

CAPABILITY FOR MEASUREMENT OF O/U RATIOS IN AS-DISCHARGED DEFECTED CANDU FUEL

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ABSTRACT

Coulometric titration was used to measure the O/U ratios of small samples taken from a CANDU fuel element that defected during in-reactor service. Fuel samples were heated to 1000°C in reducing atmospheres, and the amount of oxygen released by the sample was recorded as a function of time. The reproducibility of the method is excellent, and the verification of the techniques was demonstrated. In one fuel element, coulometric titration measurements of samples taken 6 cm from a debris-fretting defect showed that, at that location, the fuel samples had been oxidized during their in-reactor residence to $\text{UO}_{2.044 \pm 0.002}$. The next step is to measure variations of O/U as a function of distance from a fuel defect.

1.0 INTRODUCTION

UO_2 fuel can readily absorb oxygen in oxidizing environments to become UO_{2+x} or, in larger amounts, to form a new phase, such as U_4O_9 , U_3O_8 or even UO_3 . These different oxide forms are possible because uranium can exist with valencies of 4, 5 or 6. Compared to UO_2 , the more oxidized forms have different thermal conductivities, fission-product release properties, and may have degraded physical strength and integrity. Altered fuel properties due to oxidation may lead to altered in-reactor performance.

The oxygen-to-uranium ratio, O/U, is the ratio of the number of oxygen atoms divided by the number of uranium atoms in a fuel sample. For example, stoichiometric UO_2 has an O/U of 2.000, whereas U_4O_9 has an O/U of 2.250. In irradiated fuel, some fission-product atoms occupy uranium atom sites. This complicates the concept of the O/U ratio, but common practice is to count substitution atoms as uranium atoms. Sometimes, O/M is written instead of O/U (M includes all substitution atoms), but O/U is used throughout this paper.

If sheath defects occur during irradiation; then coolant enters the fuel element, leading to the oxidation of the fuel. The oxidation of defected fuel is a complex process, and is not well understood [1, 2]. It is difficult to predict the extent of UO_2 oxidation that will occur in-reactor, because of the hydrogen generation in the fuel that results in parallel fuel oxidation and Zircaloy hydriding. O/U measurements can be used to indicate the extent of oxidation, i.e., the volume of fuel affected, and the magnitude of oxidation as a function of position within that volume. The development of the capability to measure O/U in as-discharged, defected CANDU fuel is the main subject of this paper.

The common method that is used to measure O/U ratios in UO_2 is the gravimetric technique. That is, weight changes are carefully monitored in-situ while the oxygen potential of the surrounding atmosphere is changed. However, this is inappropriate for irradiated fuel, because the sample weights that are required for gravimetry are relatively large (about 2 g), and the associated radioactivity is too large for operator handling outside a shielded cell, while the cost of setting up such equipment in a shielded cell seems prohibitive.

The techniques applied at Chalk River utilize the method of *coulometric titration* (CT), which is described in Section 2. Samples that weigh only 100-200 mg, and that can be handled safely in a glove box, generate accurate, reproducible measurements. This paper describes the CT method and its application to samples of CANDU fuel.

Over the last three decades, substantial effort worldwide has focused on measuring the O/U ratios of UO_2 as a function of the oxygen potential of the surrounding atmosphere [3, 4]. Such measurements allow the amount of oxidation of UO_2 at equilibrium to be predicted as a function of sintering atmosphere. If such measurements were extended to irradiated fuel, then the amount of oxygen that a fuel could absorb as a function of O/U would change, due to normal phenomena (e.g., to extended burnup), or due to water in-leakage to fuel with defected sheaths during in-reactor service. However, the measurements have only been made on unirradiated UO_2 , although recent work has also been performed on UO_2 with additives such as burnable poisons [5]. Knowledge of the behaviour of irradiated fuel O/U in oxidizing potentials is also required. The methods that are described here have been successfully applied to irradiated fuel.

2.0 BRIEF DESCRIPTION OF THE COULOMETRIC TITRATION TECHNIQUES

The CT equipment simply measures the amount of oxygen that a sample gives off or absorbs in a controlled atmosphere. At the same time, the equipment can be used to control the atmosphere at the sample. Hence, the oxygen state (i.e., the O/U ratio) of a fuel sample can be measured, by heating the sample in an atmosphere that is designed to reduce the fuel matrix to UO_2 , and by measuring the amount of oxygen given off. If the sample was oxidized while in-reactor, then it will release oxygen during the CT test; if not, then it will not release oxygen.

Figure 1 shows a schematic diagram of the basics of the operation of the CT equipment. A reducing gas (e.g., Ar + 1300 ppm H_2) flows through cell 1 into the (unheated) sample furnace, and then into cell 2, where just enough oxygen is added, to convert all the H_2 to H_2O . The oxygen is added by passing a current of oxygen ions from the surrounding air through the ceramic cell wall at 700°C into the gas. The composition of the gas in cell 2 is continually monitored, and a feedback loop continually adjusts the current, in order to supply the precise amount of oxygen that is necessary to convert all H_2 to H_2O . (For this reason, the current is termed *titration* current.) As the sample heats up in the furnace and reduces to UO_2 , it releases oxygen. This oxygen converts some of the H_2 to H_2O in the flowing gas, and the current in cell 2 that is required to convert the remaining H_2 to H_2O decreases. This decrease is measured and integrated, until the sample completely reduces to UO_2 and stops giving off further oxygen. The integrated value can then be converted to obtain the total oxygen given off by the sample; thus, the initial O/U ratio of the sample can be obtained.

The CT cells are made of zirconia doped with calcia, which permits oxygen ion (O^{2-}) current at 700°C, but no free electron current at that temperature. This ensures that all current that is measured in the cells represents oxygen transport from the air atmosphere that surrounds the cells into the gas atmosphere inside the cells.

3.0 SAMPLE PREPARATION

3.1 Crushed Samples

For all work described here, CT measurements were obtained from chips of UO_2 (100 to 200 mg) that were obtained from longitudinal segments, 3-5 mm in length, which were cut from fuel elements. Fuel samples were intentionally broken and pieces were selected. No information on the radial location of the source of the chips was obtained. The chips were crushed to powder in a hot cell using a mortar and pestle, and were transferred to the CT glove box. In the glove box, each crushed-powder sample was placed in a quartz-glass sample holder, and was weighed and installed in the CT furnace for O/U measurement. Radiological constraints required that only one sample be transferred from the hot cell to the glove box at a time, and that it be returned to the hot cell before the next sample was transferred. Improved sample preparation methods, described in the next section, were subsequently developed and will be used in the future.

3.2 Precise Location Drilling

For future work, a method was sought that could produce samples from specific radial locations in the irradiated fuel, without introducing extraneous chemical or stabilizing agents to the fuel. The method that was developed uses a small diamond drill to obtain samples by drilling small holes at precise radial locations. This process produces a fine powder from a known location. The powder that collected around the rim of the hole was transferred to a plastic vial with a screw top by inverting the sample over a funnel that emptied into the vial, and by tapping gently. Drill diameters of 1.8 mm and 2.1 mm were tested. For low burnup fuel (about 100 MWh/kgU and low powers), the drills produced an easy-to-manage powder. For much higher burnup fuel (about 500 MWh/kgU), the initial contact of the drill with the fuel surface often produced chips before powder was produced. However, it was easy to separate these relatively large chips by sieving. Thus, the method is satisfactory for both low and high burnup fuels.

4.0 MEASUREMENT OF O/U RATIO

4.1 Issues Discovered and Resolved

During the commissioning of the CT equipment, several issues regarding the obtaining of proper O/U results were discovered and resolved:

1. *Sample-holder glassware.* New sample-holder glassware is required for each test to prevent the cross-contamination of samples. A small oxidation peak during heat-up occurs when using new sample-holder glassware. Therefore, all new sample-holder glassware is pre-conditioned by a heat treatment in the CT equipment under test conditions, but with no fuel sample.
2. *Transport of volatile fission products.* It was discovered that cesium (Cs) damaged the CT cells. Two or three cells stopped working completely after only one or two tests with irradiated fuel, before this fact was discovered. Originally, Cs was not thought to cause these malfunctions, because only a small amount of Cs is released from the tiny fuel chips, and most of this is deposited on the steel tubing before the gas reaches the cell. Nevertheless, when a stainless steel frit (i.e., a 30-cm-long filter with 50- μ m pores) was placed in the flow path between the sample and the downstream cell, all Cs was adsorbed onto the frit walls, and no further problems with the cells occurred due to this issue.
3. *Mass-flow controller.* Constant gas flow is required, so that the titration current (of oxygen ions) that is used to convert all H_2 to H_2O in the downstream cell is constant. When the sample heats up and begins to release oxygen, changes in the current can be unambiguously attributed to this oxygen release, and they will not be confused with gas-flow changes (Figure 2, for example, shows such a flat baseline). Irregularities in the downstream cell current were observed, and were attributed to unstable gas flow. A replacement gas mass-flow controller was installed, which corrected this problem.
4. *Leaks.* Due to the use of the frit to capture volatile fission products, a pressure of 5 to 10 kPa (1 to 2 psi) in the gas atmosphere developed. Subsequent irregularities led to the search for, discovery of, and correction of several leaks that had not been previously apparent. Furthermore, it was discovered that some new cells had leaks at some of the fittings. Finally, due to careful helium leak-detection methods, it was discovered that some of the newest cells leaked through the ceramic wall itself. These findings have been sent to the manufacturer. We now carefully perform helium leak testing on all cells prior to use.
5. *Kinetics.* For some tests, insufficient time was allowed for the system to come to full equilibrium (i.e., no further oxygen absorption), until it was appreciated that the kinetics could be very slow. Tests that were performed in a heavily reducing atmosphere to reduce samples to near-perfect stoichiometry, such as those described in this report for irradiated fuel only required a few hours to reach equilibrium. However, in oxidative atmospheres, many hours or even days were required for equilibrium to be reached, which was partly due to the use of an Ar atmosphere with only a small amount (0.1 %) of the active components, H_2/H_2O . Tests that were performed on UO_2 without allowing sufficient time for equilibrium to be reached did not give results that agreed with those in the literature. However, once this effect was understood and sufficient time was allowed,

results on unirradiated UO_2 agreed with those in the literature. No tests have been performed to date on irradiated UO_2 .

4.2 Fuel Samples

The fuel that was chosen for the measurements came from a low-burnup (80 MWh/kgU), low power (23-28 kW/m) fuel element that had been previously examined in hot cells and had been determined to have both primary (debris fretting) and secondary defects. Chips were taken from a location that was 6 cm from the primary defect. Each chip was ground into powder in the hot cells, before being transferred to the glove box for O/U measurements.

5.0 EQUIPMENT VERIFICATION

Before beginning a series of tests, and periodically throughout a long campaign, tests are performed to help indicate the proper operation of the CT system. These tests are described, below.

5.1 U_3O_8 Reduction Test

In this test, a sample of unirradiated UO_2 is oxidized in an oxygen atmosphere in the sample furnace at 500°C . This process converts the sample to U_3O_8 , as has been confirmed by subsequent X-ray diffraction (XRD) analysis and by weight-change measurements. The CT ceramic cells cannot be turned on during this process to measure oxygen absorption, because the high oxygen content would destroy the cells. Following this oxidation process, the flowing gas is changed to Ar+1300 ppm H_2 , the standard reducing gas, the equipment is turned on, and the U_3O_8 is reduced back to UO_2 , while the equipment measures the amount of oxygen released during the process. This result is then compared to the amount of oxygen that is calculated to be necessary to convert U_3O_8 to UO_2 .

Figure 2 shows the results of one of these tests. The O/U of the sample changed by 0.674 during the test, compared to an expected value of 0.667, or a 1 % error. This demonstrates sufficient equipment accuracy for future planned tests on defected fuel.

5.2 Null Sample Test to Compare Results from Cell 1 and Cell 2

In this test (see Figure 3 and Table 1), the equipment is operated with Ar-1300 ppm H_2 gas, as usual, but with no test-sample. As per normal operation, cell 2 (the CT cell downstream of the sample furnace) is operated to convert all H_2 in the gas stream to H_2O , and the current that is needed to accomplish this is monitored. Then, a small current of oxygen is fed into the gas in cell 1, i.e., the upstream cell, which has the same capabilities for oxygen transport through the cell wall as the downstream cell. Since this converts some of the H_2 to H_2O , the titration current in cell 2 should immediately drop by exactly the same amount as the applied current in cell 1. Figure 3 shows ten such changes, five with a relatively large upstream current and five with a much lower current. This tests the cells over the extremes in expected usage. The downstream cell current changed almost immediately when the upstream cell current changed. This behaviour

is important, because it shows that cell 2 can track oxygen release from the sample, without smearing the release over a longer period of time and possibly compromising accuracy. The current in cell 2 also changed by almost exactly the same amount as that in cell 1. Table 1 shows representative values, obtained near the middle of each test, of the upstream and downstream cell currents. No averaging of values over individual tests was done. The table also shows that the sum of these two currents for each test is about constant, as expected. To facilitate comparison, deviation from the mean value, 11514 μA is also shown. At present, it is not understood why the downstream currents for tests 9 and 10 have a small slope, nor why the current sum for test 9, which has the lowest value of upstream current, showed a larger deviation from the mean than the other tests. If the current were in error by 40 μA over the full period of a 2 h test, then the error in O/U for a 100 mg sample of UO_2 would be 0.004, which is acceptable for tests on defected fuel elements. Thus, these tests confirm the acceptable operation of the cells and the leak-tightness of the gas lines.

5.3 Comparison With Literature

As the result of many measurements, the variation of the O/U ratio for unirradiated UO_2 as a function of oxygen potential at 1000°C and 1200°C is well known, although there is considerable scatter in the data. Thus, measurements of O/U as a function of oxygen potential at one of these temperatures constitute a good check that all aspects of the system are operating properly. Figure 4 shows measurements that were obtained at 1000°C compared to two representative sets of values from the literature. As indicated in Section 4.1, tests at high oxygen potentials required long times to achieve equilibrium. Above about -250 kJ/mol, tests required prohibitively long times. Alternative methods are being evaluated to achieve higher oxygen potentials, including the use of CO/CO_2 gas instead of the $\text{H}_2/\text{H}_2\text{O}$ gas that is currently used.

6.0 RESULTS AND DISCUSSION

The results of tests on four nominally identical samples, taken 6 cm from the primary defect, are shown in Figure 5. Each graph plots the sample temperature and titration current (of oxygen ions) in cell 2 as a function of time for one test. Deviation below the baseline indicates that the sample was releasing oxygen into the gas atmosphere. Each test showed that oxygen release from the sample occurred above about 700°C. The values listed in the figures show the area of each peak (in terms of the change in O/U ratio that the peak represents).

The average O/U obtained for this series of tests was 0.044, with a standard deviation of 0.0025, or less than 6 % of the mean value. The scatter in data, which is small and acceptable, may be due to real variations in O/U of the samples, or due to system inaccuracy when measuring very small values of released oxygen (0.2 to 0.3 mg) from the 100 to 150 mg samples of fuel that were used for these tests.

The CT equipment is now operating as expected, and excellent results are being obtained. With proper care, absolute values of fuel oxidation can be measured with good accuracy, and relative values of oxidation for samples from different locations in the same fuel rod can be determined

even more accurately. At the present time, the exact value of any systematic error introduced by the measurement methods is not known. The only measure we have of the systematic error is the value obtained for the known U_3O_8 sample, and this yields an error of between 1% and 5%. Even if the systematic error were 5 %, it would be less than the scatter between samples. Furthermore, the systematic error is less important than scatter between measurements for relative measurements, i.e., for determining how O/U changes with distance from the fuel defect. Thus, by periodically performing equipment checks to ensure that all components are operating properly without leaks, systematic error is expected to be less than 5 % at worst, and less than 1 % at best.

7.0 SUMMARY AND CONCLUSIONS

The CT laboratory for measuring O/U ratios in irradiated fuel has been successfully commissioned, and methods of operation have been developed to provide consistently reliable measurements. There were several hurdles to overcome to develop proper methods for making O/U measurements. These challenges included determining that some as-manufactured CT cells had gas leaks at joints and through the ceramic wall. Another issue was the determination that trace quantities of Cs, released from the irradiated fuel and transported to the CT cell, damaged the CT cell. The use and pre-test conditioning of new glassware for each test, and the replacement of an inaccurate gas mass-flow controller were additional issues. The careful checking and controlling of these issues led to repeatable O/U measurements from a fuel element with a defect in the sheath.

Repeatable O/U measurements were demonstrated on four irradiated fuel samples, 100 mg to 200 mg each, taken from a fuel element that had defected during operation in a power reactor. The averages of the CT measurements of O/U were 2.044 ± 0.0025 at the 6-cm location. Earlier tests gave similar results on samples that were obtained 5 cm from the defect, but have not been shown here because they were made before all the issues, especially leaks, had been understood and corrected.

The scatter in the results for these four tests (for the samples obtained 6 cm from the defect), after all leaks had been detected and corrected, was 13 % (the difference between the highest and lowest values measured). However, the standard deviation in these four tests was only 6 % of the mean. The systematic error of the measuring system for the reduction of U_3O_8 to UO_2 for three tests was less than 5%.

For the tests described in this report, UO_2 chips were obtained from fuel samples by mechanical impact, and the chips were crushed to powder in a mortar and pestle. Information about the radial location of the samples from within the fuel rod was not obtainable. Improved methods were developed for future work, which will provide the radial location.

These improved methods utilize 1.8 mm-diameter drills. Fine powder is obtained directly from a specific location by drilling a hole. The powder collects around the rim of the hole, the sample and holder are inverted over a funnel that contains a screen to sieve out chips, and the powder is collected in plastic vials for transfer to the O/U laboratory.

8.0 FUTURE WORK

The utilization of these sample preparation methods with the CT equipment will enable a map of oxidation versus axial and radial location relative to the defect to be obtained, and this work has been planned for COG in 2001-02.

These tests will be followed by measurements of the manner in which O/U changes with oxygen potential in irradiated fuel. There are no such measurements in the literature.

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TABLE 1: REPRESENTATIVE VALUES (NEAR THE MIDDLE OF EACH TEST) OF THE UPSTREAM AND DOWNSTREAM CELL CURRENTS (μA) FOR THE 10 TESTS SHOWN IN FIGURE 3.

Test #	1	2	3	4	5	6	7	8	9	10
Upstr.	10000	10500	9998	9500	10000	999	1500	1000	499	999
Down	1523	1025	1516	2018	1522	10511	10017	10510	10976	10530
Total	11523	11525	11514	11518	11522	11510	11517	11510	11475	11529
Difference from mean	9	11	0	4	8	-4	3	-4	-39	15

TABLE 2: O/U CHANGES MEASURED FOR FOUR NOMINALLY IDENTICAL SAMPLES OBTAINED 6 CM FROM THE PRIMARY FUEL DEFECT.

Test Name	Change in O/U*
R010314A	-0.041
R010316A	-0.044
R010320A	-0.047
R010322A	-0.045
Mean and Std. Dev.	-0.044 \pm 0.0025
Std. Dev. (% of Mean)	6 %

* Part of the variation in O/U values may be real, since a radial variation in O/U is expected, and part may be scatter from the measurements.

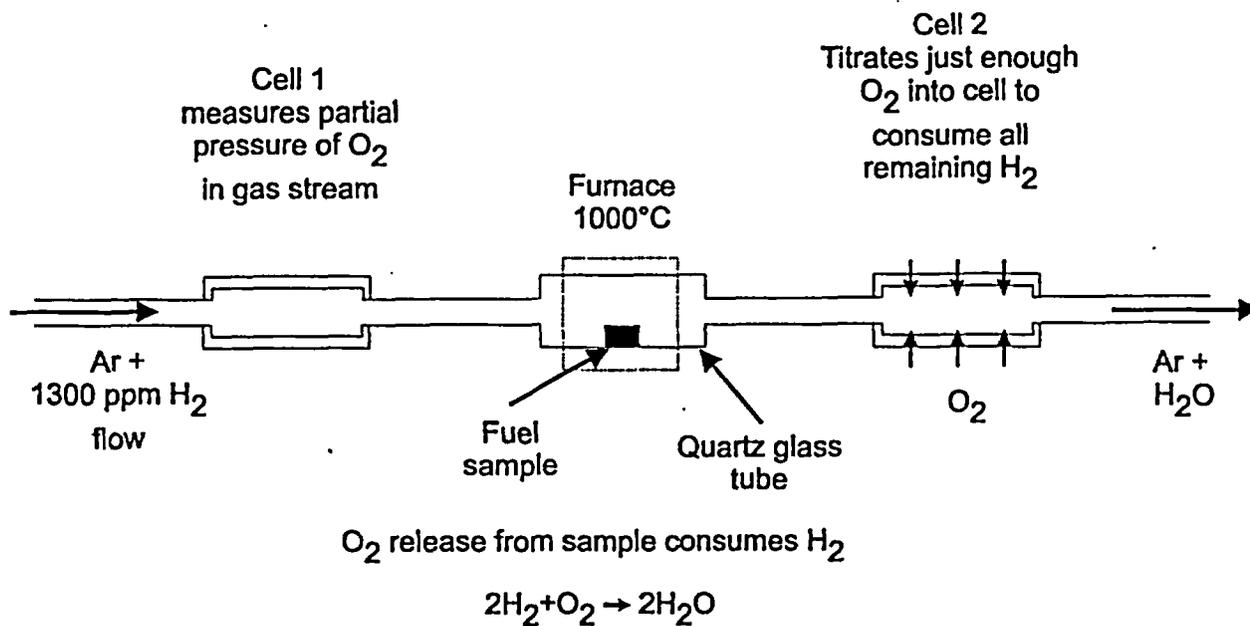


FIGURE 1. SIMPLIFIED SCHEMATIC DIAGRAM OF COULOMETRIC TITRATION APPARATUS

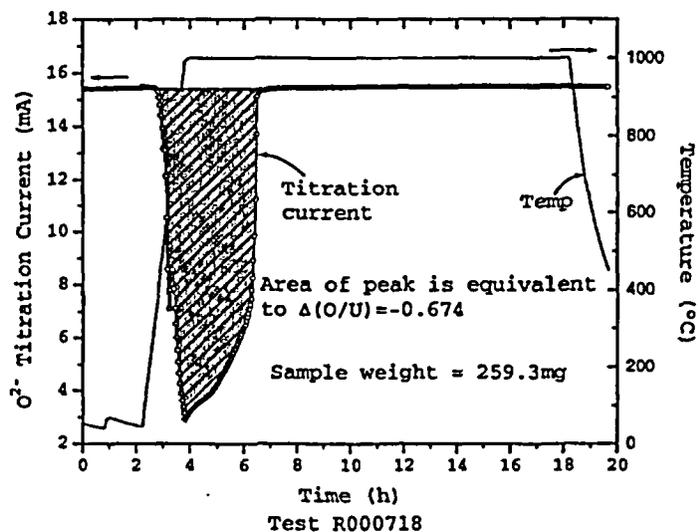


FIGURE 2. EQUIPMENT CHECK—REDUCTION OF U₃O₈ TO UO₂ IN FLOWING AR+1300 PPM H₂ AT 1000°C.

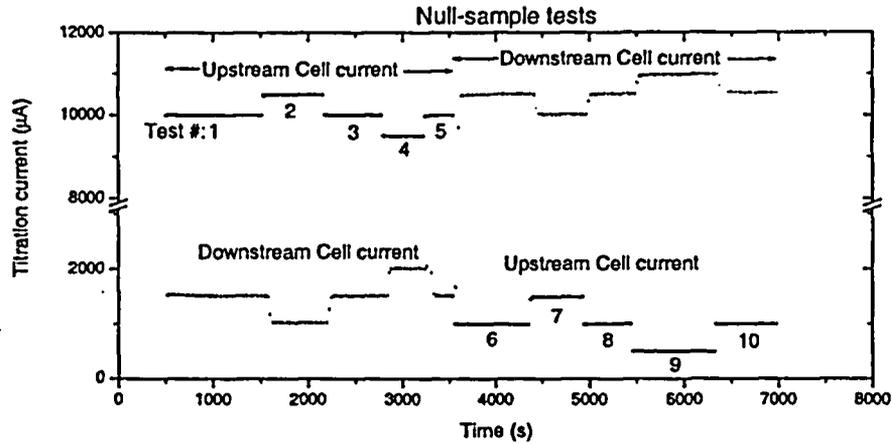


FIGURE 3. EQUIPMENT CHECK—RESULTS OF A NULL-SAMPLE SERIES OF TESTS SHOWING THE RESPONSE OF THE DOWNSTREAM CELL TITRATION-CURRENT TO IMPOSED CHANGES IN OXYGEN CONTENT OF GAS IN UPSTREAM CELL.

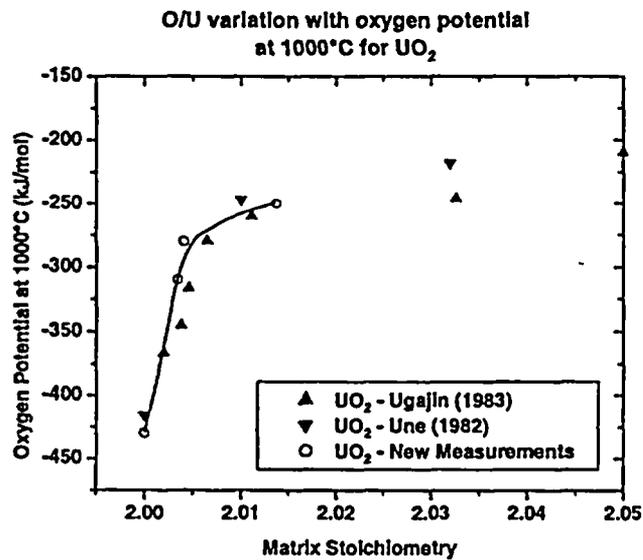


FIGURE 4. LITERATURE DATA AND NEW MEASUREMENTS SHOWING OXYGEN POTENTIAL VERSUS O/U RATIO FOR UO_2 .

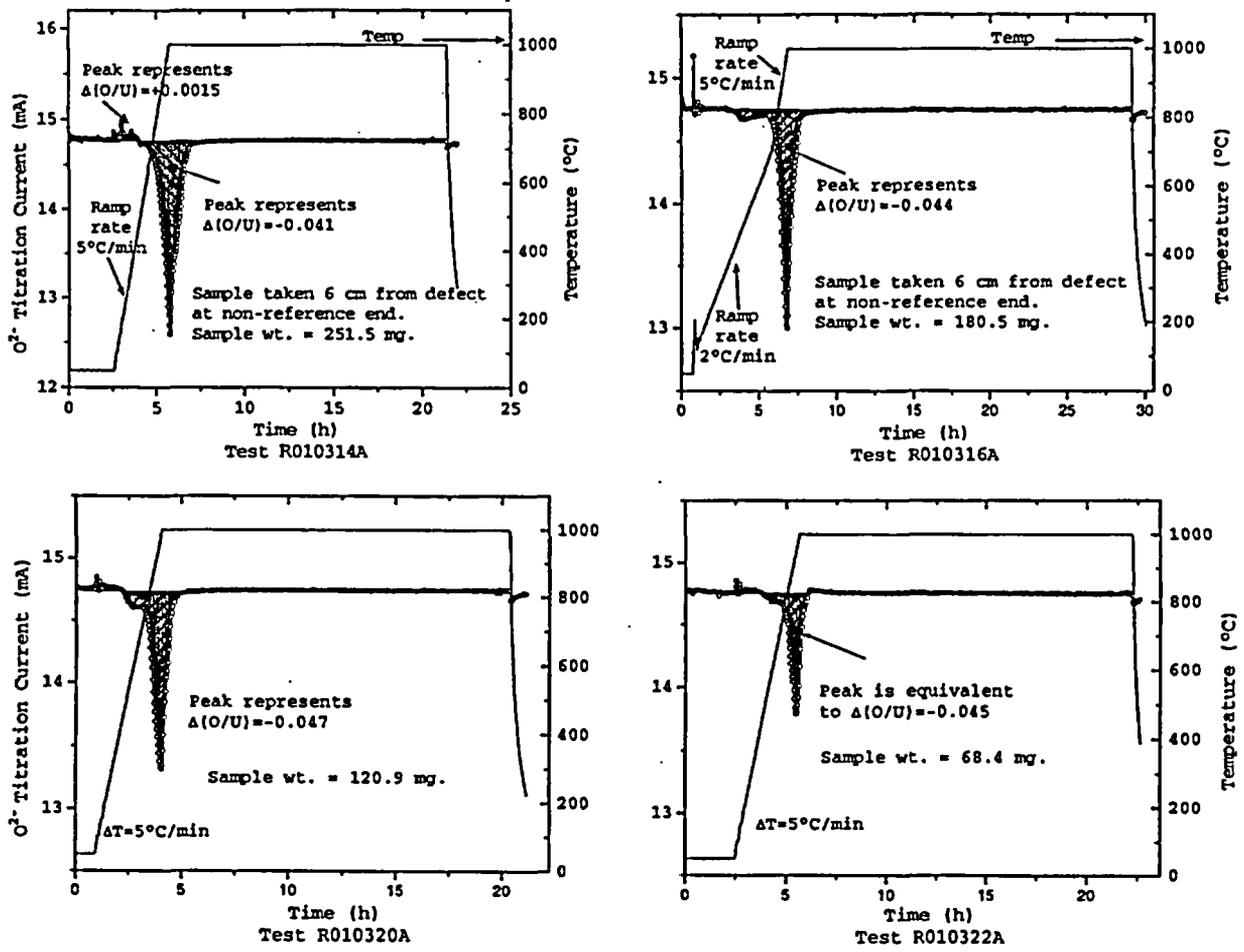


FIGURE 5. RESULTS OF O/U MEASUREMENTS ON FOUR FUEL SAMPLES TAKEN 6 CM FROM FUEL DEFECT.