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ESTABLISHMENT
OF PRELIMINARY REQUIREMENTS
FOR FFTF COVER GAS PURITY
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ESTABLISHMENT OF PRELIMINARY REQUIREMENTS
FOR FFTF COVER GAS PURITY

H. P. Maffei

Engineering Department
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October 1969

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ESTABLISHMENT OF PRELIMINARY REQUIREMENTS
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H. P. Maffei

ABSTRACT

Preliminary FFTF cover gas impurity requirements for methane and carbon monoxide have been determined. The requirements are based on the reaction rates of the impurities with molten sodium for various coolant temperatures assuming that all of the carbon introduced into the system will eventually carburize the stainless steel fuel cladding. Kinetic reaction rates of methane and carbon monoxide with sodium at various temperatures have been determined and are presented. Recommendations have also been made for minimum oxygen concentration for the nitrogen cover gas blanket system.

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ESTABLISHMENT OF PRELIMINARY REQUIREMENTS FOR FFTF COVER GAS PURITY

H. P. Maffei

INTRODUCTION

A necessary feature of FFTF will be the provision of appropriate inert gas blankets for various reactor locations. The conceptual system design description No. 82 states that⁽¹⁾ "inert gases will be used in FFTF applications to provide atmospheres that will prevent undesirable chemical changes of sodium, fuels, or test materials." Two inert gases have been selected for FFTF.⁽¹⁾ Argon will be used as a cover gas for molten sodium systems, and nitrogen will be used as an inert atmosphere for equipment cells. These gases were selected on the basis of several criteria. Among these was one treating the control of material damaging impurities.

ARGON COVER GAS

The various impurities considered for argon cover gas are nitrogen, hydrogen, oxygen, water vapor, methane, carbon monoxide, and carbon dioxide. These impurities probably appear in the cover gas through air inleakage and by reduction of carbonaceous impurities. These impurities can damage reactor fuels and components as well as increase sodium frost buildup rates and sodium plugging temperature. Carbon bearing impurities will react with molten sodium to introduce carbon into the coolant and thereby increase the possibility of carburizing the austenitic stainless steel fuel cladding and structural components. Nitrogen in the cover gas could lead to nitriding of sodium covered stainless steel components. Oxygen and water vapor will react very rapidly with molten sodium to form sodium oxide and in the case of water vapor also sodium hydride. Sodium oxide and sodium hydride will increase plugging temperatures of the coolant. The presence of any of these impurities in the

cover gas could add to the sodium frost buildup rates in the gas plenum. These frost deposits may lead to damage of rotational or sliding reactor seals on closures.

Ultimately, cover gas impurity levels must be established for FFTF which will not overburden sodium and gas purification systems and become detrimental to reactor components, fuels, or sodium coolant. Tests have been performed to establish preliminary specifications for methane and carbon monoxide impurity levels. Tests are planned to establish specifications for the remaining impurities. Oxygen, carbon dioxide, or water vapor specifications must be established for the feed cover gas rather than for cover gases that have equilibrated over molten sodium because these substances react rapidly with sodium and, therefore, will be removed before they can be measured.⁽²⁾ Limits on nitrogen impurities in the cover gas will be established to prevent nitriding of sodium covered stainless steel components. It has been shown that austenitic stainless steel in sodium will nitride with a pure nitrogen cover gas.⁽³⁾ Since the nitrogen may be present in the FFTF cover gas, the effect of partial pressures (0.1 to 1%) of nitrogen must be determined.

Numerous investigators have observed that carbon bearing liquid sodium, by causing carburization of the austenitic stainless steel structure components or fuel cladding, can consequently modify their chemical and mechanical properties considerably. Anderson and Sneesby⁽⁴⁾ report that, at 650 °C (1202 °F), 304 SS with an initial carbon content of 0.05% can carburize up to 1% in the equilibrium phase in the presence of sodium containing only 25 ppm carbon. It is therefore important that the carbon containing impurities such as methane and carbon monoxide in the argon cover gas be maintained at sufficiently low concentrations to minimize the carburization potential of the sodium coolant. The purpose of this report

is to establish preliminary standards for methane and carbon monoxide primary cover gas impurities satisfying this criteria. Definition of required impurity levels is also required to define the need for recirculating gas purification equipment on the FFTF cover gas.

INERT NITROGEN ATMOSPHERE

Nitrogen has been chosen as an inert atmosphere for equipment cells which normally contain the primary sodium storage and processing systems, the reactor vessel, and the primary sodium heat transport systems.⁽¹⁾ The most important criterion for selection of the inert gas as presented in the CSDD No. 82 states⁽¹⁾ that "the inert gas must prevent serious chemical reactions which would occur if air came in contact with molten sodium." "...sodium will not react with nitrogen as far as is known. Atmospheres of less than 4% oxygen in the lower ranges of humidity do not permit serious sodium-oxygen or sodium-water reactions to occur." It has been shown⁽⁵⁾ that sodium will not react with atmospheres containing 4% oxygen if the water content of the inert gas is less than 0.1 ppm. At water concentrations of 1 ppm, vigorous combustion will occur when the ignition temperature of sodium is exceeded. Water reaction at 10 ppm will occur below the sodium ignition temperature. It therefore appears that the moisture content of the nitrogen inert gas should be maintained at approximately 0.1 ppm.

A second CSDD criterion states⁽¹⁾ that "the inert gas must facilitate control of material damaging impurities, and must not itself damage materials or equipment." The use of nitrogen introduces the possibility of nitriding the stainless steel components such as thin bellows, and the outside of sodium piping systems. It is known that heavily nitrided stainless steel is more prone to failure through loss of ductility. Nitriding of stainless steel occurs readily under proper conditions of temperature and reducing atmospheres. D. J. Keller⁽⁶⁾ and

B. E. Farrel⁽⁷⁾ report the possibility of inhibiting the nitriding of stainless steels by the presence of small concentrations of oxygen in the nitrogen gas.

Preliminary requirements for nitrogen cover gas established to inhibit the nitriding of stainless steel are also reported herein.

SODIUM COVER GAS BLANKET

EXPERIMENTAL

Methane-Sodium Reaction

The reaction of methane impurity in both helium and argon with molten sodium was measured at 800 °F, 1000 °F, 1200 °F, and 1400 °F. The tests were conducted in a glass recirculating gas system employing 304 SS capsules containing molten sodium. A diagram of the system is shown in Figures 1 and 2. Two liters of cover gas at 760 mm of Hg pressure and containing nominally 100 ppm of methane were recirculated over the sodium in the stainless steel capsules and through a 10 cm³ sampling coil by means of a glass Toepler pump. Except for the experiments to determine the effect of sodium volume and surface areas, each capsule contained 100 cm³ of sodium with a surface area of 14.1 cm². The effect of sodium volume was investigated by increasing the amount of sodium to 250 cm³ and 500 cm³, respectively.

In order to investigate the effect of sodium surface areas, the capsule geometry was changed to provide sodium surface areas of 4.4 cm² and 9.7 cm² with 100 cm³ of sodium, and 74.8 cm² with 200 cm³ of sodium. All of the sodium contained less than 10 ppm oxygen. In every experimental run, the resultant decrease of methane concentration with time in the recirculating gas was measured by diverting the gas in the sampling coil to a gas chromatograph. The chromatograph employed a β ionization detector for helium cover gas, and a flame ionization detector for argon cover gas.

FIGURE 1. Schematic of Sodium Cover Gas Interaction System

FIGURE 2. Reaction Vessel

In addition to the investigation of methane-sodium reaction rates, two runs were made to determine the products of the reaction. In the first run, the distribution of the carbon reaction product(s) in the sodium was determined. Sodium samples obtained at various levels from the sodium pool in the stainless steel capsules and from the condensed sodium on the capsule walls were analyzed for carbon.

The identification of the methane-sodium reaction product(s) was accomplished by reacting 1.0 mg of methane with 19 g of sodium at 1200 °F in a stainless steel capsule. The sodium was then analyzed for carbon by a modified sodium amalgamation technique.⁽⁸⁾ The sodium in the capsule was removed by amalgamation with mercury and the amalgam was transferred to a reaction flask. Water was then added to the flask to hydrolyze the carbon compounds contained with the amalgam, and the resulting gases were trapped cryogenically in a liquid nitrogen trap. The condensed gases in the cryogenic trap were then analyzed by gas chromatography. Separate analyses were made of the sodium pool and the condensed sodium on the capsule walls. The sodium amalgams from both runs were analyzed for total sodium content to establish the amounts of condensed sodium and pool sodium.

Carbon Monoxide-Sodium Reaction

The reaction of carbon monoxide impurity in argon with molten sodium was measured at 500 °F, 650 °F, and 800 °F. The tests were conducted by flowing argon containing 900 ppm CO over 100 g of molten sodium contained in a stainless steel capsule, shown in Figure 2. The effluent gas from the capsule was then measured with an infrared carbon monoxide analyzer. Various gas flows (100 to 400 ml/min) over the sodium were used at the three test temperatures. Each run was continued until a reaction equilibrium was established, at which time the CO concentration in the effluent gas was noted. A flow diagram of the reaction apparatus is shown in Figure 3.

FIGURE 3. Flow Diagram of CO-Na Reaction Apparatus

DISCUSSION

Methane-Sodium Reaction

The investigation of the reaction of methane with molten sodium was initiated using helium cover gas, the reference blanket gas for FFTF at that time. The reaction rate studies were changed to argon with the subsequent change to argon for the FFTF cover gas.

The reaction of methane in helium with molten sodium at the various test temperatures is shown in Figure 4. It can be seen that the reaction is temperature dependent. At 800 °F, the reaction proceeded very slowly and reached a value of approximately 70 ppm methane in 24 hr. At the higher test temperatures (1000 °F, 1200 °F, and 1400 °F), the reaction proceeded virtually to completion in less than 24 hr at 1000 °F and 1200 °F, and in less than 4 hr at 1400 °F. Figure 5 demonstrates that the methane-sodium reaction in argon cover gas is similar to that found in helium cover gas. At 800 °F, the reaction reached a value of 61 ppm in 24 hr and, at the higher test temperatures, proceeded to completion in essentially the same time periods as for the helium cover gas.

It was determined that, at these test temperatures, the methane did not decompose upon contact with the hot stainless steel capsule walls and these data therefore represent true methane-sodium reactions. This finding was demonstrated by heating a test capsule containing no sodium to 1400 °F for a period of six hr with no resultant decrease in the methane concentration of the argon cover gas recirculating through the capsule.

The reaction of methane with sodium probably proceeds as follows:

FIGURE 4. Reaction of Methane and Sodium in Helium Cover Gas

FIGURE 5. Reaction of Methane and Sodium in Argon Cover Gas

The reaction, being bimolecular, suggests a second order kinetic reaction rate which may be expressed as:

$$\frac{dx}{dt} = -k x^2$$

where x is equal to the methane concentration at time t . If this equation is integrated from zero time when $x = a$ (the original methane concentration) to any time t , the following expression is derived:

$$\frac{a - x}{x} = a k t$$

A resulting straight line plot of $\frac{a - x}{x}$ versus t would then verify a second order reaction for the process.

Figures 6 through 8 verify that the methane-sodium reaction with argon at the different test temperatures follows the relationship expressed in the previous equation and is second order. These plots are typical for helium cover gas at the same test temperatures. The rate constants, k , derived by a least squares fit from these plots, are presented in Figure 9. It can be seen that the rate constants determined for argon cover gas at the different test temperatures are on the same order of magnitude to those derived for the helium cover gas. This similarity in magnitude indicates the methane-sodium reaction rate to be largely independent of helium or argon cover gas. The rate constants, k , indicate an activation energy for the methane-sodium reaction of 19.5 kcal/g-mole as derived from the plot slope of the variation of reaction rates with temperature.

The establishment of methane-impurity limits for FFTF cover gas requires not only the determination of methane-sodium reaction rates but also the determination of the controlling variables(s) for the reaction and the behavior of the carbon added to the sodium. Various investigations were performed to

FIGURE 6. Plot of $\frac{a-x}{x}$ Versus Time at 500 °F for Sodium-Methane Reaction

FIGURE 7. Plot of $\frac{a-x}{x}$ Versus Time at Temperatures Shown for Sodium-Methane Reaction

FIGURE 9. Variation of Reaction Rate with Temperature

establish the reaction variables. The parameters investigated included sodium volume, sodium surface area, gas plenum volume, and gas plenum surface area. In addition, the disposition of the sodium carbide formed from the reaction of methane and sodium was also determined. All of these investigations were performed at either 1000 or 1200 °F.

The finding that the methane-sodium reaction is independent of liquid sodium volumes or surface areas and occurs in the sodium vapor phase is shown in Table 1.

TABLE 1. *Reaction Rates of Methane and Sodiums at 1200 °F*

<u>Liquid Sodium Surface Area, cm²</u>	<u>Liquid Sodium Volume, ml</u>	<u>Reaction Rate Constant, k(ppm⁻¹ hr⁻¹)</u>
14.1	500	0.01
14.1	250	0.01
9.7	100	0.03
4.4	100	0.02
14.1	100	0.02
74.8	200	0.02
74.8	200	0.02

It can be seen that reaction rates are not affected by increasing sodium volumes or surface areas.

It was also found that reaction rates at constant temperature do not change with different gas plenum volumes as long as the methane and sodium vapor concentrations remain constant. The data in Table 2 demonstrate this finding.

TABLE 2. *Methane-Sodium Reaction Rates at Various Gas Plenum Volumes (1000 °F)*

<u>Gas Plenum Volume, liter</u>	<u>Reaction Rate Constant, k(ppm⁻¹ hr⁻¹)</u>
0.286	0.0016
	0.0017
	0.0012
	0.0012
	0.0014
0.686	0.0012
	0.0012
1.580	0.0012
	0.0012

No effect on reaction rate constants can be seen from increasing the gas plenum reaction volume from 0.286 to 1.580 liters.

It was felt that if the sodium-methane reaction occurred in the vapor phase, the carbon compound formed during the reaction of methane and sodium should be found in higher concentrations in the condensed sodium on the capsule walls and probably on the surface of the sodium pool. This aspect was investigated and found to be true by reacting 1 mg of methane with sodium in a capsule heated to 1200 °F and containing 100 gm of sodium. Sodium samples were taken from different levels of the sodium pool and from the condensed sodium on the capsule wall for carbon analyses. The results are shown in Figure 10. Referring to this figure, the sodium was sampled as follows:

- After Exposure, "U" tube was attached to short stub at bottom of capsule by means of a swagelock fitting.
- Capsule was heated and sodium was allowed to flow into sample tube.
- Sample tube was removed and sodium analyzed.
- Capsule was opened and sample of pool sodium obtained.

It was found that the condensed sodium from the capsule walls contained 370 ppm of carbon, whereas the top portion of the sodium pool contained 45 ppm of carbon as compared to 0 to 20 ppm for the remainder of the sodium pool.

The reaction product of the sodium-methane reaction was determined as probably sodium carbide. Hydrolyses of the sodium amalgam and residue, obtained from amalgamating sodium previously reacted with methane, yielded 1.86×10^{-6} moles of acetylene. This amount is equivalent to 1.86×10^{-6} moles of sodium carbide. Acetylene is formed from the reaction of sodium carbide with water as shown by the following equation:

FIGURE 10. Carbon Analyses for Sodium in Stainless Steel Capsules after Adding 1 mg CH_4

All of the acetylene was evolved from the condensed sodium amalgam and none from the sodium pool in the bottom of the capsule in agreement with the total carbon distribution previously shown. From the equation for the reaction of sodium and methane,

it can be seen that 1.86×10^{-6} mole of sodium carbide is equivalent to 0.0595 mg of methane. This amount of reaction product was found in 2.5 g of sodium from the total of 19 g originally in the capsule. Of the remaining 16.5 g of sodium, 6 g were recovered from the pool to leave 10.5 g unaccounted for. The 10.5 g of sodium were believed to have reacted with the methane and then condensed in the vapor trap outside of the capsule. Therefore, 0.0595 mg of methane in 2.5 g of sodium would be equivalent to 0.31 mg of methane recovered for 13 grams of sodium, amounting to a 30% recovery of the 1 mg of methane reacting with sodium. The low recovery is probably due to the loss of carbon residue during the transfer of the amalgam from the stainless steel capsule to the reaction flask. The possibility of higher Na_2C_2 concentrations in the unrecovered sodium in the vapor trap is also a possibility.

Allowable Methane Impurity Content of FFTF Cover Gas

The establishment of a methane impurity specification for the FFTF primary cover gas blanket requires the consideration of at least two factors. The first of these factors is the chemical effect of the introduction of dissolved carbon impurities into the sodium coolant. The second concerns the effect of solid impurities which could be introduced into the reactor systems from the interaction of sodium and cover gas impurities.

It has been reported by various investigators that austenitic stainless steels carburize readily from carbon-bearing liquid sodium at temperatures of 1000 °F and higher.

Anderson⁽⁴⁾ has shown that, although sodium containing 15 to 18 ppm carbon is in virtual equilibrium with uncarburized 304 SS at 1200 °F, carbon saturated liquid sodium at a temperature between 1000 and 1300 °F will carburize 304 SS to a surface carbon content of 2.7 to 3.35% after less than 1 hr exposure. The solubility of carbon in sodium containing 40 ppm O₂ has been reported to range from 32 ppm at 147 °C (296 °F) to 74 ppm at 700 °C (1292 °F).⁽⁹⁾ It should be mentioned that this data has been reported to be in error by more recent work performed at Argonne National Laboratories. C. Lunar⁽¹⁰⁾ reports that previous solubility results probably measured unfilterable carbonaceous particles in the sodium with invariably higher carbon values than equilibrium solubility. The author further states that "the true solubility of elemental carbon in sodium is less than 0.005 ppm up to 450 °C."

Thin 304 SS sheet exposed to these high carburizing potentials soon becomes severely embrittled and will tolerate no plastic deformation. Anderson⁽⁴⁾ has also shown that the surface carbon content of austenitic stainless steel decreases with decreasing carbon content of the liquid sodium and reaches a point at which the carburization effect is negligible in regard to the mechanical properties of the stainless steel. It is therefore important that sources of carbon addition to the sodium, such as methane-sodium interactions, be carefully controlled.

Deposits of solid impurities such as elemental carbon, sodium carbonate, sodium frosts, and decomposition products of hydrocarbons could interfere with mechanical components of the reactor and could also cause flow blockages of the sodium coolant. Condensation of sodium frosts resulting from interactions of sodium and various carbonaceous impurities could interfere with the rotational operation of reactor seal plugs as well as the linear motion of various shafts which must extend through

the reactor cover and gas plenum into the molten sodium. Solid impurities in the molten sodium could cause flow blockage of the coolant and also impair the mechanical operation of components within the molten sodium. It has also been reported that the presence of carbon in a sodium loop can result in plugging temperatures not in agreement with the oxygen-saturated temperatures.⁽¹¹⁾

The extent to which the operation of a sodium-cooled fast reactor may be curtailed by the presence of sodium frost formations and undissolved impurities and sodium is not known. Additional studies will be required to correlate these possible effects if they truly exist. Although information and technology in this one phase is lacking, establishment of a preliminary FFTF methane cover gas specification is possible.

The preliminary FFTF methane cover gas specification is based on the allowable carbon pickup of the fuel cladding, comprising the hottest and most critical stainless steel in the system. Given an allowable fuel clad carbon pickup in a given life time and knowing the reaction rates of methane with sodium as a function of temperature, a limit for the total allowable cover gas content of CH_4 as a function of sodium temperatures could be established. By conservatively assuming that all carbon added to the system would be ultimately absorbed by the fuel clad, the need for accurate data on carburization rates of stainless steel to set a preliminary cover gas allowance could be eliminated.

Sinizer and Pearson⁽¹²⁾ selected a surface carbon content of 0.5% in type 304 SS as the safe operating limit at SRE. They stated that, by maintaining surface carbon content below 0.5%, the service life from the standpoint of carburization could be considered infinite. Earlier, Anderson⁽⁴⁾ reported that 0.3% surface carbon had negligible effects on the mechanical properties of stainless steel. The Liquid Metal

Engineering Center (LMEC) recommends⁽¹³⁾ that a maximum of 0.5% surface carbon should be considered as the state-of-the-art criterion for an 18-8 stainless steel system.

The present FFTF fuel system design comprises 76 driver fuels each containing 217 fuel pins of 0.230 in. in diameter. The active core portion (heat generating surface) will be 36 in. in length. The temperature differential over this distance will be 300 °F. If carburization is assumed to occur in the hottest portion of the cladding within a 100 °F differential, the length and location of the affected zone would then comprise top 12 in. of the fueled region of the pins. The present design also specifies a stainless steel cladding thickness of 14 mils. As a minimum, the outer two mils of clad will be allowable for corrosion and attack by the sodium coolant. Therefore, if the carbon in the outer two mils of cladding is permitted to reach a concentration of 0.5%, the carbon concentration in the remainder of the cladding would remain at less than 0.5%.

With the criteria thus established, the total maximum carbon which may be added to the system is calculated as follows:

$$\begin{aligned}
 & (16492 \text{ fuel pins})(0.230 \text{ in.})(12 \text{ in.} \pi 0.002) \frac{(16.39 \text{ cm}^3)}{\text{in.}^3} \\
 & = 4688 \text{ cm}^3 \text{ stainless steel} \\
 & \frac{(4688 \text{ cm}^3)(7.6 \text{ gm/cm}^3)}{1000 \text{ gm/K}_g} = 35.6 \text{ K}_g \text{ stainless steel}
 \end{aligned}$$

An allowable carbon concentration of 0.5% would amount to an increase of 0.44% over the original carbon concentration of 0.06% in the stainless steel. Therefore, $(35.6 \text{ K}_g)(0.0044) = 0.16 \text{ K}_g$ of allowable carbon pickup. This amount would be equivalent to 0.21 K_g or 13 moles of pure methane. With a reactor core life of one year, the maximum amount of methane that may be allowed to react with the sodium coolant would be

13 moles per year of 0.0015 moles/hr. A FFTF primary cover gas volume of 2830 liters (100 ft³) of argon would result in a decrease of the methane concentration in the argon cover gas at a rate of:

$$\frac{(0.0015 \text{ moles/l})(22.4 \text{ l/moles at STP})(10^6)}{2830} = 11.9 \text{ ppm/hr}$$

The maximum allowable methane concentration in the primary cover gas may be calculated for various coolant temperatures by employing the previously shown kinetic equation

$$-\frac{dx}{dt} = kx^2$$

where

$\frac{dx}{dt}$ = the allowable reaction rate of 11.3 ppm/hr

k = the reaction rate constant for various coolant temperatures. (See Figure 9)

x = the allowable methane concentrations in the primary cover gas.

The calculated maximum allowable methane concentrations for coolant temperatures of 800 °F to 1400 °F are shown below:

Coolant Temperature, °F	Reaction Rate Constant, k (ppm ⁻¹ hr ⁻¹)	Maximum CH ₄ Concentration, ppm
500	0.0000044	1645
800	0.00035	184
1000	0.0025	69
1200	0.011	33
1400	0.035	18

A graphical representation of these limits is shown in Figure 11.

FIGURE 11. Maximum Allowable Methane Concentration at Various Coolant Temperatures Based on Reaction Rates

Carbon Monoxide-Sodium Reaction

The preliminary investigation disclosed the carbon monoxide reaction with molten sodium to proceed very rapidly at 800 °F, but considerably slower as the temperature of the sodium was lowered to 500 °F. The amount of carbon monoxide reacted with the sodium at various gas flow rates and sodium temperatures is shown in the following table:

<u>Temperature, °F</u>	<u>Gas Flow Rate, ml/min</u>	<u>CO Reacted,* %</u>
800	100	91
	200	82
	300	78
	375	68
	400	65
650	200	53
	200	75
	200	72
	400	60
	400	51
500	100	12

* Original concentration of CO in argon was 900 ppm.

It can be seen that considerably less carbon monoxide reacted as the temperature of the sodium was lowered. At 800 °F, 91% of the CO was consumed with a cover gas flow rate of 100 ml/min whereas, at 500 °F, only 12% of the CO was consumed at the same flow rate.

It has been shown⁽¹⁴⁾ that for a backmix flow reactor system in which there is essentially no volume change, the following equation may be used for calculating rate constants:

$$\gamma = \frac{1}{k C_{AO}^{n-1}} \left[\frac{X_A (1 + X_A)^n}{(1 - X_A)^n} \right],$$

where:

γ = the ratio of system volume to flow rate of CO,
 C_{AO} = concentration of CO in the argon cover gas,

X_A = fraction of CO reacted,

n = kinetic order of reaction.

Applying the preliminary data for the reaction of carbon monoxide with sodium to the preceding equation, rate constants for each temperature for both first and second order reactions have been derived as follows:

Temperature, °F	Gas Flow Rate, ml/min	Reaction Rate Constant, k (min^{-1})	
		$n = 1$	$n = 2$
800	100	2.2	0.0.053
	200	1.8	0.0.036
	300	2.0	0.0.018
	375	1.4	0.0.008
	400	1.3	0.0.006
650	200	0.4	0.0.001
	200	1.1	0.0.009
	200	0.9	0.0.006
	400	0.7	0.0.002
	400	1.0	0.0.005
500	100	0.2	0 0.0002

Except for one low value at 650 °F and 200 ml/min flow rate there appears to be generally good agreement between the rate constant determined for first order reaction at the temperatures of 650 and 800 °F. The average deviations for the rate constants, assuming first order reaction are $\pm 26\%$ for the 800 °F test temperature and $\pm 19\%$ for the 650 °F test temperature. This compares to the much larger deviations of $\pm 115\%$ for 800 °F test temperatures and $\pm 64\%$ for 650 °F test temperatures when a second order reaction is assumed. This preliminary data therefore show that the reaction of carbon monoxide and sodium is of first order and indicates an activation energy of 11.3 kcal/g-mole for the reaction.

Allowable Carbon Monoxide Impurity Specifications for FFTF
Cover Gas

Preliminary specifications for maximum carbon monoxide concentrations in the primary cover gas at various coolant temperatures can be established in a similar manner as for the methane limits (based on reaction rates). On this basis, the allowable CO concentrations may be calculated by means of the following equation for a first order reaction:

$$-\gamma_A = k C_A$$

where:

γ_A = the allowable reaction rate of 11.3 ppm/hr (previously established)

k = the reaction rate constant for various coolant temperatures

C_A = the allowable carbon monoxide concentration in the primary cover gas.

The allowable CO concentrations for coolant temperatures of 500 to 800 °F are shown below.

<u>Coolant Temperature</u>	<u>Reaction Rate Constant k (hr⁻¹)</u>	<u>Maximum CO Concentration</u>
500 °F	12	1 ppm
650 °F	49	0.2 ppm
800 °F	104	0.1 ppm

It should be reiterated that these are only preliminary specifications and based on reaction rates with the assumption that all of the carbon introduced from the reaction will eventually carburize the fuel clad. Before a final specification may be established, several additional factors must be investigated. The products of the CO-Na reaction must be identified.

The relationship of these products to the sodium carburizing potential of stainless steel must be established and the effect of the "frost" and reaction products on mechanical components in the gas plenum must be determined. These will be investigated in the continuing work of this program.

NITROGEN INERT GAS ATMOSPHERE

EXPERIMENTAL

The inhibiting effect of oxygen on stainless steel nitriding was investigated by exposing samples of 304 SS and 316 SS to flowing nitrogen gas containing 500 ppm and 5000 ppm oxygen, respectively. The samples were exposed to temperatures of 1000 °F and 1400 °F for periods of 1 month, 3 months, and 6 months. Following each exposure period, duplicate samples were removed for chemical nitrogen analyses and metallurgical examination. The effects of crevices and welds on both the 304 and 316 SS were also investigated.

DISCUSSION

It was found that as little as 500 ppm of oxygen in nitrogen will inhibit nitriding of stainless steel at 1000 °F. At 1400 °F, stainless steel samples would nitride with 500 ppm of oxygen, but oxygen concentrations of 5000 ppm were found to inhibit them. Except for the nitrided samples, there was no detectable increase in nitrogen concentration of the stainless steel for any of the exposures up to six months, as determined by both vacuum fusion, and by analyses and metallography. This observation also applies to the welded and crevice samples as the plain samples for both 304 and 316 SS.

Metallography of the stainless steel samples exposed to 1400 °F nitrogen containing 500 ppm oxygen showed no nitride case formation during the entire exposure period, although vacuum fusion analyses showed a continuous buildup of nitrogen

in all of the samples of 304 and 316 SS for the six-month exposure period. After the first month of exposure, the nitrogen concentration in the samples had increased by approximately 150 ppm as compared to approximately a 400 ppm increase after six months exposure. This comparison is shown in the following table.

Exposure Time, mo	Type of SS Sample	Increase in Nitrogen Concentration of Samples Exposed at 1400 °F and 500 ppm O ₂ , ppm	
1	304 plain		130
	welded		150
	crevice		150
	316 plain		190
	welded		170
	crevice		--
3	304 plain		280
	welded		230
	crevice		--
	316 plain		190
	welded		240
	crevice		250
6	304 plain		390
	welded		400
	crevice		--
	316 plain		410
	welded		--
	crevice		380

No apparent differences in the nitriding rate of 304 SS and 316 SS can be seen in these data. There also appear to be no crevice or weld effects on the nitriding. None of the samples revealed excessive corrosion by the oxygen. The maximum corrosion rates measured averaged less than 0.1 mils/year for samples exposed at 1400 °F.

The preceding data confirm previously published work at temperatures higher than expected at FFTF showing the optimum oxygen concentration for nitride prevention to be 0.5 vol% at temperatures of 1500 to 1650 °F.⁽⁶⁾ It is therefore recommended that the nitrogen cover gas blanket for the FFTF equipment cells contain a minimum of 0.5 vol% oxygen.

CONCLUSIONS

Preliminary recommendations for both methane and carbon monoxide impurities in the primary argon cover gas blanket have been established. These recommendations are:

- The maximum allowable methane concentration ranges are from 213 ppm at a sodium coolant temperature of 800 °F, to 18 ppm at a sodium coolant temperature of 1400 °F.
- The maximum allowable carbon monoxide concentration ranges are from 1 ppm at a sodium coolant temperature of 500 °F to 0.1 ppm at a sodium coolant temperature of 800 °F.

The requirements are based on the reaction rates of the impurities with molten sodium for various coolant temperatures, assuming that all carbon introduced into the sodium coolant will eventually carburize the stainless steel fuel cladding. It must be emphasized that prior to establishing final standards, additional studies must be conducted. These studies include:

- The effect of the undissolved reaction products on the reactor mechanical components plated out in the gas plenum,
- The effect of the undissolved reaction products on the sodium coolant flows, and
- The determination of the sodium carburizing potential as related to these cover gas impurities.

It is also recommended that the nitrogen cover gas blanket for the equipment cells contain a minimum oxygen concentration of 0.5 vol% to prevent nitriding of the stainless steel components.

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