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GAS-COOLED REACTOR COOLANT CHOICE

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Contract No. W-7405-eng-26

REACTOR PROJECTS DIVISION

GAS-COOLED REACTOR COOLANT CHOICE

Staff of the ORNL
Gas-Cooled Reactor Project

DATE ISSUED

MAY 21 1959

OAK RIDGE NATIONAL LABORATORY
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GAS-COOLED REACTOR COOLANT CHOICE

ABSTRACT

This report is a compilation of the technical information presently available which bears on the problem of selecting a coolant for the graphite-moderated gas-cooled reactor. The problems with respect to helium containment and availability, the status of the technology on carbon dioxide–graphite reactions, the influence of coolant choice on power cost, and the compatibility of carbon dioxide with various fuel cladding materials are discussed.

HELIUM CONTAINMENT PROBLEM

CONTAINMENT EXPERIENCE

The GCR-2 helium-cooled graphite-moderated reactor described in report ORNL-2500 (ref 1) included an operating system that consisted of the following equipment:

1	50-ft-dia sphere
4	20-ft dia, 40-ft-high cylindrical steam generators
4	axial-flow helium blowers with motors contained in the system
4	60-in.-dia butterfly control valves
4	30-in.-dia butterfly control valves
800 ft	60-in.-dia pipe
120 ft	30-in.-dia pipe
24	60-in.-dia expansion joints
8	30-in.-dia expansion joints

The total system volume was 105,000 ft^3, and the system was to be filled with 940,000 scf of helium.

The economic evaluation of the system was based on containing helium in the system at 300 psia and 450°F with a gas temperature of 1000°F in the vessel discharge piping. The system was to be completely welded. The maximum allowable leakage was specified as 1% of the system volume per day, which would cost 0.05 mill/kwhr at a price of $22.70/1000 scf.

The question of whether the system leakage could be limited to the specified losses has been open to much positive and negative speculation. The results of a survey carried out to determine whether experience with other helium installations would support the optimism of the GCR-2 designers is described here. The possible sources of leakage in the GCR-2 helium systems are:

1. diffusion of helium through the metal walls;
2. leakage through welded connections;
3. leakage past valve stems, through valve packing, or through bellows seals;
4. leakage through electrical connections;
5. losses at the fuel element sampling connections or other instrument leads;
6. losses through compressor seals, if used.

The diffusion of helium through metals has been a common cause for concern among helium users. There is a marked difference in the performance of cast and wrought metal products with respect to helium leakage. It is an accepted fact throughout industry that castings are generally unsatisfactory. Although it is not universally true that castings will not contain helium, there are cases (for example, some cast valves) in which castings which would satisfactorily hold air have been found to leak helium. Techniques for producing

[1] *The ORNL Gas-Cooled Reactor*, ORNL-2500 (April 1, 1958).

helium-tight castings would require special investigation and perhaps development work. On the other hand, leakage of helium through wrought steel materials, such as rolled plate, extruded or drawn piping and tubing, and forged shapes, has been established to be nil when the material has been previously inspected and found to be free of defects. Commercially available material without special manufacturing requirements has proved acceptable in this respect. Premo[2] states that his company has thoroughly investigated the matter and has fully established this premise. The conclusion is further borne out by the use of large quantities of plate and pipe in the helium storage facilities of the Naval Air Station at Bainbridge, Maryland, and Lakehurst, New Jersey, and at the Bureau of Mines at Amarillo, Texas. All these installations report that they have no difficulty with leakage when storing helium at pressures up to 2000 psig. The Edwards Rocket Base at Edwards, California, reports similar experience with stainless steel containers at pressures up to 6000 psig. The Bureau of Mines reports that it uses forged steel tanks for helium shipment by tank truck throughout the United States and experiences no measurable leakage at pressures up to 2000 psig.

There has been little experience, however, with high-temperature systems for helium storage. Reactor studies by Sanderson & Porter are predicated on the use of helium at pressures from 50 to 100 atmospheres and temperatures up to 1500°F. They state that they have found no evidence to indicate that helium diffusion through metal walls will be increased significantly by high temperatures if the metal is metallurgically sound. Many high- and low-alloy steels have been leak-tested at high temperatures for various experimental purposes in connection with nuclear reactor work at ORNL, and no evidence of change in leakage characteristics has been reported. It would appear, then, that the high operating temperature of the gas-cooled reactor will not materially affect the helium-leakage problem. This observation must be qualified by the fact that no test data have been collected which are specifically pertinent to helium leakage under pressure at elevated temperatures. The possibility exists that there may be some phenomena not heretofore encountered in test work which might accelerate the helium-leakage rates.

Experience of others with leakage through welded joints was also investigated. In all cases it was stated that if the welds were made by fully qualified welders and thereafter inspected in accordance with ASME Unfired Pressure Vessel Code practice, no leakage difficulties were experienced. At the Edwards Rocket Base the helium storage system is tested by mass spectrometry and constantly monitored, and a leakage rate below that detectable with their test instruments is maintained.

The loss of helium through valves was also discussed. All sources report difficulty with packed valves; however, the rate of leakage is not substantial. The Bureau of Mines at Amarillo, Texas, which has a storage capacity of 7.5 million scf, reports that losses in that system are probably in the neighborhood of 0.1%/day from all sources. At Edwards Rocket Base, where bellows-sealed valves are used, no detectable leakage past the valve stems has been observed.

There is no experience with helium leakage past electrical connections. A comparable problem has been encountered in the pressurized-water reactors which are required to contain radioactive vapors. The Shippingport Reactor designers report that the seal developed for this application has been adequate. Donnelan[3] states that a "mass spectrometer–tight" seal which would hold 2000 psi has been developed and that the adaptation of a seal of this type to contain helium would be a straightforward engineering problem.

Two types of instrument connections were considered as potential sources of leakage. The first type, sampling tubes and pressure taps, which are essentially welded connections, fall within the scope of the previous discussion concerning the tightness of welded connections. The second type includes primarily thermocouple leads that may be treated in the same manner as electrical connections.

The above discussion leads to the conclusion that an all-welded system which can meet the helium leakage requirements can be constructed without the development of new technology. The prospects appear hopeful for obtaining a compressor

[2]K. Premo, "Helium Components and Systems Development Problems," in *Helium Symposium*, Robertshaw-Fulton Controls Co., Anaheim, California, 1957.

[3]Private communication from L. Donnelan of Allis-Chalmers Mfg. Co. to R. D. Stulting and M. Bender of ORNL.

shaft seal which can meet the helium-cooled reactor requirements, and, while this is unnecessary to the successful execution of the design, it would be a desirable feature from the standpoint of improved access for direct maintenance.

Acceptance of these conclusions, should not, however, preclude cognizance of the several design requirements. The GCR-2 design was based on off-stream fuel loading in an unpressurized system, since continuous fuel loading would be a difficult accomplishment for a helium system. Undoubtedly, a substantial amount of development work would be necessary to produce a seal which would permit a fuel-loading machine to be connected and disconnected remotely without significant loss of helium. Further, the anticipated long fuel lifetime, which is essential to the economic success of the system, makes continuous fuel loading an unnecessary complication, but not an undesirable one. A continuous-loading system for a CO_2-cooled reactor would undoubtedly require a less complex sealing system because of larger leakage allowances and would consequently be easier to design.

In spite of the emphasis which has been placed on an all-welded system, the use of bolted and gasketed connections has not been shown to be impractical. Connections of this type are used in high-vacuum systems and in some helium systems.[4] The reliability of this type of connection must be established by test experience.

The bellows-sealed butterfly valve is another possibility which should be considered. The sealing problem is straightforward, but in order to obtain the desired flexibility, the bellows wall must be thin, and a counterbalancing pressure may be required to limit pressure stresses. While the counterbalancing pressure could be applied with air, the valve would have to be carefully tested to assure complete integrity of the bellows seal.

Finally, it should be noted that while the economic incentive to obtain a leakage specification of less than 1% of the system volume per day is not great for the GCR-2 design, a smaller 40-Mw prototype reactor would have a higher helium cost factor per unit of energy output (about 0.25 mill/kwhr) that would represent a significant part of the operating budget. Furthermore, the design of a system of greater tightness would reduce the drain on the helium resources and remove a substantial part of the objection to the use of helium in the reactor export market. Since no evidence of the impracticability of obtaining a tighter system has been uncovered, it is suggested that a system designed to limit losses to 0.1% of the system volume per day be used as a goal for helium-cooled reactor installations rather than the 1% specified for the GCR-2 (ref 1).

HELIUM AVAILABILITY

A survey was also made of the helium supply available for use in gas-cooled reactors. Usage during the years 1957 and 1958 and the projected usage during 1959 and 1960 are estimated by the Bureau of Mines as:

1957	281.5 million scf
1958	387.1 million scf
1959	432.7 million scf
1960	464.6 million scf

Of the 1960 estimate, 12 million scf, or 2.6%, is allocated for nuclear reactors.

Recently the Bureau of Mines has proposed the construction of 13 recovery plants capable of increasing helium recovery to 2.4 billion scf per year by 1975. If this proposal is implemented, a 32-billion scf reserve of helium would be developed by 1975. The new construction would cause an increase in the helium price from $19.00/1000 scf to $44.50/1000 scf. The GCR-2 helium cost would increase only from 0.05 to 0.12 mill/kwhr when the price increase became effective, and thus the price increase would have little effect on the over-all power cost of a GCR-2 type of reactor.

The proposed expansion of the helium-recovery system by the Bureau of Mines would make sufficient helium available to support a substantial portion of the United States electrical power for at least 50 years. This conclusion is drawn from the fact that the Bureau of Mines proposes a helium-recovery capacity of 2.4 billion scf per year by 1975, while the projected domestic usage in that year would be 1.2 billion scf. The difference between the capacity and the usage indicates that 1.2 billion scf of excess capacity per year would be available for nuclear power plants. Some of the production sources included in the conservation plan of the Bureau of Mines may be nearly exhausted by the

[4] W. H. Lawrence, "Operational Helium," in *Helium Symposium*, Robertshaw-Fulton Controls Co., Anaheim, California, 1957.

year 1975, while others with lower helium concentrations that are not presently included in the plan presumably could be developed, if required.

The 13 fields included in the recovery plan have 119 billion scf of recoverable helium of which 72.5 billion is to be recovered under the current plan. The Bureau of Mines expects that, by 1975, 11.5 billion scf will have been exhausted. In the same year, helium usage is estimated at 1.5 billion scf, including nuclear power plant usage. Nonnuclear usage would, of course, be somewhat less than 1.5 billion scf, but for the period 1975 to 2005, it would probably be fair to estimate that the average yearly nonnuclear usage would approach 1.5 billion scf. The total nonnuclear consumption would thus be 45 billion scf during the period 1975 to 2005. If this quantity plus the 11.5 billion scf utilized up to 1975 is subtracted from the total of 72.5 billion scf to be recovered, the remaining 16 billion scf of helium appears to be available for nuclear power plants. If the conservative helium usage values given for GCR-2 (ref 1) are used as the basis, it is estimated that a 225-Mw reactor would use 3,440,000 scf of helium per year. During the anticipated nuclear power plant lifetime of 20 years, 69 million scf of helium would be used. The 16 billion scf of helium available for nuclear reactors would thus permit operation of 233 nuclear power plants of 225-Mw capacity, which would have a total capacity of 52,300 Mw. This represents 56.5% of the United States 1955 steam-electrical capacity of 92,000 Mw. By expanding the Bureau of Mines helium conservation plan to include recovery of the remaining 46.5 billion scf of helium which is potentially available but not now included, the amount of nuclear electrical power which could be supported is 204,000 Mw.

Such expansion might, however, not be practical or necessary. As outlined above, experience in the United States has shown that it is reasonable to expect to be able to limit leakage to a rate of 0.1% of the system volume per day. Further, it is possible that higher capacity plants than the ORNL GCR-2 can be built without increasing the helium consumption rate. On the basis of a 0.1% per day leakage rate, rather than 1% per day as used for the GCR-2 calculations, the 16 billion scf of helium available (from 1975 to 2005) under the current Bureau of Mines conservation proposal would support GCR-2 type plants with a capacity of 523,000 Mw. It is of interest to note that if the 10-year doubling time for electrical capacity in the United States is used as a criterion, the steam-electrical capacity in the United States, compared with that existing in 1955, should be:

1955	92,000 Mw
1965	184,000 Mw
1975	368,000 Mw
1985	736,000 Mw

The potential helium supply of 16 billion scf for nuclear power under the current Bureau of Mines helium conservation proposal might support virtually all the steam-electrical capacity constructed between 1965 and 1985.

The fact that the helium supply is limited should not lead to the conclusion that the future of this type of gas-cooled reactor is restricted. Experience with gas containment and advances in high-temperature materials technology will ultimately permit helium to be displaced as a coolant by some higher performance fluid, such as hydrogen, in gas-cooled reactor systems.

The short-range picture is, perhaps, less attractive. According to a recent announcement of the Joint Committee on Atomic Energy, the United States plans to be able to produce power competitively in foreign markets in five years and in domestic markets in ten years. This would mean that competitive foreign reactors would have to be available in the year 1963 and competitive domestic reactors in 1968. The principal foreign nuclear power markets are probably the United Kingdom and the Euratom group. These are reported[5] to require, respectively, 6000-Mw capacity in 1965 and 15,000-Mw capacity in 1967. The United Kingdom program is predicated on the use of CO_2-cooled reactors, and thus the United Kingdom should probably not be considered in short-range helium-usage planning. The Euratom group, therefore, represents the major potential user. If the GCR-2 plant with 1% per day losses is again used as a reference, it may be seen that 67 such plants would be required to meet the Euratom demands through 1967. These plants would use 230 million

[5] *A Target for Euratom*, Report submitted by Mr. Louis Armand, Mr. Franz Etzel, and Mr. Francesco Giordani at the request of the governments of Belgium, France, German Federal Republic, Italy, Luxembourg, and the Netherlands, May 1957.

scf of helium per year or 1.64 times the quantity that will be supplied to nongovernment users in the United States in 1960. (If the inference from the Bureau of Mines data is correct, the nongovernment usage is increasing at the rate of 20 million scf per year, so, in 1967, it would be 280 million scf, a more realistic comparative value than the 1960 figure.) The need for immediate action to implement the Bureau of Mines conservation plan is indicated if domestic helium is to be utilized in a foreign reactor market. These expanded production facilities could meet the needs of a foreign reactor market up to 1967 and could continue for an extended period if the leakage rates could be cut to 0.1% of the system volume per day. (The 15,000-Mw capacity required by the Euratom group would require only 23 million scf per year in the latter case.)

AVAILABILITY OF HELIUM IN FOREIGN COUNTRIES

Little is known about the availability of helium outside the North American continent. Information gained from a search of the literature indicates that the existing deposits are of such low concentration as to be prohibitively expensive to separate with currently used methods; it is also apparent that the meager information found in the course of the search is not sufficient to justify a conclusion that there are no substantial helium deposits outside the United States. The Bureau of Mines has tested only a few samples from foreign sources, and these have not shown the presence of significant quantities of helium. A more extensive search for foreign helium resources would be desirable if helium is to be considered as a coolant for export nuclear power reactors.

The Air Reduction Company was contacted concerning overseas shipments of helium gas, and it was learned that either gaseous or liquid helium could be shipped satisfactorily. It was suggested that use be made of the tank cars presently used for helium transportation. The tank cars hold about 250,000 scf of helium in gaseous form and cost about $100,000 each. Two such units could probably maintain a supply of helium for a GCR-2 type of plant.

The Bureau of Aeronautics in Washington was consulted about the transportation of liquid helium. The Bureau of Aeronautics is planning a 100,000- to 300,000-scfd liquifier for installation at Amarillo, Texas, in 1960. It was stated that liquid helium could be shipped by rail without difficulty, and presumably water shipment would be equally satisfactory provided the shipment time was not substantially longer than 2 weeks, since helium vaporization would cause a gradual increase in pressure in the container. The time period could be extended by designing shipping containers for higher pressures or for additional storage capacity.

The economics of water shipment suggest that overseas transport should not be substantially more costly than rail transport on a mileage basis. It costs only about $0.006/scf to transport liquid helium from Amarillo, Texas, to Oak Ridge, Tennessee, and thus it appears that the cost of water shipment to Europe would not be prohibitive. One shipper in the New York area indicated that a 35,000-scf helium trailer could be shipped from New York to Calais, France, for $0.03/scf. If this cost were added to a probable maximum cost of $0.015/scf for shipment to New York, the total cost would be $0.045/scf. With this shipping cost added to the projected price for helium of $0.044/scf, based on the Bureau of Mines conservation plan price, the total cost would be $0.089/scf. If ORNL GCR-2 consumption rates are used as a basis, the helium contribution to power cost would be approximately 0.2 mill/kwhr at Calais, France. Overseas shipping rates vary because of the shipping regulations of the various countries, and negotiations would be necessary to obtain competitive rates to various countries.

STATUS OF TECHNOLOGY OF CARBON DIOXIDE–GRAPHITE REACTIONS

REACTION OF CARBON DIOXIDE WITH GRAPHITE IN THE ABSENCE OF RADIATION

Most of the available information on the reactions of CO_2 with graphite is not applicable to reactor studies because it relates to grades of graphite that are more reactive than reactor grades of graphite and does not include data on the effects of radiation. Studies of reactor-grade graphites have been, to a large degree, performed at Hanford or by the British, and the data presented in the following sections have been drawn mainly from these sources. The British have studied the reactions of CO_2 and graphite in closed-flow systems, but little information has been made available. Information on studies of the effects of such factors as flow rates and the partial pressures of CO_2 and CO is similarly incomplete.

Reaction Rate Data

Rate data for the thermally induced reaction of CO_2 and graphite, as reported by Burton[6] and Walker,[7] are given in Table 1 and Fig. 1, as extrapolated to cover the temperature range 300 to 900°C. Burton used a 0.426-in. by 1-in. cylinder of CSF graphite having a surface area of 0.30 to 0.40 m^2/g, a temperature range of 850 to 1000°C, and a CO_2 flow rate of 100 cm^3/min. A ½-in. by 2-in. cylinder of Speers Carbon Co. graphite was used by Walker at 900 to 1200°C, with a CO_2 flow rate of 2 liters/min. Measurements were made at essentially 1 atm of CO_2 pressure, and the gas was not recycled. The agreement between the results is satisfactory in view of the fact that different graphites were used, and it appears reasonable to assume that rates of this order would be applicable to the reactor grades of graphite. The higher rates reported by Walker probably resulted from the greater surface area of the graphite used.

Factors Affecting the Reaction Rate

Surface Area. – The rate of reaction between graphite and CO_2 is markedly affected by the available graphite surface. A very effective method of increasing the surface area is through oxidation, as shown by the studies of Spalaris[8] and of Walker.[7] Nitrogen adsorption-desorption isotherms were used to determine the surface area and pore size distribution as a function of the degree of oxidation by CO_2. The surface area was found to increase with increasing degree of oxidation, with the most rapid increase occurring during the initial slight oxidation; the reaction rate also increases rapidly during the period of most rapid increase of the surface area. Two of the principal distribution peaks in the micropore structure of graphite occur at radii of 20 to 35 and 90 to 150 Å. The intensity of the peak at 20 to 35 Å increases rapidly between zero and about 2% oxidation, decreases between 2 and 6% oxidation, and remains essentially constant

[6] H. H. Burton, HW-23169 (Jan. 2, 1952); HW-24489 (May 15, 1952); HW-24676 (June 5, 1952). (Classified).

[7] P. L. Walker, Jr., R. J. Foresti, Jr., and C. C. Wright, *Ind. Eng. Chem.* **45**, 1703 (1953).

[8] C. N. Spalaris, HW-29082 (July 14, 1953). (Classified).

Table 1. Reaction Rates for the Thermally Induced Reaction of Carbon Dioxide and Graphite

Temperature (°C)	Percentage Weight Loss in 1000 Days	
	Burton	Walker
300	1.4×10^{-9}	8.2×10^{-6}
400	4.4×10^{-6}	4.3×10^{-3}
500	1.5×10^{-3}	4.6×10^{-1}
550	1.8×10^{-2}	3.1
600	1.5×10^{-1}	16
650	1.1	72
700	6	2.7×10^{2}
750	30	9.8×10^{2}
800	1.2×10^{2}	2.9×10^{3}
850	4.1×10^{2}	7.7×10^{3}
900	1.4×10^{3}	2.1×10^{4}
Activation Energy, kcal/mole	61.5	48

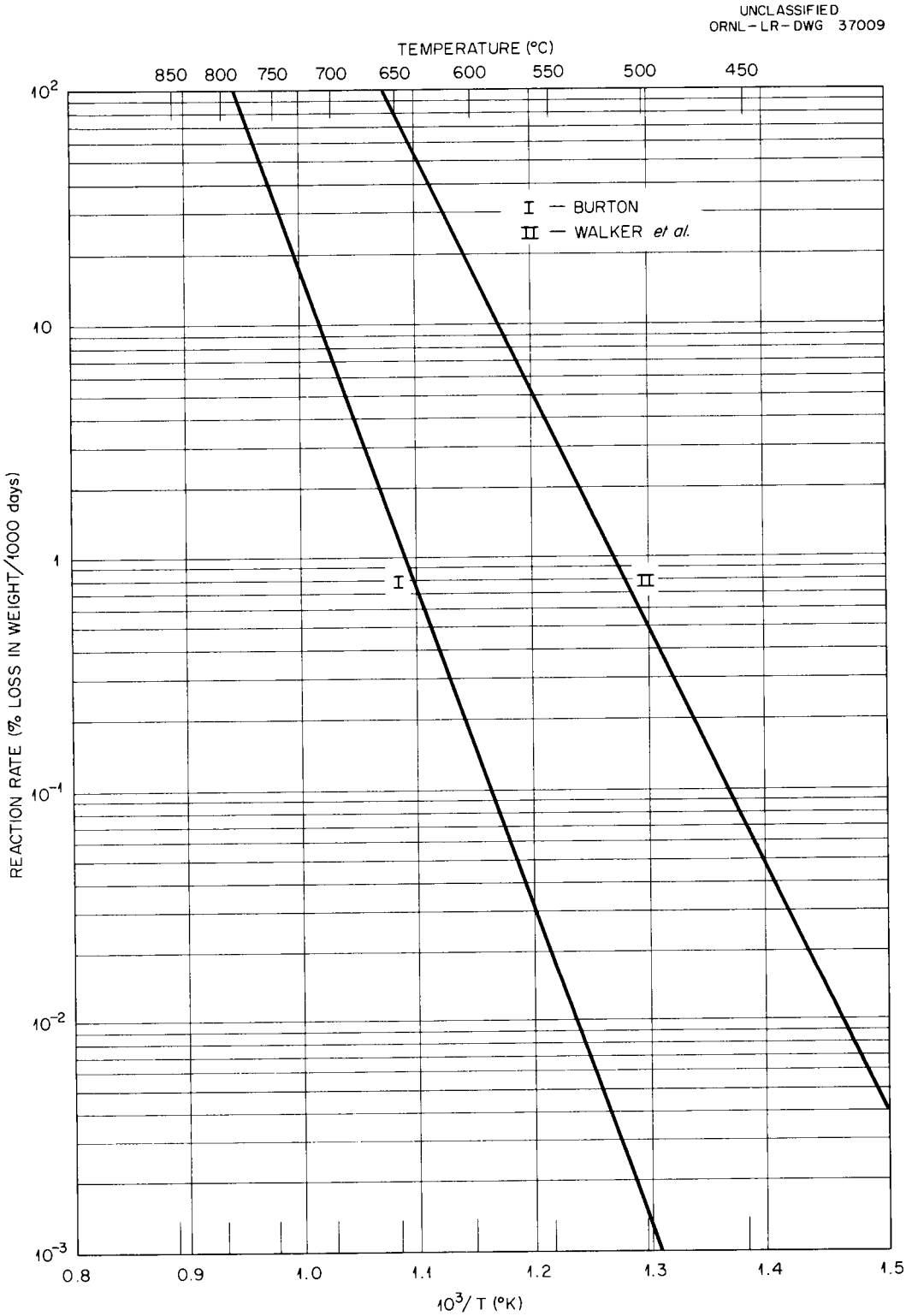

Fig. 1. Reaction Rate of Thermally Induced Reaction Between CO_2 and Graphite.

from 6 to 30% oxidation. The intensity of the peak at 90 to 150 Å increases up to about 6% oxidation and changes very little thereafter. It is postulated that the rapid increases in surface area and reaction rate are the result of the 20- to 35-Å pores being unblocked during the early stages of oxidation. Subsequently, as the pores enlarge, the rate of surface-area increase diminishes, and above 6% oxidation there is probably generalized attack of the graphite crystal that is characterized by a constant reaction rate, which results from dynamic balance between internal diffusion and the chemical reaction. This is the reaction rate which is commonly reported.

Another method of increasing the surface area would be to cut up the graphite. Spalaris[9] studied the reaction rates of CSF graphite using a 1-in. by 1-in. cylinder with a surface area of 0.32 m^2/g and disks cut from another cylinder having a surface area of 0.56 m^2/g. Oxidation in CO_2 at 1000°C showed that increasing the initial area by a factor of about 2 increased the reaction rate by a factor of about 3. Thus, it is evident that part of the inaccessible pore space can be opened by reducing the size of the graphite specimens, as well as by oxidizing the binding material and/or the crystallites blocking the entrance to these pores. This suggests that data obtained for small specimens cannot safely be extrapolated to data for graphite bars.

Prior Irradiation. – Hanford work[10] has shown that the reaction rates with CO_2 for a sample of CSF graphite subjected to an in-pile exposure of 3.1×10^{20} neutrons/cm^2 are about four times as large as the rates found for virgin CSF graphite at 950 to 1000°C. Activation energies of 61.5 and 51.5 kcal/mole were found for the virgin and irradiated graphite samples, respectively. Similar effects on the reaction rate for the O_2-graphite system were observed. Spalaris[8] noted that the irradiated samples had larger surface areas than virgin samples at comparable percentages of weight loss, which indicated that an increase in surface area was produced by irradiation.

Type of Graphite. – The reactivity of a particular type of graphite with CO_2 is mainly a function of the available surface area. The various types of reactor-grade graphite produced in this country probably do not have large differences in reactivity. Small variations in density may be unimportant. For example, Hanford has used KC graphite with a density of 1.70–1.80 g/cm^3 and CSF with a density of 1.60–1.65 g/cm^3 and found no important difference in reactivity.[10] Although it is possible to produce special grades of graphite which, while having the same density, may vary widely in surface area, the use of such types of graphite in reactors is not likely. The type of binder could have some effect on reactivity, since the reaction with CO_2 involves the removal of blockages from the pores and the blockages may be binding material and/or poorly crystallized material, but departure from the use of standard binders in reactor graphite also seems improbable. Likewise the use of low-density graphite, which would be likely to be more reactive, does not appear to be probable.

Pressure and Flow Rate of Gas. – For a heterogeneous reaction such as that between CO_2 and graphite, the reactive sites on the graphite surface are of prime importance. It would appear that, at moderate pressures and flow rates of CO_2, the availability of the sites would be the rate-controlling factor. It is generally agreed that a rapid reaction of CO_2 occurs at the reactive sites that gives rise to CO, which passes into the gas phase, and to a surface oxide or an oxygenated surface.[11–13] The oxygenated surface undergoes slow decomposition and also gives rise to CO, which may either leave the surface or remain adsorbed on it. An adsorption-desorption equilibrium is established for CO in which part of the reaction sites on the carbon surface are occupied by CO and hence are not available for the initial CO_2 reaction. An increase in the partial pressure of CO would be expected to retard the over-all reaction by blocking more reaction sites.

There is little information available on the effect of CO_2 and CO pressures and flow rates. Gadsby *et al.*[11] studied the reaction of CO_2 with charcoal and gave an expression for the over-all reaction

[9] C. N. Spalaris, *Role of Surface Area in the Kinetics of Oxidation of Graphite*, HW-31928 (May 24, 1954). (Declassified, TID-1112).

[10] R. E. Woodley, AEC Technical Cooperation Program, U.K.-U.S.A., *Discussions on Graphite Oxidation – Hanford Contribution*, WASH-690 (April 16, 1956). (Classified).

[11] J. Gadsby, F. J. Long, P. Sleightholm, and K. W. Sykes, *Proc. Roy. Soc.* A193, 357 (1948).

[12] W. E. J. Broom and M. W. Travers, *Proc. Roy. Soc.* 135A, 512 (1932).

[13] F. Bonner and J. Turkevich, *J. Am. Chem. Soc.* 73, 561 (1951).

rate for CO_2 pressures from 10 to 760 mm Hg, with the following three stages taken into account:

1. initial CO_2 reaction with carbon,
2. evaporation of adsorbed oxygen with atoms of carbon from the surface,
3. adsorption-desorption of CO on carbon surface.

It is doubtful, however, that the expression has any valid application to graphite.

Studies[14] at Hanford have shown that the reaction rate of the CO_2-graphite system becomes constant at some definite flow rate and that an increase in the flow rate above this value does not increase the reaction rate as measured by the concentration of CO in the effluent gases. A decrease in the ratio of surface area to volume of the graphite (radius of a cylindrical sample of given length is increased) requires a higher flow rate to reach the constant reaction rate. Other studies[15] have shown that if the partial pressure of CO_2 is reduced by the addition of helium, the reaction rate is decreased. Thus it appears that the reaction rate is dependent on the partial pressure of CO_2. The addition of small amounts (3.4%) of CO to the CO_2 has been shown[16] to reduce the reaction rates in the temperature range 850 to 1025°C. The data show, however, that with increasing temperature the logarithm of the reaction rate for the mixture approaches that for pure CO_2 asymptotically. Thus the inhibiting effect of the CO appears to be less at the higher temperatures as a result of increased desorption of CO from the surface at the higher temperatures. Since these studies were not conducted in closed flow systems, no information is available on steady-state conditions.

Thermodynamic Equilibrium Data

The equilibrium concentrations of CO for the reaction $CO_2\ (g) + C\ (s) \rightleftharpoons 2CO\ (g)$ at various temperatures and pressures are given in Table 2. These values are of academic interest only, since it is realized that for the systems of interest the steady-state conditions differ significantly from the thermodynamic equilibrium state.

RADIATION-INDUCED REACTION OF CARBON DIOXIDE WITH GRAPHITE

The intense radiation present in a reactor may lead to chemical reactions which would not otherwise occur except at much higher temperatures. The reaction of graphite with CO_2 is radiation induced through the ionized and excited gas molecules, that is, the active species or short-lived intermediates of CO_2. Some of the available information on the radiation behavior of this system is presented in the following sections, but it will be apparent that the over-all picture is quite complex and incomplete.

Decomposition of CO_2

The decomposition of CO_2 by in-pile irradiation in the absence of graphite occurs to a limited

[14] R. E. Woodley, HW-34154 (Dec. 15, 1954). (Classified).

[15] H. H. Burton, HW-26618 (Jan. 12, 1953). (Classified).

[16] H. H. Burton, HW-24676 (June 5, 1952). (Classified).

Table 2. Thermodynamic Equilibrium Concentrations of Carbon Monoxide at Various Temperatures and Pressures for the Reaction: $CO_2\ (g) + C\ (s) \rightleftharpoons 2CO\ (g)$

Temperature (°C)	CO (mole %)					
	At 1 atm	At 5 atm	At 10 atm	At 15 atm	At 20 atm	At 25 atm
350	0.28	0.13	0.07	0.06	0.05	0.04
400	0.94	0.42	0.30	0.24	0.20	0.18
450	2.8	1.2	0.88	0.72	0.62	0.56
500	7	3.2	2.2	1.8	1.6	1.4
550	15	6.6	4.6	3.8	3.3	3
600	32	14	10	8.2	7.2	6.4

extent. Woodley[17] reports that approximately 1% of the CO_2 is decomposed, while studies by Harteck and Dondes[18] of samples irradiated in the Brookhaven reactor gave about 0.1% decomposition. Davidge and Marsh[19] reported a maximum final CO concentration of 8×10^{-3}% at 325°C using a CO_2 pressure of 75 cm of Hg and an exposure of 5.25×10^{17} neutrons/cm^2. The gas-phase processes have been represented as follows:[20]

$$CO_2 = CO + O \quad (1)$$

$$O + O\ (\text{wall}) = O_2 \quad (2)$$

$$O + O_2 = O_3 \quad (3)$$

$$O_3 + CO = CO_2 + O_2 \quad (4)$$

In the presence of a graphite surface, atomic oxygen or ozone will react to form adsorbed CO or a surface oxide layer. Davidge and Marsh[19] give the following scheme for the reaction of graphite with the oxygen resulting from CO_2 decomposition.

$$2CO_2 = 2CO + 2O \quad (5)$$

$$2O + 2O_2 = 2O_3 \quad (6)$$

$$2O_3 + C = CO_2 + 2O_2 \quad (7)$$

or

$$2O_3 + 2C = 2CO + 2O_2 \quad (8)$$

A combination of reactions 5, 6, and 7 or of 5, 6, and 8 yields $CO_2 + C = 2CO$, with the first combination giving one molecule of CO per molecule of CO_2 dissociated and the second twice as much CO. The British admit that this is speculative and conclude only that the forward reaction

$$CO_2 + C = 2CO$$

proceeds through an intermediary having a mean life comparable to or shorter than 1 min, the time of circulation in their experimental system.

The thermal reaction is inhibited by adsorbed CO on the graphite surface, and a similar inhibiting effect would be expected for a radiation-induced reaction unless the absorbed layer is removed by by some means. Woodley[21] found that the gamma-induced reaction for graphite exposed to CO_2 in the MTR canal gamma facility was suppressed by adsorbed CO, whereas exposure in the Hanford pile[17] gave results which indicate that the CO was not an effective inhibitor. The graphite temperature, in either case, was not sufficiently high to desorb the CO, and the difference in behavior is thought to be due to the desorption of CO in-pile by the energetic neutrons. While this implies a continuing reaction with the graphite and a resulting buildup of CO, the CO according to reaction 4, as well as the suboxide polymers, will become competitors for the ozone molecules and give rise to an equilibrium state in which the rate of reduction of CO_2 will be equal to its rate of formation.

Decomposition of CO

The decomposition of CO under irradiation was observed by Lind and Bardwell[22] and was more recently investigated by Woodley.[17,21] The latter exposed samples of CO in both the MTR canal gamma facilities and a Hanford pile and observed the formation of carbon suboxide polymers in both facilities. Systems containing graphite and CO_2 gave polymers in-pile but not in the gamma facility. Woodley believes that the following mechanism may be used to explain the in-pile decomposition of CO:

$$CO = C + O \quad (9)$$

$$C + CO + M = C_2O + M \quad (10)$$

$$C_2O + CO + M = C_3O_2 + M \quad (11)$$

$$C_3O_2 + CO + M = C_4O_3 + M \quad (12)$$

$$C_3O_2 + O = C_2O + CO_2 \quad (13a)$$

$$C_4O_3 + O = C_3O_2 + CO_2 \quad (13b)$$

$$C\ (\text{wall}) = \text{graphite} \quad (14)$$

$$C_2O,\ C_3O_2,\ C_4O_3\ (\text{wall}) = \text{polymers} \quad (15)$$

One molecule of CO is primarily dissociated per ion pair as in reaction 9, but four additional

[17] R. E. Woodley, *The Promotion of Chemical Reaction by Pile Radiation*, p 25, HW-40142 (Nov. 22, 1955).

[18] P. Harteck and S. Dondes, *J. Chem. Phys.* 23, 902 (1955).

[19] P. C. Davidge and W. R. Marsh, *The Effect of Pile Radiation on the Carbon Dioxide-Graphite Reaction*, AERE-C/R-1374 (Jan. 1956).

[20] J. O. Hirschfelder and H. S. Taylor, *J. Chem. Phys.* 6, 783 (1938).

[21] R. E. Woodley, *Promotion of Chemical Reaction in Gas-Graphite Systems by Gamma Radiation*, HW-31929 (May 24, 1954). (Declassified, AEC 1556).

[22] S. C. Lind and D. C. Bardwell, *J. Am. Chem. Soc.* 47, 2675 (1925).

molecules of CO are subsequently consumed in the processes represented by reactions 10 and 11, plus either reactions 12 to 13*b* and back to 12 or 13*a* to 11 and then to 12. These reactions lead to the overall-all reactions

$$5CO = CO_2 + C_4O_3$$

and

$$XC_4O_3 = (C_4O_3)_x$$

which are believed to occur at least during the initial period of irradiation. For the studies[21] in the gamma facility, the ratio of moles of CO decomposed to moles of CO_2 formed remained constant at 5. In the case of in-pile radiation, the ratio is not constant, and in the fringe areas of the reactor is approximately 4, corresponding to

$$4CO = CO_2 + C_3O_2$$

and

$$XC_3O_2 = (C_3O_2)_x$$

Woodley believes that the lower value of the in-pile ratio is due to a degradation of the suboxide polymers by the energetic neutrons, as follows:

$$(C_JO_K)_1 = (C_{J-m}O_{K-m})_1 + mCO$$

$$(C_JO_K)_1 = (C_{J-m}O_{K-2m})_1 + mCO_2$$

The CO formed can subsequently decompose, as before, but the reverse of either of the two processes given does not readily occur. As a result, carbon suboxide polymers with increased percentages of carbon are formed with increasing in-pile exposure. It is believed that the formation of C_4O_3 predominates initially, reaches a maximum, and decreases as its rate of degradation exceeds its rate of formation. A similar behavior was postulated for C_3O_2, but with the maximum occurring at a higher total dosage. The formation of elemental carbon would continually increase and might result in a solid composed largely of carbon after a long exposure. The color of the solid changes from reddish brown for short exposures to dark brown for longer exposures. It is believed that the polymerization occurs, in part, in the gas phase, but there also is some indication that the surface may be instrumental in initiating polymerization.

British Reaction Rate Data

The British have made studies of the CO_2-graphite reaction in closed flow systems in connection with their gas-cooled reactor program. Davidge and Marsh[19] have reported the results obtained with a glass loop at temperatures up to 350°C in BEPO. Experiments carried out with AGXP graphite and flowing CO_2 with the reactor at zero power gave a reaction rate of less than 2.5×10^{-4} mg of CO per hour at 350°C. The lowest reaction rate found under similar conditions with the reactor at power was 3.6×10^{-3} mg of CO per hour (0.03 wt %/1000 days). The increase in the reaction rate that occurs under irradiation is evident from these values. The rate of reaction was found to be proportional to the reactor power and therefore to neutron flux and dose rate over the range studied. The reaction rate of the radiation-induced reaction was only doubled upon increasing the temperature from 30 to 300°C. It was anticipated that the thermal reaction would mask the effect of radiation at temperatures of 500°C and above because of the small temperature coefficient.

A marked effect was noted upon reversing the gas flow. The geometry was such that under normal flow the gas passed through a container of small volume, over the graphite, and then through a container of large volume. The reaction rate was doubled if the CO_2 passed through the large-volume container before passing over the graphite. It was concluded from this large effect that the reaction is controlled more by energy deposition in the gas than by energy deposition in the graphite. The energy deposition in the gas is, in turn, affected by the decomposition of CO_2 by radiation to oxidizing intermediates, which may either react with graphite or reform CO_2. It was assumed also that the mean life of the intermediates must be less than or comparable with the time of circulation of the gas (1 min). Otherwise, the position of the large volume with respect to the graphite would not have produced a marked effect on the reaction rate. An increase in pressure should increase the reaction rate, since the mass of gas irradiated would be increased. Experimentally, it was found that a sevenfold increase in pressure (28 to 220 cm of Hg) increased the reaction rate by a factor of less than 3. The rate of reaction would be expected to be low at a very low flow rate, since most of the intermediates will have recombined before they reach the graphite, even though nearly every intermediate reaching the graphite should react. The time of contact over the graphite will be short at high flow rates, and therefore a low rate of reaction should also occur under these conditions. At intermediate flow rates an appreciable fraction

of the intermediates should reach the graphite, as well as react with it, to produce a maximum reaction rate at some optimum flow rate. For the experimental conditions used, the fact that the rate of reaction decreased with increasing flow rates above 1 g/min indicated that at flow rates greater than 1 g/min the optimum flow rate had been exceeded. A single experiment was run in which 0.87% water vapor was added to the CO_2. This addition had no effect on the rate of reaction. The exact steady-state concentration of CO at one atmosphere pressure of CO_2 probably lies between 0.034 and 0.6% at 350°C. The equilibrium CO concentration in the absence of radiation is 0.27% at this temperature. It is not possible to say whether radiation shifts the steady-state CO concentration or not, but it is believed that the radiation equilibrium will depend on the geometry of the system. One of the conclusions reached by the British workers follows: "The observed variations in rate caused by altering the geometrical conditions of the experiment and the possibility that graphite was not being removed uniformly from the samples in these experiments suggest that it might be quite misleading to attempt any calculation of burning rates of graphite in a gas-cooled reactor from these data."

EFFECTIVENESS OF COATINGS ON GRAPHITE

Coatings on graphite have been studied for many years at several laboratories. The coatings, which are designed to improve erosion resistance and/or corrosion resistance, have usually been restricted to the carbides or to carbide and metal mixtures. The techniques for applying them generally fall into the following categories: vapor deposition, flame spraying, coating with a slurry, and immersion in a liquid metal.

The coatings designed to protect graphite from erosion have been more successful than those designed to prevent corrosion or reaction with an active atmosphere. Until very recently there have been no coatings which gave any degree of permanent resistance to oxidation. For gas-cooled power reactor application coatings are desirable which give protection from oxidation over very long periods of time. In the particular case of the CO_2-cooled reactor the coatings must be essentially impermeable in order to inhibit the reaction of CO_2 with graphite. It may be seen that a permeable coating would subject the graphite base material to the oxidizing action of CO_2; there would be gradual removal of graphite; and the mechanical properties of the graphite would be seriously affected. In turn, there might be spalling of the coating and exposure of more of the graphite.

The most promising coating for graphite at the present time is the silicon–silicon carbide coating developed by Minnesota Mining and Mfg. Co. It is the only coating which offers a good possibility of being impermeable, as well as fulfilling the other requirements of low cross section, good thermal conductivity, refractoriness, and resistance to thermal fracture and spalling. This coating has been applied to graphite only on a laboratory scale and has been satisfactory only on a special grade of isotropic graphite produced by the Great Lakes Carbon Corporation. Questions remain as to whether the process could be scaled up to produce the large quantities and sizes required and whether sufficient special graphite could be obtained.

While the various available coatings for graphite should certainly be tested, the possibility of using pure silicon carbide sleeves should be considered. Silicon carbide has the inherent advantage of complete resistance to corrosion by CO_2; it is refractory; and it has a low cross section. There exists, also, a well-established fabrication technology, and production facilities are available for fabricating sleeves of the required sizes.

INFLUENCE OF REACTIONS ON REACTOR PERFORMANCE

Relationship of Available Reaction Data to a High-Temperature Gas-Cooled Reactor System

An examination of the available data for the reaction between CO_2 and graphite suggests that it is impossible to formulate any reliable estimate of the losses of graphite or the deposition of carbon either for the reactor as a whole or for any particular region within the reactor. The evidence at hand suggests that in the temperature region 550 to 600°C the thermal reaction of CO_2 with graphite controls the rate of oxidation of the graphite by overshadowing the radiation-induced reaction. If it is assumed that the maximum graphite temperature in an enriched gas-cooled reactor of the type contemplated will not exceed 550°C, the radiation-induced reaction is the one to be considered. This reaction apparently has a very small temperature coefficient so far as the forward part of the reaction is concerned. If the value of 0.13 tons/yr for the

graphite burnout in the Calder Hall reactor is used as a base, it is estimated that the higher temperature of the proposed GCR probably would not increase the graphite burnout by more than 50%.

The distribution of the graphite burnout is also of interest. Results from the British model-channel experiment suggest that the maximum oxidation rates occur between the gas inlet and the center of the reactor. In the case of the model-channel experiment the maximum flux occurred at the center of the channel and the maximum temperature at the outlet area. Thus, the maximum reaction rates were observed in relatively cool areas outside the maximum flux area. This behavior may be explained by a mechanism involving the decomposition of CO_2 by radiation with the formation of oxidizing intermediates, probably ozone and/or atomic oxygen, which have limited lives. These intermediates may either react with the graphite or be destroyed by reaction with CO or its decomposition products. The model-channel results suggest that between the inlet and center the oxidizing intermediates are most effective in reacting with graphite. In other words their destruction by CO and its decomposition products is not as great in this area as farther downstream where the concentrations of CO and its decomposition products are larger because more CO has been formed and after formation has been exposed to increased dosages of radiation. The important point, however, is that the reaction is controlled more by energy deposition in the gas than in the graphite. One may guess that the weight-loss distribution in the channels of the proposed GCR will be similar to that observed in the model-channel experiment.

An increase in pressure of the CO_2 would be expected to increase the oxidation rate of the graphite simply because more oxidizing intermediates would be produced per unit volume. It is not clear, however, just what relationship exists between the rate of oxidation and pressure in the high-pressure regions. Calder Hall experience suggests that the loss of graphite is linear with respect to the CO_2 pressure, but data demonstrating this are not available. The glass loop experiments in BEPO showed that an increase in pressure from 28 to 220 cm Hg increased the reaction rate by a factor of 3. The geometry of the system probably influences the pressure effect to a considerable extent. It appears likely that an increase in the CO_2 pressure from 100 to 300 or 400 psi would cause a significant increase in the reaction rate. Whether or not the pressure effect is linear in this pressure region is not known, but it is believed that an increase by a factor of 3 or 4 in the reaction rate is the maximum likely to occur upon increasing the pressure from 100 to 300 or 400 psi, and the effect may be considerably less.

The effect of flow rate on the oxidation rate of graphite is also obscure, particularly at high flow rates. It would be expected that the mean life of the oxidizing intermediates and the contact time required for the reaction of the intermediate with the graphite would determine the particular flow rate (constant pressure) required to produce the maximum oxidation rate. At low flow rates the intermediates will have ample time to react with the graphite, but many of them will have reacted in the gas phase before reaching the surface. At the other extreme the contact time is short, but many intermediates survive to reach the surface. The maximum reaction rate would be expected to occur between these extremes. This behavior was found experimentally in the glass loop exposed in BEPO. No information is accessible on the effect of flow rate on the oxidation of graphite in either the model-channel or the Calder Hall reactor. It might be assumed that the flow rate in Calder Hall is sufficiently high that the oxidation rate is less than the maximum attainable at some lower flow rate. If this were the case, the projected flow rate for the GCR-2 might influence the reaction rate to only a small degree. This is probably oversimplifying the case, however, since the pressure and geometry are related to the flow rate.

Although an estimate might be made of the initial rate of oxidation, this rate would decrease with increasing CO concentrations, and eventually a radiation-induced equilibrium would prevail. In actual reactor operations, leakage would influence the steady-state conditions. The large leakage of the Calder Hall reactor mainly determines the steady-state conditions, namely a CO concentration of 0.35% at 196 Mw and 100 psi. At a state in which the CO concentration is constant, its rate of formation is balanced by its decomposition plus that lost through leakage. The decomposition of CO under irradiation proceeds through polymerized suboxides, and the mechanism is believed to be quite complex. The effect of temperature on this decomposition is not understood, and consequently the regions in which the decomposition attains a

maximum are open to speculation. This decomposition could be of considerable importance if it is promoted in the cooler regions of the reactor and results in deposition of solids on the heat exchanger surfaces. (The catalytic decomposition of CO by the metal surfaces could conceivably occur, although it does not appear likely in view of the inactive state of the metal surfaces present.) Calder Hall experience sheds no light on this question, since no positive evidence for the deposition of carbon has been observed despite an estimated burnout of 0.13 tons of graphite per year. It is true that a good share of the carbon has been lost from the system, as CO, as a result of the high leakage rates. The model-channel experiment indicates that some burnout of graphite occurs along the entire length of the channel, and, if this is true, it suggests that carbon is deposited outside of the channel.

As mentioned previously, the steady-state value for CO in the Calder Hall reactors is about 0.35% and is limited mainly by the leakage rate. A steady-state value of about 1% CO was found in the model channel at a flux of one-fifth and a flow rate of one-half those prevailing in the Calder Hall reactors. This difference in CO levels is, again, to a large degree, due to the high leakage rate of the Calder Hall reactors. The glass loop experiment in BEPO[19] gave a steady-state concentration of CO somewhere between 0.3 and 0.64%.

Calder Hall operations suggest, as indicated above, that in reactor operation the leakage rate may play a dominant role in establishing the steady-state conditions, and the same may be the case for the GCR-2. If the burnout of graphite is of prime concern, the leakage rate should be kept as low as practical, since loss of CO favors the forward reaction. On the other hand, if the formation of solids from the decomposition of CO is troublesome, leak tightness of the reactor is not so important. In addition to the leakage rate, such factors as maximum temperature, temperature gradients, radiation dosage, pressure, flow rate, resonance time in relation to transit time, gas-to-graphite volume ratio, and ratio of in-pile gas volume to out-of-pile gas volume must be considered in arriving at the steady-state conditions.

Influence of Exit Gas Temperature on Performance

The mean temperature of the gas leaving the reactor is likely to be set as a result of a compromise between reactor performance and steam system performance. Since the ultimate limiting temperature in the reactor is usually the fuel surface temperature, good reactor performance does not favor a very high gas outlet temperature. The high heat transfer coefficients attainable with gas coolants tend to require high gas velocity, and hence high pumping power, and therefore, within limits, it proves to be more advantageous to secure good heat transfer performance by means of a large temperature difference between fuel and coolant. Good steam system performance on the other hand is promoted by a high gas outlet temperature, which not only permits improvement in the thermal efficiency of the power recovery cycle, but also may lead to substantially smaller, and, hence, less costly, power recovery equipment. This improvement results from a high temperature difference in the steam generator, from reduced mass flow of the coolant and the consequent reduction in pressure drop, from higher steam temperature and pressure with lower flow rate, or from some combination of these effects. Offsetting these advantages, in part, is the possibility that higher temperatures will require the use of more costly materials, both in the steam system and in the gas piping.

To ascertain what combination of the numerous variables of the entire system will produce the lowest cost power and to determine how sensitive the power cost is to such variables as the gas outlet temperature, would be a difficult and tedious task that would require the evaluation of many individual cases. The problem is seriously complicated by the fact that most of the variables commonly used to describe the reactor and power recovery system are not independent, and therefore the results that are obtained and the conclusions that are drawn from a parametric survey depend critically on the assumptions made and on which variables are held constant.

Several studies have been made from which one may attempt to determine the effect of gas outlet temperature on power cost. One of these is the survey made at Hanford,[23] in which the system is characterized by the gas outlet temperature, the reactor temperature differential, the total thermal power, and the fuel tube specific power in kilowatts per foot of fuel element. In this study, the cooling channel diameter was held fixed at one-half the

[23] *A Parametric Study of the Gas-Cooled Reactor Concept*, HW-54727 (Rev) (March 1, 1958).

equivalent lattice cell diameter for all cases studied, and the number and size of fuel rods per fuel element cluster was determined by the allowable wall temperature and the specified moderator-to-uranium ratio. The fuel surface temperature was fixed at 1500°F. Subject to these restrictions, it was concluded that the power costs are not very sensitive to gas outlet temperature in the range of 1000 to 1200°F, when other variables are optimized, and, indeed for some cases, the net power cost appeared to be lower with a 1000°F outlet temperature than with a 1200°F outlet temperature.

A parametric survey of reactor performance has been initiated at ORNL, with the significant independent variables being gas pressure, inlet and outlet gas temperature, fuel surface temperature, number of fuel rods per cluster, and the gas-channel physical diameter. Among the preliminary results obtained thus far are the contribution of the reactor and gas system cost to the net power cost as a function of gas outlet temperature for various values of the other variables. Some of the results are presented in Table 3 (next section), which presents a comparison of performance at 1000 and 900°F gas outlet temperatures, for a 1200°F maximum fuel element surface temperature. Over a range of nearly a factor of 2 in heat output per channel, it may be seen that the lower gas temperature results in slightly better reactor performance. The effect is more pronounced as more heat is extracted per channel and is slightly greater for CO_2 than for helium.

On the other hand, a study of the effect of gas outlet temperature on steam system performance made in connection with the GCR-2 study[24] indicated a cost incentive of about 0.25 mill/kwhr per 100°F to increase the gas temperature. Thus, the opposite effects of gas temperature on reactor and steam system performance will tend to produce a broad minimum in power cost with respect to gas temperature. The location of this minimum will certainly depend on other design variables and has not been determined exactly in the case of the GCR-2. It would appear, however, that the power cost is not very sensitive to gas temperatures within 100°F of the optimum.

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[24] *The ORNL Gas-Cooled Reactor*, Part 3, p 9.24, Fig. 9.4, ORNL-2500 (April 1, 1958).

INFLUENCE OF COOLANT CHOICE ON REACTOR PERFORMANCE

BASIS FOR COMPARISON OF COOLANTS

One of the criteria of suitability of a given fluid as a nuclear reactor coolant is its ability to provide high rates of heat transfer from the fuel to the coolant stream and high rates of transport of heat from the reactor to the thermodynamic cycle. A distinction must be made between these two processes since they are functions of different properties of the gas. The former is dependent on the conductivity and the Reynolds and Prandtl numbers; the latter is a function of the molar heat capacity. Carbon dioxide, for instance, has excellent heat transport properties, but is relatively poor from a standpoint of heat transfer, while helium is just the reverse. The amount of pumping power required to remove a given quantity of heat from a reactor under given conditions of system pressure and temperature is therefore an index of its quality as a coolant.

The expression $m\mathrm{Pr}^{2/3}/(mC_p)^3$, where m is the molecular weight of the gas, Pr is the Prandtl number, and mC_p is the molar heat capacity, has often been presented as an index of heat transfer efficiency of gases.[25,26] The derivation of this expression involves, however, the assumption that the effective diameter of the heat transfer channel is an independent variable. This cannot be the case for a given fuel element configuration if the heat flux and the temperatures of the fuel element surface and the coolant stream are fixed. It has been shown[27] that under the above constraints the channel equivalent diameter has a strong influence on the pumping power required.

The best basis for comparison of different coolants is the unit net power cost of the system optimized separately for the two gases, with care being taken that no parameter be allowed to vary except as required by specific coolant properties. For instance, a comparison made by allowing a higher fuel element surface temperature in one case than in the other would not be equable. The present cost estimates are based on those portions of the plant which are chargeable directly to the primary coolant circuit, that is, the pressure vessel, graphite, ducting, blower, and blower power. Costs of fuel, steam generators, and turbine-generator machinery are not closely related to the properties of the coolant and are excluded. When the range of independent parameters has been sufficiently narrowed on this simplified basis, the more important cases can be examined on the basis of total unit power cost. Table 3 gives the partial power

[25] Sanderson and Porter, Rpt. No. DC-29.224, Sec. 1959-1.2 (July 15, 1955).

[26] J. Diamond and W. B. Hall, *Journal of the British Nuclear Energy Conference* 1, 227 (1956).

[27] G. Samuels, *Comparison of Gases for Use as the Coolant in a Gas-Cooled Reactor*, ORNL CF-58-4-108 (April 28, 1958).

Table 3. Some Comparisons of Partial Power Costs for Helium- and CO_2-Cooled Power Reactors

Coolant Outlet Temperature (°F)	Fuel Element Surface Temperature (°F)	Power Per Channel (Mw)	Equivalent Diameter (in.)		Pumping Power (percentage of total electrical power output)		Cost* (mills/kwhr)	
			He	CO_2	He	CO_2	He	CO_2
1000	1300	0.80	3.74	3.35	2.40	3.72	1.04	1.07
		0.97	3.69	3.30	3.75	5.93	0.935	1.01
		1.40	3.60	3.23	8.69	14.00	1.09	1.68
1000	1200	0.82	3.41	3.10	4.17	6.94	1.10	1.20
		1.00	3.38	3.05	6.65	11.10	1.07	1.37
		1.44	3.30	3.00	15.64	26.50	2.05	4.69
900	1200	0.82	3.85	3.42	3.72	5.76	1.09	1.15
		1.00	3.80	3.38	5.78	9.09	1.04	1.21
		1.44	3.71	3.31	13.4	19.5	1.52	3.15

*Costs are calculated on the basis of 700 channels 20 ft long with seven 0.8-in.-dia fuel rods. Coolant gas pressure taken as 485 psi and inlet temperature as 450°F. Cost includes reactor and gas system.

cost, as described above, together with the channel equivalent diameter and the percentage of the gross electric power used for pumping carbon-dioxide or helium for three combinations of coolant outlet and fuel element surface temperatures. The cost information is plotted vs power per channel in Fig. 2.

It may be seen that, for any given set of heat flux and temperature conditions over the ranges covered, the use of helium results in consistently lower power costs than does the use of carbon dioxide. The difference is small at heat rates of about 0.8 Mw (th) per channel, but the costs diverge rapidly at higher rates. The GCR-2 system, for example, at the design output of 700 Mw (th), if operated at a helium gas pressure of 485 psia, would have an average heat rate of 0.7 Mw (th) per

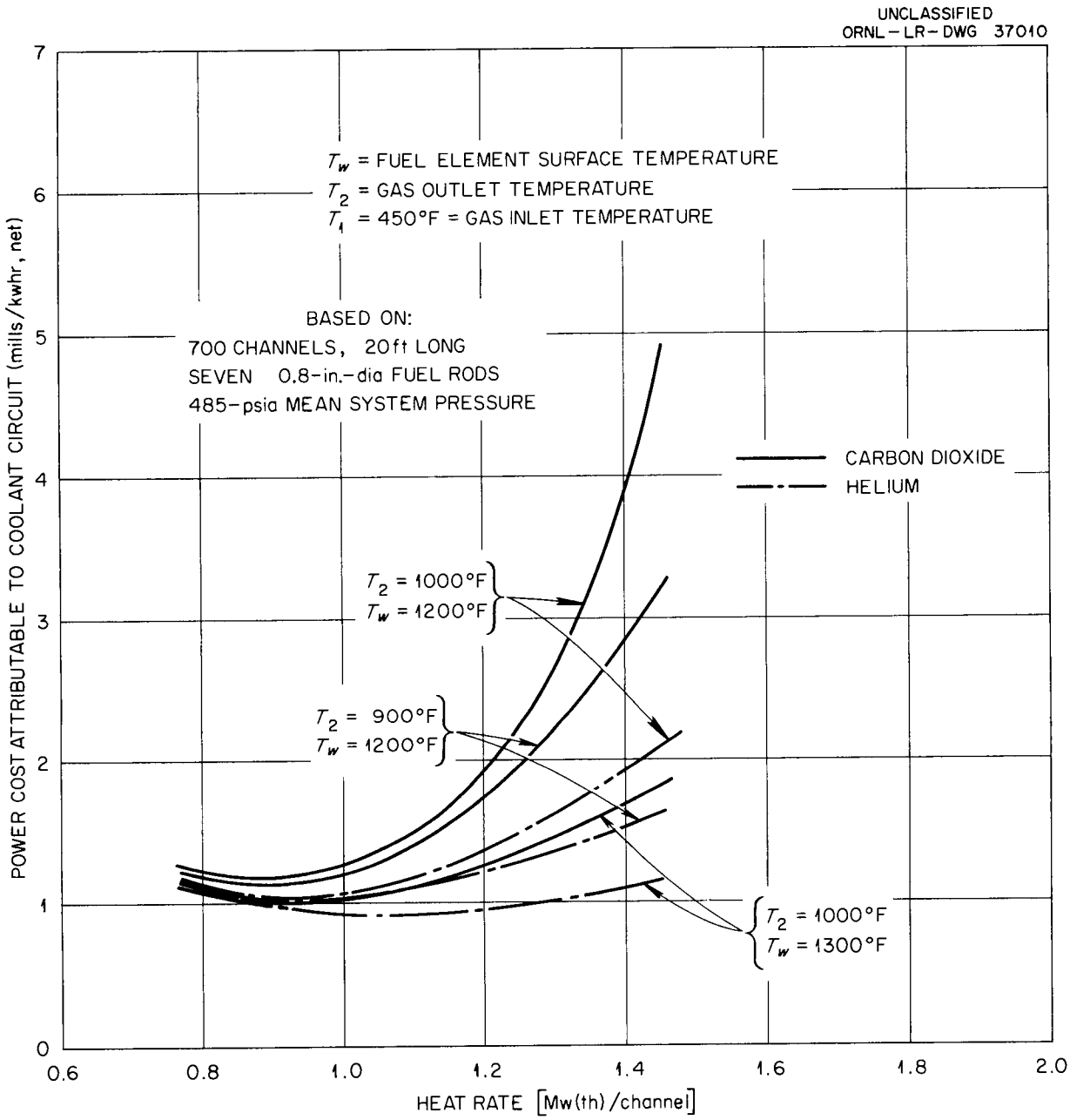

Fig. 2. Power Cost Attributable to Coolant Circuit.

channel. The GCR-2 study showed, however, that reduced power costs would result if the output were increased to approximately 1100 Mw (th), which corresponds to 1.1 Mw (th) per channel. At this point, the partial power cost of a carbon dioxide system would be approximately 40% higher than that of a helium system.

Aside from the question of chemical compatibility of carbon dioxide and graphite, it appears that the advantage of using helium is not great below heat rates corresponding to approximately 0.7 Mw (th) per channel. Current interest, however, is in high heat rates. There is some interest in reactors having low heat rates per channel for prototype or pilot plant experiments.

INTERCHANGEABILITY OF COOLANTS

The physical properties of the most attractive coolants (hydrogen, helium, water vapor, or carbon dioxide) are such that they do not permit interchangeability in a given reactor system at the same heat flux and temperature conditions. Hydrogen and helium are close to being interchangeable, as are carbon dioxide and water vapor, but interchanging the light and heavy gases would necessitate major changes in the operating conditions or the system components.

The volumetric capacity of the coolant circulating blower is directly related to the volumetric heat capacity of the coolant, and the blower head is affected by those properties of the coolant which influence the heat transfer coefficients. Interchanges between the light and heavy gases therefore call for changes in head and flow which cannot be accomplished in a turbodynamic blower by speed change alone. It would be necessary to change the blower design and replace the drive motors with units of different rating if helium and carbon dioxide, for instance, were interchanged.

COMPATIBILITY OF FUEL CLADDING MATERIALS WITH CARBON DIOXIDE

The compatibility of a cladding material with a coolant gas must be evaluated from two standpoints: (1) the maximum temperature at which long-time operation will be feasible, and (2) the hazards associated with a short-time excursion to much higher temperatures than the operating temperature. An ideal system from the compatibility standpoint is one in which the temperature limits are set by considerations other than the reaction between the cladding material and the coolant and in which no hazards exist. This section is a discussion of the degree to which these conditions are met with magnesium alloys, beryllium, and the austenitic stainless steels in contact with CO_2 in a reactor environment. The compatibility with CO_2 of the impervious or coated graphite materials that might be used as fuel cladding is the same as that for the previously discussed sleeve material, and therefore no further discussion of these materials is required.

The discussion which follows is based almost entirely on out-of-pile oxidation information. There is an unfortunate lack of information on the effects of radiation on the oxidation characteristics of metals, but the general experience has been that radiation does not produce major increases in oxidation rates. Thus the effects of radiation are assumed to be negligible.

MAGNESIUM ALLOYS

The following conclusions may be derived from the existing information on the reaction between Mg and CO_2 in a reactor environment:[28,29]

1. Magnox C (1% Al, 0.05% Be, balance Mg) is the most promising magnesium alloy for use as a cladding material. In bulk forms it is compatible with CO_2 to temperatures above its melting point of 645°C.

2. A possible hazard exists with Magnox C in a CO_2-cooled reactor, if the temperature of the cladding exceeds the melting point.

3. The low strength of magnesium alloys at elevated temperatures limits their usefulness as cladding materials.

[28] H. Inouye, *The Reactions of Magnesium and Magnesium Alloys with Gases at High Temperatures*, ORNL CF-58-1-93 (Jan. 20, 1958).

[29] J. L. Scott, *An Analysis of the Mg-CO Reaction in Terms of a Reactor Environment*, ORNL CF-58-5-100 (May 15, 1958).

BERYLLIUM

Huddle[30] has reported that the oxidation resistance of beryllium is excellent below 750°C. This temperature is above the temperature at which swelling has been observed to occur (700°C),[31] so the compatibility of beryllium with CO_2 may be considered to be good. Swelling is caused by the helium produced by (n,α) reactions. Since beryllium does not ignite in air, there is no hazard associated with its use in contact with CO_2 in a gas-cooled reactor.

AUSTENITIC STAINLESS STEELS

The austenitic stainless steels are particularly noted for their oxidation resistance and high strength at elevated temperatures, so they come to the fore as fuel cladding materials for operating temperatures in the range 600 to 1100°C, despite their relatively high neutron-absorption cross sections. The improved properties of the austenitic stainless steels relative to ordinary steels are derived from beneficial additions of nickel and chromium. Two basic types of stainless steels are in common use: the 18% Cr–8% Ni types and the more expensive 25% Cr–20% Ni types. In air the limiting temperature for 18% Cr–8% Ni steels is about 870°C and for the 25% Cr–20% Ni steels it is about 1150°C.[32] In addition, the oxide film, which is responsible for the excellent oxidation resistance, does not spall when the material is thermally cycled.

The behavior of the austenitic stainless steels in a reactor cooled with CO_2 is difficult to predict. Pure CO_2 is oxidizing to steels and stainless steels at all temperatures,[33] and the rate of scaling

[30] R. A. U. Huddle, "Oxidation Behaviour of Reactor Metals," p 79 in *Problems in Nuclear Engineering* 1, D. J. Hughes, S. McLain, and C. Williams (eds.), Pergamon, New York, 1957.

[31] H. M. Finniston, private communication to J. L. Scott, Nov. 1, 1957.

[32] W. O. Binder, "Heat-Resistant Alloys," p 644 in *Corrosion Handbook*, H. H. Uhlig (ed.), Wiley, New York, 1948.

[33] J. B. Austin and M. J. Day, "Chemical Equilibrium as a Guide in the Control of Furnace Atmospheres – A Review of Equilibrium Data," p 20 in *Controlled Atmospheres*, American Society for Metals, 1942.

attack in CO_2 is less than in air;[34] however, the reaction between CO_2 and the graphite moderator will produce some CO, as discussed previously. The resulting atmosphere could be oxidizing or reducing, depending on the CO_2-to-CO ratio, the temperature, and the composition of the stainless steel. Since the temperature would be expected to fluctuate widely during the course of operation of a reactor and the fuel elements may be periodically moved to increase the fuel burnup, the stainless steel might be exposed to cyclic oxidizing and reducing conditions.

Such conditions could result in a variety of harmful effects to the austenitic stainless steel. If the CO content were sufficiently high in a localized region of the reactor, the stainless steel might be heavily carburized. Although carburization increases the creep strength of stainless steel, it also results in embrittlement. Further, since chromium carbide is more stable than iron carbide, the chromium reacts preferentially with carbon when carburization occurs. In this way the amount of chromium in solid solution is reduced. Since 12% Cr in solid solution is required for good oxidation resistance, a heavily carburized stainless steel exposed to an oxidizing atmosphere would be expected to be rapidly attacked.

Another harmful effect could result from the reducing action of mixtures of CO and CO_2. Since the protective oxide film on stainless steels contains some Fe_2O_3, as well as the stable spinel $FeO{\cdot}Cr_2O_3$, the reduction of Fe_2O_3 by CO could loosen the protective film and result in selective internal oxidation of chromium in the alloy. Such attack, which would seriously impair the mechanical properties, would be similar to the phenomenon called "green rot," which has been observed in nickel-chromium alloys exposed to a CO atmosphere.[35]

A third type of attack which can occur when stainless steels are exposed to alternating oxidizing and reducing conditions is the so-called "metal dusting." Metal dusting is the mechanical removal of particles of metal or oxide from the surface because of the formation of solid carbon beneath the particles in regions where the decomposition of carbon monoxide is possible (400 to 700°C). The process has been observed to result in the rapid deterioration of metal rails leading into annealing furnaces in regions where the opening and closing of doors leads to cycles of oxidizing and reducing conditions. The mechanism for this type of attack is similar to that described by Baukloh for the rapid attack of cast iron in CO.[36] In the present case, a film would be formed during the oxidizing cycle which would contain both $FeO{\cdot}Cr_2O_3$ and F_2O_3.[37] On the reducing cycle the Fe_2O_3 would be reduced to metallic iron. The $FeO{\cdot}Cr_2O_3$ is sufficiently stable that it would not be reduced even in pure CO. If the mixture of CO and CO_2 happened to be sufficiently reducing, some of the CO might be reduced to solid carbon at the metal surface in such a way that the resulting stresses would mechanically fracture the remaining oxide film. A second oxidation cycle would result in the formation of a new film with the consumption of more metal. A sequence of such cycles could lead to the destruction of the fuel capsule wall.

A consideration of the above effects indicates that, from the metallurgical standpoint, the CO concentration in a CO_2-cooled reactor should be limited to the order of 1%. The difficulties associated with limiting the CO are connected with the development of a completely impervious coating on the graphite, as previously discussed. If the atmosphere consists only of CO_2, the life of stainless steel in the reactor environment should exceed its life in air. Thus, type 304 stainless steel would be expected to perform satisfactorily up to 870°C; no hazard exists up to the melting point of the alloy (1400°C).

If an alloy with higher strength than that of type 304 stainless steel at elevated temperatures is required, type 310 stainless steel (25% Cr, 20% Ni) is recommended, since its oxidation resistance is superior to that of type 304 stainless steel. Type 316 stainless steel (18% Cr, 8% Ni, 2% Mo) is not

[34] J. B. Austin and R. W. Gurry, "Iron and Steel," p 636 in *Corrosion Handbook*, H. H. Uhlig (ed.), Wiley, New York, 1948.

[35] H. R. Copson and F. S. Lang, *Some Experiments on Internal Green Rot Oxidation of Nickel-Chromium Alloys*, The International Nickel Company, Inc., Research Laboratory, TP: No. 277.

[36] W. Baukloh, "Concerning the Destructive Effects of CO and Gases Containing CO," *Chem. Fabrik* 13, 101 (March 1940).

[37] H. M. McCullough, M. G. Fontana, F. H. Beck, "Formation of Oxides on Some Stainless Steels at High Temperatures," *Trans. Am. Soc. Metals* 43, 404 (1951).

recommended for use in CO_2, because of the possible accelerated oxidation due to the highly corrosive MoO_3 which might be formed. This type of corrosion, which has been observed in all steels containing molybdenum, is most likely to occur in those regions of the reactor where the localized gas flow rate is low.[38] For the same reason, alloys containing vanadium as a strengthener are to be avoided.

If type 310 stainless steel were selected as the cladding material, extensive studies would have to be carried out to determine the susceptibility of the material to sigma-phase embrittlement under conditions of the reactor operation.

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[38] A. deS. Brasunas and N. J. Grant, "Accelerated Oxidation of Metals at High Temperatures," *Trans. Am. Soc. Metals* 44, 1117 (1952).

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