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TITLE
REACTIVITY OF UO_3

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REACTIVITY OF UO_3

The term "reactivity" when used in connection with the properties of UO_3 is basically a RATIO of reaction rates and has meaning only when the particular reactions involved, and the conditions under which the reactions are carried out, have been specified. A reactivity term is used at Mallinkrodt and Fernald which is applicable only to the sequence of reactions involved in the reduction of UO_3 to metal. The "reactivity" (or "reactivity ratio" as it is sometimes called) which is of interest at HAPO, is a relative measure of the extent to which the UO_3 may be converted to UF_4 in the reduction and hydrofluorination steps of the process used in the preparation of the uranium for introduction into the diffusion process at Oak Ridge and Paducah. It is a completely arbitrary unit, expressing the ratio between the per cent conversion to UF_4 of a sample of Hanford UO_3 and the per cent conversion to UF_4 of a primary standard sample of UO_3, origirally obtained from the Mallinkrodt Chemical Works, when reacted in accordance with a standard analytical procedure. The primary standard was selected from a lot of material which was observed to give good conversion to UF_4. In practice, the determination is made from secondary standards, which are currently supplied by Oak Ridge. The procedure in the laboratory is to take aliquots of the unknown and of the standard, reduce each to UO_2, then to react the UO_2 with HF, each step being carefully controlled. A quantative determination of the UF_4 is made for each sample and the per cent conversion of the UO_3 to UF_4 is calculated. The reactivity is then reported as

W. M. Barty

$$\text{Reactivity} = \frac{\% \text{ conversion to } UF_4 \text{ of unknown sample}}{\% \text{ conversion to } UF_4 \text{ of standard sample}}$$

Thus samples which react to a greater extent than the standard sample may have reactivities greater than unity.

At Oak Ridge, the uranium trioxide is reduced to UO_2 by heating in an atmosphere of hydrogen on vibrating trays. The UO_2 thus produced is then converted to UF_4 ("green salt") by further heating in an atmosphere of hydrogen fluoride. These steps are much less expensive than the subsequent step of fluorination to UF_6 in an atmosphere of fluorine, but the purity of the UF_4 has a marked effect on the rate at which conversion to UF_6 takes place, and on the quantity of fluorine gas required to convert all the uranium present to UF_6. For example, UO_3 of poor reactivity may yield UF_4 containing substantial amounts of UO_2F_2, a compound which may be converted to UF_6 when heated in a fluorine atmosphere, (Equation: $UO_2F_2 + 4F_2 \rightarrow UF_6 + 2F_2O$) but which in the process may require up to 4 times as much fluorine as UF_4, the fluorine costing approximately 10 times as much as HF. The economic advantage of UO_3 of high reactivity is immediately apparent and it has been stated that each increase in reactivity of 0.1 (in the reactivity range of 1.0) would result in savings at Oak Ridge of $100,000 annually.

Many factors such as particle size, crystalline form, amount of impurities, water of crystallization, etc., are believed to influence the reactivity of the UO_3.

The UO_3 can be made more reactive by converting it to the monohydrate, and a plant for this purpose was designed but never constructed. Occasionally, samples of ordinary UO_3 are run against a monohydrate standard which, when tested under the Less Rigorous Hydrofluorination Conditions Employed, is about twice as reactive as the conventional standard. This method is used only as a research tool in examining very reactive material.

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