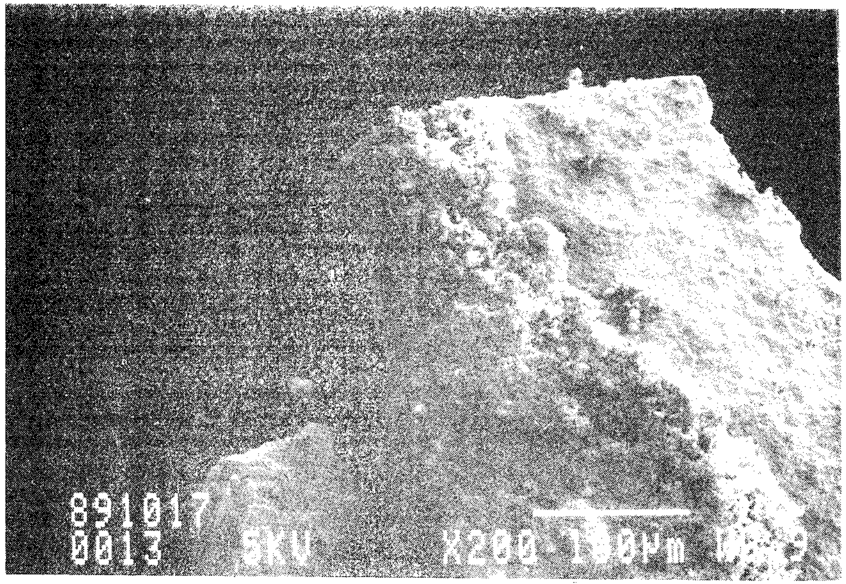
3c) x10

Detail of fuel:
half A.
(See Fig. 1)

3d) x40

Detail of deposit Clad
crust at upper end of
clad half B.
(See Fig. 2)

<u>Fig. 4</u> Detail of deposit crust
at upper end of clad
half A.
(See Fig. 1)



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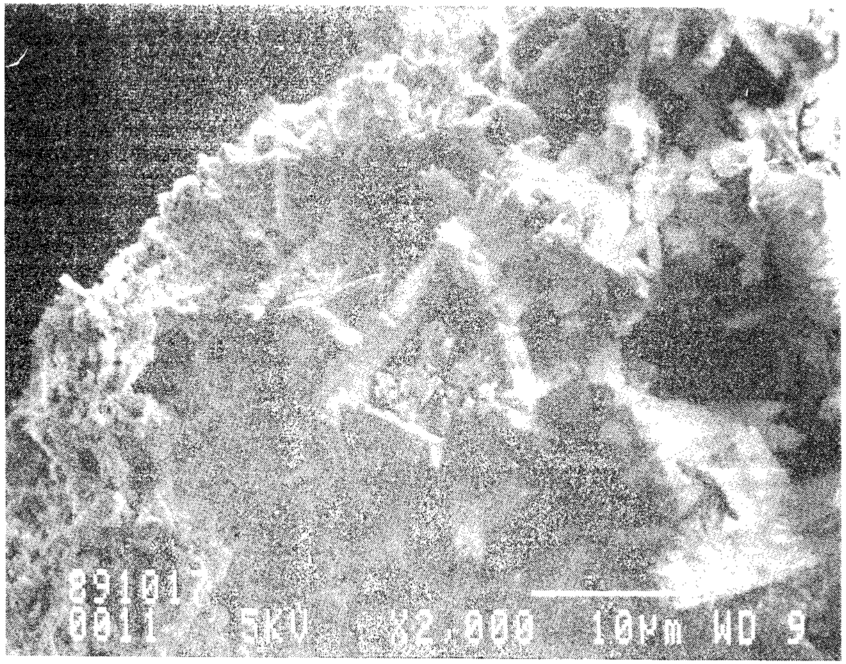

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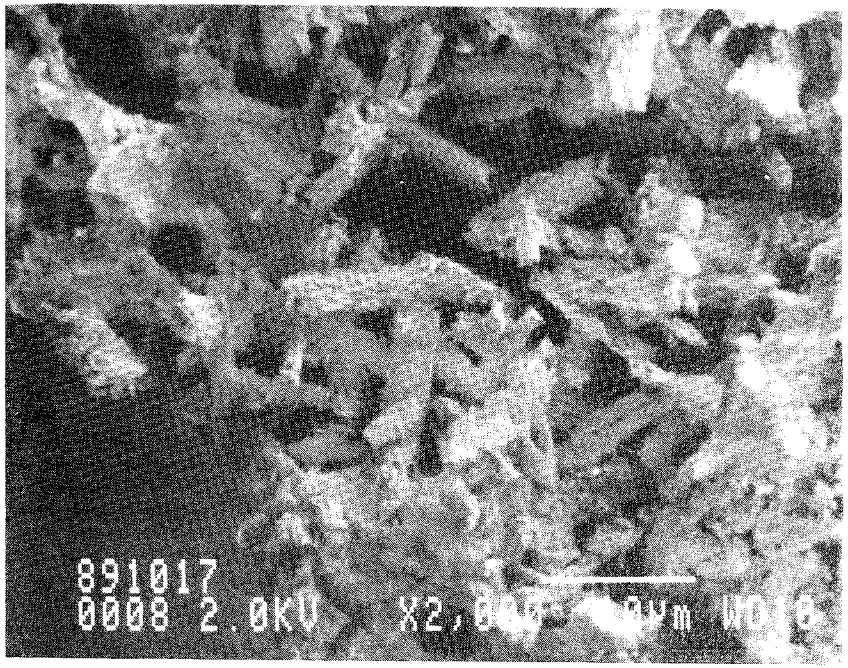

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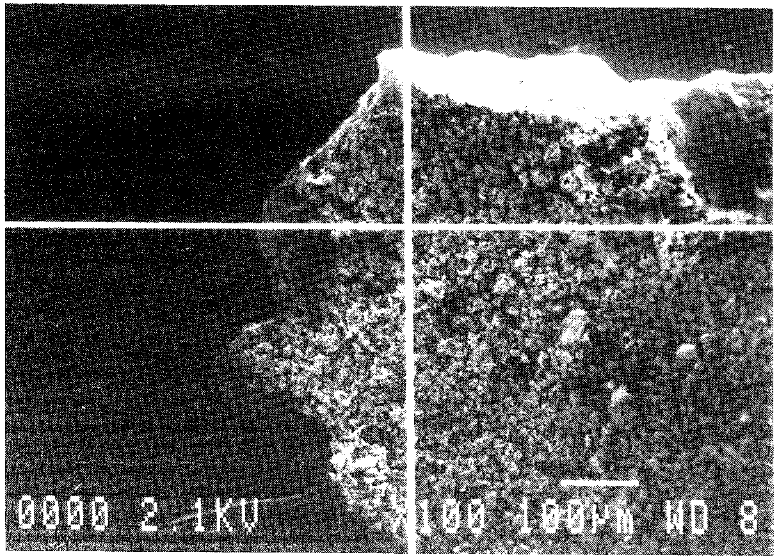
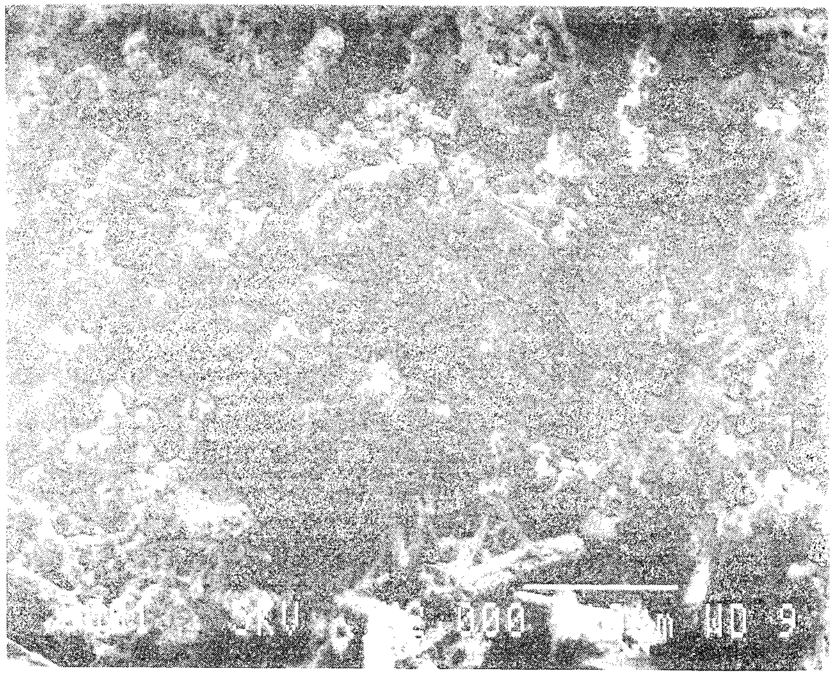


5a)

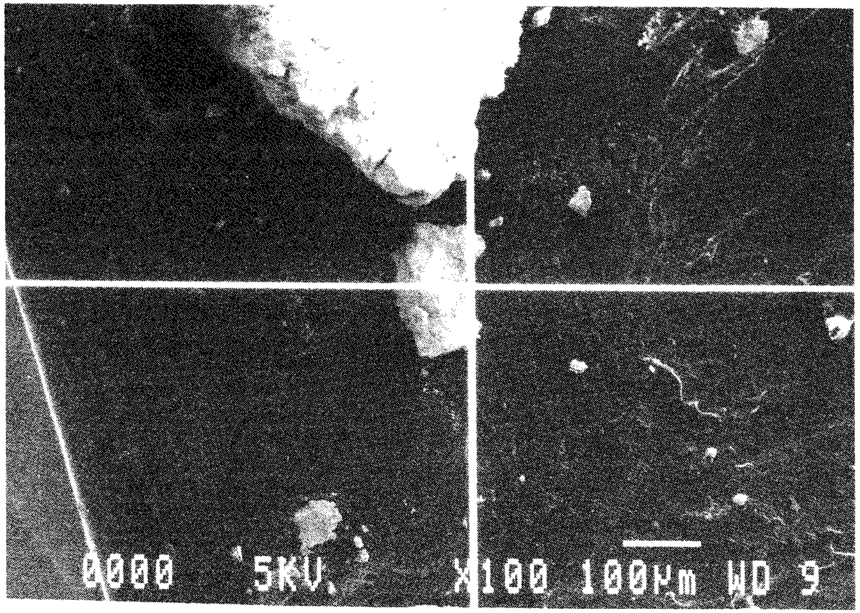
Fig. 5 Detail of deposit crust at upper end of clad half A. (See Fig. 1)



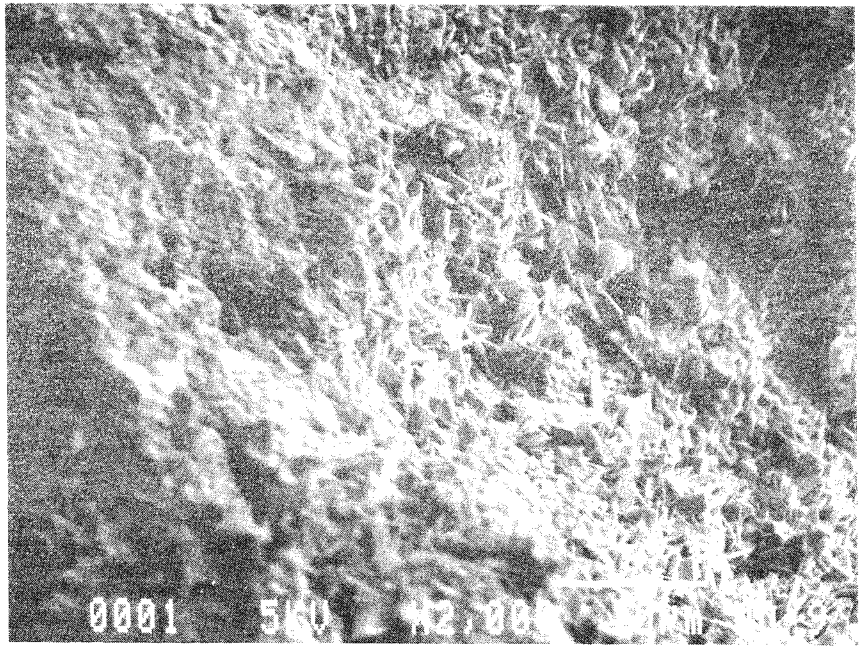
5b)

5c)

Fig. 6 Detail of small fragment of surface crust.



6a)



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6c)

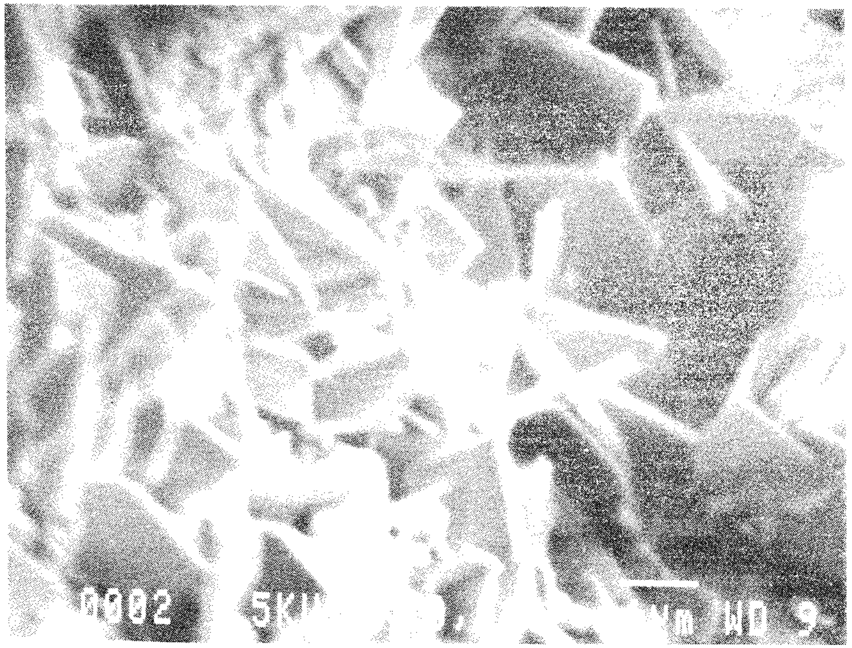
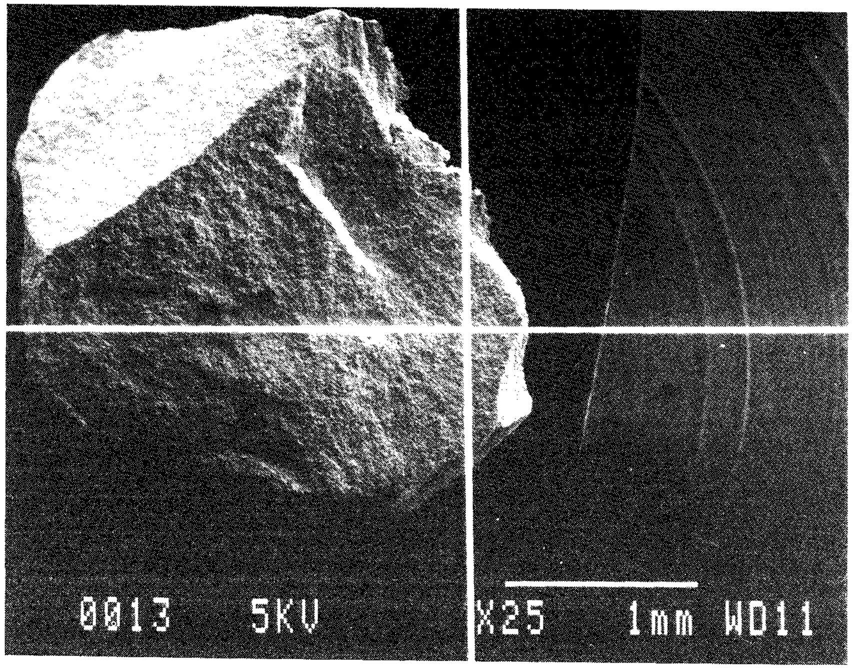
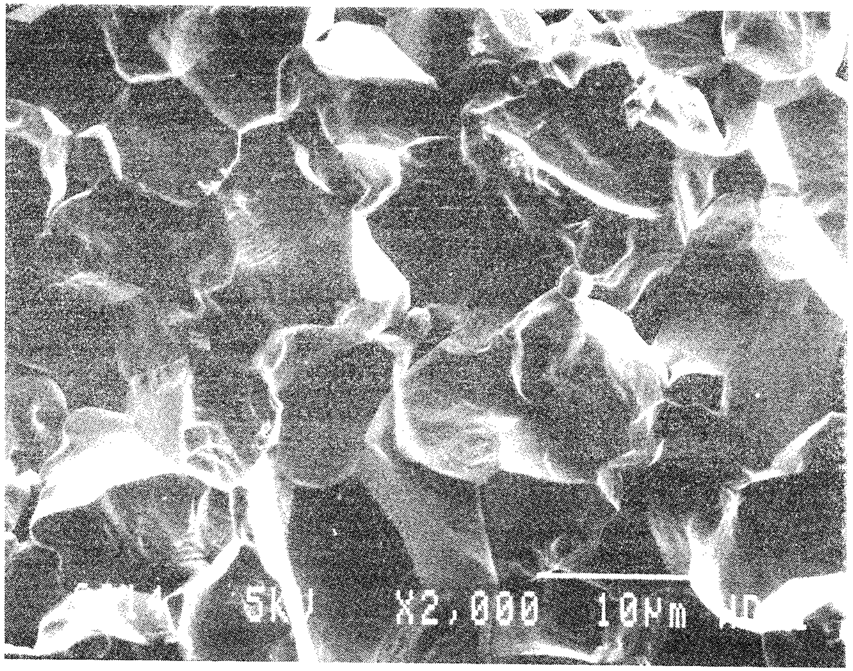


Fig. 7 Detail of fresh fracture surface.



7a)



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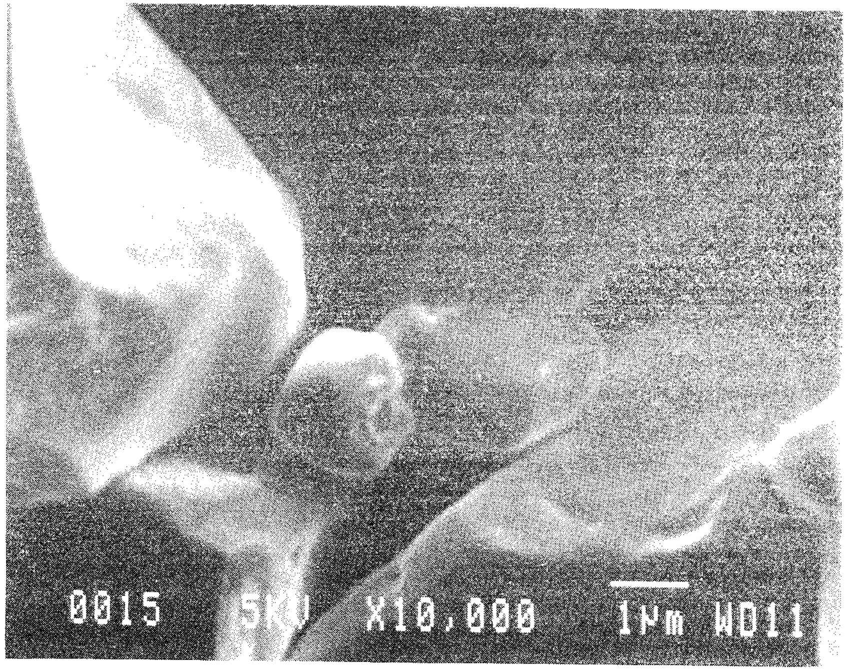
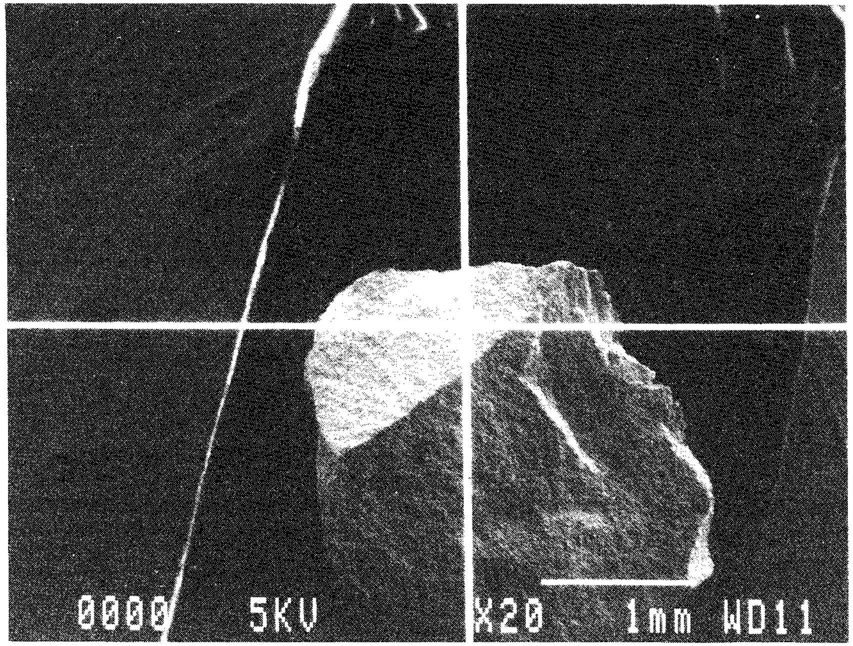


7c)

Fig. 8 Detail of corroded fragment surface.

8a)



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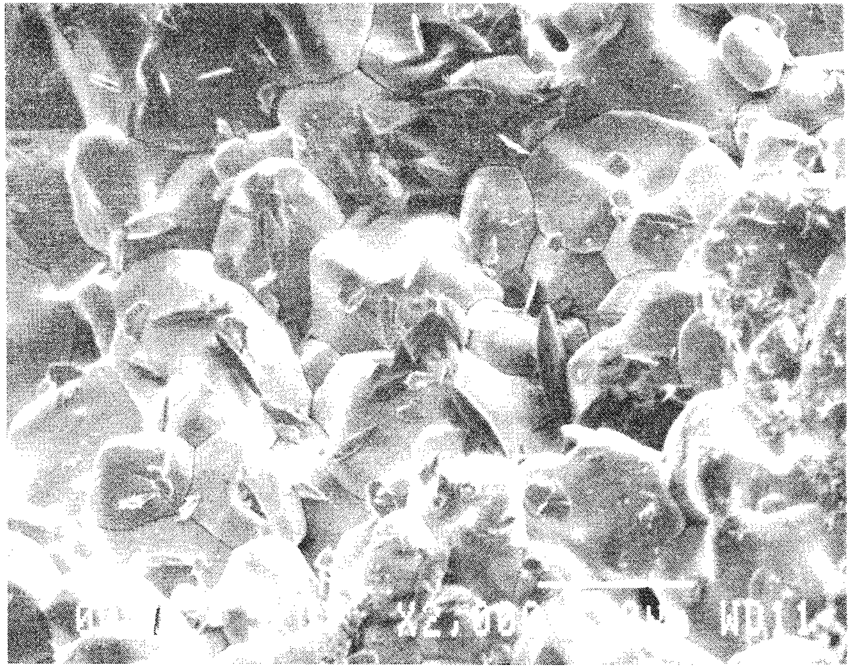

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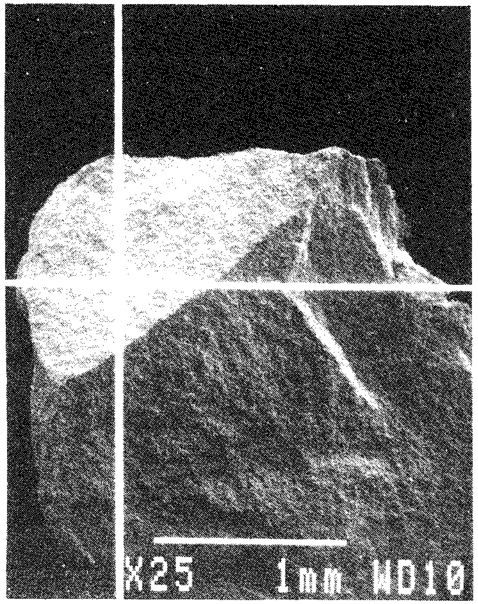


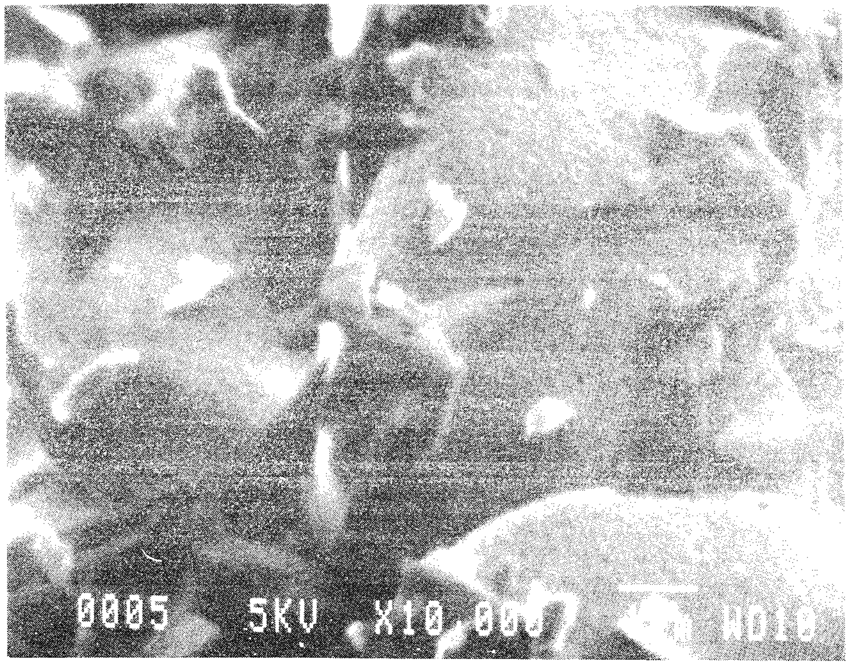
9a)

9b)

Fig. 9 Detail of corroded fragment surface.

9c)

9d)



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Statistical estimation and stochastic simulation using PROPER
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R.S. Forsyth, U-B. Eklund, O. Mattsson, D. Schrire
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March 1990

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Potential effects of bacteria on radionuclide transport from a Swedish high level nuclear waste repository

Karsten Pedersen
University of Gothenburg, Department of General and Marine Microbiology, Gothenburg
January 1990

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Yngve Albinsson, Birgit Sätmark,
Ingemar Engkvist, W. Johansson
Department of Nuclear Chemistry,
Chalmers University of Technology, Gothenburg
April 1990