LETTER TO THE EDITOR

REACTOR IRRADIATION OF LANTHANUM OXIDE SAMPLES

Dear Sir:

While most chemists are aware that lanthanum is a very basic element, it is perhaps not as generally realized that this fact makes its oxide behave atypically as compared to the other rare earth oxides. This was brought home to us in a forceful manner when we were recently asked to investigate an incident at the Argonne CP-5 reactor that eventually involved a substantial amount of decontamination time and expense.

A half-gram sample of 99.9% lanthanum oxide as received from the manufacturer had been oven-dried for several hours at 110°C, then sealed into a 1-cm-i.d. quartz capsule about three inches in length. It was then irradiated in the Argonne Research Reactor, CP-5, for a total exposure of about 1.5×10^{19} n/cm^2. During this period the tube broke, a fact that was discovered too late to avoid considerable contamination of the reactor building when the sample was removed from the irradiation thimble.

In the course of investigating the incident, separate samples of the original La_2O_3 were dried for 2 and 24 h at 110°C. The weight loss in each case was about 0.2%. On one-hour ignition at 850°C, however, the total loss in weight became 14.23%. Mass spectrometric examination of the released gases showed the material to be essentially all H_2O with only a trace of CO_2 present. A sample of the original oxide was then analyzed thermogravimetrically, with the results shown in Fig. 1. Material which had been ignited at 850° was subsequently exposed to a humid atmosphere for 18 h and re-run. The second thermogravimetric curve was essentially identical with the first. Ignited samples of cerium(III), praseodymium, and neodymium oxides were similarly exposed to moist air for about a week, then analyzed thermogravimetrically. Essentially no weight loss was seen for the Ce or Nd, and only a very small loss (with no sharp break in the curve) for Pr.

The first break in Fig. 1 corresponds roughly to the loss of two waters per molecule of La_2O_3, the second break to the loss of one H_2O.

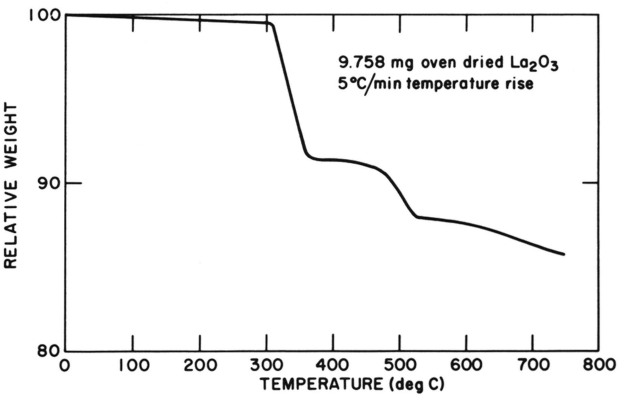

Fig. 1. Thermogravimetric analysis of oven-dried lanthanum oxide.

It would seem probable that the reactor accident occurred when water adsorbed by the lanthanum oxide was decomposed into hydrogen and oxygen during the irradiation. The resulting pressure buildup could have caused the tube to rupture, although since similar samples had been irradiated previously without trouble, the particular tube used may have also had some undetected imperfection. In any event, the obvious recommendation is that all lanthanum oxide samples exposed to reactor irradiation be ignited, not simply dried, immediately before being sealed into the sample tube.

The original drying experiments were carried out by P. E. Peterson and the mass spectrometric analysis of the gas by L. F. Krout, both members of the Argonne Analytical Chemistry Section. This letter is based on work performed under the auspices of the USAEC.

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