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SUMMARY

Deposits of sodium and sodium oxide aerosol particles on heat exchanger surfaces following a molten sodium release within a closed loop cell of the FFTF can represent a serious resistance to heat flow. The magnitude of the added heat flow resistance is dependent upon the thickness of the deposit and its heat transfer coefficient. The latter value is influenced principally by the bulk density of the deposit. Bulk density measurements of sodium oxides generated in less than 2% O_2 atmospheres and deposited inside ducts dynamically, indicate that the sodium oxide layer contains mostly gas trapped in a very porous solid. Heat transfer coefficient measurements confirm that the deposited layer has heat transfer characteristics that are similar to a stagnant layer of nitrogen gas of equal thickness.

The fission gas holdup beds for the FFTF will also remove ^{41}Ar from the argon cover gas. The efficiency of the removal of ^{41}Ar depends, among other factors, on the adsorption capacity of the charcoal in the holdup beds. The adsorption coefficients of argon on Pittsburgh PCB charcoal at temperatures from $-75^\circ C$ to $-140^\circ C$ and pressures from 5 to 140 psig were determined experimentally. These adsorption coefficients increased with decrease in temperature, as expected. However, the increase in adsorption with pressure was much less than one-to-one, especially at the lower temperatures. Thus, a three-fold increase in pressure at $-75^\circ C$ resulted in only a 50% increase in the adsorption coefficient, and a six-fold increase in pressure at $-140^\circ C$ resulted in only a 20% increase in adsorption coefficient.

These measurements, when plotted as a function of the Polanyi potential, were in good agreement with data in the literature for adsorption at subatmospheric pressures. These new results permit the effect of pressure on the adsorption of krypton from an argon carrier gas to be analyzed as a function of the quantity of adsorbed argon and explain the strong effect that the pressure of the argon carrier gas has on the adsorption of krypton at low temperatures. From the standpoint of reactor safety, these new data permit one to 1) calculate the removal of ^{41}Ar in the holdup beds and 2) determine the effect of argon adsorption on the holdup of krypton and xenon.

The chemical composition of sodium aerosol particles depends upon the oxygen content of the atmosphere enclosing the molten metal. Sodium peroxide is formed in normal atmospheres, sodium monoxide in low oxygen atmospheres, and sodium metal in inert atmospheres. Oxide mixtures occur as the initial oxygen content of the atmosphere is consumed by reactions. Reactions also take place between sodium and the other normal constituents of the atmosphere, i.e., water vapor and carbon dioxide. A method is described to determine the chemical composition of aerosol particles formed in nitrogen atmospheres containing less than 10% air.

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Heat Transfer Properties of Sodium Oxide Particles Deposited from an Aerosol

R. R. Hall & M. W. First

I. Sodium Aerosol Studies

A. Introduction

Our previous reports (1),(2),(3) describe laboratory investigations of the rate of deposition of sodium aerosol particles in a 3-tube heat exchanger simulator. These investigations were extended with the aid of a 7-tube heat exchanger simulator and additional measurements of deposition rate have been made.

If sodium oxide (Na_2O)⁽⁴⁾ deposits in a shell and tube heat exchanger, it will lower the heat transfer capability of the apparatus. Although the thermal conductivity of elemental sodium and many of its common reaction products can be found in handbooks and similar sources, these values refer to the behavior of pure substances when compacted to their theoretical density and have no close or predictable relationship to the thermal conductivity of these same materials when deposited as highly porous layers composed of finely divided particles of mixed chemical composition. A familiar example will serve to illustrate this difference: ice with a density of 57.5 lb/cu.ft. has a thermal conductivity of 1.3 Btu/hr(sq.ft.)(°F/ft.) whereas compacted snow has a bulk density of 34.7 lb/cu.ft. and a thermal conductivity of only 0.27. This shows the enormous change which occurs in heat flow characteristics when the bulk density of a material differs significantly

from its true density. Freshly fallen snow, which often has a bulk density as low as 6 lb/cu.ft., has even poorer heat flow characteristics, indicating the overriding influence of tiny occluded air spaces on heat transmission rates through porous materials. To aid in heat exchanger design, investigations have been conducted to determine the thermal conductivity of sodium oxide deposits.

B. Rationale and Procedures

The thermal conductivity of a material may be determined directly by measuring the thickness, temperature gradient, cross sectional area, and the rate of heat transmission. As it is not easy to make temperature gradient measurements in sodium oxide deposits, and as extreme accuracy is not needed for engineering estimates of the effect of oxide deposits on heat transfer capability, an indirect method was used to obtain the thermal conductivity of sodium oxide deposits. Basically the method consisted of:

1. Measuring the overall heat transfer resistance when the heat exchanger was clean.
2. Measuring the overall heat transfer resistance after the sodium oxide had been deposited.
3. Measuring the thickness of the sodium oxide deposit
4. Calculating thermal conductivity of the sodium oxide deposit with the formula derived in the following paragraph.

A simplified design equation for a heat exchanger is:

$$q = UA\Delta T_{lm} \quad (1)$$

Where:

q = rate of heat transfer, Btu/hr

U = overall heat transfer coefficient $\frac{\text{Btu}}{\text{hr.ft}^2\text{.}^\circ\text{F}}$

A = area associated with the controlling heat transfer resistance, in this case the inside area of the heat exchanger tubes, ft^2

ΔT_{lm} = log mean temperature difference between the hot and cold fluids in countercurrent flow, $^\circ\text{F}$

The following assumptions have been made:

1. The overall heat transfer coefficient (U) is constant through the heat exchanger.
2. The specific heats of the two fluids are independent of temperature.
3. The mass rate of flow of both fluids is constant.

The term $\frac{1}{UA}$ is commonly defined as the overall heat transfer resistance. From equation 1, it can be seen that $1/UA$ equals $\Delta T_{lm}/q$. In this paper, both terms, $\left(\frac{1}{UA}\right)$ and $\left(\Delta T_{lm}/q\right)$ are referred to as heat transfer resistances. For a countercurrent double-pipe heat exchanger, the overall heat transfer resistance is equal to the sum of the individual resistances:

$$\left(\frac{1}{UA}\right)_C = \frac{1}{h_2 A_2} + \frac{R_3 - R_2}{K_T A_T} + \frac{1}{h_3 A_3} \quad (2)$$

Where :

$\left(\frac{1}{UA}\right)_C$ = overall heat transfer resistance when no deposit is present, Btu/hr°F

h_2 = heat transfer coefficient between the gas and the pipe wall, $\frac{\text{Btu}}{\text{hr.ft}^2\text{°F}}$

A_2 = inside area of the pipe, ft²

$R_3 - R_2$ = wall thickness of the pipe, ft

K_T = thermal conductivity of the pipe, $\frac{\text{Btu}}{\text{hr.ft}^2\text{°F/ft}}$

A_T = mean area of the pipe, $\left(\frac{\text{inside area} + \text{outside}}{2}\right)$, ft² +

h_3 = heat transfer coefficient between the inside pipe wall and the coolant, Btu/hr.ft²°F

A_3 = outside area of the inner pipe, ft²

Similarly, the heat transfer resistance after the sodium oxide has deposited is:

$$\left(\frac{1}{UA}\right)_D = \frac{1}{h_1 A_1} + \frac{t}{K_D A_D} + \frac{1}{h_w A_z} + \frac{R_3 - R_2}{K_T A_T} + \frac{1}{h_3 A_3} \quad (3)$$

Where:

- $\left(\frac{1}{UA}\right)_D$ = overall heat transfer resistance when the deposit is present, $\frac{\text{Btu}}{\text{hr}^{\circ}\text{F}}$
- h_1 = heat transfer coefficient between the gas and the deposit, $\text{Btu/hr.ft}^2\text{°F}$
- A_1 = inside area of the deposit, ft^2
- t = thickness of the deposit, ft
- K_D = thermal conductivity of the deposit, $\text{Btu/hr.ft}^2\text{°F/ft}$
- A_D = mean area of the deposit, ft^2
- h_w = heat transfer coefficient between the deposit and the pipe wall, $\text{Btu/hr.ft}^2\text{°F}$

Subtracting equation 2 from equation 3 yields:

$$\left(\frac{1}{UA}\right)_D - \left(\frac{1}{UA}\right)_C = \left(\frac{1}{h_1 A_1} - \frac{1}{h_2 A_2}\right) + \frac{t}{K_d A_d} + \frac{1}{h_w A_2} \quad (4)$$

From Perry's Chemical Engineers' Handbook⁽⁵⁾, the heat transfer coefficient (h_2) between the gas and the clean pipe wall equals $11 \text{ Btu/hr.ft}^2\text{°F}$. If the thickness of the deposit is .08 inches and the thermal conductivity of the deposit is $\frac{.16 \text{ Btu}}{\text{hr.ft}^2(\text{°F/ft})}$,

then:

$$\frac{1}{h_2 A_2} = \frac{1}{11 A_2} \quad (5)$$

and:

$$\frac{t}{K_d A_d} = \frac{1}{2kA_d} \quad (6)$$

From equations 5 and 6, it can be seen that when the heat transfer resistance between the gas and the clean tube wall $\left(\frac{1}{h_1 A_1}\right)$ and the heat transfer resistance between the gas and the sodium oxide deposit $\left(\frac{1}{h_2 A_2}\right)$ differ by 5% or less, the term $\left(\frac{1}{h_1 A_1} - \frac{1}{h_2 A_2}\right)$ will be less than 10% of the term $\frac{t}{K_d A_d}$. Therefore, the term $\left(\frac{1}{h_1 A_1} - \frac{1}{h_2 A_2}\right)$ is not significant in an engineering estimate of the thermal conductivity of a sodium oxide deposit. The heat transfer coefficient between two pieces of rough aluminum in intimate contact at atmospheric pressure is $\frac{500 \text{ Btu}}{\text{hr.ft}^2\text{°F}}$. (6) As the

sodium oxide deposit will be in intimate contact with the tube wall, the value of h_w is assumed to be 500 Btu/hr.ft²°F and the term $\frac{1}{h_w A_2}$ becomes less than 3% of the term $\frac{t}{K_d A_d}$ and is not significant. Therefore, equation 4 can be simplified to:

$$\left(\frac{1}{UA}\right)_D - \left(\frac{1}{UA}\right)_C = \frac{t}{K_d A_d} \quad (7)$$

Solving for K_d yields:

$$K_d = \frac{t}{A_d \left(\left(\frac{1}{UA}\right)_D - \left(\frac{1}{UA}\right)_C \right)} \quad (8)$$

From equation 1:

$$\frac{1}{UA} = \frac{\Delta T_{lm}}{q} \quad (9)$$

Substituting in equation 8 yields the design equation:

$$K_d = \frac{t}{A_d \left(\left(\frac{\Delta T_{lm}}{q} \right)_D - \left(\frac{\Delta T_{lm}}{q} \right)_C \right)} \quad (10)$$

The value of q is calculated from the heat removed from the gas as follows:

$$q = Q \rho C_p (T_1 - T_o) \quad (11)$$

Where:

Q = flow rate, ft^3/hr

ρ = gas density, lb/ft^3

C_p = gas specific heat, $\text{Btu}/\text{lb}^\circ\text{F}$

T_1 = gas temperature entering the heat exchanger, $^\circ\text{F}$

T_o = gas temperature leaving the heat exchanger, $^\circ\text{F}$

The sodium oxide aerosol was generated in a 3300 ft^3 chamber filled with an atmosphere composed of 1% oxygen, and 99% nitrogen. A 6" x 6" x 6" steel pot with four 2000 watt electrical heaters

in the bottom was used to vaporize 3-6 pounds of metallic sodium over a 2 to 6 hour period. During the sodium vaporization period, the sodium oxide aerosol was circulated through the inner tubes of the heat exchanger until a reasonably thick deposit was achieved. After the aerosol in the chamber settled, thermometers were inserted immediately upstream and downstream from the heat exchange section and the heat exchanger operated until an equilibrium condition was reached. Next, the apparatus was disassembled and the thickness of the sodium oxide deposit measured. As the heat exchanger had already been run clean before the aerosol was generated, the next step was to use equations 10 and 11 to calculate the thermal conductivity of the sodium oxide deposit.

C. Experimental arrangement and measurements

The experimental arrangement and equipment were similar to the equipment used in our previous sodium deposition experiments which were described and pictured in some detail in our previous reports. Fig. 1-1 is a schematic diagram of the experiment. Two different heat exchangers were used in the study. The first consisted of seven tubes, each 7.5 ft long, having an inside diameter of 0.53 in. As there was some doubt as to the effective total heat transfer area of the tube bundle because of crowding together of the tubes, a double-pipe heat exchanger was constructed. The double-pipe heat exchanger was 7.1 feet long and the inside pipe was 2.067-in, I.D. Temperatures were measured with identical

FIGURE 1-1. APPARATUS FOR MEASURING HEAT TRANSFER COEFFICIENT.

0°-50°C thermometers marked in 0.1°C subdivisions and placed immediately upstream and downstream of the heat exchanger. The gas flow rate through the heat exchanger was measured with a Venturi meter.

Problems were encountered in measuring the thickness of the sodium oxide deposit. Close-up photographs of the entrance and exit were taken and enlarged. This method yielded good measurements of the thickness at the entrance and exit but, because of deposit discontinuities, it was not possible to calculate with certainty the average thickness in the tubes. However, as the total amount of sodium deposited in the tubes during each run could be measured accurately by chemical analysis, it would be possible to calculate the average thickness if the bulk density of the deposit was known.

Seven methods were used to find the bulk density of the deposit. In Method No. 1, the total deposit in the entry plenum of the seven tube bundle was removed and analyzed for sodium. The volume of the space was determined by filling with water. Method No. 2 consisted of scraping a bulk sample of the deposit from an outlet pipe into a 25cc vial and analyzing for total sodium. Method No. 3 was to place Millipore filters on the walls of the two inch diameter heat exchanger pipe. After sodium oxide had deposited, the Millipore filters were removed and the thickness of the deposit measured with a depth gauge. The deposit on the

Millipore filter was then analyzed for total sodium and the density of the deposit calculated. In Method No. 4 a thin, flat piece of copper shim stock (7 mil) was used in place of the Millipore filter to overcome the difficulty caused by breakage during removal from the pipe. Method No. 5 was to calculate the density from the thickness at the entry and exit using enlarged photographs of the entrance and exit on the assumption that the deposit varied linearly from entrance to exit. None of the above measurements proved to be entirely satisfactory. Therefore, for Method No. 6, a four foot long square lucite pipe was constructed with a removable bottom so that measurements could be made easily with a depth gauge. Next, an attempt was made to get a very large deposit in the square pipe by evaporating 11 pounds of sodium in the aerosol chamber over a period of 9 hours. Very little sodium oxide was deposited on the bottom section of the rectangular pipe but a 0.45 cm thick deposit was found on the top section. After the thickness of the deposit was measured, it was removed with a spatula and analyzed for sodium. This Method, No. 7, is believed to be the most accurate determination of the density of the sodium oxide deposit. The bulk density calculated from Method No. 7 was 0.029 gm/cc expressed as elemental sodium. During this same experiment, some of the sodium oxide deposited at the end of the tube in an easily measureable, triangular cake-like deposit whose bulk density was 0.11 gm/cc (Method No. 8). The appearance of the deposit removed from the walls was very much more powdery

than the material removed from the end of the tube and its bulk density (0.029 gm/cc) was obviously far less than that of the caked deposit (0.11 gm/cc). Table 1-1 lists all of the density measurements determined by each of the methods mentioned above.

D. Experimental Results

Initially, experiments were conducted with a seven-tube heat exchanger. First, the clean heat transfer resistance was measured and then the sodium aerosol was allowed to flow through the tubes for 1-2 hours to form a reasonably thick deposit. Next, the suspended sodium oxide particles in the chamber were allowed to settle and the clean chamber atmosphere was circulated through the heat exchanger until a temperature equilibrium was reached with the coolant. After measuring the thickness of the deposit, the thermal conductivity was calculated.

Various methods were used to cool the seven tube bundle. At first, natural convection of ambient air was used but this did not result in significant heat transfer. Next, room air, blown parallel to the tubes at high velocity was used for cooling, but, the heat transfer rate was still low and the resulting temperature differentials too small for accurate measurement. When cool air was used as the coolant, adequate temperature differentials were observed and the thermal conductivity of the sodium oxide deposit was calculated to be $0.16 \text{ Btu/hr.ft}^2(^{\circ}\text{F/ft})$ based on a deposit density of $0.029 \text{ gm}^{\text{Na}}/\text{cc}$. The data from the above experiment is listed as experiment 1 in Table 1-2.

DENSITY MEASUREMENTS

TABLE 1-1

Method*	Measured Thickness Deposit cm	Total Volume Deposit cm ³	Total wt as Na gm	Density lb/ft ³	gm/cc	%O ₂ in atmosphere in which aerosol formed
1		110	8.7	4.99	0.080	1.3
2.		25	1.59	3.93	0.063	
3	0.038	0.192	0.0182	5.93	0.095	1.1
	0.040	0.216	0.0175	5.05	0.081	1.1
4	0.059	0.121	0.004	2.06	0.033	1.4
5	0.0188	305	33.6	6.86	0.110	1.3
	0.02	350	35	6.24	0.100	
	0.061	182	8	2.75	0.044	0.81
6	0.218	2.41	0.06	1.56	0.025	1.5
7	0.45	53.4	1.55	1.81	0.029	1.5
8	0.5	.90	0.7	6.8	0.109	1.5

* see text

HEAT TRANSFER EXPERIMENTS

TABLE 1-2

Experiment	K	Flow Rate cfm	Aerosol Temperature		Coolant Temperature		Deposit as gm Na	Thickness of Deposit, in.
	$\frac{\text{Btu}}{\text{hr.ft}^2(^{\circ}\text{F/ft})}$		Upstream $^{\circ}\text{C}$	Downstream $^{\circ}\text{C}$	In $^{\circ}\text{C}$	Out $^{\circ}\text{C}$		
1. 7-tubes, cool air	.16	38.6	33.54	27.1	22.67		33.6	.081
1a. Same as above but no deposit		38.6	31.425	26.35	24.25			
2. 1 tube, cold water	.12	62.6	48.1	41.9	21.8	22.3	12.8	.05
2a. Same as above but no deposit		62.6	46.1	39.1	22.4	22.9		
3. 1 tube cold water	.13	62.6	45.68	39.18	20.7	21.2	8.0	.031
3a. Same as above but no deposit			44.3	37.9	21.8	22.8		
4. 1 tube, cold water	.056	62.6	46.7	41.3	19.65	20.2	13	.054

1-14

The remainder of the heat transfer experiments were conducted with a double pipe heat exchanger. To achieve a thick deposit, the aerosol was circulated through the exchanger for 5-6 hours. Ice water, pumped countercurrent to the gas flow at 5 gal/min, was used as the coolant in the initial double pipe experiment but, as the dew point of the gas was above 32°F, water condensed on the sodium oxide deposit and ruined the experiment. For the next run, cold tap water was used as the coolant and the nitrogen recirculated through the inner heat exchange pipe was heated to obtain large temperature differentials. This method worked well and was repeated twice more. Two measurements of thermal conductivity were in very close agreement, i.e., 0.12 and 0.13 Btu/hr.ft²(°F/ft) but the third, 0.056 Btu/hr.ft²(°F/ft) was lower. No explanation is offered for the low result.

E. Conclusion

The effect of deposited sodium oxide on the performance characteristics of a heat exchanger is likely to be detrimental when the total amount of sodium deposited in the tubes is enough to produce a coating in excess of .01-.02 inches. If the deposit has approximately the same bulk density as the deposits that were measured, the uncertainty in the density will not seriously effect the design of the heat exchanger.

The magnitude of the effect of the sodium oxide deposit on the design of the proposed heat exchanger can be calculated in the following manner. Assume the heat exchanger will contain

2000 tubes, each 8 ft. long, 0.53" I.D. and 0.75" O.D. and that the velocity of the nitrogen gas through the tubes will be 90 ft/sec. From Perry's Chemical Engineers' Handbook⁽⁵⁾, the inside heat transfer coefficient from the gas to the tube wall will be 11 Btu/hr.ft²°F. Since the heat transfer resistance of the tube wall and the outside film is not large, the overall heat transfer coefficient will probably be about 10 Btu/hr.ft²°F. The overall heat transfer resistance can be calculated from the following formula:

$$\left(\frac{1}{UA}\right)_D = \left(\frac{1}{UA}\right)_C + \frac{t}{K_d A_d} \quad (12)$$

In order to calculate, t , the thickness of the deposit, the amount of sodium deposited must be known. For this example, it has been assumed that 6.125 lbs. sodium deposited in the 2000 tubes. The thickness of the deposit may be calculated by trial and error from the following equations:

$$t = \frac{4m}{\rho N L \pi (D_1 + D_2)} \quad (13)$$

Where:

m = mass deposited, lbs.

ρ = Bulk density of the deposit, .029 gm/cm³, 1.81 lbs/ft³

N = number of tubes

L = length of each tube, ft

D_1 = diameter with the deposit present, ft

D_2 = diameter when the tube is clean, ft

Solving equation 13 yields:

$$t = 0.00333\text{-ft or } 0.04\text{-in}$$

The mean area of the deposit, if the thickness of the deposit is small compared to the diameter, may be found from the following:

$$A_d = \frac{NL\pi}{2} (D_1 + D_2) \quad (14)$$

The calculated value of A_d for this example is 2051 ft^2

The inside area, A , of the 2000 tubes is 2219 ft^2

The thermal conductivity of the deposit may be calculated from the following:

$$K_d = \frac{t}{A_d \left(\left(\frac{\Delta T_{lm}}{q} \right)_D - \left(\frac{\Delta T_{lm}}{q} \right)_C \right)} \quad (15)$$

where all the symbols refer to experimentally measured quantities. The value for K_d is $0.14 \text{ Btu/hr.ft}^2\text{°F/ft}$. The heat transfer resistance when the 0.04-in thick deposit is present is:

$$\left(\frac{1}{UA}\right)_D = \frac{1}{\left(\frac{10 \text{ Btu}}{\text{hr.ft}^2\text{°F/ft}}\right)(2219)} + \left(\frac{.00333 \text{ ft}}{\left(\frac{.14 \text{ Btu}}{\text{hr.ft}^2\text{°F/ft}}\right)(2051 \text{ ft}^2)}\right) \quad (16)$$

$$\left(\frac{1}{UA}\right)_D = 0.0000451 + 0.00001160$$

$$\left(\frac{1}{UA}\right)_D = .0000567$$

The value of U_D can be calculated now and is found to be 7.95 Btu/hr.ft²°F; i.e., 20% less than the clean heat transfer coefficient for the exchanger. If more sodium had been deposited and the resultant deposit became twice as thick, U_D would equal 6.60 Btu/hr.ft²°F; i.e., 34% less than the clean heat transfer coefficient for the exchanger. If less sodium had been deposited and the resultant deposit was one half as thick as the original example, U_D would equal $\frac{8.85 \text{ Btu}}{\text{hr.ft}^2\text{°F}}$, i.e., 11% less than the clean heat transfer coefficient for the exchanger.

The effect of any uncertainty in the HACL determination of the density of the sodium oxide deposit is small and can be calculated from equations 12-16. It has already been assumed that the full scale FFTF deposit will have the same density as the experimental deposit. If the density was 3.62 lb Na/ft³ instead of 1.81 lb Na/ft³, the thermal conductivity would become 0.0690 Btu/hr.ft²(°F/ft). For 6.125-lb sodium deposited, the thickness would be 0.001592-ft and the mean area of the deposit

would be 2139 ft². Recalculating U_D yields a value of 8.00 Btu/hr.ft²°F which is only 5% higher than the original value of 7.95 Btu/hr.ft²°F confirming the statement that a small error in the density figure will not greatly affect the heat exchange calculation.

It is possible that the density and composition of the FFTF deposit may differ from the experimental deposit. The following can be used to calculate the Na₂O volume fraction of the deposit:

$$V = 1 - \frac{\rho_{Na_2O} - \rho}{\rho_{Na_2O} - \rho_{N_2}}$$

Where:

ρ_{Na_2O} = true density of sodium oxide, lb/ft³

ρ = bulk density of the deposit, lb/ft³

ρ_{N_2} = density of nitrogen, lb/ft³

From the above, it can be calculated that only about 1.7% of the volume of the deposit is Na₂O, the remainder being N₂. Various papers ^{6,7,8} indicate that the thermal conductivity of a powder with such a low volume fraction of solids depends mainly on the type of gas and not on the type of solid material. So long as the bulk density of the deposit is the same as the bulk density of the experimental deposit, it should make little difference whether it

is Na_2O , Na_2O_2 , Na, or some mixture. If the density of the actual deposit is greater than the density in the HACL experiments, then the thermal conductivity will be higher and the deposit thinner. Both factors will mean that the heat exchanger will perform better than the design. Similarly, if the density of the FFTF deposit is less than the experimental deposit, the thermal conductivity will be lower. The percentage change in the thermal conductivity should be less than half the percentage change in the density.

Information from the literature generally predicts that a powder that is only 1.7 volume percent solids should have a lower thermal conductivity than was found during these experiments. The predicted value for the thermal conductivity of the sodium oxide deposit is about $.02 \text{ Btu/hr.ft}^2\text{°F/ft}$, just a little higher than nitrogen which is $.0155 \text{ Btu/hr.ft}^2\text{°F/ft}$. However, predictions may not be accurate since they do not consider the irregular shapes of the particle, which could change the amount of heat conducted between the particles. Our value may be higher than the predicted value because we assumed that the heat transfer coefficient between the gas and the clean tube wall is almost the same as the heat transfer coefficient between the gas and the sodium oxide deposit. If the heat transfer coefficient between the gas and the sodium oxide deposit was higher, then it would cause our value for the thermal conductivity to be high. However, if the same assumption

is made in the design of the full scale heat exchanger, a thermal conductivity of $.14 \text{ Btu/hr.ft}^2\text{°F/ft}$ should represent the situation with sufficient accuracy.

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Adsorption of Argon on Activated Charcoal

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Introduction

The argon adsorption studies reported here were primarily designed to provide design data for the removal of ^{41}Ar in the FFTF fission gas adsorption beds. Over the range of temperatures and pressures of interest for the FFTF design the measured values of the adsorption coefficient for argon ranged from 0.1 to 0.3 liters(STP)/gm charcoal. Several months after these data were taken, large scale experimental tests at Hanford, Washington, confirmed the applicability of this laboratory scale data.

Argon adsorption data also important to a theoretical understanding of the nature of krypton and xenon adsorption from an argon carrier gas. Use of the analysis made possible by this data permits a far more accurate prediction of the effects of temperature and pressure on fission gas adsorption from an argon carrier gas.

Experimental

The test system used here has been described⁽¹⁾. In these earlier tests, either ^{85}Kr or ^{133}Xe was injected into a stream of argon carrier gas and the adsorption coefficients of these isotopes calculated from their breakthrough times in passing through a bed of charcoal maintained at the desired temperature and pressure. We could have used ^{41}Ar in the same system to determine the

adsorption coefficient for argon, but it was far simpler, after allowing the beds to reach equilibrium with argon, to measure the volume of argon released from the bed as the bed passed from test conditions to ambient temperature and pressure. There would be about 7 cc argon remaining per gram of charcoal⁽²⁾ at the end of each test run and this value was added from the test data to give the total quantity of argon - measured at STP - adsorbed on the charcoal at the indicated temperature and pressure. Correction factors for the dead volume of the test system were obtained by carrying out similar tests using helium in place of the argon adsorbate.

Fig. 2-1 shows the test apparatus. The sorbent bed used in these experiments was 21.3 grams of 12 x 30 mesh Pittsburgh PCB charcoal contained in a 6 inch by 3/4 inch diameter iron pipe. The argon, obtained from Union Carbide Co. (Linde Division) was at least 99.96% (by volume) argon.

Discussion of Results

The primary objective of this study - determination of the adsorption coefficients for argon on activated charcoal - is given in Fig. 2-2. These measurements were made across the range of temperatures and pressures to be employed in the FFTF charcoal adsorption beds and thus should prove useful for design calculations. As expected, the adsorption coefficient increased as temperature decreased. The effect of pressure, however, was less noticeable at the lower temperatures. At -75°C, increasing the

2-3

FIGURE 2-1. SCHEMATIC DRAWING OF EXPERIMENTAL APPARATUS.

FIGURE 2-2. ARGON ADSORPTION COEFFICIENTS.
SORBENT: PITTSBURGH PCB CHARCOAL.

pressure from 3.7 to 10.5 atmospheres increased the adsorption coefficient from 0.12 to 0.175 liters/gm charcoal, but at -140°C the adsorption coefficient changed from 0.255 to only 0.30 liters/gm as the pressure increased from 1.65 to 10.5 atmospheres.

It is interesting to note that the data show saturation effects: the quantity of adsorbed argon, divided by the absolute pressure, decreases with increasing pressure. This effect is attributed to the selective coverage (or saturation) of the more active adsorption sites by argon at the lower pressures. Saturation effects in the adsorption of argon on Pittsburgh PCB activated charcoal was reported earlier by Grant and Manes⁽³⁾. Their study, however, was carried out at subatmospheric pressures and, therefore, not directly applicable to FFF design.

When the procedure of Polanyi⁽⁴⁾ is used to plot our data, all points fall on a single line (See Fig. 2-3). In Fig. 2-3, the ordinate is the quantity of argon adsorbed per gram of charcoal, expressed as volume of liquid argon at a temperature at which the vapor pressure is the adsorption pressure. The abscissa $(P/P_s) \log_{10}(f_s/f)$ is proportional to c , the work required to compress the unadsorbed gas into unit volume of adsorbed phase. In this expression:

T = absolute temperature, $^{\circ}\text{K}$

V_b = volume of a mole of liquefied carrier gas at the adsorption pressure

f_s = fugacity of liquefied carrier gas at temperature of adsorption, atmospheres

f = fugacity of carrier gas, atmospheres.

FIGURE 23. POLANYI PLOT OF ARGON ADSORPTION ON PITTSBURGH PCB CHARCOAL.

At temperatures above the critical temperature the pressure (or the fugacity), of the liquid phase must be extrapolated. Over what range of temperatures this extrapolation can be carried out is not known, but for nitrogen⁽⁵⁾, similar calculations have nearly been extended to room temperature.

The information necessary to convert our adsorption data to a Polanyi plot is shown in Figs 2-4 & 2-5, which give respectively the density and fugacity of liquid argon.

The potential theory of Polanyi is essentially a thermodynamic theory which does not demand a precise physical description of the mechanism of adsorption⁽⁴⁾. Put into its simplest terms, this theory states that ϕ , the volume of material in the adsorbed phase per unit weight of stationary phase, is a single valued function of ϵ . Fig. 2-6 shows the best fitting line for our data compared with a similar line for the data of Grant and Manes⁽³⁾. These lines are very close to each other, further justifying the use of the Polanyi correlation for the temperatures and pressures under consideration. This agreement is important for this study because it shows that the Polanyi procedure can be used to correlate argon adsorption data over a wide range of conditions. This has the practical result of permitting the argon adsorption coefficients to be predicted with some confidence even for temperatures and pressures where no data are available.

Application to Krypton Adsorption Data

Previously it was found that the adsorption of krypton from

FIGURE 2-4 DENSITY OF LIQUID ARGON IN EQUILIBRIUM WITH THE VAPOR.

FIGURE 26 COMPARISON OF ADSORPTION MEASUREMENTS.

an argon carrier gas can give rise to a strange result: at a sufficiently low temperature the adsorption of krypton decreases with increase in pressure. From the standpoint of reactor safety, the result is quite important, for increasing the pressure of the carrier gas actually degrades the ability of the bed to retain krypton and xenon. In the earlier report, it was suggested that this was related to phenomena associated with the critical temperatures. The present analysis, however, suggests that this is more likely the result of adsorbed argon interfering with the adsorption of krypton.

Following this suggestion we plotted the adsorption coefficient (liters of adsorbed krypton gas at STP per gram of charcoal per atmosphere of krypton) as a function of the volume of liquid argon adsorbed on the charcoal (See Fig. 2-7). The estimates for krypton adsorption at zero argon coverage were obtained by using adsorption data for krypton in a helium carrier gas. The resulting plot of this data is a family of parallel curves.

Analysis of the data in Fig. 2-7 shows that this adsorption of argon is the explanation of the unusual pressure effect reported earlier. In Fig. 2-7, we have a series of parallel curves in place of adsorption isotherms which may rise or fall with respect with pressure. This consistency can be accomplished only if the adsorption of argon is the cause of the irregularities reported before.

Also in Fig. 2-7 we see the very strong effect that adsorbed argon has in reducing the adsorption of krypton - the effective

FIGURE 2-7. EFFECT OF ADSORBED ARGON ON THE KRYPTON ADSORPTION COEFFICIENT.

adsorption coefficients are reduced by factors of 100 to 10,000 over the temperatures and pressures covered experimentally.

Finally, we believe we have a useful procedure for predicting the interference of other carrier gases on the adsorption of fission gases. An accurate correlation of this effect will make the design of fission gas adsorption beds far more precise.

Comparison with large-scale argon adsorption data

Several months after this adsorption data was obtained, Kabele⁽⁶⁾ ran pilot plant studies of the adsorption of argon on charcoal. His experimental procedure used the delay time of a pulse of ^{41}Ar injected into the bed. Fig. 2-8 shows his calculated argon adsorption coefficients superimposed with data taken from this laboratory. Within experimental error there is no difference between these adsorption coefficients.

FIGURE 2. ARGON ADSORPTION COEFFICIENT AS DETERMINED BY KABELE. REFERENCE 6

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Chemical Analysis of Sodium Aerosols

Avram Gold

A scheme was worked out to determine the chemical composition of a sodium aerosol generated in a controlled atmosphere of nitrogen containing < 2% O_2 . The composition of the aerosol was known from previous work to be primarily sodium oxide (Na_2O) with small amounts of sodium peroxide (Na_2O_2) and carbonate (Na_2CO_3).

Since Na_2O_2 is not stable in alkaline solution:

a volumetric determination of O_2 liberated upon solution of the analytical sample in a closed system was deemed most suitable for peroxide determination. The $NaOH-Na_2CO_3$ mixture remaining could then be determined by titration to two end points either colorimetrically (with phenolphthalein and methyl orange) or with a pH meter.

The composition of the aerosol could then be determined as follows:

Peroxide:

$$\text{Moles } O_2 = \frac{PV}{RT}$$

P = Atmospheric Pressure
V = Volume of gas collected
R = gas constant
T = Room temperature ($^{\circ}K$)

$$\text{Moles } Na_2O_2 = 2 \times \text{moles } O_2 \text{ (from equation 1)}$$

Carbonate:

Moles Na_2CO_3 = normality of HCl x volume (l) of acid to reach 2nd end point from first end point.

Hydroxide (Oxide):

Moles NaOH = normality of HCl x volume (l) required to reach 1st end point

- 2 x moles Na_2O_2 (from equation 1)

- moles carbonate.

A diagram of the apparatus is shown in Fig 3-1.

The sample was collected in the 3-necked flask (with stopcocks 1 and 2 in place and a stopper in the middle neck) by drawing the aerosol through the apparatus from stopcock 1 to 2. The aerosol is trapped on the glass wool plug. Originally, stopcocks with 1mm bores were used, but with the narrow bore, an adequate flow rate was hard to maintain and samples of only 100-150 mg could be collected. Stopcocks with 4mm bores have been substituted and it is expected that samples on the order of 1g may be collected.

After collection, dry nitrogen was flushed through the system via stopcock 2, exiting through the middle neck while the dropping funnel (containing ~ 10ml distilled water) and the line to the gas buret were put in place. The nitrogen was then shut off and the system equilibrated with atmospheric pressure through stopcock 3. The system was closed to the atmosphere and the water added. Analyses of mixtures of known composition indicated that complete decomposition

FIGURE 3-1. ANALYSIS APPARATUS FOR AEROSOL.

of Na_2O_2 would require boiling the solution for two 5 minute intervals. Blank runs on samples containing no peroxide showed that the volume readings on the gas buret would return to 0.2 to 0.5ml after ~ 20 minutes for thermal equilibration. At 23°, this corresponds to an error of +1 to +3mg Na_2O_2 . Since this is an absolute error, its significance decreases with sample size and increasing Na_2O_2 content.

After boiling the sample as described, allowing the temperature to equilibrate about 20 minutes and recording the volume of O_2 the contents of the 3-necked flask were thoroughly rinsed into a flask or beaker for determination of Na_2CO_3 -NaOH by titration.

Fig. 3-2 shows the pH meter titration curve for a 404mg sample of fresh reagent grade NaOH labeled 97%min NaOH. A reasonable estimate is that a second end point within 0.4ml of the first could still be detected, corresponding to ~ 2mg Na_2CO_3 . For a 1g sample this amount corresponds to a 0.2% limit of detection.

Future aerosol experiments will utilize an atmosphere containing little or no oxygen resulting in the possibility of metallic sodium in the aerosol. The above analytical scheme can be accommodated to analyze for sodium. Upon solution in water, sodium will react

to evolve hydrogen which will be collected in the gas buret along with any O_2 from peroxide present. The gas in the buret

RUN NO. 3	404.6 MG.
	WEIGHED SAMPLE
ML. TO e.p. NO. 1	1.72 + 19.60
ML. TO e.p. NO. 2	1.39
MG. Na_2CO_3	7.4 MG.
MG. NaOH	393 MG.
TOTAL	400.4 MG.
% WT. Na_2CO_3	1.8%

FIGURE 3-2. NaOH - Na_2CO_3 TITRATION CURVE.

may be quantitatively analyzed for H_2 and O_2 by GPC calibrated with a standard sample.

There is a possibility that if Na_2O_2 , Na_2O , and metallic Na coexist in the aerosol, the reaction

would occur if Na did not react quickly enough with water. This possibility might be investigated by adding metallic Na to an aqueous solution containing a known amount of sodium oxide and running the analysis. The extent to which reaction (2) occurs could be determined by the amount of gas liberated and GPC analysis of the gas for H_2 and O_2 .

Table 3-1

Composition of Aerosol Samples Analyzed.

	mg	mg	mg
Na_2O_2	15	36	9
NaOH	176	188	65
Na_2CO_3	3	18	5.3
	Sample 1	Sample 2	Sample 3

CONSULTATIONS & PUBLICATIONS

On November 28, 1972, Mr. Thomas Kabele of the Westinghouse-Hanford, visited Boston to confer with members of the Harvard Air Cleaning Laboratory on the latest design considerations for the noble gas adsorption system for the FFTF. The major discussion was related to the effects of nitrogen carrier gas on the adsorption of krypton and xenon as a function of temperature and pressure.

Dr. First conferred on a weekly basis with Mr. Wayne Madsen and others at Bechtel Corp., San Francisco, regarding progress on sodium aerosol studies for the FFTF H & V systems throughout this period.

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