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GAS COOLED POWER REACTOR COOLANT CHOICE

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GAS COOLED POWER REACTOR COOLANT CHOICE

The selection of a gas coolant has been the subject of considerable attention during recent U.S. studies of the gas cooled reactor concept.^(1,2,3) The most likely coolant prospects are helium and carbon dioxide, each with its peculiar advantages and disadvantages. Prominently listed among helium's disadvantages is the difficulty with which it is contained in a complex system, especially at high temperature and pressure. Similarly, any discussion of the pros and cons of carbon dioxide includes as a disadvantage the fact that graphite temperatures must be limited in the presence of carbon dioxide and nuclear radiation.

Considerable importance is ascribed to these disadvantages of the respective gases, largely owing to the lack of directly applicable data. Although the technology of both gases is quite well developed for specific applications, the region of interest to the Gas Cooled Power Reactor Program has not been completely explored. Applicable data that might be useful in choosing between helium and carbon dioxide are presented in this report along with some interpretation. Such interpretation is, of course, subject to error, and the reader is cautioned to note the limitations that are placed on the conclusions.

SUMMARY

The current status of helium and carbon dioxide technology is described in the light of the Gas Cooled Power Reactor Program requirements. The problem of containing high pressure helium at high temperature is discussed and it is concluded that, by proper attention to the design, construction and maintenance of a plant, a high degree of helium leak-tightness can be achieved at small additional cost when compared to a carbon dioxide system. What is more, the cost of making up helium losses in a practically achievable system is estimated to be small compared to other fixed and operating costs.

Graphite-carbon dioxide reaction data are reviewed. It is shown that carbon dioxide at atmospheric pressure and low flow rates should be compatible with a graphite moderator up to 525 C (975 F). No data are available at the high pressures and flow rates that would be encountered in power reactors. Significantly higher oxidation rates may result, however, perhaps limiting bulk moderator temperatures to 450-500 C (842-932 F). Improved carbon materials, protective coatings and inhibitors, and/or operating practices may be developed that will allow significant future increases in these limiting temperatures.

PART I. THE USE OF HELIUM AS REACTOR COOLANT

One basis for comparing helium and carbon dioxide, when used as the primary coolant in a gas-cooled reactor, is on relative leakage rates. This is a natural comparison which arises because: (1) Helium is known as a "leaky gas" and (2) The British have experienced high leakage rates from their carbon dioxide cooled reactor. Leakage is undesirable because of the cost of make-up gas, the release of radioactive gases into reactor operating areas, and the

release of any gas (CO_2 or He) into operating areas in sufficient quantity to deplete the oxygen concentration. It is understood that this latter type of leakage has been found to be more serious in the British reactors than the contaminated leakage.

If the various methods of leaking are examined, we can see that helium leakage is comparable with other gases including CO_2 . Three methods of leakage can be considered: (1) Orifice flow, through large passages short in relative length, (2) Viscous flow, through small passages long in relative length and (3) Molecular flow, through passages whose width approaches the mean free path of the gas molecules.

With an orifice type flow it can be shown at the pressures and temperatures under consideration, that the volume of helium leakage will be one and one-half to three times that of CO_2 for a given opening. On a weight comparison basis four to six times as much CO_2 as He would be lost under similar conditions. For viscous flow, where the volume leakage is inversely proportional to the viscosity, helium leakage will be 12 to 28 per cent more than CO_2 . Again the weight loss of CO_2 will be greater than helium by a factor of eight to ten.

In molecular flow the volume leakage is proportional to the reciprocal of the square root of the gas density. This gives a helium volume leakage of three and one-third times that of CO_2 . The corresponding weight loss of CO_2 to helium is $3-1/3 : 1$. Thus it can be seen that helium leakage and CO_2 leakage are in the same range. The cost of make-up gas, with helium at five times the cost of CO_2 , would have to be evaluated based on plant leakage. For small volume leakages this make-up cost would be negligible, when compared to other fixed and operating costs.

Experience with large CO_2 and helium systems at Hanford and Oak Ridge has shown that both high and low pressure gas systems can be constructed and operated on a relatively leak-tight basis if proper precautions are taken. Similar experience has been noted at the Bureau of Mines helium recovery plants. Further technology of large, high pressure, high temperature, gas systems is available from chemical industry which substantiates that such systems can be made relatively leak free.

To obtain leak-tight systems requires considerable effort to be devoted in design and construction towards achieving this goal, with particular care devoted to the prevention or elimination of all possible leak points. Furthermore, provisions must be made for detecting leaks if they do occur. Construction of such a system calls for constant quality control and high standards of workmanship. Operation of the system, including maintenance, calls for a continuation of these high standards.

These high standards of design, construction, and operation, while they may not be common industrial practice, are normal for atomic energy installations, specialized chemical industries and central station practice. It has been estimated that these standards increase construction costs for piping systems 10 to 15 per cent over normal costs. This increase is not at all excessive when compared with the increases that are already paid by atomic energy installations to attain better than normal quality and cleanliness.

A gas-cooled reactor operating at the temperatures and pressures under consideration is a very specialized plant. Making the system relatively leak-tight is

possible if this goal is set when design starts and is carried through operation and maintenance of the plant. The premium paid for the elimination of leaks is not excessive considering other costs of the plant.

Further discussion of these considerations may be found in HW-54727, HW-54727 ADD, and General Motors Corporation Study Report for Contract MA 1252, and the Ford Instrument Company Study Report for Contract AT (30-3)-250 (FI Co. No. 102). Other important factors that must be considered in choosing between helium and carbon dioxide are their relative availability and reliability of supply, and the influence of these factors on the attitude of the foreign market. These items are considered outside the scope of this report and are therefore not discussed.

In summary, it is our opinion that the problem of helium leakage in a gas-cooled reactor would not be significantly greater than that which would be encountered with the use of carbon dioxide as the reactor coolant. Special equipment, seals, turbomachinery, etc. are not available or significantly more fully developed for use with carbon dioxide than they are for use with helium as the same basic problems are present with either gas. In fact more attention has probably been given to the development of leak free helium systems in certain specialized applications and industries than to the development of similar carbon dioxide systems due to the greater economic incentive to prevent helium leakage. It is our belief that a satisfactory leak free system for helium service can be built if sufficient attention is given to the design, procurement, and construction of the system. The leak free system may be attained at a relatively small additional cost when compared to other piping systems.

PART II. THE USE OF CARBON DIOXIDE AS REACTOR COOLANT

The rate of oxidation of graphite by carbon dioxide depends upon a number of variables which include the graphite temperature, radiation intensity, gas composition and flow rate, pressure, and any physical properties of the graphite which affect the extent of its surface area available for reaction. It is the object of this part of the report to review the factors affecting the rate of reaction of carbon dioxide with graphite and to discuss their application to the CO₂-cooled partially enriched reactor proposed in a recent feasibility study by Kaiser Engineers and ACF Industries.(2)

A. The Effect of Temperature on Graphite Oxidation

1. Radiation Absent

A survey of the technical literature disclosed no comprehensive studies of the reaction rate between graphite and carbon dioxide in the absence of radiation in the temperature range pertinent to the proposed gas cooled reactor (240-600 C, 464-1112 F). Over this range of temperatures, the

thermally induced reaction is slow enough to be of no concern in graphite moderated reactors. Recent British tests⁽⁵⁾ with graphite lamp filaments in pure CO₂ showed no failures occurred below 600 C and no evidence of carbon loss was found after 400 days. It was postulated that the reaction below 700 C takes place in two steps: (1) oxidation of the carbon surface and formation of a surface oxide; (2) decomposition of the surface oxide to carbon monoxide. A small amount of Hanford data shows that the rate of weight loss due to oxidation at 650 C - 700 C is appreciable, on the order of 10 to 25 per cent per 1000 days.

Precise Hanford laboratory studies were conducted at higher temperatures (850-1025 C, 1562-1877 F). It was found that rates calculated as per cent weight loss/day follow the Arrhenius equation, that is, they increase exponentially with temperature. At 975 C (1778 F) unirradiated graphite oxidized at the rate of 2.6 per cent per day while irradiated samples lost 11 per cent per day. The temperature dependence of the rate also differed slightly as indicated by an activation energy of 61.5 kcal/mole for unirradiated samples compared with a value of 51.5 kcal/mole for irradiated samples.

2. Radiation Present

Reactor radiation induces chemical reactions at temperatures much lower than are normally required in the absence of radiation. The irradiation of pure carbon dioxide in the absence of graphite at 40 C results in the rapid attainment of an equilibrium state in which about one per cent of the carbon dioxide is decomposed to carbon monoxide and oxygen.⁽⁶⁾ The low temperature (30 C) exposure of graphite to Hanford fluxes in capsules containing carbon dioxide results in the formation of carbon monoxide. A portion of the resultant carbon monoxide eventually decomposes to form carbon dioxide and a solid polymer of one or more of the carbon suboxides.

In another experiment at Hanford flux⁽⁷⁾ a blue solid deposited on graphite samples exposed to carbon dioxide in the cooler downstream region of an in-reactor facility. Upon heating the solid to 230 C in the laboratory, a thin trail of white smoke was observed. The weight lost after heating at 350 C for three hours was exactly equal to the weight gained during exposure in the reactor. Formation of solid polymer would not be expected in a high temperature gas cooled reactor.

The radiation induced oxidation rate is rather insensitive to temperature from 175-430 C as evidenced by the small activation energy of 1 to 3 kcal/mole.⁽⁸⁾ A value of 2.5 kcal/mole was obtained at Chalk River for the in-reactor reaction of graphite with air.⁽⁹⁾

Further investigations at Hanford of the CO₂-graphite reaction under irradiation at higher temperatures were conducted to determine the temperature at which the thermal reaction rate would become important. Graphite oxidation rates were measured in-reactor and ex-reactor at 500-670 C with carbon dioxide-helium gas mixtures containing 50-85 per cent carbon dioxide.⁽¹⁰⁾

It was found that the oxidation rate begins to increase exponentially with temperature at 600-650 C (1112-1202 F). Oxidation rates of approximately 2 per cent per thousand operating days at Hanford flux were measured for the temperature range of 525-575 C and for the temperature range 650-700 C the rate increased to about 15 per cent per thousand operating days. Gas flow over the 0.4 inch diameter samples was 25 ± 10 liters per minute (ca. 0.8 ft/sec) and gas pressure was maintained slightly above atmospheric. The oxidation rate of samples in the reactor was compared directly with the rate out of the reactor under similar conditions. The data indicate that radiation induced chemical reactions play a small role in graphite oxidation at 650-700 C. The effect of radiation on possible mass transfer of carbon and stability of graphite coatings was not investigated.

Graphite irradiated inside a hollow uranium cylinder in the BEPO reactor where the energy absorption per neutron per square centimeter was increased by a factor of three or more indicated that this variable has little significant effect on the rate of reaction.⁽¹¹⁾ Experiments at different reactor power levels from 2 MW to 6 MW indicated that the rate of carbon monoxide production was a linear function of radiation intensity. The temperature in these experiments was only 350 C and the CO₂ pressure was less than one atmosphere.

In the British model channel experiment, carbon dioxide was circulated at a pressure of 7 atmospheres over graphite in a thermal flux of about 10^{12} nv.⁽¹²⁾ Inlet and outlet gas temperatures were 140 C and 336 C respectively. The mean loss from the whole in-pile channel was about 0.02 per cent per year with a maximum loss of 0.15 per cent for a few circumferential samples.

B. EFFECT OF GAS COMPOSITION ON GRAPHITE OXIDATION

The effect of carbon monoxide addition on the rate of oxidation of graphite by carbon dioxide has been determined in the absence of radiation from 850 to 1025 C.⁽¹³⁾ The added carbon monoxide is most effective in reducing the rate at the lower temperatures. At 850 C the rate was 0.3 gm/gm-year in 100 per cent CO₂ vs. 0.062 gm/gm-year in 3 per cent CO - 97 per cent CO₂. Presumably CO is produced rapidly at the higher temperatures and a small additional amount results in little change in the rate.

The effect of carbon monoxide addition on the CO₂-graphite reaction in the presence of radiation has been determined by exposing graphite samples in a reactor to carbon dioxide containing 5, 15, and 25 per cent carbon monoxide by volume.⁽¹⁴⁾ The results have shown that, while the burnout rate was reduced from 3 per cent per thousand operating days to 0.5 per cent/thousand operating days in the region of highest temperature (400 C) and neutron flux, the use of a gas mixture containing 95 per cent carbon dioxide plus 5 per cent carbon monoxide simply displaced the maximum burnout rate upstream from the region of highest temperature and neutron flux without significantly affecting its magnitude. The use of gas mixtures containing 15 per cent and 25 per cent carbon monoxide results in the deposition of carbon suboxide polymers and/or carbon in the cooler fringe regions where the temperature was estimated to be less than 150 C.

The addition of helium to the carbon dioxide before passing it over the graphite samples results in a decreased rate of reaction at all helium concentrations⁽¹⁵⁾,

thereby showing that the reaction rate is dependent on the partial pressure of carbon dioxide in the influent gas as would be expected.

When static systems of graphite and liquid water are exposed to reactor radiation at 40 C, the reaction results in the formation of carbon dioxide and hydrogen. The preliminary steps are probably the decomposition of the water into hydrogen and oxygen followed by the reaction of oxygen with the graphite to form carbon dioxide.⁽⁶⁾ The presence of 0.9 per cent water vapor in a BEPO CO₂-graphite flow system has been reported to have no significant effect on the rate of graphite oxidation at 350 C by CO₂.⁽¹¹⁾

C. EFFECT OF SAMPLE GEOMETRY ON GRAPHITE OXIDATION

Upon comparison of in-reactor oxidation rates obtained by the concurrent exposure of cylindrical samples with different radii, it has been found that 0.40 inch diameter samples are oxidized at a rate from about two to almost ten times faster than the rate for samples with a diameter of 1.125 inches.⁽¹⁶⁾ This difference in rates is probably a direct consequence of a difference in specific surface areas, i.e. surface areas per unit weight. In the case of larger samples, a greater portion of the internal surface area is not readily available for reaction and only slowly becomes available as a result of the removal of pore blockages and poorly crystallized material by oxidation. The average in-reactor rate of oxidation of 4" x 4" x 12" graphite bars was 0.26 per cent per thousand operating days at a temperature of 500-540 C compared to 2 per cent per thousand operating days for 0.42 inch samples oxidized under similar temperature conditions.⁽¹⁰⁾

D. APPLICATION OF GRAPHITE-CO₂ TECHNOLOGY TO THE KAISER-ACF 44 MW PROTOTYPE PARTIALLY ENRICHED REACTOR

The feasibility study of the Kaiser-ACF reactor requires that replaceable graphite sleeves be employed to support the fuel assemblies and to assure that the bulk moderator is not exposed to the high temperature CO₂ (240 C inlet and 540 C outlet). It is proposed that the sleeves be protected with a thin silicon carbide coating. The mass velocity of the coolant in a central channel would be 5.6×10^5 lb/hr-ft² at about 400 psia.

At present there is no experience on the behavior of graphite under these conditions. Hanford experience has been limited to low flow, low pressure conditions, although the temperatures have been in the range of interest to the present discussion. In attempting to estimate a maximum graphite moderator temperature the question arises: "What is the maximum amount of oxidation that can be tolerated?" The strength of the moderator will decrease as oxidation proceeds.⁽¹⁷⁾ If it is assumed that a loss of 50 per cent in mechanical strength can be tolerated over a period of 20 years then the rate should not exceed 1.5 per cent per thousand days. If these assumptions are made, the use of 100 per cent CO₂ at atmospheric pressure and low flow rate would limit graphite temperatures to a maximum of about 525 C. The high flow rate and pressure in a CO₂ cooled reactor would be expected to increase the reaction rate somewhat. Based upon present technology it appears that the bulk moderator of the Kaiser-ACF reactor should be limited to 450-500 C (842-932 F). A development program may show that improved carbon materials can be made or

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inhibitors, such as phosphates, can be added in trace amounts which will reduce the oxidation rate and allow a significant increase in the maximum graphite temperature. To our knowledge no detailed design of the Kaiser-ACF reactor is yet available which would allow the estimation of the bulk moderator temperature. It is our suggestion that the design be completed in enough detail at an early date to allow a reliable estimate of the moderator temperature.

The oxidation rate of the graphite sleeves can likely be reduced by a silicon carbide coating, and it is not unreasonable to hope that an expendable graphite sleeve might be operated at 538 C (1000 F). Additional studies will be required before the magnitude of the rate reduction under prototypical conditions can be estimated. The radiation stability of the protective coating also needs to be demonstrated.

There is likely to be some mass transfer of carbon in a CO₂-graphite recirculating system. Experiments described in this report and elsewhere have demonstrated that this occurs. However, this has never caused an operational problem in the Hanford or Calder reactors. If the CO concentration is kept low and temperatures in the coolant system are above about 230 C (446 F), it is unlikely that carbon suboxide will deposit. These postulations should be confirmed, however, in a prototypical gas loop.

The prototype design provides for graphite growth. However, at about 300 C graphite begins to contract from radiation damage. This will occur whether the coolant is CO₂ or some other gas. The contraction rate is low compared to the expansion rate at 30 C and will depend on the temperature, type of graphite and neutron exposure. Stored energy accumulation will likely be low except in the fringe regions. Reliable estimates of the moderator temperature will indicate whether a stored energy problem exists.

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