

ZEOTROPIC MIXTURES OF HALOCARBONS AS WORKING FLUIDS
IN BINARY GEOTHERMAL POWER GENERATION CYCLES

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The performance of Rankine cycle binary systems for geothermal power generation using a hydrothermal resource has been investigated as a part of the U. S. Department of Energy, Geothermal Technology Division (DOE/GTD) Heat Cycle Research Program. To date, in addition to many pure fluids, mixtures of Paraffin-type hydrocarbons and water-ammonia mixtures have been investigated. This paper gives the results of consideration of mixtures of halocarbons as working fluids in these power cycles. The performance of mixtures of Refrigerant-114 (R-114) and Refrigerant-22 (R-22) in combinations from pure R-114 to pure R-22 was calculated for such cycles. Various alternatives were considered: 1. minimum geofluid outlet temperature constraint/no constraint, 2. dry turbine expansion/expansion through vapor dome, 3. use of turbine exhaust gas recuperator/no recuperator.

Results of the study indicate that the halocarbon mixtures are at least as good as the hydrocarbon mixtures previously analyzed for a 360 F resource. The magnitude of the net geofluid effectiveness (net energy produced per unit mass geofluid flow) for the R-114/R-22 mixtures is the same as for the best hydrocarbon mixture previously analyzed. The percentage improvement in effectiveness in using mixtures over using the pure fluids as working fluids is comparable for both classes of working fluids.

Introduction

The performance of Rankine cycle binary systems for power generation using hydrothermal resources has been investigated, and those systems are now being used in a number of applications. The selection of a working fluid to maximize performance and/or minimize cost of production of electrical energy for a particular resource is a primary concern. The use of paraffin-series hydrocarbons alone and in binary mixtures has been studied fairly extensively by Demuth and Kochan^{1,2} and Milora and Tester³. Bliem⁴ mixtures of water and ammonia. Milora and Tester³ have shown that pure halocarbons (Freons) are comparable with the hydrocarbons in performance. Demuth and Kochan² showed an increase in performance of binary mixtures of the hydrocarbons over the pure hydrocarbon of about 7 to 9 percent. One would expect similar increases for the halocarbons. The Freon Products Laboratory of E. I. Du Pont de Nemours & Company has recently developed computer programs to determine the thermodynamic properties of binary mixtures of the Freons.⁵ Data for two such mixtures are available. Because of all of these developments, it was decided that this would be a good time to investigate halocarbon mixtures in geothermal Rankine cycle systems. The purpose of the present work was to conduct a preliminary

investigation of the halocarbons; it was not to be an exhaustive study. Therefore, this report investigates only one promising mixture, R-22 and R-114, realizing that there are, probably, better mixtures. However, all of the information needed to develop the thermodynamic data required in the analysis was available for this mixture.

Overall, the paper discusses the feasibility of using mixtures of halocarbons in geothermal power plants. The next section contains a discussion of the halocarbons as represented by the standard refrigerants and their possible applicability. This is followed by a section on the approach and assumptions made in the study. Results and conclusions are presented in the final sections. The work is discussed in more detail in Reference 6.

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Halocarbon Working Fluids

Halocarbons or halogenated hydrocarbons have been used as refrigerants for a long period of time. These substances have been synthetically produced, particularly for their refrigerating properties, by the substitution of a halogen for one or more of the hydrogen atoms in methane, ethane and propane. The halogens used are fluorine, chlorine and sometimes bromine. The American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE) has developed a numerical system for designation different refrigerants. The last digit in the designation (the one on the right) indicates the number of fluorine atoms in the molecule formed. The second digit from the right is one more than the number of hydrogen atoms remaining, and the third digit is one less than the number of carbon atoms (blank indicating methane structure; 1, ethane structure and 2, propane structure). If bromine is used, this designation is followed by a B with the number of bromine atoms after the B.

Figure 1 shows the critical pressures and temperatures of some of these refrigerants. Experimental values are shown by the open circles are the methane-based halocarbons (10-40), and by the open squares for some of the ethane-based halocarbons. The shaded circles and squares represent computed values for critical properties deduced from the molecular structure of the compound. Experimental values for the paraffin-series hydrocarbons are shown on the plot, as references, in small closed triangles. The dashed line connects the normal form of each of the hydrocarbons from ethane (C₂) through heptane (C₇). The other triangles are the isomers of each hydrocarbon (for example, the triangle at C₄ not on the line is isobutane and

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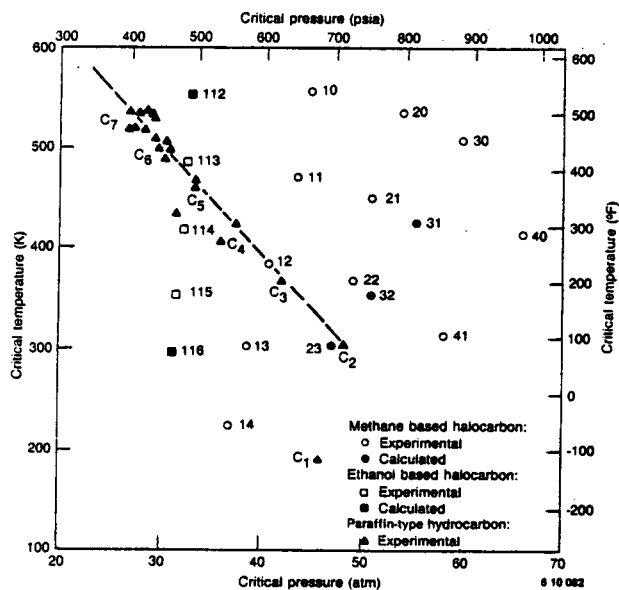


Fig. 1 Critical States for Hydrocarbons and Halocarbons

the point on the line is normal butane). It can be seen that the halocarbons have critical states which bracket the range of critical states for the hydrocarbons.

The choice of a halocarbon mixture for this initial study was made using the information in Figure 1. It was felt that mixture critical temperature was an important parameter in determination of thermodynamic performance. Previous studies 1,2 indicated that the best performance for a 360 F resource was obtained with mixtures of isobutane and a very small quantity of heptane (4 percent by mass), and propane with 5 percent hexane. To a first approximation, the mixture critical temperature is the mole-weighted average of the constituent critical temperatures. It was, therefore, felt that halocarbons spanning the range of critical temperatures between isobutane and propane might give good thermodynamic results. Refrigerant-22 and 114 fit the desired criterion. Du Pont had supplied the interaction parameter needed to represent this mixture with their computer codes, so no additional experimental work was necessary to determine the thermodynamic properties of any mixture of these refrigerants.

One additional point may be deduced from Figure 1. The earlier studies of mixtures of the paraffin-type hydrocarbons indicated that a binary mixture gave as high a thermodynamic performance as a tertiary mixture of these hydrocarbons. The mole-weighted average critical pressure gives a first order approximation of the mixture critical pressure. This approximation is not as good as the similar approximation for temperatures, but it is close. (In fact, the mixture critical pressure may be somewhat above the mole-weighted average.) Using the approximation, a binary mixture state would be plotted along the straight line connecting the components. A tertiary mixture state would be

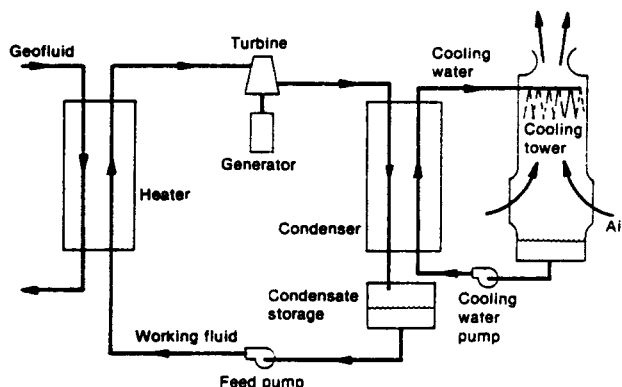
within the triangle connecting the three substances. The paraffin-type hydrocarbons are grouped so close to a straight line that it is doubtful that significant difference could be seen between two or three component mixtures. With the halocarbons, however, there would be a substantial difference. Therefore, is an additional degree of freedom results for mixtures of halocarbons, and the critical pressure of the mixture in addition to critical temperature could be tailored to the desired requirements. It is felt that three component mixtures of the halocarbons should be investigated to determine if this conjecture is correct.

Approach and Assumptions

The system performance for a simple Rankine cycle was calculated using assumptions consistent with those used in References 1, 2, and 4 (the hydrocarbon and ammonia-water analyses). Mixtures from pure R-114 to pure R-22 were used as working fluids. The following subsections describe the cycles, list the assumptions made in the analysis, and then describe the analytical procedure. A more complete discussion of the approach is given in Reference 6 along with a computer which was used to determine the cycle performance.

Binary Geothermal Cycle Descriptions

The working fluid in a binary geothermal electric power plant undergoes the processes of a Rankine thermodynamic cycle. Figure 2, which is a schematic diagram of a simple binary geothermal cycle, illustrates these processes as well as the major components of the plant. Starting at the condensate storage tank, the working fluid is pumped from the condenser pressure to the heater pressure. Heat is transferred from the geofluid to the working fluid in the heater (a shell-and-tube heat exchanger). In most of the cycles analyzed, the heater pressure was above the mixture critical pressure so there was no discrete change of phase in the heater. If the pressure is less than the critical pressure, the heater is a preheater, boiler and superheater. The working fluid is heated to the appropriate turbine inlet temperature. The working fluid vapor then flows through the turbine, producing work at the turbine shaft. The turbine drives



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Fig. 2 Simple Binary Geothermal Cycle

the generator, which produces the electrical work. The turbine-exhaust working fluid is then condensed (after being desuperheated, if necessary) in the condenser, and the heat is transferred to cooling water. This heat is rejected, in turn, to atmospheric air using a wet cooling tower. The condensed working fluid is then returned to the condensate storage tank and the cycle is repeated.

In many instances, there is enough energy at a high enough temperature in the turbine exhaust, to preheat of the working fluid going to the heater. A recuperator may be added to the cycle to accomplish this task as is shown in Figure 3. This modification is particularly useful when the limit on the geofluid outlet temperature is imposed. In these applications, the recuperator allows the working-fluid-to-geofluid-flow ratio to be changed in order to increase the geofluid effectiveness. The heat rejected is also reduced, but this is a small effect. In the case where there is no minimum imposed on the geofluid outlet temperature, recuperation is generally not worthwhile because only the heat rejected is decreased which gives a small increment in geofluid effectiveness at the expense of a more complex system.

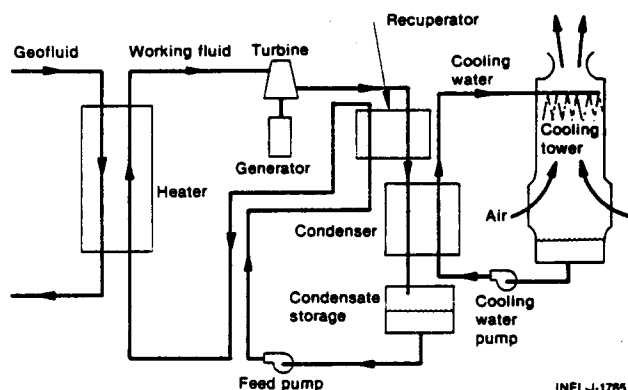


Fig. 3 Binary Geothermal Cycle with Turbine-Exhaust Recuperator

Thermodynamic Assumptions

The assumptions made in this analysis are essentially the same assumptions that were made in previous working fluid studies.^{1,2,4} The assumptions are:

1. The geofluid supplied to the plant was liquid at 360 F and was slightly subcooled.
2. Cooling water was supplied to the condenser from a wet cooling tower. The wet-bulb temperature was assumed to be 60 F and the tower approach temperature difference was 10 F. Therefore, cooling water entered the condenser at 70 F. The parasitic power requirements were estimated as described in References 1 and 2.
3. Pinch point temperature differences in the heater and condenser were taken to be 10 F. The pinch point in the recuperator was assumed to be 9 F.
4. Pump and turbine isentropic efficiencies were assumed to be 80 and 85 percent, respectively. Electrical losses were not included.
5. Geofluid pumping requirements (at a given

geofluid flow rate) were assumed to be the same in all cases and those parasitics were not included.

6. Component, valve and piping pressure drops were neglected.

7. Geofluid properties were assumed to be those of pure water and were taken from the ASME Steam Tables⁷ as were cooling water properties. The working fluid properties were taken from the Du Pont computer codes.

5 The properties are obtained using the Redlich-Kwong equation of state with Soave's modifications, including binary interaction coefficients. The liquid density is provided by the user. Superheated vapor properties were taken from SUPERTABLE, bubble and dew points were taken from SATTABLE (each of which generated a hard-copy table), and the two-phase properties between the bubble point and the dew point were obtained from an interactive program CYCLE.

Some inconsistencies were noted in the properties of the halocarbon mixtures in the compressed liquid state. The resolution of these inconsistencies is discussed in detail in Reference 6.

Method of Analysis

A computer program was written which will perform a thermodynamic cycle analysis using the assumptions listed in the previous section. A listing of the program along with input instructions and the results of a typical run are given in the appendix to Reference 6. Thermodynamic properties (sets of temperature, enthalpy and entropy) are input at the heater pressure and the condenser pressure with a temperature range to cover the possible operating range of the system. A turbine inlet temperature or entropy is specified, and the program analyzes four cases: no geofluid outlet temperature restriction with and without a recuperator, and a specified minimum geofluid outlet temperature with and without a recuperator.

Mixtures from 0 to 100 percent R-114 were analyzed (every 25 % from 0 to 75 % R-114, and then every 5 % to 100 %). For each mixture, a heater pressure was chosen and the turbine inlet temperature varied from the point which would give an isentropic turbine outlet state with 10% moisture to the point at which a pinch point occurs at the heater outlet (350 F). The temperature at which the geofluid effectiveness was a maximum was determined for four cases: 1. no minimum geofluid outlet temperature limit (10 F pinch point) with an isentropic turbine expansion which avoided the two-phase region (without a recuperator). 2. no minimum geofluid outlet temperature limit with an isentropic turbine expansion which could pass through the two-phase region (without a recuperator). 3. 160 F minimum geofluid outlet temperature without a recuperator. 4. 160 F minimum geofluid outlet temperature limit with a recuperator. The initial data showed that the gains in performance adding a recuperator to a system with no minimum geofluid temperature limit was generally less than 0.1% for reasons noted in the previous section. This gain could not offset the added

complexity and capital cost of a recuperator. Therefore, no recuperators were considered when there was no geofluid temperature constraint. Similarly, no system with a 160 F geofluid outlet temperature limit produced an optimum value with an expansion which passed through the two-phase region. Indeed, in most cases, maximum performance occurred near the point with maximum turbine inlet temperature.

The optimum turbine inlet temperature was found for each pressure for each case mentioned above. In general, the turbine inlet temperatures were different for the different cases. (This was more optimization than was done in the previous studies^{1,2,4}.)

On the condensing side, the working fluid pressure was obtained using the following rules (to avoid a separate optimization): If the condensing range (difference between the dew point and the bubble point) was less than 20 F, the dew point was taken to be 105 F. If the condensing range was greater than 20 F, the bubble point was taken to be 85 F. These are also the rules that were used in the previous analysis^{1,2,4}. Some recent analyses have indicated that optimization of the condenser pressure may change the results to some extent; this behavior should be examined further for the near optimum cases.

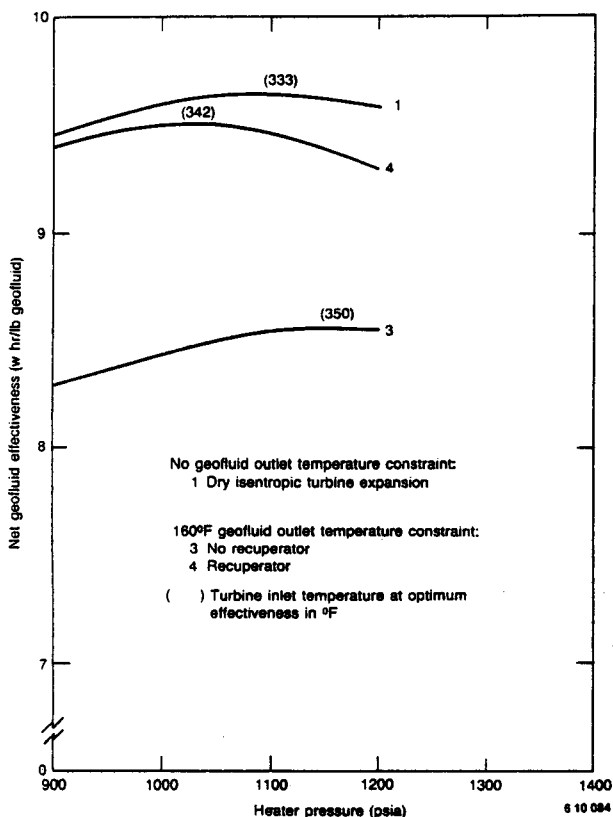


Fig. 4 Cycle Performance for a 50% R-114
50% R-22 Mixture

Results

The results of the analysis discussed in the previous section are shown in Figures 4 and 5. Figure 4 gives the results for a mixture containing 50 % by mass R-114, the composition giving the maximum geofluid effectiveness. Figure 5 gives the same results for a mixture containing 95 % by mass of R-114.

Notice that there is no curve for expanding through the dome (Case 2) in Figure 4. It was found that unless the fluid properties resulted in a drying effect on expansion, there was no calculated performance gain by going into the dome (even with the optimistic assumption of no turbine efficiency degradation with moisture). At each pressure, the turbine inlet temperature was varied to obtain the maximum geofluid effectiveness under the assumptions of each of the remaining three single-phase-expansion cases: 1) no geofluid outlet temperature constraint, 3) 160 F geofluid outlet temperature constraint without a recuperator, and 4) 160 F geofluid outlet temperature constraint with a recuperator. The turbine inlet temperature at the maximum effectiveness is noted on the figure for each case. Normally, the constrained-outlet-temperature cases optimized at higher heater pressures and turbine inlet temperatures than did the unconstrained cases. The constrained-temperature case without a recuperator optimized at a higher temperature and

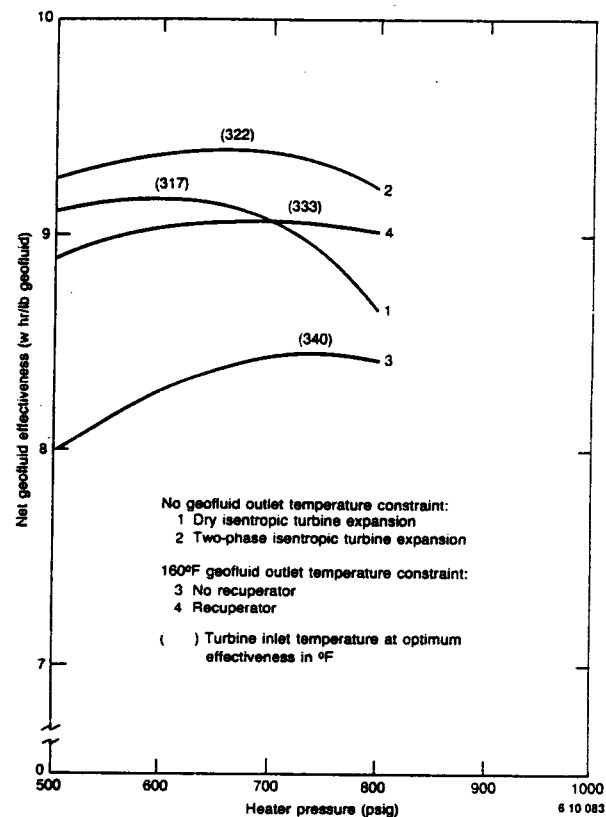


Fig. 5 Cycle Performance for a 95% R-114
5% R-22 Mixture

pressure than the case with a recuperator. Indeed, the unrecuperated, constrained case usually maximized at the point at which the turbine inlet temperature was as high as possible (350 F) giving a pinch point at the heater outlet.

Similar results are shown in Figure 5 for the 95 % R-114 case. Here, the turbine expansion is drying so a performance improvement is possible by expanding through the two-phase dome. In general, the maximum geofluid effectiveness is achieved with the isentropic expansion ending on the saturation line; in some cases, however, the outlet state was slightly superheated.

Figure 6 shows the maximum performance for each of the four cases as a function of mixture composition. Note that the two-phase turbine expansion through the dome shows improvement over a dry isentropic turbine expansion only for compositions with 65% or more R-114. (Pure R-114 dries on expansion while R-22 wets on expansion.) Two relative maxima appear on each curve. Past cycle analyses for hydrocarbon mixtures have not shown this effect. Reference

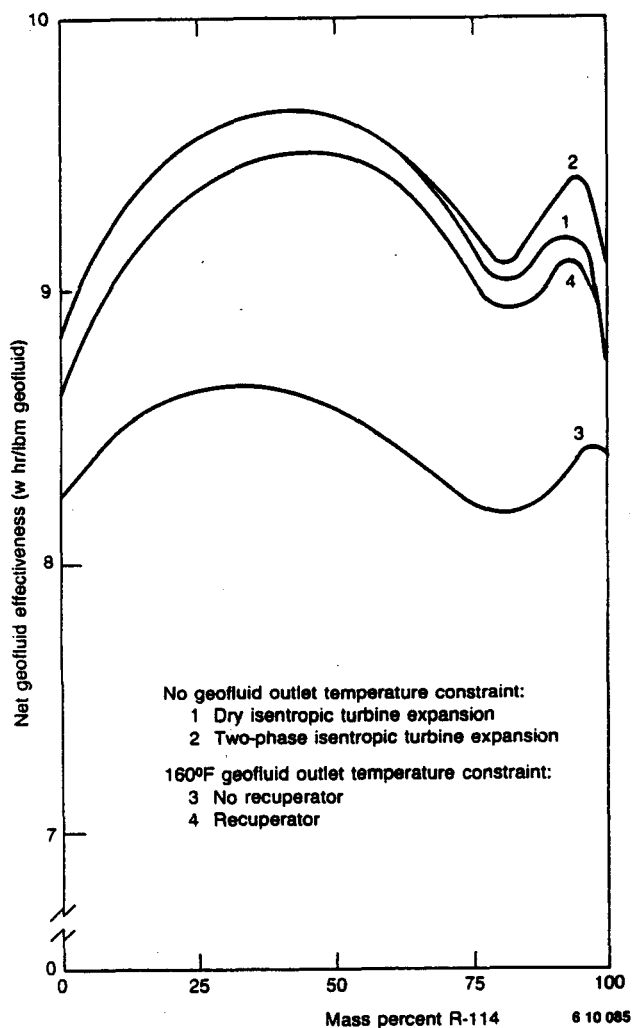


Fig. 6 Maximum Cycle Performance as a Function of R-114 Content

1, however, only considered a small range of compositions, especially for those mixtures with sharply peaked performance curves such as propane-hexane and isobutane-heptane mixtures. Closer examination of these curves indicates that the slopes of the curves must change and at least an inflection point (if not a lesser maximum) must occur, prior to reaching the pure heavy constituent. With the halocarbon mixtures considered in this report, the pure components have approximately equal performance, while with the hydrocarbon mixtures mentioned above, the performance of the pure heavy constituent is quite a bit lower than that of the pure light component. Therefore, where two maxima appear with the halocarbons, possibly only one exists with the hydrocarbons (or at least the second maximum will be much lower than those shown in Reference 1).

For the R-114/R-22 mixture, the maximum performance occurs at compositions between 30 and 50% R-114. The maximum is very flat and therefore system performance will not be sensitive to changes in composition. The lower maximum occurs at a composition of 90 to 95% R-114 and is considerably more peaked. For the unconstrained outlet temperature case, the second maximum is 2.7% lower than the highest maximum if wet isentropic turbine expansion (through the dome) is allowed, and 5.0% lower if the isentropic expansion is forced to remain dry. For the case in which the geofluid outlet temperature is constrained to remain above 160 F, the second maximum is 2.6% lower than the highest maximum. The use of an exhaust gas recuperator with the constrained geofluid-temperature produced an effectiveness curve having a maximum within 1.4% of the unconstrained maximum.

Conclusions and Recommendations

The results of the study and the conclusions reached are summarized below:

1. The performance of halocarbon binary geothermal cycles appears to be as good as that of hydrocarbons as measured by the net geofluid effectiveness (watt-hr/lb geofluid flow). The highest values of geofluid effectiveness are in the range from 9 to 10 watt-hr/lb geofluid for both types of working fluids.

2. The incremental increase in performance with halocarbon mixtures as compared with single-component halocarbons is at least as large as that for hydrocarbon mixtures: With no geofluid outlet temperature restriction and no recuperation, a 7.8 percent increase in geofluid effectiveness was possible with a halocarbon mixture relative to a pure halocarbon for a cycle having a dry turbine expansion, and a 6.0 percent increase for a cycle with expansion through vapor dome. With the 160 F geofluid outlet temperature restriction an increase of 3.0 percent with no turbine exhaust recuperator was observed for this mixture and an 8.8 percent increase with a recuperator.

3. Turbine exhaust recuperation increases the optimum performance with the 160 F geofluid outlet temperature limit to

within 1.4 percent of the optimum performance with no limit on outlet geofluid temperature. The unrecuperated case with the restriction is 10.3 percent below the unrestricted case. These results are similar to those noted for the hydrocarbon mixtures.

4. There is some indication that tertiary mixtures may give better results than binary mixtures for the halocarbons (while this was not the case for the paraffin-series hydrocarbons).

As a result of this preliminary study, the following recommendations are made:

1. Further study of the halocarbon mixtures as working fluids in geothermal power plants should be conducted. This work should include: a. A study to investigate the effect of optimizing the condenser pressure on performance. b. Thermodynamic performance studies of other halocarbon mixtures (including tertiary mixtures). c. A second law (availability) analysis of the systems. d. Studies estimating the cost of electricity for a halocarbon plant relative to a hydrocarbon plant.

2. A more critical look at the thermodynamic properties of the halocarbon mixtures should be taken. The effort might also require the use of other thermodynamic modeling of the fluid mixtures such as the extended corresponding states model of the National Bureau of Standards. The Du Pont code predicts the thermodynamic properties of binary mixtures only; if tertiary mixtures are to be considered, other models would be required. Some additional experimental data would be required to determine the interaction parameters for a given mixture if extremely accurate properties are needed. However, for preliminary analyses, an approximation of these properties can be made without the additional experimental results.

Further study will verify whether mixtures of halocarbons are viable candidate working fluids for geothermal power cycles.

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