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X-ray Cells for Diffraction Analysis of Flat Powder Mounts in Contact with Liquid at Elevated Temperature and Pressure

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Abstract

Cells for obtaining X-ray diffraction patterns from flat powder mounts in contact with liquid at elevated temperature and pressure are feasible in several designs using Poulter and armored O-ring seals and windows of boron carbide or vitreous carbon. Sintered windows of diamond or cubic boron nitride, if available, would be stronger and more nearly inert chemically, but would result in higher X-ray absorption losses.

None of the designs presented is optimum for the full range of conditions considered, to 600°C and 8 kbar. The variety of materials currently available for critical cell elements permits choices to be made for particular applications.

Introduction

Measurements of total ion-exchange capacity, cation selectivity, and the amount and structure of interlayer water are needed for clay minerals under experimental conditions simulating those of deep sedimentary basins. Knowledge of these equilibrium parameters is a necessary prerequisite to developing detailed transport models describing the migration of hydrocarbons, the expulsion of interstitial brines across shale beds during compaction and tectonism, and the behavior of pollutants pumped into deep wells.

Useful in such inquiries is the basal X-ray diffraction diagram, classically obtained by scanning with a diffractometer over a flat oriented aggregate of flakes. This paper describes a cell that permits such scans for clay samples held under simulated deep-basin environments, that is, in contact with chloride brines as hot as 260°C and under as much as 2 kbar pressure. These estimates are for brine completely enclosed in a reservoir under lithostatic pressure of 7.62 km of sedimentary rock with a geothermal gradient toward the high end of the range observed in thick sedimentary sections. The *d*-spacings of greatest interest extend from about 15 Å, the first order basal diffraction for a Ca-saturated montmorillonite with two interlayers of water, to about 2 Å, the spacing for a reflection of illite that is probably the highest order basal clay-mineral diffraction of sufficient intensity to be detected through high-pressure windows. Because of the very low angles of X-ray incidence needed to obtain such large *d*-values, and because of the poor structural quality and reduced diffracting efficiency of many clay minerals, the sample area must obviously be made much larger than customary in high-pressure X-ray cells, if usable intensity maxima are to be obtained.

Whenever possible, the attempt is made in this paper to design cell elements that can withstand more severe conditions, specifically, 3 kbar at 600°C and 8 kbar at room temperature. The first of these conditions is routinely exceeded with simple cold-seal pressure vessels. On the other hand, 10 kbar has been cited (*e.g.*, Luth and Tuttle, 1963) as an approximate upper limit for externally heated, single walled vessels.

Several constraints apply to these designs: (1) A microporous plate is needed that has pores small enough to prevent passage of clay particles but large enough so that the plate does not behave as a semipermeable membrane. The pore size selected for the plate will depend upon the particle size range of the clay samples to be studied, and the discussion in this paper assumes this range to be 0.2–2 μm diameter. (2) The designs assume that superalloy high pressure tubing appropriate for experimental conditions is available. If it is not, the plugs that seal cell openings would have to be extended, at a large enough diameter to permit drilling out a central hole, even though there would be an undesirable increase in heat loss along these members. (3) The cell must have an external furnace, because it would be difficult or impossible to incorporate an internal furnace that would enclose the brine reservoir and sample. (4) The sample area is rectangular to utilize most effectively the line focus of a standard X-ray tube, 1.25 cm by 0.13 cm, even though there is some loss of cell strength because of stress concentration at rectangle corners. Although the X-ray intensity per unit area is greater for a microfocus or fine-focus tube, the total intensity is greater for the standard focus. (5) It is obviously impossible to incorporate a sample area large enough to intercept the full cross section of the incident beam at very low values of 2θ. Therefore an area is chosen that coincides with the projected area of the beam at the highest 2θ of interest, that for d equal to 2 Å.

This paper is a literature review and design survey. None of the suggested cells has yet been constructed.

Cell-Body Materials

A useful equation for comparing the mechanical properties of alloys not being weakened by creep or corrosion is one that estimates bursting strength of a thick-walled cylinder from the two short-term tensile properties, ultimate tensile strength, and yield strength at 0.2 percent offset. Comings (1956, eq. 6–70) estimates bursting pressure using the equation

$$p_b = \left(2 - \frac{\sigma_y}{\sigma_u}\right) \frac{2\sigma_y}{\sqrt{3}} \ln \mathrm{K}, \tag{1}$$

where σ_y = tensile yield strength, σ_u = ultimate tensile strength, $\mathrm{K} = (r_2/r_1)$, r_1 = bore radius, and r_2 = cylinder radius.

It is also useful to estimate cell life before creep-induced rupture takes place. To obtain this estimate, it would be helpful to relate the tensile stress applied in a creep test made upon a bar or solid cylinder to the stress distribution in a thick-walled cylinder and to the hydrostatic pressure in the latter. It seems reasonable to equate the tensile strength of the creep test to the maximum tensile stress found in the hollow cylinder. For a thick-walled cylinder subject to negligible external pressure, the maximum tensile stress is a circumferential one at the inner radius and, if the cylinder is within the region of elastic behavior in short-term tests, the relationship when the cell is first stressed is

$$\frac{\sigma'}{p_h} = \frac{\mathrm{K}^2 + 1}{\mathrm{K}^2 - 1} \tag{2}$$

(after eq. 6–10 of Comings, 1965), where σ' = tensile stress at inner radius and p_h = hydrostatic pressure.

As a region of inelastic strain forms at the inner wall and moves outward, the maximum circumferential stress exists at the boundary between the elastic and inelastic regions, and more complex equations must be used. A hydrostatic pressure as much as twice that required to initiate inelastic deformation at the inner wall in short-term tests may be required to propagate it outward (Comings, 1956, p. 161). I infer the corollary that at constant hydrostatic pressure the rate of creep-inducd strain in long-term use will decrease as the inelastically deformed zone moves outward. Hence, an estimate of cell life based upon the situation at the beginnig of deformation will be a conservative estimate. Larson-Miller diagrams, in which applied tensile stress is plotted against a parameter that linearly relates temperature to the logarithm of the time, afford a compact graphical means of summarizing stress rupture performance (see, *e.g.*, Dieter, 1961; Tetelman, 1967).

A suggested procedure for obtaining minimal creep life of an alloy under specified conditions thus involves (1) taking a fixed value of tensile stress applied in a creep test and applying it to a Larson-Miller diagram to read the times; and (2) equating this applied tensile stress to σ' in Eq. (2) and solving for p_h, the pressure parameter of experimental interest, so that p_h and time can be compared. Because this calculation presumably underestimates the creep lives of different alloys to different degrees, comparisons among several alloys will be inexact.

Table 1 presents values of p_b and cell life for several alloys, derived from published information in company literature and handbooks. Because parameters vary considerably depending upon (1) mechanical and thermal pretreatment of the test piece upon which tensile properties were measured, and (2) its diameter, *etc,* the values in Table 1 must be taken as suggestive only. Furthermore, these values do not include a safety factor and do not consider local stress concentrations and the weakening effect of radial openings in the vessel. *All such cells should be shielded adequately to contain an explosive failure.*

Of the three most corrosion-resistant alloys listed in Table 1, INCONEL 625, Haynes Alloy #25, and Hastelloy C, the first two have high and essentially identical p_b values at room temperature, but

INCONEL 625 retains a markedly higher p_b at 600°C. The Larson-Miller curves of INCONEL 625 and Haynes #25 cross at about $\sigma' = 2.8$ kbar. Below that stress level, Haynes #25 has the longer creep life; above it INCONEL 625 has. Hastelloy C has a creep life of intermediate duration throughout the entire range. Obtaining adequate cell life at 600°C and $p_h = 5.7$ kbar would require shifting to precipitation-hardened alloys such as René 41 and Udimet 700 and accepting somewhat greater corrosive attack. Udimar B-300, one of the maraging steels, is included as an example allowing very high p_b if it were possible to work at or near room temperature with noncorrosive systems such as clay plus organic liquid.

High-Pressure Tubing

Those intervals of high-pressure tubing that contain brine should be made of Co- or Ni-base superalloy to resist corrosion, particularly if the brine is at elevated temperature or pressure. If tubing is maintained in environments above ambient temperature, *e.g.*, within a furnace at the point of attachment to an X-ray cell, the need for retention of strength at temperature is also satisfied by the superalloys.

There is some maximum ratio of outer diameter to hole diameter at which tubing can be fabricated for a given superalloy, but even the technically feasible sizes are more difficult to obtain than formerly. Thus, I am no longer able to find a supplier of INCONEL X-750 tubing of 0.318 cm (0.125″) OD by 0.069 cm (0.027″) ID. Superalloy tubing 0.635 cm OD by 0.213 cm ID can be obtained from a number of high-pressure equipment companies (*e.g.*, Tube Methods Inc., Box A, Bridgeport, Pennsylvania 19405 for INCONEL X-750), but cost and delivery time are both rising rapidly, and no one company is likely to have many different superalloys to choose from. This OD/ID ratio is less favorable than that of the smaller diameter tubing, but it is easier to thread the larger tubing without undue weakening at the point where it is anchored to the cell (see Paul and Warschauer, 1956, on anchoring 0.318 cm (1/8″) OD tubing). Likewise, if the tubing is anchored by using a high-temperature brazing material of superalloy composition such as Nikrobraz 170 (Wall Colmonoy Corp., 19345 John R St., Detroit, Michigan 48203), there is somewhat less danger of sealing the bore of larger tubing. The brazing temperature for Nikrobraz 170, namely 1150–1200°C, is high enough so that strength imparted to either the tubing or the cell body by earlier heat treatment may be lost in the immediate vicinity of the brazed connection, but use of this material may still be advantageous because of the sharp reduction in the size of the opening that must be cut into the cell. The volume heated may be minimized by heating with an electron beam in vacuum and using a copper heat sink shaped for the particular geometry involved.

TABLE 1. Creep and Rupture Properties of Selected Alloys

Alloy	P_b (kbar), 20°C K=6	P_b (kbar), 600°C, K=6	Creep-Rupture Life, hrs, 600°C		
			p_h=1.4 kbar	p_h=2.8 kbar	p_h=5.7 kbar
INCONEL 625[*]	15.1	13.2	1.1×10^8	3.8×10^5	509
Haynes Alloy #25[**]	15.4	8.6	1.6×10^{10}	2.3×10^5	
Hastelloy C[***]	11.6	6.8	6.0×10^8	2.5×10^5	
René 41[†]	21.5	20.9		8.0×10^9	3.0×10^6
Udimet 700[††]	26.9	25.7		2.7×10^{11}	1.2×10^7
Udimar B-300[†††]	41.8				

[*] Int'l. Nickel Co., Huntington Alloy Products Div., Huntington, W. Va. 25720 (Hot-rolled; anneal 1-4 hrs., 927-1038°C).

[**] Cabot Corp., Stellite Div., 1020 W. Park Ave., Kokomo, Ind., 46901 (Solution heat-treated 1232-1241°C, water-quenched).

[***] Cabot Corp. (Heat-treated 1218°C, water quenched).

[†] Developed by General Electric Co., data from Special Metals Corp., New Hartford, N.Y. 13413, which markets it as Udimet 41 (1066-1079°C, 4 hours, air cool; 760°C, 16 hours, air cool).

[††] Special Metals Corp. (1177°C, 4 hours, air cool; 1079°C, 4 hours, air cool; 760°C, 16 hours, air cool).

[†††] Special Metals Corp. (816°C, 1 hour; 482°C, 3 hours, air cool).

X-ray Window Materials

An ideal window material should have a low mean atomic number to minimize absorption losses, and it should not contribute interfering diffraction features. It must be impermeable at high pressure to the fluid within the cell and strong enough over the specified temperature range, and it must remain inert both toward the internal brine and the external atmosphere.

Amorphous B gives only two diffuse X-ray diffraction rings at 2.5 and 4.3 Å and has a tensile strength in thick filaments of about 21,080 kg/cm² (= 300,000 psi) (Talley, Line, and Overman, 1965). It could probably be fabricated into plates, but clearly would not withstand chemical attack by brine.

Boron carbide, molded without binder to give essentially zero porosity and a compressive strength of 29,090 kg/cm² (414,000 psi), is available commercially ("Norbide" of Norton Company, Worcester, Massachusetts 01606) in plates from 0.318 cm (1/8″) to 1.27 cm (1/2″) thick and in solid cylinders up to 12.7 cm (5″) in diameter and several inches long. "B_4C", actually a range of compositions around $B_{12}C_3$ (Thompson, 1969), is said by the manufacturer not to be attacked by acids and alkalis at room temperature and to have good resistance to oxidizing atmospheres up to 600°C. However, this resistance is achieved by forming a self-protecting glaze at red heat, and there can be erosion well below 600°C if abrasion occurs. Furthermore, water vapor accelerates oxidation by assisting in removal of the protective boric oxide film (Thompson, 1969), so that durability of a B_4C window in a brine cell at temperature is questionable.

Diamond would seem to be an ideal window material. The largest *d*-value is 2.06 Å, and the only disadvantage is a distinctly secondary one, an increased linear absorption coefficient because of high density. It would be prohibitively expensive to obtain single crystals of diamond from which windows of the required size could be cut. Sintered diamond shapes made with Co or other metal as binder (*e.g.,* Katzman and Libby, 1971) are unacceptable because the metal would be opaque to X-rays and would be chemically attacked by the brine. Hall (1970) has hot-pressed diamond powder without binder into polycrystalline aggregates that have a compressive strength of 31,600 kg/cm² (450,000 psi) (H. T. Hall, personal communication). Disks approximately 0.18 cm thick by 0.64 cm in diameter are available commercially (Megadiamond Industries, 589 5th Ave., New York City). In the absence of information about the porosity and pore-size distribution of these plates, it is not clear whether they would be impermeable to fluid contained in a cell under high pressure.

Glassy carbon, produced by the pyrolysis of thermosetting resins, is sufficiently disordered that it yields only three broadened diffraction maxima, yet typically has room-temperature compressive strengths in the range 7027–9135 kg/cm² (100,000–130,000 psi) (Cowlard and Lewis, 1967; Bradshaw, 1972; available from Beckwith Carbon Co., 16140 Raymer St., Van Nuys, California 91406 and from Polycarbon, 7418 Fulton Ave., North Hollywood, California 91605). However, the typical values reported for flexural strength and tensile strength are only about 2038 and 1195 kg/cm², respectively (29,000 and 17,000 psi) (Cowlard and Lewis, 1967; Bradshaw, 1972; Kaae, 1972). Glassy carbon prepared at 2000°C has essentially the same tensile strength at 1600°C as at room temperature (W. G. Bradshaw, personal communication). Bradshaw (1972) describes a variation in precursor formulation that yields a glassy carbon with room temperature values of 14,050 and 2038 kg/cm² (200,000 and 29,000 psi) for compressive strength and tensile strength, respectively.

Vitreous carbon is obviously much weaker than diamond, and its broad graphite-like diffraction maxima are strong enough to be a major nuisance when attempting to define the attenuated diffraction features characteristic of some clays. But, because of its lower density, it has a much lower linear absorption coefficient for X-rays than does diamond.

Small-angle X-ray-scattering studies and its low density compared with that of graphite indicate that vitreous carbon must have considerable porosity. However, the extremely low value of room-temperature gas permeability cited for it by Taylor and Kline (1967), 10^{-10} cm²/sec, suggests that there must be a large number of very tiny pores. Fitzer and Schäfer (1970) conclude from small-angle scattering measurements that these micropores are of a uniform size that varies with pyrolysis temperature, *e.g.,* 25 Å diameter for 2200°C, and that most of the pore entrances are between 4 and 5 Å because water (molecular diameter, 2.89 Å) and methanol (3.76 Å) enter the pores but isobutanol (4.75 Å) does not.

Vitreous carbon is quite resistant to graphitization and to oxidation. Samples produced at pyrolysis temperatures of 1500°C and above, and therefore completely dehydrogenated, show no graphitization even after 15 minutes at 3200°C (Yamaguchi, 1963). Samples containing bound hydrogen can be extensively converted in minutes at 10 kbar and 2500°C (Noda and Kato, 1965; Chard *et al,* 1968), but these conditions are far beyond those of interest in this paper. Measurements of oxidation rate in dry air by Cowlard and Lewis (1967) extrapolate to only 0.00002 g/cm²hr at 600°C, although that part of the window surface along which a high-pressure seal is maintained could be a locus of stress concentration and accelerated oxidation.

However, Cowlard and Lewis (1967) report that vitreous carbon suffers a weight loss of 0.05 g/cm²hr in steam at 570–580°C. This rate corresponds to a loss of thickness of 0.1 cm from the interior window surface in less than 3 hours, and suggests that window replacement might be necessary after each run at these temperatures.

There is an obvious concern about the toxicity of Be and its compounds. They might be dispersed either as powder during machining or as vapor from a window operated at too high a temperature. Another difficulty is that Be compounds appear to be sufficiently soluble in high-pressure aqueous solutions to weaken the window and to put Be onto exchange positions of clay. Beryllium quickly forms a thin surface layer of BeO that is said to be protective against wet CO_2 to about 500°C (Werner and Inouye, 1963). However, the BeO film does not prevent pitting in distilled water at 260°C nor in chloride-containing solutions (White and Burke, 1955). Be carbide and Be nitride are obviously decomposed by water vapor at low to moderate temperatures (White and Burke, 1955). BeO in vacuum and in inert atmospheres has a very low vapor pressure (Erway and Seifert, 1951), but in high-humidity atmospheres at elevated temperatures increased weight loss occurs because of the formation of gaseous $Be(OH)_2$ (Grossweiner and Seifert, 1952). The loss rate decreases with decreasing temperature, but in a high-humidity atmosphere at 1000°C, it is still 2.0×10^{-3} g BeO/ cm^2/2 hr (Darwin and Buddery, 1960). The fact that the minimum temperature required to remove combined water from Be hydroxide is 500°C (Darwin and Buddery, 1960) suggests that BeO would not have long term stability in high pressure liquid systems even up to 600°C. BeO is attacked by HF and to a lesser extent by the other mineral acids, the rate of attack depending upon acid strength, temperature, and BeO particle size (Darwin and Buddery, 1960).

If chemical reactivity can be ignored, BeO is a reasonably attractive window material. It yields only three X-ray reflections above 2 Å, at 2.337, 2.189, and 2.061 Å (Swanson and Tatge, 1953). At room temperature, it has a compressive strength for theoretical density somewhat above 14,050 kg/cm^2 (200,000 psi) and a tensile strength of 1300 kg/cm^2 (18,500 psi); these values decrease by 35 and 45 percent respectively, if temperature is increased to 600°C (White and Burke, 1955). BeO has been hot-pressed by Kodaira and Koizumi (1971) into transparent masses of theoretical density.

Windows of Be are weaker than those of BeO, and give X-ray diffraction maxima for both Be and the BeO oxidation layer. Their use might be dictated if low absorption losses were critical.

AlB_{10} and the AlB_{12} polymorphs have an undesirably large number of reflections above 2 Å (Kohn, Katz, and Giardini, 1958; Kohn and Eckart, 1960).

One attractive possibility remains. Cubic BN, the largest *d*-spacing of which is 2.09 Å (Bundy and Wentorf, 1963), has recently been produced in polycrystalline masses with densities close to theoretical, *e.g.*, by Vereshchagin *et al* (1970) and Wakatsuki, Ichinose, and Aoki (1972). Both hexagonal and cubic BN have oxidation resistance superior to that of boron carbide; hexagonal BN begins to oxidize in air at about 770°C (Ingles and Popper, 1960).

Window Failures

For several reasons, a high-pressure window may fracture under stresses appreciably less than those predicted from the properties of the bulk solid. Parsons and Drickamer (1956) found it desirable to have synthetic CaF_2 crystals annealed at the factory to relieve local stress concentrations. This treatment would probably be advisable for all the materials that we have discussed. Vitreous-carbon windows might be weakened in two additional ways. First, the strength of vitreous carbon, like that of all glasses, depends upon surface condition (see, *e.g.*, Sugarman, 1967). Even though the windows be highly polished, increasing temperature will accentuate the importance of the remaining defects, and applying pressure along lines of sealing may deform the surface there. Second, Poulter and Wilson (1932) demonstrated many years ago that glass high-pressure windows will fracture at lower maximum pressure and will be much more likely to fracture during reduction of pressure if low viscosity liquids such as water are used to transmit pressure instead of oil or glycerine. These authors were able to prevent fracturing during pressure reduction by releasing pressure very slowly over five or ten days, and they speculated that water molecules were actually penetrating the glass. The finding of Fitzer and Schäfer (1970) that water molecules penetrate the micropores of vitreous carbon suggests that similar difficulties may be encountered with this material.

Microporous Backing Plates

Porous plate material must remain chemically inert toward the internal brine, it must have adequate strength to maintain sample rigidity during hydrostatic pressure adjustments, and for the purposes of this paper it should retain particles larger than 0.2 μm with essentially 100 percent efficiency. Because X radiation may penetrate through a sufficiently thin clay sample, it is also desirable that the porous plate not contribute interfering diffraction features.

With adequate plate thickness, pore tortuosity will result in the retention of a high proportion of particles somewhat smaller than the pore diameter. However, this blocking of pores with jumbled aggregates makes it much more difficult to clean the backing plate for use with subsequent samples. Deposition of such jumbled aggregates into the upper ends of pores during sedimentation of the clay sample onto the plate would probably not impair significantly the desired parallel flake orientation of the bulk of the sample, but a down-pressure adjustment of reservoir hydrostatic pressure during a run might conceivably force enough clay into the pores to do so. The direct solution is to seek pores with a maximum diameter of 0.1 or 0.2 μm.

No single porous plate material appears to meet all requirements. Vitreous carbon can be obtained in sized powders, and a molded porous plate of this material is an obvious possibility. However, neither diamond, vitreous carbon, nor boron carbide appears as yet to have been fabricated into porous plates. Teflon (Dupont's tetrafluoroethylene) and Kel-F (Minnesota Mining and Manufacturing Company's trifluorochloroethylene) are apparently not well suited for making very fine filters; the mean pore diameters available in porous plate (Pall Trinity Micro Corp., Cortland, New York 13045) are 9 μm for Teflon and 15 μm for Kel-F; in Teflon filter paper (Millipore Corp., Bedford, Massachusetts 01730) the smallest mean diameter available is 5 μm. Because of the desirability of monitoring ionic and colloidal Si and Al species in solution to check on possible disintegration of the alumino-silicate framework of the clay, it would be better not to use porous porcelain, alumina, or silica. Molded microporous plate of INCONEL 600, particularly resistant to attack by acidic chloride solutions, is made (Pall Trinity Micro Corp., Cortland, New York 13045), but the smallest mean pore diameter available is 5 μm. Alloys such as INCONEL 600—used either as the porous plate or for the body of the cell—will in general not contribute diffraction maxima at large enough *d*-values to be troublesome, if they are single-phase cubic materials. The phase assemblage must be checked for each such alloy.

A partial solution of the problem involves using a sheet of Nuclepore porous plastic (General Electric Co., Irradiation Processing Operation, Vallecitos Road, Pleasanton, California 94566), with pores of 0.2 μm diameter, against a porous metal plate. The pores in the plastic are chemically etched fission tracks of quite constant diameter and circularity. The plastic is said to withstand temperatures of 140°C indefinitely and to be particularly resistant to acids, but to decompose in bases and in some organic solvents.

Seals

Four types of seals are considered in this paper. Metal-to-metal cone fittings are appropriate for lines leading from a high-pressure liquid reservoir in a cell to external pressure sensors, pumps, *etc.* Nikrobraz closures are shown in Figures 1 and 2, but cone seals could as well have been used. A Poulter seal, which involves pressing two highly polished surfaces together (Poulter, 1932), is called for at the X-ray window in the design of Figure 1. Most frequently used, however, are O-rings with metal backup rings ("armored O-rings") which occupy minimal space and which Daniels and Hruschka (1957) and others find will seal to 10 kbar. The O-ring is given an initial seal by tightening a retaining ring or a closure nut. Further increase of pressure over the unsupported area forces the thin wedge of the backup ring into a metal-to-metal seal that holds even if the O-ring shrinks under pressure and leaks.

Of the materials other than metals from which O-rings are currently fabricated, Teflon is usable to the highest temperature and is the most nearly inert chemically. At atmospheric pressure the crystalline component of Teflon breaks down at 327°C (Hanford and Joyce, 1946), but the completely amorphous material that results still has a very high viscosity. The temperature at which crystallinity is lost increases 0.152°C/bar (McGeer and Duus, 1952). At atmospheric pressure significant amounts of gaseous decomposition products begin to be evolved at about 450°C. Company literature, which may include a safety margin, recommends that Teflon not be used for seals above 232°C, above 260°C, *etc.* However, Gill and Marshall (1961) were able to make 4- to 5-hour runs at 500°C and 987 bars by placing a Teflon gasket between two metal rings of triangular cross section. These authors believed that the relatively high thermal expansion of Teflon operated to create metal-to-metal seals in these runs. The brittleness and grayness of the Teflon after the runs indicated that increased pressure had not prevented considerable decomposition from occurring.

If even small amounts of specific Teflon decomposition products such as fluorine cannot be tolerated in the system because of chemical reaction with the experimental charge, the allowable maximum temperature will be lower. Dickson, Blount, and Tunell (1963) used a Teflon sample holder contained within a metal pressure vessel to measure anhydrite solubilities to 275°C without detectable adverse effects. However, some geochemists who have measured calcite solubilities believe that discrepancies observed even between 100° and 200°C may be related to decomposition of small amounts of Teflon.

Difficulties may be expected in using Teflon O-rings while studying clay-organic systems. Hughes and Robertson (1956) found that O-rings of Teflon and other organic materials go into solution in organic liquids at high pressure.

For that part of the temperature range to 600°C in which Teflon is unsuitable, there is some hope that even more temperature-resistant plastics may become available (Frazer, 1969). Failing that, designing the O-ring chamber below the backup ring with a rectangular cross section would make it possible to use a stack of flat annular gaskets of metals or alloys of increasing stiffness, although it would be difficult to find several such materials that also had adequate corrosion resistance. A more direct solution would be to go to metal sealing rings, which are available in alloys such as Haynes #25 and the INCONELS (*e.g.*, The Advanced Products Company, Defco Park Road, North Haven, Connecticut 06473; Pressure Science Incorporated, 11642 Old Baltimore Pike, Beltsville, Maryland 20705). Such sealing rings may be made of hollow tubing (APC) or have part of the tubing cross-section cut away (PSI), and they can be shaped to seal openings other than circular. Various designs have been used at least to 1200°C and to 14,050 kg/cm^2 (200,000 psi). The body of the ring obviously needs to be fairly stiff, but better seals will be obtained if the surface layer of the ring is soft enough to flow into surface imperfections in the sealing surfaces. Coatings such as Ag, In, Pb, or Cu are not sufficiently corrosion resistant for the cells under discussion, and the diffusion rate of Au into Ni-base alloys at 600°C appears to be excessive; a coating of Ni would probably be the best choice.

For the temperature range in which it is being used, the material of the backup ring should be resistant to oxidation by air, and soft enough not only to deform but also to leave the material of the main cell body unblemished. Over that pressure range in which the O-ring maintains a seal, resistance of the backup ring to liquid corrosion is not a requirement. At 260°C and 2 kbar, the extreme condition contemplated for experiments modeling basin diagenesis, stainless steel 304 is a reasonable material to try in Ni-base super-alloy cells using Teflon O-rings.

For a Poulter seal, it is sufficient to lap the facing surfaces with 0000 emery paper (Fishman and Drickamer, 1956) or equivalent abrasive. If one of these surfaces is an interior one within the cell, the hole leading to it must be circular and of some reasonably large diameter for its length, so that a rigid lathe-mounted rod can be used for polishing. If the material of the pressure vessel has a sufficiently complex structure so that diffraction maxima with *d*-values greater than 2 Å are generated from the region immediately around the sample, covering that area with a thin layer of Pt is a possibility (Jamieson, Lawson, and Nachtrieb, 1959). The largest interplanar spacings of Pt are 2.26 and 1.96 A. However, electrodeposition of Pt over a limited area on an interior surface presents technical difficulties, and a seal involving deformable material is no longer a Poulter seal. Presumably, for the seal to hold at pressures ranging up to 10 kbar, all of the Pt except that in microdepressions would have to be squeezed out so that there would be a large area of contact between the hard materials of the window and the pressure vessel.

An X-ray Cell Design for Maximum Pressure

Figure 1 illustrates a cell that incorporates two hydraulic intensifiers, one pressuring a brine reservoir, the other exercising a somewhat higher pressure to effect a Poulter seal of an X-ray window over the internal hole in the brine reservoir. The sample, mounted on a microporous backing plate assembly which is held against the X-ray window by a spring of corrosion-resistant metal such as tantalum (not shown), is loaded through the brine reservoir. As drawn, the cell body would be made from a cylinder of superalloy 15.24 cm in diameter and 38.10 cm long, and the internal pistons would have rather large diameters for their lengths to minimize bending under pressure and dragging against enclosing shaft walls. If, in fact, the dimensions shown were to prove not adequate to reach the pressure goal of 8 kbars at room temperature stated earlier, they could obviously be made so by increasing the cell body diam-

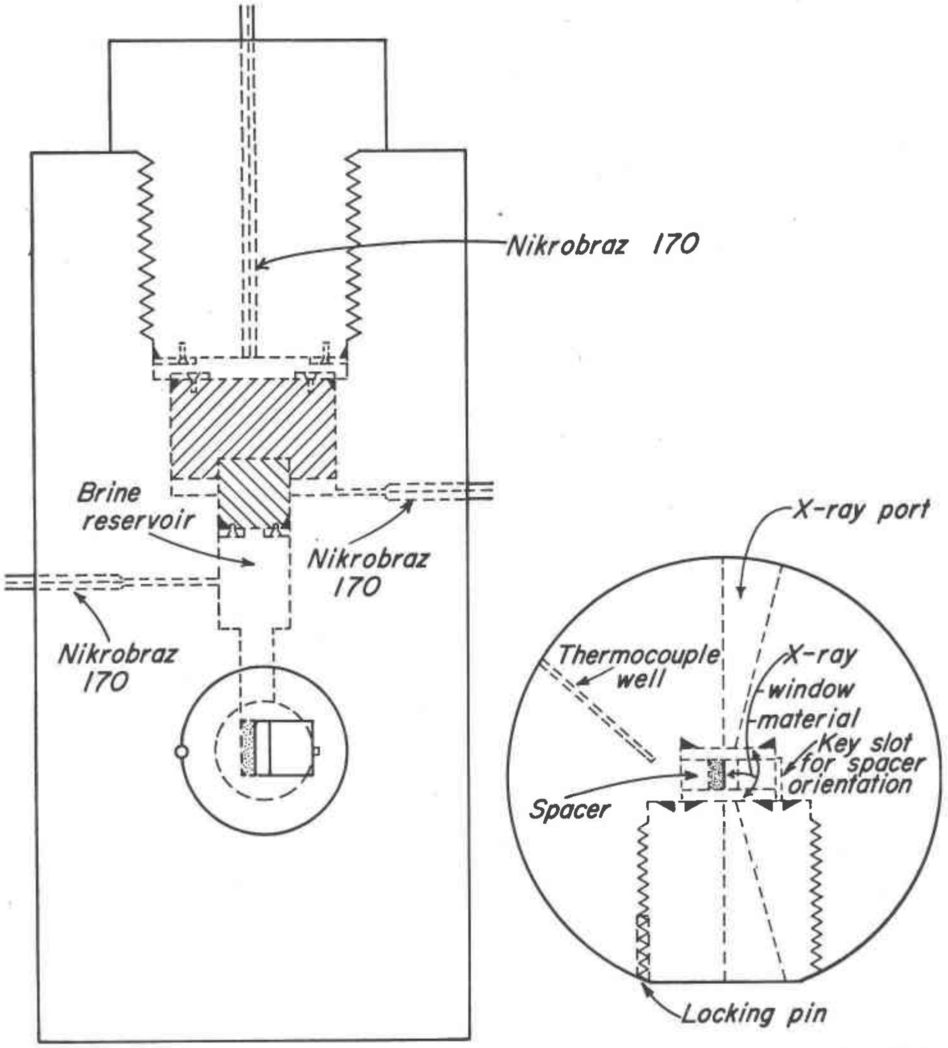

FIG. 1. Cell for studies in which high pressure is of paramount importance. The main cylinder is 38.10 cm long and 15.24 cm in diameter. Internal pistons are diagonally lined, and armored O-ring seals are shown as black triangles. Rounding of corners for stress relief is not shown.

eter, or decreasing the brine chamber and piston diameters, or shrinking an outer alloy cylinder around the cell.

This design is tailored to the desirability of using vitreous carbon in compression, because of the present inability to produce it in more nearly equidimensional blocks. The window is 2.54 × 1.91 × 0.32 cm thick and thus provides a 0.64 cm shoulder on all sides of the 1.27 × 0.64 cm sample plate. It lies within a circular area 3.18 cm in diameter that can be polished, and spacers would have to be inserted into the fan-shaped X-ray ports to hold it in position during cell assembly. If temperature and the two hydrostatic pressures were to be increased in judicious increments, it should be possible never to exert a differential pressure across the window greater than the amount necessary to maintain the Poulter seal (0.5 to 1 kbar?), and window failures like those experienced by Warschauer and Paul (1958) as a consequence of stress concentrations at points overlying the corners of rectangular apertures would be less likely.

The area reductions in the two intensifiers are such that pressures of 8 kbar in the brine reservoir and 9 kbar in the window could be achieved with a maximum external pressure of only about 1.7 kbar, within the range of simple hand pumps.

Because corrosive brine is confined within an internal chamber, the cell could be coupled to flexible stainless steel tubing [Harwood Engineering Co., South Street, Walpole, Massachusetts 02081; 0.318 cm (0.125″) OD, 0.064 cm (0.025″) ID] at sufficient distances away from the heat of the furnace. However, pressure within that brine chamber has to be calculated using a ratio of areas and is subject to error from friction of the intervening armored O-ring seals. Figure 1 includes an optional high-pressure brine line leading to an external pressure gauge or manganin cell. In practice, a separator could be placed in the line or the line could be valved off except when pressure was being read, so that brine external to the cell would not interact along a temperature gradient with that in the cell.

Calculation of the pressure that seals the window involves a ratio of areas, and there is one intervening armored O-ring seal, but this pressure need not be known as accurately as that within the brine chamber.

In natural environments where the rock or sediment mass is sufficiently cemented to support its own weight, there is, of course, a fundamental thermodynamic distinction between total (lithostatic) pressure and hydrostatic pressure. It would be possible to model these environments with the design of Figure 1 by filling the brine reservoir with a pair of porous superalloy pistons, a larger circular one driving a smaller rectangular one. With this modification, the main longitudinal pressurizing system could be used to exert a mechanical ("lithostatic") pressure upon the sample greater than the hydrostatic brine pressure maintained by an auxiliary pumping system acting through the lateral pressure line—the line normally used only for pressure monitoring. The retaining plate for the armored O-ring sealing the brine chamber, as shown in Figure 1, is quite thick and is held in place by a loosely threaded screw; thus it would be able to transmit pressure without damage. The magnitude of the mechanical stress generated by this chain of pistons could not be known very accurately, and there is a question whether it would not be more highly directional than its counterpart in nature. The sample would have to be much thinner than usual, to prevent extrusion around the edges of the backing plate; as a result, X-ray diffracted signal intensity would be decreased. The backing plate would have to be solid so that the sample could not be forced into pores, with the consequence that the rate of chemical equilibration with the brine reservoir, possible only around the edges of the plate, would be slowed. The further possibility exists of generating hydrostatic pressure with a mixture such as argon-water, so that the total hydrostatic pressure, the partial pressure of H_2O, and the mechanical pressure would all be different.

The design of Figure 1 has some obvious disadvantages. The cell would be awkward to assemble and disassemble because of its weight and because of high pressure tubing sticking out in several directions. Certainly it would be too large to fit on any standard diffractometer and would have to be fixed in a rigid housing to which an X-ray tube could be brought by flexible cable and oriented. Even though Figure 1 and the discussion thus far have assumed the use of standard dispersive X-ray diffraction, a nondispersive X-ray technique might be the only feasible way of obtaining diffraction features through a range in 2θ. Such a technique requires only a narrow X-ray port and the cell is therefore weakened minimally, but resolution is not as good as that obtainable by classical dispersive techniques. Furthermore, the semiconductor detector must be maintained at liquid nitrogen temperature even when not in use if it is not to deteriorate.

The above design shares two limitations with the designs that follow. First, electrical discharge machining needed to finish out the fan-shaped X-ray ports is time-consuming and expensive. Second, sequential measurements should be taken with increasing pressure, because with even small decreases in reservoir pressure the trapped pore fluid in the sample could retract the backing assembly and disrupt sample orientation.

An X-ray Cell For The General Electric XRD-3 Diffractometer

Figure 2 illustrates an X-ray cell, complete with furnace and positioning mechanism, that is small enough to be mounted on the XRD-3 platform, if simpler slits are substituted for the Soller slits. In use, the long axis of the cell would be vertical, and the diffractometer drive would be used to sweep through 2θ. The lower end of the brine chamber lies between two X-ray windows that are perpendicular to the X-ray beam. Leakage of brine from this region is prevented by three armored O-ring seals. Between the two windows is a superalloy spacer of thickness such that an initial seal of the O-rings can be obtained by tightening the side plug that contains one of the X-ray ports. Increasing the brine pressure to the experimental value selected then produces the desired high-pressure seal. The spacer is keyed to maintain correct orientation, and

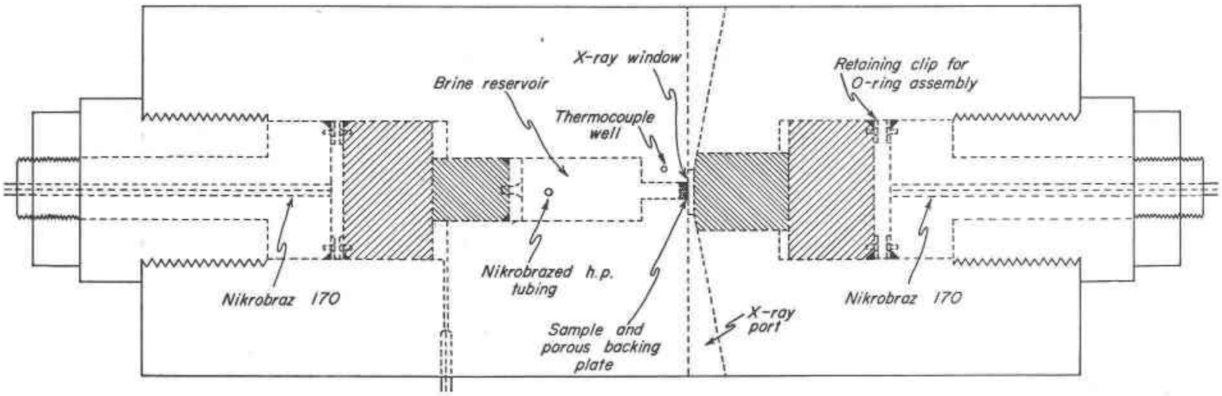

FIG. 2. Cell for use on the General Electric XRD-3 diffractometer platform (side view of cell, and top view of the portion of the cell through which the X-ray beam passes). The main cylinder is 20.32 cm long and 10.16 cm in diameter. Internal pistons are diagonally lined, and armored O-ring seals are shown as black triangles. Rounding of corners for stress relief is not shown.

a pin is inserted after assembly to fix the position of the side plug. The sandwich of porous backing plate, sample, and solid fronting plate of X-ray window material is loaded in a tantalum-ribbon spring holder through the brine chamber into a rectangular notch in the spacer. The fronting plate cannot be porous because X-ray absorption losses to aqueous chloride solution in the pores would be excessive.

Assembly of the spacer and side plug will present some challenge to machinists because, after assembly, not only must the O-rings be sealed, but also the fan-shaped X-ray port must be in proper orientation. Trial-and-error grinding to remove small thicknesses from one X-ray window may be the simplest technique. The problem will, of course, arise anew every time it is necessary to replace windows or disassemble the sample-chamber components for cleaning. Hopefully, there will be many applications in which disassembly is a rare event. Drilling a conical hole instead of a fan-shaped slit in the side plug would eliminate the orientation problem, but the plug would be weakened and the adjoining window would have to support the high pressure of the sample chamber over a greatly increased area.

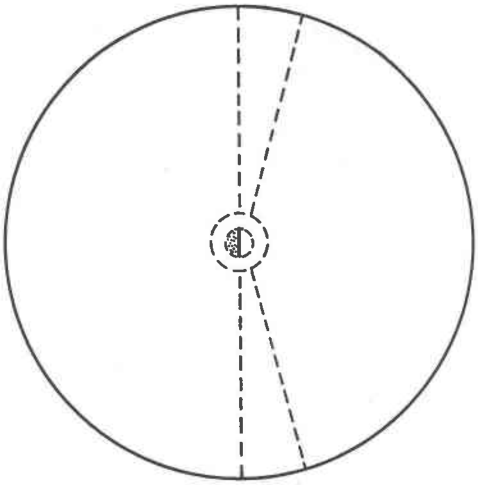

FIG. 3. Partial sketch of a cell in which the sample is held in a cup made of X-ray window material.

In addition to its compactness, this X-ray cell has some other advantages over that of Figure 1: (1) the total thickness of window material that must be traversed by X radiation has been reduced from 1.91 cm to 1.27 cm; and (2) because there is only one axial hydraulic system, which is connected to the top of the cell, the bottom can be left as a flat surface to maximize mechanical stability and ease of positioning.

Some advantages of the design of Figure 1 are lost. For example, (1) The X-ray windows must now sustain in shear the full differential between atmospheric pressure and the pressure within the brine chamber, so that the range of experimental pressures available is restricted. There is some compensating gain because the holes sealed by the windows are smaller than before, about 0.25 × 1.27 cm instead of 0.64 × 1.27 cm. (2) The maximum strength for which the cell body itself can be designed is limited, because the maximum outside diameter is fixed and an initial decision was made to hold sample area fixed. (3) The volume of the brine reservoir is about a third that of Figure 1. It could, of course, be increased within limits by lengthening the cell. (4) It is no longer possible to use porous pistons to exert a

TABLE 2. Percent Absorption Loss of Mo$K\alpha$ Radiation Passing Through Various X-Ray Window Materials for the d = 2Å and d = 15 Å Diffractions

	Density, g/cc	Linear Absorption Coefficient, μ	Path Length 1.91 cm		Path Length 1.27 cm		Path Length 0.636 cm	
			d = 2Å	d = 15Å	d = 2Å	d = 15Å	d = 2Å	d = 15Å
Diamond	3.51	2.45	99.0	99.9	95.5	99.4	79.2	97.4
Vitreous carbon	1.4	0.98	85.3	94.9	71.2	96.4	46.6	93.3
B_4C	2.50	1.26	91.9	99.0	79.2	97.4	55.4	94.4
BN (cubic)	3.48	2.84	99.5	99.9	97.3	99.7	83.8	98.0
BeO	3.01	3.21	99.8	100	98.3	99.8	87.2	98.4
Be	1.85	0.56	65.5	95.7	50.9	93.9	30.0	91.3
B (amorph)	2.35	1.06	86.7	98.3	74.0	96.8	49.3	93.7

mechanical pressure upon the sample. (5) The area of porous plate surface in contact with the brine reservoir is less than before, increasing equilibration time; moreover, it lies at one end of the sample, so that equilibration will be slower for the bottom part of the sample than for the top. (6) It is more difficult to clean the cell thoroughly of brine from the previous run. If the films of liquid trapped on surfaces between spacer and windows, spacer and cell body, and cell body and windows cannot be tolerated, disassembly of the side plug-window assembly would be required to remove them. It is because of this possible need for cleaning as well as the need to replace corrosion-weakened windows that sealing in the region of the sample is effected entirely by O-rings rather than by some combination of O-ring and Poulter seals; thus, the necessity for repolishing Poulter-seal surfaces is eliminated. (7) There is obviously a limit to the ability of a thin, brittle vitreous carbon plate to sustain the localized stresses around an O-ring seal, but the maximum pressure to which the cell can be used has already been restricted by (1) above.

The limitations of the design of Figure 2 result in considerable degree from the complexity of the cell in the region near the sample. Figure 3 sketches a simplification in which the sample assembly, held in a flat-bottomed cup of X-ray window material, is sealed by an O-ring around its top edge. Unfortunately, the cup is a structurally weak shape.

The X radiation to be used in conjunction with all three cells clearly has to be Zr-filtered Mo$K\alpha$, which displays the desired diffractions between 15 and 2 Å in the 2θ range from 2.7° to 20.5°. Shorter wavelengths compress this range whereas longer wavelengths are strongly absorbed by the window. The 15° angular aperture shown in Figure 1 for the X-ray channel is that at which the piston behind the X-ray window begins to intercept the incident X-ray beam, and is thus a function of window thickness and width. This aperture is, of course, considerably greater than that needed for the basal clay reflections if Mo$K\alpha$ radiation is used.

Obtaining adequate diffracted signal intensity is a major problem. Table 2 gives calculated absorption losses of several window materials for window path lengths of 1.91 cm (the design of Figure 1), 1.27 cm (the design of Figure 2), and 0.636 cm, at the angular positions of the 2 Å and 15 Å diffractions. About 7/8 of the incident X-ray beam falls outside the sample area at the latter angle. The calculation does not allow for absorption losses caused by the brine-saturated sample. The use of a step-scanner for automatic internal counting would make it possible to use thicker windows and would extend the usable range in 2θ.

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