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G. L. KULCINSKI

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EXPLORATION OF THE PROBLEMS ASSOCIATED WITH THE NEUTRON IRRADIATION OF SAMPLES UNDER HIGH HYDROSTATIC PRESSURES

G. L. Kulcinski

INTRODUCTION

Since the early 1950's when diamond was first synthesized, there has been a tremendous amount of interest in the use of pressure as an analytical tool. Scientists in all fields; chemistry, geology, metallurgy, solid state physics, and ceramics to name just a few, have been engaged in high pressure research of both an applied and theoretical nature. In the past fifteen years there have been eight times as many papers published in this field as in the entire period prior to 1952. This large increase in publication is further manifested by the fact that prior to 1955 there were but six laboratories with the capability of obtaining pressures greater than 25 kbar,* whereas it is now estimated that 150 laboratories can make this claim.

There have been several excellent review articles written(1-18) which explain how investigators have ingenuously adapted high pressure equipment to yield information about the crystallographic, magnetic, optical, electrical, mechanical, and thermal properties of matter while under pressure. However, one of the last areas of materials science to add this new capability to its repertoire of investigative tools has been the irradiation effects field. There are many reasons for this, and it is hoped that this report will both outline some of the major problems in this area for those not familiar with the field of atomic energy and suggest some solutions for these problems.

The object of this report then, is not to explain <u>why</u> one wishes to study the effects of pressure on materials which have been, or are about to be irradiated, but rather it will concentrate on <u>how</u> such a study can be made. Other reports(19-23) deal with the "why" of ultra-high pressure research.

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* 1 kbar $\simeq$ 1000 atmospheres

In considering the type of high pressure experiments that the nuclear metallurgist would like to perform, one finds that they fall into three general categories:

1) Preirradiation treatments
2) In-reactor studies
3) Postirradiation treatments

In reality, the requirements of the first category are no different than those of the "ordinary" high pressure scientist. Equipment for these studies has been described previously,(1) and will not be discussed here. In fact, aside from modifications to handle radioactive material, the requirements for the third category are similar to the first. It is the in-reactor equipment which demands special consideration as to size, nature of material and method of pressure generation. Therefore, the emphasis in this report will be placed on the general problems to be encountered by placing ultra-high pressure equipment in the environment of a nuclear reactor with its ionizing radiation.

The restrictions imposed on the equipment from the standpoint of the reactor will be explored first, followed by a discussion of how one can meet these restrictions. This latter topic is broken up into the three areas: pressure generation, pressure containment, and pressure transmittance.

SUMMARY AND CONCLUSIONS

Problems associated with the design of equipment to generate high hydrostatic pressures on samples which are simultaneously irradiated to a neutron fluence of 10^{18} nvt have been discussed in detail. Of necessity, some areas have been treated in a cursory and general manner and some of the points made in this analysis may be slightly modified in special cases.

Basically, the capsule incorporates a clamping type method of maintaining pressure in conjunction with the tapered cylinder pressure support concept. Pressure stability and calibration is obtained by the use of an alkali halide, immersed with the sample in a liquid metal pressure transmitting media. The liquid metal is contained by the use of a Bridgman seal arrangement. The overall dimension of such a cell could be approximately 2.75 in. in diam approximately 6 in. long, if it is constructed out of high strength, low alloy steel. This cell could accommodate a sample of slightly less than 0.25 in. in diam and 0.5 in. long which can be subjected to approximately 20 kbars of pressure while it is inside a nuclear reactor.

DISCUSSION

GENERAL DESIGN CRITERIA

Before launching into the subject, it is important that one thoroughly analyze the objectives of a particular pressure-irradiation study. One must first of all decide on the type of neutrons desired, namely fast or thermal. After this is determined, the total neutron fluence required must be known. In addition, dose rate is important in that for a required total exposure, the lower the dose rate the longer the experiment must run. Other variables such as temperature and the degree of hydrostaticity are also important in the final design of the proper pressure device.

Obviously, one cannot hope to set up design criteria for all the possible combinations of the above conditions and one is required at the onset to choose a set of conditions which will be representative of the most general case. For the sake of continuity, the design requirements for a specific pressure cell will be investigated and it is hoped that a majority of possible problems will be discussed; hence, it will be required that:

1) The pressure to the sample be hydrostatic and no less than 20 kbar
2) The in-reactor experiment run no longer than 720 hr (1 month)

3) The total fluence to exceed 10^{18} nvt fast neutrons (>1 MeV)
4) The temperature be below 200 °C
5) The sample to be 0.125 in. at its smallest dimension.

With this set of ground rules one can now address the specific limitations that a nuclear reactor imposes on such a study.

SPECIFIC LIMITATIONS IMPOSED BY REACTORS ON "IN SITU" HIGH PRESSURE EQUIPMENT

Size

Perhaps the most severe limitation from the pressure standpoint is the relatively small diameter of irradiation facilities. Table I gives the maximum diameter allowable for the irradiation facilities of various reactors currently in operation.

For closed systems, these facilities are usually cylindrically shaped so that the maximum length that can be accommodated is approximately 3 to 4 times the maximum diameter. It should be noted that the diameters in Table I are the ID of the tube and any equipment going into this facility must necessarily be smaller. The exact size of the equipment will depend on the method of cooling, and it is not unreasonable that the maximum diameter of a pressure cell in these facilities may be 10 to 15% smaller than the dimension in Table I.

With diameters greater than 3 in., the number of tubes available in a specific reactor drops to a few, or in most cases, one. In the high flux reactors, competition for these larger tubes is keen and many times one must wait for as much as a year or so before his turn comes up to use the space. In addition, since the holes are so big, a complete shutdown of the reactor is usually required to insert or remove equipment.

Normally there may be 10 to 100 different experiments running in one reactor so that reactor shutdown occurs only at specified intervals (usually 3 to 4 weeks). This procedure cuts down on the flexibility of fluence received and a cell may receive considerably more irradiation than desired.

TABLE I. Typical Data on Reactor Irradiation Facilities(a)

Reactor	Epithermal Flux x 10^{12}	Thermal Flux x 10^{12}	Gamma Intensity 10^8 rad/hr	Sample Diam-in.	No. of Tubes	Temp. °C
	Closed Systems					
Advanced TRIGA Prototype	34	23	3.1	1.4		A(b)
Argonne Research Reactor	40	50	-	0.5	17	-
CP-5	10	50	-	1.4	7	-
Advanced Test Reactor	1,000	1,000	80	3	9	A
Babcock and Wilcox Test	150	160	5	6	1	A
Reactor	70	45	1.5	1.812	4	A
Battelle Research Reactor	20	40	1	3	2	A
	10	10	0.43	8	2	A
Curtis Wright Nuclear Laboratory	10	10	0.5	8	3	A
Engineering Test	330	1,000	83	9	1	-
Reactor	25	220	8	3	4	-
Georgia Tech Research Reactor	1	-	-	4	8	38
GE Test Reactor	1,300	200	36	3	1	A
	600	220	20	1.5	-	
Hanford Production Reactors	Classified			2.75	-	A
	Classified			0.75	-	A
Plutonium Recycle Test Reactor	500	400	-	3.25	10	280
IIT Research Reactor	3	0.32	150	1.4	1	70
Industrial Reactor Lab	7	30	3	8	1	38
	200	200	8	3	1	43
	300	140	8	2	1	43
MIT Research Reactor	50	30	-	1	30	60
	10	20	-	13	1	125
Material Test Reactor	100	500	18	3	4	40
	50	400	-	6	3	Controlled
NASA PLUM Brook Reactor	200	90	50	2	12	A
	35	300	13	9	1	A
	7	150	5.4	11.75	1	A
Omega West	7	20	-	6	8	~50
Penn State Reactor	2	2	-	3	-	25
TRIGA MARK I Reactor	9	4.9	0.7	1.4	-	A
Advanced TRIGA Prototype	34	23	3.1	1.4	-	A
Western NY Nuclear Research Reactor	30	-	0.2	3	-	-
Westinghouse Test Reactor	200	84	-	2	5	55
	60	170	-	8	11	Variable
	Open Systems--Pool Type					
Air Force Nuclear	6	4	6			A(b)
Test Reactor	3	0.03	2			A
Bulk Shielding Facility	10	10	-			A
Georgia Nuclear Lab	5	12	0.15			-
Juggernaut	5	1.5	-			A
Livermore Pool Reactor(c)	50	5.0	-			A
National Bureau of Standards Reactor	100	150	5			-
Rhode Island Nuclear Science Center Reactor	20	5.6	0.01			-
U. of Illinois Reactor	5	4	0.3			-
U. of Missouri Reactor	80	500	-			A
U. of Virginia Reactor	20	10	0.4			A
Washington State Reactor	1.2	0.5	-			A
U. of Wisconsin Reactor	1	1.8	-			A
Walter Reed Army Medical Center Reactor	2	2	-			A

(a) Only the data for the tubes with the largest fast flux and the largest diameter are quoted.(24)

(b) A = Ambient temperature

(c) Maximum flux is available only in 3 in. ID tubes to core.

With diameters less than 3 in., the number of holes increases considerably which tends to reduce the waiting time for irradiation space. In addition, since smaller masses are involved, arrangements usually can be made to charge or discharge while the reactor is running. In this way one can control radiation exposures so that only the required fluence is obtained.

For these reasons, and others which will become apparent as we continue, it is assumed that pressure vessels for closed reactors should be designed with the outside diameters no larger than 2.75 in. (to fit 3 in. tubes). The lengths of these cells can be 10 to 12 in. or more. The maximum size of equipment in pool-type reactors is larger than closed systems. Equipment of up to 12 to 15 in. in diameter may be used. However, this equipment must be placed outside the core of the reactor and the fluxes in Table I are peak fluxes in the core. Since pool-type reactors are water cooled, the fast flux drops off by orders of magnitude within a few inches of the core face. It is then difficult, if not impossible, to obtain the required fast flux of 10^{18} nvt in a period of $\sim 3 \times 10^{6}$ sec (1 month).*

Large "conventional" pressure units could be used if they were placed in front of beam ports outside the reactor or in conjunction with portable neutron generators. However, the integrated fast flux would be limited between 10^{15} to 10^{16} nvt which is below our design considerations.

Accessibility in the Reactor

When placed inside a reactor, the pressure device must operate some 20 to 30 ft from its control equipment. One must design the pressure device to be self-sufficient; i. e., be completely isolated from outside control, or devise methods of generating and measuring pressures

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* The reader will notice that the fast fluxes quoted in Table I are for epithermal neutrons. This number is generally 3 to 4 times higher than the fast (>1 MeV) flux so that the minimum epithermal instantaneous flux which will satisfy our requirements is $\sim 10^{12}$ nv).

outside the reactor. This latter situation requires long lengths of pressure tubing and possibly electrical leads to be led through the reactor shielding, and in some cases through high pressure, high temperature water regions. In addition, equipment must be extremely reliable in its environment because once the reactor has started, the pressure cell cannot be easily removed, fixed, and recharged.

Neutronic Considerations

The nature of the material making up the pressure device must be such that it does not seriously disrupt the neutronics of the reactor. This means materials with large neutron cross section such as boron, cadmium, indium, hafnium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, thulium, lutetium, iridium, and mercury must be avoided in any substantial amount. Even large amounts of elements such as scandium, cobalt, rhodium, silver, tantalum, tungsten, rhenium, gold will significantly depress the flux (hence the power level) in the region of an experiment. It also goes without saying that large amounts of fissionable material such as uranium, plutonium, and thorium should be avoided.

Hazards to Reactor

From the standpoint of reactor safety, the inadvertent release of solids, liquids, or gases into the core, its moderating system, or cooling loop cannot be tolerated. This release could result from an explosion or by leakage of the pressure cell. This means that the possibility of an explosion with its very large energy releases must be avoided at all costs. Projectiles from an explosion could cause a fuel-cladding rupture, loss of coolant or moderator, or jamming of the control rod mechanism, all of which present a hazard to the environment around the reactor.

Some elements, even though not explosively released in a reactor, present a hazard by their mere presence. For example, mercury, aside from its large absorption cross section, is extremely corrosive on some cladding materials such as aluminum and zirconium. Although gallium has a more acceptable nuclear absorption cross section (3 barns), its corrosive properties are just as bad. Very small amounts of mercury or gallium could cause the failure of such cladding, thus releasing large amounts of radioactive fission products into the system.

It is common practice in the field to use BN powder for a pressure transmitting media. The release of large amounts of BN into the reactor moderating system would quite possibly cause the shutdown of a reactor. This stems from the fact that B^{10} has a very large absorption cross section. Removing the BN from the core would be, at the very least, a costly operation, and might possibly mean that the entire fuel assembly would have to be replaced.

Neutron Effects on Materials in a Pressure Cell

It goes without saying that the materials of construction must retain their mechanical and physical integrity under conditions of intense neutron and gamma ray bombardment. This coupled with the fact that the ambient temperatures inside the reactor may vary from 100 to 300 °C, aside from the heat generated by interactions with the ionizing radiation, tends to rule out organic materials for lubrication, pressure transmittance, and pressure generation. More will be said about organics in later sections.

The general effect of neutron irradiation on the mechanical properties of metals is to increase their yield strengths while reducing their ductilities.(25) Creep rates seem to be relatively unaffected by neutrons at lower stress levels, but no data are available for stresses of 100, 000 to 200, 000 psi which may be present in the members of a pressure device. It is for this reason that one would like to keep the duration of the experiment to times less than 1 month in order to reduce any relaxation-induced pressure reduction.

Transmutation effects do not seem to significantly affect the mechanical properties of metals unless one of the products of the reaction is helium or hydrogen. Some embrittlement may result from the helium and hydrogen produced by (n, α) or (n, p) reactions in some steels. Beryllium should also be avoided because of its large cross section for the $Be^9(n, \alpha)He^6$ reaction.

Postirradiation Analysis

The postirradiation investigation of the specimen is complicated by the fact that both the sample and pressure cell will be extremely radioactive. This means that normal operations that are usually performed on a work bench must be modified so they can be performed inside a "hot cell" with mechanical manipulators. Very few structural materials are immune to neutron-induced, long term radioactivity.

This means that experiments are usually "one shot" affairs and that a new cell must be made for each experiment. Needless to say, this requires the equipment to be designed for maximum simplicity and minimum cost per unit.

The restrictions outlined above apply to the sample as well as the pressure cell. Normal measurements (such as postirradiation, electrical, optical, magnetic, X-ray, or mechanical property measurements) become considerably more complex. This also requires expensive hot cell facilities and a willingness to sacrifice equipment which may become contaminated.

Summary

The pressure cell must be of cylindrical geometry with less than 2.75 in. OD and 10 to 12 in. long. It should be made of materials which do not drastically affect the neutron flux, and whose accidental release through explosion or leakage into the system will not compromise the safety of the reactor. The radiation stability of the materials must be sufficient to operate for long periods of time without degradation of mechanical properties. The pressure generating system must be able to operate for periods of time up to 1 month with little variation. It is desirable that the long term residual radioactivity be reasonably low and that the cost per unit be minimized.

PROBLEMS OF PRESSURE GENERATION IN REACTOR

In a general sense, pressure is generated within a material when its volume is reduced. This is usually accomplished by surrounding the sample with confining walls of which one or more are movable. With the exception of pressure produced in nature by gravity and shock waves, one can state that there are three methods of applying the needed force behind the "movable wall" (hereafter called the piston) to provide the necessary volume reduction. These methods are:

1) Hydraulically
    a) Gas
    b) Liquid
2) Thermally
    a) Expansions of solids, liquids, or gases
    b) Phase transformations
3) Mechanically
    a) Clamps
    b) Coil springs
    c) Disc springs

Thus far in high pressure research the hydraulic method is most commonly used, although there are several examples of mechanically actuated pistons and a very few using thermal energy.

Hydraulic Methods of Pressure Generation

Figure 1 is a schematic of how, in a general sense, pressure is applied to a sample by the hydraulic mechanism. A force, F, acts on an area, A_0, which produces a pressure, P_0, in the hydraulic pressure generator. This pressure is applied to the piston which has an area, A_2. The force acting on the piston is then P_0A_2, or FA_2/A_0. This force is fully supported by the area, A_1, so that the theoretical pressure obtained with this type of arrangement is FA_2/A_0A_1. Obviously, to obtain a large pressure we should make F/A_0 and A_2 as large as possible and A_1 as small as possible.

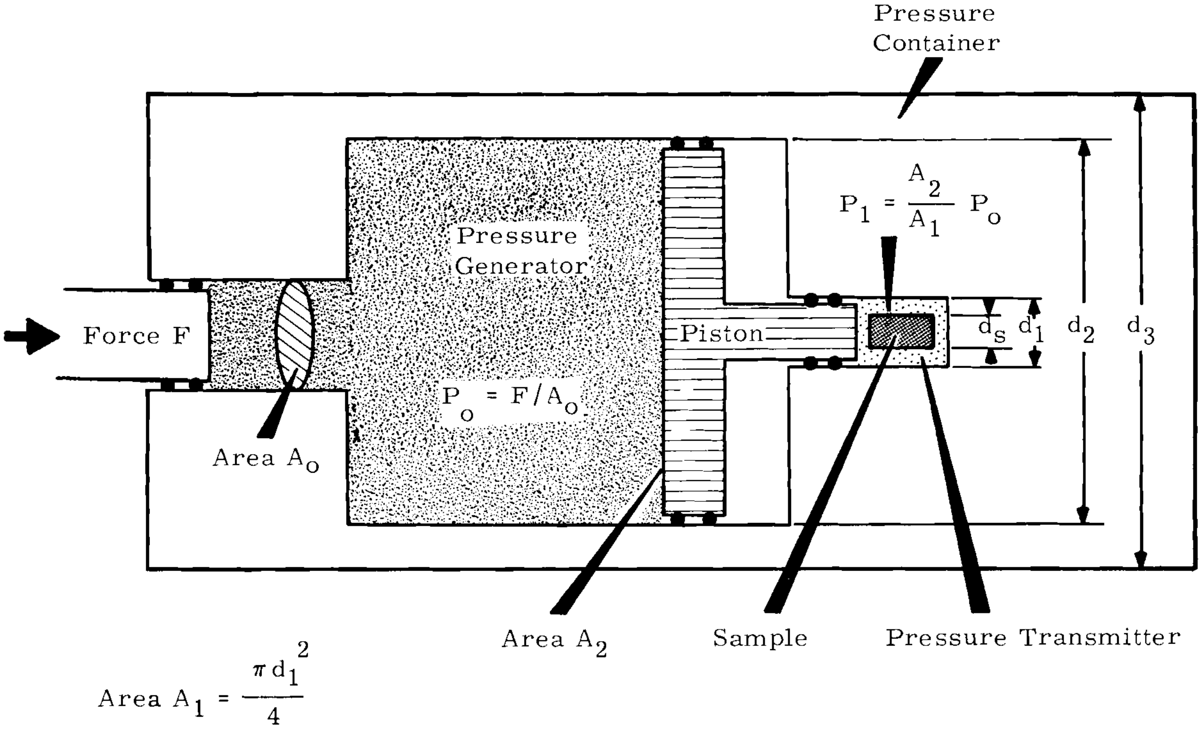

FIGURE 1. Schematic of Typical Hydrostatic Pressure Device

An upper limit has already been set on A_2; namely, it cannot exceed the maximum outside diameter decided upon in the previous section minus some reasonable wall thickness to hold P_0. There is also a lower limit on A_1. This is determined by the area of the sample, A_s. Since we require hydrostatic pressure on our sample, it must be surrounded by a pressure transmitter. More will be said about this later, but it is sufficient now to say that the transmitter must not support any shear stresses. To completely surround the sample with such a pressure transmitter, and to eliminate the edge effects of the walls, $A_1 \simeq (4\text{-}5)A_s$. At first glance this seems like a lot of area is taken up by the transmitter, but one must remember that this only corresponds to a transmitter thickness equal to the radius of the sample (~0.0625 in. in our case). The length of the sample does not affect these calculations.

The limits placed on F/A_0 depend on the maximum pressure that one can safely contain between the pressure generating equipment and the device itself. In our case, this would mean the maximum pressure we would be willing to allow in a high pressure pipe running into the reactor. This will be explored in later sections.

In order to make the ensuing discussion more meaningful, we will substitute some numbers for the quantities in Figure 1. Assume that area A_1 is ~ 0.05 in.^{2} ($d_1 \simeq 0.25$ in.) and limiting $d_2 = 2.00$ in. then $P_0 = F/A_0 \simeq 5,000$ psi.

The hydraulic pressure generator could be either a liquid or a gas. There are certain restrictions which must be placed on both of these fluids to insure safe, reproducible pressure generation. In general, they must:

- Undergo no thermal- or irradiation-induced phase transformations while under pressure.
- Possess a reasonable viscosity under irradiation at high pressures so as to adjust to minute movement of the pistons.
- Be noncorrosive and not subject to explosion.
- Not constitute a hazard to the safe operation of the reactor.

Gases

Most inorganic gases qualify as irradiation and thermally stable fluids which possess low viscosity under a few hundred to a thousand atmospheres. Consideration of corrosive and explosive properties eliminates such gases as oxygen, hydrogen, fluorine, and chlorine. Nevertheless, gases such as nitrogen and argon which successfully fulfill the first three requirements, fail the last one dramatically. The reason, of course, lies in the large amount of energy stored in gases compressed to 5,000 psi.

The rupture of high-pressure tubing or chambers which are not rigorously supported at regular intervals can be particularly dangerous. The gas escaping from the fracture will accelerate fragments (i. e., bolts, flanges, fittings, etc.) during their passage through closures. The velocity of such particles may approach ballistic proportions.

While this can be controlled by the proper design of blast barricades and venting systems, it requires considerable space and thick plates (1 to 2 in.) for suitable protection. Obviously, such space is not available in the experimental regions of present day reactors. Therefore, the placement of such a high-pressure gas system into a test reactor would require the highest possible scrutiny, which, in the experience of the author, would delay any meaningful experimental results by perhaps years.

Liquids

For pressures in the range of 5000 psi pressure, generation through the use of liquids is convenient and efficient. (Pressure transmittance at higher pressures will be treated later.) The corrosiveness of liquids can be kept to a minimum by using organics. The hazards of the gas system can be greatly reduced because of the much smaller energy storage in liquids compared with gases compressed to the same pressure and volume. As a matter of illustration, in an organic liquid compressed to 5000 psi, there is less than 0.1% of the potential energy available in a gas at 5000 psi and the same volume. The viscosities of the liquids at these pressures can be kept to a minimum by using pentane, methanol, kerosene, silicone oils or other suitable hydraulic fluids. At room temperature and <1 kbar these organics are well above their freezing points so that one need not worry about phase changes.

A major difficulty arises when one superimposes a radiation field on the experimental environment. Organic liquids have been found to be among the materials with the lowest radiation stability. In a reactor, a considerable amount of damage occurs when organics are exposed to fast neutrons which produce ionizing recoil protons; thermal neutrons which result in high energy capture gamma rays; and the high flux of fission gamma rays characteristic of the region around the core. These irradiations disturb the electronic system of the atoms and cause molecules to break up to smaller ones or recombine into larger molecules.

This process can be explained in more quantitative terms by defining G to be the number of molecules of product produced per 100 eV of energy absorbed. Table II(26) shows how three general classes of organics--saturated, unsaturated, and aromatic compounds--are affected by radiation. It can be seen that the unsaturated hydrocarbons are the least stable of the three, exhibiting considerable polymerization and destruction of material. Aromatic compounds are more resistant to damage, but nevertheless display some tendency for polymerization. Saturated hydrocarbons are free from polymerization problems, but considerable amounts of gas, mainly hydrogen, are evolved. Not only does hydrogen present an explosive hazard, but its embrittlement potential could considerably limit the strength of high-pressure tubing.

TABLE II. Summary of Radiation Yields from Organic Compounds(26)

	$G^{(a)}$		
Reaction	Saturated Hydrocarbon	Unsaturated Hydrocarbon	Aromatic Hydrocarbon
Polymerization	None	10 to 2,000	0.5 to 5
Crosslinking	~1	6 to 14	~1
Hydrogen Evolution	2 to 6	1	0.04 to 0.4
Methane Evolution	0.06 to 1	0.01 to 0.4	0.001 to 0.08
Destruction of Material	4 to 9	6 to 2,000	~1

(a) G = Number of molecules produced per 100 eV of energy absorbed.

Considering all the factors, it is evident that aromatic molecules prove to be much more stable against both pyrolytic and radiolytic damage than any other organic compounds. For this reason, considerable attention has been paid to these materials as reactor coolant fluids.(27) Within the aromatic grouping, the polyphenyl compounds display the highest threshold values for damage, on the order of 5×10^9 rads. (See Table III.) This threshold value is the radiation dose above which the performance of the material is impaired. This degradation takes the form of increased viscosity, density, molecular weight and decreased melting point and hydrogen content.(26)

TABLE III. Radiation Resistance of Various Organic Compounds(28)

	Radiation Dose (10^8 rads)(a)	
	Threshold(b)	Failure(b)
Polyphenyls	50	500
Polyphenyl Ethers	10	100
Alkyl Aromatics	10	50
Polyglycols Mineral Oils Methylphenyl Silicones Aryl Esthers	1	10
Silicates Pisiloxanes Alkyl Diesters	0.5	5
Phosphates Alkyl Silicones Olefins	0.5	1

(a) Irradiations in inert atmospheres at moderate temperatures.
(b) Based on the most sensitive lubricant property; usually viscosity or acidity. Threshold dose is the radiation dose above which performance of material is impaired. Failure applies to the dose at which a material becomes useless.

Within the polyphenyl category, compounds which present the most promise are the biphenyl, ortho-, meta-, and para-terphenyl liquids. Various mixtures of these materials (commercially called "Santowax") have been successfully used in several nuclear reactors as coolants.(27) Table IV displays some of the properties of these materials and the composition of some of the various mixtures. All of their physical properties are compatible with the reactor environment, but their high melting points require that some external source of heat be used to keep the organic from solidifying when the reactor is not operating. Table V gives some of the "G" values for the polyphenyls under neutron irradiation, and it shows that p-terphenyl is most desirable from that standpoint (compare with Table II). However, its high melting point (213 °C) would complicate its use as a pressure generator. Hence, ortho- or bi-phenyl would be more desirable choices.

TABLE IV. Properties of Biphenyl and the Terphenyls(27)

Material	Melting Point °C	Boiling Point °C	Vapor Pressure at 315 °C psia	Vapor Pressure at 427 °C psia	Viscosity at 315 °C cP
Biphenyl	69	255	47	223	0.48
Ortho-terphenyl	56	332	8	62	0.38
Meta-terphenyl	87	364	4	34	0.38
Para-terphenyl	213	385	3	28	0.42
Santowax OMP(a)	155(b)	-	3	30	0.38
Santowax R(c)	155(b)	377	3	30	0.40
Santowax OM(d)	85(b)	-	14	54	0.33

(a) o-terphenyl 12%, m-terphenyl 57%, p-terplenyl 31%
(b) Final melting point
(c) Same ratio of terphenyl isomers as OMP plus up to 10% or more of high boiling components.
(d) Biphenyl 3%, o-terphenyl 64%, m-terphenyl 32%, p-terphenyl 1%

From an irradiation standpoint, a 5×10^9 rad dose corresponds to $\sim 3 \times 10^{22}$ eV absorbed per gram of organic. This is equivalent to an integrated fast* neutron fluence of 4×10^{18} nvt or an integrated gamma fluence of $\sim 10^{19}$ photons/cm^2.(29) In reality, both forms of radiation are

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* Energy >1 MeV

present in a reactor so that the allowable fast flux to the sample may be reduced by as much as 20%(30) or more. Considering the typical fast neutron fluxes and intensities of gamma radiation shown in Table I, the allowable fast neutron fluences will be less than 10^{18} nvt. Hence, it is possible that the organic fluids may decompose before the desired fluence is reached.

TABLE V. Initial Yields in Reactor Irradiations(30)

Material	Temp.	G,[a] gas	G, HB[b]
Biphenyl	300	0. 11	0. 41
	350	0. 144	0. 58
	397	0. 155	0. 76
	360	--	0. 24
Ortho-terphenyl	300	0. 080	0. 295
	350	0. 110	0. 35
	387	0. 144	0. 445
Meta-terphenyl	300	0. 070	0. 29
	350	0. 082	0. 315
	387	0. 104	0. 335
Para-terphenyl	300	0. 062	0. 235
	350	0. 073	0. 29
	399	0. 117	0. 44
Santowax R	300	0. 064	0. 265
	350	0. 080	0. 295
	399	0. 119	0. 415
	340	--	0. 13
Santowax OM	330	--	0. 12
OMRE coolant ca.	300	--	0. 15

(a) G = number of molecules produced per 100 eV of energy absorbed.

(b) HB = high boiling liquids

What physically would happen to a biphenyl fluid at 300 to 350 °C and this exposure? There will be a slight tendency to form gas from the thermal effects alone at the rate of $\sim 10^{-4}$ ml/g/hr, and there will be a tendency to form high boiling molecules at the rate of $\sim 10^{-5}$/hr.(31) Since an experiment is not assumed to last more than 1000 hr, pyrolytic decomposition can be ignored. On the other hand, after 10^{18} nvt (fast) and with G (gas) $\simeq$ 0.11 and G (high boiler) = 0.45 (see Table V) there will be 3×10^{19} molecules of hydrogen formed ($\sim$1 ml of hydrogen gas at STP) and $\sim 1 \times 10^{20}$ high boiling molecules synthesized per gram of biphenyl. Considering that at least two molecules must be used in forming a molecule of a "high boiler," it is apparent that as much as 5% of the biphenyl molecules must be affected by the irradiation. While the above numbers are only order of magnitude estimates, they dramatically illustrate the susceptibility of organic fluids to radiation damage.

Unfortunately, data on the effect of high pressure on the melting point, viscosity and compressibility of polyphenyls are rather sparse at this time. Since the volume change on melting is positive, it is assumed that the melting point will increase with pressure. Norris(32) has found a related compound, polyphenyl ether, which shows an increase of $\sim$5 °C/kbar in its melting point. Opdycke et al.(33) find that the compressibilities of the polyphenyls to be 1.7 to 2.7×10^{-5} bar^{-1} up to 170 atm. The increase in viscosity under pressure is not known, but Bridgman(8) found that most organics display an exponential behavior in this respect. In any case, it is expected to increase.

Aside from the independent detrimental effects of pressure and irradiation, their combined effects may aggravate the polymerization of polyphenyls. Wall and Brown(34) have found that simultaneous compression (5 to 20 kbar) of acrylamide which had been previously irradiated increases the conversion to polymer. Prince(35) found that postirradiation compression of acrylamide increased the molecular weight over nonpressurized systems.

While it is risky to extend these results to the polyphenyl system, it seems logical that the combined effect of pressure and irradiation will be to induce more polymerization than irradiation at 1 atm. Hence, it appears that in experiments which require fast fluences of $>10^{18}$ nvt, it may be impossible to obtain reproducible pressures with organic fluids as pressure generators.

The question immediately arises as to the properties of water under such conditions. Even though its viscosity is reasonable(36) and it is in no danger of freezing at 5000 psi; water, like organic fluids, will be subject to radiolysis(37) $[G(H_2) \simeq 0.8,\ G(-H_2O)_{net} \simeq 3\text{-}4]$. The buildup of molecular hydrogen over a period of a month may be appreciable, possible 6 ml of hydrogen gas/g of water. Since the system is closed, there may be container embrittlement by the atomic hydrogen produced $(G(H) \simeq 2)$. In any case, one must be careful about using hydrogen containing materials as pressure generators in reactor when proper disposal of the evolved hydrogen is prevented.

Serious consideration can be given to the use of liquid metals (i. e., lithium, sodium, potassium, mercury, gallium) to transfer force generated outside the reactor to a piston inside. Mercury is ruled out because of its corrosiveness and high neutron capture cross section. The problems associated with alkali metals are also quite formidable. Sodium, potassium, or a NaK alloy would be stable under irradiation, possess the proper viscosity, be noncorrosive if properly contained, and remain a liquid under the conditions of the experiment.(38, 39) However, since most research reactors use water in one form or another, the violent reaction between the alkali metals and water, plus its tendency to burn in air, presents some serious safety problems. Technically, it is feasible to use such a system, but several design problems must be solved before such a pressure generation arrangement could be used.

Gallium possesses the same properties as the alkali metals except that it is not as reactive to water and may be handled safely in air. It is extremely corrosive at higher temperatures to all the elements except some refractories and steels. At lower temperatures it could be contained, but one would have to be extremely careful about the possibility of a leak into the reactor coolant or moderating system. If gallium were to come in contact with the hotter fuel elements, failure of the cladding material would be almost assured. Pure gallium at room temperature is not as corrosive to most structural materials as mercury,(40) but at higher temperatures this advantage disappears.

Summarizing, the difficulties of using fluids as pressure generators in-reactor we find that:

- Gases present a safety hazard from explosion,
- Organics are unstable in the ionizing atmosphere and the more radiation damage resistance fluids may be heated,
- Water presents some problems from embrittlement and hydrogen gas buildup,
- Liquid metals present a safety hazard resulting from their reactivity and corrosiveness.

Thermal Methods for Pressure Generation

One of the major technical problems faced in using hydraulic fluids to generate the force behind our "piston" is the fact that the pressure must be generated outside the reactor and led some 20 to 30 ft through various shields, pressure vessels, coolant and moderating media, and finally to the vicinity of the core itself. Hence, it seems desirable to eliminate this complex arrangement and make the pressure unit self-contained; i. e., require no outside equipment to generate the force required to act on the piston. Methods of doing this are discussed in the following sections.

Expansion of Solids, Liquids, and Gases

If, instead of using a working medium to transfer the force generated outside the reactor to the piston inside, one simply closes off the chamber behind the piston in Figure 1 and applies heat to a solid or liquid at constant volume, a similar force can be generated (see Figure 2). This type of pressure generation is particularly attractive because there is no longer a need for lengthy tubing and remote operating procedures.

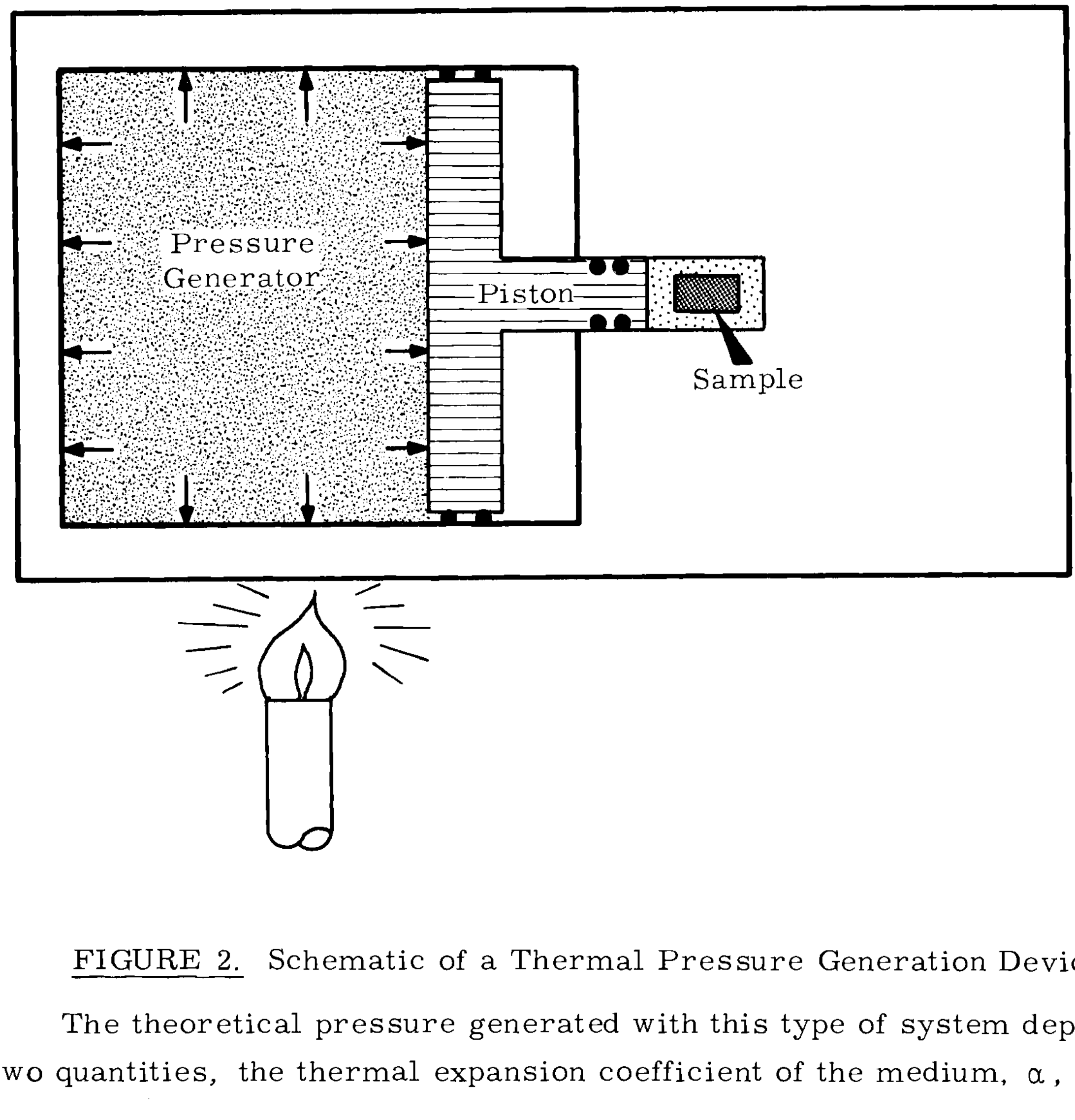

FIGURE 2. Schematic of a Thermal Pressure Generation Device

The theoretical pressure generated with this type of system depends on two quantities, the thermal expansion coefficient of the medium, α, and its compressibility β. From thermodynamics, the relationship for the pressure generated per degree rise in T temperature is

$$\frac{\partial P}{\partial T}_V = -\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T} = \frac{\alpha}{\beta} \tag{1}$$

When investigating the suitability of various systems for this arrangement one finds that gases can be eliminated immediately because of their high compressibility and the wide range of temperatures needed for significant pressure generation. For liquids, water gives a value of ~5 atm/°C while for most organics it is raised to 12 atm/°C at 1 atm.(41) Both of these values increase with pressure because of the decrease on compressibility at higher pressures. Sodium gives a value of 18 atm/°C and it has been calculated that mercury will generate some 7000 atm when it is heated at constant volume from -30 °C to 200 °C.(41) This would give an average $(\partial P/\partial T)_V$ of ~30 atm/°C.

In principle, solids can be used for the expanding medium behind the piston, but they "suffer" from a finite ability to withstand shear stresses. Hence, one cannot simply use the volume thermal expansion coefficient, but must instead use an empirical value that lies somewhere between the linear and volume coefficient. Table VI lists the available thermal expansion coefficients and compressibilities for most materials of interest. From this table one can see that because of the lower compressibilities of metals, pressure coefficients of ~5 to 27 atm/° C are possible even though one uses the linear thermal expansion coefficient.

It must be remembered that the values in Table VI are theoretical which assumes that despite the temperature and pressure changes within the generator, the volume of the generator will remain constant. Realistically, due to the finite compressibility, thermal expansion and elastic properties of materials of construction, as well as the necessary movement

TABLE VI. Thermal Expansion and Compressibility Coefficients for Various Elements

Element	Temp. °C	Linear Expansion Coefficient $°C^{-1} \times 10^6$	Cubic Expansion Coefficient $°C^{-1} \times 10^6$	Compressibility$^{(a)}$ $b^{-1} \times 10^{-6}$	$(\partial P/\partial T)_v$ Linear Coefficient bar/°C	$(\partial P/\partial T)_v$ Cubic Coefficient bar/°C
			Solids			
Al	20	25.5	$69^{(c)}$	1.3	19.5	53
Sb	20	12	31	$2.2^{(b)}$	5.5	14
As	10-90	3.9	~10.7	$1.8^{(b)}$	2.2	6
Be	20-100	12.3	~36.9	0.9	13.7	41
Bi	19-100	13.5	40	2.9	4.7	14
Cd	20	28.8	$93.3^{(c)}$	2.0	14.5	47
C						
Diamond	40	1.2	3.5	$0.2^{(d)}$	6	17.5
Graphite	40	7.9	~23.7	1.8	4.3	13
Cr	20-100	6.8	~20.4	0.5	13.6	40.8
Co	40	12.4	~37.2	0.5	24.8	74.4
Cu	25-100	16.8	~50.4	0.7	24	72
Ge		~37.5	$112.5^{(c)}$	1.4	26.7	80
Au	16-100	14.3	~42.9	0.6	24	71
IN	40	41.7	~125.1	2.5	16.7	50
Ir	40	5.7	~17.1	0.3	19	57
Fe	40	12.1	$35.1^{(c)}$	0.6	20	58
Steel	40	13	~36			
Pb	18-100	29.4	~88.2	2.4	12.2	37
Mg	20-100	26	$75.9^{(c)}$	$3.0^{(b)}$	8.7	25
Mo	25-100	4.9	~14.7	0.3	16.4	49
Ni	40	12.8	~38.4	0.5	25.6	77
Os	40	6.8	~20.4	$\sim 0.4^{(b)}$	17	51
Pd	40	11.7	35.1	0.5	23.4	70
Pt	40	9.0	27	0.4	22.5	67
Si		~23.3	$69.9^{(c)}$	$0.9^{(b)}$	26	78
Ag	20	18.8	~56.4	1.0	18.8	56.4
Ta	20-40	6.7	~20.1	0.5	13.4	40
Te	40	16.8	~50.4	$4.5^{(b)}$	3.7	11
Tl	40	30.2	~90.4	2.8	11	32
Th	0-100	12.3	~36.9	1.8	6.8	21
SN	18-100	26.9	~80.7	$1.8^{(b)}$	14.9	45
W	0-100	4.3	~12.9	0.3	14.3	43
U		~14.5	~43.4	1.0	14.5	43.4
			Liquids			
H_2O	0-33		207	$40^{(42)}$		5.2
Ice	-10-0	51	112	$10^{(d)}$	5.1	11.2
Ga	0-30	18	~54	2.0	9	27
	Liquid		120- AGIG$^{(f)}$	4.0		30
Hg	0-100		181	3.7		49
Li	186-200		$180^{(e)}$	8.7		21
Na	-188-17	62.2	201	14.2		14.2
K			$250^{(c)}$	27.5		9.1
S	13-50					
	Solid	70	233	$12.6^{(b)}$		17.7
Most Organics	RT		500-1000	$80^{(43)}$		6-12

(a) Reference 7
(b) Reference 44
(c) Reference 45
(d) WADC-TR-59-341, 1959
(e) Int. Crit. Tables, Vol. 1, p. 102, F. W. Washburn, Ed., McGraw-Hill, 1927
(f) Alusuisse Publication #65 10. 3000

Note: All linear and thermal expansion data from Reference 43 unless noted otherwise.

Note: When (~) sign appears before number in cubic thermal expansion coefficients, it means that the linear coefficient was multiplied by three.

of the piston to generate the required pressure on the sample, the coefficients will be considerably reduced. Below are listed the factors which will tend to reduce $(\partial P/\partial T)$:

- The thermal expansion of the pressure container,
- The finite compressibility of the pressure container and piston,
- The elastic tensile strain in the walls of the container,
- The compressibility of the sample and its surrounding media,
- Any free space present in the system before heating,
- Creep strength of the container.

Neglecting the last two, it can be shown (Appendix A) that the realistic pressure generating coefficient is,

$$\frac{\Delta P_g}{\Delta T} = \alpha_g - 3\alpha_w + \frac{\ell_p}{\ell_g}\alpha_p \div \left[\frac{1}{E_w}\left\{2f(K_g) + 2f(K_s)\frac{\ell_c}{\ell_g}\left(\frac{d_2}{d_1}\right)^2\frac{1}{K_g^2 - 1} + \frac{\ell_c}{\ell_g}\frac{1}{(K_s^2 - 1)}\right\} + \frac{\ell_p}{\ell_g}\frac{1}{E_p}(d_2/d_1)^2 + \beta_c\frac{\ell_c}{\ell_g}\frac{d_2^2}{d_1^2} + \beta_g\right] \quad (2)$$

where the symbols are explained in Appendix A. For a high strength steel container, with a tungsten carbide piston and values of d_3, d_2, d_1 which conform with space restrictions, it can be seen that one can generate 5000 psi (340 atm) with ~110 °C temperature rise in a 6 in. long, 2 in. diam tube of potassium, sodium, lithium (see Appendix B). It has been pointed out before that mercury and organic fluids are not desirable in a reactor environment. Sulfur has a tendency to become too viscous at the temperatures required. Gallium would provide the same pressure rise by only a 170 °C temperature rise.

The difference between the actual pressure coefficients of 3 to 3.2 atm/°C and the theoretical values of 9 to 21 atm/°C (Table VI) is a result of the finite physical properties of the pressure container and the necessary compressibility of the pressure transmitter and sample. There is a limit to the maximum pressure attainable with this technique. It depends on the rate of yield strength loss with increasing temperature. There will be a point at which one more degree rise in temperature will lower the yield strength below that stress present in the confining walls, hence causing the plastic flow of the container walls. The ΔT should be limited to 200 to 300 °C for this reason.

There is a certain amount of attractiveness in this technique, but actual working models have never been reported because other methods, to be described later, have proven to be less complicated. At first glance, the high radiation and thermal stability of metals coupled with their low compressibilities make them appear as logical materials for pressure generators. However, their finite shear strength allows them to support considerable shear stresses and makes the determination of α_g (the cubic thermal expansion coefficient of the pressure generator) much more difficult. In the general sense, one knows that α_g lies between the volume thermal coefficient and the linear coefficient, probably closer to the latter. If one examines Equation (2), he finds that $\Delta P_g/\Delta T$ is close to zero unless $\alpha_g > 3\alpha_w$ where α_w is the linear thermal expansion coefficient of the container wall. For most purposes this means a $\alpha_g > 35 \times 10^{-6}/°C$ which is higher than most linear expansion coefficients (Table VI). Therefore, unless α_g is much greater than $3\alpha_w$, the pressures generated will either be quite low (Appendix C) or the container will expand completely away from the generator.

A quick study of Table VII shows that germanium, indium, and thallium are the most promising metals to use from a pressure generating standpoint. However, the high neutron cross section of thallium eliminates this element from consideration. Even though germanium and indium have high (27 and 11 atm/°C) pressure coefficients, their relatively low linear expansion coefficients make it difficult to compensate for the thermal expansion of the pressure container.

TABLE VII. Physical Properties of Materials that are Known to Expand on Freezing

Element or Compound	Ref.	Melting Temp. °C	Molar Volume, cm^3/mole	Volume Change on Freezing %	Maximum Pressure Attainable, kbar	Temp. at Maximum Pressure °C
Sb	46	631	18.7	-0.0095	50 +	
Bi	46	271	21.5	-0.0335	22	170
Ge	46	934	13.9	-0.050	180 +	
Ga	46	30	11.8	-0.032	12	5
Si	47	1410	12.1	-0.096	50 +	
Ce	48	795	21.3	-0.0105	30	650
Pu	49	640	14.6	≃0.007	30	500
InP	47	1060	15.2	?	125 ?	700
InAs	47	942	16.8	?	95 ?	500
InSb	47	530	20.5	-0.137	20	330
GaAs	47	1238	13.6	?	50 +	
GaSb	47	706	17.3	-0.07	59	400
GaP	47	1450	12.2	?	--	-
H_2O	42	0	18.05	-0.083	2.5	-22

Phase Transformations

Thus far we have investigated the generation of pressure by continuously varying the temperature on a single-phase material. As stated before, the disadvantages of this method are the requirement of liquid materials, usually corrosive or hazardous, and the fact that as the temperature is increased the strength of the materials decrease. Phase transformations--whether solid-solid, solid-liquid, or liquid-solid--provide a considerable volume change with the added advantage that they take place at essentially constant temperature. In addition, there is more freedom for the choice of the generating material.

The proportional change in volume on melting a liquid is usually positive, that is, the solid is usually more dense than the liquid. Representative values; for this volume change on melting range from +1.65% for lithium to +6% for aluminum (see Table VIII). To obtain this amount of volume change by heating a solid alone would require ΔT = 300 to 600 °C and possibly more.

TABLE VIII. Volume Changes Associated with Certain Metals on Melting(46)

Metal	Volume at T_{mp}, cm^3/mole	$\Delta V/V$
Lithium (bcc)	13.3	0.0165
Sodium (bcc)	24.1	0.025
Potassium (bcc)	46.0	0.0255
Rubidium (bcc)	56.1	0.025
Cesium (bcc)	70.0	0.026
Aluminum (fcc)	10.5	0.060
Copper (fcc)	7.6	0.0415
Silver (fcc)	10.9	0.038
Gold (fcc)	10.7	0.051
Nickel (fcc)	7.1	0.037
Platinum (fcc)	9.5	(0.038)
Rhodium (fcc)	8.7	(0.039)
Lead (fcc)	18.9	0.035
Iron (fcc)	7.7	(0.032)
Iron (bcc)	7.7	0.030
Thallium (bcc)	17.8	0.022
Thallium (fcc)	17.8	(0.023)
Magnesium (hcp)	14.8	0.041
Zinc (hcp)	9.5	0.042
Cadmium (hcp)	13.4	0.040
Indium (fct)	16.2	0.020
Tin (bct)	16.5	0.028
Tellurium (hexagonal)	21.0	(0.020)
Antimony (rhombohedral)	18.7	-0.0095
Bismuth (rhombohedral)	21.5	-0.0335
Germanium (diamond cubic)	31.9	-0.050
Gallium (orthorhombic)	11.8	-0.032

The main disadvantages of this method are the requirements that the generator be compatible with the containing material and that the melting temperature be low enough so as to not interfere with the mechanical properties of the container. Assuming that the container is made of high strength steel, this means that the melting temperature should be below ~ 300 °C. The metals which satisfy this requirement and expand on melting are lithium (108 °C), sodium (97.8 °C), potassium (63.7 °C), rubidium (38.9 °C), cesium (28.7 °C), lead (327 °C), thallium (303 °C), indium (156 °C), and tin (232 °C). Rubidium and cesium can be ruled out because of chemical reactivity problems, and indium can be ruled out because of its nuclear properties. The higher melting points of lead, thallium, and tin make them less desirable than the lower melting alkali metals. On the other hand, one again has the problem of chemical reactivity with these latter solids. Using a modified version of Equation (A-1), (see Appendix D), it is found that one could raise the pressure in a 2 in. diam, 6 in. long cylinder of solid sodium by 393 atm (5700 psi) when increasing the temperature from 97 to 102 °C. As seen before this sample pressure could be generated by heating liquid sodium to ~240 °C. Accounting for heating the solid sodium from room temperature to ~102 °C (ΔT = 80 °C) we find that an additional 216 atm are generated. Hence, heating sodium from 20 °C to 102 °C will generate 609 atm behind a piston which is about twice that obtained by heating liquid sodium from 102 °C to 240 °C. Obviously the phase transformation method is more desirable for sodium than the continuous heating of liquid material. Much the same results are obtained when considering lithium or potassium.

Making use of a volume change due to melting usually means that the sample will be under pressure only in the reactor and when it is heated. Transporting to and from the reactor at temperatures sufficient to keep the generator melted would prove to be a nuisance to say the least. It is somewhat desirable to load the sample outside the reactor so that one is certain of the nature and magnitude of the pressure on the sample. Hence, one would desire to have the sample under pressure when the pressure cell is at ambient temperatures.

The above objective could be accomplished if one used a material that expanded upon freezing. So far there are 15 known elements or compounds which possess this property (see Table VII): water, bismuth, antimony, germanium, gallium, silicon, cerium, plutonium, InP, InAs, InSb, GaAs, GaSb, GaP. Of these elements plutonium, InP, InAs, and InSb, can be eliminated because of their nuclear properties. Of the other materials, GaAs, GaSb, GaP, K_2SiO_9, silicon, germanium, and antimony have melting points which are much too high.

The expansion of water on freezing to ice is a well known means of pressure generation. From Figure 3 one can see that if water is cooled from 0 °C at constant volume, ice I forms and the pressure rises to a value of 2, 500 atm at -22 °C when ice I transforms to ice III with a 15% contraction in volume. One disadvantage is the low temperature that must be maintained in order to keep water a solid. This may present engineering problems in view of the heating of the cell due to ambient conditions and gamma heating in the reactor.

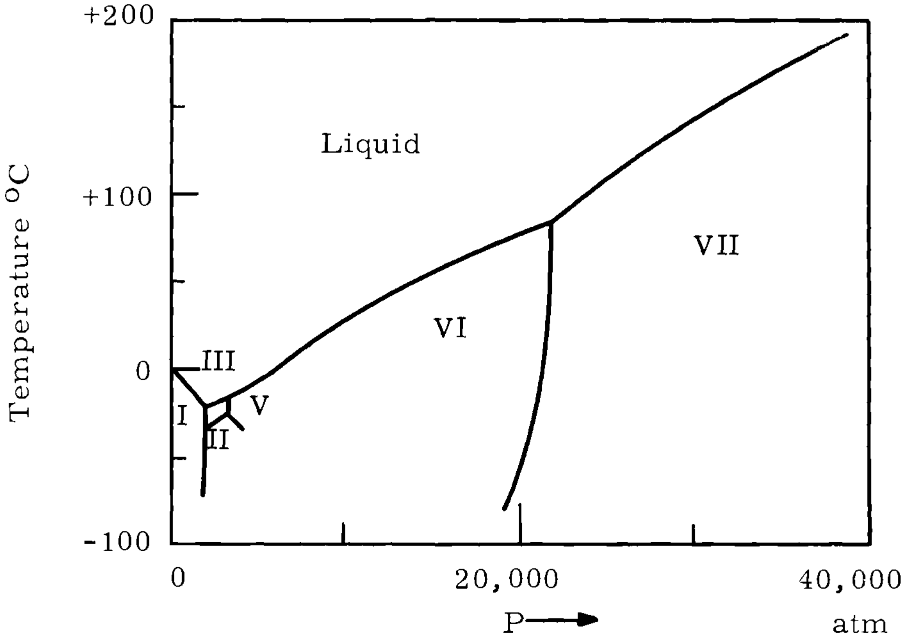

FIGURE 3. The Phase Diagram of Water in the Liquid-Solid Region(42)

Discounting water, one is left with only bismuth and gallium (Figures 4 and 5). Even gallium requires some cooling in order to stay solid (T < 5 °C). Hence, bismuth seems to be most desirable from the standpoint of: 1) large positive volume change on freezing, 2) low melting point, 3) remaining solid in normal operating range (up to 100 to 150 °C), 4) good nuclear characteristics and 5) low solubility of iron in bismuth.(51) Using

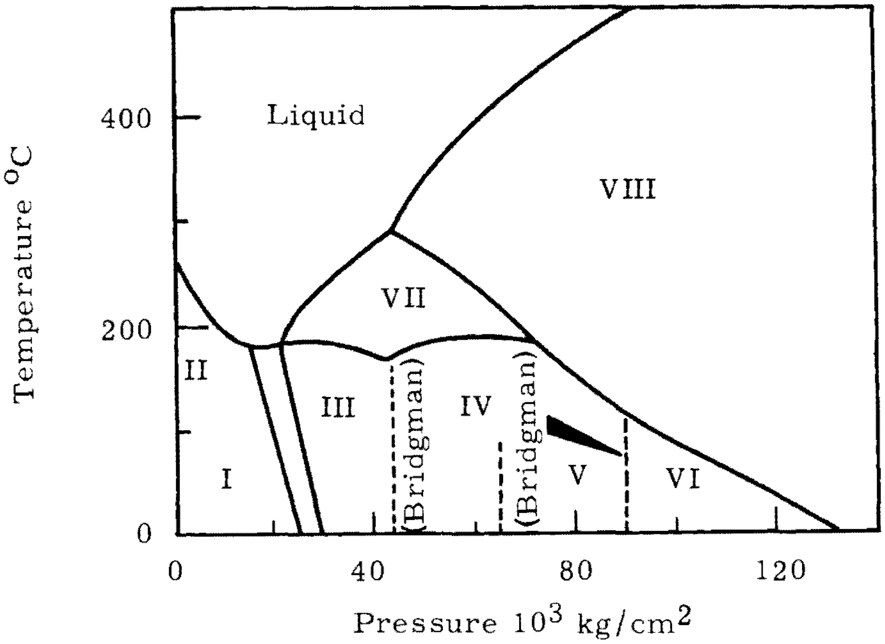

FIGURE 4. Phase Diagram for Bismuth(50)

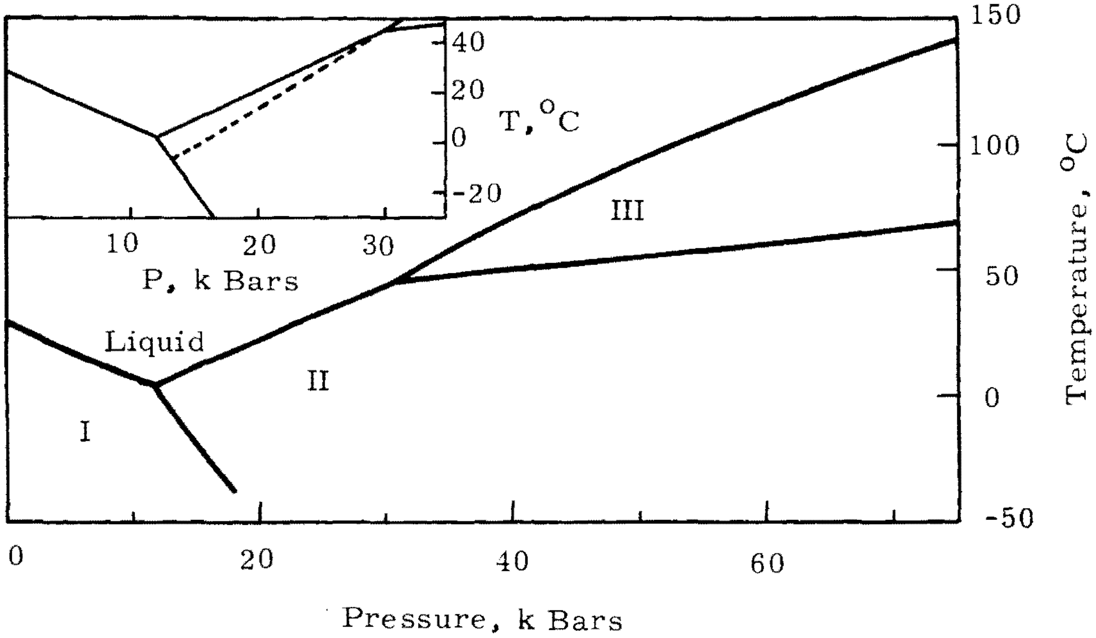

FIGURE 5. Equilibrium Phase Diagram of Gallium (from J. Phy, Chem. Solids 24, p. 14, 1963)

Equation (A-12) in Appendix D we find that for conditions outlined in that section,

$$\Delta Pg = 610 \text{ atm}$$

when bismuth is cooled from 275 °C to 150 °C. This ratio could be changed by changing the ratio of the length of pressure generator to length of sample. There will also be a slight loss of pressure (<10%) when cooling from the melting point of bismuth to ambient conditions. This latter effect is due to the larger coefficient of thermal expansion for bismuth than iron (normal container material).

Summarizing, bismuth and sodium appear to be the most attractive materials from the standpoint of thermally generating a pressure behind a high-pressure piston. It is feasible to generate 400 to 600 atm behind a piston at a temperature of ~100 °C and, depending upon the pressure magnification, 20 to 30 kbar on a 0. 25 in. diam specimen chamber.

The main disadvantage of this technique is the susceptibility of the pressure on the sample to small dimension changes whether due to thermal, mechanical, or errors in construction. To counteract this, one is forced to use a large amount of pressure generating media so that these relative errors are minimized. This considerably increases the length and weight of the cell.

Mechanical Loading

Clamps

Instead of using a hydraulic head of fluid or the thermal-induced expansion of solids or liquids, it is possible to compress the sample with an external press and lock the piston in place with a mechanical clamp. Figure 6 is a schematic of this concept. This method is attractive because all of the pressure generating operations can be performed outside the reactor, thus eliminating the need for high-pressure tubing. It also circumvents the problems associated with heating or cooling the pressure vessel under great stresses.

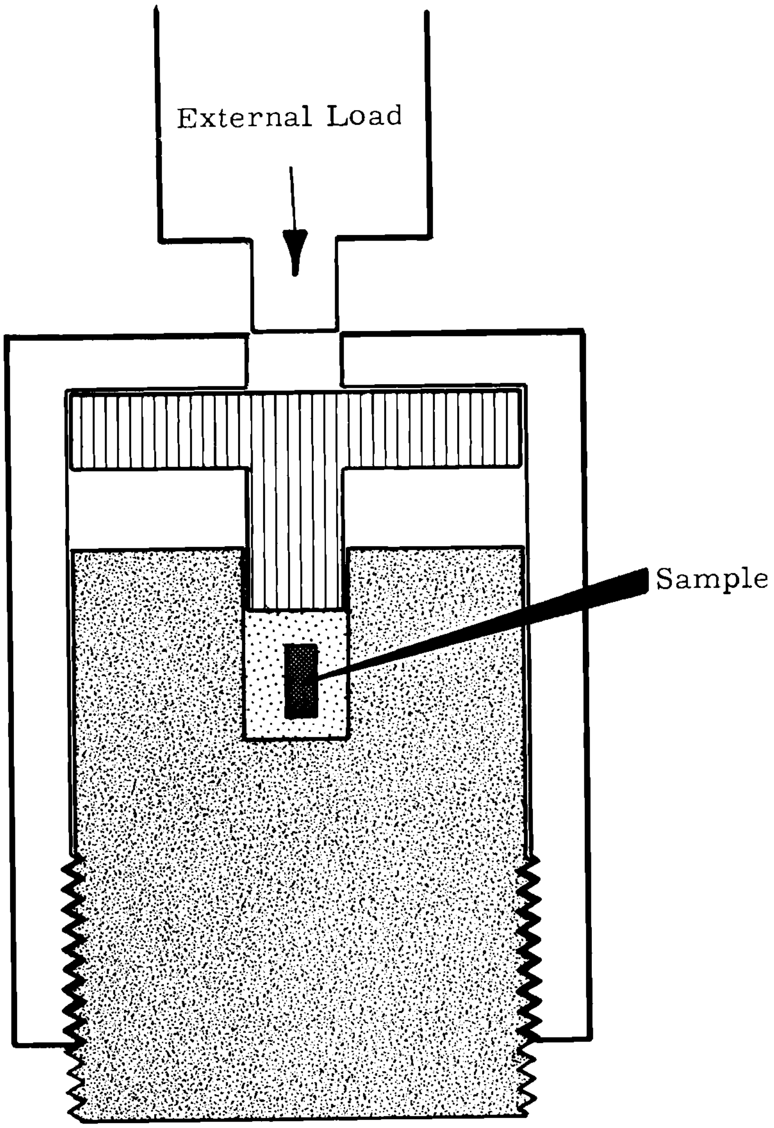

FIGURE 6. Schematic of a 'Clamped' Pressure Device

However, as with the thermal method, small dimension changes after loading, whether due to material properties or errors in tolerances, can have effects on the magnitude of pressure generated. Eliminating construction errors, factors such as elastic relaxation, creep, and even some backlash in the clamping mechanism may result in as much as 5 to 10% pressure loss to the sample. For example, in our model, 5000 psi was developed in the generator. Considering the area of the walls to be $\pi/4(2.5^2 - 2^2) = 1.76 \text{ in.}^2$, then a tensile stress of 9000 psi is developed in the walls. This stress results in a strain of 3×10^{-4}; and assuming the wall is 8 in. long (6 in. generator + wall adjacent to the piston and sample), then a 0.002 in. relaxation will occur. Considering the compressibility of the specimen chamber to be 7×10^{-6} b^{-1} and its length to be 0.5 in., then 20 kbar will result in a 0.070 in. compression of the sample.* Hence, at least 3% of the pressure could be lost by relaxation and another 2 to 3% loss is almost inevitable with a normal locking device.

Since it is desirable to maintain the pressure on the sample for periods of 1 mo or more (~1000 hr), one must worry about creep relaxation in the high pressure region where stresses can reach nearly 200,000 psi (see section on container material). If one wishes to keep the tangential creep strain to less than 10^{-4} in./in. (<1% vol change or <10% drop in pressure in our model), then the creep rate must be less than 5×10^{-8} in./in. hr. At 100 to 200 °C, it is felt that the error introduced by creep is on the order of a few percent and may be considered as part of the original 5 to 10% loss.

Coil Springs

To compensate for the relaxation effects, one would like to insert a pressure generator behind the piston that would deliver a relatively constant load regardless of minute dimension changes. A reasonable way to accomplish this is to apply the load to heavy die springs and to clamp them in place (Figure 7).

The equations which govern the load available from such a spring are:(52)

$$P = \frac{fGd^4}{8D^3}$$

where P = load
f = deflection/coil
G = torsional modulus
d = wire diameter
D = pitch diameter.

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* Does not account for sample container expansion.

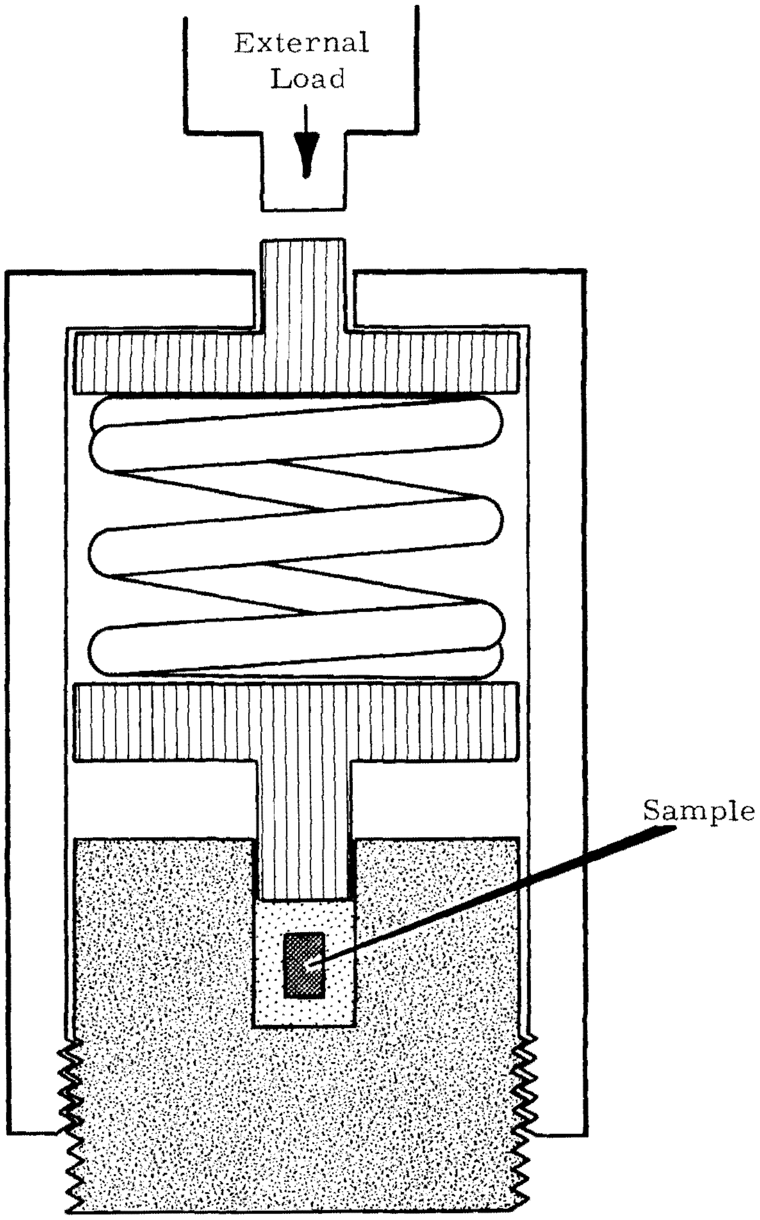


FIGURE 7. Schematic of a 'Clamped' Coil Spring Pressure Cell

Hence, to get the largest load possible, one must use material with the largest torsional modulus, select the largest wire diameter and smallest pitch diameter possible, and deflect the spring as much as one can without exceeding the maximum allowable stress. Without going into a detailed calculation, one finds that the maximum force available from a 2 in. diam, 6 in. long spring made of 0.45 in. diam wire is on the order of 2000 lb. Neglecting friction, a maximum of 2 to 3 kbars could be generated on the sample.

A relaxation in the clamping mechanism of 0.003 in. only amounts to a 0.3% loss of pressure which is much smaller than normal experimental error.

It is immediately apparent that in order to utilize this type of arrangement one must be satisfied with either lower pressures to the sample (~2 to 3 kbar) or use smaller diameter samples than 0.25 in. For example, if the diameter was reduced to ~0.062 in., then 20 kbars could be obtained.

One might question the ability of a spring to deliver relatively constant loads over a long period of time in a radiation field. R. L. Mehan(53) has examined Haynes-25 and Inconel-**X** springs which were stressed to 80,000 psi at 500 °F in water. They were irradiated from 5.9×10^{18} to 4.2×10^{19} nvt (>1 MeV) for 20 to 100 days. He found that the spring constant increased 5 to 8% and the free length decreased 2 to 3%. These counteracting effects are assumed to make the resulting change in pressure less than 5%. It is difficult to be more specific about this effect without experimentation. Hence, the conclusion is that coil springs, while offering sufficient travel to nullify elastic and thermal expansion effects, do not generate enough force to obtain the required pressure on the desired sample size. In addition there is a small, but finite, error associated with the effects of irradiation on their load delivery ability.

Disc Springs

A solution to the problem of obtaining larger loads than coil springs, but at the same time retaining a force generator which is relatively insensitive to small relaxations, lies in the use of "disc springs" (Figure 8). Unlike the coil spring where increasing length has no effect on the load, the amounts of load to be carried by a washer combination depends on the number of units used. That is, the total load is proportional to the number of washers stacked in series. In addition the total deflection depends on whether the washers are stacked in series or parallel (Figure 9).

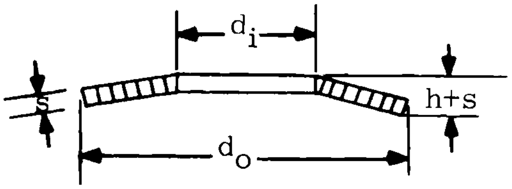


FIGURE 8. Conventional Shape of Disc Spring(54)

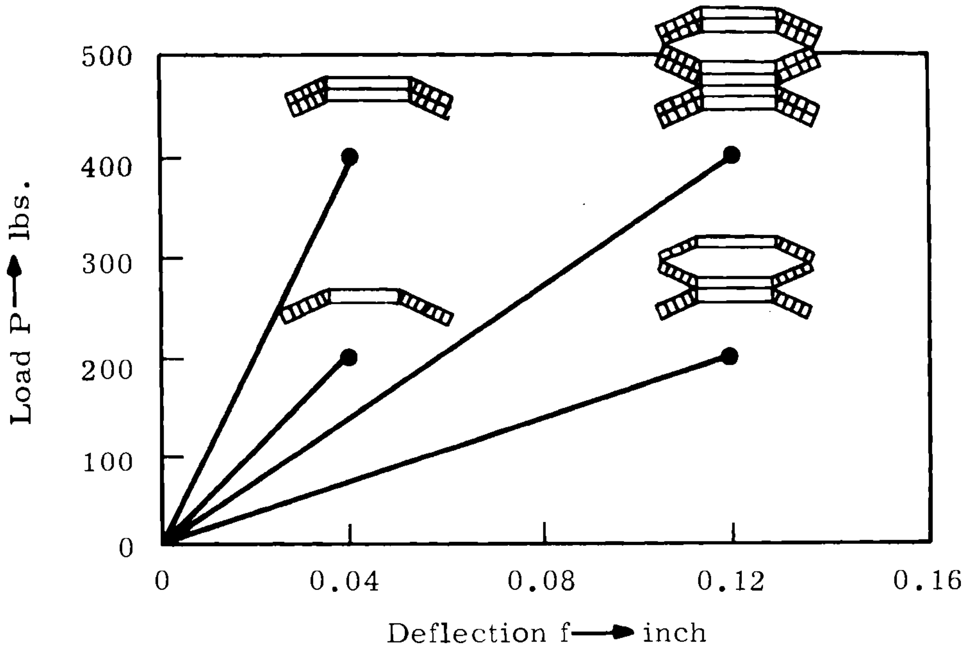


FIGURE 9. Load-Deflection Curves for Various Combinations of Disc Washer(54)

By using 6 washers of 1.97 in. OD and 1.0 in. ID, stacked in series, one can obtain a load of ~16,500 lb for a 0.032-in. deflection (Figure 10). This will generate ~20 kbar on a 0.25 in. diam sample. The total deflection at this load can be increased to 0.096 in. by using three stacks of six washers, each in parallel. A 0.003 in. change in clamping mechanism will result in only ~1% load change. The total height of this arrangement will be 2.25 in. which is compatible with the geometrical restirctions of the pressure cell.

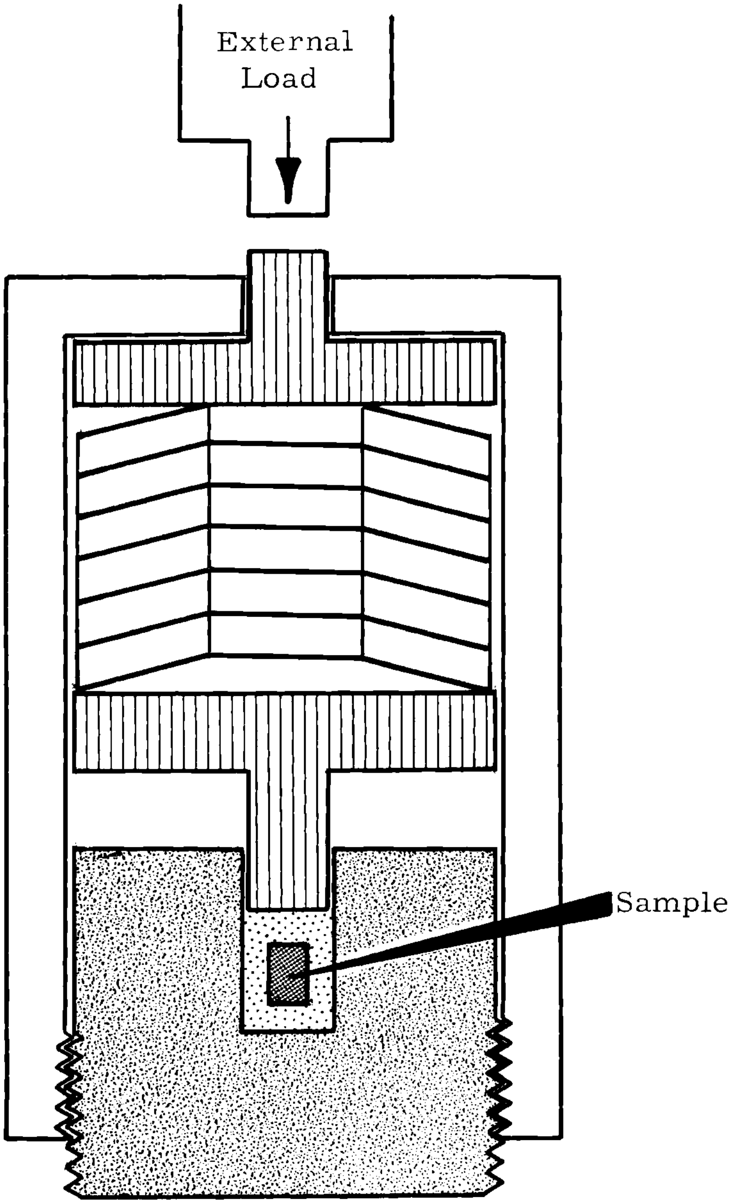


FIGURE 10. Schematic of a 'Clamped' Disc Spring Pressure Device

Since the disc spring concept depends more on the elastic deflection of the solid itself, it should be less susceptible to radiation damage than simple coil springs. For that reason, we would anticipate that, at least to fast fluences less than 10^{19} nvt, very little change in load should occur under irradiation. An additional advantage of the disc springs, as is true with coil springs and clamping devices, is the low energy storage. In applying 20 kbars to a 1/4 in. sample, only 150 ft-lb of energy is stored, which is ~0.5% of the energy available in the event of a failure in a high pressure gas system delivering the same pressure. This inherent safety is very important when one considers the consequences of a chamber rupture. It is thought that disc springs offer the best method for mechanically generating the required load and are superior to hydraulic or thermal methods for the following additional reasons: they can safely deliver large loads at adjustable deflections, they are stable to irradiation, corrosion, and thermal environments, and then allow generation of the pressure outside the reactor where it can be properly measured and controlled.

With further modifications to the pressure container and pressure transmitter, the simple clamp method can be improved still further. This will be discussed later.

PRESSURE CONTAINMENT

As was stated earlier, a necessary requirement in the generation of pressure is the reduction in volume of the sample due to the inward movement of the walls that initially confine the specimen. There are at least three different methods by which one can realize the above objectives:

- Provide massive, rigid, close fitting walls around a sliding piston
- Provide thin gaskets to keep the sample from extruding between two advancing surfaces
- Provide high shear strength material which, by extruding between the piston and close fitting walls, prevents the expulsion of the sample as the pistons are advanced.

Examples of the first technique include simple and supported piston-cylinder devices. The second technique is exemplified by Bridgman anvils. Examples of the third technique include Belt, Girdle Tetrahedral, and Cubic devices. The reader is referred to Reference (1) for a more detailed description of these devices.

While all three of these methods could be applied in the reactor, only 1 and 3 are capable of generating hydrostatic pressure. Number 1 can be used up to 20 to 30 kbar beyond which it is necessary to go to the third method. Method number 1 will be used as a basis for detailed discussion.

We have been tacitly assuming a piston and cylinder geometry in our schematic drawings of Figures 1, 2, 6, 7, and 10. In those cases we have assumed that the confining walls around the sample behave elastically regardless of the pressure contained. We have also assumed that fit between the walls is so close that none of the pressure transmitting media is lost around the piston. In reality the container has finite strength and one must design the piston so that the transmitting media dose not extrude around the piston.

It is then more convenient to treat the container problem in two parts: the confining walls and the piston. This is necessary since the maximum pressures attainable will depend on the strengths of the materials involved and because the walls are not usually subject to the same stresses or made of the same material as the piston. Following a brief analysis we will examine the problem of pressure transmitter extrusion.

Cylinder Walls

The maximum allowable pressures generated in a thin walled cylinder can be obtained from the familiar "thin wall" formula,

$$P_{i_{max}} = \frac{2t}{D_i} \sigma_y \tag{3}$$

where $P_{i_{max}}$ is the maximum internal pressure,

t is the wall thickness,

D_i is the internal diameter of the cylinder and is assumed to be >>2t,

σ_y is the elastic limit of the wall material.

Therefore, considering the elastic limits of most materials of construction, Table IX, we find that P_i is limited to ~50,000 psi (~3 kbar).

TABLE IX. Representative Values for the Strength of Common Metals at Room Temperature

Material	State[(a)]	Yield Stress Limit 1000 psi	Ultimate Stress Limit 1000 psi	Reference
Lead			1.5	12
2S-AL	A	5	13	55
5250 AL	A	14	29	55
6061-AL		43		55
7000-AL		91		55
Copper	W		59	12
Nickel	W		113	12
Zircaloy-II		61	67	(b)
Monel	Drawn	95	125	8
Be-Cu alloy	H		210	55
Inconel	W	90	112	8
Hastelloy-B		65	140	8
SAE-1020	A	40	60	55
-8630	A	60	90	55
-4340	A	67	109	55
-4340	H	255	290	(c)
Mild Steel	W	65	110	12
Stainless Steels				
410		150	200	8
431		185	270	8
301		40	100	8
347		35	85	8
Maraging Steel		290	337	8

(a) A = Annealed
H = Hardened
W = Worked

(b) Nucleonics Data Sheet #30

(c) The Tensile and Impact Properties of Quenched and Tempered Nickel Alloy Steels in Different Sizes, the Int. Nickel Company, 1946.

Increasing the thickness of the cylinder wall such that $2t >> D_i$ modifies Equation (3) to(7)

$$P_{i_{max}} = \frac{K^2 - 1}{K^2 + 1} \frac{\sigma_{ty}}{\sqrt{3}} \tag{4}$$

where K = ratio of outside diameter/inside diameter

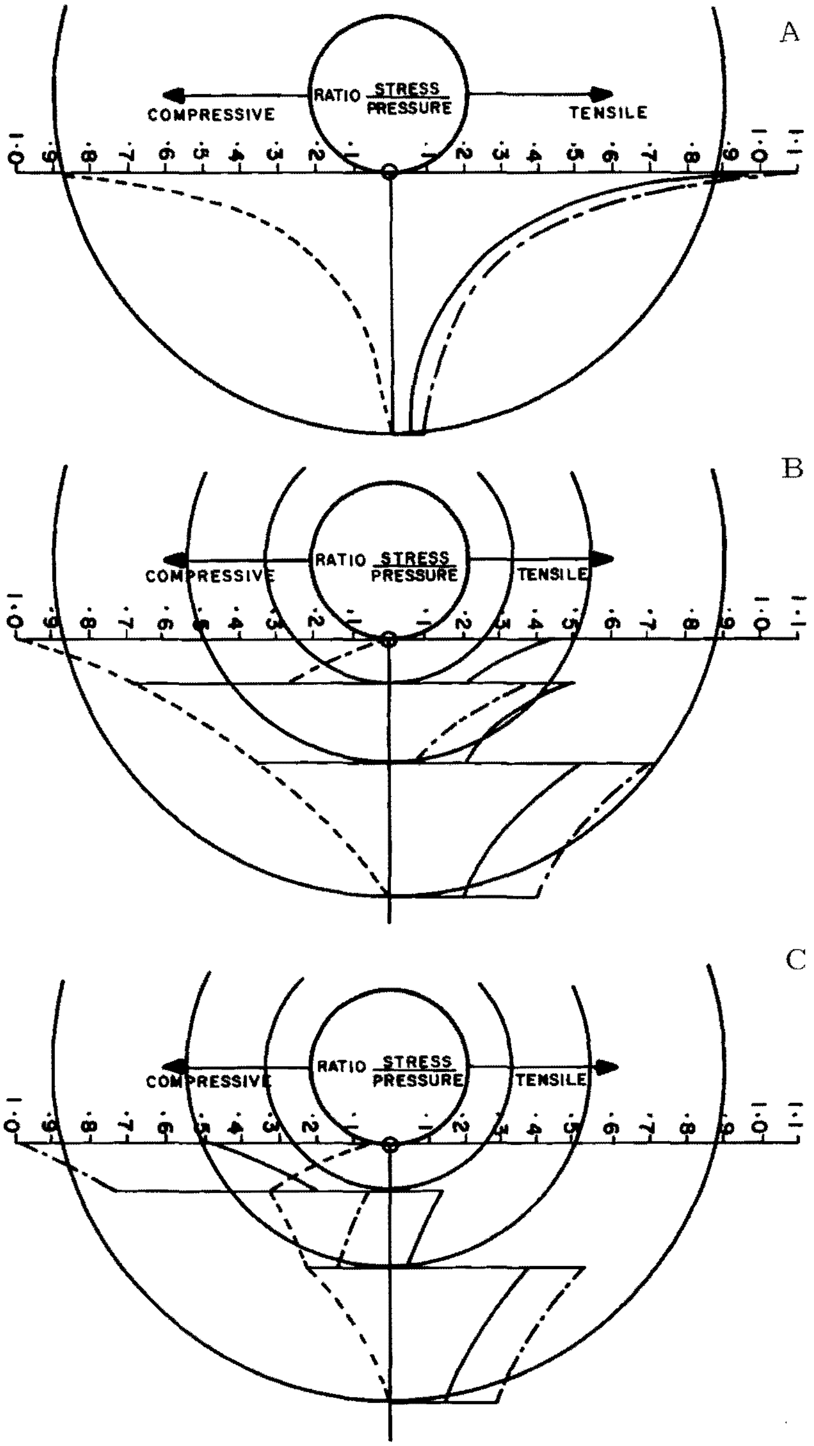
σ_{ty} = is the yield stress in tension of the wall material.

This means that an infinitely thick cylinder will yield at ~0. 58 σ_{ty} or ~150, 000 psi (10 kbar) for the strongest materials available. As a matter of fact, it is useless to make K greater than 3 or 4. This can be realized from the fact that in going from K = 3 to K = 4 there is only a 5% increase in strength obtained at the cost of an increase of 77% in volume.

The problem is that the whole cylinder does not cooperate in sharing the load. The inner layers of material are subjected to much higher stresses than those on the outer edge. Figure 11-A illustrates this point by plotting the compressure and tensile stresses as function of radius in a pressurized cylinder. Figure 11-B and 11-C show how this stress distribution is altered by the use of supporting cylinders.

It must be emphasized that the $P_{i_{max}}$ in Equation (4) is not the pressure at which the cylinder fails, but it is rather the pressure at which the inner surface of the cylinder begins to plastically deform. Figure 12 shows the relationship between the bursting pressure and yield pressure for an alloy steel. Notice the effect of increasing K beyond 2 as it pertains to the start of overstrain.

To construct a reliable apparatus developing pressures in excess of 10, 000 atm, a new approach is necessary. To further increase the allowable pressure inside the vessel, it is necessary to subject the vessel to an external pressure which will assist in balancing the internal pressure.



A. Simple Cylinder with Internal Pressure Acting
B. Ideal Triplex Cylinder with Internal Pressure Acting
C. Ideal Triplex Cylinder Showing Residual Stresses
Stresses: Shear ——— Hoop —-—- Radial ------

FIGURE 11. Stresses for Cylinders Having a Diameter Ratio of 4.5 to 1(55)

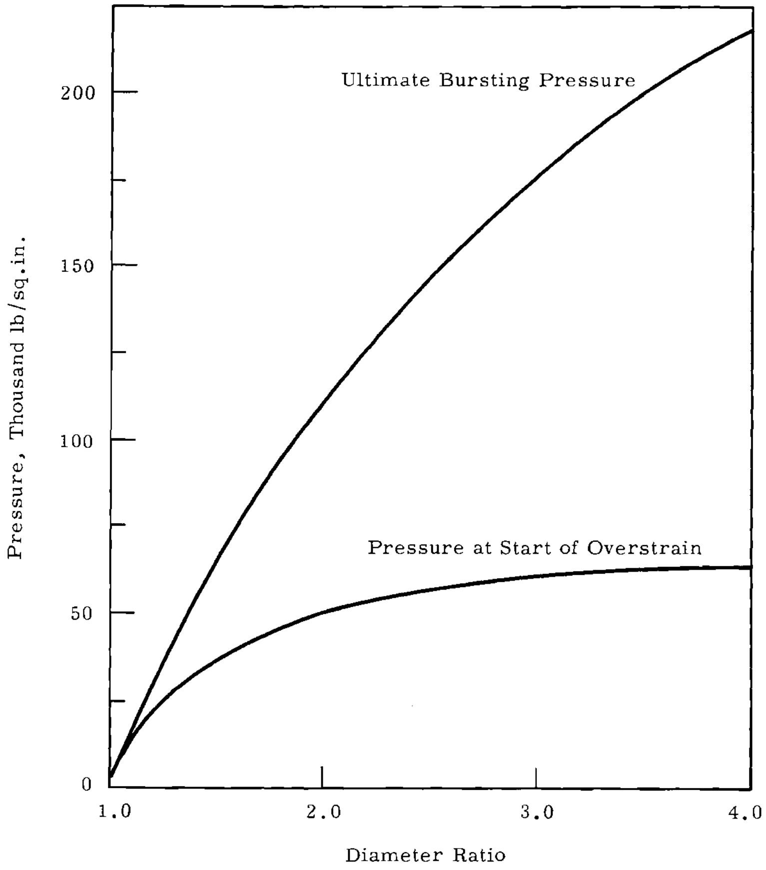


FIGURE 12. Point where Overstrain Begins, Compared with Bursting Pressure for a Cylinder of Alloy Steel Having a Tensile Strength of 137,000 lb/in.^{2} (56)

This can be done in several ways. All involve the same basic but familiar principle -- namely, reinforcing a core tube either by shrinking other tubes over it or by winding around it layers of continuous wire or strip. In this way a residual tensile stress is developed in the outer layers and a corresponding compression is developed in the core. When the pressure load is applied, compression in the core cancels out some of the resulting tensile stressing at the expense of increased tension in the lightly stressed outer layers. Figures 11-A and 11-B show how the stresses appear in a multicylinder arrangement before and after loading. Theoretically, assuming the compressive yield stress equals the tensile yield stress, the maximum pressure now attainable with this arrangement is,

$$P_{i_{max}} \simeq \frac{2}{\sqrt{3}} \sigma_{ty} \qquad (5)$$

or twice that of the unsupported cylinder.

Bridgman(3) has developed a marked improvement on the shrink-fit method for maximum pressures less than 20 to 30 kbar (Figure 13). It consists of making the inner vessel conical and forcing it into a complementary conical sleeve, so that it becomes compressed in the same way as a wedge. A simple analysis shows that if the inner core is pushed into the sleeve by a thrust, F, the supporting pressure, P_p, on the outside of the cone is

$$P_p = \frac{F}{\pi(r_2^2 - r_1^2) + \pi H(r_1 + r_2)\,\mu \cos \alpha} \qquad (6)$$

where the dimensions refer to Figure 13.

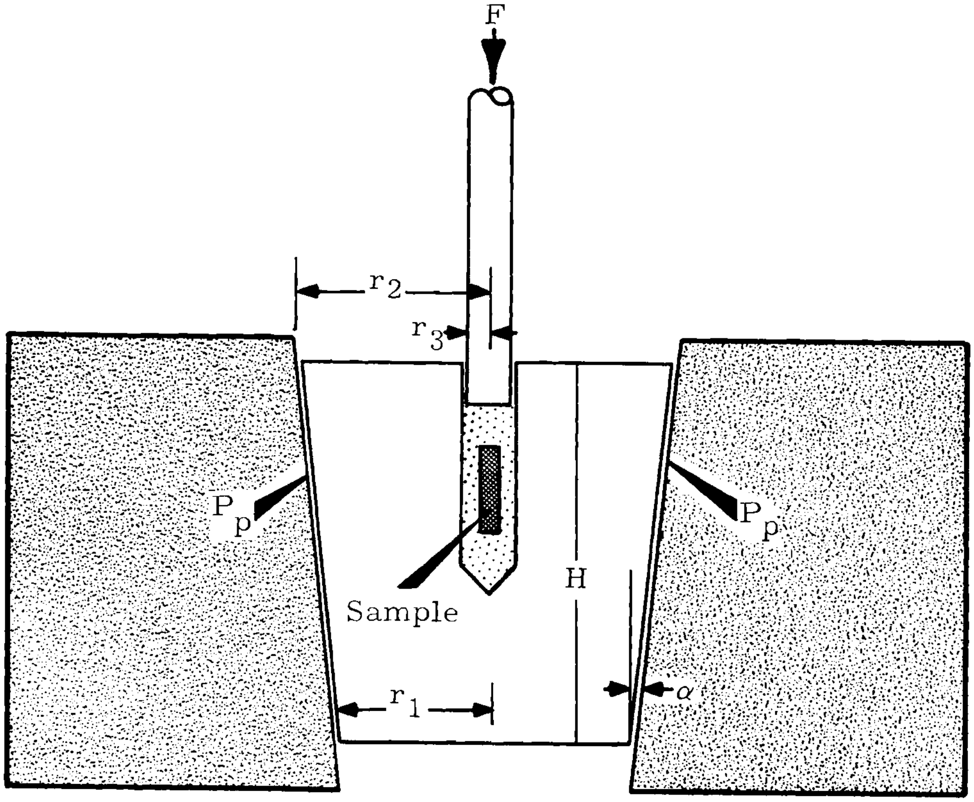


FIGURE 13. Schematic of Bridgman's Method of Providing External Support for a Pressure Vessel

To give a numerical example, if

$F = 14,700$ lb

Sample chamber diameter = 0.25 in.

$r_2 = 0.335$ in.

$r_1 = 0.269$ in.

$\mu = 0.02$

$H = 1.5$ in.

$\alpha = 2.5°$

$$P_p = \frac{14,700}{\pi(0.335^2 - 0.269^2) + \pi(1.5)(0.604)(0.02)}$$

$$P_p \simeq 5.5 \text{ kbar}$$

Assuming no friction along the sample walls the pressure on the sample is 300,000 psi (~20 kbar). In the absence of a supporting pressure, the fibers along the sample chamber wall would be subjected to >400,000 psi tensile stress! However, the supporting pressure of 81,000 psi is magnified to ~200,000 psi compressive stress on the inner fibers so that at maximum pressure (20 kbar), the absolute tangential tensile stress on the inner chamber walls is only ~230,000 psi (~16 kbar). These stresses allow the walls to remain close to the elastic region during the generation of the pressure.

As stated before, the main advantages of this device is that the supporting pressure and chamber pressure both rise together and fall together, thus reducing the tendency of the sample to extrude around the piston. It is also much simpler to construct than the shrink-fit ring designs.

In considering the problems previously encountered with the finite relaxation of the cell, the Bridgman method of supporting the inner cylinder has one more added advantage. The amount that the cylinder moves into the sleeve will contribute to the total amount of takeup by the outer sleeve. This can amount to as much as 0.050 in. in the sample cell in Figure 14. This extra takeup acts somewhat in the same manner as a spring and tends to reduce the error associated with container relaxation. It may even make the disc-spring concept less advantageous than the simpler clamp mechanism.

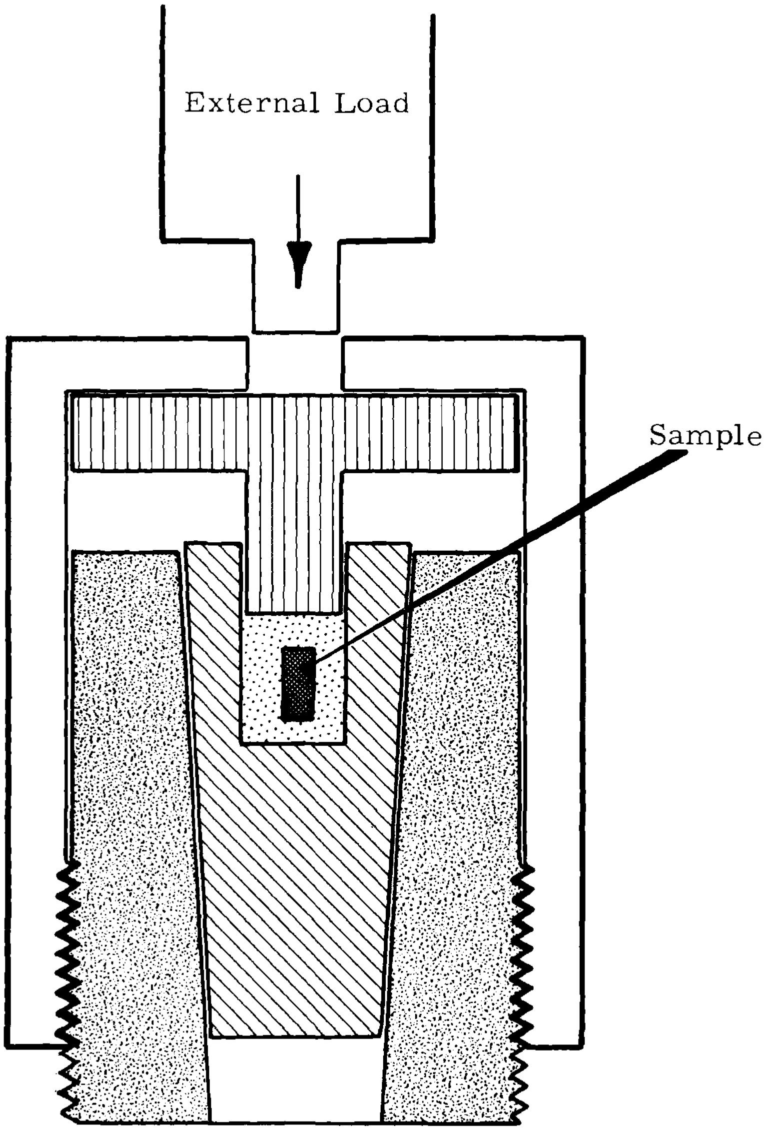


FIGURE 14. Schematic of a 'Clamped' Pressure Device Using the Supported Cylinder Concept.

As seen from Table IX, the highest strength materials of construction for pressure cells are:

- 4340 steels
- Maraging steels.

The strongest maraging steels contain 6 to 7% or more of cobalt which is undesirable inside the reactor (Table X). The maraging steels without cobalt are usually not much stronger than the best 4340 steels.

TABLE X. Typical Composition of Maraging and 4340 Steels

Element	Maraging Steels(a) 12 Ni-5 Cr-3 Mo	Maraging Steels(a) 18 Ni-Grade 300	4340 Steel(b)
C	0.025	0.03	0.38-0.43
Mn	0.08	0.01	0.60-0.80
P	0.008	0.010	
S	0.010	0.010	
Si	0.08	0.10	
Ni	12.0	17-19	1.65-2.00
Cr	4.75	--	0.7-0.9
Mo	3.00	4.6-5.1	0.2-0.3
Ti	0.25	0.6-0.8	
Al	0.30	0.05-0.15	
B	0.002	--	
Co	--	8-9.5	
Fe	--	Balance	Balance
Max. Yield Stress	190,000	290,000	225,000

(a) United States Steel, report No. ADUSS-94034, 1964
(b) The International Nickel Company, report No. A-68, 1946

From a nuclear standpoint the 4340 steels are acceptable. The major long-lived radioactive isotope is Fe^{59} with a 45 day half life. However, its parent isotope, Fe^{58}, is only present in 0.33% abundance and has a cross section of ~1 b. It can be shown that the activity of 1 g of 4340 which has decayed for 30 days after an exposure to 5×10^{18} nvt thermal flux is only ~2.5 mr/hr at 1 ft.

The effects of irradiation on the mechanical properties of 4340 have been studied and it is generally found that the yield and ultimate strengths increase while there is a slight reduction in ductility (Figure 15a, b, c). None of these effects is very serious at the anticipated exposures.

The steel does have a tendency to corrode in an aqueous environment, but should present no problems for runs <1000 hr. A 4340 steel pressure device could also be clad with a noncorroding material to eliminate this problem.

Data Points	Reference	Irradiation Temperature,°C	Test Temp.°C	Preirradiation Condition,etc.
1	(58)	67	Room	As Quenched from 1650°F
2	(58)	67	Room	800°F, Draw
3	(58)	67	Room	1000°F, Draw
4	(58)	67	Room	1200°F, Draw
5	(58)	67	Room	1600°F, Draw

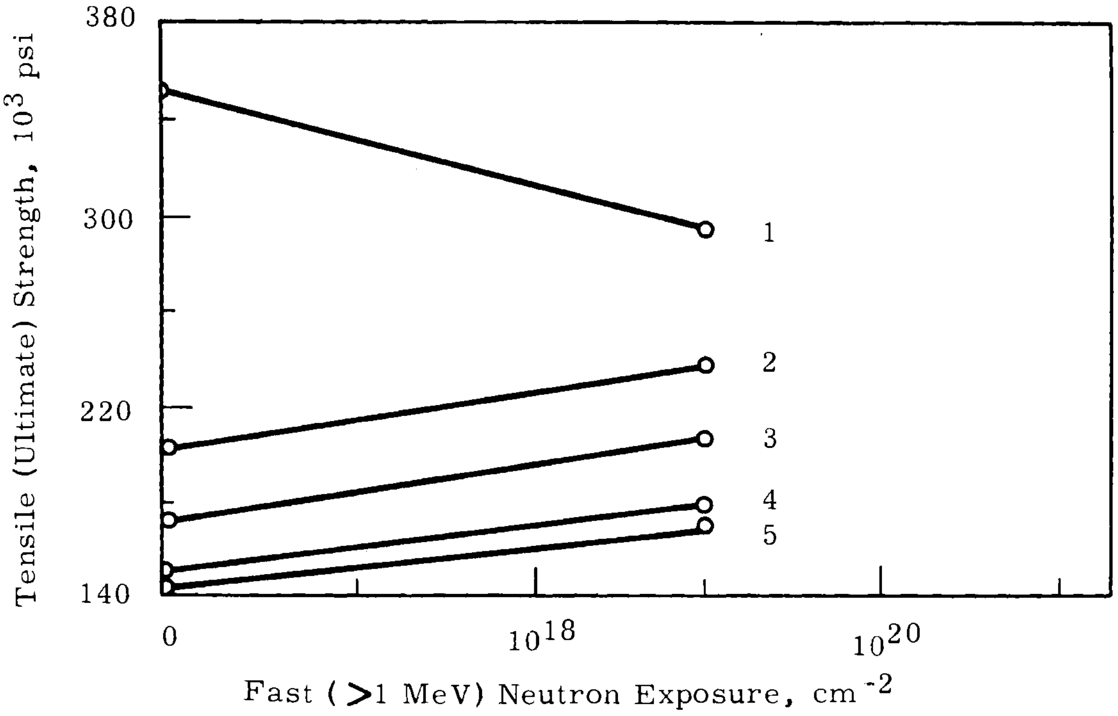


FIGURE 15.a Tensile Strength of SAE-4340

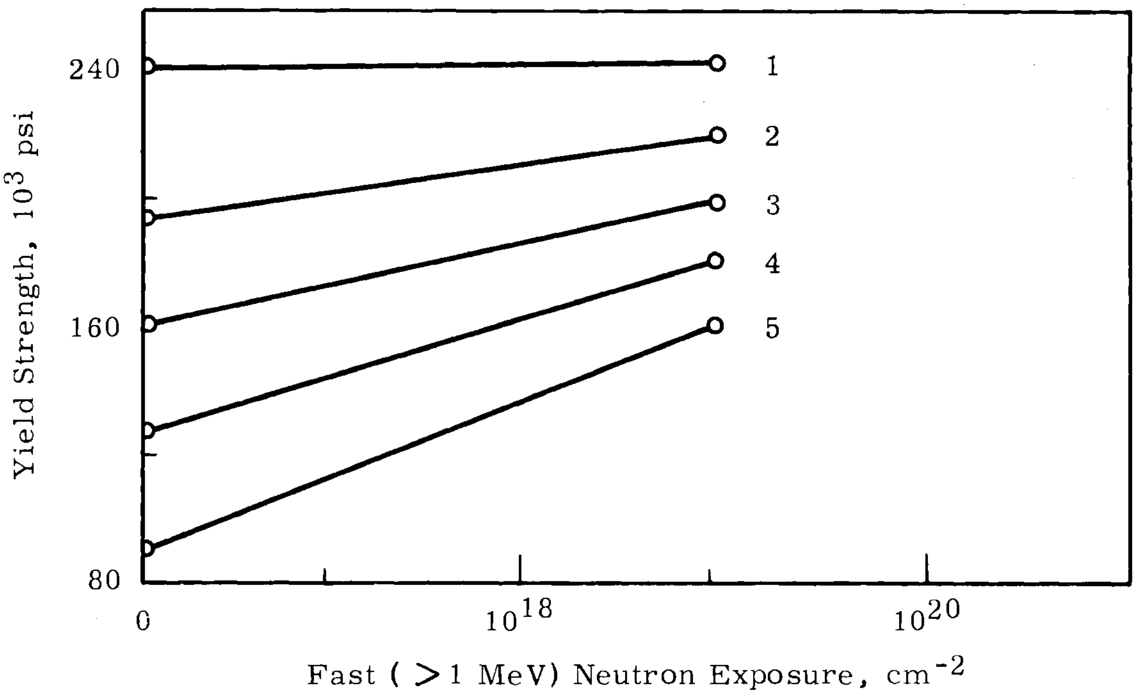


FIGURE 15.b. Yield Strength of SAE-4340

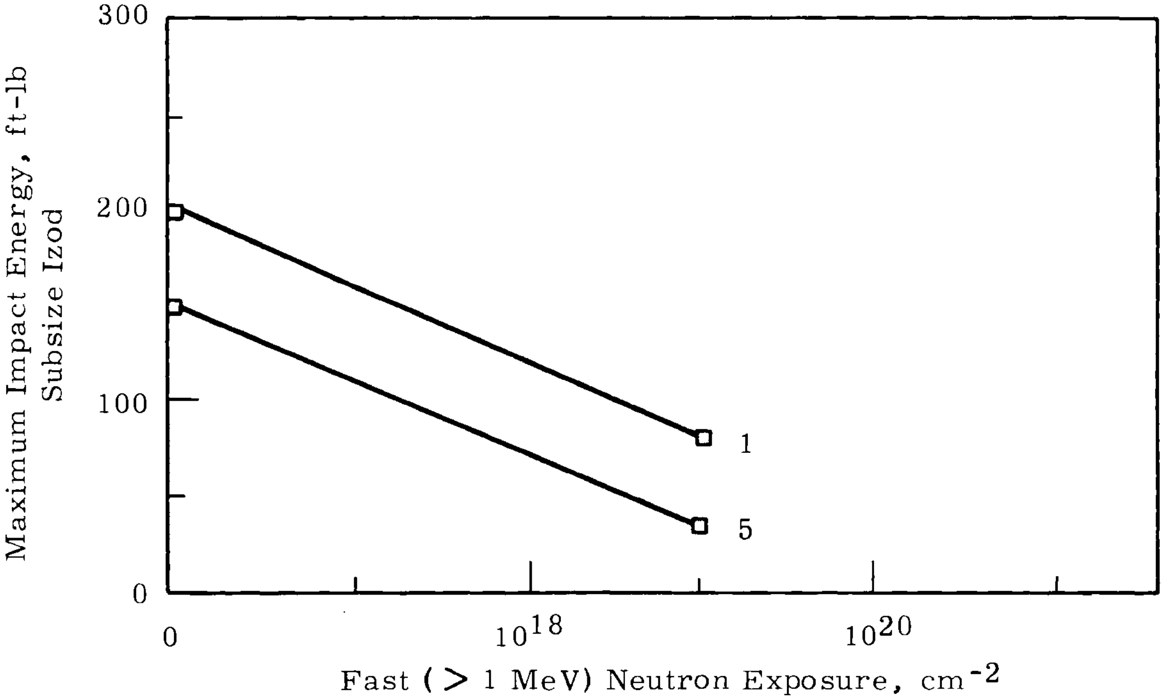


FIGURE 15.c. Impact Energy of SAE-4340

It has been found in practice that steels harder than RC-50 or with carbon content of more than 0.6% will not withstand sufficient elongation before rupture. On the other hand, if the hardness is below RC-40, the bore will enlarge under loading. With these limits in mind and considering the properties presented in Figure 16, a 4340 steel with RC-46, $\sigma y \simeq 200,000$ psi, should suffice for the wall components prior to irradiation. Even with a 10% increase in hardness and yield strength due to irradiation ($\sim 5 \times 10^{18}$ nvt), the pressure vessel should retain enough ductility for our purposes.

Piston Material

The major problem in picking a suitable piston material is to find one which has a sufficiently large compressive yield limit. One material, cemented tungsten carbide, is superior to other materials in this respect.

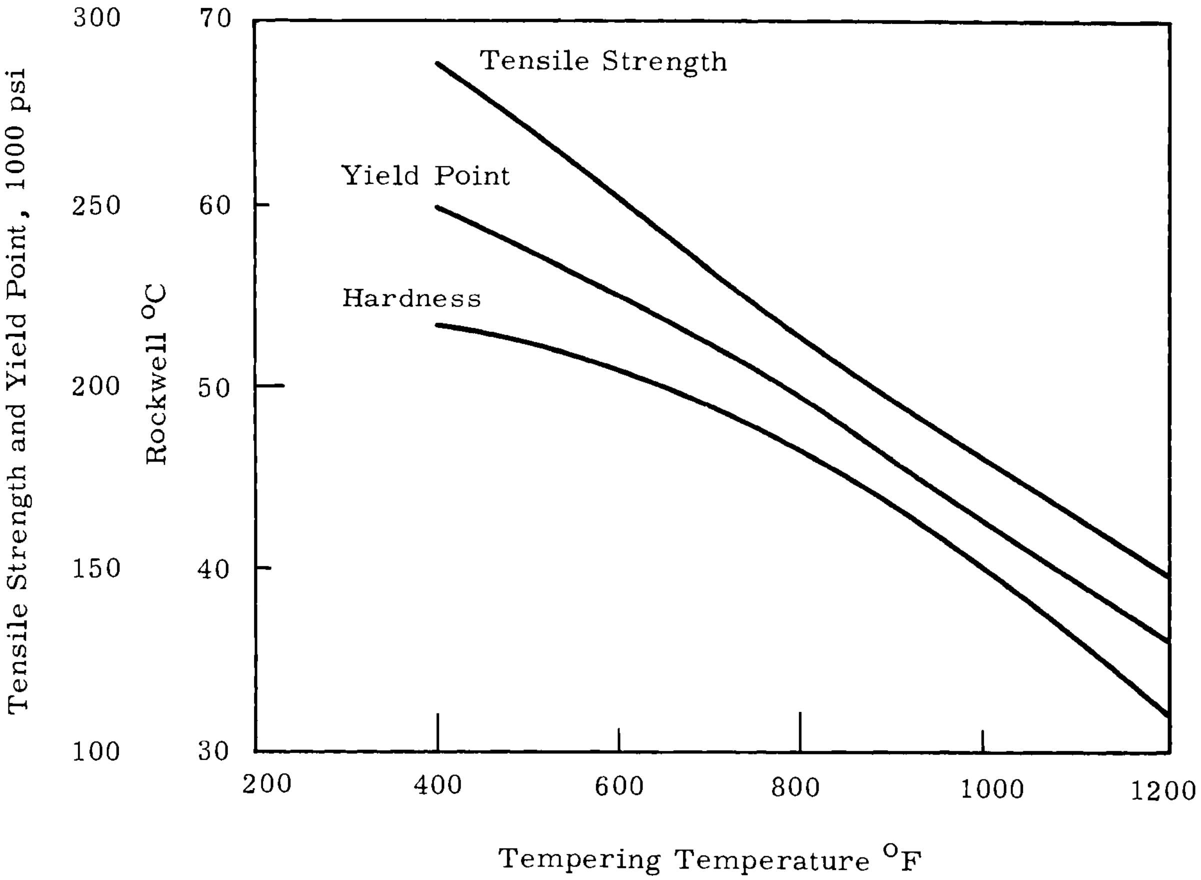


FIGURE 16. Properties of Oil Quenched and Tempered 4340 Steels (International Nickel Company, Report No. A-68, 1956)

Its compressive strength is 800,000 psi (~50 kbar).(57) As seen from Table XI, this material usually contains cobalt as a cementing agent in 5 to 6% quantities. Again this is undesirable from the nuclear standpoint.

Since the requirements for our hypothetical pressure cell do not exceed 20 kbar (300,000 psi) it is possible to use hardened steel as a piston. Substitutes such as Carpenter Hampden steel hardened to RC-60-63 and Carpenter Speed Star Steel, RC-65-66, can be used to pressures of 20 to 30 kbar at room temperature. The compositions of possible piston materials are listed in Table XI.

TABLE XI. Typical Chemical Compositions of Possible Materials for High Pressure Pistons

	WC		Carpenter	
	GE 999	GE 883	Hampden Steel	Speed Star Steel
W	91	88.25	-	6.25
C	6	5.75	2.1	0.82
Co	3	6	-	--
Cr			12.0	4.25
Mo				5.00
V				1.90
Fe			Balance	Balance

Piston Design

Aside from picking the proper material for the construction of a piston, one must also consider the problem of keeping the sample and pressure transmitting medium from leaking out of the high pressure region. Obviously, the strongest materials in nature are useless unless the system is designed properly.

If the sample and/or pressure transmitting medium are solid, it is usually sufficient to design the piston for a sliding fit in the pressure cylinder under no load conditions (see Figure 17). Under load, the cylinder walls expand slightly as does the piston, but because of the selection of different construction materials, the walls usually expand to a greater extent. When this happens some of the sample can extrude past the piston face into the gap between the cylinder and piston walls (Figure 17B). The finite shear strength of the extruded solid and frictional effects on the walls keeps this loss of material to a minimum. In some cases, a circular ring of triangular cross section can be placed around the piston to prevent extrusion of the sample material. The ring material will extrude in the place of the sample (Figure 17D).

When the sample or the transmitting medium around the sample is liquid, definite problems are associated with the configuration in Figure 17. The low shear strength of liquids even under high pressure will permit them to flow around the piston and possibly out of the system. Various seals and "O" ring designs have been conceived to solve this problem, but none of them work as well as the seal invented by P. W. Bridgman(7) (Figure 18).

In this arrangement a hole is drilled along the axis of the piston. Into this hole a close fitting stem from a mushroom plug is fitted. The head of the mushroom is also cylindrical and fits accurately to the internal diameter of the cylinder. The stem is threaded so that it can be pulled out easily.

A soft ring of packing material is placed around the stem of the plug and the stem is then inserted into the axial hole in the piston. When a load is applied to the piston, generating a pressure in the liquid below the piston, the pressure inside the packing material also rises. In fact, because the cross-sectional area of the packing material is less than the cross-sectional area of the piston, the pressure in the packing material is greater than that on the sample. Consequently, this seal will not allow the liquid to escape between the packing and the wall.

The packing material must be stable with respect to the fluid it is trying to contain and must be able to flow under pressure. Copper and lead are suitable for organic fluids, but one must be more selective

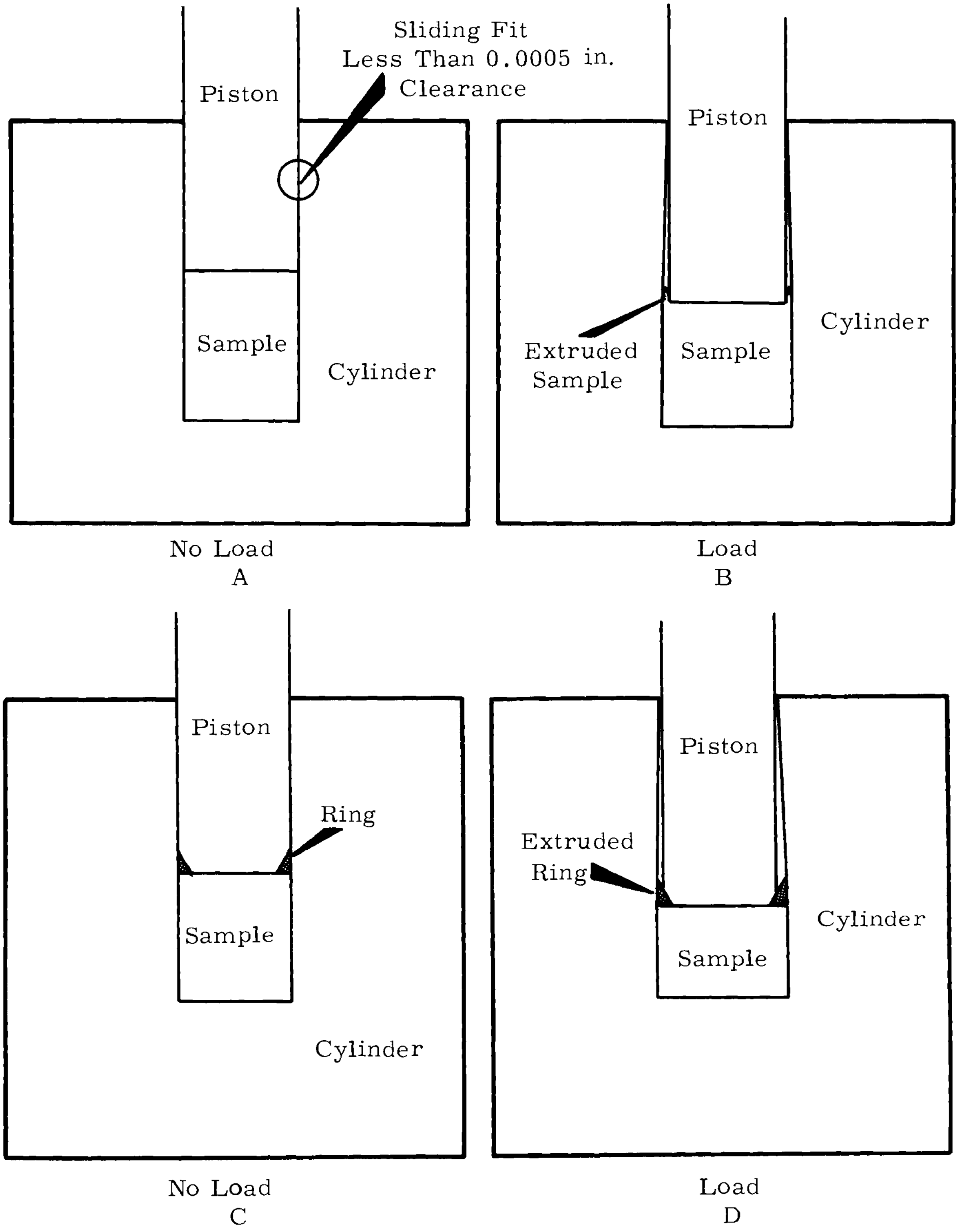


FIGURE 17. Extrusion Problems in a Piston-Cylinder Apparatus with Solid Pressure Transmitter

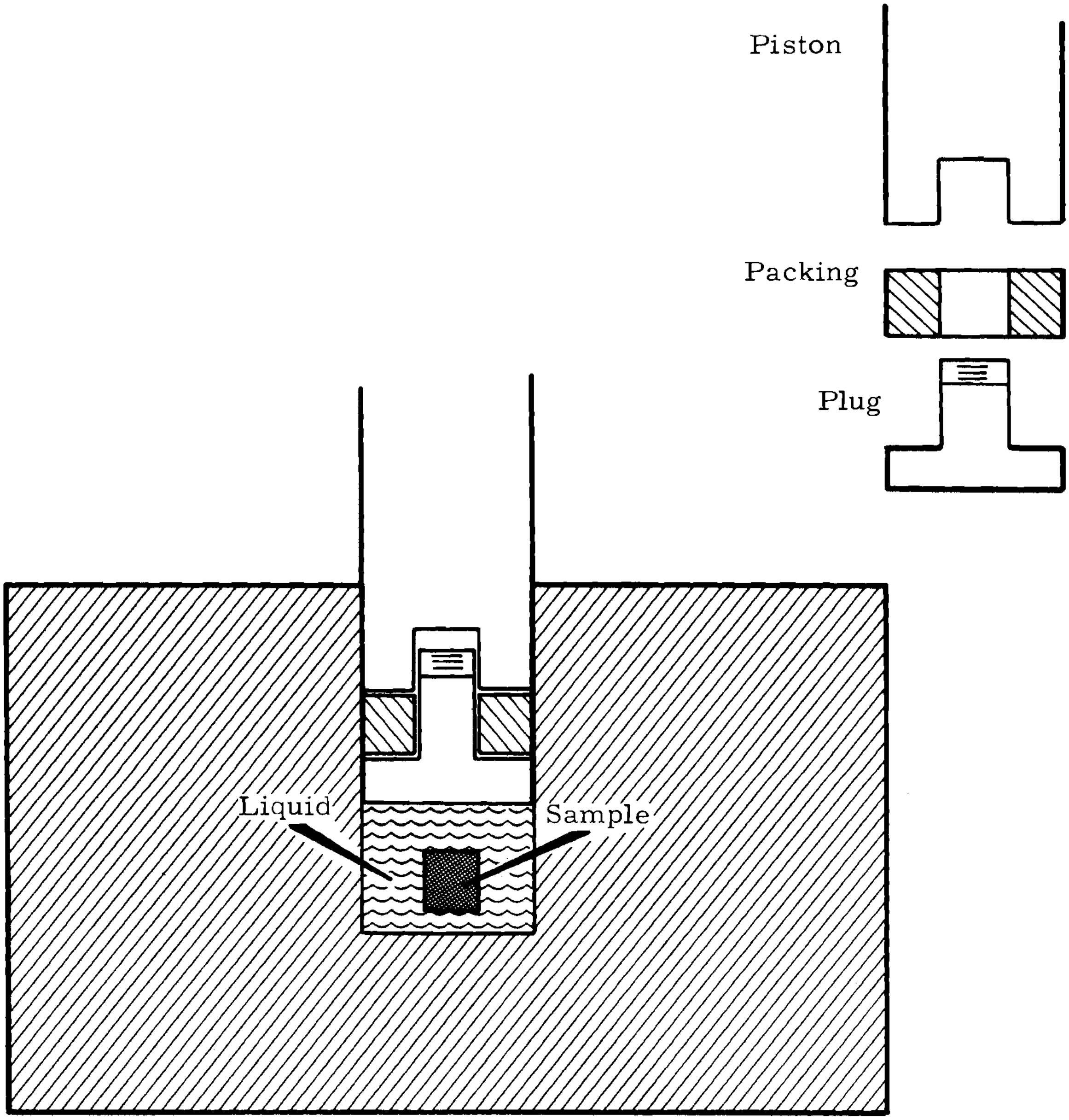


FIGURE 18. Schematic of Bridgman Seal

when working with the liquid metals (i. e. sodium, potassium, mercury, or gallium). Their extreme corrosiveness limits the available materials to a select few. Copper is not compatible with potassium, mercury, or gallium even at moderate temperatures.(59, 60) However, copper may be used in conjunction with NaK to moderate temperatures.(39) Lead is not compatible with liquid potassium, mercury, or sodium,(59) and has limited resistance to liquid gallium up to 300°.(60) Aluminum is not compatible with liquid gallium,(60) or mercury,(60) but can be used with the alkali metals.(59)

Packing materials are not limited to metals. Inorganic powders which are resistant to the contained fluids can also be used. Materials such as BeO, Al_2O_3, SiO_2, ZrO_2, and graphite are possibilities for use with NaK, mercury, or gallium.(59, 60) The powders are first pressed into pellets and then machined to proper dimensions. The washer can then be placed between the plug and piston much in the same manner as metals.

PRESSURE TRANSMITTANCE

Assuming that the problems of pressure generation and pressure containment have been solved, one must then be sure that the pressure transmitted to the sample is truly hydrostatic. Analogous to the case of pressure generation, the transmitter must:

- Transmit pressure hydrostatically (support no shear stresses) at all times
- Undergo no thermal or irradiation induced phase transformations under pressure
- Be noncorrosive and chemically compatible with the sample
- Not constitute a hazard to the reactor or interfere with its operation.

Gases

In general, gases satisfy requirements 1 through 3 below 10, 000 atm. Above 10, 000 atm there are only six elemental gases that remain in the gaseous form; helium, H_2, neon, N_2, argon and

O_2 (see Table XII). The gases H_2 and O_2 are not used because of their explosive nature; helium is undesirable because of its high diffusivity; and argon must be heated if it is to be used much above 10 kbar. Nitrogen is cheaper and as satisfactory as neon; however, energy storage and safety presents the same problems as in the case of pressure generators (see pages 4 through 9). It is also physically difficult to "pack" enough gas into the sample chamber to allow for the high compressibility of gases. Both of these reasons tend to preclude the use of gases for effective pressure transmitters in reactor.

TABLE XII. The Melting Properties of the So-Called "Permanent Gases"

	Temp °K	1, 000 atm(a) Temp °K	3, 500 atm(b) Temp °K	10, 000 atm(c) Temp °K
He	0. 9	14	40	
H_2	14. 0	35	60	
Ne	24. 5		62	
N_2	63. 2	82	120	185
Ar	83. 9	104		280
O_2	54. 7	65	83	
CH_4	89. 1			

(a) Reference (50)
(b) Reference (36)
(c) Reference (51), p. 66

Liquids

For pressures in the range of 15, 000 to 450, 000 psi (1, 000 to 30, 000 atm), pressure transmission by means of liquids is convenient and efficient. The corrosiveness of the liquids can be kept to a minimum by using organics. The hazards of a gas system are greatly reduced because of the smaller energy storage in compressed liquid as compared to a gas at the same pressure. However, even though organic liquids satisfy two of the requirements for pressure generation, their increased viscosity and possible solidification constitute significant problems in the very high pressure region above 30 kbar.

Bridgman(7) has studied the viscosity of the most promising organic systems with respect to pressure and finds that the viscosity increases exponentially (see Figure 19). Above 30 kbar at room temperature, only 4 normal liquids remain liquid: iso- and n-propanol, n-amyl alcohol, and n-butyl bromide. The viscosities of i-propanol, n-amyl alcohol, n-Buty Bromide at 30 kbar are about 10^5 poise.(62) When the viscosities of fluids approach this order of magnitude, considerable problems of fluid flow are encountered. It is known that pressure gradients of a few kbars per centimeter take minutes to relax at viscosities of 10^6 poise or greater. Even n-propanol whose viscosity at 30 kbar is about 10^3 poise will approach this region before 40 kbar. However, since our maximum desired pressure is <20 kbars, isopentane and methanol appear to be satisfactory in the absence of irradiation.

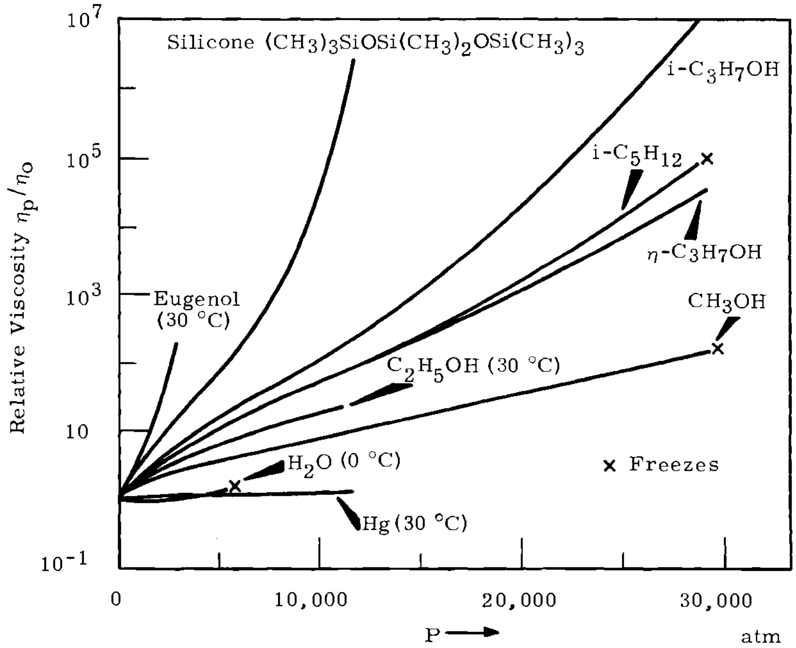


FIGURE 19. The Viscosities of Some Compressed Liquids. The Measurements were made at Room Temperature Unless it is Otherwise Indicated.(6)

As stated before (pages 4 through 9), organic liquids are quite susceptible to ionizing radiation. It has been shown that the most radiation damage resistant fluids belong to the polyphenyl group. However, even these organics are severely decomposed at fast fluences of 10^{18} nvt. Under extreme pressures this maximum allowable exposure is expected to be even lower. In addition, pressure tends to raise the melting points of most organic fluids. This means that the temperature of the cell would have to be above 70 to 100 °C at all times to prevent the freezing of the organic which would destroy the desired hydrostatic conditions. Considering these factors, organic fluids are an undesirable choice for a pressure transmitting medium.

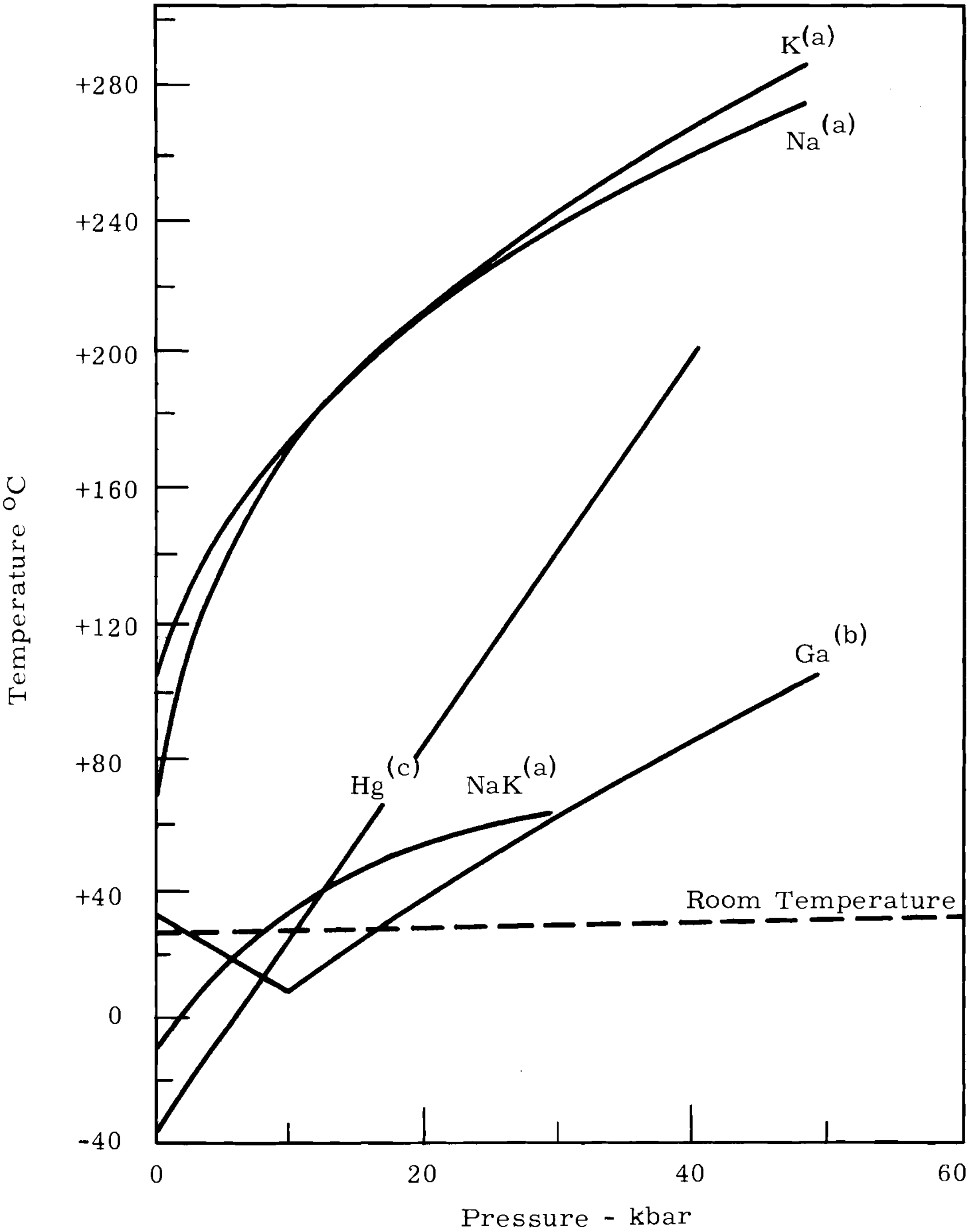
Liquid metals such as sodium, potassium, NaK, mercury, or gallium are very attractive from both thermal- and radiation-stability standpoints. The melting points of these materials as a function of pressure are shown in Figure 20. It can be seen that the melting points of sodium and potassium are quite high at 20 kbar which would tend to preclude their use. Mercury, gallium and NaK all have melting points below 60 °C at 20 kbar, and gallium will be liquid above 30 °C at that pressure.

The viscosity of mercury increases by only 50% under 10 kbar(6) so that there will be no problems of hydrostaticity even at 20 kbar or more. The same should be true for NaK and gallium.

The compressibilities of the liquid metals are

mercury(44)	3.7×10^{-6} b^{-1}
gallium(7)	4×10^{-6} b^{-1}
sodium(66)	35×10^{-6} b^{-1} at 1 atm
	10×10^{-6} b^{-1} in range 1 to 20 kbar.

All three metals have drawbacks when considering their corrosive properties. NaK burns when it comes in contact with water vapor, and both gallium and mercury are quite corrosive.



(a) Reference (63)
(b) Reference (64)
(c) Reference (65)

FIGURE 20. Melting Points of Liquid Metals as a Function of Pressure

One can narrow the field further by eliminating mercury. Its nuclear properties ($\sigma_a \simeq 360$ b) make it undesirable in large quantities. Since it is equally as corrosive as gallium to most structural materials and sample materials of interest, its higher melting point makes it even less desirable than gallium. Gallium and NaK have neutron absorption cross sections of ~3 and ~1. 7 b, respectively.

In choosing between NaK and gallium, NaK is suitable for use with such elements as uranium, aluminum, iron, copper, and the refractory elements, while gallium can be used with lead, iron, and the refractory elements.

While both gallium and NaK are corrosive to materials of construction, gallium is relatively stable in air. The violent reaction of NaK with water vapor makes loading and unloading the transmitter rather complicated. In addition, the possibility of a failure of the pressure cell with release of the reactive metal into the system is doubly hazardous with NaK. Both sodium and potassium have short-lived radioisotopes. This makes their activity quite high within a few minutes after being removed from the reactor. If NaK should burn, the subsequent smoke would be radioactive and would present a personnel hazard in the area. For this reason, gallium is favored with NaK for use in the reactor when compatibility problems are favorable.

The containment of the liquid transmitter can be accomplished in two ways:

1) A seal on the piston (i. e. , Bridgman seal)
2) Confine the liquid to a collapsible can which is then acted on directly by the piston.

The first method has already been described; therefore, the second method will be discussed here. There have been many designs of collapsible cans, all of which provide a mechanism by which the fluid can be compressed uniaxially while remaining around the sample (Figure 21). One design is to machine the upper and lower parts of the can so that they can slide over one another as the piston advances. The fit between the sliding portions is made sufficiently loose to allow extrusion of the fluid at 1 atm. Under external pressure (and subsequent internal pressure) the sliding walls usually fit quite closely. Ordinarily, little or no fluid is lost.

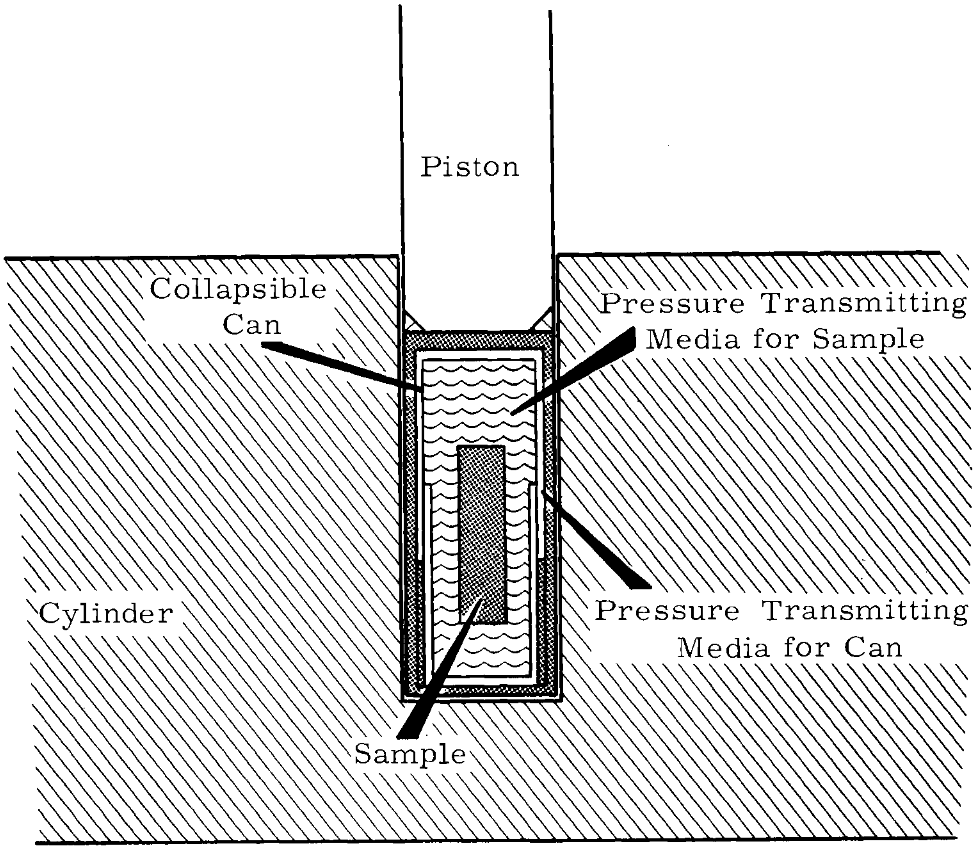


FIGURE 21. Schematic of Collapsible Can Arrangement

From our previous requirements, that is, an 0. 25 in. diam pressure chamber, we see that the maximum diameter of allowable sample is between 0. 25 in. and 0. 15 in. for a completely liquid environment, or <0. 15 in. for a collapsible can arrangement. The smaller sample size in the latter case is due to the fact that we must surround the sample with liquid, can, and quasihydrostatic material to transmit the pressure to the can.

CALIBRATION AND PRESSURE STABILITY

In the simplest case one can compute the pressure on a sample by dividing the force by the area on which it acts. In reality, frictional effects along the cylinder walls, finite container relaxation, and uncertainty in the precise area over which the pressure acts, will tend to reduce confidence in pressure deduced from the ideal F/A ratio. In order to compensate for these effects, one usually measures the force required to promote a phase transformation which occurs at a known pressure. This point can be determined by a variety of measurements; electrical resistance, differential thermal analysis (DTA), or volume changes.

By far the simplest technique in a piston and cylinder device is the measurement of volume change. This consists of substituting a calibrating material in place of the sample and measuring the piston travel as a function of load applied. When the phase transformation takes place, there is usually a large negative volume change in the calibrant. This results in a discontinuous advance of the piston at relatively constant load and provides the desired calibration point.

The electrical technique is widely used at pressures above 25 kbar by noting the resistance of such elements as bismuth, ytterbium, thallium, and barium as a function of load. When these elements undergo a phase transition (Bi-25.4 kbar, Tl-37 kbar, Yb-39.5 kbar, Ba-59 kbar), a discontinuous change in resistance from one phase to another is found. The load at which this discontinuity occurs provides the calibration point in this case. Since we were concerned with relatively lower pressures (<20 kbar), this technique is not as functional as the volume change measurement.

The DTA measurements are considerably more complex than either of the previous measurements, hence not as desirable as the volume change method.

There are several compounds which undergo phase transitions below 20 kbar, and a few are listed in Table XIII.

TABLE XIII. Selected Compounds Which Under Phase Transition at Room Temperature and Below 20 kbar

Compound	Transition Pressure, (kbar)	$\Delta V/Vo$	Reference
KNO_3	2. 3		10
AgI	2. 9		10
RbI	3. 6	0. 139	67
CuI	4. 0		68
RbBr	4. 2	~0. 135	67
RbCl	5. 3(67)	0. 146(69)	
RbF	6. 2		70
TlBr	6. 5		10
$NaNO_2$	14. 5		9
KF	15. 2	0. 108	70
KI	17. 4	0. 222	67
KBr	17. 5	0. 193	67
KCl	19. 2	0. 183	71
CsF	20. 0	0. 100	70

In order to measure the pressure that the sample experiences, the calibrant should be subjected to the same environment as the sample; that is, it should be immersed in the pressure transmitting media. In our case this media was chosen to be either gallium or NaK. Hence, we must now consider the possibility of reaction between the calibrant and transmitting media.

Since the Na^+, K^+, and Ga^{+++} anions are much more chemically reactive than Ag^+, Cu^+, or Tl^+, it seems likely that the halides of the latter metals will react when immersed in NaK or gallium. The affinity of NaK or gallium for oxygen would also tend to rule out KNO_3

and $NaNO_2$. This leaves potassium and rubidium halides or CsF. The rubidium salts are good for low-pressure <6 kbar calibration and the potassium and cesium salts are good for the higher-pressure (~20 kbar) calibration.

Referring to "The Thermochemical Properties of the Oxides, Fluorides, and Chlorides to 2500 °K" by A. Glassner, ANL-5750, 1958, we can obtain some idea of the relative stability of the calibrating compounds in relation to NaX, KX, and GaX_3 (X stands for a halide atom as seen in Table XIV). Among the fluorides, the free energy for formation of NaF is more negative than KF which is more negative than RbF at 300 °K. Since the free energy of formation for the NaK eutectic is only a fraction of a kilocalorie/mole at that temperature, both RbF and KF would appear to be unstable in such an environment. However, both RbF and KF have more negative free energies of formation per gram atom of fluorine GaF_3; therefore, they should be stable in gallium.

The chlorides, bromides, and iodides of rubidium and potassium should be stable both in NaK or gallium by the above reasoning and the data in Table XIV.

Either RbCl or KCl seem to be appropriate choices for a calibration media. They can be used in both gallium or NaK, and KCl will give a calibration point close to the maximum pressure desired (CsF could also be used).

An added and quite important advantage to be obtained by using the alkali halides in the pressure transmitter is the stability with which a constant presure may be maintained. As outlined earlier, a mechanical clamping device seemed most appropriate for an in-reactor device. The major disadvantage of such an arrangement was that slight relaxations in the clamping mechanisms could have large effects on the magnitude of the generated pressure, especially in systems where the pressure transmitter has a low compressibility. This uncertainty can be greatly reduced by inserting a pellet of KCl, for example, in the pressure transmitting medium along with the sample. As the pressure is raised, the piston will advance by an amount determined by the overall compressibility of the specimen cell. However, at 19.2 kbar the KCl will transform to a more dense phase allowing the piston to advance discontinuously. This will provide a calibration point.

TABLE XIV. Free Energy of Formation of Various Alkali Halides (from ANL-5750)

Compound	ΔF_f at 27 °C Kcal/mole Per gram atom of Halide
	Fluorides
NaF	-129
KF	-127
RbF	-125
CsF	-124
GaF_3	-80
	Chlorides
RbCl	-99
KCl	-97
NaCl	-92
$GaCl_3$	-37
	Bromides(a)
RbBr	-92
KBr	-92
NaBr	-87
$GaBr_3$	≃ -31
	Iodides(a)
RbI	-78
KI	-77
NaI	-69
GaI_3	≃ -20

(a) Reference (43)

If the pressure is now raised slightly beyond the KCl transition point and the piston clamped in place, we can be reasonably sure that the pressure to the sample will not fall below the reverse transition pressure. If the piston were to retract, slightly lowering the pressure in the sample chamber below 19.2 kbar, some of the KCl would transform back to the low pressure phase accompanied by an increase in volume. The KCl will continue to transform until it makes up for the change in volume due to the piston retraction. When the pressure is back to 19.2 kbar the reversion will stop. It will be as if we had a "pressure buffer" in the system to maintain a constant hydrostatic stress on the sample. The use of this technique along with the moving cylinder arrangement should eliminate the advantage in selecting disc springs for the system.

While it is possible to obtain many different pressures by varying the alkali halide in the medium, it may be desirable to be able to maintain a constant pressure anywhere within the 0 to 20 kbar range. This could be done by replacing the metallic washer in the Bridgman seal (see Piston Design) with the alkali halide. By varying the ratio of the cross-sectional area of the washer to the area of the piston, one could maintain any pressure between 1 to 2 kbar and 20 kbars.

For example, assume that we wish to generate a pressure of 10 kbar in our specimen chamber which is 0.25 in. in diameter. By using KCl as a washer material and making its cross-sectional area equal 0.0255 in.^{2}, we will obtain the 19.2 kbar transition in the washer when the pressure on the pressure transmitter is 10 kbar. This would mean that the unsupported area (the area of the hole inside the washer) should be ~0.024 in.^{2} which would make the diameter inside the washer equal to 0.175 in. Hence, by varying the washer and plug arrangement of Figure 17 along with the washer material, we should be able to maintain any pressure desired below 20 kbars. The accuracy of this technique is estimated to be ±5%.

SUGGESTIONS

After analysis of the problem of ultra-high hydrostatic pressure generation inside nuclear reactors, several points stand out.

- A clamp-type mechanism is preferred over the normal hydraulic systems.

- Gases and organic liquids are not very well-suited to the generation of hydrostatic pressures inside a nuclear reactor.
- Liquid metals such as NaK and gallium, while possessing some definite drawbacks, appear to be the only radiation, thermal and pressure stable fluids available to transmit pressures greater than 20 kbar in a reactor.
- Low alloy, high strength steels are favored for materials of construction.
- A method of pressure support is required to generate pressures greater than 10 kbars.
- Special seals are required to contain the liquid metal pressure transmitter at high pressure.
- The question of long term pressure stability can be solved by the use of a 'pressure buffer' which can also serve as a calibrant.

A general type of cell which is suited for in-reactor high pressure work is shown in Figure 22. Models of this cell have been constructed and operated at Pacific Northwest Laboratories (PNL). Future reports will describe in more detail the operation of this particular cell. In general, the load is applied to the piston by an external press. The piston movement resulting from the compression of the sample and pressure transmitting media, the phase change of the calibrant, and the movement of the inner cylinder into an outer support sleeve, is taken up by the clamping mechanism. After the external load is removed, small changes in the pressure to the sample are compensated by a reversion of the calibrant to its low-pressure form. This cell takes advantage of the Bridgman supported cylinder concept to generate pressure greater than 10 kbars and the Bridgman packing principle to keep the liquid metal pressure transmitter from escaping.

The cell in Figure 22 is only one of many types that have been designed at PNL. Modifications to this cell can be made to meet specific problems such as smaller diameter irradiation facilities, peculiar sample geometries, higher temperature situations, or sample-liquid metal compatibility problems.

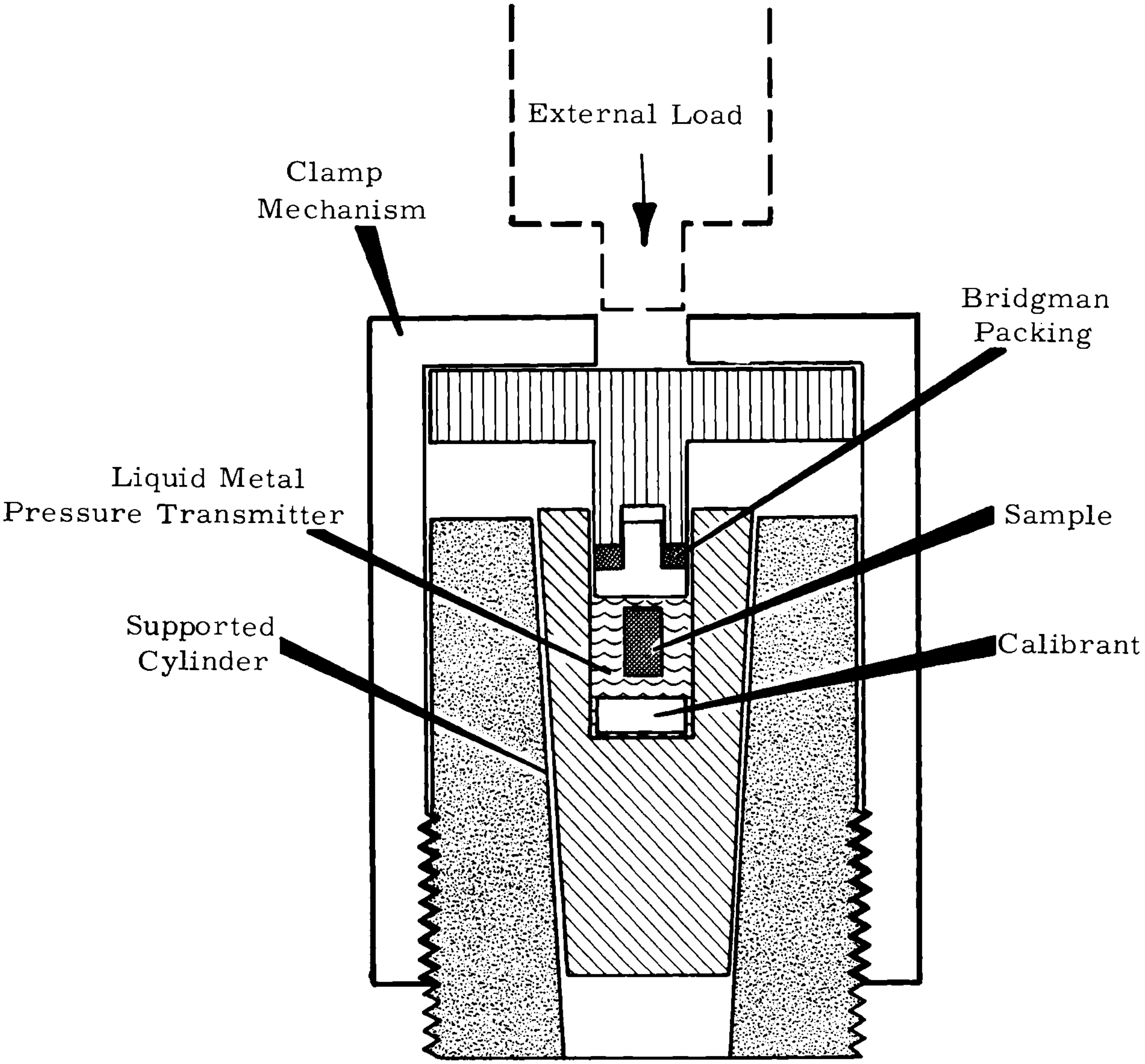


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FIGURE 22. Schematic of Proposed In-Reactor Hydrostatic Pressure Cell

Since this is the first known investigation of the problems associated with the design of such equipment, it is hoped that this report will stimulate others into making the improvements and refinements necessary to allow a broader range of studies to be made. It is anticipated that in the near future scientists will be able to vary the temperature at will on a sample under pressure in a reactor as well as obtaining 'in situ' electrical resistance and magnetic measurements. The study of the phase stability of materials under irradiation will also be an area of importance. If the equipment problems can be solved, a difficult but not impossible task, these areas of investigation will become extremely active in the next few years.

APPENDICES

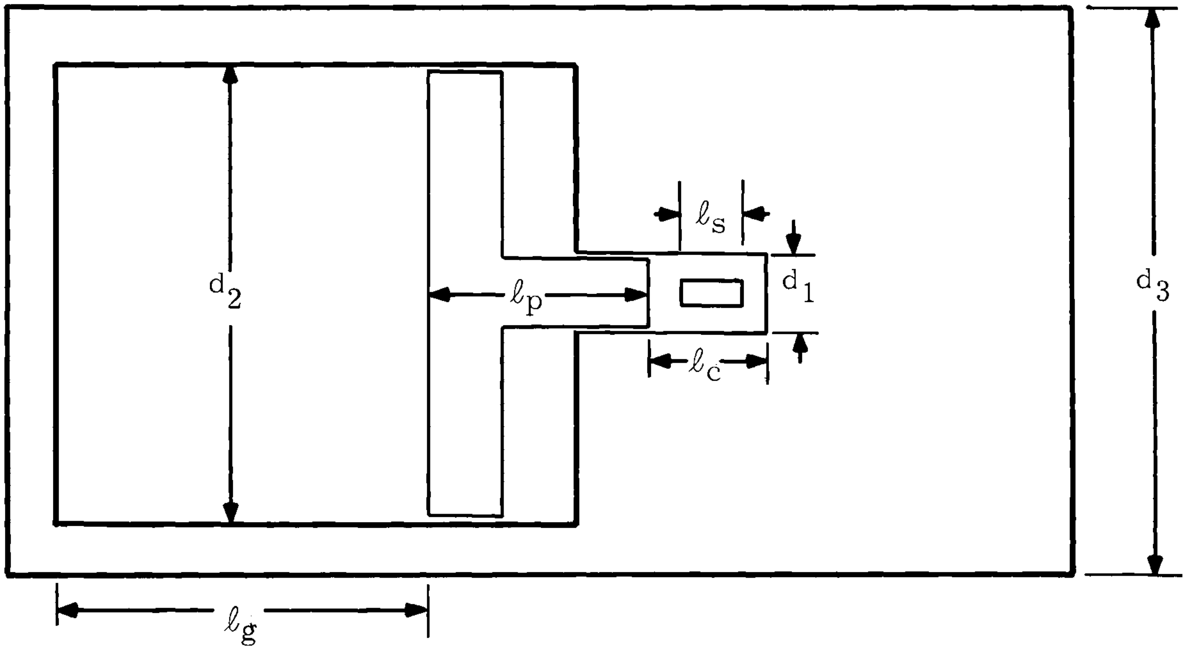
APPENDIX A

CALCULATION OF THEORETICAL PRESSURES DEVELOPED BY THERMAL METHODS

In the ideal case the pressure generated by a substance heated at a constant volume is (Equation 1)

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha_g}{\beta_g} \tag{A-1}$$

In reality, as the temperature of the system is raised, the container holding the pressure generator and the piston will expand. In addition to the thermal effects, the container will relax elastically, the piston will shorten, and the sample and its pressure transmitting medium will be compressed due to the pressure generated. The change in the volume available to the generator can be accounted for by: (See Figure A-1 for explanation of dimensions.)



(Linear) α_w = Thermal Expansion Coefficient of Container Wall
(Linear) α_p = Thermal Expansion Coefficient of Piston
(Volume) α_g = Thermal Expansion Coefficient of Generator
(Volume) α_t = Thermal Expansion Coefficient of Pressure Transmitter
(Volume) α_s = Thermal Expansion Coefficient of Sample

FIGURE A-1. Schematic of Cell for Thermal Pressure Generation

- Thermal expansion of container for pressure generator

$$\Delta V \simeq \left(\frac{\pi d_2^2}{4}\right)\left(\ell_g \alpha_w\right) \Delta T + \ell_g \frac{\pi}{4} \left[(d_2 + \Delta d)^2 - d_2^2\right]$$

$$= \frac{\pi d_2^2 \ell_g \alpha_w \Delta T}{4} + \frac{\ell_g \pi d_2^2}{2} \alpha_w \Delta T$$

$$\Delta V \simeq \frac{3}{4} \pi d_2^2 \ell_g \alpha_w \Delta T \qquad \text{(A-2)}$$

- Thermal expansion of piston

$$\Delta V \simeq \frac{\pi d_2^2}{4} \ell_p \alpha_p \Delta T \qquad \text{(A-3)}$$

- Radial elastic expansion of container walls

a) Walls around pressure generator

$$\Delta V = \frac{\pi}{4} \left[(d_2 + \Delta d)^2 - d_2^2\right] \ell_g$$

$$\Delta V = \ell_g \frac{\pi}{2} d_2 \Delta d$$

$$\Delta V = \ell_g \frac{\pi}{2} d_2^2 \frac{P_g}{E_w} f(K_g) \qquad \text{(A-4)}$$

where$^{(7)}$ $f(K_g) = \dfrac{1.3 K_g^2 - 0.4}{K_g^2 - 1}$

$K_g = \dfrac{OD}{ID}$ of walls holding pressure generator

E_w = Youngs modulus of wall

b) Sample chamber

$$\Delta V \simeq \ell_c \frac{\pi d_2^2}{2} \left(\frac{d_2}{d_1}\right)^2 \frac{P_g}{E_w} f(K_s) \qquad \text{(A-5)}$$

where $K_s = \dfrac{OD}{ID}$ of walls holding the pressure transmitter.

- Axial elastic expansion of container walls

  a) Pressure generator chamber

$$\Delta V \simeq \frac{\pi d_2^2}{4} \ell_g \frac{P_g}{E_w} \frac{1}{K_g^2 - 1} \tag{A-6}$$

  b) Sample chamber

$$\Delta V \simeq \frac{\pi d_1^2}{4} \ell_c \left(\frac{d_2}{d_1}\right)^2 \frac{P_g}{E_w} \frac{1}{K_s^2 - 1} \tag{A-7}$$

- Compressibility of the piston

$$\Delta V \simeq \frac{\pi d_2^2}{4} \ell_p \frac{P_g}{E_p} \frac{d_2^2}{d_1^2} \tag{A-8}$$

- Compressibility of sample and pressure transmitting medium

$$\Delta V \simeq \beta_c P_g \frac{d_2^2}{d_1^2} \ell_c \pi \frac{d_2^2}{4} \tag{A-9}$$

where β_c = average compressibility of the sample and pressure transmitting medium.

$$\beta_c = \left[\frac{d_s^2 \ell_s}{d_1^2 \ell_c} \beta_s + \left(1 - \frac{d_s^2 \ell_s}{d_1^2 \ell_c}\right) \beta_{PT} \right]$$

$$\beta_c = \beta_{PT} + \frac{d_s^2 \ell_s}{d_1^2 \ell_c} (\beta_s - \beta_{PT})$$

where β_{PT} = compressibility of pressure transmitter

β_s = compressibility of sample

Equation A-1 can be rewritten as:

$$P_g \simeq \frac{\text{Corrected volume change due to } \Delta T/\text{original volume}}{\text{Compressibility of pressure generator}}$$

or

$$\frac{\pi d_2^2 \ell_g}{4} P_g \beta_g = \Delta T \left[\alpha_g \frac{\pi d_2^2 \ell_g}{4} - \frac{3\pi d_2^2 \ell_g \alpha_w}{4} + \frac{\pi d_2^2 \ell_p \alpha_p}{4} \right]$$

$$- \frac{\pi d_2^2}{2} \frac{P_g}{E_w} \left\{ \ell_g f(K_g) + \ell_c \left(\frac{d_2}{d_1} \right)^2 f(K_s) \right\}$$

$$- \frac{\pi d_2^2}{4} \frac{P_g}{E_w} \left\{ \frac{\ell_g}{K_g^2 - 1} + \frac{\ell_c}{K_s^2 - 1} \right\} - \frac{\pi d_2^2}{4} \ell_p \frac{P_g}{E_p} \frac{d_2^2}{d_1^2}$$

$$- \frac{\pi d_2}{4} \beta_c P_g \frac{d_2^2}{d_1^2} \ell_c \quad .$$

Upon rearranging terms,

$$P_g \beta_g = \Delta T \left[\alpha_g - 3\alpha_w + \frac{\ell_p}{\ell_g} \alpha_p \right] - P_g \left[\frac{2}{E_w} \left\{ f(K_g) \right. \right.$$

$$\left. + \frac{\ell_c}{\ell_g} f(K_s) \left(\frac{d_2}{d_1} \right)^2 \right\} + \frac{1}{E_w} \left\{ \frac{1}{K_g^2 - 1} + \frac{\ell_c}{\ell_g} \frac{1}{(K_s^2 - 1)} \right\}$$

$$\left. + \frac{\ell_p}{\ell_g E_p} \left(\frac{d_2}{d_1} \right)^2 + \frac{\ell_c}{\ell_g} \beta_c \frac{d_2^2}{d_1^2} \right]$$

or

$$\frac{P_g}{\Delta T} = \left(\alpha_g - 3\alpha_w + \frac{\ell_p}{\ell_g} \alpha_p \right) \Bigg/ \left[\frac{1}{E_w} \left\{ 2f(K_g) + \frac{2\ell_c}{\ell_g} f(K_s) \left(\frac{d_2}{d_1} \right)^2 \right. \right.$$

$$\left. + \frac{1}{(K_g^2 - 1)} \right\} + \frac{\ell_c}{\ell_g} \frac{1}{(K_s^2 - 1)} + \frac{\ell_p}{\ell_g} \frac{1}{E_p} \left(\frac{d_2}{d_1} \right)^2$$

$$\left. + \beta_c \frac{\ell_c}{\ell_g} \frac{d_2^2}{d_1^2} + \beta_g \right] \qquad \text{(A-10)}$$

From Equation (A-10) there are some obvious and not so obvious comments that might be made. Generally, one wishes to have α_g, α_p, E_w, and E_p as large as possible and α_w, β_c, and β_g as small as possible. It is not so clear what ratios of ℓ_p, ℓ_g, and ℓ_c are desirable, although the ratios of d_1, d_2, and d_3 are fixed by space limitations and size of sample desired. The proper values of ℓ_p, ℓ_g, and ℓ_c will be more apparent in the following appendices.

APPENDIX B

USE OF ALKALI METALS AS THERMAL PRESSURE GENERATORS

Temperature Rise required for generation of 20 kbar in a 0.25 in. diam cylinder with lithium, sodium, or potassium pressure generators.

Assume: Geometry in Figure A-1, $d_1 = 0.25$ in., $d_2 = 2$ in., $d_3 = 2.5$ in.

$\alpha_p = 4.42 \times 10^{-6}$ (WC) $\qquad \alpha_\omega = 10^{-5}$

$K_g = 1.25 \qquad K_s = 10$

$f(K_g) = 3.82 \qquad f(K_s) = 1.46$

$E_w = 2 \times 10^6 b$

$E_p = 6 \times 10^6 b$

$\frac{d_2}{d_1} = 8$

Then Equation (A-10) becomes

$$\frac{\Delta P_g}{\Delta T} = \alpha_g - 3 \times 10^{-5} + \frac{\ell_p}{\ell_g} 4.4 \times 10^{-6} \div \left[\frac{1}{2 \times 10^6} \left(7.64 + 187 \frac{\ell_c}{\ell_g} + 1.79 + 0\right) + \frac{1}{6 \times 10^6} \frac{\ell_p}{\ell_g} \times 64 + \beta_c \frac{\ell_c}{\ell_g} 64 + \beta_g \right]$$

$$\frac{\Delta P_g}{\Delta T} \simeq \left[\alpha_g - 3 \times 10^{-5} + \frac{\ell_p}{\ell_g} 4.4 \times 10^{-6} \right] \Big/ \left[4.7 \times 10^{-6} + 10.7 \times 10^{-6} \frac{\ell_p}{\ell_g} \left(93.5 \times 10^{-6} + 64 \beta_c\right) \frac{\ell_c}{\ell_g} + \beta_g \right]$$

For Na, $\beta_g = 1.4 \times 10^{-5} \qquad \alpha_g = 2.0 \times 10^{-4}$

assume $\beta_c = 7 \times 10^{-6}$

$$\frac{\Delta P_g}{\Delta T} = \left[1.7 \times 10^{-4} + \frac{\ell_p}{\ell_g}\, 4.4 \times 10^{-6}\right] \Big/ \left[18.7 \times 10^{-6} + 10.7 \times 10^{-6} \frac{\ell_p}{\ell_g} + 450 \frac{\ell_c}{\ell_g} \times 10^{-6}\right] \qquad \text{(A-11)}$$

Realistic minimum values of $\ell_c \simeq 0.5$ in. and $\ell_p = 0.5$.

Since Equation (A-11) is rather insensitive to ℓ_p / ℓ_g in the range 0 to 10 but quite sensitive to ℓ_c / ℓ_g we should make ℓ_g as large as possible. If one places a 10 in. limit on the overall size of the pressure apparatus, this leaves ~6 to 7 in. for maximum value of ℓ_g. Choosing

$\ell_c = 0.5$ in.
$\ell_p = 0.5$ in.
$\ell_g = 6$ in.

yields

$$\frac{\Delta P_g}{\Delta T} = \frac{1.7 \times 10^{-4}}{18.7 \times 10^{-6} + 44.5 \times 10^{-6}} = \frac{170}{62.7} = 2.7 \text{ bar/°C} \quad .$$

Choosing

$\ell_c = 0.5$ in.
$\ell_p = 0.5$ in.
$\ell_g = 0.5$ in.

yields

$$\frac{\Delta P_g}{\Delta T} = \frac{174}{18.7 + 10.7 + 540} = \frac{174}{569.4} = 0.31 \text{ bar/°C} \quad .$$

Hence our design should seek to maximum ℓ_g. Referring to the original problem (i.e., 20 kbar on sample), we find that

$$\Delta T \simeq 116\ °\text{C} \quad .$$

Owing to the fact that Equation (A-10) is more sensitive to changes in thermal expansion than compressibility, one finds that $(\partial P/\partial T)_V$ for lithium is ~2.6 bar/°C.

Potassium gives

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{2.2 \times 10^{-4}}{75.7 \times 10^{-6}} = 2.9 \text{ bar/°C} \quad .$$

APPENDIX C

USE OF ALUMINUM, LEAD, AND GERMANIUM AS PRESSURE GENERATORS

Using the same experimental arrangement as in Appendix B

Aluminum

$$\frac{\Delta P_g}{\Delta T} = 25 \times 10^{-6} - 30 \times 10^{-6} + \frac{1}{12} \left(4.4 \times 10^{-6}\right) \div \left[4.7 \times 10^{-6} + \frac{10.7}{12} \times 10^{-6} + \frac{540}{12} \times 10^{-6} + 1.1 \times 10^{-6}\right]$$

$$= \frac{-5 \times 10^{-6}}{57.6 \times 10^{-6}}$$

$\frac{\Delta P_g}{\Delta T} \simeq 0$ because the walls expand away from the generator

Lead

$$\frac{\Delta P_g}{\Delta T} = \frac{\sim 0}{51.6 \times 10^{-6}}$$

Germanium

$$\frac{\Delta P_g}{\Delta T} = \frac{7.5 \times 10^{-6}}{51.9 \times 10^{-6}} \simeq 0.15 \text{ bar/}^\circ\text{C}$$

Hence, to generate 340 bar, it would be necessary to raise the temperature of the germanium to >2000 °C, far above the melting point.

APPENDIX D

PRESSURE GENERATED BY MELTING SODIUM AT CONSTANT VOLUME

We will neglect the pressure increase due to thermal expansion caused by the small ΔT required to melt the sodium. It will also be assumed that the melting point is unaffected by the pressure increase. This assumption will be checked later. We can modify Equation (A-10) by replacing the volume change due to thermal expansion by the volume change due to melting. The corrected volume of the pressure generator due to the mechanical properties of the walls will be included as before. Hence

$$P_g \simeq \Delta V_m(\mathrm{Na}) \Bigg/ \left[\frac{1}{E_w} \left\{ 2f(K_g) + \frac{2\ell_c}{\ell_g} f(K_s) \left(\frac{d_2}{d_1}\right)^2 \frac{1}{K_g^2 - 1} + \frac{\ell_c}{\ell_g} \frac{1}{(K_s^2 - 1)} \right\} + \frac{\ell_p}{\ell_g} \frac{1}{E_p} \left(\frac{d_2}{d_1}\right)^2 + \beta_c \frac{\ell_c}{\ell_g} \frac{d_2^2}{d_1^2} + \beta_g \right] \qquad \text{(A-12)}$$

Using the same numerical constants as in Appendix B, namely

$K_g = 1.25$ $\qquad K_2 \geqq 4$

$f(K_g) = 3.82$

$f(K_s) = 1.46$

$E_w = 2 \times 10^6 b$

$E_p = 6 \times 10^6 b$

$\frac{d_2}{d_1} = 8$ $\qquad d_3 = 2.5$ in. $\qquad d_2 = 2$ in. $\qquad d_1 = 0.25$ in.

$\ell_c = 0.5$ in. $\qquad \beta_c = 7 \times 10^{-6}$

$\ell_p = 0.5$ in. $\qquad \beta_g = 1.4 \times 10^{-5}$

$\ell_g = 6$ in.

we get

$$P_g = 0.025 \Bigg/ \left[\frac{1}{2 \times 10^6} \left\{ 2 \times 3.82 + \frac{2}{12} \times 1.46 \times 64 + \frac{1}{56} + \tilde{0} \right\} \right.$$

$$\left. + \frac{1}{12} \times \frac{64}{6 \times 10^6} + \frac{7 \times 10^{-6}}{12} \times 64 + 1.4 \times 10^{-5} \right]$$

$$= 0.025 \Bigg/ \left[\frac{23.3}{2 \times 10^6} + 0.89 \times 10^{-6} + 37.2 \times 10^{-6} + 14 \times 10^{-6} \right]$$

$$P_g = \frac{2.5 \times 10^{-2}}{6.37 \times 10^{-5}} = 393 \text{ bar (5700 psi)}$$

To check our assumption about the effect of pressure on the melting point of sodium, we find that it is raised no more than 2 to 3 °C.(35) The pressure on the sample in this case would be ~25,000 atm and could be varied by changing the ℓ_c/ℓ_g ratio.

To account for the pressure generation in heating the solid from 20 to 100 °C, we find Equation (A-10)

$$\Delta P = 80 \times \frac{\left(\alpha_g - 3 \times 10^{-5} + \ell_p/\ell_g \; 4.4 \times 10^{-6} \right)}{63.7 \times 10^{-6}}$$

$$\Delta P = \frac{80}{63.7} \times 10^6 \, (156 \times 10^{-6}) = 196 \text{ bar} \quad .$$

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