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CHEMICAL PROBLEMS IN ADVANCED GAS-COOLED REACTORS*

Advanced gas-cooled reactors, in general, aim for relatively high temperature operation. Accordingly, chemical problems largely involve gas and solid phase chemistry where chemical reactions and physicochemical processes occur at elevated temperatures (to order of 2500°K or 4000°F). The high temperatures require that the fuel bodies and moderator be made of refractory materials such as oxides, carbides and graphite and may preclude the use of a metal cladding. For example, stainless steel, Inconel or Hastelloy cladding are limited to temperatures of the order of 1500 to 1800°F because of strength and chemical reactivity considerations.

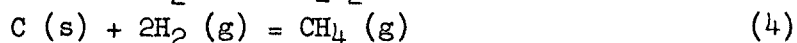
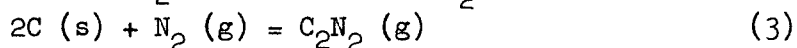
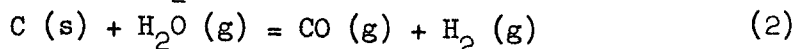
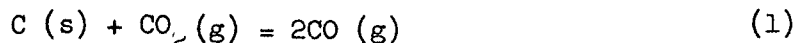
From the reactor components viewpoint, two important areas of concern are:

- A. Reactor materials, which include questions on the:
 1. Diffusion or vaporization of fissile, fertile and burnable poison materials from the fuel bodies.
 2. Phase transition temperatures and melting points which may fix the limit of the operating temperature.
 3. Diffusion of fission products from fuel bodies and their diffusion through ceramic or metal cladding materials.
 4. Chemical reactions of the coolant or impurities in the coolant which have a deleterious effect such as erosion or embrittlement on reactor materials.
- B. The reactor primary coolant system, which includes questions on the:
 1. Fission product release characteristics of the reactor fuel elements.
 2. Characteristic and behavior of devices such as fission product traps, for decontaminating the coolant or, more desirably, for preventing significant fission product activity from entering the main coolant stream.

* This is a summary of work being carried out under the HTGR Research and Development Program at General Atomic. The work is being done under Contract No. AT(04-3)-314 with the U. S. Atomic Energy Commission

3. Concentration level of oxidizing, carburizing, or nitriding impurities which must be maintained in the coolant and the means for purifying the coolant.
4. Nature and distribution of deposited radioactivities and methods and reagents for their removal.

Almost all of the problems of reactor materials and the primary coolant systems involved mass transfer. Reversible endothermic reactions such as those of simple vaporization will lead to transfer from hot to cold zones. Besides this, there are volatilization reactions wherein the coolant or coolant impurities may participate as reactants and lead to mass transfer. Thus the following can lead to carbon transfer in a gas-cooled graphite reactor:



The first three reactions will transfer carbon from hot to cold zones, while (4) will tend to do the reverse.

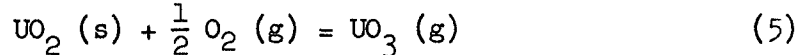
Reactions (1) and (2) are especially important in a helium-cooled, unclad-graphite reactor.¹ Thus, in the forward direction they can lead to graphite erosion or an increase of graphite permeability (to fission products), while in the reverse direction they can lead to carbon deposition in purge gas passageways and possible embrittlement by carburization of metal piping and baffles in the coolant system. The problem of the chemist, in this case, is to determine the rate(s) of the controlling reaction(s) for specific reactor materials of interest as a function of temperature and composition so as to fix the permissible impurity levels. Studies under way at General Atomic indicate that carbon may deposit as cementite (Fe_3C) in iron or steel at temperatures of interest ($\sim 1200^\circ\text{F}$) and at low partial pressures of CO and H_2 (2×10^{-3} atm or less) and lead to embrittlement. The question to be answered is at what concentrations, temperatures and periods of exposure is the strength of primary coolant loop materials significantly affected.

Substantial mass transfer can be expected from gas phase diffusion across a gap due to equilibrium concentration shifts when the gap boundaries are at different temperatures. Thus, due to the water gas reaction shift

with a 5 mil gap between graphite surfaces running at 1100°K (1520°F) and 1000°K (1340°F) a transfer of up to 480 mg/cm² of carbon is theoretically possible in 1000 days if H₂ and CO impurities are each present at 100 ppm in 300 psia helium coolant. This will drop to 4.8 mg/cm² for a 10 ppm impurity level.

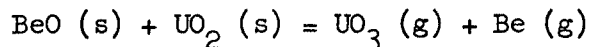
Reaction (3) will cause graphite erosion in a nitrogen-cooled, high-temperature graphite and could lead to serious mass transfer problems.² Reaction (4) makes it unwise to consider using hydrogen as a coolant in direct contact with graphite.

Coolant impurities can also lead to fuel migration. Thus in a reactor with unclad ceramic oxide fuel bodies (such as BeO-UO₂) oxygen at low partial pressures can lead to a serious fuel vaporization due to the reaction



at temperatures of order of 1300°K (1880°F).^{3,4}

Also in a BeO-UO₂ fuel body the reaction



will enhance BeO volatility (which vaporizes primarily as Be and O atoms) and lead to fuel (U) migration. For example, at 2500°K (4040°F) we have for BeO alone and BeO mixed with UO₂ the following partial pressures:

	<u>BeO</u>	<u>BeO + UO₂</u>
P _{Be}	1.4 x 10 ⁻⁵ (atm)	2.8 x 10 ⁻⁴ (atm)
P _{UO₃}	-	2.8 x 10 ⁻⁴
P _{UO₂}	-	7.8 x 10 ⁻⁵
P _O	1.4 x 10 ⁻⁵	7 x 10 ⁻⁷

The chemical constitution of the fuel body environment will be important in determining both fuel (Th, U and Pu) migration and fission product release. Fuel bodies for gas-cooled reactors must be highly refractory and usually comprise oxides or carbides and graphite (although nitride or sulphide systems are conceivable). Thus, the fuel environment is ordinarily dominated by either oxygen or carbon. In the case of fission product elements (of yields greater than 0.1) in UO₂, the expected molecular forms at higher temperatures (>1500°K or 2240°F) are as follows:

<u>Oxides</u>	<u>Metals</u>	<u>Elemental Gases</u>
Zr Sr	Mo	Kr Br
La Ba	Te	Xe I
Rare earths	Rh	Rb Se
Y	Pd	Cs Te

and at lower temperatures, I, Br, Te and Se will combine with (become anions of) Cs, Rb, Ba and Sr.⁵ On the other hand, when these fission products are formed in a carbide-graphite fuel material, they are expected to be in the following molecular forms at higher temperatures:

<u>Carbides</u>	<u>Metals</u>	<u>Elemental Gases</u>
Zr Ce	Tc	Sr Kr Br
Mo Pr	Ru	Ba Xe I
Y Nd	Rh	Sm Rb Se
La Pm	Pd	Eu Cs Te

Of the elements in the form of gases, Sr, Ba, Sm and Eu will condense most readily and tend at lower temperatures ($<1500^{\circ}\text{K}$) to react with any CO impurity present in the coolant to form oxides.

Accordingly, at high temperatures the more volatile fission product elements of groups V, VI, VII, O, I, II and III (including As, Se, Br, Kr, Rb, Sr, Cd, Sb, Te, I, Xe, Cs, Ba, Sm and Eu) will tend to escape from the refractory fuel bodies after some delay. The initial delaying process is one of diffusion of the fission fragment from oxide, carbide or graphite crystallites in which they are lodged upon completion of the fission recoil process.⁶ In the case of oxide fuel bodies (as of UO_2), SrO, BaO, SmO and EuO will form solid solutions and will tend to be held back much more than in the case of carbide-graphite fuel bodies.

In general, volatile fission product activities must be removed from the reactor coolant. This is best done if they are at relatively high partial pressures (order of 10^{-6} to 10^{-5} atmospheres) and preferably are kept out of the main stream. This is accomplished in the HTGR system⁷ by purging the fuel elements with helium and trapping fission products from the gas before it is returned to the primary circuit.

Activated charcoal appears to be a most useful reagent for solving the fission product trapping problem. Browning and coworkers⁸ at Oak Ridge

have shown room temperature and refrigerated charcoal beds to be effective in holding iodine and delaying or holding xenon and krypton fission products. Recent work at General Atomic has indicated activated charcoal will be a most effective trap for cesium (and presumably rubidium) at elevated temperatures (800-1000°K).⁹ Also previous studies of activated charcoal-iodine adsorption¹⁰ and current studies on CuI and AgI adsorption and the chromatographic column action of copper or silver metal impregnated charcoal beds at elevated temperatures indicate substantial holding or delaying action for metal impregnated activated charcoal fission product traps placed inside a gas-cooled reactor fuel element.

In regards to the minimization of high temperature vaporization processes, carbide-graphite systems appear to have a substantial edge over oxide systems. This is due to the fact that fuel material (Th or U) oxides are more volatile than these metals as carbide in the presence of carbon. Furthermore, oxide molecules of the actinide elements and some of the refractory fission products (such as UO, UO₂, UO₃, ThO, ThO₂, ZrO, ZrO₂, MoO, MoO₂, MoO₃, RuO₂) can participate in high temperature vaporization processes, particularly if excess oxygen is present.¹¹ On the other hand, the presence of carbon results in the formation of stable carbides and the lowering of the vapor pressures of these elements. Or, as in the case of ruthenium, where a stable carbide is not formed, the element is maintained in its refractory elemental form since carbon reacts preferentially with oxygen or volatile oxides to form CO. This is related to the rather great stability of CO (dissociation energy, D° = 256 kcal/mole). Vaporization process would appear to limit carbide-graphite reactor systems fuel to the order of 2400°K (3860°F) and oxide systems to temperatures of approximately 400°K (720°F) lower. Vapor pressures at 2000 and 2500°K pertinent to oxide and carbide-graphite fueled reactors are given in Table 1.

Table 1

Vapor Pressures of Advanced Gas-Cooled Reactor Fuel Materials*

<u>Species</u>	<u>2000°K (atm)</u>	<u>2500°K (atm)</u>
UO ₂ (g) over UO ₂ (s)	8 x 10 ⁻⁴	8 x 10 ⁻⁵
Be (g) + O (g) over BeO (s)	3 x 10 ⁻⁸	3 x 10 ⁻⁵
ThO ₂ (g) over ThO ₂ (s)	3 x 10 ⁻⁹	4 x 10 ⁻⁶
B (g) over "B ₄ C" + C	5 x 10 ⁻⁸	5 x 10 ⁻⁵
U (g) over UC ₂ + C	2 x 10 ⁻¹⁰	5 x 10 ⁻⁷
C ₁ (g) + C ₂ (g) + C ₃ (g) over graphite	6 x 10 ⁻¹¹	7 x 10 ⁻⁷
Th (g) over ThC ₂ + C	1.2 x 10 ⁻¹²	5 x 10 ⁻⁹

* Based on data of Brewer,¹² Sinke and Stull¹³ and Ackermann, Gilles and Thorn.¹⁴

These vapor pressures, in many cases, are based on rather meager experimental data and thus are only tentative values. Accordingly, further experimental work on vapor pressures and vaporization processes of various reactor material at high temperature is definitely required.

Other gas-cooled reactor chemical problems connected with questions on fission product behavior and control and the temperature limitations of carbide-graphite fuel elements include the following:

(1) The nature of fission product plate-out such as of I and Cs from a coolant stream and techniques for decontaminating surfaces supporting such deposits.

(2) Whether surface diffusion (on internal pores) is an important process in determining the migration of thorium and uranium in graphite at very high temperatures ($\geq 2300^{\circ}\text{K}$ or 3680°F) and in determining the permeation of graphite by cesium at moderately high temperatures ($900\text{-}1500^{\circ}\text{K}$ or $1160\text{-}2240^{\circ}\text{F}$).

(3) The melting temperatures of $\text{ThC}_2\text{-UC}_2$ phases containing fission products and in the presence of graphite (i.e., what are the eutectic temperatures and related phase data?) The limiting temperature in reactor operation imposed by melting of these phases appears to be of the order of $2600\text{-}2700^{\circ}\text{K}$ ($4220\text{-}4400^{\circ}\text{F}$), but needs further delineation.

It is to be noted that a number of active investigations on chemistry and materials problems of advanced gas-cooled reactors are being carried out in this country under the sponsorship of the USAEC and the Defense Department,¹⁵ and abroad including work on the OEEC sponsored High Temperature Reactor Project - Dragon.¹⁶ Accordingly, it is hoped that in a relatively short span of time many of the questions mentioned here will be answered to the satisfaction of engineers and designers of these reactors.

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