

SOLUBILITY OF UNIRRADIATED FUEL IN GRANITIC GROUNDWATER

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ABSTRACT

The simulation of groundwater conditions in the planned granitic repositories of spent nuclear fuel has shown to play an essential role in the dissolution studies of uranium oxide. The role of the low oxygen content in the water is especially essential. Therefore, the dissolution experiments of unirradiated uranium oxide pellets in this work are being carried out in oxygen-free containers and a glove box, and in an anaerobic autoclave system which was developed within this project. Two different synthetic groundwaters were employed in the tests, one of which corresponds to the undisturbed groundwater deep in the granitic bedrock. Another synthetic water with high carbonate content takes into account the effects of bentonite present around the spent fuel canisters in the repository. Also two natural groundwaters were applied. Oxygen concentrations as low as 0.8 µg/l have been observed in the waters inside the anaerobic glove box. The reducing conditions have been maintained fairly reliably in the recent experiments. The pH values are controlled in order to remain in steps between 4.5 and 11, and the redox potentials +0.1...-0.4 V. The temperatures are kept at 25 °C and 60 °C. Under reducing or mildly oxidizing conditions and within the pH values 8...9 the solubility limit of uranium has stayed between 0.02 mg/l and 1.4 mg/l. The higher value corresponds with a higher redox potential.

BACKGROUND AND OBJECTIVE

The up-to-date Finnish plans for the management of spent nuclear fuel do not comprise reprocessing. Therefore, the safety assessments are concentrated upon the direct disposal of spent fuel starting in the year 2020. The proposed repository will be excavated in hard precambrian bedrock at a depth of 500 m.

The dissolution rate of spent fuel is needed for the safety analysis as the source term. The dissolution tests at our laboratory are made by using unirradiated uranium oxide fuel.¹ As a matter of fact, spent fuel matrix itself is the innermost of the barriers between the active nuclides and the biosphere. The solubility of uranium is important since uranium is the single most abundant element in spent fuel. The release of many other nuclides, especially actinides, is dependent on the matrix dissolution.

The characterization of the disposal conditions is going on and gives more detailed information. It serves as a basis for the experiments which are intended to produce dissolution data in simulated disposal conditions.

The maximum temperature at the surface of a fuel canister will be around 70 °C 40 years after the disposal and below 30 °C 10 000 years later². The pressure will be 5 MPa plus a conceivable swelling pressure of bentonite clay which is thought to be used as a buffer material. Swelling pressures up to 3 MPa have been registered³.

Chemical conditions in laboratory experiments similar to those in a vault in granitic bedrock are very laborious to achieve. The main reasons are:
1) an oxygen-free atmosphere with approximately

10 ppm or less oxygen in the gas is difficult to maintain in a glove box, 2) a typical groundwater system is very sensible towards disturbances, 3) groundwater can accidentally be oxidized in an instant but will return to the reduced state very slowly, 4) the chemical conditions in a repository change with time and place, 5) the reactions are not fully understood, 6) a sensible instrumentation is needed for detecting small concentrations and for measuring very high impedance voltage sources and 7) all the afore-mentioned combined with high pressures.

The solubility limit of U(VI) is considerably higher than that of U(IV). Traces of oxygen are harmful since it leads to the oxidized form U(VI). Thus the redox potential is an essential indicator in the experimental studies.

Also a high carbonate concentration increases the UO₂ dissolution rate⁴. The lowest solubility as a function of pH stays in the region of neutral water. The aim of this project has been to clarify the influence of these parameters.

The first dissolution experiments were performed in air saturated waters. Those experiments were followed by tests performed in double wall containers which were filled with nitrogen. A noteworthy improvement was the introduction of an anaerobic cabinet and an anaerobic autoclave system.

EXPERIMENTAL

The experimental studies are performed in three set-ups : 1) in double wall plastic containers filled with nitrogen, 2) in an anaerobic glove box, and 3) in an autoclave system especially developed for these experiments.

The specimens are unirradiated sintered uranium dioxide pellets. They enter the tests as such without extra polishing. In the beginning the waters are changed more frequently in order to remove the high oxides of uranium, mainly U(VI), that potentially exist on the surface.

The pH value and the redox potential (Eh) of water are measured in every sample. The analytical determinations of uranium are made by activation analysis from the waters. A scanning electron microscope with an energy dispersive spectrometer and an X-ray diffractometer were utilized in the analysis of surface layers of two fuel pellets.

Waters

Altogether four types of groundwaters were used. Two of them were natural and the other two were synthetic. The compositions are listed in TABLE I. Deionized water served as a reference.

Samples of natural granitic groundwaters were collected at shallow depths in the Stripa mine in Sweden and in a bore hole (-70 m) at the Olkiluoto nuclear power plant site in Finland. The waters were in contact with air during the sampling.

One synthetic groundwater is intended to correspond with the undisturbed chemical conditions deep in the granitic bedrock⁵. The low carbonate content (120 mg/l HCO₃) is specific to this water. Another synthetic groundwater⁶ simulates the effect of bentonite clay which has been proposed for a buffer material. Descriptive are its high carbonate (400...600 mg/l HCO₃) and sodium concentrations.

Double wall containers

The use of nitrogen filled polyethylene vessels which are placed in larger plastic containers (Fig. 1) offers a cost-effective way to start anaerobic dissolution experiments. The system can also readily be used at elevated temperatures in heat chambers.

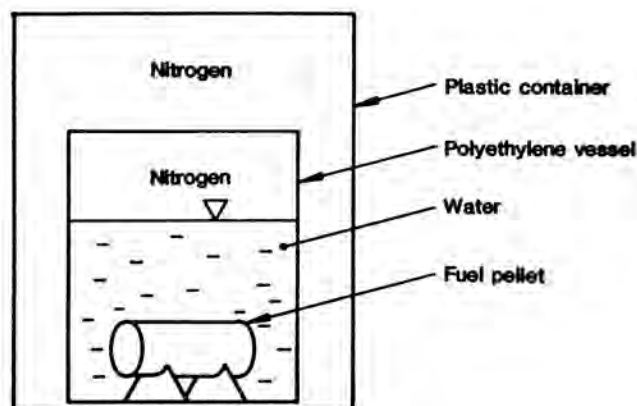


Fig. 1. A double wall container.

TABLE I

Groundwater compositions.

| Component | Dimension | Olkiluoto groundwater (Sample YD2, 70m, 30.8.1982) (natural) | Stripa groundwater (Sample M3/82-09/1) (natural) | Undisturbed granite groundwater ⁵ (synthetic I) | Groundwater in the presence of bentonite clay ⁶ (synthetic II) |
|-----------------------|--------------------------------|--------------------------------------------------------------|--------------------------------------------------|------------------------------------------------------------|---------------------------------------------------------------------------|
| pH | 1 | 8.2 | 8.3 | 8...9 | 8...9 |
| Eh | V | - | - | -0.1 | -0.4...0 |
| Alkalinity | mval/l | 5.9 | 1.4 | - | - |
| Electric conductivity | mS/m | 8.7 | 28 | - | - |
| Permanganate number | KMnO ₄ | 50 | 4 | - | - |
| Phosphate | PO ₄ ³⁻ | .011 | < 0.1 | - | 0.01 |
| | HPO ₄ ²⁻ | - | - | - | 0.4 |
| Sulphate | SO ₄ ²⁻ | 180 | 6.0 | 9.6 | 50 |
| Chloride | Cl ⁻ | 20 | 37 | 70 | 80 |
| Fluoride | F ⁻ | 0.47 | 5.3 | - | 7.5 |
| Bicarbonate | HCO ₃ ⁻ | 360 | 86 | 120 | 400...600 |
| Nitrite | NO ₂ ⁻ | < 0.1 | < 0.001 | - | - |
| Nitrate | NO ₃ ⁻ | < 0.1 | < 0.02 | - | - |
| Iron | Fe ^{tot} | 0.04 | < 0.02 | (2...3) | < 5 |
| Silica | SiO ₂ | 13 (Si) | < 1 | 12 | 20 |
| Potassium | K ⁺ | 17 | 0.26 | 3.9 | 5 |
| Sodium | Na ⁺ | 77 | 50 | 65 | 300...500 |
| Ammonium | NH ₄ ⁺ | < 0.01 | < 0.01 | - | - |
| Calcium | Ca ²⁺ | 69 | 14 | 18 | 20 |
| Magnesium | Mg ²⁺ | 39 | 0.25 | 4.3 | 5 |
| Manganese | Mn ²⁺ | 1.3 | < 0.02 | - | - |

The natural groundwaters were deaerated by flushing with nitrogen gas. The oxygen content of the samples at 60 °C increased to 2...3 mg/l. At 25 °C the oxygen content stayed below 0.01 mg/l. As a reference, the oxygen content of air saturated water is 8.5 mg/l.

Anaerobic glove box

Most of the present studies are in progress in an anaerobic glove box. Thus it is possible to carry out complicated maneuvers without oxidizing conditions. The low oxygen concentration is maintained by using a mixture of high purity nitrogen gas (minimum 99.998 % N₂) and a small fraction of hydrogen. The share of hydrogen is to combine with oxygen by means of a catalyzer. The continuous oxygen analysis has regularly indicated a concentration of 10 ppm O₂ in the atmosphere.

Anaerobic autoclave system

An autoclave system⁷ was developed for the simulation of hydrostatic pressure and temperature rise in the disposal vault. The system block scheme is shown in Fig. 2. The specimen stays in an oxygen-free environment during the water changes which are carried out isobaric and isothermal. The system is pressurized with nitrogen up to 20 MPa. Thus the upper limit of temperature is 100 °C. The surfaces in contact with water have a polytetrafluoroethylene (PTFE) coating, the valves forming an exception.

The volume of each pressure vessel is 210 cm³. Thus the standard value 0.1 m for the ratio leachant volume to the geometric surface area of the specimen (V/S-ratio) can be used with the common fuel pellets.

The dissolution vessel is shown in Fig. 3. The instrumentation involves pressure, temperature and redox potential sensors.

The redox sensitive electrode couple was developed during the project⁷. The reference electrode is an Ag/AgCl cell with saturated KCl filling. A platinum wire serves as a measuring electrode. However, experience has convinced us that a glassy carbon electrode would be more suitable for measurements in groundwaters.

In order to prepare the leachant it can be deoxygenated by flushing it with nitrogen gas and preheating it in the supply vessel. The oxygen content during a test has not been measured but the redox potentials have proven the conditions to remain reducing.

Dissolution rate of uranium

The dissolution rate of uranium was determined by using the ISO 6961 standard⁸ method.⁹ The test conditions are listed in the TABLE II. The groundwater types refer to the ones presented in the TABLE I. The sensitivity of the oxygen analyzer was 0.01 mg/l. Therefore more accurate oxygen contents were not available.

The standard value of the V/S-ratio is in the range 0.1...0.2 m. The dissolution periods are lengthened during the test. After the sixth week the periods last one month.

The test series D was carried out at high pressure, 10 MPa.

Solubility limit of uranium

The conditions for the solubility limit determinations of uranium are included in TABLE II. The conditions range from reducing to mildly oxidizing ones. The test temperatures are 25 °C and 60 °C.

The pH value is controlled in series F between 4 and 12. Preliminary results are given in this paper. The pH is adjusted by varying the composition HCO₃⁻ - CO₃²⁻ - OH⁻ - H⁺. Series G with various redox potential levels through +0.1 V to -0.4 V has recently been started. The redox potential is controlled with Fe(II) content.

The experiments concerning the solubility limit of uranium will be continued until it begins to precipitate during a period, or the equilibrium concentration is attained.

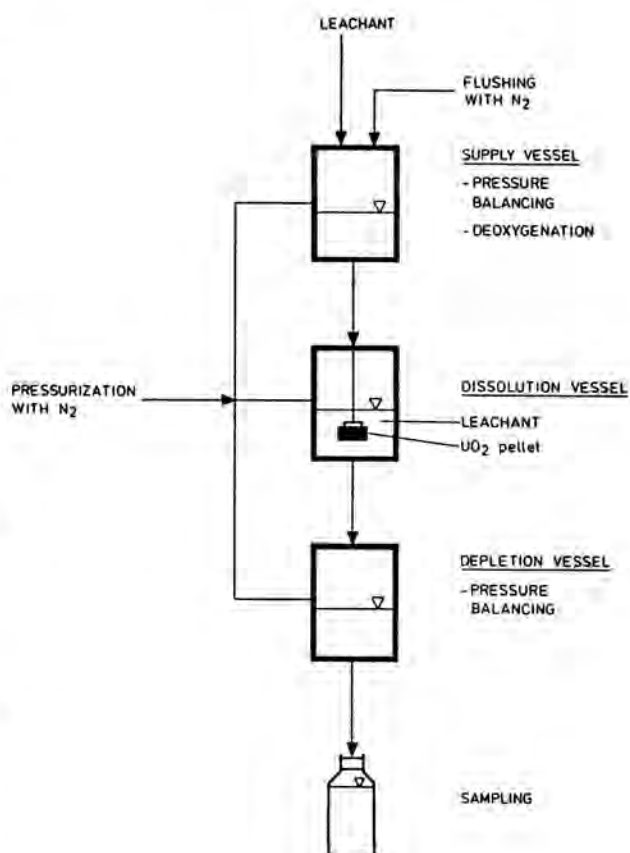


Fig. 2. A simplified system diagram of the autoclave system.

TABLE II
Test conditions.

| Series | Dissolution rate test | Solubility limit test | Water type | Pressure (MPa) | Temperature (°C) | Oxygen content (mg/l) | Comment |
|--------|-----------------------|-----------------------|------------------------|----------------|------------------|-----------------------|---------|
| A | X | | Deionized | 0.1 | 25 | 8...9 | |
| B | X | X | Natural groundwaters | 0.1 | 25 | < 0.01 | |
| C | X | | " | 0.1 | 60 | 2...3 | |
| D | X | | 01kiluoto groundwater | 10 | 60 | < 0.01 | a |
| E | | X | Natural groundwaters | 0.1 | 60 | 2...3 | |
| F | | X | Synthetic groundwaters | 0.1 | 25 | 0.001 | b |
| G | | X | " | 0.1 | 25 | 0.001 | b |

a) Deduced from Eh.

b) The test has recently been started.

RESULTS

Dissolution rate

The uranium dissolution rates varied from $2 \cdot 10^{-8}$ to $2 \cdot 10^{-7}$ g cm⁻² d⁻¹ as can be seen in TABLE III. The pH value was kept between 8 and 9.

The dissolution rate in air-saturated deionized water was approximately as low as or lower than in the groundwaters despite the presence of oxygen. This is probably caused by the carbonate in the groundwaters which enhances the dissolution rate. No great difference was observed between the natural groundwaters in the oxygen-free conditions.

TABLE III
Dissolution rates of uranium⁹

| Water | Oxygen content (mg/l) | Temp. (°C) | Dissolution rate (g cm ⁻² d ⁻¹) | Time |
|--------------------------|-----------------------|------------|--------------------------------------------------------|-------------|
| Deionized | 8...9 | 25 | $5 \cdot 10^{-8}$ | After 732 d |
| Air-saturated | | | | |
| 01kiluoto groundwater | < 0.01 | 25 | $1 \cdot 10^{-7}$ | After 612 d |
| Oxygen-free | | | | |
| Stripa groundwater | " | 25 | $2 \cdot 10^{-7}$ | " |
| 01kiluoto groundwater | 2...3 | 60 | $2 \cdot 10^{-8}$ | " |
| Mildly oxidizing | | | | |
| Stripa groundwater | " | 60 | $2 \cdot 10^{-7}$ | " |
| Literature ¹⁰ | - | - | $10^{-9} \dots 10^{-6}$ | - |

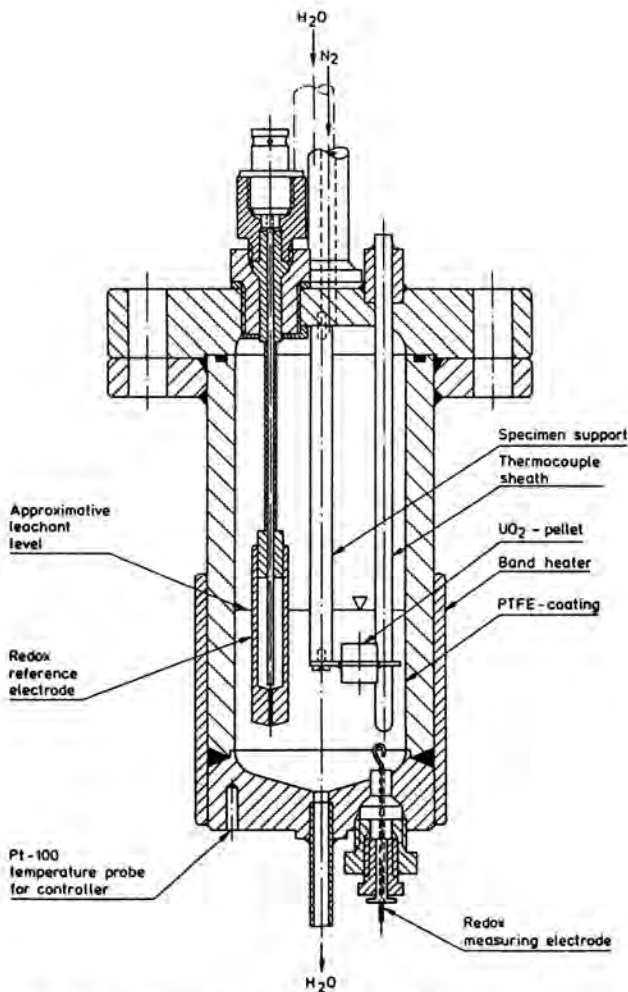


Fig. 3. The dissolution vessel of the autoclave system.

According to the theoretical calculations for the pure water-uranium system the solubility of uranium decreases with increasing temperature in weakly basic solutions with reducing conditions¹⁰. This seems to have had an effect because the dissolution rates of uranium in the groundwaters were equal or lower at 60 °C than at 25 °C in spite of the higher oxygen content at 60 °C.

No clear difference between the dissolution rates at different pressures can be observed. The comparison of the results is difficult because the oxygen content in the waters did not remain similar.

Solubility limit

The solubility limit varied in the natural groundwaters between 0.02 and 0.6 mg U/l (TABLE IV). The influence of Eh is so strong that the solubility stays lower with a higher carbonate content if a low Eh is maintained.

The surface layer of two UO₂ pellets from test series B were examined with scanning electron microscopy (SEM). Figures 5, 6 and 7 represent the pellets before and after the test. The dissolution in the Stripa groundwater left almost no visible coating. The energy dispersive spectrum still revealed clearly silica and iron in the thin and irregular deposit (Fig. 6). Traces of aluminum, sulphur and chlorine were also detected.

The pellet immersed in the Olkiluoto groundwater, on the contrary, had a thick homogenous CaCO₃ layer. Calcium was the only element detected with SEM. CaCO₃ was specified with X-ray diffractometry.

The solubility in the synthetic groundwaters is measured at different pH values (Fig. 4). The preliminary results show a strong dependence on pH in the synthetic groundwater with high carbonate content.

It seems as if the higher total carbonate content would not have any influence on uranium solubility at pH 8...9, within the values predicted

for deep groundwater. The solubility is considerably increased at the other pH values. This requires, however, further studies.

The results should be taken as tentative ones. The measurements will be continued.

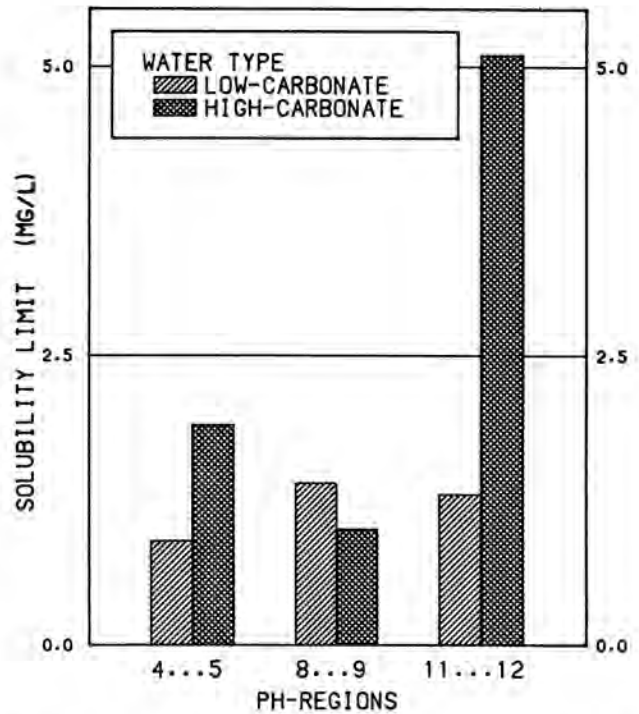


Fig 4. Solubility limit of uranium as a function of pH. The low-carbonate water refers to Synthetic groundwater I and the high-carbonate water to Synthetic groundwater II.

TABLE IV

Solubility limits of uranium in synthetic and natural groundwaters. The concentration of dissolved oxygen was below 0.01 mg/l and pH was kept between 8 and 9.

| Water type | Eh (V) | Total carbonate HCO ₃ (mg/l) | Uranium solubility (mg/l) |
|--------------------------------------------------------------|-------------|-----------------------------------------|---------------------------|
| Synthetic groundwater I (undisturbed repository conditions) | -0.1 | 120 | 1.4 |
| Synthetic groundwater II (effect of bentonite clay included) | " | 600 | 1.0 |
| Olkiluoto groundwater (natural) | -0.4...-0.2 | 360 | 0.02...0.2 |
| Stripa groundwater (natural) | -0.3...0 | 86 | 0.04...0.6 |

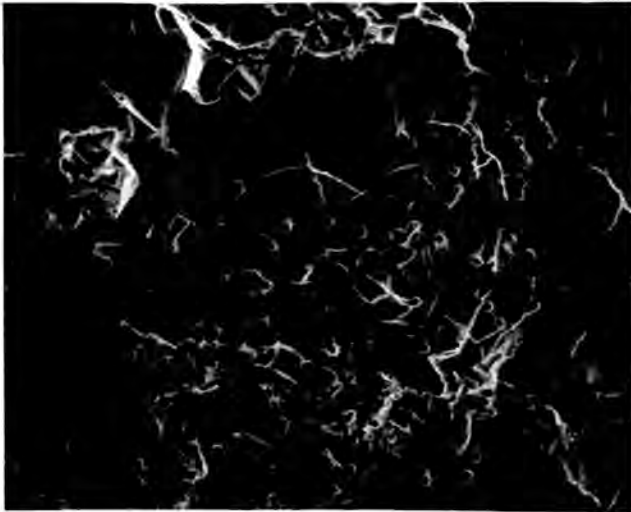


Fig. 5. The surface of a UO_2 pellet before the dissolution test. The magnification is 700.

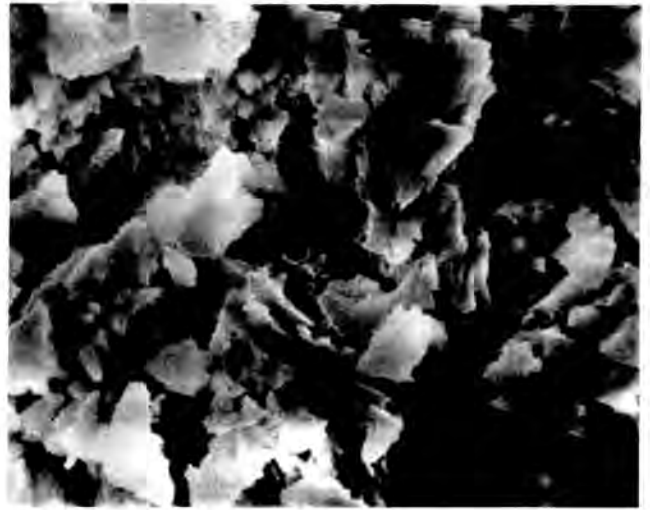


Fig. 7. The surface of a UO_2 pellet which was immersed in high-carbonate Olkiluoto groundwater. The crystalline formation is $CaCO_3$. The magnification is 2000.

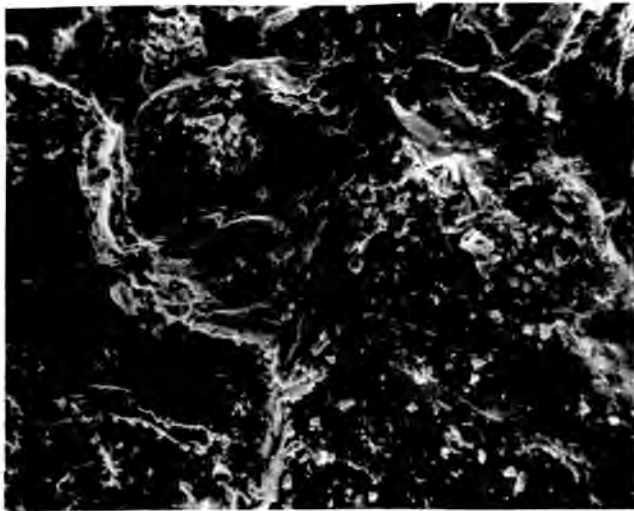


Fig. 6. The surface layer of a UO_2 pellet after dissolution in Stripa groundwater. The magnification is 700.

DISCUSSION AND CONCLUSIONS

Spent fuel is not considered to be applied in the dissolution tests in Finland in the near future. Unirradiated fuel offers along with the much more convenient working conditions also a better possibility to arrange an oxygen-free experimental environment. Radiolysis products such as oxygen and hydrogen peroxide can be added into the groundwater when needed to simulate the near-field conditions after the canister break-down.

The results presented in this paper are the first ones obtained in this context at our institute. In the beginning the oxygen content of the water was unstable which causes interpretation difficulties of the results. In the most recent experiments the reducing conditions were kept reliably. The solubility limits of uranium as a function of pH are only tentative values from longer test series. The determination of the solubility as a function of Eh is also in progress. The determination of the dissolution rate has not been included in further plans.

The solubility of uranium in granite groundwater varies strongly with the groundwater conditions. In normal conditions in an intact repository the system performance is not very sensitive toward the variations in the solubility limit. Thus there is no need of high accuracy in the source term estimation - provided that the repository and the geosphere are reliable and effective⁶. In this case the use of the solubility limit for the safety analysis is relevant because the solubility limit will be attained due to an extremely low water exchange.

In an abnormal condition when the water flow rate is high and the path from the vault to the biosphere is shorter, the dissolution rate of uranium is a proper quantity. Then the significance of the source term becomes emphasized.

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