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Characterization of the Stoichiometric Ratio O/U in UO_2 Samples by Gravimetric and Voltammetric Methods

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Abstract The gravimetric and voltametric methods for determination of non-stoichiometry O/U ratio in uranium dioxide used as nuclear fuel are evaluate in this work. The oxidation of uranium oxide is very complex due to many phase changes and the gravimetric and voltametric methods do not detect these phase changes. To evaluate both methods is requiring to do Rietveld methods by X-ray diffraction data to identify the uranium oxides phase changes. The results show that voltametric and gravimetric methods are precise but not accurate techniques for determination of non stoichiometry uranium dioxide samples.

Introduction

In the sinterized UO_{2+x} pellets, the relation between O/Me affects a series of phenomenon that happen during its irradiation process, such as, the reaction between fuel and cladding (Zircaloy tubes), fuel plasticity, retention of the fission gases, conductivity and the coefficient of the uranium inter-diffusion. The uranium oxides present a non-stoichiometry composition, i.e. O/U different of two, even when the system presents only one phase [1,2,3,4].

In the sense of maintaining the electric neutrality in the crystal, when the oxygen ions are removed or added, is necessary that some cations should change its valence. Therefore, the uranium ions in the UO_{2+x} will form a mixture of ions U^{+4} and U^{+5} or even U^{+4} and U^{+6}.

The stoichiometry deviation create the formation of Frenckel defects in the sub-lattice of the oxygen ions, which is accommodated in the interstitials of the fluorite structure [5,6]. Due to its high performance to form several non-stoichiometry oxides, the uranium oxides were already well characterized, four phases stables UO_2 , U_4O_9 , U_3O_8 and UO_3 , and several additional oxides stables U_3O_7, U_2O_5 [4].

The factors that affect the stoichiometry of the UO_2 are:

- Temperature: The predominant oxidation reaction varies with the chemical adsorption (less than - 130°C) through the oxidation surface, (-130 to 100°C) for a volume formation of U_3O_7 / U_4O_9, (100 to 250°C), nucleation and growth of the U_3O_8 (>250°C) [7,8].
- Oxygen partial pressure: Below -13 kPa the oxygen pressure has a larger influence in the oxidation rate of the UO_2 powder, but in higher pressures it has a small effect [9].
- Storage: The storage in air results in a slow oxidation rate. The reason of such behavior is not well understood but it might be related to the formation of a fine superficial layer of oxidize material [10].
- Particle size: The behavior of the UO_2 oxidation varies from pirophoric for extremely fine powders, obeying a nucleation rate and growth sigmoidal [11].

Through the years many techniques were developed searching the determination of the relation O/Me in several types of nuclear fuels. The techniques frequently used for that determination are volumetric, voltametric and gravimetric techniques [12,13].

Through these techniques, stoichiometry results are obtained with good precision and accuracy. Besides the stoichiometry, these techniques determine the average uranium oxidation states.
The objective of this work is to evaluate the gravimetric and voltametric techniques with relation to its application in the determination of the O/U ratio in the uranium dioxide. The Rietveld method by X-ray diffraction data is applied to identify the phase changes and to quantify the present phase as well.

Experimental Procedure

The determination of the O/U ratio by gravimetric method, was performance inside a "glove box ", within nitrogen atmosphere, controlled humidity (<20%) and an analytic balance (4 decimals digits) to sample weight. Interlinked to this system, it has a quartz tube, 25mm (I.D.), coupled to a resistive oven for the samples thermal treatment.
The sample used in this work was the uranium oxide powder, U_3O_8 , obtained from Ammonium Uranil Diuranate and Uranil Ammonium Tricarbonate (DUA/TCAU) calcination process supplied by the Department of Chemical Engineering / IPEN. The powder U_3O_8 samples were reduced to UO_2 in hydrogen atmosphere at different conditions of time and temperature.
The gravimetric method is based on the determination of mass variation when the uranium oxide non-stoichiometry becomes stoichiometry. The mass variation corresponds to the loss or gain of oxygen. The following (Eq. 1) calculate the O/U ratio:

$$O/U = (mi/mf) \times 17.5417 - 14.8750 \quad \text{(Eq.1)}$$

where: O/U = stoichiometry ratio
m_i = initial mass (g)
m_f = final mass (g)

The gravimetric analyses use an initial mass of UO_{2+x} (1g), into the oven at temperature of 800°C during 4 hours at oxydant atmosphere.
The voltametric method is based on the UO_2 powder or pellet inside a non-oxidizer medium, measurement of the hexavalent uranium UO_2^{+2} present in this sample, then with another part of the initial solution, is oxidized all the rest of uranium and finally the total uranium is determinate.
The tetravalent uranium is calculated by the difference between the amount of total uranium and the amount of uranium hexavalent [13]. The stoichiometric value of the O/U ratio is calculated applying the following (Eq. 2):

$$O/U = 3U(VI)\ (\%) + 2U(IV)\ (\%) / Ut\ (\%) \quad \text{(|Eq.2)}$$

The voltametric analysis consist in weighed 0.1 g of UO_2 (powder or pellets), dissolved inside 2ml of a hot solution of H_2SO_4 and 1ml of H_3PO_4 then is transfer into a 10 ml balloon with H_2SO_4 1M (solution A). From the solution A is pipette 1 ml into a glass cup of 25 ml and it is added 1 ml of HNO_3 and 2 ml H_2O_2. Heated until the total elimination of the oxygenated water and the white fumes. Finally transferred into a balloon of 10 ml (solution B).
An aliquot from the solution A and another from the solution B is transferred, separately, into a polarographic cell, where U(VI) it is determined in the solution A and the total uranium (Ut) in the solution B, using the voltametric technical with electrolytic supports H_2SO_4 1 M. The uranium IV value present in the UO_2 is obtained, substracting the amount of total uranium (Ut) and the U (IV).

Results and discussion

The X-ray diffraction data was used to the Rietveld refinement, (program DBWS9411) [13] and the crystallographic parameters were obtained by the data based of ICCD. The difratograms was obtained with step of 0.020, counting time of 10 s with 2θ between 200 and 1200°.

Table 1 Final results of the lattice parameter, stoichiometry ratio and phase percent, using the voltametric and gravimetric method.

Sample	Gravimetric O/U	Voltametric O/U	Phase 1 (%)	Phase 2 (%)	Lin. Regr. a_0 (nm)	Rietveld a_0 (nm)	Phase 1 a_0 (nm)	Phase 2 a_0 (nm)
A11	2.22	2.30	38.41	61.59	0.54638	0.5465	0.4467	0.5467
A14	2.08	2.10	13.57	86.43	0.54605	0.54501	0.54467	0.5467
A15	2.04	2.08	35.78	64.22	0.54595	0.54559	0.54467	0.5467
A17	2.03	2.10	52.77	47.23	0.54598	0.54347	0.54467	0.5463
A3	1.99	2.03	64.24	35.76	0.54512	0.5450	0.54467	0.5463
A5	2.05	2.03	100	--	0.54665	0.54633	0.54665	--
A6	2.01	2.01	100	--	0.54669	0.54612	0.54665	--
A9	2,02	2.02	100	--	0.54659	0.5465	0.54659	--
B1	2.00	2.8	35.89	64.15	0.54549	0.54479	0.54521	0.5467
B2	2.00	2.08	40.95	59.05	0.54595	0.54476	0.54528	0.5467
C1	2.13	2.22	28.19	71.81	0.54632	0.54615	0.54528	0.5467
C2	2.16	2.19	29.69	70.31	0.54534	0.54515	0.54467	0.5467
C3	2.20	2.51	14.51	85.49	0.54653	0.5458	0.54467	0.5467
S10	2.05	2.30	34.93	65.07	0.54456	--	0.54464	0.5467
S11	2.04	2.04	100	--	0.54417	0.54393	0.54417	--
S12	2.00	2.03	76.34	23.66	0.54428	0.54428	0.5450	0.5462
S13	2.00	2.08	28.7	71.3	0.54418	0.51189	0.5450	0.5462
Z1	2.10	2.08	34.89	65.11	0.54484	0.54441	0.5450	0.5462
Z2	2.15	2.19	62.08	37.92	0.54630	0.54470	0.54467	0.5467
Z3	2.32	2.20	57.61	42.39	0.54503	0.53809	0.54467	0.5467
Z4	2.12	2.16	61.64	38.36	0.54531	0.54206	0.54467	0.5467

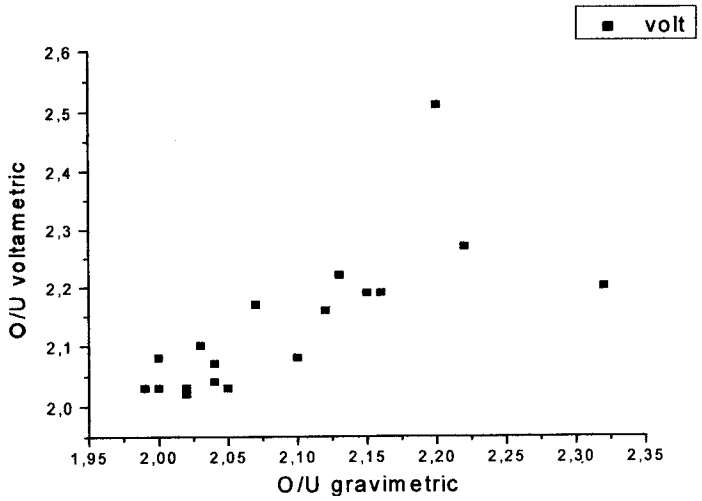

Fig. 1: Correlation between Gravimetric and Voltametric methods for all samples O/U ratio data.

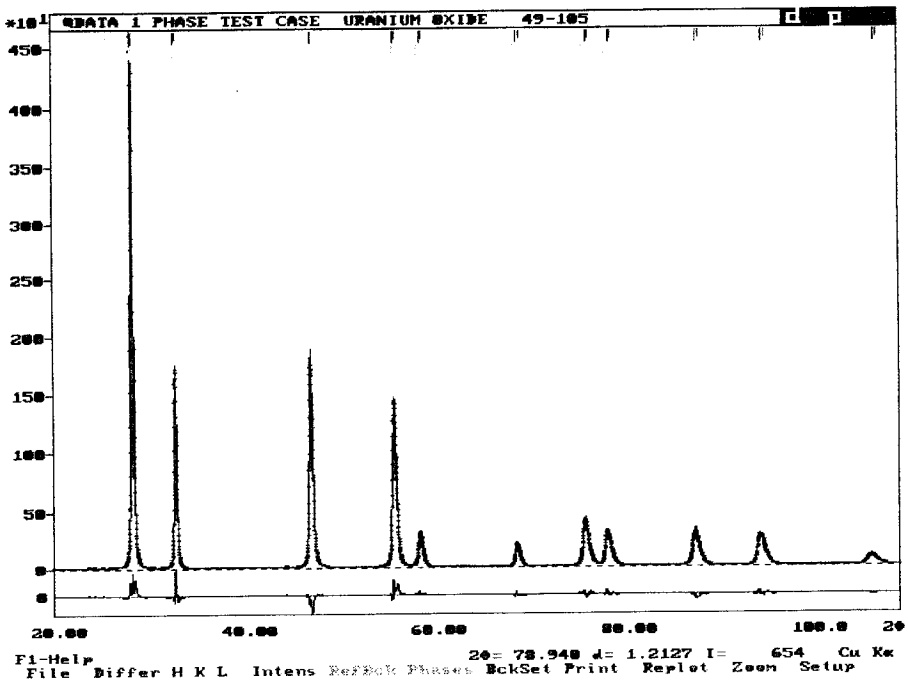

Fig. 2: X-ray diffratogram from A3 sample with Rietveld adjust.

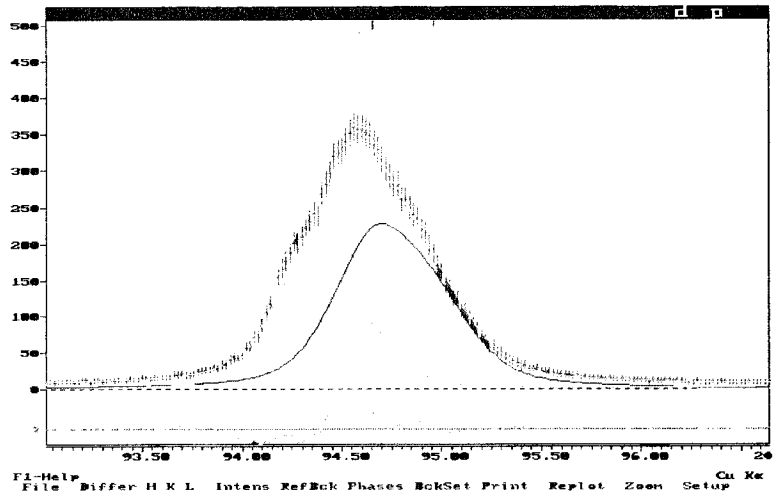

Fig. 3: X-ray diffratogram from A3 sample. Detail of the peak (333).

Fig. 1 shows the stoichiometry O/U ratio data from all the analyzed samples. The results do not present a good correlation between both techniques, meaning these techniques should be better evaluated to obtain the exactly O/U ratio. In the Fig. 1 is observed that the voltametric O/U values are systematically larger than the thermo gravimetric values.

The difference among the results can be due to the complexity of the system oxygen-uranium, besides inherent experimental problems of the techniques that do not consider structural factors of the system oxygen-uranium, and others parameters that were not completely understood [13]. The following factors are:

-The reducing atmosphere that has low pressure of oxygen and high pressure of hydrogen and the relative humidity of the air around (20%), can take to the formation of fine layer of UO_3, U_4O_9, UO_{2+x}, U_3O_7, defects in the crystalline lattice of the interphase between the phases and adsorption of H_2O.

-The solubility limit of the interstitial oxygen in the UO_2 structure forming UO_{2+x} is low as described by Smith, Blackburn and Hoeskstra [7,9,13] at different pressure and temperature conditions. All these factors can form vacancies in the crystalline structure of the several compounds formed during the UO_2 reduction.

-The gravimetric technique measures the variation of oxygen in the oxidation of the UO_{2+x} to U_3O_8, and it should be for small values of x, due to the low solubility of the oxygen. The data obtained by gravimetric technique for higher values of " x ", can be distorted due to the presence of defects in the phase crystalline lattice that are going to be formed.

-The voltametric technique does not detect the presence of the ions 5+, which presence increases the value of the ratio O/U. On the other hand the presence of impurities such Fe, Cu, Cd and V, take to mistakes in the sense of increasing the values of O/U because it has a very close reduction potential of the U potential.

For a better understanding of these results, the X-ray diffraction technique was used, this is not the best indicated technique for the determination of the relation O/U ratio, but it supplies fundamental information on the crystalline structure of the uranium oxides, and will allow evaluate and validate the results obtained by voltametric and gravimetric techniques.

The occupation of the oxygen in the lattice implies in the change of the uranium valence from 4+ to 5+ and/or 6+ with linear variation of the lattice parameter. Besides, the diffraction technique, with the aid of the Rietveld method can detect the presence of another phase that had been formed during the reaction.
Fig. 2 and 3 illustrate the presence of two phases in the sample A3, these phases can not be detected by the voltametric and gravimetric techniques. On the other hand only the X-ray diffraction data do not supply a reliable estimation of the O/U ratio.
The literature diverges, if the UO_2 coexists with the U_4O_9 or U_3O_7 or both. It was chosen the phase U_4O_9 because this possesses the structure fcc, the same as UO_2. The phase U_3O_7 has tetragonal structure and produce also some doublets, which were not detected.
The four samples, that can be classified as non-stoichiometry uranium oxide, are A5, A6, A9 and S11 samples because present right values to the excess of oxygen either by the voltametric or thermogravimetric techniques, besides presents only one phase.

Conclusions

Gravimetric and voltametric are precise but not accurate techniques for determination of the non-stoichiometry uranium dioxide samples. The analysis of the O/U ratio by gravimetric and voltametric methods should be made together with the analysis of the X-ray diffraction, because this technique determines the phases and it allows to evaluate and to validate the results obtained by voltametric and gravimetric techniques.

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