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ARAB REPUBLIC OF EGYPT
ATOMIC ENERGY ESTABLISHMENT
NUCLEAR CHEMISTRY DEPARTMENT

STOICHIOMETRY OF THE U_3O_8 PHASE FORMED DURING
CALCINATION OF SOME URANIUM COMPOUNDS

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S.A. El-Feky, M. Y. Farah and N.H. Rofail

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INTRODUCTION

Although recent work has shown U_3O_8 phase to be the decomposition product obtained after calcining uranyl nitrate, sulphate or ammonium uranate, neither the necessary conditions for obtaining stoichiometric U_3O_8 nor the details of the reaction have been established. Presence of sulphate or nitrate ions during preparation greatly affects the O/U of the obtained oxides and the physico-chemical properties of uranium tetrafluoride prepared afterwards from it [1-3].

The aim of the present investigation was to study the effect of calcination regimes on the stoichiometry of the U_3O_8 phase produced by the thermal decomposition of uranyl nitrate, sulphate, and ammonium uranate, which was prepared by precipitation from nuclear-pure uranyl sulphate. Stoichiometry of the U_3O_8 phase formed during calcination of ammonium uranate precipitated from nuclear pure uranyl nitrate solution was reported before [1].

EXPERIMENTAL

Ammonium uranate was precipitated from nuclear-pure uranyl sulphate solution using analar ammonia liquor at pH 7. Uranyl nitrate and sulphate crystals were of nuclear grade purity. A sample layer of uranium compounds, 0.3 or 1.5-cm thick, was placed on a quartz tray and ignited in a muffle furnace at temperature ranging from 600 to 1100 °C for different durations. Stoichiometry of the U_3O_8 phase was determined titrimetrically with cerium (IV) sulphate as reported before [17].

RESULTS AND DISCUSSION

Figure 1 indicates that ignition of 0.3 and 1.5-cm thick layers of uranyl nitrate crystals at 750 °C for 3 h yields oxides with O/U equal to 2.666 and 2.667 respectively while ignition above 750 °C yields hypostoichiometric oxides. Chemical analysis indicates that oxides obtained below 750 °C still contain nitrate impurities. Vita et al. [4] and Breuns et al. [5] stated, without definition of thickness of layers, that ignition at Ca. 1000 °C for 2 h produces U_3O_8 that is nearly stoichiometric.

Ignition of uranyl sulphate crystals to U_3O_8 oxides of sulphur and oxygen was found to start at about 690 °C and to proceed over a temperature range of 690 - 800 °C depending upon time and thickness of layer. Fig. 1 indicates that ignition of 0.3 and 1.5-cm thick layers of uranyl sulphate crystals at 850 °C for 3 h yields oxides with O/U ratio equal to 2.666 and 2.668 respectively.

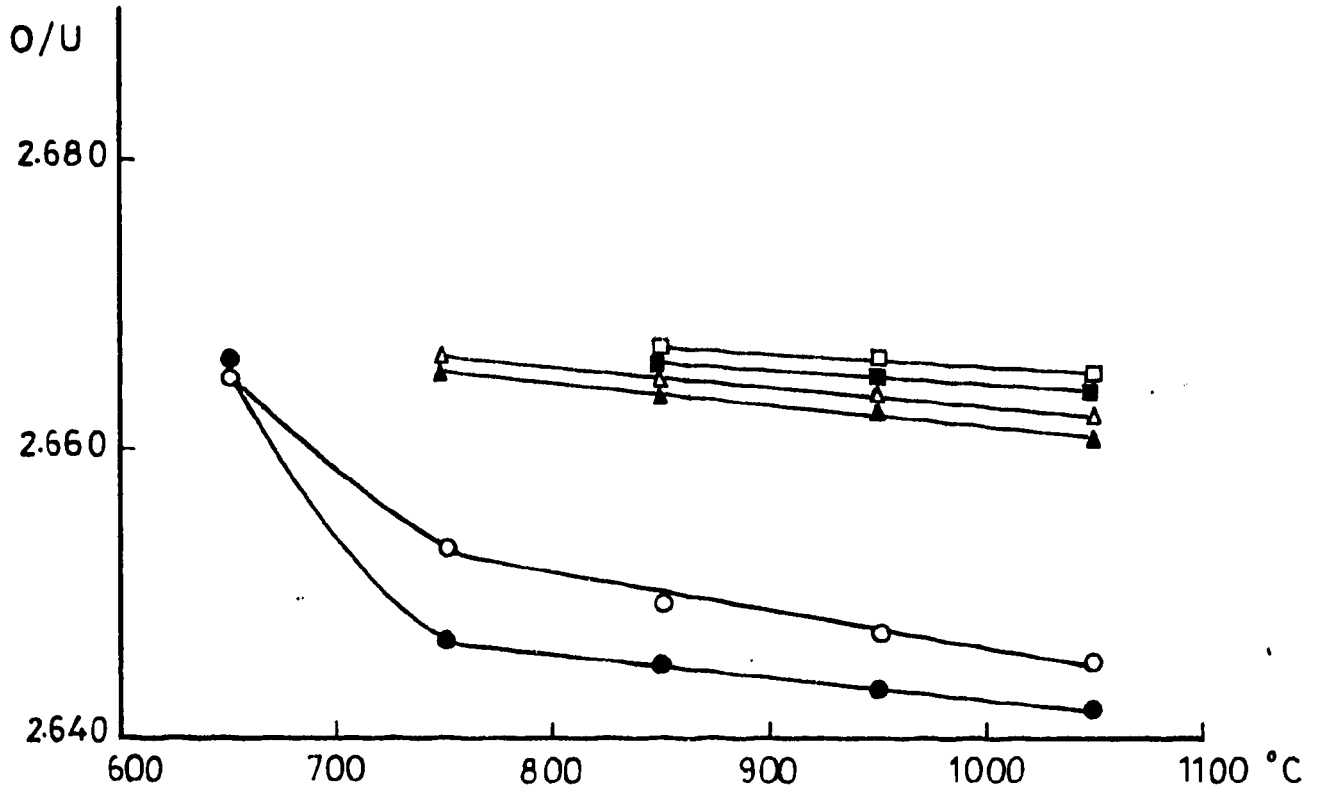


Fig.(1) : Effect of calcination temperature on the O / U ratio of the U_3O_8 phase

- 0.3—cm thick ammonium uranate
- 1.5—cm " " "
- 0.3—cm thick uranyl sulphate
- 1.5—cm " " "
- ▲▲ 0.3—cm thick uranyl nitrate
- △△ 1.5—cm " " "

-- Average of 3 independent estimations

-- The standard deviation on the average = ± 0.004

Chemical analysis indicated that oxides obtained below 800° C even for 2 h still contain sulphate impurities. Ignition of 0.3-cm thick layer at 750° C for 6 h produces oxide with O/U equal to 2.666, a result which agrees with that of Karl [6] who stated, without definition of layer thickness, that ignition, at 750° C in air to constant weight yields U_3O_8 that is nearly stoichiometric.

Figure 1 indicates also that ignition of 0.3 and 1.5-cm thick layers of ammonium uranate at 650° C for 3 h yields oxides with O/U equal to 2.666 and 2.665 respectively. Chemical analysis indicates that above 650° C, the U_3O_8 phase is significantly oxygen-deficient, below 650° C the U_3O_8 phase is oxygen-rich with an O/U ratio greater than 2.667, a result which agrees with that of other workers [7]. This reaction is described before [1].

Figure 1 indicated also that ignition at temperatures higher than that at which stoichiometric U_3O_8 is formed yields in every case oxygen-deficient oxides. Deviation from stoichiometry, even small, is significant because it affects the accuracy of the uranium analysis. Results indicate that departure of oxygen in thick calcined layers is less than in thin ones, presumably the oxygen is retarded from evolution within the thicker layer. Fig. 2 indicates that there is no need for ignition more than 6 h.

Figure 3 indicates that the O/U ratio decreased with decreasing surface area presumably due to microsintering. The same figure indicates also that the stoichiometry of the U_3O_8 phase depends mainly on the nature of the precursor and its thermal treatment.

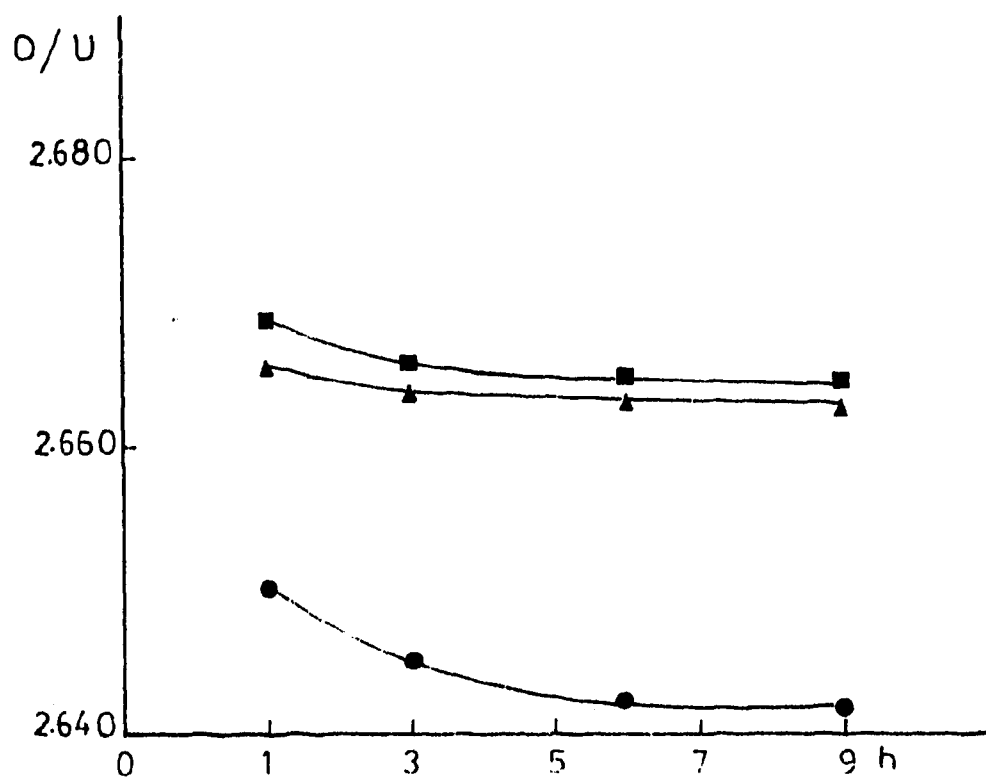


Fig. (2) : Effect of duration of calcination on O / U ratio of U_3O_8 phase formed at $850^\circ C$

- ■ 0.3— cm thick uranyl sulphate
- ▲ ▲ 0.3— cm thick uranyl nitrate
- ● 0.3— cm thick ammonium uranate

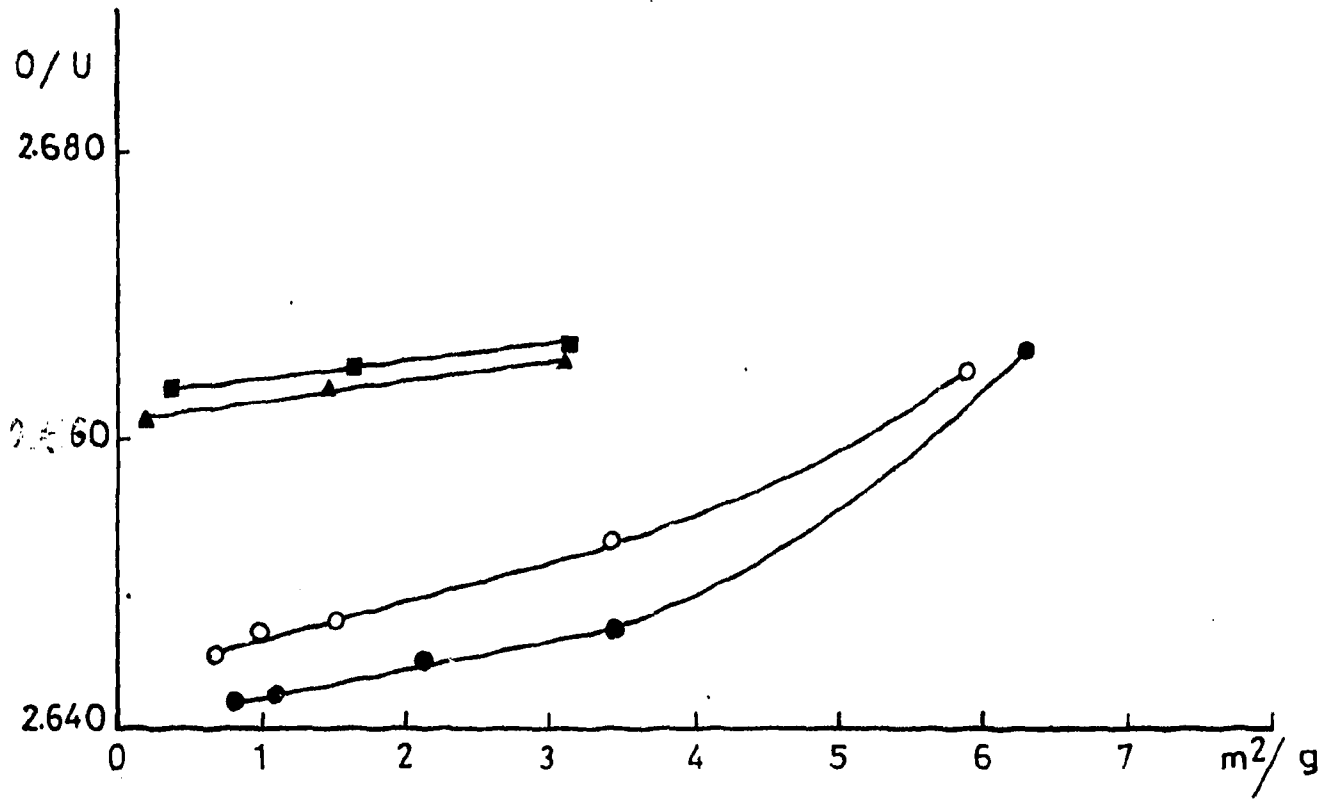


Fig.(3): Effect of surface area on the O/U ratio of U_3O_8 phase

- 0.3-cm thick ammonium uranate
- 1.5-cm " " "
- ▲-▲ 1.5-cm thick uranyl nitrate
- 1.5-cm thick uranyl sulphate

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