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Part 1. Gd$_2$ O$_3$ microspheres preparation from the sol-gel method

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(FIAT)

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— sol preparation,
— gelation and spheroidization,
— thermal treatment (presintering and sintering).

The sol has been prepared by peptization at 80°C for 30 minutes of freshly precipitaded gadolinium hydroxide with nitrate ions as stabilizing electrolyte. The concentration of sol was about 2M and the NO $_{3/Gd}$ molar ratio in the range 0.12-0.27.
The gelation and spheroidization were carried out in a tapered column through dehydratation and gelation by an aliphatic long chain alcohol.
The gelled microspheres have been presintered under vacuum up to 950°C for a total time of about 10 hours in order to decompose the gadolinium hydroxide, nitrate, carbonate and the adsorbed organic substances.
The presintered microspheres have been hydrogen sintered for 2-3 hours at 1600-1700°C : microspheres with sintered density very near to the theoretical value have been obtained.

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KEYWORDS

COLLOIDS
REPROCESSING
GELATION
SINTERING
GADOLINIUM HYDROXIDES
ALCOHOLS
POISONING
FUELS
METALS

CONTENTS

1. INTRODUCTION *

In early 1951, A.Radkowsky (1, 2) of the Office of the Naval Reactors (United State Atomic Energy Commission) formulated the principle of burnable poison. The basic idea was to introduce into the core an absorber of cross-section greater of the fuel, the depletion of which would compensate for both the depletion of fuel and the accumulation of fission-product poison; in other words, Radkowsky showed that the use of burnable poison would permit greatly increasing the endurance of a core. Previous trials, in fact, of controlling the long-lived cores solely from the control rods, had introduced such severe mechanical and nuclear design problems, the penalities resulting made these cores less appealing and their practical feasability highly questionable.
On the other hand, the use of burnable poison showed many problems.
For instance, since the total control of the core varies in a complex manner with the life, and the rate of burnup of burnable poison must be in agreement to reactivity change resulting from the fuel depletion, burnable poison must have :
a) design geometries which enable their consumption at a rate consistent with fuel depletion and
b) concentration so that no burnable poison residue remains at the end of the reactor core life.
So in order to have the complete consumption of the burnable poison, its absorption cross section must exceed that of fuel (since the core must have a quite large reactivity, when all the poison has been burned). However if the poison to fuel cross section ratio is too large, the poison will be immediately depleted, almost nullifying the advantages of using the burnable poison.

The best compromise among these opposite requirements has been obtained through the use of the self-shielded poisons (3), as microspheres of different diameter calculated in order to nullify the poison residue at the wanted core-life period.

The elements most suitable for these applications are boron, erbium, cadmium, samarium and gadolinium. The moderately high thermal neutron cross section of ^{10}B makes boron suitable for either short-term control in very diluted quantities or for longer periods of control with modest self-shielding. Erbium, cadmium, samarium and gadolinium are the best choice when self-shielded poisons are requested.

The burnable poisons can be incorporated in the reactor core into the fuel cladding or as temporary auxiliary controls in the form of removable inserts: both concepts showed many difficulties, so the most technically feasible long range concept seems to be the incorporation of the burnable poison as microspheres of different diameters in uranium dioxide fuel.

Furthermore, it may be noted that the homogenous incorporation of rare earth oxides microspheres into UO_2 can be accomplished by processes that are essentially the same as those used for pure urania fuel. UO_2 homogeneously mixed with erbia powder was used for the second fuel reload of the Dresden reactor and for the third fuel reload was used gadolinia powder as burnable poison. (4,5)

This paper describes the preparation of gadolinia microspheres through the sol-gel process for use as burnable poisons for nuclear fuel.

2. EXPERIMENTAL

It is well known that the sol-gel methods for the preparation of metal oxide microspheres (6-13) include the following steps:

(a) preparation of a colloidal dispersion (sol) carrying the metal ions,
(b) spheroidization of said solution into droplets of the wanted diameter, and drying of said droplets into solid (gel) microspheres, and finally
(c) thermal treatment in order to convert the microspheres of gel into high density ceramic bodies.

2.1. Preparation of gadolinia colloidal dispersions (sols)

The preparation of gadolinia colloidal dispersions has been obtained through the precipitation of gadolinium hydroxide from its nitrate and subsequent peptization of this precipitate; the process can be seen as a condensation in the first step (precipitation) and as a dispersion in the second step (peptization) (14). However the precipitation is without doubt the most influencing step in the course of the whole preparation. The particle-size distribution of a precipitate is determined by the relative rates of two processes, the nucleation and the crystal growth.

If the precipitation is carried out so that a few nuclei are formed, precipitation will be slow, crystals large and purity high. On the other hand, if the precipitation is carried out in such a manner to produce numerous nuclei, precipitation will be rapid with formation of a very fine precipitate of low purity.

In order to effect nucleation it is necessary that the solution be supersaturated and that the probability of nucleation increase very rapidly with supersaturation.

The nucleation rate is given by

$$N = A \exp \left(- \frac{\Delta G}{RT} \right) \qquad (1)$$

where N is the number of nuclei formed per volume unit and time unit, A is a proportionality constant, R and T have the usual significance and ΔG is the overall excess free energy of particle, i.e. the work of nucleation. This is given by the following equation:

$$W = \frac{16 \pi \sigma^3 M^2}{3 \left(RT \ln \frac{c}{c_s} \right)^2 \rho^2} \qquad (2)$$

where σ is the interfacial energy of the solid-liquid system, M and ρ are respectively the molecular weight and the density of the solid, c is the actual concentration and c_s the saturation concentration.

At consequence the relation for the nucleation rate will be as follows:

$$N = A \exp \left[- \frac{16 \pi \sigma^3 M^2}{3 R^3 T^3 \rho^2 (\ln \frac{c}{c_s})^2} \right] \qquad (1')$$

One can see that an increase of the ratio $\frac{c}{c_s}$ strongly increases the nucleation rate and thus increasing the concentration of the reagents it will obtain a higher number of nuclei and a fine precipitate.

The rate of crystal growth can be interpreted in term of diffusion of the crystallizing substance to the surface of crystals (15) although in other cases it may be interpreted by deposition of new molecules on the existing crystals (16). In the first case the linear growth of a crystal is proportional to the degree of supersaturation $(c-c_s)$ and inversely proportional to the diameter of the crystal. In the second case the linear growth is independent of both these parameters. It is to be pointed that many other factors influence the crystal growth, such as stirring rate, adsorbed substances, temperature, crystal imperfections, etc. From the foregoing discussion it results that the conditions for the formation of a colloidal precipitate are principally related to the supersaturation degree. This is in agreement with the old rule of von Weimarn (17) according to whom colloidal systems of insoluble salts are formed by the mixing of very concentrated solutions. In fact in these conditions the total amount of insoluble substance formed is greater, but the number of nuclei found is more than proportionally larger and thus the particles formed remain small. However operating in such a manner there is flocculation of the sol for the large amount of accompanying electrolytes.

In order to check the validity of the above summarized theoretical considerations, different gadolinia colloidal dispersions have been prepared.

Colloidal dispersions of some rare-earth hydroxides are known from long time (18-24) but the colloidal dispersions of gadolinium hydroxide have not been yet studied extensively. Also the works of Hardy and collaborators (25-28) on the lanthanide hydroxides dispersions from the sol-gel process point of view are principally concerned with the praseodynium, europium and neodymium hydroxides, while data on gadolinium hydroxide are very poor.

The preparation of gadolinium hydroxide colloidal dispersions was carried out according to the following procedure. A solution (different for each experiment) of gadolinium nitrate pentahydrate, $Gd(NO_3)_3$. 5 H_2O, 99.9% of title was added to a 2M solution of ammonia. The precipitate $Gd(OH)_3$ was washed for the first time with concentrated NH_4OH and then with deionized CO_2-free water, as long as nitrate ions adsorbed were constant, then the precipitate was dispersed in wanted quantity of diluted nitric acid and heated to peptization for the required time. The final sol concentration as $Gd(OH)_3$ was about 2M.

The colloidal dispersions obtained were characterized through chemical and physical determinations. The total gadolinium concentration in the sol was determined by slow evaporation of a measured sample and then calcination to Gd_2O_3 at 1000°C. The nitrate ions concentration was determined by reduction to NH_3 by Devarda alloy and subsequent absorption in standard H_2SO_4 through a classical Kjeldhal apparatus. The carbonate ions were determined by liberating the carbon dioxide through attack by hydrochloric acid and absorbing it in ascarite (29). The pH was determined potentiometrically with a Metrohm Model 300 B pH meter. The specimens for the electron microscopy observations were prepared through a dilution of 0.01 ml colloidal dispersion into 100 ml deionized, CO_2-free water. One drop of this diluted dispersion was placed on a carbon-covered copper grid and then inserted in the electron microscope. Electrical conductivity was measured at 25°C and 1 Kc with a Radiometer type CDM 2 apparatus. The semiquantitative electrical behaviour of sol was evaluated by a Burton apparatus (30).

The first set of experiments is carried out in order to observe the influence of the initial gadolinium nitrate concentration on the formation of the colloidal dispersion. For these experiments a constant quantity of peptization agent (nitrate ions) is added to the hydroxide precipitate without taking into account the adsorbed nitrate ions. The results are summarized in tab 1. The main conclusions are the following:

a) the nitrate ions adsorbed by the precipitate increase increasing the gadolinium nitrate concentration;

b) in all cases a net variation of the pH of dispersion before and after peptization was observed;

c) no significant differences in pH among the various dispersions were observed;

d) only for one precipitation concentration (0.2 M) a relatively homogeneous sol has been obtained;

e) in all the other cases the dispersions are to be considered as formed by two types of sols, a sol with rod like units and a sol with spherical and apparently amorphous units;

f) from a semiquantitative point of view it is possible to see that the length of rods decreases increasing the gadolinium concentration during the precipitation.

In order to check the right influence of the nitrate ions, another
set of experiments has been carried out with a total constant amount
of nitrate ions in the gadolinium hydroxide precipitate. The results
of these experiments are summarized in tab. 2 : the conclusions are
that also these dispersions are formed by two different types of
sol except for 0.2M gadolinium nitrate solution, even if the
dimensional difference between the two sols are smaller than that
observed in the previous experiment.

Since a monodisperse colloidal solution has the best behaviour for
the sol-gel process, the influence of the aging time and temperature
has been examined on colloidal dispersions obtained by the 0.2M
gadolinium nitrate solution. The experiments have been carried out
at room temperature and at 80°C for a soaking time long enough to
obtain a good crystallization. Fig. 1 shows the results obtained at
room temperature, while the fig. 2 shows the results obtained at
80°C. The main conclusions are that the sol is completely crystallized
after 30 min. at 80°C, while very long time periods are requested
if a room temperature aging is desired.

The results of the additional physico-chemical determinations on the
colloidal dispersion are the following:

- the electrophoretic measurements showed that the gadolinium hydroxide
  is a positively charged colloid with nitrate ions and perhaps
  hydroxide ions as controions;
- the electron diffraction pattern on a single crystal of gadolinium
  hydroxide shows an exagonal simmetry, accordingly with X-ray data
  (31) (fig. 3);
- the electrical conductivity measurements, though they are not very
  significative because of the great amount of electrolyte added, give
  a specific conductivity value of $1.53 \cdot 10^{-2}$ mho . cm^{-1} for the
  dispersion prepared from a 0.2M gadolinium nitrate solution.

In conclusion from the results obtained it is possible to hypothyze
that the colloidal dispersions of gadolinium hydroxide have the
following chemical composition:

$$\left[x \ Gd \ (OH)_3 \ . \ nH_2O \ . \ zGdO \right]^{z+} + (z-y) \ NO_3^- + y \ OH^-$$
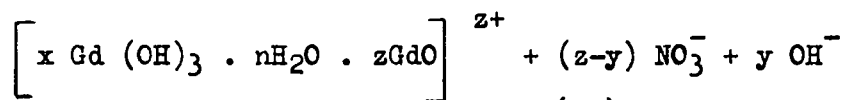
Accordingly to Milazzo's classification (32) the colloid is to be
considered etheromolecular and the ratio $\frac{z}{z-y}$ is from 0.12 to 0.27
depending upon the preparation conditions.

Finally the existence of two sols can be ascribed to non-homogeneous
conditions of precipitation. The different dimensions of the sol can
be explained on the basis of nucleation rate, being it higher increas
ing of the precipitation concentration, even if several other
physico-chemical parameters can influence it. The lower influence
on dimensional variation of the sol in the experiences with $\overline{NO_3}/Gd$
molar ratio constant can give an indication on the great Gd influence
of the ionic atmosphere solution during the peptization step.

2.2. Spheroidization and gelation of colloidal dispersions of gadolinium hydroxide

In order to have the gelation of gadolinium hydroxide colloidal dispersions under microspheres form two fundamental conditions must be fulfilled:

a) the colloidal dispersion must be spheroidized by immission in a medium poorly-mixable with water;

b) a sol-gel transition must occur through the formation of a relatively rigid structure.

The media poorly-mixable with water are generally aliphatic long chain alcohols. The "Octylol", an aliphatic commercial long chain alcohol, produced by Shell, is a good choice for the spheroidization and gelation of colloidal dispersions of gadolinium hydroxide. Amyl alcohol and N-ethyl-2-hexanol gave also good results. In order to stabilize the droplets of the colloidal dispersion during the gelation, small quantities (0.5 $\%$)of a surfactant agent have been added: a good behaviour for this application has shown the Span 80, a sorbitan monooleate produced by Atlas Chemical Industries.
The sol-gel transition occurs through contemporary dehydratation and sensitisation phenomena.

A sketch of apparatus utilized for the spheroidization and gelation is shown in fig. 4. In order to obtain an isotropic gelation, the fluid dynamics of the column has been studied in such way that the microspheres are maintained in continuous suspension and rotation: in particular, this effect has been obtained through three apropriate fluid fluxes operating in the column, one coaxial with the nozzle, one raising and one transversal. A general view of the apparatus is shown in fig. 5. The size of the microspheres in the range 200μ - 1mm can be regulated by the sol immission rate and by the nozzle diameter.

The time necessary for obtaining the complete gelation of the sol depends from the concentration of the colloidal dispersion and the size of droplets. Experiments on the kinetics of dehydratation have been carried out on the colloidal dispersion from 0.2M gadolinium nitrate solution, because it is formed by a single phase and at consequence the gelation and spheroidization is uniform and more reproducible . The same solution has been utilized for the gadolinia microspheres production. The kinetic experiments are performed through the determination of the water extracted from the "Octylol" doped with different water contents; the water content of the "Octylol" was determined through the electrometric Karl Fischer method. Fig. 6 summarizes the results of the dehydratation kinetic experiments: it can be seen that in all cases the water in the column is constant after 20 min. and that the amount of water from microspheres to gelation mixture decreases when the equilibrium is reached by increasing the initial water concentration in the column (fig. 7). No significative differences in dehydratation kinetics were

detected by operating with different amounts (in the range 0.5 - 2%) of surfactant agent.

It is to be pointed that the dehydratation is perhaps the main parameter in gelation process but it is not the only one. In fact after dehydratation time (20') a dimensional variation can be qualitatively detected that can be attributed to a "breakdown" of the microsphere. Fig. 8 shows the gadolinia microspheres as gelled.

2.3. Thermal Treatment of gelled microspheres

The whole thermal treatment involves two steps:

a) transformation of gelled microspheres to dried microspheres of gadolinium oxide (presintering) and

b) densification of dried microspheres until a value of 95-98% T.D. is obtained (sintering).

The chemical composition of the raw microspheres involves the presence of gadolinium hydroxide with small quantities of gadolinium nitrate, gadolinium carbonate and gelation mixture. A complete elimination of the decomposition products is, as it is well know (33, 34), necessary if microspheres with a density near to the theoretical value must be obtained. In order to establish which are the evaporation and decomposition temperatures of the products present in the gelled microspheres, a single batch of microspheres was placed in a platinum boat and heated in vacuo. Every fifty degrees and every quarter of an hour the vacuum was released through a soda lime tube, the boat weighted and then replaced in vacuo until constant weight was raised. The results obtained are plotted in fig. 9. A soaking time of one hour for each temperature has been necessary for obtaining constant weight (weight variation less than 2% is considered constant weight).

On the basis of these results, the presintering thermal cycle shown in fig. 10 has been adopted. In order to determine the variation induced in the gelled microspheres at the different steps of the presintering cycle, the microspheres have been heat treated at each step and physically and chemically analysed after these steps. The following determinations have been performed:

- apparent density carried out through the mercury picnometry with a modified Fascia and Johnston apparatus (35)

- total surface area carried out through the measurements of the nitrogen absorbed and the utilization of the Brunauer, Emmet and Teller equation

- nitrate and carbonate content through the above reported methods.

The results of these determinations are summarized in table 3.

Another determination carried out on the microsphere subjected to each

step of the presintering cycle has been the total pore size distribution
determined through the mercury penetration: the results are shown in
fig. 11. (36).

The main conclusions drawn from the results of these analyses are the
following:

- the apparent density of the gelled microspheres is quite low: no
  densification has been obtained during the presintering cycle; at the
  end of the presintering treatment the microspheres have an apparent
  density of 27% of the theoretical value;

- the total surface area of the gelled microspheres is higher than the
  value obtained by the current ceramic grade powders; these values of
  the total surface area mean that it will be possible to obtain, also
  with very low apparent density of the microspheres, very dense
  sintered bodies; on the other hand great attention must be given to
  the presintering treatment because it is very easy to obtain a very
  dense skin before a complete elimination of the volatile and
  decomposable substances contained in the microspheres; in this case
  the microspheres swell during the sintering appearing very strong
  and hard but poorly densified (fig. 12);

- through the presintering cycle, a complete decomposition of the
  hydroxides, nitrates and carbonates of gadolinium has been obtained;

- through the examination of the pore distribution of the gelled
  microspheres, it can be deduced that initially the pores are very
  small and lower than 0.03μ (the lower limit of the sensitivity of
  the apparatus).

The determination of the total carbon contained in the presintered
microspheres has been carried out through a standard extraction
method (LECO apparatus): no carbon content has been detected within
the sensitivity limits of the method (15 ppm). No presence of carbon
in the presintered microspheres is a very important fact because it
means that no carbide formation is possible during the sintering
treatment.

The micrographic aspect of the presintered microspheres carried out
through an ultramicrotome specimen preparation and an electron
microscopy observation is shown in fig. 13: it can be seen the basket
weave structure where the single particles of the colloidal dispersion
are still evident.

The presintered microspheres have been sintered both in hydrogen
atmosphere with a molybdenum heated furnace up to 1700° C and in air
with a silite heated furnace up to 1500° C. The raise and the fall in
temperature has been maintained in the range of 300° C/hr.   Fig. 14
shows the densification curves obtained in hydrogen and in air. It can
be observed a slight improvement in densification rate for thermal
treatments performed in air. That is to be considered anomalous
because most oxides present an increase of sintering rate in hydrogen
atmosphere, due to the formation of lattice defects in the crystal

structure. (37, 38). Unfortunately, it is impossible to perform an air thermal treatment at temperatures higher than 1500° C and this temperature is not high enough to obtain microspheres at the desired density. Through an hydrogen treatment at 1700° C, instead, microspheres at a density very near to the theoretical value have been obtained. A slow variation in densification rate has been observed in the range 1300 - 1500° C: it is possible to consider the Gd_2O_3 cubic - monoclinic phase transformation responsible for this effect: in fact during the transformation the theoretical density increases from 7.64 g/cm^3 (cubic phase) to 8.33 g/cm^3 (monoclinic phase). The transformation starts at 1300°C and it is to be considered irreversible (39), also if some literature works report the transformation as reversible (40-41). Our experiments performed through the annealing of the Gd_2O_3 monoclinic phase for 840 hours at 950° temperature where the cubic phase is stable, have showed through X - ray analysis the irreversibility of the transformation monoclinic phase - cubic phase. Fortunately, during the phase transformation no craks or morphological modifications have been observed: this favourable effect is due to the poor density of the microspheres when the phase transformation occurs.

The value of the apparent density plotted in fig. 14 has been determined through the mercury picnometry: it has been seen that microsphere density determinations performed through the classic carbon tetrachloride picnometric method are wrong because the open porosity of the microsphere (that is almost the total value) is not considered in the density determination. Also an evaluation of the density of the microspheres through the optical micrographic aspect can be in error owing to the poor resolution of the optical microscopy through which it is impossible to see the small pores contained in the microspheres: through the electron microscopy, in fact, these pores can be seen (fig. 15)

In order to evaluate the changes induced in the microspheres during the sintering treatment total surface area and pore size distribution measurements have been performed with microspheres at different degree of sintering densification. Fig. 16, and fig. 17 show the surface area and pore - size distribution values: it has been confirmed through the surface area determination that the densification rate is higher in air that in hydrogen atmosphere and that the complete densification of the microspheres is obtained solely in the temperature range of 1600 - 1700°C; the pore size distribution meausurements, instead, show that the fine porosity shifts during the densification from 0.08 - 0.10 micron for density of about 40% T.D. to 0.2 - 0.25 micron for density of 70-75% T.D.; it can be seen, in addition, a small increase in the coarse porosity with the increasing of the sintered density of the microspheres; this pore size distribution is in good agreement with the pore distribution of the ceramic compacts submitted to a sintering cycle (42).

Fig. 18 shows some cross sections of Gd_2O_3 microspheres (98% T.D.).
The same microspheres after chemical etching are shown in fig.19; it can
be seen the distinctive type of twinning present in the Gd_2O_3 structure.

3. C O N C L U S I O N S

Gd_2O_3 sintered microspheres (95 - 98% of the theoretical value of the
density) have been prepared through the sol - gel method.

The sol has been prepared through precipitation by ammonia of gadolinium
hydroxide from a 0.2M gadolinium nitrate solution; after washing, the
precipitate has been added of diluted nitric acid until a NO_3/Gd molar
ratio of about 0.15 was raised; then peptized by heating at 80°C for 30
minutes.
The gelled microspheres have been obtained through spheroidization and
gelation of sol by immission in an aliphatic long chain alcohol (i. e.
"Octylol", a commercial product manifacturated by Shell).

The gelled microspheres have been presintered under vacuum up to 950° C
for a total time of about 10 hours in order to decompose the gadolinium
hydroxide, nitrate, carbonate and the adsorbed organic substances.
The presintered microspheres have been hydrogen sintered for 2-3 hours
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| Gadolinium nitrate concentration before precipitation of Gd(OH)$_3$	pH after		Temperature of peptization (°C)	Time of peptization (hrs)	NO_3^-/Gd mole ratio	Size and shape of particles
	dispersion in diluted HNO$_3$	peptization				
0.05	9.2	6.2	80	0.50	0.123	Many crystalline rods from 1900 to 4700 Å long and 190 to 300 Å wide; a few spherical amorphous particles 20÷ 40 Å in diameter.
0.2	9.5	6.4	80	0.50	0.152	All crystalline rods, single or as bundles from 1200 to 2600 Å long and 120 to 240 Å wide.
0.5	9.2	6.3	80	0.50	0.168	Crystalline rods from 1050 to 2600 Å long and 90 to 200 Å wide; a few amorphous spherical particles 20÷40 Å in diameter.
1	9.2	6.3	80	0.50	0.192	Crystalline rods from 1050 to 2600 Å long and 90 to 200 Å wide; a few amorphous spherical particles 20÷40 Å in diameter.
2	9.2	6.1	80	0.50	0.270	Many crystalline rods from 650 to 2100 Å long and 120 to 230 Å wide; few spherical amorphous particles from 20 to 50 Å in diameter.

Scale ⊢————⊣ = 5000 Å

TAB. 1 - Properties of gadolinia colloidal dispersions obtained through different gadolinium nitrate concentrations during precipitation and different NO_3^-/Gd molar ratio.

Gadolinium nitrate concentration before precipitation of Gd(OH)$_3$	pH after		Temperature of peptization (°C)	Time of peptization (hrs)	NO$_3$/Gd mole ratio	Size and shape of particles
	dispersion in diluted HNO$_3$	peptization				
0.05	9.3	6.3	80	0.50	.159	Many crystalline rods from 1200 Å to 2900 Å long and 150 Å to 240 Å wide; few spherical amorphous particles from 20 to 40 Å in diameter.
0.2	9.5	6.5	80	0.50	0.152	All crystalline rods single or as bundles from 1200 Å to 2600 Å long and 120 to 240 Å wide.
0.5	9.3	6.2	80	0.50	0.163	Many crystalline rods from 1200 Å to 1900 Å long and 120 Å to 190 Å wide; many spherical amorphous particles from 20 to 50 Å wide.
1	9.3	6.2	80	0.50	0.149	Many crystalline rods from 950 Å to 3600 Å long and 190 Å to 240 Å wide; a few amorphous spherical particles 20÷40 Å in diameter.
2	9.3	6.3	80	0.50	0.139	Many crystalline rods from 1200 Å to 4050 Å long and 120 Å wide; a many amorphous spherical particles 20÷40 Å in diameter.

Scale ├———┤ = 5000 Å

TAB. 2 — Properties of gadolinia colloidal dispersions obtained through different gadolinium nitrate concentrations during precipitation and about constant NO$_3^-$/Gd molar ratio.
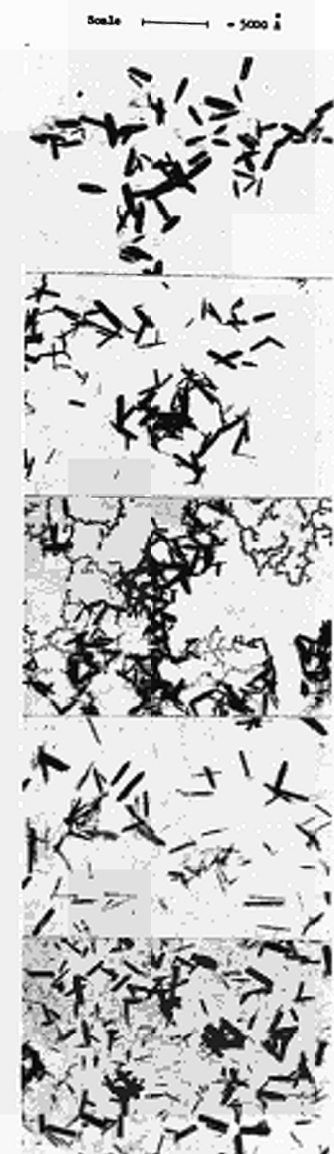
TAB. 3 - Evolution during presintering of physico-chemical properties of 800μ gelled gadolinia microspheres (sol prepared from gadolinium nitrate 0.2 M solution)

	Micro-spheres as gelled	After a constant weight thermal treatment				
		350°C	500°C	650°C	800°C	950°C
Apparent density, g. cm^{-3}	-	1.93	1.87	1.81	1.99	2.1
Specific surface area (BET), m^2 g^{-1}	22.1	34.5	27.9	31.5	22.1	19.1
NO_3^- content, as ppm of nitrogen	8,150	3,530	1,920	330	30	non detectable
CO_3^{--} content, as ppm of carbon (x)	3,950	2,920	1,730	650	50	non detectable

(x) The summarized data are characteristic of our experimental procedure: variation in CO_3^{--} content can occur changing the storage time, the CO_2^{in} atmosphere and in water, the starting materials and the experimental procedure.
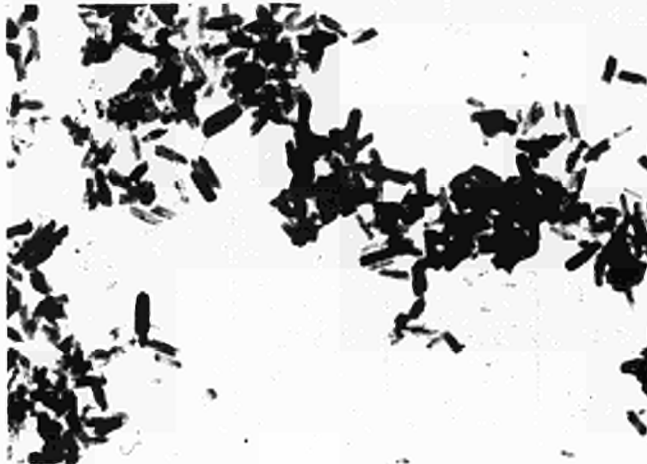
Scale ├──────┤ = 5000 Å

FIG. 1 – Effect of different room temperature aging times on the morphologic aspect of gadolinia colloidal dispersions prepared from gadolinium nitrate 0.2M solution (above: after 12 hrs; below: after 48 hrs).

Scale ⊢————⊣ = 5000 Å
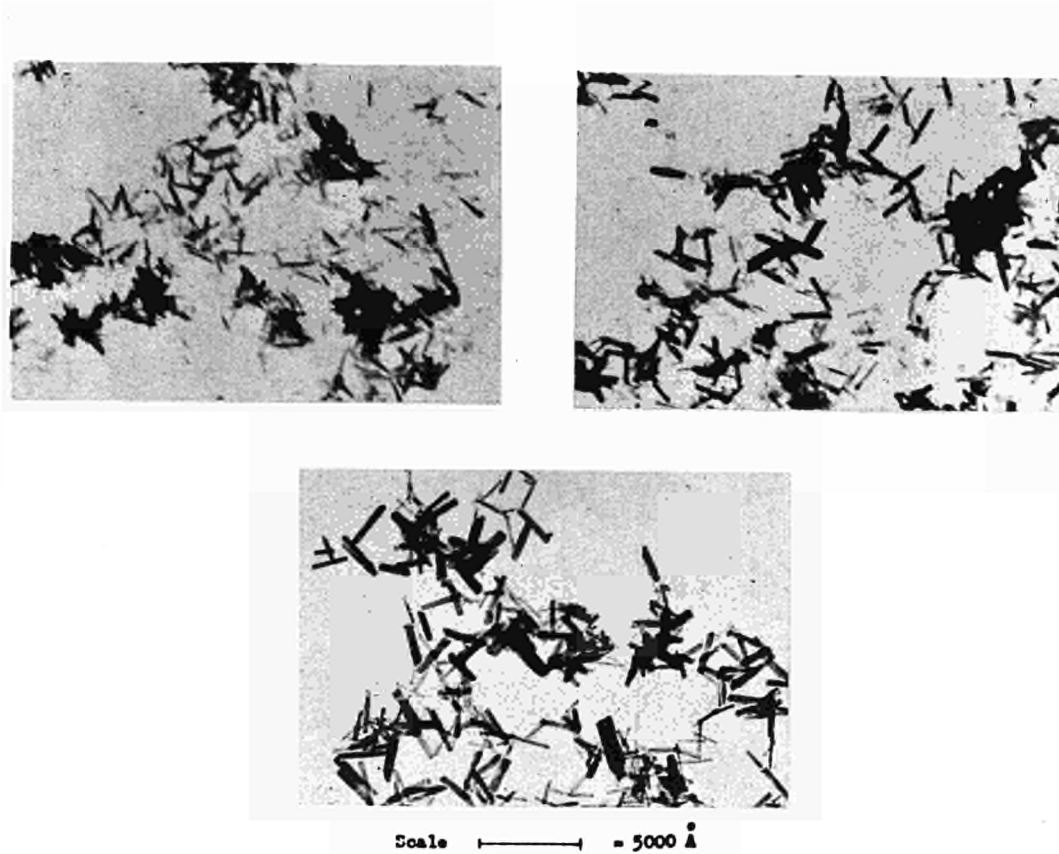
FIG. 2 – Effect of different 80°C aging times on the morphologic
aspect of gadolinia colloidal dispersions prepared from
gadolinium nitrate 0.2M solution (right above: after
5 min.; left above: after 15 min.; below: after 30 min.)
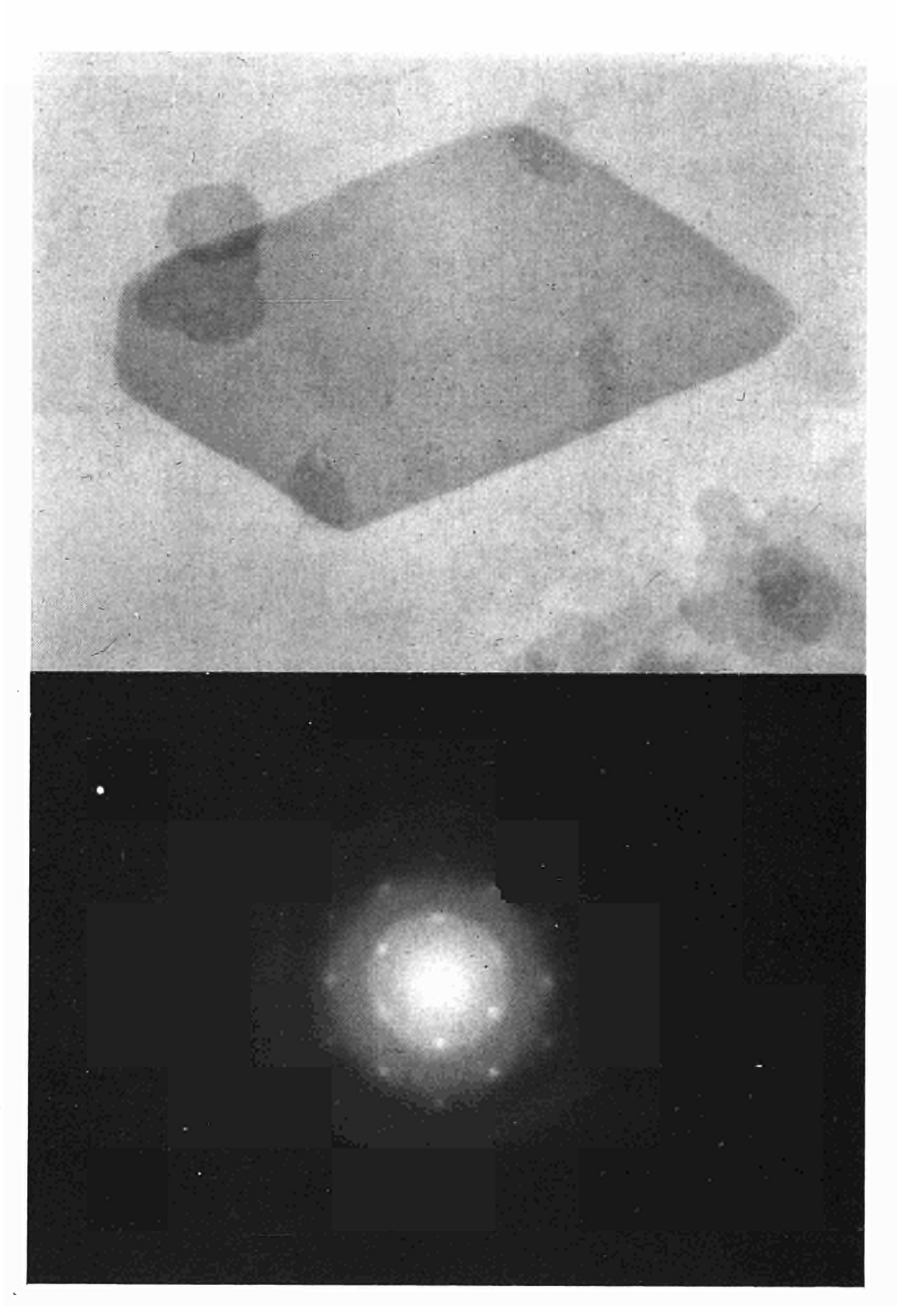
FIG. 3 - Electron diffraction pattern (75 KV) on a single crystal
of gadolinium hydroxide (40,000 x)

Aqueous sol from syringe pump

Two - Fluid nozzle

FL

Tapered column

FL

FL

Product collector
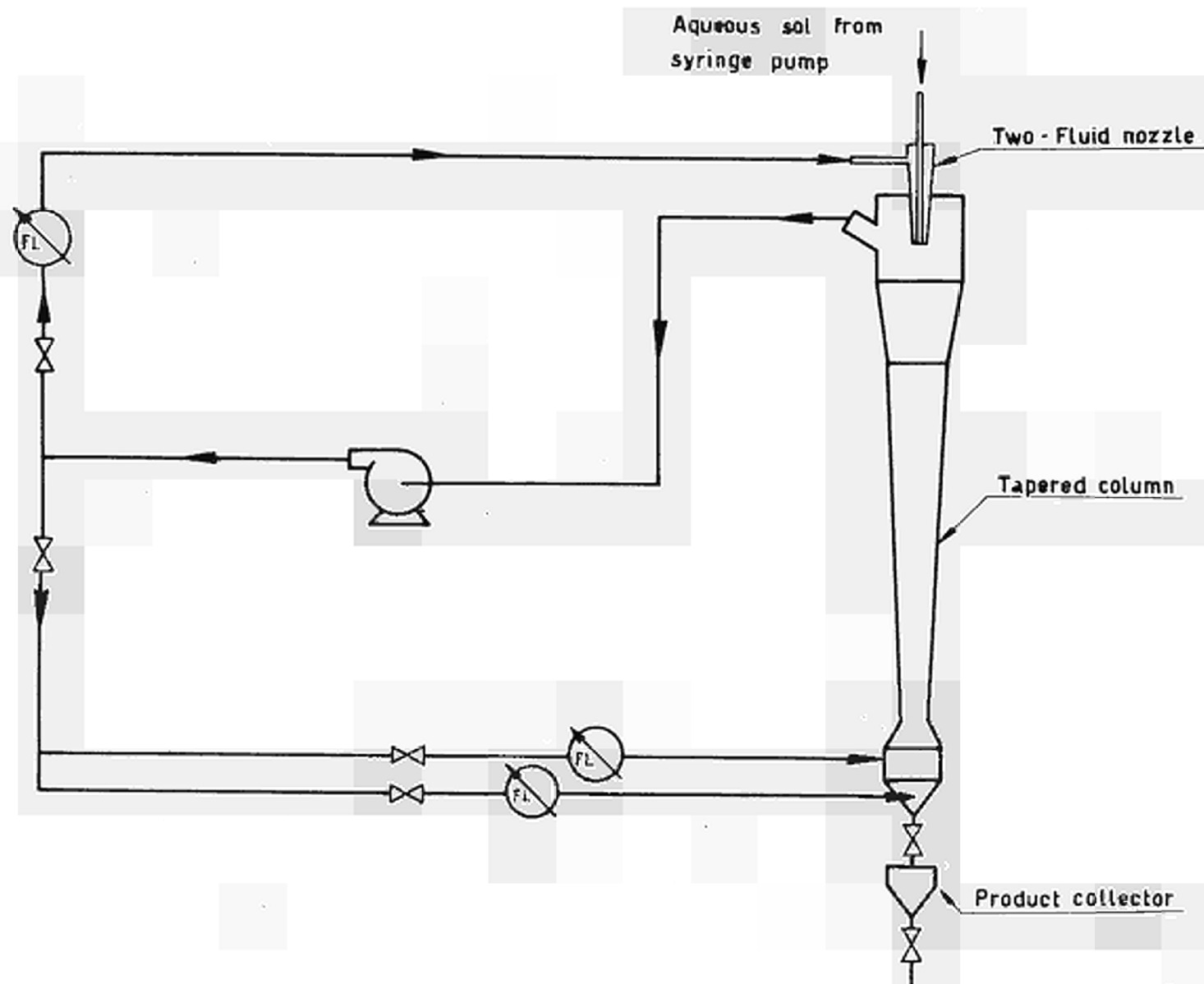
FIG. 4 - Sketch of apparatus for spheroidization and gelation of gadolinia colloidal dispersions.
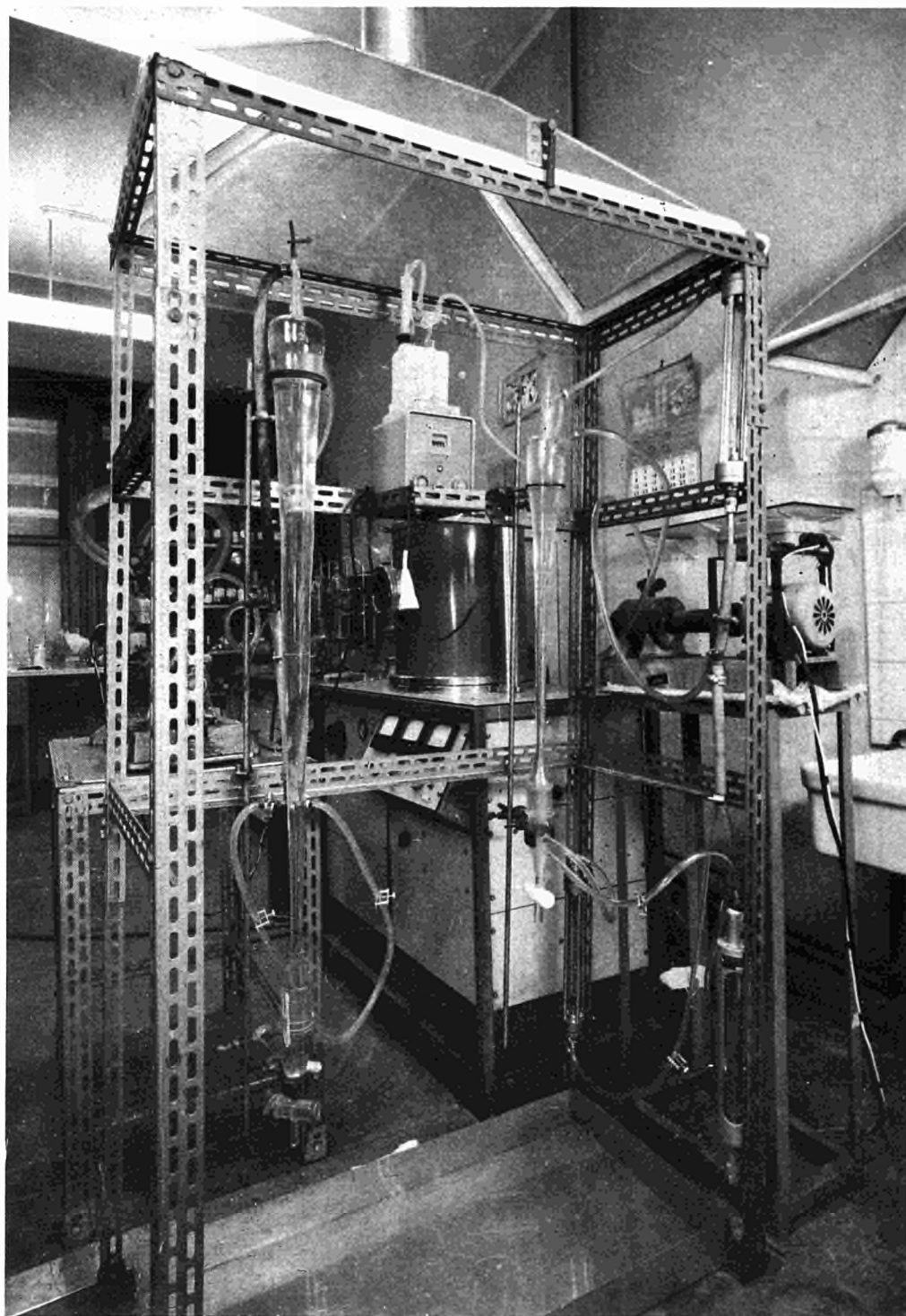
FIG. 5 - Apparatus for spheroidization and gelation of gadolinia
colloidal dispersions.
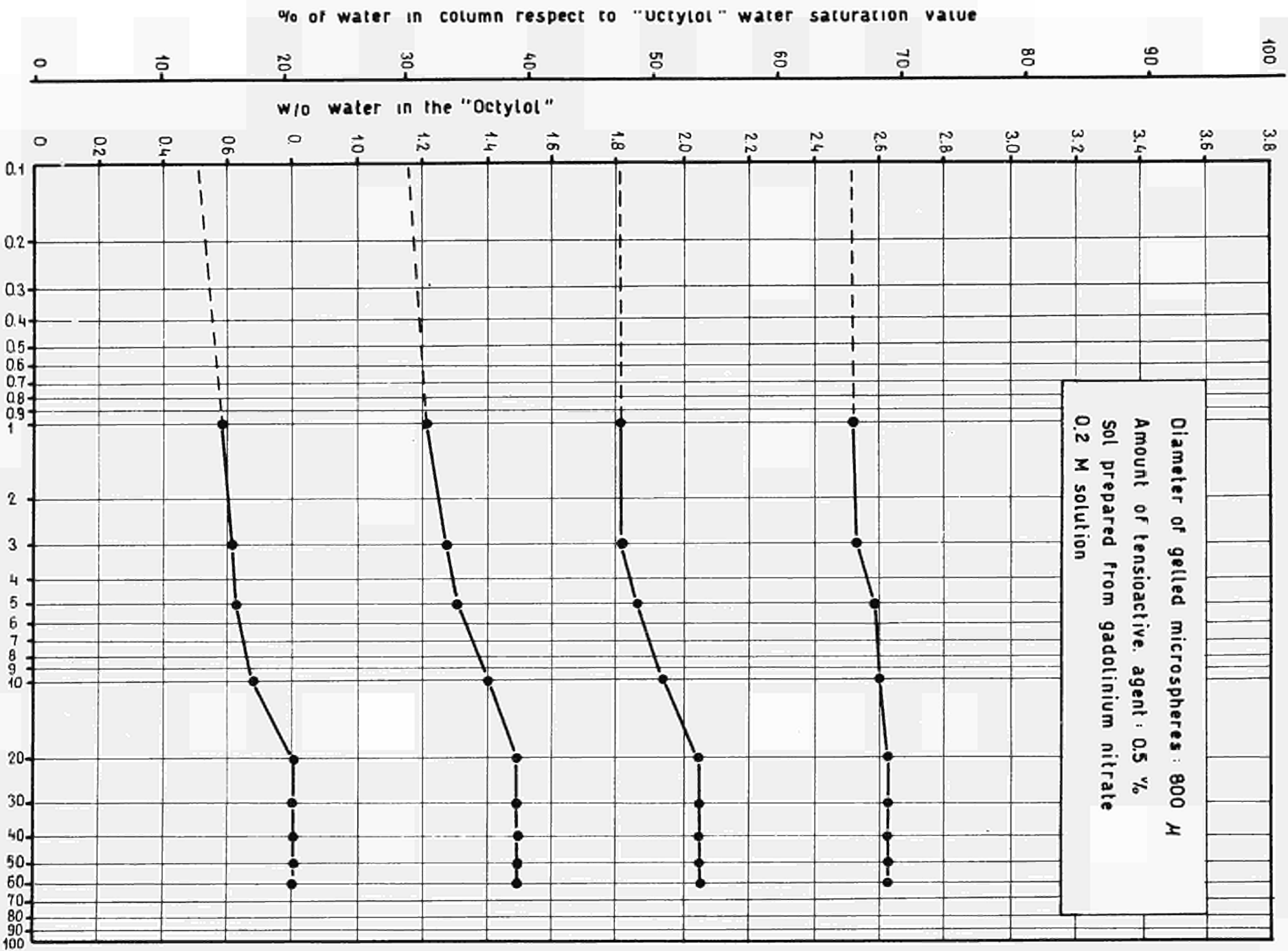
FIG. 6 - Kinetics of dehydratation of gadolinia colloidal dispersions in "Octylol" doped with different water contents.
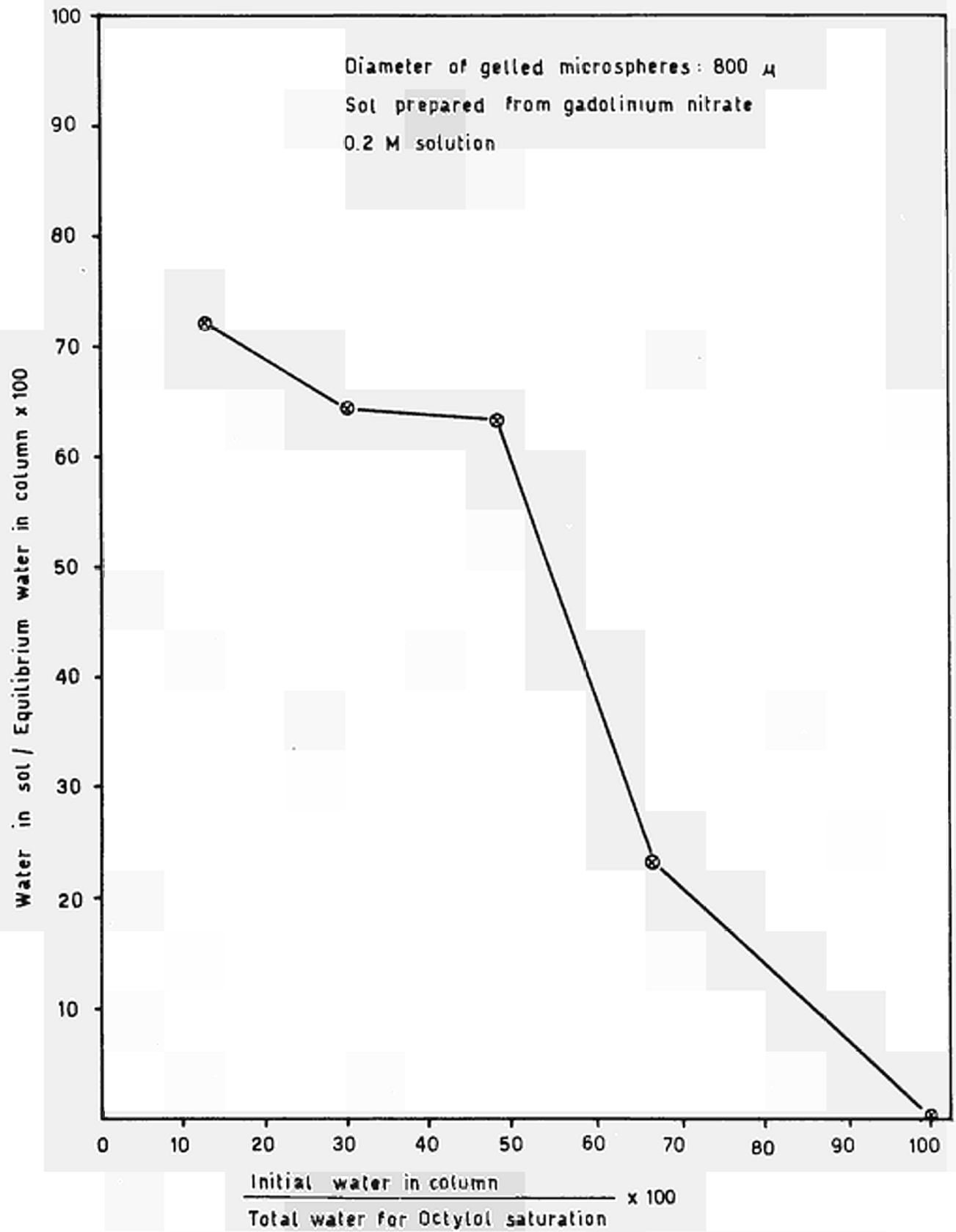
FIG. 7 - Water extracted from gadolinia colloidal dispersions by
"Octylol" doped with different water contents.
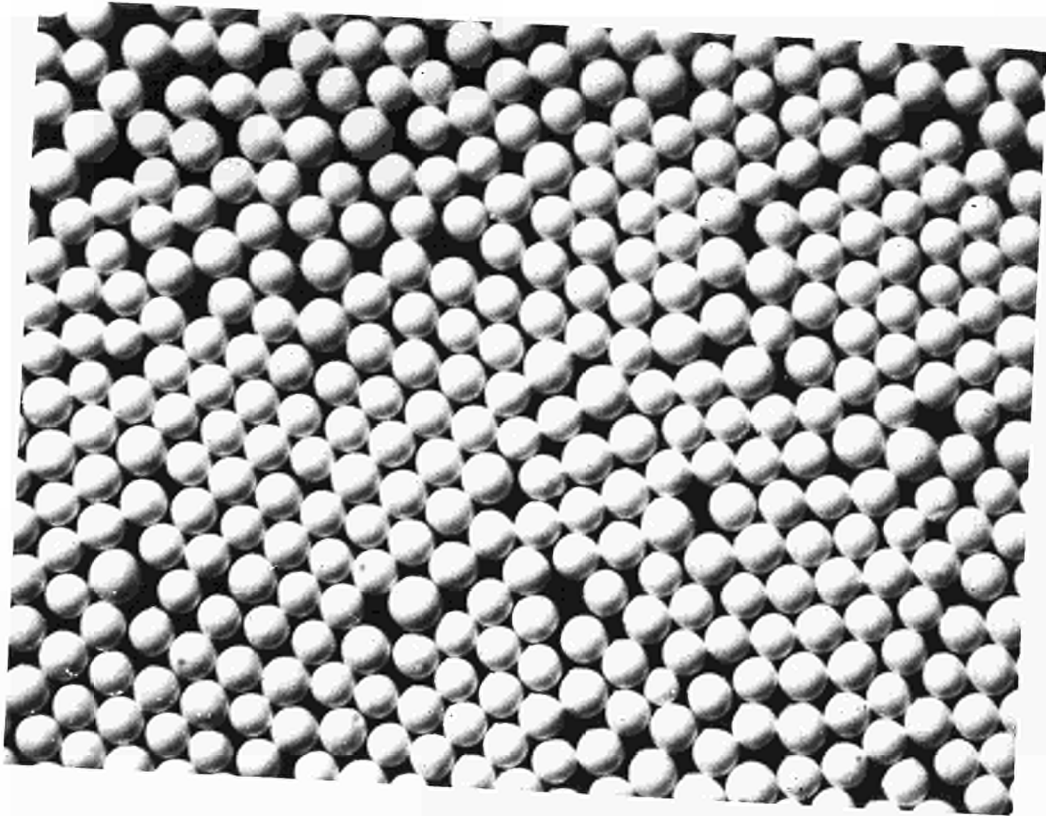
FIG. 8 - Gadolinia microspheres as gelled.   (20 x)
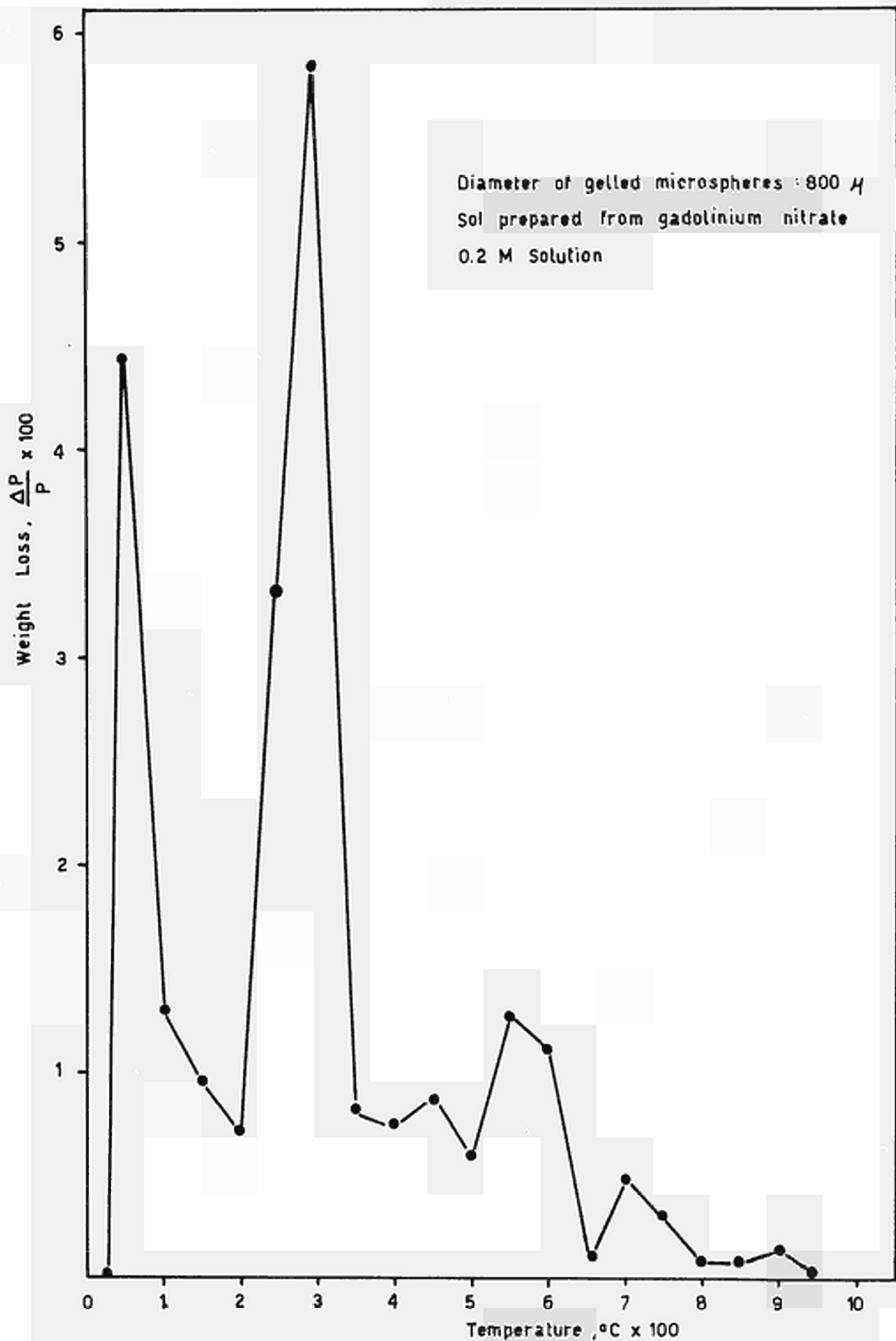
FIG. 9 - Differential weight variation during the presintering cycle of gadolinia microspheres.

Diameter of gelled microspheres : 800 μ

Sol prepared from gadolinium nitrate

0.2 M solution
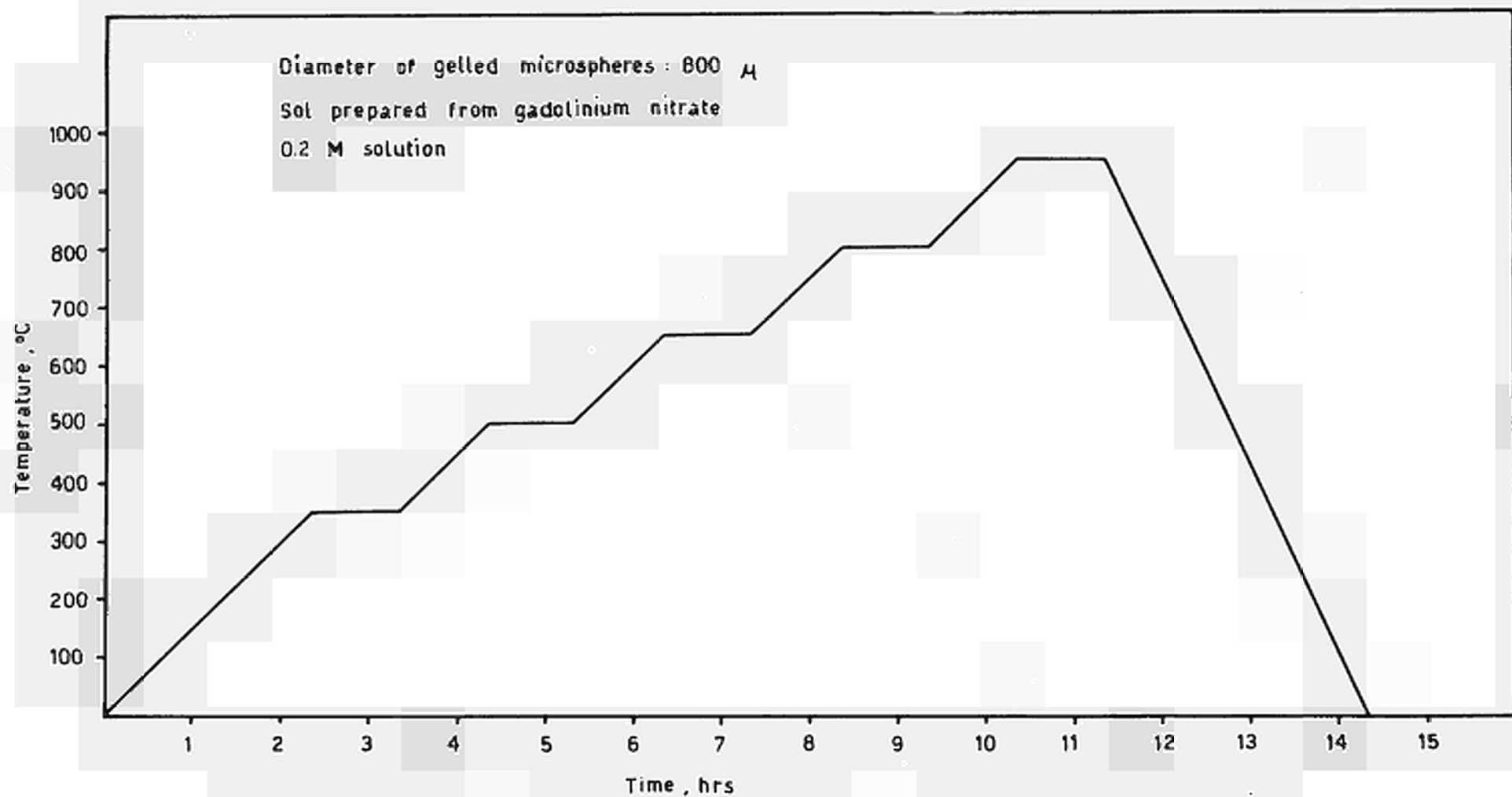
FIG. 10 — Optimized presintering thermal cycle for gadolinia microspheres.

Equivalent Pore Diameter, μ

Diameter of gelled microspheres : 800 μ

Sol prepared from gadolinium nitrate

0.2 M Solution

Legend		
—●—	After a 25 °C constant weight thermal treatment
—■—	After a 150 °C constant weight thermal treatment
—▲—	After a 350 °C constant weight thermal treatment
—○—	After a 500 °C constant weight thermal treatment
—□—	After a 600 °C constant weight thermal treatment
—○—	After a 800 °C constant weight thermal treatment
—○—	After a 950 °C constant weight thermal treatment

Pore Volume Occupied by Mercury , cm³/g

Absolute pressure, psi

FIG. 11 — Open porosity distribution for gadolinia microspheres
after a constant weight thermal treatment.
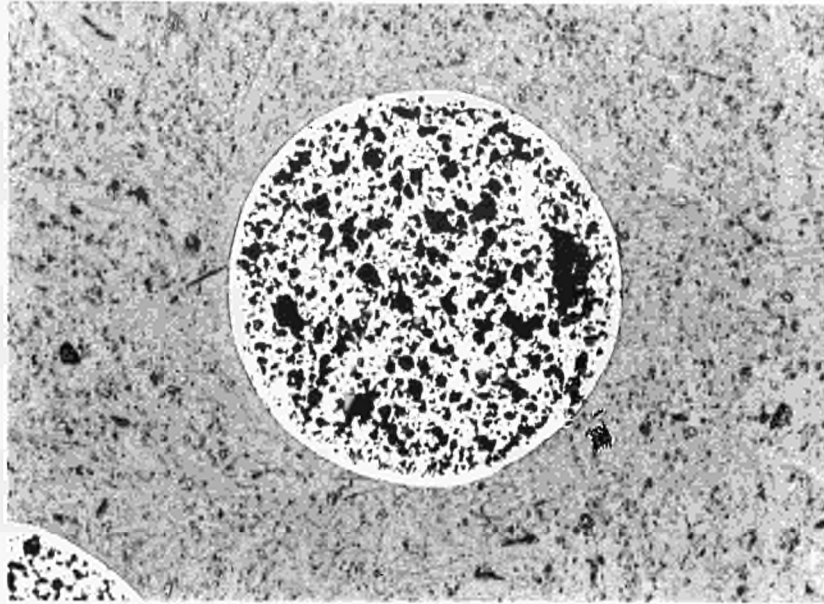
FIG. 12 - A gadolinia microsphere with a fast presintering treatment (500°C/hr).

FIG. 13 – Thin section of presintered gadolinia microspheres (42,000 x) (courtesy of Reichert, Wien).
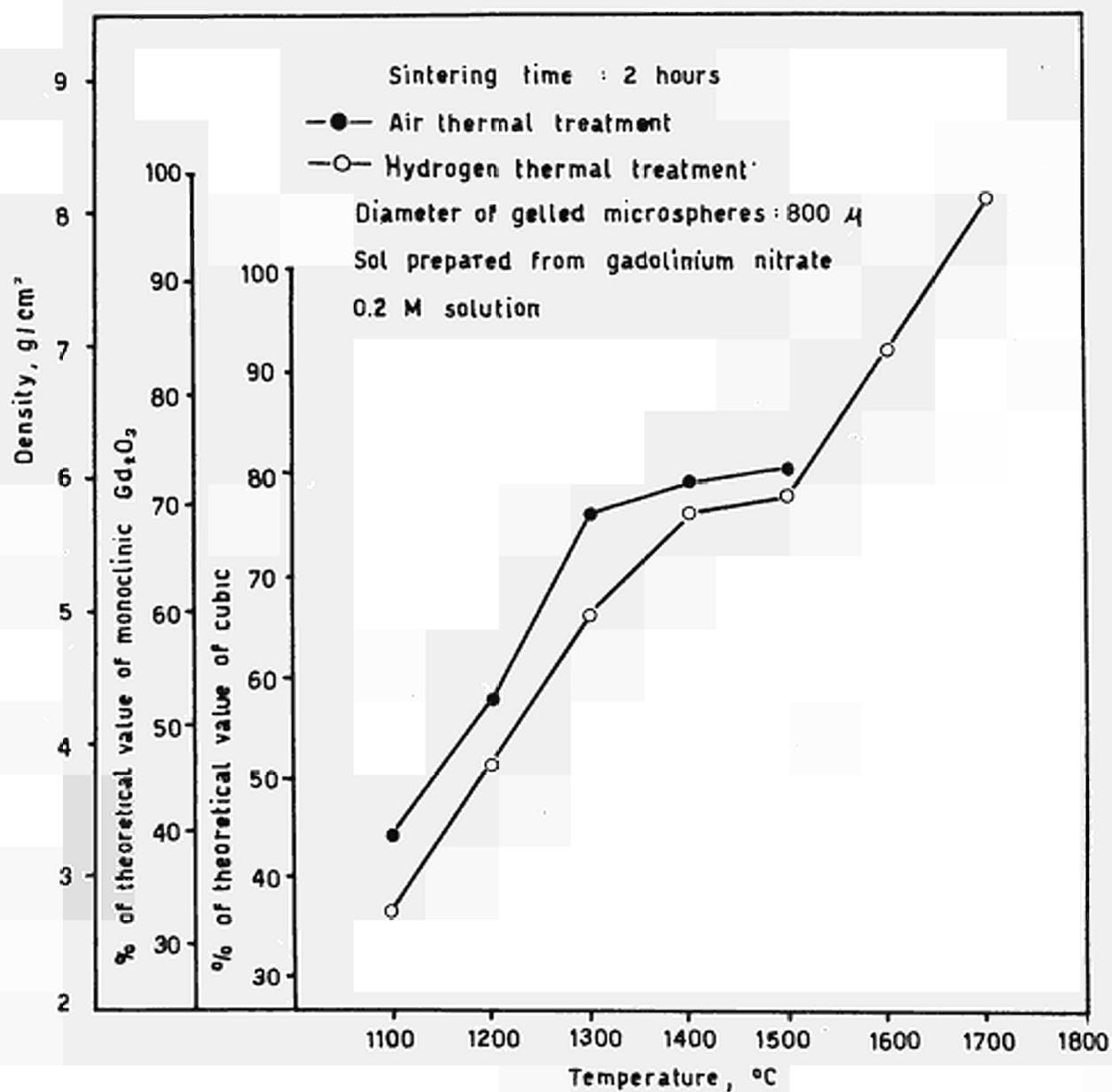
FIG. 14 — Sintered densities versus temperature for hydrogen and air
thermal treated gadolinia microspheres.
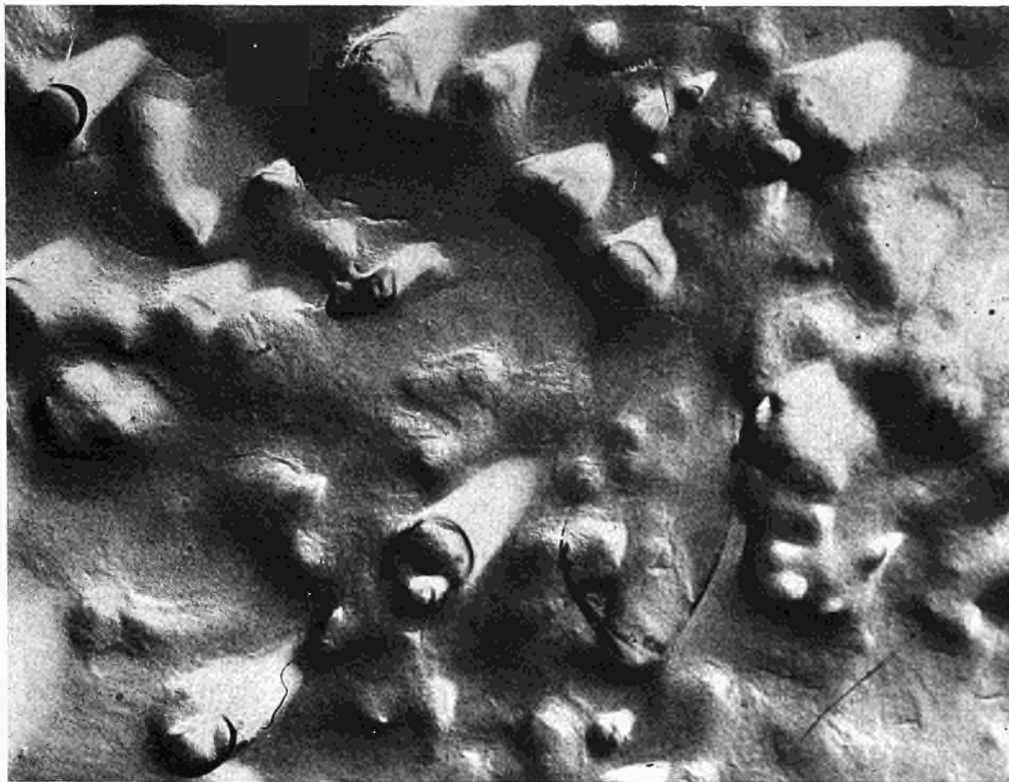
FIG. 15 - Electron micrograph of replicated fracture surface of gadolinia microspheres   (20,700 x)
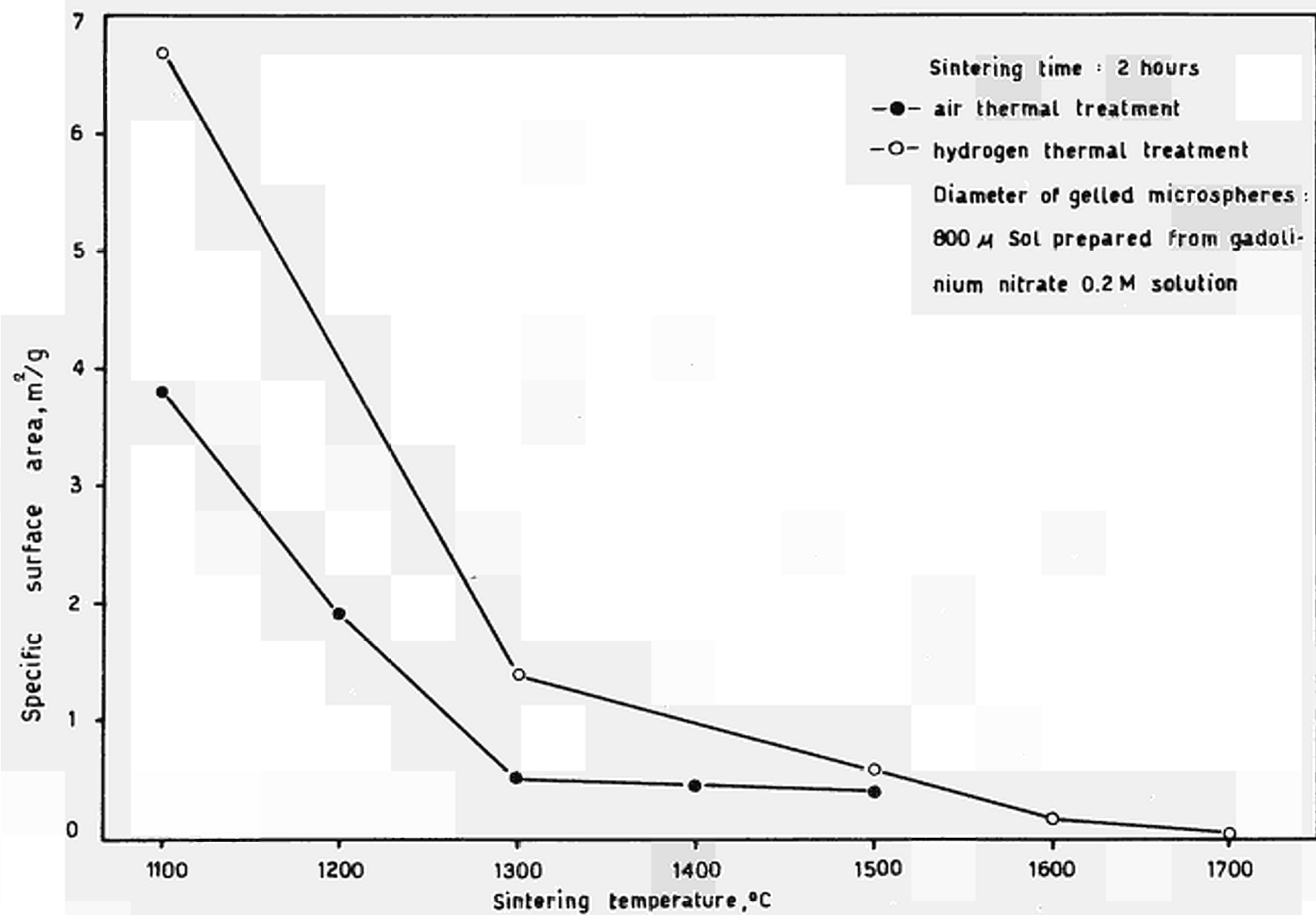
FIG. 16 — Variation of specific surface area (BET) values for gadolinia microspheres during air and hydrogen sintering.
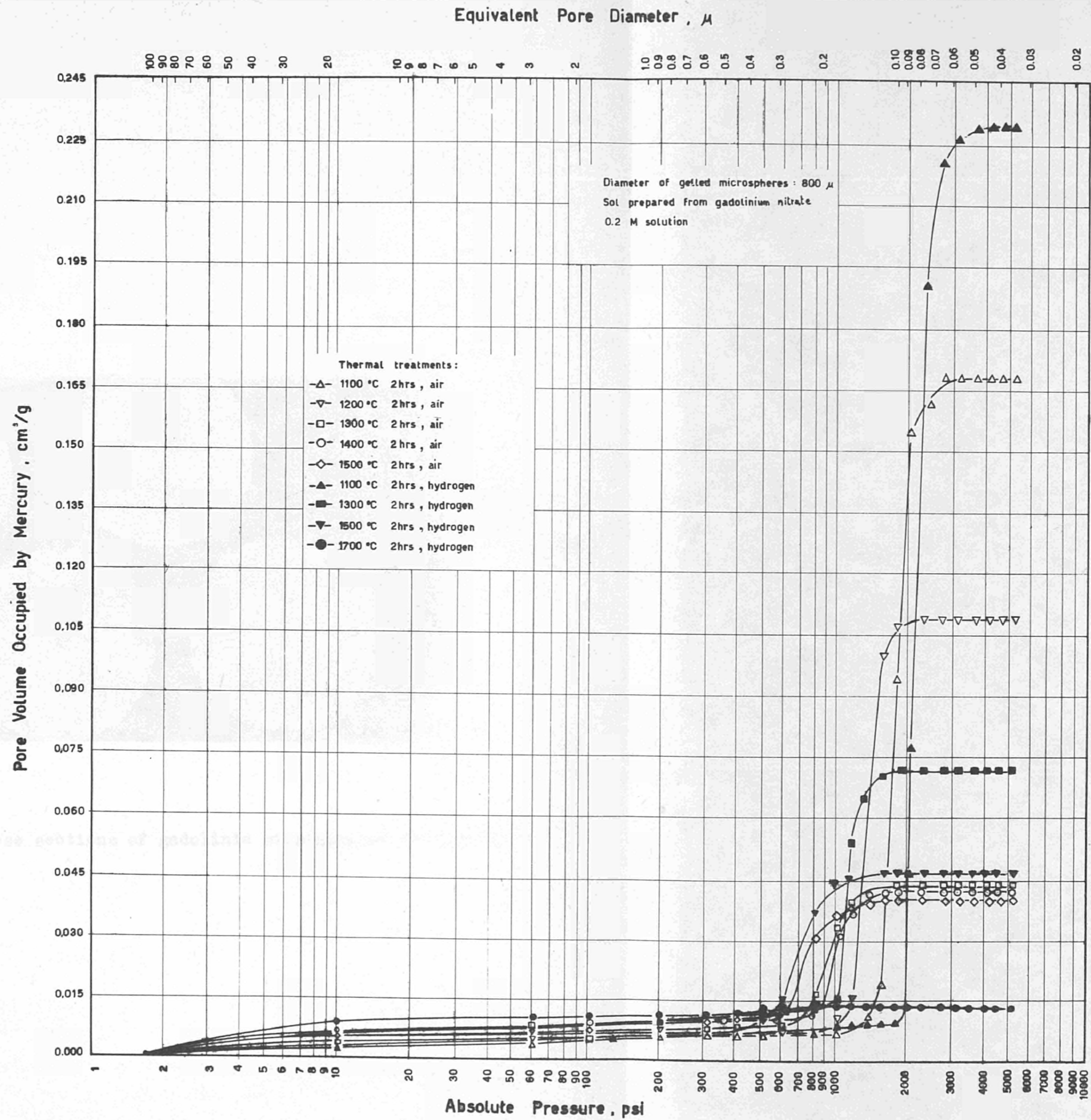
FIG. 17 – Open porosity distribution for gadolinia microspheres air and hydrogen thermal treated.
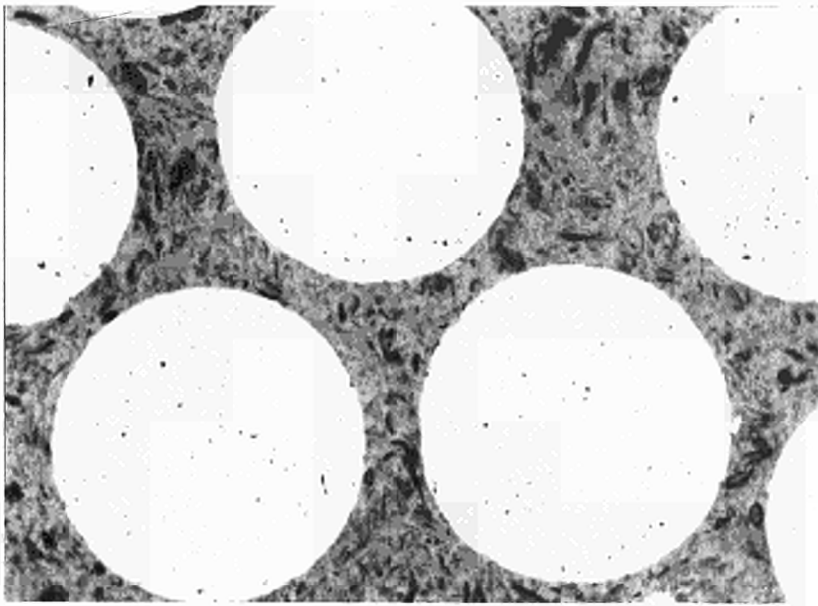
FIG. 18 - Cross sections of gadolinia microspheres 98% T.D. (120 x).
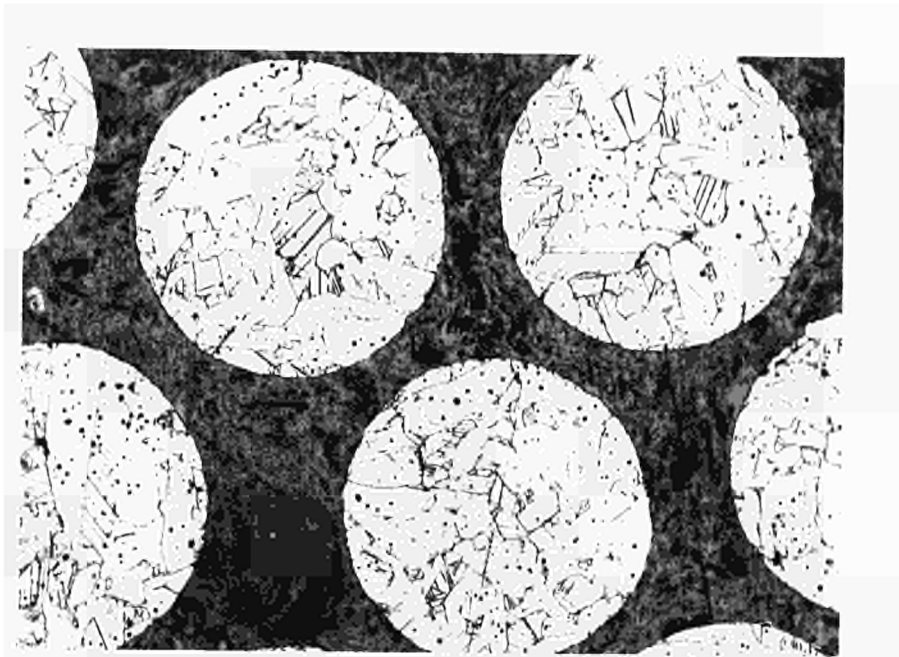
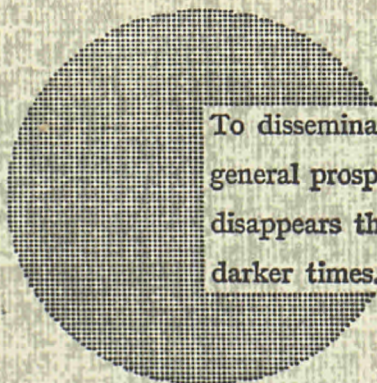FIG. 19 – Cross sections of gadolinia microspheres 98% T.D., etched (120 x).

To disseminate knowledge is to disseminate prosperity — I mean general prosperity and not individual riches — and with prosperity disappears the greater part of the evil which is our heritage from darker times.

Alfred Nobel

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