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CERAMIC AND CERMET TARGETS*

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ABSTRACT

Use of isotopic materials as targets in high temperature environments, e.g., reactor cores, requires that chemically stable forms of the isotopes be employed. Usually oxides are compatible with temperatures >1600 K, although some light element oxides exhibit some volatility at temperatures >1300 K. Especially in the case of heavy elements, the relatively low melting points of the metals, poor compatibility of the metals with encapsulation materials, and high chemical reactivity at moderate temperatures preclude the use of metal targets. However, encapsulation of ceramic targets has been successfully performed yielding high integrity samples. If hydrogen-reducible metals are mixed with the isotope(s), malleable, high strength, corrosion resistant targets can be rolled which contain a ceramic phase of isotope oxide. Isotope dilutions, additions of metals to form the metal matrix of a cermet target, and subsequent homogenization of all components are performed by dissolution in molten urea followed by calcination and compaction into the desired target form.

INTRODUCTION

For more than 20 years, Oak Ridge National Laboratory personnel have prepared unique and exacting specimens of separated stable and radioactive nuclides in physical forms compatible with research in physics, chemistry, and metallurgy. Although not always used for studying subatomic particle interactions with specific nuclei, most samples have been used in this manner by researchers throughout the world. Isotope samples in "target" form can assume physical shapes such as thin films, wires, rods, castings, spheres, and many others. To shape these target samples a variety of methods are employed. However, it is not always possible to prepare the required target either because insufficient material is available, or reduction of a compound form of the nuclide to the element is not feasible, or the end product would not be physically and/or chemically compatible with the temperature or other materials to be used in the desired experiment.

To circumvent some of the above described problems, a technique has been developed to prepare shaped ceramics or cermets (metal-ceramic mixtures) which have the ability to withstand enhanced temperature regimes and yet have readily definable composition and high uniformity of nuclidic distribution. Ceramic materials are, for the most part, more compatible with encapsulation materials than are elemental forms and almost always have lower vapor pressures and better chemical stability so that their use in vacuum or under oxidizing conditions is permissible.

This paper describes methods of preparation of ceramic and cermet starting materials for target preparation, methods of compaction and forming, and the characteristics of resultant specimens.

EXPERIMENTAL DEVELOPMENT

In 1971 W. D. Box reported at the Third International Symposium on Research Materials and Nuclear Measurements on the preparation of neutron dosimetry samples usable in reactor core regimes for the purpose of measuring neutron flux and energy distributions. In this work, powdered oxides of a variety of separated stable and radioactive nuclides were encapsulated in high purity vanadium containers having an outer diameter of 1.25 mm and lengths varying from 3 mm to about 10 mm. Each capsule was uniquely identifiable and contained well-analyzed material, the quantity of which was determined by weight-by-difference on a microbalance. Masses of contained material per capsule varied from 0.1 mg to 9 mg with a measured error of $\pm 1\%$. Preparation of these dosimeters was tedious and subject to error resulting in frequent sample rejection because of the inherent difficulty in handling the powdered materials. Closure welding, decontamination and weighing-by-difference measurements all resulted in time-consuming and error-producing events which subsequently caused the unit cost of acceptable samples to be high.

Chemical Treatment

Recent developments have permitted preparation of similar samples at a cost approaching 50% of the earlier costs. A method whereby desired nuclides could be prepared as easily formed and sinterable powders has been achieved in which the nuclide of interest is dissolved and subsequently precipitated from a molten urea solution (450 K). Dilutions of the nuclide of interest with inert materials, e.g., 1% $^{239}PuO_2$ in MgO, have been prepared in this manner as well as pure materials.

The process simply involves quantitative dissolution of materials containing the nuclides of interest in nitric acid (or directly in molten urea when possible) and addition of urea so that the urea-to-nitrate concentration ratio exceeds 5:1. In batch processing this ratio must be exceeded to avoid severe ebullation during the precipitation process and the subsequent thermal decomposition of excess urea. After precipitation is complete, excess urea is decomposed at temperatures >450 K and eventual calcination of the material at approximately 1110 K in air quantitatively produces a uniform particle size powder.

Depending upon the urea-to-nitrate concentration ratio, particle size can be controlled in the range of 0.05 μm diam to 10 μm diam, the smaller diameter being formed from solutions containing the larger urea concentration. If easily sinterable materials are desired, the particle size should be small. For example, thoria (ThO_2) whose melting point is ∿3500 K, has been sintered into a translucent body of approximately 98% theoretical density at 1720 K when the ceramic powder was produced by precipitation from a 20:1 mole ratio of urea to nitrate ion.

Of importance is the ease with which chemical composition of the oxide powders can be controlled and the subsequent shaping and densification into the desired physical form is achieved. Because the "urea process" is quantitative, dissolution of carefully compounded admixtures of materials at the beginning of the process result directly in the same composition of the precipitated powder in the end, the only possible variation arising from volatility of a component at the required calcination or sintering temperature. Dilutions of isotopically pure materials in MgO and Al_2O_3 have been prepared in which variation of composition did not occur to more than $\pm 0.1\%$ after the physical form was produced.

Physical Forming Procedures

Depending on the physical shape of the target sample, a variety of forming and densification procedures can be used. In the case of neutron dosimetry materials noted above, a "wire" form of the ceramic containing the nuclide(s) of interest is most desirable. By mixing the calcined powder prepared from the urea process with a lubricant-binder material, e.g., 2% polyethylene in paraffin, wire can be extruded, Figure 1. Subsequent heating of the formed material in MgO tubes, Figure 2, causes the powder to sinter (the binder being thermally volatilized and/or chemically decomposed) with resulting densities >90% of the theoretical value. High-fired MgO tubes are used to contain the "green" extruded material during the sintering process so that straightness of the wire is maintained.

A system for continuous extrusion of green material is shown in Figure 3 wherein wire is spooled on a reel after extrusion. As much as 100 m of wire has been produced by this latter technique with a single loading of the extrusion die. Typical dosimeter wires produced by this

procedure are shown in Figure 4. A photomicrograph of sintered thoria is shown in Figure 5 to illustrate the high density structure achieved by the sintering of urea-produced ceramic powder.

The efficacy of extrusion of sinterable isotope-bearing ceramics is dramatically illustrated by our preparation of $^{244}Cm_2O_3$ ribbon of rectangular cross-section. Lengths of 21 mm of 3.0 mm x 6 mm cross-section Cm_2O_3 were required for material compatibility and radiation damage studies. By extrusion using a Roger A. Reed Corp. wax (known as No. 77030) as the binder and subsequent sintering these samples were prepared. Resultant density was 59.4% of the theoretical value. Since samples were required to be fitted to +0.0 mm, -0.05 mm, in terms of thickness, width, and length, the extrusion die nozzle dimensions were defined after determining shrinkage of the extruded material upon sintering at 1700 K. The extrusion die assembly, extruded and sintered samples, and the sample holder is shown in Figure 6. All operations with this material were performed in an argon atmosphere glove box to maintain the sesquioxide composition. Heat generated by the ^{244}Cm decay required the use of a high melting point wax binder (noted above) and extrusion and sintering were required to be performed within 12 hr because radiation degradation of the wax precluded satisfactory forming if longer periods were involved.

Another forming method is hot pressing which has been employed to produce disc-shaped samples of actinide oxides as used in neutron reaction rate measurements. Powders produced by the urea process are easily densified in ATJ graphite dies by hot pressing at temperatures of 1100-2000 K and at pressures of 14-34 MPa (2000-5000 psi). A schematic representation of a typical hot press used for this purpose is illustrated in Figure 7.

The hot pressing procedure is used to form rods of an actinide oxide which can be sawed, subsequent to pressing, using an abrasive wheel or a diamond saw. Densities approaching 98% of theoretical have been achieved and circular wafers of approximately 4-mm thickness have been produced from actinide oxides including americium. Because of the hazardous nature of these materials, such samples must be encapsulated for handling and/or insertion into a reactor core zone. To encapsulate disk-shaped samples a thermal pressure bonding technique was developed. A typical pressure bonding system is shown in Figures 8 and 9. Copper or aluminum has been used to encapsulate the isotope samples by this technique.

The pressure bonding apparatus is simply a circular die prepared from tungsten carbide which will not deform significantly under pressures of 14-28 mPa (2000-4000 psi) and temperatures of approximately 750 K. Preformed discs of encapsulating metal, Figure 8, are inserted and the ceramic actinide disc is centered in the metal sandwich. Subsequent pressure and heating by electrical resistance in the die at the periphery of the capsule results in a bond which, when examined metallographically, shows no definable interface between the metal layers. The outer sleeve surrounding the ram of the die is used both to center the composite pieces in the die and to subsequently shear the finished capsule to the appropriate diameter.

RESULTS

Use of urea-produced oxide powders permit preparation of unique ceramic and cermet target samples. Dilutions of specific isotope nuclei can be produced by addition of the diluent nuclide in the dissolution step of the urea process which results in essentially atomic homogenization of the mixed species. By this preparative process, a wide variety of pure and diluted isotope samples have been prepared, Table 1.

Table 1. Varieties of Extruded-Sintered Ceramic Wires Produced by the Isotope Research Materials Laboratory

Composition	Diameter (mm)	Length, m
$^{232}ThO_2$	0.5,0.7	350
$^{233}UO_2$	0.5,0.7	350
$^{235}UO_2$	0.5,0.7	350
$^{238}UO_2$	0.5,0.7	350
$^{237}NpO_2$	0.5,0.7	350
$^{239}PuO_2$	0.5,0.7	350
Sc_2O_3	0.5,0.7	350
1% $^{233}UO_2$-MgO	0.5,0.7	300
1% $^{235}UO_2$-MgO	0.5,0.7	610
1% $^{238}UO_2$-MgO	0.5,0.7	610
1% $^{237}NpO_2$-MgO	0.5,0.7	610
1% $^{239}PuO_2$-MgO	0.5,0.7	610
1% $^{232}ThO_2$-MgO	0.5,0.7	610
16% $^{61}NiO_2$-MgO	0.8,1.2	50
1% CoO-MgO	0.5,0.7	610
$^{238}UO_2$	4.8	0.5
$^{238}UO_2$ (Tubing)	4.8 o.d.,2.8 i.d.	0.5

Extrusion of coprecipitated and calcined oxides can be performed to shape materials into desired forms having very narrow dimensional tolerances. Table 1 notes the variety of shapes and sizes that have been formed by extrusion. Preparation of samples of this type would be impossible by other methods, especially where highly radioactive and toxic materials are required. The urea process and subsequent forming processes are readily compatible with a glove box environment and have been used in this mode at ORNL.

If urea-precipitated powder contains a reducible cation(s) species, subsequent heating of the species in a reducing atmosphere yields a metal phase of uniform distribution on a nearly atomic scale in the mixture. Subsequent compaction and densification of such a mixture results in a cermet in which the ceramic phase is microencapsulated in a metallic phase. Composition of the metal and ceramic phases can be tailored by additions at the beginning of the urea process.

Depending upon the quantity and composition of the metal phase, it is possible to form cermets (and alloys) which are malleable and formable by standard rolling and forging techniques. For example, actinide oxide in a copper or nickel matrix can be formed by rolling into highly uniform foils. Provided the concentration of the ceramic phase is insufficient to harden the matrix metal to a nonmalleable condition, thin foils can be rolled nearly to thicknesses achievable with the pure metal. Distribution uniformity of >99% have been achieved in this manner. Cermets are amenable to cold forming under pressure and excellent samples suitable for cross-section measurements can be prepared in this manner.

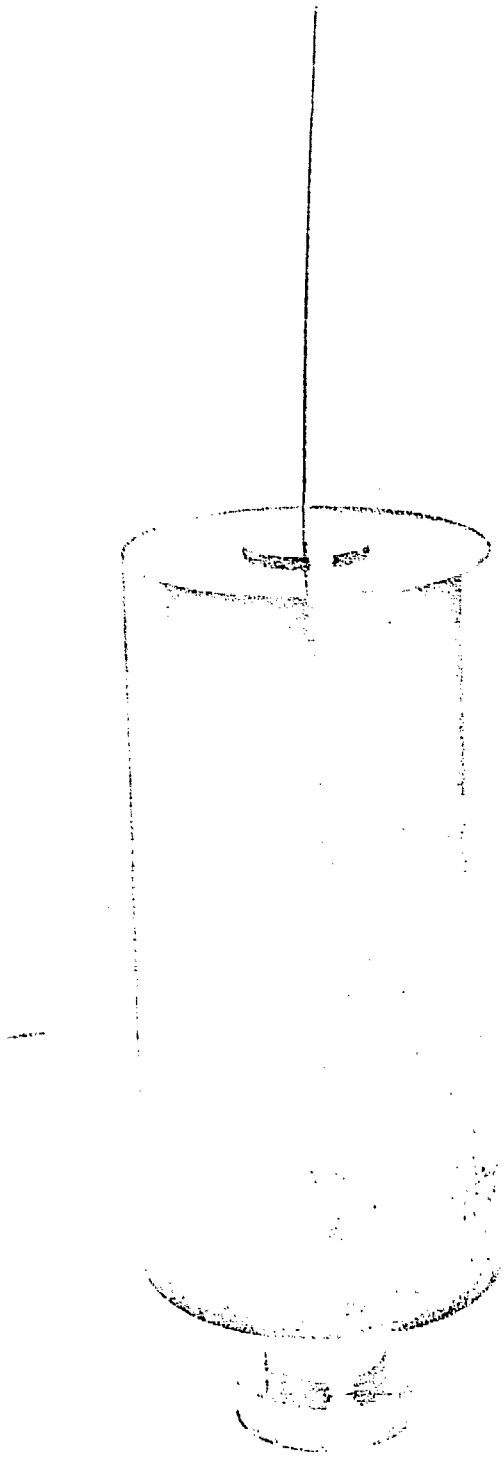
Finally, it should be recognized that this technique is applicable to preparation of thick samples of many difficult to handle isotopes, e.g., Ru, Ir. Dispersion of these elements in metal matrices is sometimes the only method of achieving a desired sample thickness or configuration. Unusual shapes can be prepared from urea-precipitated materials. A specific case in point was the preparation of 12-mm diam UO_2 tubing with a 2-mm wall thickness. This material was prepared by extrusion in tube form using a wax binder. Because of shrinkage upon sintering, the green extruded samples were about twice the diameter of the final densified specimens.

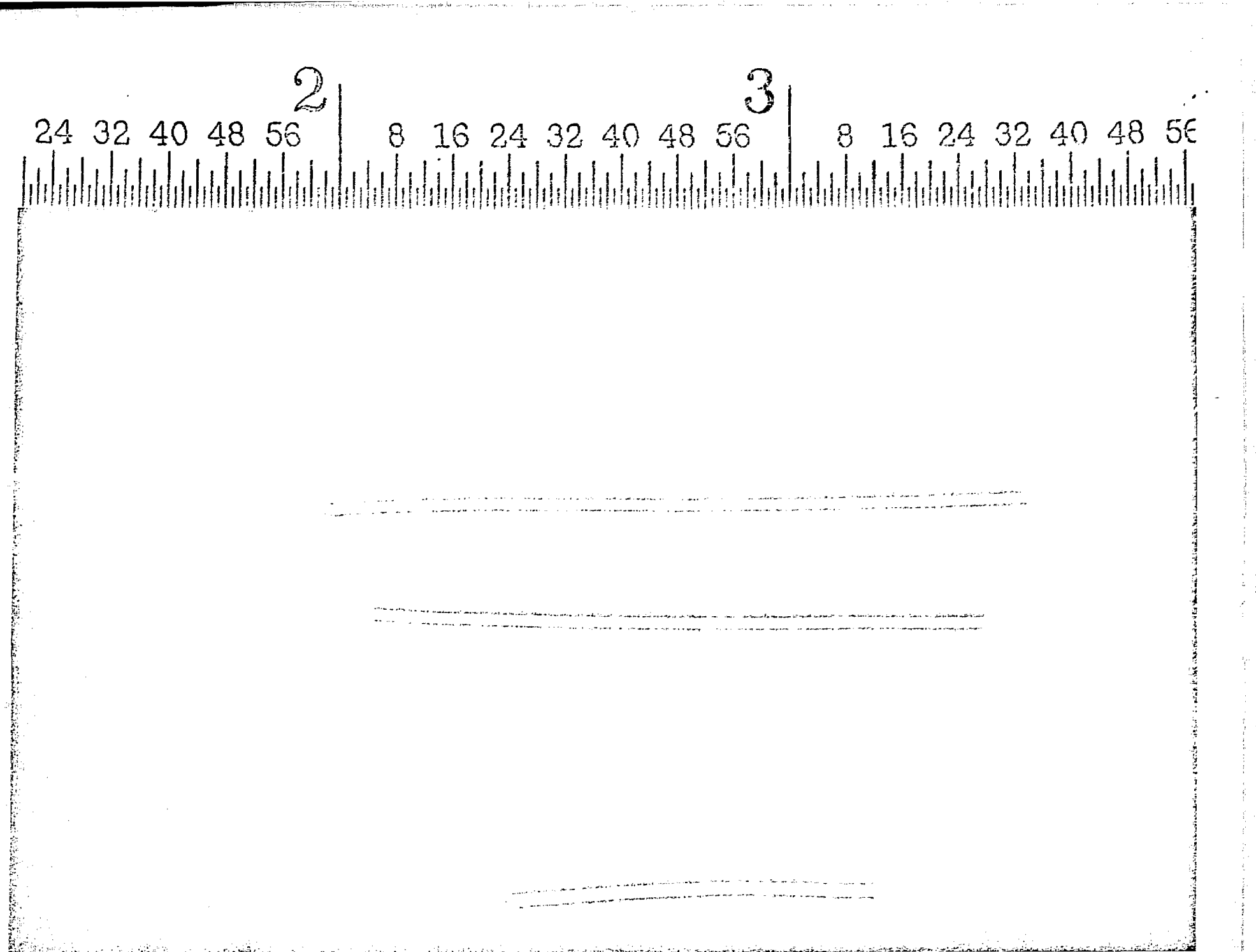
CONCLUSIONS

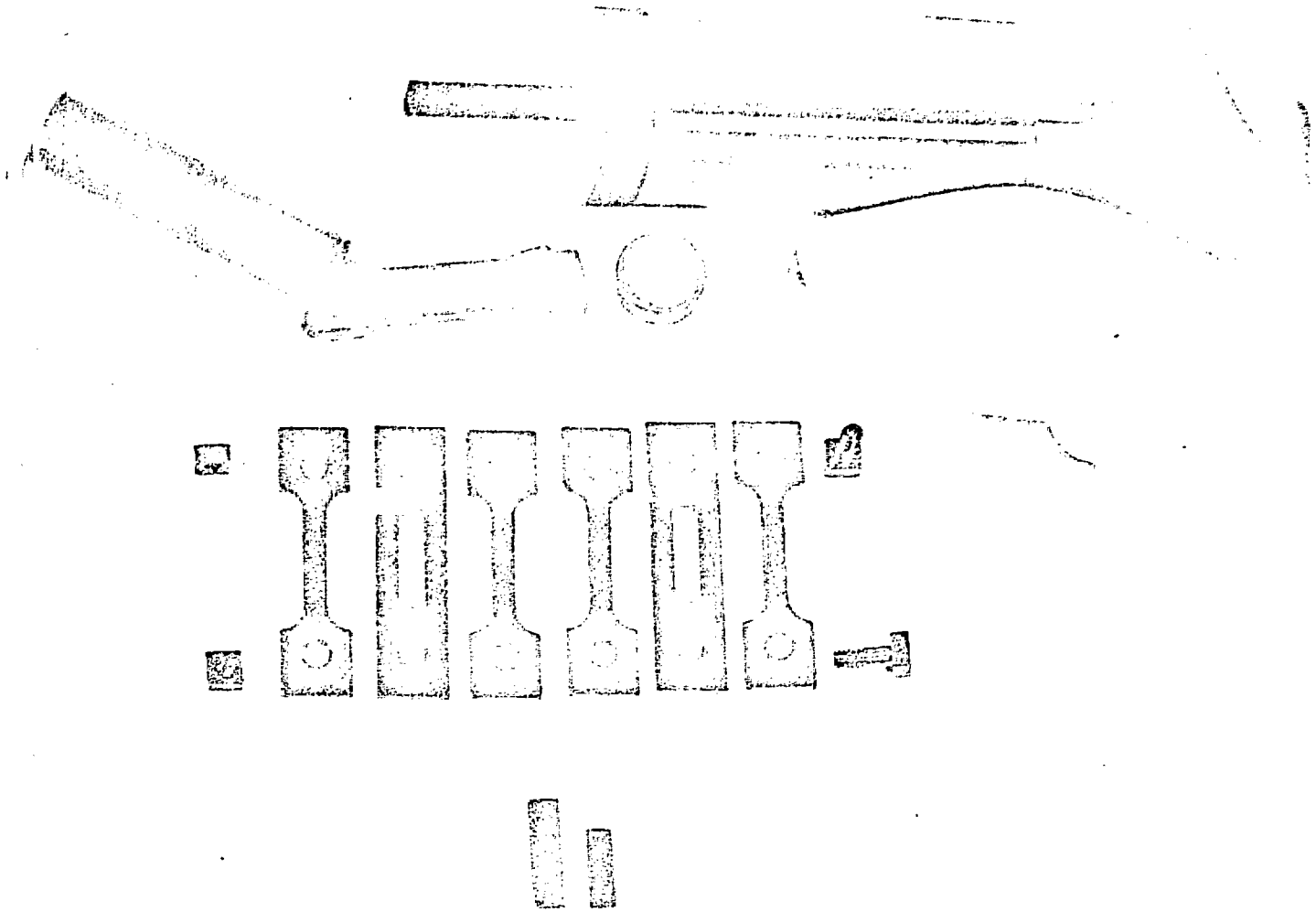
The urea precipitation process together with a variety of physical forming methods adds considerable versatility to target and other form preparation capability. The technique is especially adaptable to the forming of sinterable ceramic samples and offers an alternative preparative method for some hard-to-handle materials. Preparative processes are amenable to glove box operations and are very useful in producing high quality actinide samples. Cermets containing desired nuclei in the ceramic phase can be cold-compacted and even formed by rolling and forging. Although not a panacea for all target preparative problems, ceramic and cermet target forms may be the only applicable specimen forms suitable for the experimental environment in which they are to be used. The relatively simple thermal pressure bonding method of sample encapsulation offers an additional dimension of versatility in providing leak-tight, reactor compatible samples.

FIGURE LIST

Figure No.	
1	Green ceramic wire extruded from a steel die using 2% polyethylene in paraffin as the binder-lubricant.
2	Magnesia tubes are used to contain green extruded ceramic wire so as to maintain straightness during sintering.
3	Continuous extrusion of green wire and subsequent spooling permits up to 100 m lengths to be formed.
4	Typical dosimeter wires as formed by extrusion and sintering. From top to bottom: UO_2, 1% CoO-MgO, Sc_2O_3, Mn, 13% NiO-MgO.
5	Surface structure of a ThO_2 extruded and sintered wire illustrates high density structure. Note extrusion mark at top of photomicrograph (9000X)
6	Cm_2O_3 extrusion with a wax binder produced ribbons suitable for sintering. Illustrated is the extrusion die, green and sintered material, and sample holder assemblies. Ribbon samples before and after sintering are shown at the bottom of the photograph.
7	Hot press schematic diagram illustrates simplicity of preparation of flat, disk-shaped actinide oxide samples.
8	A disassembled view of thermal pressure bonding die is shown in photograph. At lower center-right is shown a ceramic, hot-pressed disk of UO_2 to be encapsulated in the copper shell on which it rests. Larger copper capsules are then bonded around the small inner capsule (No. 41 shown in illustration).
9	A pressure bonding die assembly in the closed position is shown; assembly used to form large capsule enclosures is illustrated in Figure 7. High current-low voltage power is used to heat the capsule parts under pressure by resistive heating. Outer sleeve (middle of photograph) is used to center capsule components and to shear expanded metal to appropriate diameter after press-bonding.







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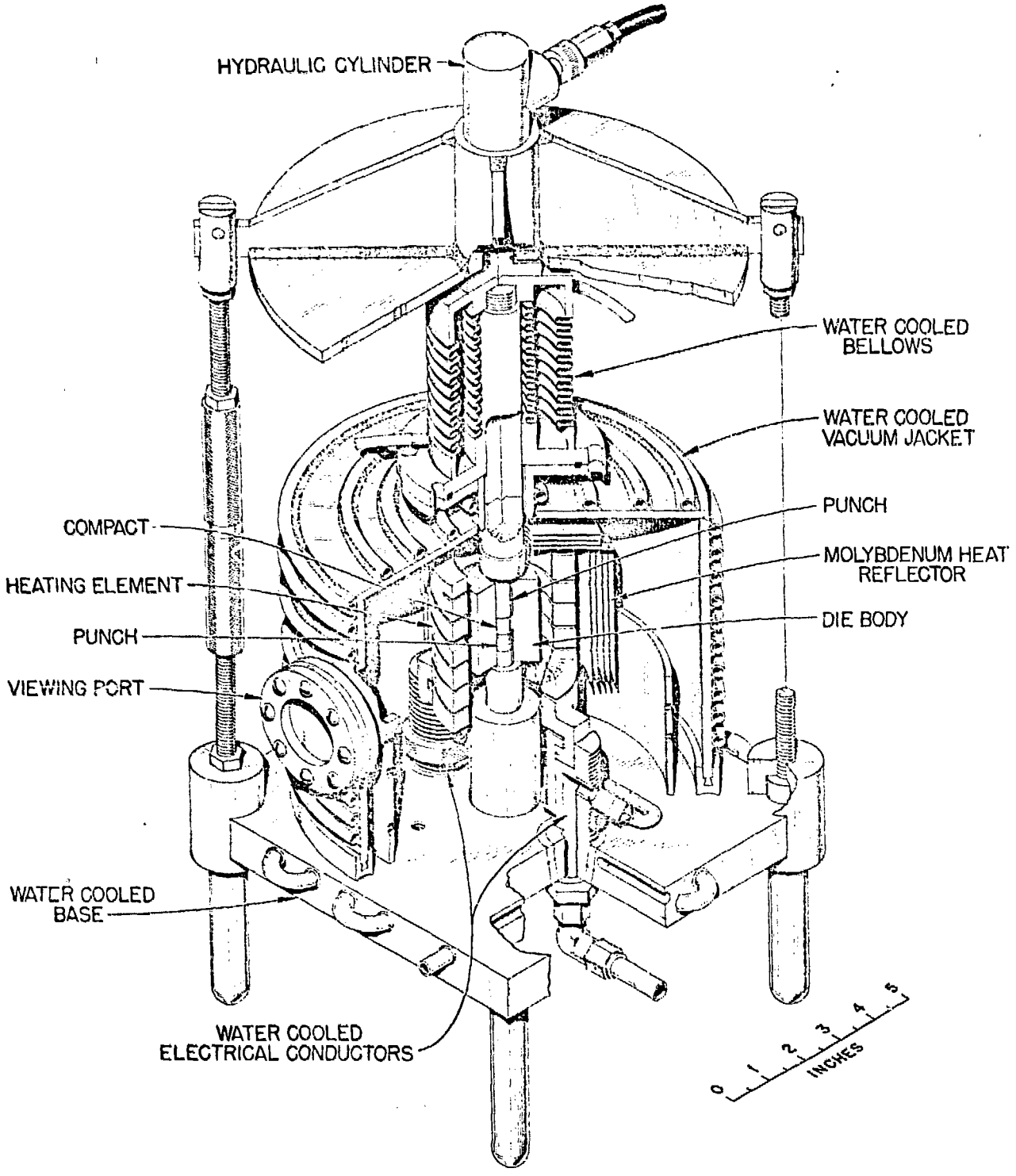
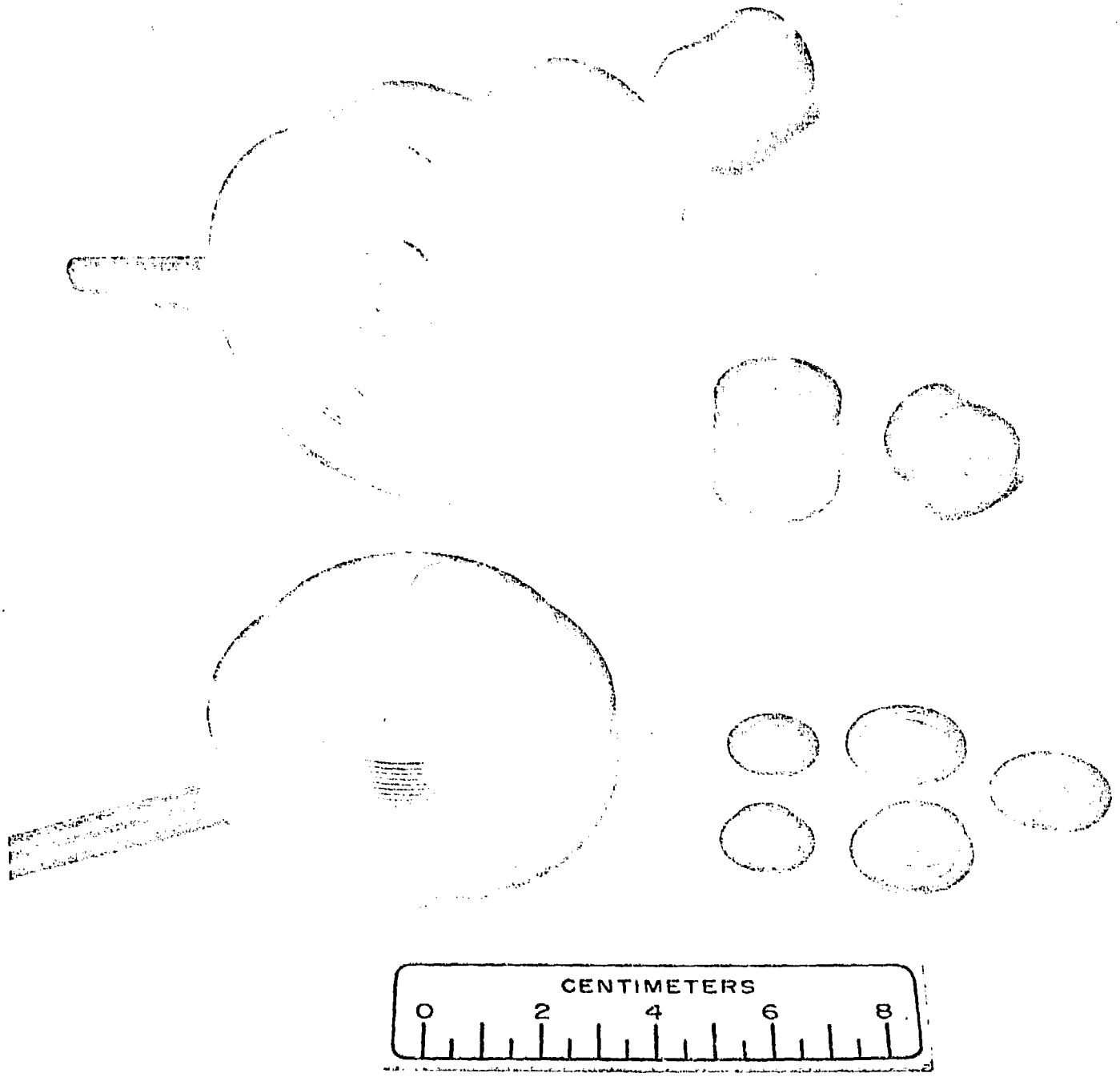


Miniature Hot Press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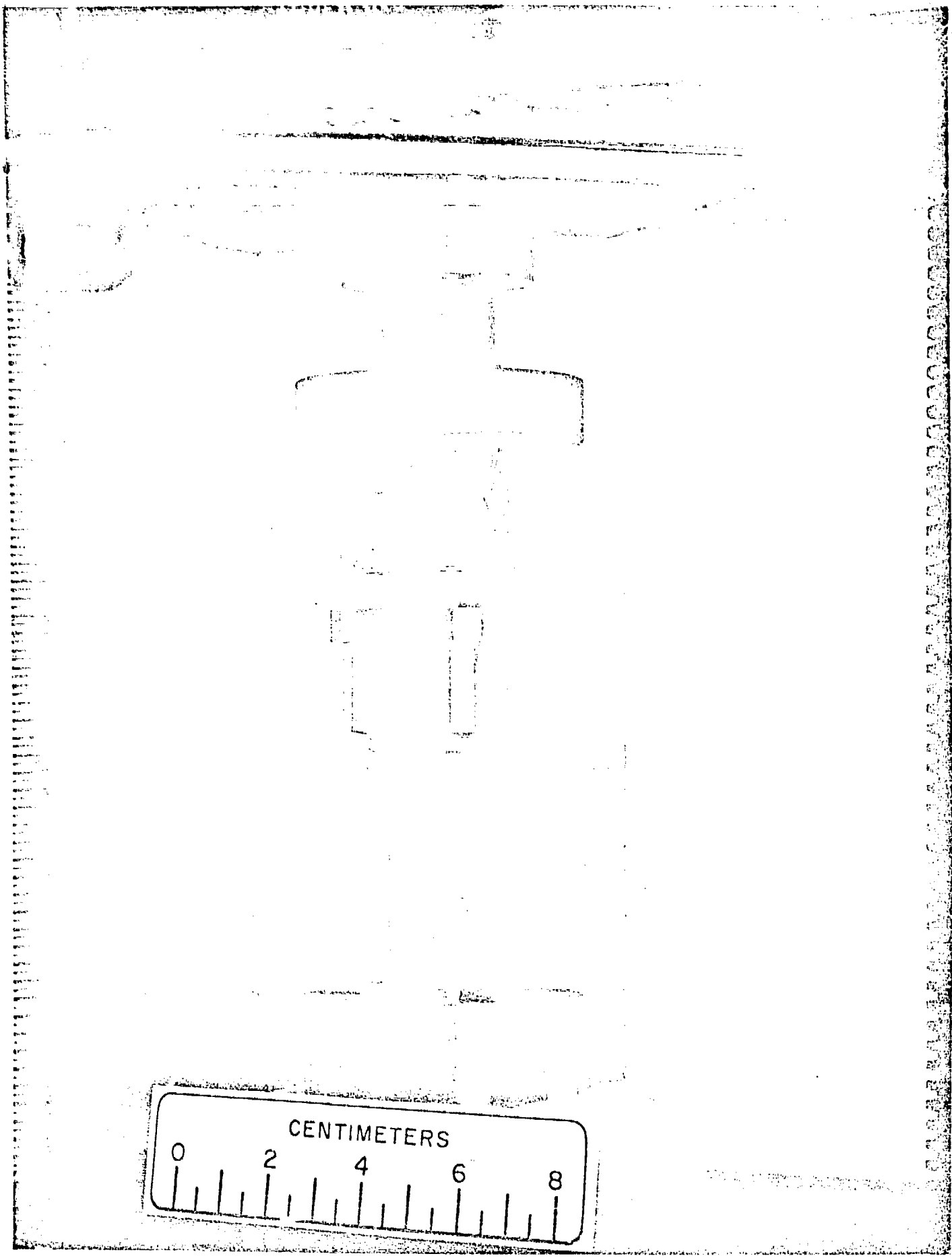
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