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Differential thermal analysis of some irradiated materials

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Abstract

Differential thermal analysis has been successfully applied to highly radioactive irradiated materials through use of a disposable sample holder and appropriate remotely-operated equipment; measurement of the temperature at which radiation damage is annealed, as well as the quantity of energy released, has been obtained. In the cases of irradiated, amorphous U_3O_8 and Al_2O_3, the energy release associated with the return of crystallinity was measured; results of the measurements indicate that these amorphous materials are supercooled liquids, that is, true glasses. Negative runs were obtained on differential thermal analysis runs on UO_2 and $ZrO_2{-}UO_2$.

Introduction

The hundred-year history of the differential thermal analysis (DTA) technique has been reviewed by Smothers and Chiang (1958). Basically, the apparatus consists of two thermocouples connected to form a hypothetical hot-and-cold junction of dissimilar metals. One of these junctions is embedded in a sample of the material to be studied; the other is embedded in an inert material of comparable thermal properties. The two materials are then subjected to a uniform increase in temperature. Any exothermic or endothermic reaction in the sample produces a temperature difference, and therefore a detectable signal. A recorder profile provides data on the magnitude of each reaction, as well as the temperature at which it occurs. The area under the curve is proportional to the enthalpy of the reaction (Sturm, 1961). If the weight of the sample is known and the machine has been calibrated with known substances, the differential thermal analyzer can be used as a microcalorimeter.

Childs and McGurn (1959) used differential thermal analysis to measure the energy released when slightly irradiated U_3O_8 is heated to 250°C. They found that 21.4 kcal/mole was released, a value that corresponds reasonably well with the heats of fusion of comparable metal oxides. The heat of fusion of U_3O_8 was and is unavailable, since the material decomposes into U_4O_9 and oxygen before melting. Childs and McGurn found that the stored energy reached this saturation value at about 5.5×10^{15} fissions/cc. On the basis of the difference in enthalpy between the unirradiated and irradiated states, the irradiated material could be identified as a supercooled liquid, *i.e.* a true glass. This is in agreement with Boyko *et al.* (1958) and Berman *et al.* (1960), who observed that the X-ray diffractogram of U_3O_8 disappears after comparable exposures.

In order to extend these observations to other irradiated materials, a differential thermal analyzer designed specifically for heavily-shielded remote operation was constructed inside one of the "Hot Laboratory" cells at Bettis Atomic Power Laboratory. After the apparatus was calibrated with nonradioactive materials, samples of irradiated Al_2O_3–UO_2, ZrO_2–UO_2, and U_3O_8 were run.

Amorphous solid materials, in the sense here used, are those in which the discrete X-ray diffractograms characteristic of crystalline materials are not observed. Metamict materials are a class of amorphous materials in which there is good reason to believe that the crystal structure has been destroyed by radiation; in the case of minerals, the radioactive material is generally observable. It is often possible to cause these materials to crystallize by heating them to a temperature considerably below the melting point, and annealing out the radiation damage.

The term "glass" refers to the relationship between an amorphous solid material and the liquid of the molten state. It is possible to move from one of these

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states to the other without encountering the phenomena associated with a change of phase—a sudden change of properties, a two-phase field, or a temperature at which an absorption or release of energy is noted.

Description of equipment

The equipment consists of: (a) a small muffle furnace mounted in a bell jar; (b) a sample holder with thermocouples mounted on the furnace door; and (c) a furnace controller, d-c amplifier, recorder, vacuum pump, and helium tank located outside the cell. The furnace door, sample holder, and thermocouple assembly are remotely attachable and disposable. There are insulated, gas-tight "Feed-through" electrical contacts in the floor of the bell jar for the thermocouples and the furnace power, and also a tubing connection through which the bell jar may be evacuated and back-filled with helium.

The furnace is a small platinum-wound unit, 5 cm in internal diameter, manufactured for dental purposes by the S. S. White Dental Manufacturing Co. Furnace control is through a Pt:Pt-10%Rh thermocouple separate from the DTA thermocouples. At first the sample block was stainless steel; in later experiments Lavite (fired talc) was used. The sample block measured 2.5 × 2.5 × 4 cm; the 4-cm dimension was along the centerline through the two sample holes. These holes were drilled in the top surface, each 13 mm deep and 6 mm in diameter, with axes along the centerline 13 mm apart. Similar holes were drilled in the face at right angles to these, to connect with the bottoms of the previous holes; these were fitted with Alundum thermocouple tubing containing the thermocouples. The thermocouple tubing was cemented into holes in the furnace door, and served as a mechanical support for the sample assembly. Sauereisen cement was used to assemble the pieces. Chromel and Alumel were originally used for the DTA thermocouples, the central link being Alumel. Later, when the sample block was changed to Lavite, Pt:Pt-10%Rh thermocouples were used, the central link being Pt-10%Rh. The furnace controller was set to increase the temperature linearly at a rate of 10°C per minute.

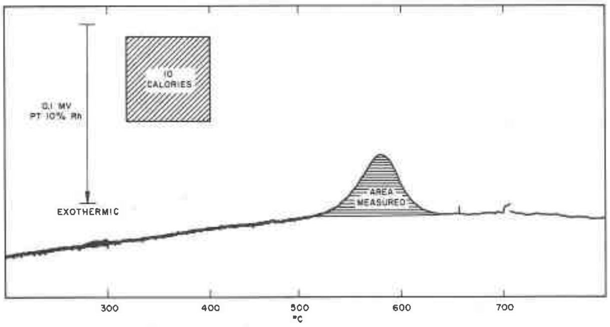

Fig. 1. Typical calibration run, using K_2SO_4 inversion.

The following reactions were used for calibration:
The dehydration of $CaSO_4 \cdot 2H_2O$ at 150–200°C
The melting of Pb at 327°C
The low-quartz high-quartz transformation at 573°C
The inversion of K_2SO_4 at 583°C
The decomposition of $CaCO_3$ above 750°C

Areas under the chart peaks were measured and divided by the known response of the thermocouple system at that particular temperature in millivolts per degree. This result was divided into the known energy release of the weighed sample, to give a coefficient that represented calories per square centimeter of peak area. This calibration is shown graphically in the figures of this paper. A typical calibration run is shown as Figure 1.

Experimental procedure

One of the sample wells was loaded outside the hot laboratory area with unirradiated inert alumina, and the entire sample assembly was weighed. The irradiated sample was then ground wet by a 50-cc vibratory mill inside the cell. This mill was a cylinder lined with SiC, using SiC balls, and sealed with rubber O-rings. Approximately 2 gm of sample and a comparable amount of water were placed in the cylinder, which was then clamped to an eccentric linkage driven by an 1800-rpm motor. The assembly was oscillated through a 5-cm arc for 3 minutes. The resulting slurry was transferred to the second sample well, the sample holder meanwhile having been placed in the hot cell.

The sample holder was then dried in a low-temperature vacuum furnace. The sample was next compacted with a blunt tool, using the hot-laboratory manipulators. More slurry was added, and the drying and compacting was repeated, until the sample well was filled. Temperature during the drying operation did not exceed 100°C. Finally, the entire sample holder assembly was weighed, and the weight of the sample was obtained by difference.

The sample holder was placed in the furnace using the manipulators. The thermocouple leads were clamped to the appropriate terminals, and the bell jar was lowered. The bell jar was evacuated twice and back-filled with helium. Runs made *in vacuo* proved unsatisfactory; apparently, the conductivity of the interstitial gas was necessary for narrow, well-defined peaks.

Certain Al_2O_3–UO_2 samples were deliberately oxidized in air at 400°C for 1 hour before the run in order to show that the peaks observed at higher temperatures did not result from the oxidation of UO_2 to U_3O_8.

The furnace controller then raised the temperature at a rate of 10°C per minute to 1100°C, then lowered it at a comparable rate to avoid cracking of the insulation of the furnace. After the run a portion of the sample, now usually partially sintered, was broken out for study with the remotely-operated X-ray diffraction unit, which used a shielded monochromator and pulse-height discrimination to reduce the background caused by gamma rays emanating from the sample. The remainder of the sample was discarded, together with the sample holder.

Description of samples

Among the materials run were irradiated samples of Al_2O_3–21wt% UO_2, Al_2O_3–80wt% UO_2, pure UO_2, U_3O_8, and ZrO_2–34wt% UO_2. The Al_2O_3 and U_3O_8 materials were irradiated in aluminum capsules at Brookhaven National Laboratory (Berman *et al.*, 1960). The other materials had been fabricated into sintered plates, clad in Zircaloy, and irradiated at reactors at NRTS or Chalk River under conditions simulating those of a pressurized water reactor (Bleiberg *et al.*, 1962). The Zircaloy cladding was removed from these samples with a remotely-operated rotary saw.

The Al_2O_3–UO_2 samples consisted before irradiation of the two materials, essentially in their pure state, sintered together to form a two-phase mixture. There was little solid solution between the two components; however, the particle size (10 μm) was such that all of the alumina was within the range of fission-fragment recoil from the urania particles. Upon very slight irradiation, the material increased about 20 percent in volume. X-ray examination showed no diffraction peaks from the alumina (Berman *et al.*, 1960). These results have been confirmed by Wait, of AERE, who also found that the alumina diffractogram disappeared at about 7 × 10^{15} fissions/cc. The U_3O_8 had also been transformed to an amorphous state by very slight pile irradiation.

The zirconia–urania materials had been sintered at 1700°C, and consisted, before irradiation, of appropriate amounts of the two phases in equilibrium at this temperature, according to the binary phase diagram (Cohen and Schaner, 1962). Both phases were tetragonal when cooled to room temperature; one contained approximately 29 weight percent urania, the other 65 weight percent urania, the balance in both cases being zirconia. After irradiation to 2.15 × 10^{21} fissions/cc, the material had been homogenized into a single cubic phase. Certain samples of the same composition removed after 6 × 10^{20} fissions/cc consisted of a single tetragonal phase (Rubin *et al.*, 1962).

In contrast with the materials described above, the X-ray diffractogram of UO_2 changes very little when the material is exposed to reactor irradiation (Daniel *et al.*, 1962). A sharp fluorite-type diffractogram is observed in very highly irradiated material. Changes in unit-cell size are minor, and can largely be attributed to point-defect formation at low exposures and possibly to fission-liberated oxygen. The major physical changes observed in the irradiation of UO_2, aside from the formation of radioactive nuclei, are dimensional changes that can largely be attributed to fission-generated krypton and xenon, as well as less-volatile nuclides.

The fission-fragment-induced phase changes in the other materials produced metastable states. It was expected that heating in the course of the DTA runs would destroy these metastable states and cause the samples to return to the more stable states represented by the unirradiated materials. When this occurred, the apparatus would detect the energy released as an exothermic reaction, and would also show the temperature at which the radiation damage was annealed out.

Experimental results

The samples submitted to DTA, together with their weight and in-pile exposure, the energy release observed, and the temperature of the maximum of the DTA peak, are listed in Table I. The samples with "A" entries in the calibration column were run with Chromel–Alumel thermocouples in a stainless steel block with Alundum liners for the sample wells. The sample with "P" entries were run with Pt:Pt-10%Rh thermocouples in a Lavite block.

In some cases, Sauereisen cement was used to coat the thermocouple wires up to the bead to ensure that the reading would reflect the temperature at the center of the sample. This procedure proved unnecessary and undesirable; the Sauereisen introduced exothermic peaks of its own between 550 and 650°C. Fortunately, these could be recognized and elimi-

Table 1. Energy release of irradiated materials measured by DTA

Material	Calibration	Fiss/cc $\times 10^{-20}$	Sample Wt(mg)	Calories	Kcal/mole	Peaks (deg C)	Remarks
Al_2O_3-21wt% UO_2	A	0.92	843	9.81	1.50*	790,750	
			863	14.15	2.11*	690	
			1225	13.56	1.42*	770	Saueresen peaks eliminated graphically
			1233	17.02	1.77*	790,700	Deliberately oxidized
			1619	29.61	2.35*	730	Deliberately oxidized
	A	6.9	630	9.13	1.87*	700	Loosely packed
Al_2O_3-80wt% UO_2	P	0.07	1120	10.17	4.63*	890	Sample holder not full
			1270	15.06	6.05*	880	Considerable zero drift
U_3O_8	A	0.0004	319	11.00	29.0	230	
UO_2	P	1.6	738	None			
	P	1.3	1316	None			
	A	0.6	915	None			Saueresen peaks only
ZrO_2-34wt% UO_2	P	21.5	550	None			

* In Al_2O_3-UO_2 samples, kcal/mole values refer to moles of Al_2O_3.

Calibration A -- Stainless steel sample block, Chromel-Alumel thermocouples.
Calibration P -- Lavite block, Pt:Pt10%Rh thermocouples.

nated graphically. The thermograms affected are noted in Table I.

Figure 2 shows a DTA run obtained with a sample of U_3O_8 irradiated to 4×10^{16} fissions/cc. A sharp exothermic reaction is observed between 180 and 260°C, with the maximum of the peak at about 230°C. The 319-mg sample released 11.0 calories, for an energy release of 29.0 kcal/mole. This result agrees well with that of Childs and McGurn (1959), who measured a release of 21.4 kcal/mole at 250°C from material in which radiation damage had become saturated. The X-ray diffraction pattern of our sample, which had been completely destroyed by the pile irradiation, was completely restored after the DTA run.

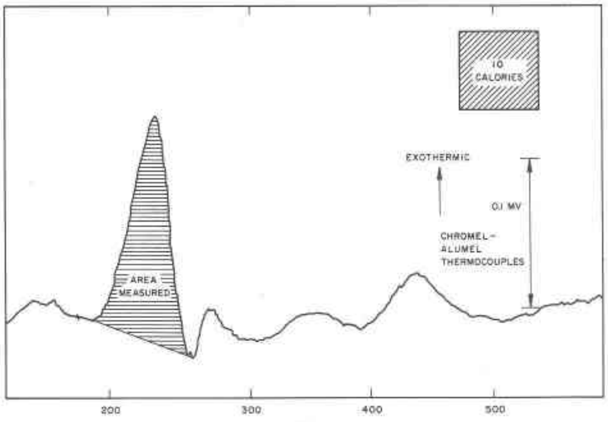

Fig. 2. Differential thermogram of U_3O_8 irradiated to 4×10^{16} fissions/cc.

Figure 3 shows a selection of the differential thermograms obtained from the irradiated urania–alumina samples. They show broad peaks, *i.e.* fairly slow exothermic reactions, between 650 and 850°C. Some of the profiles show evidence of partial resolution into two peaks, such as would be expected in a two-stage reaction.

The stored energy represented by the peaks from Al_2O_3–21wt% UO_2 samples, irradiated to 9.2×10^{19} fissions/cc, varies from 1.42 to 2.35 kcal/mole, with an average of 1.84. The heat of fusion of alumina, at its melting point of 2040°C, is 26 kcal/mole. The energy released in the annealing of radiation damage from these samples is clearly only a small fraction of that figure. It was necessary to eliminate the possibility that the peaks observed were due to the oxidation of the urania by air incompletely removed by the vacuum pumping and helium flushing. Two samples were therefore deliberately oxidized to convert the UO_2 constituent to U_3O_8; this was done by heating in air at 400°C for one hour. These samples then produced differential thermograms similar in nature and magnitude to the other Al_2O_3–21wt% UO_2 samples, although no further oxidation of the urania could have taken place.

A diffractogram of one of the samples of Al_2O_3–

UO_2 after the DTA run is shown in Figure 4. Peaks associated with alumina are observed, and the crystallinity of the material has apparently recovered. The apparent reduced intensity of the lowermost diffractogram is due to the small sample and to the compromises in efficiency and sensitivity that were necessary in building a diffractometer for highly radioactive materials. The uppermost diffractogram was made with a conventional diffractometer.

The Al_2O_3–80wt% UO_2 material was subjected to much less intense reactor irradiation, and reached an exposure of 7 × 10^{18} fissions/cc. The energy release measured from two such samples was 6.05 and 4.63 kcal/mole Al_2O_3. Both values are considerably higher than those obtained from Al_2O_3–21wt% UO_2, although still well below the heat of fusion.

Table I also lists three samples of UO_2 and one of ZrO_2–UO_2 from which differential thermograms were obtained. The results were essentially negative. No well-defined, reproducible reaction peaks were obtained. In the case of the ZrO_2–UO_2, the absence of peaks indicates that the two-hour run with temperature increasing to 1000°C was insufficient to permit the sample to return from a single cubic phase to the more stable condition of a two-phase mixture. It is also possible that the difference in enthalpy between the two states is too small to measure or that the reaction is too slow to produce a well-defined peak.

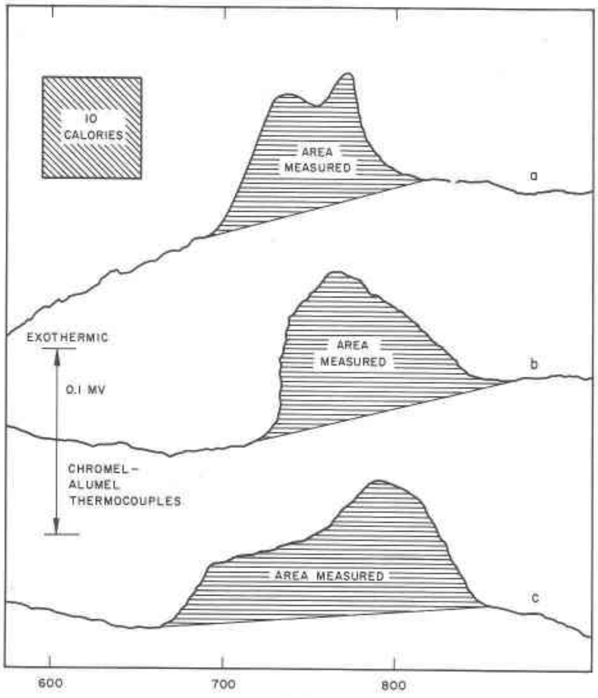

Fig. 3. Differential thermograms of Al_2O_3–21 wt% UO_2 irradiated to 9 × 10^{19} fissions/cc. Weight of samples: (a) 843 mg, (b) 1225 mg, (c) 1233 mg. Sample c was deliberately oxidized.

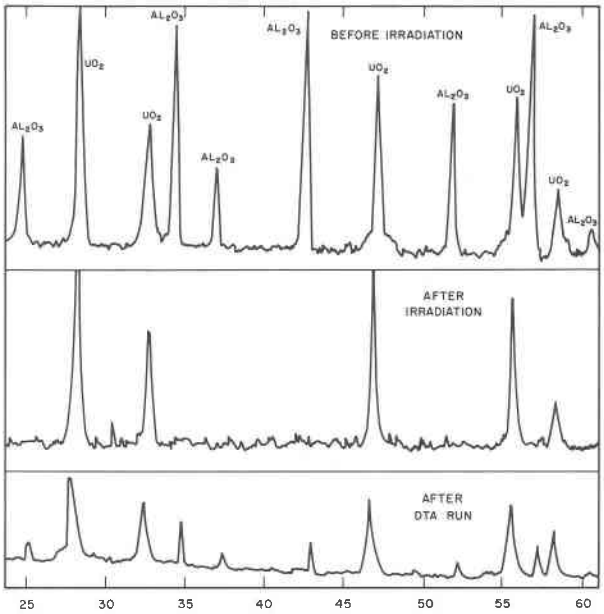

Fig. 4. X-ray diffractograms of a sample of Al_2O_3–21 wt% UO_2 irradiated to 9.2 × 10^{19} fissions/cc. Corresponds to sample b in Fig. 3.

Discussion and conclusion

The X-ray diffraction pattern of U_3O_8 disappears when the material is exposed to a small amount of pile irradiation. The question arises whether the resulting amorphous material corresponds to the metamict state in natural minerals, and whether it can correctly be called a glass, that is, a supercooled liquid.

Glasses are metastable. Their enthalpy lies above that of the corresponding crystalline substance by an amount equal to the latent heat of fusion after an appropriate temperature correction is made. This temperature correction takes into account the difference in heat capacity between the glass and the crystalline solid in the temperature interval from the annealing temperature to the melting point. These heat capacities are not available for the amorphous forms of some of the materials studied; the corrections, however, are probably not very large when compared to the value of the heat of fusion.

The heat of fusion of U_3O_8 cannot be measured directly, since the compound decomposes before melting into UO_{2+x} and oxygen. The present experiments, and those of Childs and McGurn, have shown that irradiated amorphous U_3O_8 returns to the crystalline state when heated to 150–250°C, releasing 20–30 kcal/mole. This quantity of energy can hardly represent anything but the latent heat of fusion, and amorphous irradiated U_3O_8 can correctly be described as a glass.

Al_2O_3 also becomes amorphous, as judged by the disappearance of diffraction peaks, when subjected to fission fragment bombardment. In the case of Al_2O_3–21wt% UO_2, for which the exposure is on the order of 10^{20} fissions/cc, the crystal structure is restored between 700 and 800°C. The energy release accompanying this event is, however, far less than the heat of fusion of alumina. The average of six determinations on irradiated Al_2O_3–21wt% UO_2 is 1.84 kcal/mole of Al_2O_3. The measured value for the heat of fusion at the melting point is 26 kcal/mole.

There are a number of possible interpretations of these data. Conceivably some energy is being produced slowly all during heating and cannot be distinguished from the background represented by the slightly drifting zero point. A second possibility is that the amorphous material may be in a metastable state with an energy above that of the crystalline state, but much below that projected for a supercooled liquid, and should not be considered continuous with the liquid material occurring above the melting point.

Two samples of Al_2O_3–80wt% UO_2 irradiated to 7×10^{18} fissions/cc gave a very different picture. The temperature of energy release was higher—about 880°C; the peak was sharper, indicating a faster reaction; and the quantity of energy released for a given weight of alumina was far higher—about 6 kcal/mole. However, it still fell far short of the heat of fusion, 26 kcal/mole.

The Al_2O_3–21wt% UO_2 samples and the Al_2O_3–80wt% UO_2 samples differ in fission fragment exposure as well as in bulk composition. However, both consist of nearly pure alumina and nearly pure urania grains, in differing amounts, sintered together. It is probable that the different concentration of fission fragments, rather than bulk composition, is primarily responsible for the differences observed between the differential thermograms of the two materials.

In cylindrical ceramic fuel elements that reach high temperatures, columnar crystal grains form a radial pattern in the interior, and fission fragments already formed are largely excluded from this material in the process of recrystallization. No such mechanisms are feasible for amorphous materials. Unless the fission products actually diffuse outside the fuel body—as is the case, for instance, with a portion of the fission gases—they are apparently distributed randomly, in true solution, and affect the properties of the material accordingly.

If the fission fragments in supercooled alumina liquid serve to nucleate the recrystallization, then a small concentration can bring about a considerable change in properties. The change from 0.7 to 9×10^{19} fissions/cc (and twice those numbers of fission fragments) can well account for the difference in temperature at which the annealing of the lattice damage takes place (880 and 770°C, respectively).

The irradiation damage in U_3O_8 is annealed at a very much lower temperature (230°C). In this case, the structure of the material is such that the depth of the energy wells associated with the metastable, irradiation-damaged state is very much shallower than is the case with Al_2O_3.

The irradiation exposures of the samples range over five orders of magnitude, and represent material that happened to be available, as well as observations for which elucidation was required. However, the available evidence indicates that the changes in crystallinity, where they occurred, took place at a comparatively low exposure, and that additional exposure, perhaps orders of magnitude, had comparatively minor effects.

It is questionable whether the decrease in energy release on recrystallization can be ascribed to the fission fragments in solution. The X-ray diffractograms indicate that the material is amorphous. A true glass should release, on recrystallization, a quantity of heat equal to the heat of fusion, after appropriate corrections are made for the difference in heat capacity between the crystalline solid and the glass between the temperature of recrystallization and the melting point. However, it seems even more doubtful to assign the fission-damaged alumina to some metastable state between the crystalline solid and the supercooled liquid, in view of the difference in energy release between the less-irradiated and more-irradiated samples. Surely, the metastable state does not cover the entire band of energies from 1.8 to 6 kcal/mole above the crystalline state.

The fission-damaged amorphous alumina can be tentatively described, on the X-ray and density change evidence and by analogy with U_3O_8, as a glass, that is, a supercooled liquid. The annealing is therefore analogous to the devitrification of a glass, and the fission fragment ions act essentially like the ions of non-glass-formers when they are introduced into a glass; they provide nuclei around which ordered structures can form, and they decrease the stability of the glass. It is suggested that analogous processes occur in the annealing of metamict minerals, with alpha-decay products playing a role comparable to the fission fragments.

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