DATE ISSUED DEC 3 1971

ORNL
MASTER COPY

OAK RIDGE NATIONAL LABORATORY
OPERATED BY
UNION CARBIDE CORPORATION
NUCLEAR DIVISION
POST OFFICE BOX X
OAK RIDGE, TENNESSEE 37830

~~Internal Use Only~~

ORNL
CENTRAL FILES NUMBER
71-8-10

DATE: August 6, 1971

SUBJECT: A Review of Possible Choices for Secondary Coolants for Molten Salt Reactors

TO: Distribution

FROM: J. P. Sanders

Abstract

A review has been made of various choices for secondary coolants in a molten salt reactor system which has as its primary fuel salt a ^{7}LiF-BeF_2-ThF_4-UF_4 mixture. Special consideration was given to inhibiting the migration of tritium from the primary salt through the secondary salt to the steam system. At the same time the performance characteristics of these coolants, the associated inventory costs, their compatibility with the fuel salt, steam, and the cell environment, and the materials required to contain the coolants were summarized for future reference. Three groups of coolants were considered; these were (a) molten salts and sodium hydroxide, (b) liquid metals, and (c) gases at a high or moderate pressure.

Of the coolants which were considered, there appeared to be no real incentive for a choice other than the sodium fluoroborate which is currently being studied. It appears that it might be possible to contain a small concentration of hydroxl ion in complex in this coolant which could be continuously removed and replaced to function as a trap for the tritium. A present disadvantage of the sodium fluoroborate appears to be its high liquidus temperature of 725°F. A lower melting point fluoride mix of LiF, NaF and BeF_2 with a liquidus temperature of 640°F or a mix of LiCl and KCl with a liquidus temperature of 680°F appear to be alternatives.

[redacted]

Full release per David Hamrin 2/4/04

Sodium with a melting point of 208°F is the best choice of the liquid metals; several design problems are introduced through the choice of sodium as a secondary coolant and no real incentive exists to select this as a coolant unless the lower melting temperature is desired. Of the gases, helium is the best choice; however, with this, or any other gas, it is necessary to design a secondary loop which operates at relatively high pressures. Accurate evaluation of helium as a secondary coolant will require considerable investigation into possible designs for such a secondary system.

Keywords: *review, *coolants, *MSBR, *secondary salts, physical properties, performance, tritium, capital costs, materials, inventories, fluoroborates, fluorides, sodium hydroxide, chlorides, liquid metal, gases.

[redacted]

CONTENTS

		Page
1.	INTRODUCTION	1
2.	PHYSICAL PROPERTY VALUES	4
3.	COMPARISON OF PHYSICAL PERFORMANCE OF COOLANTS	8
4.	INVENTORY COSTS	13
5.	THE SIGNIFICANCE OF THE MELTING OR LIQUIDUS TEMPERATURE OF THE SECONDARY COOLANT IN MOLTEN-SALT REACTOR SYSTEM DESIGN	16
6.	EFFECTIVENESS OF COOLANTS IN TRITIUM HOLDUP	22
7.	COMPATIBILITY OF SECONDARY COOLANTS WITH THE PRIMARY SALT, STEAM, AND THE CELL ENVIRONMENT	28
	7.1 Compatibility With the Primary Fluid	28
	7.1.1 With the molten salts as secondary coolants	29
	7.1.1.1 Sodium fluoroborate	29
	7.1.1.2 Lithium fluoride–beryllium fluoride	30
	7.1.1.3 FLINAK and the "low melting point" fluoride	30
	7.1.1.4 The chloride salts	31
	7.1.1.5 Sodium hydroxide, the nitrates, and the carbonates	31
	7.1.2 With liquid metals as secondary coolants	33
	7.1.2.1 Sodium and NaK	33
	7.1.2.2 Bismuth and lead	34
	7.1.2.3 Mercury	34
	7.1.3 With gases as secondary coolants	34
	7.1.3.1 Helium	35
	7.1.3.2 Hydrogen	35
	7.1.3.3 Water vapor	36
	7.1.3.4 Air	36
	7.1.3.5 Nitrogen	36
	7.1.3.6 Carbon dioxide	36
	7.1.3.7 Conclusions	36
	7.2 Compatibility with Steam	37
	7.3 Compatibility with the Cell Environment	37

Page

8. MATERIALS OF CONTAINMENT 38

8.1 Containment Materials for the Various Secondary Coolant Systems 38

8.1.1 Materials of construction for molten salts as secondary coolants 40

8.1.1.1 Fluoride salts 40

8.1.1.2 Chloride salts 42

8.1.1.3 Sodium hydroxide 43

8.1.1.4 Nitrates 45

8.1.1.5 Carbonates 45

8.1.2 Materials of construction for liquid metals as secondary coolants 45

8.1.2.1 Sodium 46

8.1.2.2 Sodium–potassium (NaK) 46

8.1.2.3 Bismuth 46

8.1.2.4 Bismuth–lead 47

8.1.2.5 Lead 47

8.1.2.6 Mercury 47

8.1.3 Materials of construction for gases as secondary coolants 48

8.1.3.1 Helium 48

8.1.3.2 Hydrogen 48

8.1.3.3 Water vapor 48

8.1.3.4 Air 48

8.1.3.5 Nitrogen 48

8.1.3.6 Carbon dioxide 48

8.2 Containment Materials for Various Secondary Coolants in Conjunction With the Primary Salt 49

8.2.1 Materials with molten salts as secondary coolants 49

8.2.1.1 Fluoride salts 49

8.2.1.2 Chloride salts 51

8.2.1.3 Sodium hydroxide 51

8.2.1.4 Nitrates and carbonates 51

Page

8.2.2 Materials with liquid metals as secondary coolants 51
8.2.2.1 Sodium and NaK 51
8.2.2.2 Bismuth and bismuth–lead 51
8.2.2.3 Mercury 51
8.2.2.4 Lead 51
8.2.3 Materials of construction for gases as secondary coolants 52
8.3 Containment Materials for Various Secondary Coolants in Conjunction With Steam 52
8.3.1 Materials with molten salts as secondary coolants 52
8.3.1.1 Fluoride salts 52
8.3.1.2 Chloride salts 53
8.3.1.3 Sodium hydroxide 53
8.3.1.4 Nitrates and carbonates 53
8.3.2 Materials with liquid metals as secondary coolants 53
8.3.2.1 Sodium and NaK 53
8.3.2.2 Bismuth, lead, and bismuth–lead 53
8.3.2.3 Mercury 53
8.3.3 Materials with gases as secondary coolants 53
8.4 Literature Sources 54
8.5 Summary and Conclusions Concerning Materials of Construction 54
9. OTHER POSSIBLE COOLANTS OMITTED FROM THE PREVIOUS PRESENTATION 61
9.1 Alternate Fluoride Salts 61
9.2 The Cyanides 63
9.3 Organic Secondary Coolants 63
9.4 Sulfur 63
9.5 Haloaluminates 64
10. SUMMARY AND CONCLUSIONS 65
11. ACKNOWLEDGMENTS 70

LIST OF TABLES

		Page
Table 1.	Possible Choices for Molten Salt Reactor Secondary Coolants Which Were Considered in this Study	3
Table 2.	Physical Properties of the Coolants at 1000°F (538°C)	6
Table 3.	Melting Temperatures for the Coolants	7
Table 4.	Comparison Factors for Secondary Coolants at 1000°F..	12
Table 5.	Cost of Secondary Coolants, Estimated Total Inventories, and Estimated Total Inventory Costs	15
Table 6.	Allowable Stresses and Design Pressures for Various Materials	56
Table 7.	Performance of Materials in Contact with the Secondary Coolant Only	58
Table 8.	Performance of Materials in Contact with the Secondary Coolant and the Fuel Salt	59
Table 9.	Performance of Materials in Contact with the Secondary Coolant and with Steam	60

1. INTRODUCTION

A review of possible choices for secondary coolants for molten-salt reactors has been initiated. Several problems prompted this coolant study. Sodium fluoroborate, which had been investigated most extensively as a possible secondary coolant, seemed to be more corrosive than was desirable; there was concern about the effects of the mixing of this coolant with the fuel salt in the event of a primary heat exchanger tube rupture; and the pressure of the required BF_3 cover gas would be greater than one atmosphere at temperatures of 1300°F and above which might develop under abnormal operating conditions. An additional problem which prompted this study was the consideration of the secondary coolant as a tritium trap or a tritium reservoir for that tritium which migrated from the primary salt through the heat transfer area of the primary heat exchanger.

These have not been the only characteristics of the secondary coolant considered in this study; an effort has been made to bring together as much additional information from all possible sources which would concern the performance of the secondary coolant in the molten-salt reactor system. This information includes the physical properties of the coolant; possible materials of containment for the coolant itself and for the coolant in conjunction with both the primary salt and with steam; the compatibility of the coolant with the primary salt, the steam, and the reactor cell environment; the cost and availability of the coolant; safety considerations in the use and handling of the coolant; and any other general information.

The ultimate purpose of this study is to evaluate the various coolants in a reactor system design which will be optimized for the characteristics of that coolant. Since it will not be practical to develop a design for each choice for the secondary coolant, the coolants have been grouped into three categories, viz., molten salts, liquid metals, and gases, and it is postulated that a design which will be developed for the category will be, at least, partially optimum for each of the coolants in that category. A comparison of the characteristics of each coolant in the optimized design of the category should then provide a basis for the selection of the ultimate optimum coolant.

As the first phase of this study, the characteristics of the more obvious choices for coolants in each of the three categories have been collected and tabulated. The choices include nine molten-salt mixtures, six liquid metal coolants or mixtures, and six different gases each considered as a high-pressure gas (1000 psia) and a low-pressure gas (250 psia). A list of these choices is presented in Table 1 which gives the composition of the mixtures following a special designation which will be used in referencing the particular coolant in subsequent tabulations. The designations have been selected to be compatible with the characters printed by the standard teletype machine so that subsequent tabulated data can be printed by this unit.

This report has received an initial review by several members of the MSR Program and has been revised to incorporate many of their comments. It is issued at this time as a Central Files (CF) report for comment by the entire staff prior to final revision and publication as a Technical Memorandum (TM). Comments or corrections that will make the report more useful will be appreciated. All information in the report should be considered tentative until the revised report is issued.

Table 1. Possible Choices for Molten Salt Reactor Secondary Coolants Which Were Considered in this Study

Designation	Composition
NA BF4-NA F	92 m/o $NaBF_4$, 8 m/o NaF
LI F--BE F2	66 m/o LiF, 34 m/o BeF_2
FLINAK	46.5 m/o LiF, 11.5 m/o NaF, 42.0 m/o KF
NA+K F--ZR F4	10.0 m/o NaF, 48.2 m/o KF, 42.0 m/o ZrF_4
NA ØH	100 o/o NaOH
LI CL--K CL	59.0 m/o LiCl, 41.0 m/o KCl
NITRATES	6.9 m/o $NaNO_3$, 48.5 m/o $NaNO_2$, 44.6 m/o KNO_3
LMP FLUORIDES	35.0 m/o LiF, 27.0 m/o NaF, 38.0 m/o BeF_2
CARBØNATES	43.5 m/o Li_2CO_3, 31.5 m/o Na_2CO_3, 25.0 m/o K_2CO_3
SØDIUM	100 o/o Na
NAK	44 w/o K, 56 w/o Na
BISMUTH	100 o/o Bi
PB--BI	55 w/o Bi, 45 w/o Pb
MERCURY	100 o/o Hg
LEAD	100 o/o Pb
HELIUM(HP)	100 o/o He at 1000 psia
HELIUM(LP)	100 o/o He at 250 psia
HYDRØGEN(HP)	100 o/o H_2 at 1000 psia
HYDRØGEN(LP)	100 o/o H_2 at 250 psia
WATER(HP)	100 o/o H_2O at 1000 psia
WATER(LP)	100 o/o H_2O at 250 psia
AIR(HP)	Air (79 m/o N_2, 21 m/o O_2) at 1000 psia
AIR(LP)	Air (79 m/o N_2, 21 m/o O_2) at 250 psia
NITRØGEN(HP)	100 o/o N_2 at 1000 psia
NITRØGEN(LP)	100 o/o N_2 at 250 psia
CØ2(HP)	100 o/o CO_2 at 1000 psia
CØ2(LP)	100 o/o CO_2 at 250 psia

Note: m/o designates mole per cent; w/o designates weight per cent; where the designation is not significant as for pure components and compounds, o/o indicates per cent.

2. PHYSICAL PROPERTY VALUES

Physical property values for each of the coolants are presented in Table 2. With the exception of mercury, all physical properties are given for the coolant at 1000°F; property values for mercury are given for a temperature of 600°F because values were not readily available at the higher temperature and no accurate method of extrapolation to this temperature existed.

For the most part, physical property values for the molten-salt mixtures were obtained from the following references:

1. S. Cantor, Editor, "Physical Properties of Molten-Salt Reactor Fuel, Coolant, and Flush Salts," USAEC Report ORNL-TM-2316, Oak Ridge National Laboratory, August 1968.
2. J. R. McWherter, "MSBR Mark I Primary and Secondary Salts and their Physical Properties," internal memorandum, MSR 68-135, Rev. 1, Sept. 27, 1968; revised Feb. 12, 1969.
3. H. A. McLain, "Revised MSBR Secondary Salt Viscosity Correlations," internal memorandum, MSR 69-103, Oct. 27, 1969.
4. J. W. Cooke, internal memorandum, MSR 68-123.
5. H. F. McDuffie, et al., "Assessment of Molten Salts as Intermediate Coolants for LMFBR's," USAEC Report ORNL-TM-2696, Oak Ridge National Laboratory, Sept. 3, 1969.
6. S. McLain and J. H. Martens, Editors, Reactor Handbook, 2nd Ed., Interscience Publishers, New York (1964).
7. H. W. Hoffman and S. I. Cohen, "Fused Salt Heat Transfer--Part III: Forced-Convection Heat Transfer in Circular Tubes Containing the Salt Mixture $NaNO_2$–$NaNO_3$–KNO_3," USAEC Report ORNL-2433, Oak Ridge National Laboratory, March 1, 1960.

Additional information for the liquid metal properties was obtained from:

8. John G. Yevick, Editor, Fast Reactor Technology: Plant Design, The MIT Press (1966).

Gas properties were obtained from:

9. J. Hilsenrath and Y. S. Touloukian, "The Viscosity, Thermal Conductivity, and Prandtl Number for Air, O_2, N_2, NO, H_2, CO, CO_2, H_2O, He, and A," Trans. ASME, August 1954, pp. 967–985.
10. National Bureau of Standards, "Tables of Thermal Properties of Gases," Circular 564.
11. International Critical Tables.

12. Fluid Properties Handbook, Missile and Space System, Douglas Aircraft Company, Inc.

13. C. A. Meyer, et al., Thermodynamic and Transport Properties of Steam, ASME, 1967.

14. E.R.G. Eckert and R. M. Drake, Jr., Heat and Mass Transfer, 2nd Ed., McGraw-Hill Book Company, Inc., New York (1959).

Most of the physical property data are well established with the exception of the thermal conductivities. For some fluids, various references indicated values for the thermal conductivity of a certain coolant which differed by a factor of 4 or more. In these cases, the value of more recent origin or of the more careful investigator was selected.

All of the last group of proposed coolants are gases at normal ambient temperatures (or slightly above ambient for CO_2). The melting point for the remainder of the coolants is given in Table 3. With the exception of mercury, all of the coolants listed in Table 3 have vapor pressure less than 1 atmosphere at the normal operating temperatures of the secondary loop of the current design for MSR. Mercury has a vapor pressure of 1 atmosphere at 674°F and a vapor pressure of 12 atmospheres at 1000°F.

Table 2. Physical Properties of the Coolants at 1000F (538C)

Secondary Coolant	Density (lb/cu ft)	Viscosity (lb/ft-hr)	Thermal Conductivity (Btu/hr-ft-F)	Heat Capacity (Btu/lb-F)
NA BF4-NA F	116.90	3.355	.2660	.3600
LI F--BE F2	124.06	28.780	.5780	.5700
FLINAK	133.36	16.560	.7500	.4410
NA+K F-ZR F4	159.82	22.730	.5780	.2500
NA OH	91.52	3.797	.6048	.5074
LI CL--K CL	100.29	4.707	.4870	.3015
NITRATES	108.33	1.030	.1900	.3730
LMP FLUORIDE	124.80	28.180	.4000	.5900
CARBONATE	125.00	18.272	.2000	.4130
SODIUM	51.20	.558	37.80	.3350
NAK	48.80	.479	16.40	.3070
BISMUTH	608.00	4.320	9.00	.0369
PB-BI	623.00	3.010	8.14	.0333
MERCURY(600F)	802.00	2.090	8.10	.0320
LEAD	650.00	4.100	8.90	.0346
HELIUM(HP)	.25510	.0958	.1740	1.2424
HELIUM(LP)	.06378	.0958	.1720	1.2421
HYDROGEN(HP)	.12868	.0425	.2380	3.4800
HYDROGEN(LP)	.03217	.0425	.2380	3.4775
WATER(HP)	1.20550	.0741	.0460	.5650
WATER(LP)	.29085	.0730	.0440	.5250
AIR(HP)	1.85100	.0877	.0330	.2650
AIR(LP)	.46300	.0800	.0320	.2640
NITROGEN(HP)	1.78800	.0930	.0330	.2770
NITROGEN(LP)	.44700	.0900	.0320	.2750
CO2(HP)	2.80900	.0810	.0381	.2860
CO2(LP)	.70200	.0800	.0380	.2810

Table 3. Melting Temperatures for the Coolants

Secondary Coolant	Melting Temperature (Degrees F)
NA BF4-NA F	725
LI F--BE F2	856
FLINAK	851
NA+K F--ZR F4	725
NA OH	318
LI CL--K CL	680
NITRATES	288
LMP FLUORIDE	640
CARBONATE	747
SODIUM	208
NAK	66
BISMUTH	520
PB-BI	257
MERCURY	-38
LEAD	621

For the molten salt mixtures, the melting temperature that is indicated is the liquidus temperature for the composition in Table 1.

3. COMPARISON OF PHYSICAL PERFORMANCE OF COOLANTS

In order to compare the performance of the various choices of coolants within any one group on the basis of their physical properties alone, certain factors have been formulated. It was assumed that the two aspects of the coolant system which would affect the economics of the reactor operation were the heat transfer area requirements and the circulator power requirements.

If we assume that the same temperature regime is maintained for all reactor designs employing all choices of coolants within a group, then the heat transfer area requirements in both the primary and secondary heat exchangers are related directly to the reciprocal of the film heat transfer coefficient (neglecting the contribution to the resistance to heat transfer by the tube wall and by the film of fluid on the other side of the wall). According to current designs the secondary coolant will be in the shell of the primary heat exchanger to minimize fuel salt inventory and in the shell of the secondary heat exchanger so that the high pressure steam will be inside the tubes.

The heat transfer coefficient for flow outside of tubes is given by the equation,*

$$\frac{h_m D_o}{k_f} = 0.33 \left(\frac{C_p \mu}{k}\right)_f^{1/3} \left(\frac{D_o G_{max}}{\mu_f}\right)^{0.6} \qquad (1)$$

where h_m is the mean heat transfer coefficient for the tubes in the bundle, D_o is the outside diameter of the tubes in the bundle, k is the thermal conductivity of the fluid, C_p is the heat capacity of the fluid, and μ is the viscosity of the fluid. The subscript f indicates that the fluid properties are to be evaluated at a theoretical film temperature which is defined as the average of the mean bulk fluid temperature and the surface temperature of the tube wall. G_{max} indicates the maximum mass velocity (mass per unit time per unit minimum flow area) of the fluid in the bundle. G_{max} can also be written as ρV_{max} where ρ is the fluid density and V_{max} is the maximum linear velocity of the fluid in the bundle.

*W. H. McAdams, Heat Transmission, 3rd Ed., McGraw-Hill Book Company, Inc., New York (1954), p. 272.

The density of the fluid should be evaluated at the mean bulk fluid temperature since it is a measure of the total momentum in the fluid. It has been suggested that all of the coolant properties can be evaluated at the bulk temperature if the exponent of the Prandtl number ($C_p\mu/k$) is changed to a value of 0.4 when heat is transferred into the fluid and a value of 0.3 when heat is transferred out of the fluid. In the secondary loop, heat is transferred into the coolant in the primary heat exchanger and out of the coolant in the steam generator. Since the area requirements in the primary heat exchanger will probably be more critical in the reactor system design, an exponent of 0.4 will be used. For any given reactor power, the heat load for the various coolant choices will be approximately the same (they will differ only by the differences in pumping power required in this loop), and within any of the three groups of coolants, the temperature regimes will be about the same, the heat transfer area requirement can then be expressed as

$$A \approx \frac{\mu^{0.2} D^{0.4}}{C_p^{0.4}\, k^{0.6}\, \rho^{0.3}\, (\rho V^2)^{0.3}} \qquad (2)$$

If the assumption is made that for all system designs for coolants in the same group the same outside tube diameter and the same work per unit volume (ρV^2) is maintained for all choices within that group, the total heat transfer area requirement can be expressed as follows:

$$A \approx \frac{\mu^{0.2}}{C_p^{0.4}\, k^{0.6}\, \rho^{0.3}} \qquad (3)$$

The assumption that the same work per unit volume exists for the various choices of coolants within a group can be interpreted as assuming that pumping power requirements are similar.

The value of this area factor, based on the values and units indicated in Table 2, is shown for each of the coolant choices in Table 4. These values should not be used for comparing the performance of coolants among the three groups (i.e., between liquid metals and gases or between molten salts and liquid metals); they should only be used as an indication of the relative area requirement of a coolant within a group.

An expression for the work requirement of the circulator in the secondary loop would be the product of the volumetric flow rate and the pressure loss around the loop. If the major contribution to the pressure loss is fluid friction, an empirical expression for the friction factor of the form

$$f \approx \left(\frac{DV\rho}{\mu}\right)^{-0.2} \tag{4}$$

can be used to generate a factor indicating the relative circulator power. For this calculation, in addition to assuming the same equivalent hydraulic diameter for each system, we shall assume the same effective flow area and the same mass velocity (i.e., linear velocity multiplied by density). Implicit in this set of assumptions is that the product of the heat capacity and the temperature change around the loop is a constant. We then find that

$$\text{Work} \approx \frac{\mu^{0.2}}{\rho^2} \tag{5}$$

If we call this the work factor, we find the relative values listed in Table 4. Again the factors among various groups should not be compared.

If for any of the groups of coolants, the area requirements and circulator power requirements are of similar importance, we may combine the equations used above with the assumptions of similar hydraulic diameters and similar mass velocities to get a combined term which has the form

$$\text{Combined} \approx \frac{\mu^{0.40}}{\rho^{2.6} k^{0.6} C_p^{0.4}} \tag{6}$$

Again this factor is listed in Table 4 for the three groups of coolants. It is felt that this factor is the more significant of the three. Note that the last factor cannot be obtained by multiplying the first two since the first was based on the assumption of similar work requirements per unit volume of coolant and the last two were based on similar mass velocities.

If it is assumed that the system is to be designed with similar pressure losses, then the comparison factor reduces to the density multiplied by the heat capacity (this is actually the volumetric heat capacity). The

reciprocal of this product is listed as the transport factor. This indicates, if the pressure gradient around the secondary loop is an important design consideration, a coolant with a low value for the transport factor will be the most favorable choice.

If systems with similar head losses are assumed, then the heat capacity is the important physical property. If the secondary circulator is to be limited by design considerations to some maximum developed head, the fluid with the highest heat capacity will be the most favorable choice.

The Prandtl number also is an indication of the relative ease of heat transport to momentum transport (pressure drop) on a molecular basis. The coolant in any group with the lowest value of the Prandtl number, will obviously contribute the most on a molecular basis to the transfer of heat. Fluids with higher values of the Prandtl number will require more circulator work, adding momentum to the coolant, to achieve the same heat transfer.

Table 4. Comparison Factors for Secondary Coolants at 1000F

Secondary Coolant	Area Factor	Work Factor	Combined Factor	Transport Factor	Prandtl Number
NA BF4-NA F	1.70	1.27	1.502	1.750	4.541
LI F--BE F2	1.34	1.74	1.588	1.041	28.382
FLINAK	1.11	1.35	1.000	1.252	9.737
NA+K F-ZR F4	1.65	1.00	1.040	1.843	9.831
NA OH	1.00	2.13	1.588	1.586	3.186
LI CL--K CL	1.42	1.85	1.914	2.435	2.914
NITRATES	1.66	1.17	1.378	1.822	2.022
LMP FLUORIDE	1.64	1.71	1.908	1.000	41.565
CARBONATE	2.63	1.56	2.793	1.426	37.732
SODIUM	1.00	188.41	116.946	1.496	.00495
NAK	1.68	201.16	213.023	1.713	.00897
BISMUTH	4.10	2.01	2.436	1.144	.01771
PB-BI	4.19	1.78	2.190	1.237	.01231
MERCURY(600F)	3.68	1.00	1.000	1.000	.00826
LEAD	4.11	1.74	2.071	1.141	.01594
HELIUM(HP)	1.75	125.4	122.18	2.535	.6840
HELIUM(LP)	2.66	2005.9	4521.98	10.141	.6918
HYDROGEN(HP)	1.00	418.9	287.07	1.794	.6214
HYDROGEN(LP)	1.52	6701.2	10554.47	7.181	.6210
WATER(HP)	3.17	5.3	5.92	1.180	.9101
WATER(LP)	5.12	91.4	250.96	5.261	.8710
AIR(HP)	4.76	2.3	3.43	1.638	.7043
AIR(LP)	7.23	36.7	123.86	6.573	.6600
NITROGEN(HP)	4.78	2.5	3.78	1.622	.7806
NITROGEN(LP)	7.36	40.3	139.96	6.535	.7734
CO2(HP)	3.68	1.0	1.00	1.000	.6080
CO2(LP)	5.61	16.0	36.93	4.073	.5916

Minimum Values of the Factors in Each Group are:

Factor	Molten Salts	Liquid Metals	Gases
Area	5.9748E-01	4.7867E-02	1.4133E+00
Work	7.3124E-05	1.8017E-06	7.6664E-02
Combined	1.5127E-05	4.2663E-08	2.9245E-01
Transport	1.3581E-02	3.8965E-02	1.2448E+00

4. INVENTORY COSTS

An important consideration in making a choice among some of the possible secondary coolants is the inventory charge associated with the use of that coolant. This total charge is a product of the total volume of secondary system, the density of the secondary coolant, and the cost of the coolant per unit weight. The product of the first two terms is, of course, the total weight of coolant which is required for the system.

In Table 5, an estimate is shown for the relative volumes of secondary systems for 1000-MW(e) reactors for the various choices of coolant. These estimates are based on extrapolations from available designs or design estimates plus a consideration of the "Area Factor" and the "Combined Factor" of Table 4. Multiplication of this estimated volume by the densities in Table 2 produces the estimated weight of the coolant inventory which is shown in Table 5.

The unit costs for the coolants were obtained with the assistance of J. M. Campbell of the Union Carbide Purchasing Department; he obtained preliminary bids from vendors where possible. All costs exclude shipping costs; however, the incremental difference in cost which would be made by including this factor is probably less than some of the present cost uncertainties. Most of the vendors were not prepared to quote on the basis of the shipment of quantities as large as those indicated in the inventory lists. Bids indicated that for most items the unit cost would decrease as the size of the order increased; where this factor appeared to be significant, extrapolation of the available information was made to estimate the cost in quantities as indicated in Table 5.

For some of the compounds, very small differences in the amount of impurities made quite significant changes (by a factor of 10) in the unit cost of the material. Since it was assumed that any reactor plant would have some continuous processing facilities for the purification of the coolant, choices were made to accept the compound with slight impurities if it appeared that the impurities could be removed with relative ease during chemical processing and if it appeared that the impurities would not be detrimental to the secondary system during this cleanup procedure.

Some of the unit costs listed in Table 5 may appear to be unusual due to the presence of certain impurities. For example, the cost of "air" is relatively high because atmospheric air could not be used as a secondary coolant due to the activation of the small percentage of argon which it contains. Air, for a secondary coolant, would have to be synthesized from liquid oxygen and nitrogen. Carbon dioxide and hydrogen are both relatively expensive due to the difficulty of removing small amounts of water vapor which occur in the commercially available products.

Special consideration must be given to those choices for secondary coolants which contain lithium. It appears at the present time that the primary salt will be $LiF-BeF_2$ (the eutectic of lithium fluoride and beryllium fluoride) with the addition of uranium and thorium fluorides. The lithium in this mixture must be enriched in lithium-7 to decrease the number of neutrons which are absorbed in this component. If lithium is also a constituent of the secondary coolant, and if the secondary coolant becomes mixed with the primary salt through leakage in the primary heat exchanger, then the lithium in the primary salt will become diluted with the lithium-6 of the secondary coolant unless the lithium in that coolant is also enriched in lithium-7.

It is obvious that the use of the isotopically-enriched lithium in the secondary coolant will increase significantly the cost of this component. In Table 5, for those secondary coolants which contain lithium, the costs are indicated for the coolant constituted both with natural lithium and with lithium which is 99.995% lithium-7. The cost of the additional inventory charges which are incurred when enriched lithium is used must be balanced against the possible cost of replacing the primary coolant in the event of a primary heat exchanger failure or, as an alternative, allowing any lithium-6 which is introduced into the primary loop to be "burned out" during subsequent reactor operation.

The relative total inventory costs are given in the last column of Table 5.

Table 5. Cost of Secondary Coolants, Estimated Total Inventories, and Estimated Total Inventory Costs

Secondary Coolant	Estimated Inventory Volume (cubic feet)	Weight (pounds)	Unit Cost ($/pound)	Total Inventory Cost (million $)
NA BF4--NA F	8500	993650	.371	.369
LI F--BE F2	10000	1240600	5.200	6.451
WITH LITHIUM-7			11.920	14.788
FLINAK	8500	1133560	1.095	1.241
WITH LITHIUM-7			5.111	5.794
NA+K F--ZR F4	8500	1358470	2.074	2.817
NA OH	8000	732160	.250	.183
LI CL--K CL	8500	852465	.509	.434
WITH LITHIUM-7			4.140	3.529
NITRATES	7000	758310	.150	.114
LMP FLUORIDES	11000	1372800	4.342	5.961
WITH LITHIUM-7			7.944	10.906
CARBONATES	10000	1250000	.256	.320
WITH LITHIUM-7			3.370	4.212
SODIUM	4500	230400	.400	.092
NAK	4500	219600	.800	.176
BISMUTH	5000	3040000	6.000	18.240
PB--BI	5000	3115000	3.380	10.529
MERCURY	5000	4010000	12.750	51.127
LEAD	5500	3575000	.180	.643
HELIUM(HP)	20000	5102	9.500	.048469
HELIUM(LP)	20000	1276	9.500	.012118
HYDROGEN(HP)	20000	2574	14.157	.036434
HYDROGEN(LP)	20000	643	14.157	.009109
WATER(HP)	20000	24110	.010	.000241
WATER(LP)	20000	5817	.010	.000058
AIR(HP)	20000	37020	.616	.022804
AIR(LP)	20000	9260	.616	.005704
NITROGEN(HP)	20000	35760	.688	.024603
NITROGEN(LP)	20000	35760	.688	.024603
CO2(HP)	20000	56180	1.438	.080787
CO2(LP)	20000	14040	1.438	.020190

All prices are for components which are 99 per cent pure. No transportation costs have been included; prices are F.O.B. vendor.

Unless otherwise noted, prices for lithium compounds are for the naturally occurring element. Enriched lithium compounds are assumed to contain 99.995 per cent LITHIUM-7 priced at $120/kg. No chemical conversion cost for this lithium is included.

5. THE SIGNIFICANCE OF THE MELTING OR LIQUIDUS TEMPERATURE OF THE SECONDARY COOLANT IN MOLTEN-SALT REACTOR SYSTEM DESIGN

The group of gases that are to be considered for secondary coolants do not approach either a solid or liquid state (with the exception of carbon dioxide) at reactor conditions from ambient to normal operation. The liquid metals retain the liquid state (with the exception of lead and bismuth) at temperatures near or below the normal boiling point of water (212°F). The group of molten salts which are included in this study have liquidus temperatures ranging from approximately 300°F to temperatures greater than 850°F. It appears, therefore, that the values of the melting or liquidus temperature will only have importance when comparing various members within the groups of liquid metals or molten salts.

While it is not obvious that the local formation of a solid phase in the circulating secondary coolant system will be detrimental to the efficient performance of the system, the design of the system and the selection of a coolant which eliminates this possibility have certain advantages. Such a system and coolant combination would not require feedwater temperatures and flow control instrumentation with the complexity and redundancy of systems that possess the potential for subcooling the secondary coolant.

If a solid phase which does not adhere to the channel walls is formed in the coolant, then this solid will be carried by the coolant to other parts of the loop. Progressive formation of solid will lead to the generation of a "slush" within the secondary coolant system. Again, this effect may not be detrimental as long as the solid phase can be converted back to the liquid phase through the addition of heat or an adjustment of the relative coolant composition.

A system with the potential of freezing the secondary coolant can be operated successfully without the production of a solid phase. Such a system would have a feedwater temperature to the steam generator which was below the melting or liquidus temperature of the coolant. During normal, full-power operation the thermal gradient that is required for transferring the total heat load in the steam generator is greater than the difference in these temperatures. A control problem is involved in

satisfactory operation during rapid changes in power level that result from either a reactor scram or a turbine trip, or both. Under these conditions the heat load is rapidly reduced and freezing will occur unless both the feedwater flow rate and possibly also the secondary coolant flow rate are coincidently reduced in accordance with a predetermined program.

As the difference by which the melting or liquidus temperature of the coolant exceeds the feedwater temperature increases, the requirements for the control of the flow rates and temperatures of both the secondary coolant and the feedwater system during these transients become more stringent. Greater sensitivity, reliability, and redundancy must be included in the design of the two control systems, unless the consequences of the formation of the solid phase within the secondary coolant system are considered to be of minor importance. The evaluation of these consequences can be made only after a thorough analysis of the secondary coolant system under all possible transient conditions has been made. Comparison of the performance of different choices for coolants within a group can then be made only on the basis of a fixed system design.

The dependence of the comparison of coolant performance on detailed system design and the relatively high capital cost of feedwater and coolant control systems associated with such a design can be eliminated if the melting or liquidus temperature of the coolant is less than or equal to the feedwater temperature. As indicated above, due to the resistance to the transfer of heat between the feedwater and secondary coolant, the feedwater temperature can be lower than the melting or liquidus temperature without incurring the formation of a solid phase in the secondary system. As the feedwater temperature is lowered and the difference gets larger, however, the control requirements become much more restrictive and the instrumentation required to accomplish this control becomes more expensive. If the stipulation is made that the feedwater temperature can be no more than some limiting difference, such as 25 or 50°F, below the melting or liquidus temperature of the coolant, then the cost of the instrumentation for the various systems will be comparative.

This assumption relates the melting or liquidus temperature of the secondary coolant to a major system design parameter, the inlet feedwater temperature to the steam generator. The inlet feedwater temperature

must, in turn, be related to the steam system pressure through the pressure-temperature relationship for water and by the conventions of turbine plant design. Using the restriction of 50°F for the maximum difference between the melting or liquidus temperature of the coolant and the feedwater temperature would require that secondary coolants with melting or liquidus temperatures greater than 755°F be used with systems which had feedwater temperatures greater than 705°F. Since 705°F is the critical temperature of water, feedwater pressures for these systems must be supercritical; otherwise the feed is actually superheated steam and the entire steam generator unit becomes a superheater. This results in generally lower overall heat transfer coefficients and therefore larger heat transfer areas for any particular thermal duty.

Conventional steam turbine plant designs employ throttle pressures up to 2500 psi for subcritical systems and throttle pressure greater than 3500 psi for supercritical systems; the critical pressure of water is 3206.2 psia. The pressure loss in once-through steam generators in conventional turbine plants is in the range of 600 to 1000 psi. This pressure loss is due to frictional loss of flow in the tubes, header losses, and the loss due to orifices placed in the headers to suppress flow instabilities. Feedwater pressures usually then range from 3000 psia or greater for plants with 2400 psia throttle pressure and from 4300 psia for supercritical systems.

The opinion has been expressed that first-generation molten-salt reactor designs should not have the complicating factors in their design and operation which are associated with supercritical turbine plant cycles. If the feedwater temperature limitation that was proposed above is coupled with the stipulation that the plant design incorporates a subcritical steam cycle, a plant design is still possible. Supercritical pressure could be specified for the feedwater to improve the performance of the steam generator, and the steam cycle could be operated at subcritical pressures by allowing a larger pressure drop at the throttle valve of the turbine. Since this larger pressure drop at the throttle valve would have to be supplied by the feedwater pump, the power requirements for this pump would be larger than the requirements for a subcritical cycle of similar capacity.

Present steam plant designs usually incorporate feedwater temperatures ranging from 480°F for subcritical cycles to 550°F for supercritical cycles. The specification of a feedwater temperature equal to or greater than a value of 50°F below the melting or liquidus temperature of the secondary coolant will result in departures from these standard design values for most of the possible choices of molten-salt coolants and for two possibilities for the liquid metals. These higher feedwater temperatures can be obtained through modifications in conventional steam plant design which may decrease the net power generated by the cycle and/or increase the capital cost of the turbine plant.

One method of increasing the feedwater temperature would be to simply add more feedwater heaters to the train. To limit the operating temperature of the feedwater pump, the last heaters would probably be placed in the discharge line of the pump. The units would then be high-pressure, high-temperature heat exchangers with significant heat transfer areas. For this additional feedwater heating, more extraction steam would be required. To obtain the high feedwater temperatures with a reasonable heat transfer area requirement for the last-stage feedwater heaters, either prime steam or steam extracted from the high-pressure turbine would be required.

Several methods of obtaining the high feedwater temperatures by modification of the steam generator exist. All of these methods involve heating the feedwater with steam from the unit; this steam is then returned to the unit for further heating or resuperheating. The reentrant type of steam generator performs this function internally by supplying surface inside the steam generator through which heat is transferred from the hotter stream to the entering feedwater. The same function can be performed external to the steam generator simply by extracting steam at a point, passing this steam through a conventional heat exchanger to heat the feedwater, and then returning the degraded steam to the unit. The reentrant design has the disadvantages that the internal heat transfer area is more expensive than a similar area in an external unit and that there is no control of conditions and flows for the four streams involved as there is in an external system. The external system has the disadvantage that the collection and redistribution headers for the extraction and return of the hot stream are expensive.

Another possible design is one in which the prime steam is recycled to a contact heat exchanger where it is mixed with the normal feedwater to produce a fluid with the desired inlet temperature. The disadvantage of this system is that a recirculation pump is required. This pump may be placed either in the recirculated prime steam stream, or it may be placed in the mixed stream from the contact unit. In the first configuration, the capacity of the pump is lower, but its operating temperature is that of the prime steam; in the second location, the operating temperature is the same as the feedwater temperature, but the capacity of the pump is equal to the total of the feedwater and the recirculation streams. The pressure head of the pump in both configurations would be equal to the pressure loss through the steam generator unit.

To illustrate the operation of this system, assume that it was desired to raise the feedwater temperature from 500°F to 700°F for a supercritical system with throttle conditions of 3500 psia and 1000°F. The energy that must be added to the feedwater stream is 335.5 Btu per pound of feedwater, and the amount of recirculated steam required would be 0.558 pounds per pound of feedwater. Even allowing for a 1000 psi head requirement for this recirculation pump, the theoretical work required is 4118 ft-lb per pound of recirculated steam or 2300 ft-lb per pound of normal feedwater flow. Since for a 40% efficient turbine plant with these steam conditions, the net amount of energy extracted per pound of steam to the turbine is about 543 Btu per pound, the power requirement for this recirculated steam pump is less than 0.6% of the electrical power produced.

The recirculation pumps which would be required for such a process are similar in capacity and operating conditions to recirculation pumps used in current steam plant design; the head requirements for these pumps are greater than the units in present use. The contact heat exchanger which is proposed for the design would be quite similar to attemporators used to "kill" the steam in the event of a turbine-trip in presently constructed steam plants.

The conclusions which are drawn from this discussion are:

a. If future study of possible molten salt reactor designs indicates that possible formation of a solid phase in the secondary coolant system will constitute a hazard in the reactor operation, then either the design

feedwater temperature must be above the liquidus or melting temperature of the coolant (or within a limited temperature range below the liquidus or melting temperature), or else the flow and temperature control systems for both the secondary loop and the feedwater system must be extremely reliable.

b. Within the range of possibilities just stated, it is most probable that secondary coolants which have melting or liquidus temperatures greater than 750°F will find their most economical applications in conjunction with supercritical steam cycles.

c. Selection of lower feedwater temperatures to obtain higher turbine plant efficiencies must be balanced against the increased capital costs of the instrumentation and the control systems for the feedwater system and the secondary salt system.

d. Higher feedwater temperatures can be obtained by several methods that are available within the scope of present technology. One method, which is available, is the recirculation of prime steam to a contact heat exchanger; this method of increasing the feedwater temperature from 500 to 700°F would result in less than a 0.6% reduction in electrical power production from a plant with an overall efficiency of 40%.

6. EFFECTIVENESS OF COOLANTS IN TRITIUM HOLDUP

To be effective in preventing the tritium which is formed in the primary coolant loop from migrating by diffusion through the heat exchanger surfaces first to the secondary salt and then to the steam or the reactor cell, the secondary coolant must exhibit one of the following effective mechanisms. The coolant may contain atoms which are exchanged with the tritium atom, and these "captured" tritium atoms may then either be removed as a chemical component or they may be stored in the coolant for its lifetime. The coolant can also retain the tritium if it contains a constituent which will chemically combine with the tritium. Again, the tritium can be removed from the coolant by a chemical process which removes and replaces the constituent; or if the constituent is present in large concentration in the coolant, the inventory of tritium may be allowed to build up over the lifetime of coolant use.

The atom which obviously will be most easily changed with tritium is the normal hydrogen atom which is chemically identical. The only coolants which have been considered in this review that contain hydrogen atoms are NaOH, H_2, and H_2O. If any of these three choices were employed as the secondary coolant, the concentration of hydrogen atoms in the secondary coolant would be so great that the law of mass action would cause the normal hydrogen atoms to diffuse out of the system in preference to the tritium atoms. The more rapid diffusion of the hydrogen which was replaced by the tritium would actually be enhanced by the comparative weight ratio.

Collecting the tritium in such a "reservoir" as the secondary coolant would have one major disadvantage. The molecules of coolant which contained the tritium (such as NaOT and HT) cannot be separated chemically from the molecules containing normal hydrogen. The secondary coolant would therefore be always contaminated with the tritium until it was removed by natural radioactive decay (12.3 year half-life) or until it was removed by physical processing of the coolant. Physical processing of NaOH would probably not be practical. Since NaOH is the hydrous form of Na_2O, it might be possible to liberate all of the tritium and hydrogen through the application of heat and appropriate reducing agents. Physical

separation of tritium and hydrogen has been considered practical. The mixture of tritium and hydrogen could be separated by low temperature distillation, or they could be combined with oxygen to form a mixture of light and very heavy water, and the separation might be made with existing equipment used for the production of heavy water.

If the aspects of physical separation of the tritium from reservoirs are neglected temporarily, the consequences of the handling and storage of a large quantity of secondary coolant can be considered. After contamination with the tritium, the entire inventory of coolant must be contained and stored for an indefinite period. While the secondary coolant is in the reactor system, storage presents no problem. If a reactor is shut down after a planned 30-year lifetime, the cost of storage of the coolant would probably not be prohibitive. In the case of using hydrogen as a secondary coolant, it could be converted to water for storage. The principal problem arises, however, if the coolant must be replaced one or more times during the design lifetime of the reactor. Replacement could be required, if, for example, the secondary coolant became contaminated with fission products from the primary loop. If the tritium could not be effectively removed from these replaced volumes of secondary coolant, the cost of storing an undetermined number of these volumes could be prohibitive from an economic standpoint.

The better alternative for tritium holdup in the secondary coolant appears to be the addition of a limited amount of a constituent which either contains hydrogen atoms which will be exchanged with the tritium or a constituent which will chemically combine with the tritium and which would be present in relatively minute quantities. This constituent should be one which could be removed with relative ease by chemical processing. It should also be chemically inert with respect to the major component or components of the secondary coolant and to the materials of construction of the system. It should be stable in the thermal and irradiation environment of the secondary salt system.

Several constituents are available in the category of hydrogen-containing compounds which may be added in small concentrations to the choices of secondary coolants which are being considered. The most obvious choice is hydrogen gas. Neglecting the consideration of hydrogen gas

itself as a secondary coolant, hydrogen gas may be added in small concentration to any of the other choices of gaseous secondary coolants without adverse effect; a possible exception is carbon dioxide. With mixtures of hydrogen and carbon dioxide under high temperature and pressure, there would be the formation of some carbonic acid gas and carbon monoxide that might induce corrosion of the system piping.

All of the choices for molten salt or liquid metal coolants would require an overpressure of a gaseous phase at some point in the secondary system piping. This gas-liquid interface is usually maintained over the liquid phase in the pump bowl of molten-salt systems; otherwise the interface would be at the point at which the secondary system pressure was regulated. Normally this gas phase will consist of an inert gas such as helium or nitrogen plus a partial pressure of the secondary coolant or one of its degradation products. For example, in the case of sodium fluoroborate, a substantial partial overpressure of boron trifluoride gas is required to maintain the proper coolant composition.

For most of the choices of liquid metal and molten salt secondary coolants, it would be possible to add hydrogen gas to the gaseous phase. If equipment was incorporated in the secondary coolant loop so that hydrogen in an inert carrier gas could be added and stripped from the liquid phase, tritium in the coolant would then be carried with the hydrogen to the gas phase. The hydrogen and tritium mixture would be continually removed and replaced; this hydrogen could contain a high percentage of the tritium which was transported to the secondary coolant if the proper concentrations and contact areas were provided. Separation of the hydrogen gas from an inert gas such as helium or nitrogen could be accomplished by the catalytic oxidation of hydrogen to water followed by its removal in a cold trap or drying medium. Removal of hydrogen from some of the other gaseous mixtures might prove more of a processing problem.

One of the major disadvantages in the use of overpressures of H_2 is the possibility of its forming an explosive mixture with atmospheric oxygen in the event of inleakage to the reactor cell. The concentration of hydrogen can be kept so low, however, that explosive limits can never be reached, and inert gas blanketing of the reactor cell can exclude atmospheric oxygen in all but the most catastrophic accident.

Another constituent which would be compatible with most of the choices for molten salt, if not the liquid metal coolants, is the addition of hydrogen fluoride or one of the other hydrogen halides. Use of any of these additives would depend upon their compatibility with the materials of construction for the secondary loop. If the halide is already a constituent of the molten salt coolant, the addition and removal of the hydrogen halide should be relatively easy, and the addition of the hydrogen halide should not affect the corrosion rate of the coolant.

A hydrogen-containing constituent which might be a natural contaminant in many coolants is water. In very small concentrations, the hydroxyl ion forms a complex with some of the components of molten-salt mixtures. For example, in the lithium fluoride–beryllium fluoride system, a complex $Be(OH)^-$ is formed. A hydrogenous form of sodium fluoroborate can be obtained through a complex with the hydroxl ion in the form of $NaBF_3OH^-$. Normal "drying" procedures can be used to remove the moisture during chemical processing, and a slight amount of moisture could be allowed to recontaminate the salt before it was returned to the system.

Several of the choices for molten salt coolants present the possibility of maintaining a small amount of the acid represented in the salt. For example, small amounts of nitric acid could be maintained in the nitrate salts without affecting their vapor pressure substantially or their corrosion performance. Carbonic acid is not sufficiently stable to be maintained in the carbonate mixtures, but it is possible that a sufficient concentration of the bicarbonate ion HCO_3^- could be maintained to act as a tritium trap.

In the category of liquid metal coolants, particularly the alkali metals, a small concentration of the hydroxide would supply the hydrogen atoms which could be interchanged with the tritium. The metal hydrides constitute a group of hydrogen-containing compounds which might feasibly be added to either the liquid metals or the molten salts. Also the ammonium salt is a feasible constituent for use with some of the choices for molten-salt coolants.

Tritium can be retained in the secondary coolant through the addition of a constituent (probably in small concentration) with the oxidation potential to convert the tritium to its ionic state and maintain it in that

state. Oxidation in this concept refers to the process of stripping an electron from the tritium atom and producing in the coolant the positively charged tritium ion which may then associate with negative ionic species in the coolant. The added constituent must, therefore, have a reduction potential--that is, an affinity for electrons--which is greater than tritium (hydrogen). In the normal chemical processing of the secondary coolant, the oxidation-reduction potential of the coolant can be adjusted, the tritium will be released in the diatomic state and can be stripped from the coolant with an inert gas stream.

Tritium which diffuses through the heat transfer surface of the primary heat exchanger will exist either as the dimer or a pseudo-dimer through association with the electrons in the outer shells of the atoms of the wall structure. Oxidation of the dimer structure in solution will result in the association of the ionic component with anionic constituents in the coolant to prevent further diffusion of the tritium. Tritium which is formed by nucleonic reactions within the secondary coolant will probably first exist in the ionic state; however, it will be reduced by the constituents of the coolant or containment material which are above tritium (hydrogen) in the electromotive series. These components would include lithium, potassium, sodium, magnesium, beryllium, aluminum, manganese, chromium, iron, cobalt, nickel, tin, and lead, as examples.

The added oxidizing constituent, which is reduced in the process, must have sufficient potential to convert the tritium to its ionic state, and, at the same time, it must not convert the materials of construction of the secondary system to ionic species. A limited number of "getters" are available for the various choices of secondary coolants and the accompanying choices of materials of construction.

For example, C. F. Weaver indicated in a letter dated March 1, 1971, that in a fluoride-containing molten-salt coolant, if it was desired to convert T_2 to TF in a system with nickel containment, it would be necessary to have an oxidizing agent with a free energy of formation between −65 kcal/gr-atom of fluorine and −62 kcal/gr-atom of fluorine. The first value corresponds to the free energy of formation of TF at 1000°K, and the second value corresponds to the free energy of formation of NiF_2. The only agent which meets this criterion is germanium which is, at best,

a borderline possibility. If the containment material is molybdenum, then germanium is an acceptable material. If the system is lined with copper, then possible agents are germanium, molybdenum, arsenic, or antimony; the last is again a borderline choice. All of these oxidizing agents except arsenic and antimony would exist in the molten-salt mixture in the tetravalent state; arsenic and antimony would be pentavalent. All would be oxidized to the trivalent state in the reduction of tritium.

In the primary salt, it is possible to retain tritium through the introduction of either uranium or thorium at a reduced valence to serve as an oxidizing agent.

7. COMPATIBILITY OF SECONDARY COOLANTS WITH THE PRIMARY SALT, STEAM, AND THE CELL ENVIRONMENT

The compatibility of the various choices for secondary coolants with the primary system fluid, with the water in the steam generator, and with the cell environment must be considered. It will be assumed that the primary system fluid is a eutectic mixture of lithium and beryllium fluorides Li_2BeF_4 and relatively small percentages (~10%) of thorium and uranium fluorides. The cell will be assumed to be filled with an inert gas such as helium or nitrogen or a mixture of carbon dioxide and nitrogen formed by the combustion of hydrocarbons with air followed by scrubbing and drying.

7.1 Compatibility With the Primary Fluid

There are two major points of concern if leakage in the primary heat exchanger allows the secondary coolant to mix with the fluid in the primary loop. First, there is the concern that an exothermic reaction between the two fluids would propagate the leakage and mixing rate so that ultimately either or both of the two systems would be ruptured. Second, there is the concern that the addition of limited amounts of secondary coolant to the primary system would result in a concentration of the fissile material and produce a critical mass outside of the core region or excessive reactivity within the core region. Fissile material could be concentrated either by the precipitation of the material from the primary fluid (such as the precipitation of uranium oxide) or preferential absorption of the fissile material in the small volume secondary coolant.

Of secondary importance is a consideration of the possibility of an insoluble precipitate formed within the primary system which would prevent further attempts to circulate the primary fluid through that portion of the system, or the possibility that contamination of the primary fluid by the secondary coolant would adversely affect the nuclear characteristics of the fluid. In the first instance, a portion of the primary system piping and associated components would have to be replaced, and in the second instance, either the expensive primary fluid would have to be

chemically processed or replaced, or the adverse characteristics would have to be tolerated in the future operation of the reactor.

7.1.1 With the molten salts as secondary coolants

7.1.1.1 Sodium fluoroborate. The sodium fluoroborate ($NaBF_4$–NaF appears to be the choice at present for a secondary coolant for molten-salt reactors with Li_2BeF_4 plus fluorides of uranium and thorium as the primary salt. Some experimental study has been given to the possible mixing of these two salts; however, more detailed qualitative analysis of the dynamic characteristics of the interaction are required. No violent exothermic reactions occur when fluoroborates are mixed with steam or with fluoride fuel salts. In fact, it has been discovered that fluoroborates are immiscible with molten mixtures of lithium and beryllium fluorides over a significant range of conditions. Uranium and other tri- and tetravalent elements are not extracted into fluoroborates, and the only high-melting compound that might be formed is sodium fluoride. There is some migration of LiF to the fluoroborate phase, and replacement of NaF by LiF in the $NaBF_4$ complex results in an almost immediate release of BF_3 gas. The detailed consequences of mixing of the fuel salt with the sodium fluoroborate depend on (a) the rate of mixing of the two streams, (b) the solubility of the BF_3 gas in the resultant phase, (c) the relative temperatures of the two fluids, (d) the kinetics of reactions between the distributed components, and (e) which fluid constitutes the continuous phase. Present evaluation of all of these factors indicates that there is no mechanism for the concentration of uranium to produce a critical configuration and no compounds will be formed which cannot be redissolved through the addition of appropriate chemical agents.

Operation of a test loop (containing residues of this fluoride salt) with a flushing charge of NaF–$NaBF_4$ did, however, reveal the deposition of a green salt in the upper region of the pump bowl. The composition of the salt was essentially $7NaF \cdot 6(Th,U)F_4$, suggesting that either entrainment of the residue or solution-deposition of it had occurred, along with some replacement of Li by Na; although more study of this phenomenon is indicated, there is no information available to cause alarm over the possibility of accidental mixing of fluoroborates with fluoride salts. For

MSBR use, moreover, the accidental introduction of fluoroborates into the circulating fuel would cause a large reactivity decrease because of the boron, and thus even a small leak would be quickly detected. The boron could be easily removed from the fuel salt by treatment with HF.

7.1.1.2 Lithium fluoride–beryllium fluoride. Lithium fluoride–beryllium fluoride mixtures (L_2B) would be compatible with the primary salt since it is the major component of the presently proposed fuel salt. Introduction of the secondary salt into the primary system would have the effect of reducing the fissile concentration in the primary salt. The major adverse consequence would be the introduction of lithium-6 into the primary salt in the event that the secondary salt did not contain lithium which had been isotopically enriched in lithium-7. The result of such a mixing would either require that the primary fuel salt be replaced or that uranium concentration of this salt would be increased and the lithium-6 which was introduced be allowed to "burn" out. The latter course would probably be more favorable if the amount of lithium-6 introduced were small; if the amount was large, then a detailed economic consideration would have to be made to determine the course of action.

The use of L_2B which was enriched in lithium-7 as the secondary coolant would eliminate any mixing problems. This would increase the inventory charge for the secondary salt as indicated in Table 5. L_2B as a secondary coolant has the disadvantage of having a relatively high liquidus temperature as indicated in Table 3. This liquidus temperature can be lowered by adding higher concentrations of beryllium; however, this addition results in a much higher viscosity for the mixture.

7.1.1.3 FLINAK and the "low melting point" fluoride. The comments which might be made concerning FLINAK are essentially the same as those for L_2B. It has the compound LiF in common with the primary coolant, and NaF and KF are analogous compounds. Mixing with the primary coolant would probably produce no reaction, but the secondary coolant would have to contain lithium enriched in ^7Li to avoid problems with the primary salt nuclear characteristics following a mixing accident. These same statements apply to the "low melting point" fluoride mixture.

7.1.1.4 The chloride salts. The problems resulting from the use of a mixture of lithium and potassium chlorides as a secondary coolant following a mixing accident would differ from those encountered with L_2B and FLINAK only in that the chloride ion would be present. Following a mixing accident, the chloride ion could be removed from the primary salt through the use of HF gas. The presence of the chloride ion might introduce some corrosion problems if trace quantities were left in the primary loop; however, most of the proposed materials of construction for this loop are resistant to this attack, and, if the chloride salt were used as the secondary coolant, the materials of construction in the secondary loop should also be resistant.

7.1.1.5 Sodium hydroxide, the nitrates, and the carbonates. The compatibility of the primary salt with NaOH, the nitrates, and carbonates may be considered as a group principally because they are all oxygen-containing compounds. They differ to some degree in the availability of the oxygen for chemical reaction--or, more exactly, their free energy of formation with respect to the compounds in the primary salt. In considering the consequences of these compounds mixing with the primary salt, it is necessary not only to consider the reaction products which result from the combination of the chemical components, but it is also necessary to consider both the mixing rates and reaction rates.

For example, the mixture of any of these secondary coolants will result in the formation of both uranium and thorium oxides which are essentially insoluble in either of the molten mixtures. If this mixing occurs as the result of a small crack in the tubing of the primary heat exchanger, then the formation of the oxides at the point of the mixing may form a "scab" which results in a type of "self-healing" reaction to small leaks between the systems.

On the other hand, if massive mixing occurs as a result of the double-ended rupture of a tube in the primary heat exchanger, a large amount of oxide precipitate will be formed. Depending upon the relative fluid velocities, this precipitate may either be carried around the coolant loop, or it may precipitate in the place where it is formed, or it may precipitate in some section of the system where the fluid velocities are low.

If the precipitate remains in suspension in the loop, it is possible that it can be collected and chemically reconverted to a soluble fluoride. If it precipitated at the point of formation, say in the primary heat exchanger, to the extent that flow through that part of the system is blocked, then the resolution of the uranium and thorium would be practically impossible. The melting point of the uranium and thorium oxides are well above (~4500°F) the temperatures that the materials of construction can contain, and adequate agitation for effective chemical resolution would be difficult. This same problem would exist if precipitation of the oxides occurred at any other inaccessible point in the primary system. It might be feasible, if this precipitation and flow blockage did occur, to remove the system component which was involved (such as a heat exchanger) and replace it with another unit.

A fortunate circumstance is that the conditions which cause the precipitation of the oxides of uranium will also cause the oxides of thorium to precipitate. Therefore, the formation of a critical configuration outside of the core is not probable.

Mixing of the secondary coolants containing carbonates, nitrates, or hydroxides with the primary salt will result in the formation of some gaseous components. The relative amount of gas evolved and the relative evolution rate will decrease in the order just listed. In the first case, the gaseous product will be carbon dioxide, in the second it will be oxides of nitrogen, and in the last, it will be hydrogen fluoride.

Another potential problem for a violent chemical reaction exists if the nitrates penetrate the primary circulating system to the point of entering the graphite moderator lattice. This is not a probable situation since this coolant mixture is less dense than the fuel salt; it will be buoyed out of the core region as long as the fuel salt is present. If the fuel salt has been dumped into the drain system, any inleakage of this secondary salt should be carried with it. Finally, a rapid reaction between the graphite and the molten nitrate salts occurs only over a particular range of relative compositions and within a range of interactive surface to volume ratios. If the nitrates are to be considered in detail, an experimental investigation will have to be made to determine the limit of these ranges.

7.1.2 With liquid metals as secondary coolants

7.1.2.1 Sodium and Nak. The introduction of either sodium or NaK, when used as secondary coolants, into the primary loop will produce similar results. The only difference is that the higher reactivity of the potassium in the NaK may produce slightly higher reaction rates. In either case, all of the metallic species in the primary salt, with the exception of lithium, will tend to be reduced to their elemental forms by the introduction of the alkali metals.

The uranium metal will be formed most easily and present indications are that it will tend to agglomerate or sinter into particulate size. Some thorium metal may also be formed with the uranium, but this will depend upon the relative concentrations of these two species at the reaction site. Beryllium will not begin to be produced in metallic form until all of the uranium and thorium have been depleted from the primary salt at the point of the reaction.

The consequence of these events is that a critical mass of uranium can be collected outside of the core since the total inventory of fissile material in a 1000-MW(e) reactor approaches 1500 kg, and a critical mass under partially reflected conditions may be on the order of 2 kg. If the uranium does not collect in the system, then the possibility still exists of introducing a surge of uranium into the core which may produce a sharp reactivity increase. On the positive side of the picture, a small leak would begin to remove uranium from the primary salt and cause a detectable change in the reactor operational mode.

Of the reactions which have been discussed thus far between the primary salt and possible secondary coolants, the reaction of elemental sodium or potassium to produce metallic thorium, uranium, and/or beryllium are the only ones which will liberate significant amounts of energy. The maximum energy release will be less than 1 kcal per gram of sodium or potassium introduced into the system. Because of the relatively low concentration of uranium and thorium, which must be reduced first, there will not be a concentrated site for the energy release unless there is violent agitation at the point of mixing. Also, because of the relatively high thermal conductivity of the liquid metal, concentrated energy release

sites will have their effect reduced if the liquid metal phase is continuous. The conclusion is that the potential of depositing large amounts of energy at a local site in the mixed coolants is relatively low.

7.1.2.2 Bismuth and lead. Bismuth and lead, or a mixture of the two, can be allowed to contact the primary salt with relatively little effect as long as they do not contain any active metallic constituents which might result from erosion of the containment material of the secondary loop. Any metallic impurity which is in the elemental state will have the tendency of reducing the thorium and uranium of the primary salt to their elemental states. The thorium and uranium would then be extracted in the bismuth or lead phase which would be essentially immiscible with the primary salt. This effect can be eliminated by continuously processing the coolant to restrict the concentration of metallic corrosion products.

7.1.2.3 Mercury. The same statements which were made for lead and bismuth also apply to mercury. The major difference in the response of the primary system following the introduction of mercury would be due to the higher vapor pressure of the mercury at the system operation temperature. The normal boiling temperature of mercury, where the vapor pressure is equal to one atmosphere, is 674°F (357°C). At 600°C (1112°F) which is about the mean temperature of the primary system, the vapor pressure of mercury is almost 23 atmospheres (336 psia).

7.1.3 With gases as secondary coolants

The problem encountered with the use of any of the gases as secondary coolants for molten-salt reactors is the same as that which was just cited for the use of mercury, the introduction of a pressure surge to the primary system. In Table 2, the physical properties of the gases are listed at a high pressure (1000 psia) and a lower pressure (250 psia). It is obvious that the high-pressure gas is a more efficient coolant; however, the consequences of a system at 1000 psia leaking to the primary system are obviously worse than the consequences which might be encountered with a system at 250 psia. It is obvious that the primary loop must be designed

so that the admission of the higher pressure of the secondary loop will not result in major damage to the primary loop.

Several design alternatives have been discussed which would allow the use of a high-pressure system in the secondary loop. First, the higher pressure could be used as the design pressure for the primary loop. This would result in a system which would be considerably more expensive to fabricate; in addition to thicker wall requirements for a system with relatively expensive piping material, the seals for pumps and valves would be complicated. Second, the primary system could be equipped with rupture disks which would allow the fuel salt to "blow off" into the drain tank in the event of an over pressure. The problem with this design alternative is that the inertial effects of the fuel salt might cause the primary system to fail before the pressure wave reached the rupture disk. The third alternative would be to pressurize the entire cell which contained the primary and secondary loops and then design the piping and components to withstand the pressure differential. This would mean that the reactor would have to be scrammed and the system depressurized in the event of a drop in pressure in the containment cell. A further complication is that there would be the tendency for leakage outward of the containment cell rather than inward, a more desirable containment situation. A pressurized containment cell, however, appears to be the best solution of the three which are cited.

7.1.3.1 Helium. If the problems associated with the higher secondary loop pressure are bypassed, the following comments can be made concerning the use of the various gases as secondary coolants. Helium appears to be the best choice of those gases listed in Table 1. It is chemically inert, and, therefore, there will be no chemical reaction with the primary salt. With the exception of hydrogen, it has superior heat transfer performance; it transports more heat per unit weight of gas circulated.

7.1.3.2 Hydrogen. Hydrogen does have the best heat transport performance characteristics, and it is readily available. It does present an explosion hazard when mixed with atmospheric oxygen over a large range

of concentrations. This would probably eliminate it for consideration as a component in a nuclear plant.

7.1.3.3 Water vapor. Water vapor which is the least expensive choice for a secondary coolant presents about the same problems when mixed with the primary salt as the oxygen-containing molten salts which were considered previously (hydroxides, nitrates, and carbonates). Addition of water vapor to the primary salt would result in the precipitation of the oxides of uranium and thorium.

7.1.3.4 Air. The oxygen in "synthetic air" used as a secondary coolant would not be as available for formation of the oxides of uranium and thorium; however, this process would still exist. Because of the similarity in heat transport performance, there would be no advantage in using mixtures of oxygen and nitrogen in preference to pure nitrogen.

7.1.3.5 Nitrogen. Nitrogen is another inert gas with respect to chemical reactions with the primary salt. It is less expensive than helium, but it is much less efficient as a heat transport fluid.

7.1.3.6 Carbon dioxide. The use of carbon dioxide as a secondary coolant would result in the same chemical reactions with the primary salt as the carbonate molten salts.

7.1.3.7 Conclusions. The conclusion that might be drawn from these statements about the gaseous choices for secondary coolants is that helium appears to be the best choice as long as it is available and not prohibitively expensive. From availability studies which are made within the gas-cooled reactor program, it appears that a supply of helium from natural gas deposits will be available in sufficient quantity to support a relatively large reactor power industry. At the time that this supply becomes exhausted, it will be possible to extract helium from the atmosphere at a cost which is not prohibitive.

7.2 Compatibility With Steam

The major points of concern in considering the compatibility of the various choices for secondary coolants with water and steam in the event of a leak or rupture in the steam generator turbine are (a) violent reactions, (b) the creation of extremely corrosive reaction products, or (c) the production of reaction products which may plug either the coolant system or the steam system and make subsequent repair difficult. Previous work* has indicated that the sodium fluoroborate, in particular, and the fluorides, in general, do not undergo violent reactions on mixing with water. None of the other choices of molten salts for secondary coolants undergo significant exothermic chemical reactions when mixed with water. If these salts are cooled below their liquidus temperature by the feedwater stream, a solid phase will be formed; however, they can all be melted under normal system operating temperatures and most are soluble in water so that they can be washed from the steam system.

In the category of liquid metals, both sodium and potassium will undergo a rapid reaction with water with the significant evolution of heat and also hydrogen gas. The hydrogen which is evolved results in an explosive hazard if an inert atmosphere is not maintained over the system.

No problem is encountered if any of the possible gaseous secondary coolants are allowed to mix with steam or water.

7.3 Compatibility With the Cell Environment

The cell environment will most likely be a blanket of inert gas. This could be nitrogen, which is obtained from an air liquification process, or it could be the combustion products from the careful combustion of natural gas in air followed by scrubbing and drying. In either case, there should be no possibilities of chemical reaction or unusual corrosion as long as moisture is excluded from the cell. A simultaneous rupture of the steam system and the secondary coolant system could produce reactions

---

*H. F. McDuffie et al., "Assessment of Molten Salts as Intermediate Coolants for LMFBR's," USAEC Report ORNL-TM-2696, Oak Ridge National Laboratory, Sept. 3, 1969.

outside of the system piping; the events in this case would be similar to those discussed with reference to the compatibility of the secondary coolants with water and steam.

The exception to the preceding statements is hydrogen. If it is used as a secondary coolant and a situation develops in which it is introduced into the cell, then it must be considered that the same situation might either introduce ambient oxygen to the cell or allow further leakage of the hydrogen to the ambient. In either case, the development of an explosion hazard is possible.

8. MATERIALS OF CONTAINMENT

A primary consideration in the selection of a secondary coolant for a molten-salt reactor system is the choice of materials from which the piping and components of the secondary system may be fabricated. Three areas must be considered. One area includes the piping and components which are outside of both the primary and secondary heat exchangers; in this area any material which is compatible with the secondary coolant at its operating temperature and pressure will be acceptable. The second area is the tubing and headers of the primary heat exchanger where the materials of construction are in contact with both the primary fuel salt and the secondary coolant, and the third area of consideration is the tubing and headers of the secondary heat exchanger or steam generator where the material is in contact with both the secondary salt and feedwater and steam.

If a different material of construction is selected for any of these three areas, then consideration must be given to any problems which could result at the point where the two different materials are joined in the secondary system.

In the following paragraphs, it will be assumed that the materials of construction are operating nominally in the range from 1000 to 1300°F when the strength of the material is considered. In the steam generator, additional considerations must be given to the performance of the material in contact with feedwater in the range of 400°F unless the steam system is designed to preheat the inlet stream to temperatures in the range of 700°F as discussed in the previous section on the significance of the liquidus temperature of the coolant.

8.1 Containment Materials for the Various Secondary Coolant Systems

When those sections of the secondary coolant systems outside of the primary and secondary heat exchangers are considered, only the resistance of the material of construction by the secondary coolant must be considered; it can be assumed that the environment outside of the piping

and components can be kept sufficiently non-corrosive so that it need not be considered. In addition to the resistance to corrosion by the particular choice for a secondary coolant, the strength of the material at the operating temperature and pressure, the applicability of the material to the fabrication of the piping and components, and the cost of the material must be considered.

8.1.1 Materials of construction for molten salts as secondary coolants

8.1.1.1 Fluoride salts. Molten fluorides are excellent fluxing agents for the removal of oxide films. In the fluoride salt mixtures, the corrosion resistance of a metal or alloy cannot be maintained by a protective oxide film. Corrosion is controlled by the thermodynamic driving forces of the reactions involved. If the bulk of the metal fluorides in the coolant are more stable than the metal fluorides of the structural metal, there is little tendency for corrosion to occur. The relative ease of fluoride formation by alloying constituents has been related to the free energy of formation of the respective fluorides and increases in the following order: tungsten, molybdenum, niobium, nickel, iron, chromium, vanadium, zirconium, titanium, and aluminum. Results of corrosion studies have indicated that corrosion in molten fluoride systems involves the attainment of thermodynamic equilibrium between the fluoride melt and the container metal and that the chemical activities of the alloying constituents can be approximated by their atom fractions.*

In the more common high-temperature structural alloys, chromium has the greatest tendency to form a fluoride, because of the higher free energy of formation of CrF_2, which will go into solution in the fluoride salts. The presence of any oxidizing constituents in the molten salt will tend to promote this reaction until the buildup of the reduction products tends to stifle the formation of more "noble" metal fluorides such as FeF_2 because of the mass action effect. Thus, in chromium-containing base-metal alloys, corrosion, for the most part, is selective to chromium. Impurities in the melt, such as iron or nickel, increase the corrosion of the alloy due to the reduction of these fluorides by chromium in the alloy.

*Chapter VII, Corrosion in Fluid Fuel Reactors (page 46).

$$FeF_2 + Cr \rightleftarrows CrF_2 + Fe$$

The dissolution of oxide films from the metal surface can also cause selective removal of chromium by the following mechanism,

$$2Fe^{+++} + Cr \rightleftarrows 2Fe + 3Cr^{++}$$

where the original iron existed as the oxide in the film.

Nickel-base alloys generally have excellent compatibility with molten fluoride salts, since NiF_2 has a relatively low free energy of formation. As a consequence, the Hastelloy series of alloys has shown very good resistance to corrosion by molten fluoride salts. Particularly good performance was obtained from Hastelloy-B and C, and in particular, Hastelloy-N (INOR-8) which was used as the material of construction in the Molten Salt Reactor Experiment. Some attack has been indicated at temperatures above 700°C (1292°F).

Steel is not generally resistant to molten fluoride salts at high temperatures. Static studies at 700°C revealed very rapid attack within 600 hours on most of the common types of stainless steels by a mixture of lithium and uranium fluoride. Long-term tests with type 304L stainless steel, however, revealed a corrosion rate of about 2 mpy after exposures of 44,000 hours at a maximum temperature of 675°C by a mixture of lithium and beryllium fuel salts.

Molybdenum and niobium appear to be resistant to molten fluoride salts at temperatures to 816°C (1500°F). Vanadium and tantalum were attached to a depth of 1 mil in 100 hours at these temperatures. At 700°C gold and rhodium resisted attack by a mixture of sodium and uranium fluorides; platinum was slightly attacked, and copper was rapidly attacked. Other studies indicated that copper possesses excellent compatibility with fluoride salts.

For the containment of the sodium fluoroborate as a secondary coolant, Hastelloy-N is the most favored material of construction, although Inconel is a possibility. The present cost of Hastelloy-N, however, is about $20 per pound. Inconel 600 has performed reasonably well as a pump impeller even under cavitation conditions and exposure to mixtures of sodium, zirconium, and uranium fluorides (50-46-4) at temperatures in the range of

600 to 760°C. Its long-term use as reactor system piping, however, is still questionable. Alloys of nickel and molybdenum would probably provide satisfactory service, and nickel would be satisfactory for temperatures less than 1000°F. A duplex pipe of nickel inside of a stronger material would probably be satisfactory and more economical.

For L_2B in the absence of the fluorides of uranium and thorium which are found in the fuel salts, experiments have indicated that satisfactory materials of construction include Inconel, Ni–Mo alloys, Hastelloy-N, and 304 SS.

Based on the previous considerations, FLINAK could probably be contained in Ni–Mo alloys, Ni for temperatures less than 1000°F, and Hastelloy-N. Nickel-lined duplex piping is also a possibility.

The "low melting point" fluoride mixture which differs from the L_2B only in that NaF is substituted for some of the LiF could be contained in the same materials that have been specified for the L_2B. With this salt, and for some of the other fluoride salts, there is the possibility that some of the stainless steel can be used in the system piping and components if the coolant can be kept free of oxidizing agents. Leakage of the primary salt into a secondary system which contained fluoride salts as secondary coolants would introduce (along with the radioactive fission products which are undesirable in the secondary loop) the fluorides of uranium and thorium which will result in the oxidation of both the chromium and iron in the stainless steels. These mechanisms will be discussed in the following section on compatibility of the materials with the secondary salt in conjunction with the primary salt.

8.1.1.2 Chloride salts. As with fluorides, in reactions between chlorides and free elements of other elements at high temperatures, there is a tendency for the chloride which has the higher heat of formation per equivalent of chloride to be formed. Thus, zirconium, titanium, manganese, zinc, and thallium react with the chlorides of a large number of other elements whose chlorides have a lesser heat of formation. Conversely, those chlorides which have a low heat of formation per equivalent of chloride tend to be reduced to the free metallic element.

Also, as with fluorides, the presence of air over a chloride melt causes rapid corrosion of metals such as titanium, zirconium, and stainless steel. The presence of small amounts of water in a chloride mix can cause failure of stainless steels due to intergranular stress corrosion cracking.

As with the fluorides, Hastelloy-N appears to be a satisfactory material of construction for loop components and piping which is in contact with a molten chloride mix; this, however, is an expensive material of construction. Again, it is possible that nickel with a small percentage of alloying constituents might be used where temperatures are less than 1000°F, and a duplex tube with a nickel liner can be used at higher temperatures. Type 347 stainless steel might be used if the salt is maintained free of oxidizing agents and moisture; use of this material, however, is questionable.

8.1.1.3 Sodium hydroxide. The reaction between NaOH and various metals may be characterized by the following equation:

$$2\ NaOH + Me \rightarrow Na_2O + MeO\ (\text{or } NaMeO) + H_2$$

where "Me" indicates the metal, "MeO" is the metal oxide, and "NaMeO" represents the sodium metallite. Each metal tends to form its most stable or common oxide; the various metals differ only in the rate of reaction and their valence state. In general, but not exclusively, those metals which form stable oxides are least corrosion-resistant while those which form unstable oxides are most resistant. Thus, iron, chromium, beryllium, titanium, manganese, and iron-base alloys that form stable oxides are not corrosion-resistant and corrode according to the previous equation.

On the other hand, nickel, copper, gold, Monel 400, and probably silver and cobalt that form unstable oxides also exhibit one or more of the following secondary reactions:

$$MeO + H_2 \rightarrow Me + H_2O$$

$$Na_2O + 1/2\ H_2 \rightarrow NaOH + Na$$

$$H_2O + Na \rightarrow NaOH + 1/2\ H_2$$

The first two reactions are reversible for nickel, copper, and probably cobalt and only these metals or some of their alloys attain a definite equilibria (and low corrosion rates) because the sum of these three reactions is the reverse of the reaction given at the first of this section. Only these metals are protected from corrosion by a hydrogen partial pressure above the molten NaOH.

Active metals such as zirconium may generate sodium more rapidly (by the middle equation above) than it can be oxidized (by the last of the reactions shown above). Sodium hydroxide is also reported to be reduced to sodium or sodium hydride by magnesium, chromium, tungsten, iron, cobalt, or nickel. With gold and silver, the reaction forming NaOH and Na (middle, above) is not reversible because an alloy is formed with the metallic sodium and the reaction goes to completion.

All of the above metals can react further if the hydrogen which is produced is removed from the system as follows:

$$Na_2O + Me \rightarrow MeO + 2\ Na$$

This reaction will go to completion if the sodium is continuously removed or is alloyed.

These reactions indicate that hydrogen is beneficial as a cover gas with nickel, copper, and cobalt alloys. Conversely, an oxygen cover gas increases the oxidation rate of the metals in the molten hydroxide.

The position of a metal in an electrochemical order in NaOH does not appear to give an indication of its relative corrosion behavior. The reported electrochemical order for metals in NaOH at 340°C (644°F) is W, Mo, Cd, Pb, Cu, Ag, Au, Pt, Fe, Ni, Ta, Nb, and Zr.

It appears that there are really no good materials for the containment of NaOH under the conditions which will be encountered in the secondary loop of a molten-salt reactor system. Nickel, which is used as a material of construction for evaporators used to concentrate commercial NaOH, is not satisfactory from structural considerations at temperature approaching or above 1000°F. It is possible that a nickel-base alloy with an agent such as 15% molybdenum could be used; however, study supporting this statement is not complete. Monel might be an acceptable metal at lower temperatures also. For any of the choices, the maintenance of a hydrogen

pressure over the NaOH will be helpful in limiting corrosion. Loop tests have also shown that corrosion rates increase in NaOH systems both with increasing temperature and with increasing fluid velocities.

8.1.1.4 Nitrates. The nitrates in the form of a mixture of 6.9% $NaNO_3$, 48.5% $NaNO_2$, and 44.6% KNO_3 have been used for over 20 years as a heat-transfer salt. It is marketed by the DuPont Chemical Corporation by the trade name of Hitec, and it is sometimes designated as HTS for High-Temperature Salt. Early literature indicated that it decomposed at temperatures above 538°C (1000°F); however, more recent studies have indicated that, with proper overpressures and careful exclusion of contaminants, particularly water, stability could be maintained at temperatures significantly above 1100°F.

Operation of these systems has indicated that, at temperatures below 1000°F, most common materials of reactor construction can satisfactorily contain the nitrate mixture; these materials include the stainless steels, Inconel, and the high-nickel base alloys. The latter two should also be satisfactory up to temperatures of 1200°F. No studies have been reported for systems with velocities as high as those proposed in present secondary reactor systems.

8.1.1.5 Carbonates. Low-alloy steels and stainless steels, as well as the nickel-base alloys are compatible with carbonate systems up to temperatures of 1200°F. At temperatures significantly above this, 800°C (1472°F), most of the materials of construction are attacked quite rapidly by the carbonates. In the range of temperatures from 800 to 920°C, only gold appears to have significant resistance to corrosion by the carbonate mixture.

8.1.2 Materials of construction for liquid metals as secondary coolants

One particular disadvantage in the design of heat transfer systems which employ liquid metal, particularly sodium and potassium, is the development of excessive thermal stresses in the materials of construction. This aspect of system design is a result of the very high film heat transfer coefficient which is associated with the liquid metal; this same feature for liquid metals also contributes to their favorable performance in

some parts of the system. The problem develops when it is necessary to transfer heat to a fluid whose temperature differs considerably from that of the liquid metal. Specifically, in the secondary loop, this problem would develop in the steam generator. Because of the high heat transfer coefficient to the liquid metal, the temperature of the tube walls of the steam generator will remain very close to the temperature of the liquid metal. If these same tube walls are contacted by water at the usual feedwater temperatures (about 400°F), then excessive thermal stresses are created over the pipe walls and in the adjacent tube sheets.

Several design alternatives are available to avoid the development of excessive stresses in the steam generator. One of the more obvious alternatives is the same method which is used to eliminate the possibility of freezing molten-salt secondary coolants on these same tube walls; this method is to bring the feedwater to a temperature before it enters the steam generator that is high enough to prevent excessive thermal stresses in the tubing.

8.1.2.1 Sodium. Considerable experience has been obtained in circulating sodium in heat transfer loops. For those sections of the loop outside of the primary and secondary heat exchangers, the materials of construction may be the chrom-moly steels up to temperatures of 1200°F, the 18-8 stainless steels, Incoloy-800, or Hastelloy-N.

8.1.2.2 Sodium-potassium (NaK). Due to the similarity of the coolants, the same materials of construction may be used when the secondary coolant is NaK.

8.1.2.3 Bismuth. Bismuth is quite corrosive to most metals and alloys, but its corrosivity can be reduced (particularly with respect to steel) by the addition to the bismuth of zirconium or titanium in conjunction with magnesium. The zirconium (or titanium) is believed to react with the nitrogen and/or carbon in the steel to form a protective layer of ZrN or ZrC which provides a barrier between the bismuth and the ferrous alloy substrate. The role of magnesium in conjunction with zirconium or titanium is that of a getter for the oxygen from the system; thus it prevents any oxidation of the zirconium or titanium thereby destroying their effectiveness.

8.1.2.4 Bismuth–lead. Essentially the same materials of construction that were cited for bismuth are permissible materials of construction with bismuth–lead mixtures.

8.1.2.5 Lead. Most of the materials of construction are applicable for the containment of lead that were listed as materials for use with molten bismuth. Of the ferrous alloys, the stainless steels are the least resistant to attack due to the high solubility of nickel in lead and the higher solubility of chromium (than iron) in lead. Inhibition of lead with zirconium and magnesium additions is very effective in reducing corrosion attack. A Croloy 2 1/4 loop showed no attack after 27,765 hr (>3 years) operation in lead containing 250 ppm zirconium plus magnesium at a maximum temperature of 550°C (1020°F).

The refractory metal and metal alloys are resistant to attack by lead up to temperatures of 1400°F. Unalloyed niobium and niobium with 1 w/o zirconium showed no attack in one year of operation. Molybdenum is resistant at the operating temperature. A small amount of dissolved oxygen (6 ppm) inhibits corrosion through the formation of a protective layer of $PbMoO_4$. High oxygen levels or air contamination can result in rapid oxidization of the molybdenum. Other resistant materials are tantalum, tungsten, iridium, and ruthenium. Short-term tests indicate that both zirconium and titanium are catastrophically attacked by lead; the first by alloying and the second by pitting.

8.1.2.6 Mercury. Mercury and mercury vapor in topping cycles has been contained successfully in commercial practice using 2-1/4 Croloy when certain inhibitors had been added to the mercury. In experiments for the mercury loop of the SNAP-8 experiment, Croloy 9M was used and there was some evidence of corrosive attack. Tantalum was suggested as an appropriate replacement material for the Croloy; however, this was not evaluated experimentally. It appears, however, that tantalum would be a satisfactory containment material for secondary loops of molten-salt reactors if it was shown that the Croloy would not perform satisfactorily. Tantalum, of course, presents the difficulties associated with most of the refractory metals in fabrication of piping and components.

8.1.3 Materials of construction for gases as secondary coolants

In general, none of the pure gases which have been listed as choices for secondary coolants are corrosive to the normal materials used in reactor construction. Since the gases will be maintained at relatively high pressures and temperatures, the major requirement that the material of construction must meet is that it have the required strength at the operating temperature.

8.1.3.1 Helium. For the containment of helium any of the steels which possess sufficient strength at the operating temperature are satisfactory.

8.1.3.2 Hydrogen. At elevated temperatures, hydrogen embrittlement of the ferritic materials occurs. The Hastelloys will perform satisfactorily; however, hydrogen will diffuse through all of these materials at the operating temperatures.

8.1.3.3 Water vapor. The materials adaptable to any of the current commercial steam systems can be used with the water vapor systems. Use of the stainless steel will be required at the proposed operating temperatures.

8.1.3.4 Air. The oxidation of iron-base alloys might make the use of the nickel-base alloys desirable for use with air.

8.1.3.5 Nitrogen. Since nitrogen is essentially inert with respect to most structural materials, almost any material which is suitable from a structural standpoint will be acceptable. If the possibility of introducing either oxygen or moisture into the secondary system exists, then the stainless steels should be used.

8.1.3.6 Carbon dioxide. Since carbon dioxide is particularly difficult to "dry" completely, and since the possibility of introducing moisture into the system exists if the gas secondary coolant pressure is lower than the steam system pressure, the use of the stainless steels is probably required for carbon dioxide.

8.2 Containment Materials for Various Secondary Coolants in Conjunction With the Primary Salt

In the primary heat exchanger there will be some material of construction, probably in the form of tubes, which will separate the primary fuel salt from the secondary coolant. A direct-contact heat exchanger is, of course, possible in the case where inert gases are selected as the secondary coolant; however, this would negate the desire to contain the volatile fission products in the primary loop, and it would add to the problems of tritium transport to the secondary coolant. And, unless some design which incorporates bundles of double-tube heat exchanger is utilized, a material of construction will be required for the fabrication of a tube sheet to secure the tubes of the tube bundle. The tube sheet will also be in contact with both the primary fuel salt and the secondary coolant, unless some type of inert gas blanketing is designed for one or both sides.

The importance of the fact that two types of components, that is, tubes and a tube sheet, will be in contact with both the primary salt and the secondary coolant is related to the fabrication and strength requirements. The tubes may be relatively thin-walled while the tube sheet, if the pressures of the primary and secondary system differ significantly, may be quite thick. The fabrication techniques for the tubes and for the tube sheet also differ, so that, unless one material of construction is adaptable to both processes, different metals may be required. An additional requirement is that it should be possible to make a satisfactory junction between the tubes and the tube sheet and also between the tube sheet and the shell or header of the primary heat exchanger.

8.2.1 Materials with molten salts as secondary coolants

8.2.1.1 Fluoride salts. Since the primary fluid is also a fluoride salt, it might be concluded that those materials which were listed as acceptable for the remainder of the secondary coolant system with fluoride salts would also be acceptable for this part of the system. The difference, however, exists due to the fact that the fluorides of uranium and thorium are in the primary salt and they should not be present in the secondary

salt. The UF_4 in the fuel salt can be reduced by chromium, iron, and other elements by the following methods:

$$Cr + 2\ UF_4 \rightarrow CrF_2 + UF_3$$

$$Fe + 2\ UF_4 \rightarrow FeF_2 + UF_3$$

The iron fluoride in the melt can increase the corrosion of material by the further reduction of this fluoride by

$$FeF_2 + Cr \rightleftarrows CrF_2 + Fe$$

The dissolution of oxide films from the metal surface can also cause selective removal of chromium by

$$2\ Fe^{+3}(\text{in oxide film}) + 3\ Cr \rightleftarrows 2\ Fe + 3\ Cr^{+2}$$

Consideration of this mechanism would eliminate 304 stainless steel, which was cited as a possible material for use with Li_2BeF_4 as a secondary coolant, as a material of construction for the primary heat exchanger even though the primary salt is essentially Li_2BeF_4 with the fluorides of uranium and thorium added. The remaining materials which were listed as compatible with Li_2BeF_4 as a secondary coolant will also be acceptable in the primary heat exchanger. These are Inconel, nickel-molybdenum alloys, and Hastelloy-N.

For the sodium fluoroborate, two of the materials which were previously listed for the system piping should be acceptable in the primary heat exchanger. These were nickel-molybdenum alloys and Hastelloy-N. Inconel which was questionable for use in the loop piping is still questionable for this application. Nickel cannot be used because temperatures will be greater than 1000°F during normal operation, and duplex tubing employing nickel could not be used since both sides of the tubing are exposed to fluoride salts.

The same comments apply to FLINAK as were made for the fluoroborate; however, Inconel should probably be eliminated from consideration for this coolant.

The reactions just cited would also eliminate the use of the stainless steels in conjunction with the "low-melting point" fluorides and the

fuel salt. The same materials are applicable here as were listed for L_2B. These are Inconel, nickel-molybdenum alloys, and Hastelloy-N.

8.2.1.2 Chloride salts. Hastelloy-N appears to be about the only material which could be used in the primary heat exchanger of a fluoride-fueled molten-salt system with chloride salts as secondary coolants.

8.2.1.3 Sodium hydroxide. Since there appears to be no really "good" material for the containment of sodium hydroxide at the operating conditions in the secondary loop, there is no good material for use in the primary heat exchanger. The most likely choice appears to be a nickel-molybdenum alloy, if a satisfactory material does exist.

8.2.1.4 Nitrates and carbonates. For the nitrate and carbonate salts, the material requirements for compatibility with the primary fuel salt are much more severe than those of the secondary salt. The possible materials are Inconel, nickel-molybdenum alloys, and Hastelloy-N.

8.2.2 Materials with liquid metals as secondary coolants

8.2.2.1 Sodium and NaK. Because of the reactions of the primary fuel salt with material containing iron and chromium, the materials of construction which are compatible with both sodium and NaK and the primary salt are Incoloy-800 and Hastelloy-N. Even though the Hastelloy is more expensive, it would probably be the more favorable choice for this application.

8.2.2.2 Bismuth and bismuth-lead. The only materials which would be compatible with molten bismuth and the fuel salt are the refractory materials such as molybdenum and graphite. Neither of these lend themselves to the easy fabrication of tubes or tube sheets or to junctions with other materials.

8.2.2.3 Mercury. In contact with mercury and the fuel salt, again, the refractory materials would have to be employed for tubing and tube sheets. Materials which could be used are molybdenum and tantalum.

8.2.2.4 Lead. In conjunction with the primary salt, the use of lead as a secondary coolant would require the use of niobium, molybdenum. tantalum, tungsten, or some of the other refractory metals.

8.2.3 Materials of construction for gases as secondary coolants

For most of the choices of gases for secondary coolants, the material of construction in the primary heat exchanger would be dictated by the requirements to contain the primary fuel salt. A possible exception would be for the use of air (nitrogen and oxygen) as a secondary coolant. Irradiation of the secondary coolant by the delayed neutrons of the fuel salt would result in the formation of oxides of nitrogen. Pipes containing air in an irradiation environment have been found to corrode due to these compounds.

Hydriding with hydrogen as a coolant and nitriding of the material of construction with nitrogen as a coolant have not been found in the case of the use of Hastelloy-N. Both of these reactions are possible with some of the other materials which are compatible with the primary salt.

8.3 Containment Materials for Various Secondary Coolants in Conjunction With Steam

In the secondary heat exchanger or steam generator of the secondary loop, heat must be transferred from the secondary coolant to water and steam. This unit will unquestionably have tubes to provide the heat transfer surface area. It is possible that the tubes may be joined in banks of headers so that the fabrication of a tube sheet may not be necessary. It is more probable, however, at least for the molten salt and liquid metal secondary coolants, that some type of tube sheet will be required. The materials for the construction of these components must be compatible with the secondary coolant on one side and water—steam on the other. With the possible exception of the high-pressure gases, there will be a large pressure differential across these components.

8.3.1 Materials with molten salts as secondary coolants

8.3.1.1 Fluoride salts. For the sodium fluoroborate, the use of Hastelloy-N is possible for the steam generator tubing; however, the cost of this material is approximately $20 per pound. It appears possible to use a duplex tubing with Nickel-280 bonded to Incoloy-800 on the steam side; this duplex tubing might cost about $4 per pound.

The same choices exist when L_2B is the secondary coolant or for FLINAK and the "low melting point" fluorides.

8.3.1.2 Chloride salts. For the steam generator materials, the same choices appear to exist when chloride salts are used for a secondary coolant as those for the fluoride salts.

8.3.1.3 Sodium hydroxide. If the metal temperature can be restricted in the steam generator, an alloy of nickel with 15% molybdenum might be acceptable as a material for the tubing. Monel might be used near the feedwater temperatures.

8.3.1.4 Nitrates and carbonates. The stainless steels, Inconel, and similar materials usually used for high-temperature steam-plant tubing can be used in conjunction with the nitrates and carbonates as secondary coolants.

8.3.2 Materials with liquid metals as secondary coolants

8.3.2.1 Sodium and NaK. With either sodium or NaK as secondary coolants, acceptable materials for the steam generator tubing are 2-1/4 Croloy, Incoloy-800, and Hastelloy-N.

8.3.2.2 Bismuth, lead, and bismuth-lead. In the presence of bismuth or lead, it appears that 2-1/4 Croloy could be used as the steam generator tubing if the proper inhibiting agents are added.

8.3.2.3 Mercury. With either lead or mercury as secondary coolants, 2-1/4 Croloy could be used as the material for the steam generator tubing.

8.3.3 Materials with gases as secondary coolants

For most of the gases, the resistance to the corrosion by steam controls the choice of materials for the steam generator tubing. In these cases, the Croloy or stainless steels may be used. For the use of air as a secondary coolant, oxidation of the tubing in the high-temperature section may require the use of a nickel-base alloy. In the economizer sections of most of these units, mild steel may be used as the material of construction.

8.4 Literature Sources

Two major sources of information with respect to the performance of various materials of construction in the presence of the various choices for secondary coolants and the fuel salt and steam were drafts of surveys of the literature that are, as yet, unpublished. These surveys have extensive citations of the literature; however, since these original sources of information were not thoroughly investigated, these citations have not been transferred to this presentation. Copies of these drafts are in the hands of various persons at the Laboratory, and it is anticipated that they will be available in published form sometime in the future.

One draft was prepared by H. Shimotake and J. C. Hesson at Argonne National Laboratory; it was titled: "Corrosion by Fused Salts and Heavy Liquid Metals (A Survey)," and it was dated September 1965. It was prepared for publication as an ACS Monograph; however, it was not included. Hopefully, it will be available as an ANL report.

The second draft is entitled: "Chapter VII: Corrosion in Fluid Fuel Reactors." It has just become available in published form. It is contained in a book entitled Nuclear Applications by Warren E. Berry, published in 1971 by Wiley–Interscience (New York).

8.5 Summary and Conclusions Concerning Materials of Construction

For the purpose of summarizing the information that is presented in this section, three tables have been constructed. These tables indicate the performance of various materials of construction (a) in contact with the proposed secondary coolants, (b) in contact with the secondary coolants and the fuel salt, and (c) in contact with the secondary coolants and steam. In many cases, the performance of various materials of construction can be substantially affected by the presence of certain contaminants. These points are discussed in detail in the text.

In the construction of the performance tables, a series of performance criteria are listed on the next page. Where more than one criterion was applicable, multiple designations are indicated. For example, the designation 467 indicates that the performance of the material would be

satisfactory only if certain inhibitors were present in the secondary coolant, that fabrication of the piping and components from the material of construction would be questionable or difficult, and that the material would be expensive compared to other choices. A "blank" in the table is not intended to indicate that the material is unsuitable with a particular choice of coolant; it means, rather, that a more obvious selection for a material existed and that consideration of further materials of construction for use with that coolant was not necessary. Note that generally the higher numbers indicate more favorable performance for the material.

Symbol	Performance of the Material for Designations in Tables 7, 8, 9,
Blank	Material was not considered for this use.
0	Material is not suitable for this use.
1	Material can be used at temperatures less than 1100°F.
2	Material can be used at temperatures less than 1200°F.
3	Material can be used only at pressures less than 300 psia.
4	Material can be used only if certain inhibitors are present.
5	Material can be used only if certain contaminants are excluded.
6	Material can be used but fabrication is questionable or difficult.
7	Material can be used but it is relatively expensive.
8	Material can be used but a better alternative exists.
9	Best material for the application.

In the introduction of these sections, it was stated that the materials should be considered over the range of operating temperatures from 1000°F to 1300°F. The latter temperature is above the nominal operating temperature of many parts of the secondary loop; however, this temperature may be approached during transient or adverse operating conditions in almost any part of the secondary loop. The tubes of the steam generator will, for example, approach this temperature only if the turbine-plant feedwater system fails and the steam generator blows down and "dries out" in the time period immediately following a reactor scram. It would be desirable to establish the design temperature for a component or piping at the maximum temperature which the material can reach. In some instances, it may be economically desirable to establish a lower design temperature and to make system instrumentation and control so reliable that it is highly improbable that this temperature will be exceeded.

The relationship between design temperatures and pressures for the various materials is emphasized in Table 6. For the various materials

Table 6. Allowable Stresses and Design Pressures for Various Materials

Material (ASME Designation)	Design Temperature (°F)	Maximum Allowable Stress (psi)	Maximum Design Pressures		
			Case A (psig)	Case B (psi)	Case C (psig)
Carbon Steel (A-106)	900	6,500	2,500	1,200	985
	1000	2,500	960	450	380
	1100	--			
2-1/4 Croloy (A-213)	900	13,100	5,050	2,400	1,990
	1000	7,800	3,000	1,500	1,185
	1100	4,200	1,617	800	638
	1200	2,000	700	400	304
	1300				
18-8 Stainless Steel (316H) (A-312)	900	15,500	5,970	2,800	2,360
	1000	15,300	5,890	2,700	2,325
	1100	12,400	4,770	2,300	1,885
	1200	7,400	2,850	1,400	1,125
	1300	4,100	1,580	760	625
Inconel 600 (B-167)	900	16,000	6,160	3,000	2,435
	1000	7,000	2,700	1,300	1,065
	1100	3,000	1,150	600	450
	1200	2,000	770	400	304
	1300				
Incoloy 800 (B-407, Gr. 2)	900	13,100	5,045	2,400	1,990
	1000	12,800	4,930	2,300	1,950
	1100	12,700	4,890	2,275	1,930
	1200	7,900	3,040	1,500	1,200
	1300	4,600	1,770	900	700
Hastelloy-N	900	18,000	6,930	3,200	2,750
	1000	17,000	6,550	3,000	2,585
	1100	13,000	5,000	2,400	1,975
	1200	6,000	2,310	1,200	915
	1300	3,500	1,350	680	535

indicated, the allowable stresses at the indicated maximum temperatures have been extracted from Section 8, Division 1, of the ASME Boiler and Pressure Vessel Code (July 1, 1971). To facilitate the visualization of these allowable stresses, the maximum allowable pressures have been calculated for the following cases:

Case	Designates
A	Maximum allowable internal pressure in a pipe which is 1.0 inch in inside diameter with a 0.25-inch wall thickness. (This is approximately Schedule 160 pipe.)
B	Maximum allowable external pressure with 1 psia internal pressure in the pipe indicated in Case A.
C	Maximum allowable internal pressure in a pipe with an internal diameter of 12.0 inches and wall thickness of 1.0 inch (approximately Schedule 160 pipe).

For the other materials listed in the following table, values of maximum allowable stress have not been established. The nickel would have to be a low percentage carbon alloy with a small percentage of additional material to increase its high-temperature strength. In the nickel-duplex tubing, the type of material used in the duplex would determine the strength of the resultant tubing. One of the materials cited in Table 6 would probably be the duplexing material.

Table 7. Performance of Materials in Contact with the Secondary Coolant Only

Secondary Coolant	Carbon Steel	2-1/4 Croloy	18-8 Stainless Steels	Inconel 600	Incoloy 800	Hastelloy-N	Hi-nickel Alloy	Nickel-Moly Alloy	Nickel Duplex	Molybdenum	Tantalum	Tungsten	Niobium	Carbon
NA BF4-NA F			0	5		78	1	78	9	67	67	67	67	6
LI F--BE F2			8	9		7		7		67			67	6
FLINAK						7	1	8	9	67			67	6
NA+K F-ZR F4			5			7	1	8	9	67			67	6
NA ØH						8	18	8	9					68
LI CL--K CL	1	1	5			7	1		9	67				
NITRATES	1	2	8	9	8									
LMP FLUØRIDE			5			7		8	9	67			67	6
CARBØNATE	1	2	8	9	8	7								
SØDIUM		2	9	8	8	7								
NAK		2	9	8	8	7								
BISMUTH		24	4	0	0	0	0	0	0	67	67			6
PB-BI		24	4	0	0	0	0	0	0	67	67			6
MERCURY		24									67			
LEAD		24								47	67	67	67	
HELIUM(HP)			9		8	7								
HELIUM(LP)	13	23	9			7								
HYDROGEN(HP)					8	79								
HYDROGEN(LP)	13	13	13		9	7								
WATER(HP)		2	9			7								
WATER(LP)	13	2	9			7								
AIR(HP)					9	7								
AIR(LP)	13	23	9		8	7								
NITRØGEN(HP)		24	9		78	7								
NITROGEN(LP)	13	23	9			7								
CØ2(HP)		2	9			7								
CØ2(LP)	13	23	9			7								

Table 8. Performance of Materials in Contact with the Secondary Coolant and the Fuel Salt

Secondary Coolant	Carbon Steel	2-1/4 Croloy	18-8 Stainless Steels	Inconel 600	Incoloy 800	Hastelloy-N	Hi-nickel Alloy	Nickel-Moly Alloy	Nickel Duplex	Molybdenum	Tantalum	Tungsten	Niobium	Carbon
NA BF_4-NA F			0	0		79	0	2	0	67	67	67	67	
LI F--BE F2			0	9		7		7						
FLINAK			0	0		79	0	2	0	67	67	67	67	
NA+K F-ZR F_4			0	0		79	0	2	0	67	67	67	67	
NA ØH							0	0	0					
LI CL--K CL						9								
NITRATES				8		9		8						
LMP FLUØRIDE			0	9		7		7						
CARBØNATE				8		9		8						
SØDIUM					8	79								
NAK					8	79								
BISMUTH										67				6
PB-BI										67				6
MERCURY										67	67			
LEAD										67	67	67	67	6
HELIUM(HP)						79								
HELIUM(LP)						79								
HYDRØGEN(HP)						79								
HYDRØGEN(LP)						79								
WATER(HP)						79								
WATER(LP)						79								
AIR(HP)						79								
AIR(LP)						79								
NITRØGEN(HP)						79								
NITRØGEN(LP)						79								
CØ2(HP)						79								
CØ2(LP)						79								

Table 9. Performance of Materials in Contact with the Secondary Coolant and with Steam

Secondary Coolant	Carbon Steel	2-1/4 Croloy	18-8 Stainless Steels	Inconel 600	Incoloy 800	Hastelloy-N	Hi-nickel Alloy	Nickel-Moly Alloy	Nickel Duplex	Molybdenum	Tantalum	Tungsten	Niobium	Carbon
NA BF_4-NA F						7			9					
LI F--BE F2						7			9					
FLINAK						7			9					
NA+K F-ZR_4						7			9					
NA ØH								29						
LI CL--K CL						7			9					
NITRATES		2	9	8										
LMP FLUØRIDE						7			9					
CARBØNATE			8	9										
SØDIUM		28			9	7								
NAK		28			9	7								
BISMUTH		249												
PB-BI		249												
MERCURY		29												
LEAD		249												
HELIUM(HP)		29												
HELIUM(LP)	13	29												
HYDRØGEN(HP)					8	9								
HYDRØGEN(LP)	13				8	9								
WATER(HP)		28	9											
WATER(LP)	13	28	9											
AIR(HP)		28	8	8	9									
AIR(LP)	13	28	8	8	9									
NITRØGEN(HP)		28	9											
NITRØGEN(LP)	13	28	9											
CØ2(HP)		258	8	8	9									
CØ2(LP)	135	258	9											

9. OTHER POSSIBLE COOLANTS OMITTED FROM THE PREVIOUS PRESENTATION

9.1 Alternate Fluoride Salts

A fluoride salt mixture somewhat similar to the "low melting point" (LMP) fluoride salt which has been included in the previous presentation has been suggested. In this alternate salt, the BeF_2 of the LMP fluoride would be essentially replaced with KF. The composition of the alternate salt in mole percent would be 46.5% LiF, 11.5% NaF, and 42.0% KF. The substitution of KF for BeF_2 essentially makes this a "high melting point" salt since its liquidus temperature is 455°C (851°F). The viscosity of this salt is considerably lower than the LMP fluoride, and its stability when exposed to steam is better since there is no precipitation of the beryllium oxide. Because of its high liquidus temperature (the significance of this liquidus temperature has been discussed previously), this alternate salt was not included.

Another low melting point fluoride can be obtained by replacing the LiF in the LMP fluoride with BeF_2; this would leave a salt mixture containing only NaF and BeF_2. The liquidus temperatures of these mixtures would be below 400°C (752°F); however, the viscosity would be much higher than desirable and excessive pumping power in the secondary loop would be required. The advantage of using this salt is that it contains no lithium to dilute the lithium of the primary salt in the event of a leak between the two systems. If the decision was made to make all lithium fluorides in secondary coolants from lithium enriched in lithium-7, then this salt would be considerably less expensive than the LMP fluoride. The consequences and alternatives for lithium-containing secondary salts have already been discussed. Compatibility and containment problems for this salt would be similar to those for the LMP fluoride. Because of its very high viscosity, however, this salt composition has been omitted.

It has been suggested that the composition of this NaF–BeF_2 mixture could be altered by substituting ZrF_4 or AlF_3 for some of the BeF_2. This would result in a mix which had significantly lower viscosities than the NaF–BeF_2 mix with no drastic increase in the liquidus temperature. One

alternative mixture containing NaF, KF, and ZrF_4 has been included; it has a melting temperature about the same as the sodium fluoroborate. One of the advantages of this choice is that the BF_3 cover gas that is required with the fluoroborate is eliminated. There has been some concern in the use of both ZrF_4 and AlF_3 that a solid may be condensed from the cover gas over mixtures containing these compounds. This "snow" problem, at least for the use of ZrF_4 in the concentrations proposed has been reviewed. From consideration of the vapor pressure–temperature, it appears that significant precipitation of the solid phase in the vapor space will not occur if the maximum temperature difference in any of the components exposed to this vapor is less than 80°C (150°F).

The other alternatives were omitted from this presentation due to the lack of sufficient physical property data. Conclusions concerning compatibility with the primary salt and steam and suitable materials of construction for these alternatives would be quite similar to those for the similar fluoride salts. The limit in lowering the liquidus temperature by selecting various compositions among these fluoride salts is about 315°C (599°F) which can be obtained with melts of acceptable viscosity.

For a system which incorporated a primary salt with the composition of 58% KF, 31% ZrF_4, and 11% $(Th,U)F_4$, on a mole basis, a secondary salt of 58% KF and 42% ZrF_4 was proposed. The liquidus temperature of this secondary salt was about 400°C (752°F). It did not appear to have any particular advantage for systems with Li_2BF_4 as the primary carrier salt in comparison with the other fluoride salts in the study.

Stannous fluoride has been suggested as a possible secondary coolant because of its low melting point, 215°C (419°F), and its availability in very pure form due to the current large-scale use in toothpaste. Unfortunately, this material is extremely corrosive to most materials of construction. No nickel or iron-based alloys can be used in a system with stannous fluoride; the only acceptable materials of construction are the refractory materials such as molybdenum or graphite. Neither of these materials is easily adaptable to the fabrication of the secondary system components. It might be noted that PbF_2 and BiF_3 are similar to SnF_2 in oxidizing and corrosive effect.

9.2 The Cyanides

The cyanides have been suggested as possible secondary coolants principally because of the possibility of introducing hydrogen atoms to be used as "tritium traps" in the form of either ammonium cyanide or hydrogen cyanide. Sodium cyanide, the most readily available of the group, has a melting point of 563.7°C (1046.6°F) which is too high for consideration. The CuCN—NaCN system has a eutectic melting about 350°C (660°F), and the AgCN—NaCN system has a eutectic melting about 300°C (572°F). Potassium cyanide has eutectics with AgCN and CuCN melting below 300°C (572°F). Since hydrogen atoms can be added to the other secondary coolants by methods which have been previously discussed, the added biological hazard of handling large volumes of cyanides plus some questions of stability in the radiation environment appeared to disqualify the cyanides from further consideration.

9.3 Organic Secondary Coolants

Organic materials such as Santowax OM or Santowax WR, which have low vapor pressures at the proposed operating conditions and appropriate melting temperatures, have been suggested. While the overall stability of these materials in an irradiation field is considered good, there is enough radiolitically-induced decomposition to form a significant fouling film on the heat transfer surfaces of the primary heat exchanger. If these surfaces could be cleaned at reasonable intervals, then these coolants might be considered. However, the difficulties of obtaining access to this part of the reactor system appear to be sufficient to eliminate the consideration of these compounds.

9.4 Sulfur

Molten sulfur was also proposed as a secondary coolant. The melting point of this element is extremely favorable, 119°C (246°F). Again, however, the substance is extremely corrosive, and it appears that the only suitable material of construction would be carbon.

9.5 Haloaluminates

A mixture composed of 69.5% $NaAlCl_4$, 19.5% $KAlCl_4$, and 1.0% NH_4AlCl_4 (mole percentages) has been proposed. This mixture has the advantage of providing hydrogen atoms in the NH_4AlCl_4 which can be removed by distillation and thus function as a tritium trap; it also has a liquidus temperature of 125°C (257°F). No information was available on materials of containment, but those materials which were applicable to the fluoride and chloride salts are certainly applicable to this salt. The only compatibility problem would be the reaction with steam to release HCl. More information is required on the vapor pressure of this mix, its thermal conductivity and heat capacity, and an evaluation of its performance from the corrosion standpoint.

10. SUMMARY AND CONCLUSIONS

This presentation is a review of various choices for secondary coolants in a molten-salt reactor system. It assumes that the current best choices for the secondary coolant is the sodium fluoroborate in conjunction with a primary fuel salt which is a mixture of lithium and beryllium fluorides in the mole ratio of 2:1 plus the fluorides of uranium and thorium. The study was prompted by a desire to determine a secondary coolant which would perform as well or better than the sodium fluoroborate as a heat transport medium and, at the same time, be effective in preventing the migration of tritium that was formed in the primary loop to the steam in the power cycle. It was desired that the alternative choice for a secondary coolant should also avoid some or all of the additional problems associated with the use of the fluoroborate. These problems include possible interactions with the primary salt, excessive corrosion rates, and the need for a relatively high overpressure of BF_3 gas. Secondary objectives of the study were to reveal, if it existed, a secondary coolant that would have performance characteristics superior to sodium fluoroborate, and to gather in one document information on the physical characteristics and engineering performance of other choices for secondary coolant to function as a basis for further study in this area.

Possible choices for secondary coolants were divided into three groups; these were (a) molten salts, including sodium hydroxide, (b) liquid metals, and (c) gases. It was realized that before a final decision could be made concerning the relative merits of any acceptable secondary coolant, an engineering design of a molten-salt reactor plant that was, at least to some degree, optimized for that coolant, would be required. If such a design were made for the best choice in each of the three groups indicated above, then the same design should be useful in evaluating any choice in that group.

Superior performance as a heat transfer medium for any coolant should be related to either minimizing the heat transfer area required in the system or the pumping power or both. These requirements can be related, by conventional engineering correlations, to the physical property values for the various coolants at the average loop temperature. In the

category of molten salts, NaOH and FLINAK appeared to produce the lowest area requirements and FLINAK and the mixture of NaF, KF, and ZrF_4 produced the lowest requirements based both on area and power requirements. The mixture of NaF, KF, and ZrF_4 had the lowest power requirements. The relative differences between the values were not large, however, and an appropriate system design could eliminate some of these differnces in performance characteristics.

The liquid metals, on an overall basis, indicated much smaller heat transfer area requirements; this would be expected due to the large heat transfer coefficients that are obtained with these coolants. Sodium and NaK also indicated the lowest area requirement in this group of coolants. When power requirements are considered, less favorable factors are obtained since these factors assume constant mass velocity in the piping. The group of gases produced relatively high factors indicating the requirements for heat transfer area and pumping power as would be expected.

When total inventory costs for the various choices of secondary coolants were compared, significant differences (an order of magnitude) were found only for a few of the choices; these were bismuth, bismuth–lead, and mercury in the liquid metal group. In the molten salt group, if enriched lithium-7 was used in the formulation of those choices that contained lithium, the inventory costs were increased by factors between 2 and 7 depending upon the lithium content of the coolant. For coolants which were relatively expensive with the incorporation of natural lithium, these added inventory charges corresponding to these factors were greater than $5,000,000. As would be expected the inventory charges for the gaseous coolants were significantly lower than charges for the other two groups.

Some attempt was made to relate the melting or liquidus temperature of the molten salts and the liquid metals to characteristics of the engineering design of the system and the operating characteristics of the system. On the tentative bases that it was undesirable to develop the solid phase in the secondary loop and that the feedwater temperature must approach the liquidus or melting temperature by at least 50°F, certain restrictions can be listed.

As a specific example, if the liquidus or melting temperature is in the range of 750°F, this assumption implies that the feedwater temperature should approach the critical temperature. To avoid poor performance in the steam generator, the feedwater pressures must also be supercritical.

To function effectively in the prevention of tritium migration to the steam system, the secondary coolant must either contain hydrogen atoms which can be exchanged with the tritium atoms, or it must contain chemically active groups which will react to form stable compounds with the tritium. To prevent the coolant from becoming saturated with tritium during use, it must contain a large concentration of hydrogen atoms or active groups so that it becomes a reservoir for tritium, or the hydrogen atoms or active groups must be contained in a minor component of the secondary coolant which can be removed and replenished by simple chemical processing.

Of the coolants that were considered, only sodium hydroxide, hydrogen gas, and water vapor contain sufficient hydrogen atoms to act as reservoirs. A large number of possible sources of hydrogen atoms and a limited number of compounds with active groups exist that can be added to the various coolants and removed on a continuous basis. The most significant point is that such a compound exists for the sodium fluoroborate in the form of a complex hydroxl ion which forms $NaBF_3OH^-$ in the melt. Normal "drying" procedures used to process the salt will break down this complex and remove it; then a slight amount of moisture can be allowed to reform the complex. If this low concentration of hydroxl ion does not increase the corrosive characteristics of the salt, then these mechanisms appear to be acceptable. Hydrogen fluoride gas for all of the fluoride salts or hydrogen gas or a mixture of both for the liquid metals can be a source of hydrogen atoms in the coolant which can be easily stripped and replaced by equipment similar to that used to remove the fission product gases from the primary loop.

Several consequences of mixing between the secondary coolants and the primary fuel salt or the steam need to be considered. These include exothermic reactions, precipitation of fuel material, and introduction of poisons into the primary salt. Most of the fluoride salts are chemically compatible with the fuel salt although some can reduce the uranium to a

metal. For those salts which contain lithium, much study will have to be given to the question of whether the lithium of the secondary coolant should be enriched in lithium-7. The oxygen-containing secondary salts will precipitate the oxides of uranium and thorium; consideration will have to be given both to mixing rates and reaction rates to determine the exact consequences. Most undergo rather mild reactions with steam.

The active liquid metals will also produce metallic uranium and thorium when mixed with the primary salt. Their reaction with steam is significantly exothermic. The choices for gaseous coolants appear to be compatible with both the primary salt and steam except that, again, those which contain oxygen can cause the precipitation of the oxides of uranium.

When suitable materials for containment of the various coolants are considered, satisfactory alloys appear to exist for most of the choices. The only coolant which must be eliminated on this basis is sodium hydroxide; there appears to be no satisfactory containment material at the operating temperatures. Additional consideration must be given to materials of construction for the tubes of the primary heat exchanger and the steam generators where the material is in contact with the secondary coolant and the primary salt and steam, respectively. This consideration eliminates some materials which were acceptable for use in conjunction with the coolant. Hastelloy-N (INOR-8) appears to be satisfactory in many cases; however, it is relatively expensive. Nickel-molybdenum alloys also appear to be acceptable with many of the fluoride salts. Hastelloy-N and Incoloy-800 are acceptable for sodium and potassium in conjunction with the fuel salt.

When a consideration is made of the various choices for secondary coolants by groups, there appears to be at present no characteristic of sodium fluoroborate which would exclude its consideration among the other molten salts. Most of the other possible choices in this group have potential problems which can be as difficult to relieve as those of sodium fluoroborate. One of the disadvantages of sodium fluoroborate is its relatively high liquidus temperature of 725°F; however, this is significantly lower than the temperatures of 856°F for L_2B and 851°F for FLINAK. The mixture of lithium and potassium chloride has a liquidus temperature of 680°F, and it appears to have good performance characteristics; its

only disadvantage is that it introduces another halogen in the system which, for some materials of construction, may produce additional problems. All of the lithium-containing molten-salt coolants will result in significantly higher inventory charges if it is determined that enriched lithium is required to prevent contamination of the enriched lithium of the primary salt. Both the carbonates and nitrates present compatibility problems when mixed with the primary salt.

Of the possible molten-salt coolants, it appears that sodium fluoroborate is a good choice with the chlorides and possibly the low melting point fluorides being the second and third alternative choices.

In the group of liquid metals, sodium is the obvious first choice. The bismuth, bismuth–lead, or lead coolants are too corrosive as is the mercury; in addition, mercury is too expensive and probably not available in sufficient supply. Introduction of sodium as the secondary coolant would present compatibility problems with both the primary fuel salt and the steam. In addition, incorporation of sodium as the secondary coolant would lead to design problems in the elimination of excessive thermal stresses in the tubes and tube sheets of the steam generator. The use of sodium as a secondary coolant also introduces the problem of incompatibility with the steam and possibly also problems of compatibility with the primary salt. At present, there appears to be no incentive to introduce these problems into the molten-salt reactor concept by choosing sodium in preference to a molten-salt unless the lower melting temperature of the sodium proved to be a decided advantage.

While most of the proposed gaseous coolants appear to be acceptable, helium and hydrogen have obvious advantages. Because helium has obvious advantages in safety of handling and because the use of hydrogen would provide a reservoir for tritium rather than a trap, helium appears to be the better choice. The major problem related to the use of helium as a secondary coolant is that of designing a high-pressure secondary system. Design methods do exist for such a system, but considerable evaluation will have to be given to the choice of a design which is optimized for this coolant.

11. ACKNOWLEDGMENTS

Considerable assistance was received in the preparation of this report from Roy E. Thoma, who provided physical property data, information of phase relationships and reactions between various components. S. Cantor also contributed to this body of information for some of the components. Information on the acceptable materials of construction for most of the systems was obtained from John W. Koger and Jack H. Devan. J. W. Cooke provided estimates for some thermal conductivity data for molten-salt melts that otherwise were not available. J. R. McWherter and H. A. McLain provided information on present and previous considerations of design alternatives for molten-salt systems and considerations of coolant performance criteria. Many others of the molten-salt reactor project contributed from their knowledge and experience to this information. Dunlap Scott provided a point of departure and the overall aim of the study.

ORNL-CF-71-8-10

Distribution

1. J. L. Anderson
2. C. F. Baes
3. S. E. Beall
4. M. Bender
5. E. S. Bettis
6. F. F. Blankenship
7. E. G. Bohlmann
8. G. E. Boyd
9. R. B. Briggs
10. S. Cantor
11. E. L. Compere
12. J. L. Crowley
13. F. L. Culler
14. J. R. DiStefano
15. S. J. Ditto
16. W. P. Eatherly
17. D. E. Ferguson
18. L. M. Ferris
19. J. H. Frye
20. W. K. Furlong
21. W. R. Grimes
22. A. G. Grindell
23. R. H. Guymon
24. P. N. Haubenreich
25. R. E. Helms
26. P. P. Holz
27. W. R. Huntley
28. J. J. Keyes
29. S. S. Kirslis
30. J. W. Koger
31. R. B. Korsmeyer
32. A. I. Krakoviak
33. M. I. Lundin
34. H. G. MacPherson
35. R. E. MacPherson
36. A. P. Malinauskas
37. H. E. McCoy
38. H. F. McDuffie
39. H. A. McLain
40. L. E. McNeese
41. J. R. McWherter
42. R. L. Moore
43. E. L. Nicholson
44. A. M. Perry - J. R. Engel
45-47. M. W. Rosenthal
48-52. J. P. Sanders
53. Dunlap Scott
54. J. H. Shaffer
55. R. A. Strehlow
56. R. E. Thoma
57. D. B. Trauger
58. A. M. Weinberg
59. J. R. Weir
60. M. E. Whatley
61. J. C. White - A. S. Meyer
62. R. P. Wichner
63. Gale Young
64-65. Central Research Library (CRL)
66. Document Reference Section (DRS)
67-68. Laboratory Records (LRD)
69. Laboratory Records - Record Copy (LRD-RC)