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A loop for circulating liquid lead-bismuth mixtures: corrosion studies and operation

John Charles Clifford

Iowa State University

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A LOOP FOR CIRCULATING LIQUID LEAD-BISMUTH MIXTURES: CORROSION STUDIES AND OPERATION

by

John Charles Clifford

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of The Requirements for the Degree of DOCTOR OF PHILOSOPHY

Major Subject: Chemical Engineering

Approved:

Signature was redacted for privacy.

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Signature was redacted for privacy.

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Signature was redacted for privacy.

Dean of Graduate College

Iowa State University Of Science and Technology Ames, Iowa

1960
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>SUMMARY</td>
<td>iii</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>LITERATURE SURVEY</td>
<td>9</td>
</tr>
<tr>
<td>EQUIPMENT AND PROCEDURE</td>
<td>16</td>
</tr>
<tr>
<td>EXPERIMENTAL RESULTS</td>
<td>39</td>
</tr>
<tr>
<td>Materials Comparison Tests</td>
<td>39</td>
</tr>
<tr>
<td>Removal of iron and chromium from the alloys</td>
<td>40</td>
</tr>
<tr>
<td>Metallographic examination of corroded specimens</td>
<td>59</td>
</tr>
<tr>
<td>Selection of container materials</td>
<td>80</td>
</tr>
<tr>
<td>The Effects of Various Operating Conditions on Corrosion</td>
<td>82</td>
</tr>
<tr>
<td>Specimen surface conditions</td>
<td>82</td>
</tr>
<tr>
<td>Liquid metal impurities</td>
<td>91</td>
</tr>
<tr>
<td>Relative velocity of liquid metal and container material</td>
<td>95</td>
</tr>
<tr>
<td>Liquid Metal Circulation Systems</td>
<td>95</td>
</tr>
<tr>
<td>Thermal convection loops</td>
<td>95</td>
</tr>
<tr>
<td>Forced convection loop</td>
<td>109</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>111</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>115</td>
</tr>
<tr>
<td>APPENDIX</td>
<td>116</td>
</tr>
</tbody>
</table>
SUMMARY

The comparative resistances of six ferrous alloys, containing from 0 to 26.5 per cent chromium, to attack by the eutectic melt of lead-bismuth have been investigated using an isothermal, dynamic testing technique. The 96-hour tests were conducted in the temperature range 600 to 900°C, and materials evaluations were made on the basis of the amounts of iron and chromium appearing in the melt during exposure, and on metallographic examinations of the test specimens after exposure.

It was found that chromium was selectively removed from the alloys by lead-bismuth and that the amount removed increased as the chromium content of the alloys increased. Removal of chromium was the principal reason for the deterioration of the alloys, particularly at the higher temperatures. Comparison of the corrosion resistances of the chromium-alloyed steels and a steel containing no chromium indicated that small amounts of chromium provided some corrosion resistance, but that larger amounts did not improve corrosion resistance.

On the basis of these tests two of the materials, a 2\(\frac{1}{4}\) chromium-1 molybdenum alloy steel and AISI type 430 stainless steel, appeared useable as container materials for experimental systems below 700°C. Above this temperature the deterioration of all the steels was too rapid to consider these alloys even for very short time use.
Some temporary reduction in the severity of attack of type 430 stainless steel was effected by exposing the steel surfaces to oxidizing conditions before testing. However, the protective film formed by such treatments was not continuous and did not appear to be self-healing in the presence of lead and bismuth oxides. Marked reductions in corrosion were produced by saturating the lead-bismuth with chromium before tests, but such a technique is practical with lead-bismuth only under isothermal conditions.

Several pieces of equipment, including two flanged connections, a cold trap, and a modified diaphragm pump, have been tested in circulation loops to determine their suitability in experimental lead-bismuth systems. The flanges proved satisfactory at temperatures as high as 650°C, and the cold trap effectively prevented precipitation of corrosion products in the piping of the circulation systems. The 1 gpm pump performed satisfactorily in a system operating between 400 and 500°C, and it appears suitable for use with lead-bismuth where the required flow rates are low.
INTRODUCTION

Apart from the conventional metallurgical operations involving liquid metals, perhaps the advent of nuclear energy has provided the greatest stimulus for development of liquid metals technology. With the growth of a civilian atomic energy program, liquid metals came under scrutiny first as reactor coolants and later as fuel carrier-coolants and as media for reprocessing irradiated fuel elements. Within this program the greatest interest in liquid metals to date has centered about their use as reactor coolants, and an examination of the characteristics of some heat transfer media will help to show the reasons for this interest.

Consideration of several possible heat transfer media (water, Dowtherm, HTS*, sodium, lead, bismuth, and the eutectic compositions of sodium-potassium and lead-bismuth) shows that none of these satisfies all the important characteristics of a good heat transfer medium, and that selection must be made on a compromise basis. This selection is made more difficult both by the radiation encountered in a reactor and by the desire for high thermodynamic efficiency in heat transfer.

* Heat transfer salt, a mixture of sodium nitrite and sodium and potassium nitrates.
operations, the latter necessitating high temperature operation.

In non-nuclear applications steam is used at relatively low temperatures, but as temperatures are increased the cost of containment rises rapidly because of high operating pressures and increased corrosion. Dowtherm and HTS are used at temperatures below 400 and 450°C respectively, but Dowtherm and other similar organic liquids begin to decompose above 425°C. Molten salts, although thermally stable above 550°C, do not offer good enough heat transfer properties to warrant solving increased corrosion problems.

In comparison with these media, the liquid metals have several distinct advantages. Their heat transfer coefficients in systems dynamically similar to those using Dowtherm or HTS are an order of magnitude higher. They have high thermal conductivities and, being elemental, are thermally stable. Liquid metals are stable in intense radiation fields, and several of them have low thermal neutron capture cross sections. Their boiling points are relatively high, allowing low pressure operation at high temperatures.

Some disadvantages associated with liquid metals are low volumetric heat capacities, melting points above room temperature, high induced radiation in some instances, and handling and containment problems. The latter include corrosion, instrumentation, and fire hazard. With the exception of the
eutectic composition of sodium-potassium, none of the metals mentioned are liquids at room temperature. Consequently, all lines carrying these metals must be provided with heaters to prevent solidification in case of equipment shutdown. The alkali metals react violently with water and some hydrocarbons, and in case of equipment failure would present serious fire hazards for which ordinary fire fighting equipment is useless.

Corrosion problems, the severity of which depend on the particular system, are associated with all liquid metals. Both increased temperature and the presence of oxygen make these more acute. Because oxygen promotes corrosion in a liquid metal system, vacuum tight systems, which in themselves demand specialized experience and equipment, are necessary.

A combination of several desirable characteristics of liquid metals (particularly sodium) and several undesirable characteristics of more conventional coolants has brought about limited use of sodium and sodium-potassium as reactor coolants. Some of the problems created by the undesirable characteristics of liquid sodium or sodium-potassium have been solved, and the present state of alkali liquid metals technology below 550°C perhaps is best illustrated by the liquid metal cooled reactors which have been operated in this country. These include an experimental sodium-potassium cooled fast breeder reactor, a sodium cooled power prototype, and two sodium cooled submarine propulsion systems. Three additional
sodium cooled reactors are now under construction.

Use of the heavy liquid metals in the reactor program has met with less success. A reactor concept in which a uranium-bismuth solution acts both as coolant and as fuel has been under development for about ten years. The fact that such a reactor has not been operated indicates the number of technological difficulties involved with the use of a heavy liquid metal such as bismuth. In addition to uranium-bismuth, possible liquid metal fuels under consideration include molten plutonium, and dispersions of uranium oxide in a sodium-potassium alloy or in bismuth.

Another purpose for which liquid metals have been suggested is that of high temperature fuel reprocessing, or pyrometallurgical processing, of fast reactor fuels. Present processes for removing fission products from irradiated reactor fuels are centered around liquid-liquid solvent extraction. However, these aqueous processes have some undesirable features. The metallic fuel must be converted to water soluble salts before purification and then converted back to the metallic state after completion of fission product removal. In addition, the reprocessing steps generate large quantities of radioactive liquid wastes whose handling and storage present an expensive problem.

In comparison with aqueous processing, pyrometallurgical operations hold some advantages for fast reactor fuel cycles.
Fuel is processed as a molten metal, eliminating metal-to-salt and salt-to-metal conversion steps. Relatively small quantities of radioactive wastes are generated in the purification steps, and reactor fuel inventory is decreased as a result of the reduction in length of the decay period for irradiated fuel elements.

Disadvantages of pyrometallurgical processing include all those associated with the handling of liquid metals in addition to the necessity of conducting all fuel refabrication by remote control behind heavy shielding. Remote operation is necessary because pyrometallurgical reprocessing schemes fail to remove a number of radioactive isotopes from the irradiated fuel.

The first of the pyrometallurgical processes to be tested on an engineering scale is melt refining or oxidative slagging which will be used to reprocess the fuel from a sodium cooled, experimental fast breeder reactor now under construction. The principal step, carried out at 1300°C is roughly analogous to the production of steel by the open hearth process. Certain fission products in the fuel melt are selectively oxidized by reaction with the container walls, and the products of this reaction collect in a slag phase from which the purified fuel can be separated.

Another process, designed for repurification of uranium-bismuth from the liquid metal fuel reactor, employs an extrac-
tion step during which fission products are removed from the liquid metal by contacting the uranium-bismuth with a fused chloride salt at 500°C. An alternate to this process would make use of a fused salt extraction step followed by batch distillation of the extract phase to separate fissionable material from fission products. A third extraction scheme proposes the use of molten silver, which is immiscible with uranium, as an extractant for fission products.

The most recent pyrometallurgical process to be investigated is based on fractional crystallization from low melting solvent metals. Dissolution of irradiated fuel elements in bismuth-lead-tin, zinc, or mercury would be followed by separation of fission products from fissionable material by precipitation or crystallization of intermetallic compounds or metals. The solubility changes necessary for precipitation would be effected through temperature changes or the introduction of additional constituents to the system.

These examples of heat transfer and separations operations have been presented in order to illustrate some of the areas in which liquid metals can be used and, in doing this, to show cause for the present interest in these media. From the examples it can be seen that all the actual and proposed uses of liquid metals have counterparts in more conventional engineering practice. Problems arising from the adaptation of such operations as heat transfer, fluid flow, distillation,
solvent extraction, and crystallization to difficultly handled materials have been solved in the past, and there is no reason to believe that this will not be the case with liquid metals. Indeed, the development of sodium technology shows that some progress already has been made.

As these potentially useful schemes move from a stage of basic investigation to one of process development, or, as engineering scale studies of separation methods, heat transfer, and fluid flow are initiated, a number of problems are encountered. Among the first of these are selection of container materials and basic equipment, as well as development of adequate handling techniques. Since the work reported here was intended to serve as a basis from which engineering scale studies involving liquid metals could be made, several potential container metals have been examined. These common engineering materials have been evaluated for use with a heavy liquid metal, the eutectic composition of lead-bismuth, in the temperature range of 550 to 900°C.

In addition to the examination of possible container materials, an attempt has been made to develop the techniques and equipment necessary for operation of liquid metal circulation systems in the lower portion of this temperature range. This has involved the design and testing of components for four liquid lead-bismuth circulation systems: three thermal convection loops and one forced convection loop. It is hoped
that the information resulting from these tests will aid in the design and operation of engineering scale liquid metal systems.
LITERATURE SURVEY

Several summaries of information concerning the resistance of materials to attack by liquid metals have been published during the last ten years. Among those containing information on the behavior of materials in contact with lead, bismuth, or the eutectic composition of the two are Kelman, et al. (22), Miller (26), and Gurinsky (19). A survey of these and other reports dealing with containment of lead-bismuth was made in 1958 (8), so that only a brief summary is included here.

In general, it was found that nickel and nickel containing alloys, such as the austenitic steels, are unsatisfactory container materials for liquid lead-bismuth mixtures above approximately 500°C (7, 14, 15, 29, 30). This is attributed to the preferential solution of nickel from these materials.

Within the ferritic class of steels there seems to be some variation in corrosion resistance with changing chromium content, but correlation of corrosion resistance with chromium content is difficult. Static tests conducted with these steels and the lead-bismuth eutectic melt indicate that below 650°C corrosion resistance is increased by increasing chromium content (14). At 760°C, as well as above this temperature, the trend seems to be reversed and the low chromium steels are more resistant (18). However, these conclusions stem from different investigations and the experimental conditions, al-
though superficially similar, may have differed enough that any comparisons are invalid.

If the trends noted in the lead-bismuth tests are real, static tests with bismuth should substantiate them. One would expect only the severity of attack to change since bismuth is more aggressive than the eutectic melt. However, exposure of ferritic steels to bismuth under substantially the same conditions as those employed with the eutectic melt shows that at 500°C corrosion resistance decreases with increasing chromium content (10). Above 750°C it has been reported that resistance to attack by bismuth increases with increasing chromium content (28). Although these tests contradict the trend noted in tests with the eutectic melt, there may be no basis for a comparison between the sets of investigations. It appears that the only conclusion to be drawn from work with the chromium-containing ferritic alloys is that more evidence is necessary before a correlation between chromium and corrosion resistance is attempted.

Mild carbon steels suffer moderate penetration in static lead-bismuth tests at 500°C (14), and more severe penetration in 450°C thermal loop tests (12). Their limit of usefulness in flow systems probably is below 450°C.

Static tests with iron show that it has good resistance to lead, bismuth, and the eutectic melt up to 500°C (9, 10). Bismuth seems to attack iron above 700°C (9), while lead has
little effect up to 1000°C (5). From these investigations it would seem that the useful limit of iron with lead-bismuth, under static conditions, is about 700°C. The resistance of iron to the flowing metal cannot be established.

Although a large amount of work has been done in developing liquid metal handling equipment, as illustrated by some available reviews (4, 6, 16, 24, pp. 843-865, 27), the majority of this has involved sodium and sodium-potassium. Since there are substantial differences in behavior between the alkali metals and the heavy liquid metals, most of this development work is of value only as background information.

Experience with the eutectic melt of lead-bismuth before 1950 was rather limited. In general, exclusion of oxygen from lead-bismuth systems was believed essential, making necessary the use of leaktight, weld connected systems (33).

Since that time Cygan (11, 13) has reported circulating the eutectic melt with an overhung impeller centrifugal pump. The circulation system was constructed of mild carbon steel and operated at a maximum of 370°C. A sharp-edge orifice was used to measure flow, and pressure measurements were made with seal pots and liquid level probes. Flanged joints which could be protected from direct contact with the lead-bismuth were gasketed with aluminum.

A series of thermal convection loops used to circulate lead-bismuth at a maximum of 454°C also was reported by Cygan.
These loops were of all welded construction and were fabricated either from mild steel, AISI type 410 or type 446 steel. The use of a cold trap containing a vycor encased magnet for collection of magnetic corrosion products was found to increase, very substantially, the life of the loop in which it was employed.

Operation of forced-convection lead-bismuth eutectic heat transfer systems in the 200 to 500°C range was reported by Johnson et al. (20, 21). These systems employed overhung shaft centrifugal pumps and were constructed of mild steel or a chromium-molybdenum alloy steel with both welded connections and ring joint flanges with soft iron rings. Sharp edge orifice meters with pressure taps connected to float-containing seal pots were used to determine flow rates.

Development work with the bismuth-uranium fuel system below 550°C has been reported by Raseman and Weisman (31,32), Weeks et al. (34), and Klamut et al. (23). Both thermal and forced convection loops, constructed of austenitic stainless and chromium-molybdenum alloy steels, were used. In the earlier work the fuel solutions were circulated with electromagnetic pumps in austenitic stainless steel loops. Flow was measured both with magnetic and with rounded-edge orifice flowmeters, and pressure measurements were made with seal pots containing liquid level probes. All welded construction as well as ring joint flanges with austenitic stainless steel
rings were employed. Later loops were constructed of chromium-molybdenum alloy steel and all connections in the systems were welded. Canned motor centrifugal pumps were used for circulation of the liquid metal.

Circulation of bismuth at 400°C in a chromium-molybdenum alloy steel piping system has been reported by Baker (3). The pump used was of the overhung impeller centrifugal variety and both magnetic and orifice meters were used for flow measurement. Pressure measurements were made in a manner similar to that reported by Raseman and Weisman (31).

The General Electric Company has done development work on systems using liquid lead, but literature information concerning this work is meager. In addition, both the Oak Ridge National Laboratory and The Babcock and Wilcox Company have operated liquid lead circulation systems.

Summarizing the liquid metal handling experience reported, it appears that no work has been done with the eutectic melt of lead-bismuth above 500°C and that work with bismuth has not been carried much further. In most of the cases reported the liquid metal was circulated by means of a centrifugal pump. However, these pumps, with the exception of that one developed at the Brookhaven National Laboratory (24, pp. 846-847), do not seem to have been particularly successful. The use of orifice plates for flow measurement seems satisfactory except that the necessary seal pots, connecting lines, liquid level
probes, and inert gas systems make the measuring system rather complicated. Flanged connections for lead-bismuth systems have met with success in some cases and have been found impractical in others, so that the reliability of such devices for liquid metal service is still in doubt.

In order to supplement the information reported in the literature, a survey of some 30 manufacturers of liquid metal handling equipment was made. This survey, reported in more detail earlier (8), was concerned primarily with pumps and flowmeters, which were evaluated on the basis of cost, availability, delivery time, simplicity of operation, and suitability for operation with lead-bismuth. Centrifugal pumps, which had been judged the most satisfactory on the basis of literature reports, were found to be high priced and to require long periods for delivery. In fact, the advantages normally claimed for centrifugal pumps seemed overshadowed, particularly with the smaller models, by these factors. It was decided, after investigation of flowmeters and additional pump types, that the choice lay between an electromagnetic pump-magnetic flowmeter combination and a metering diaphragm pump.

The diaphragm pump was chosen partially because of difficulties involved in operating a magnetic flowmeter in a system which would contain lead-bismuth, and partially because of cost. As far as could be determined, diaphragm pumps had not been used previously to circulate liquid metals and their
suitability for use with such media was unknown. However, the simplicity of such pumps together with the fact that they meter flow by positive displacement made test operation seem worthwhile.
EQUIPMENT AND PROCEDURE

Tests for evaluation of the resistance of materials to attack by liquid metals may be classified as static or dynamic, the former being used primarily to select from a large number of materials those few which seem most resistant. In this work no static tests were conducted, as the available literature provided a guide to the more resistant classes of materials. After selection of the most resistant materials through static tests, these materials normally are evaluated in dynamic tests where conditions approach more closely those anticipated in service. Some of the more common dynamic apparatus include rocking and spinning units in addition to thermal and forced convection loops. Spinner tests, described in more detail earlier (8), thermal convection loops, and a forced circulation loop have been used in this work.

The first spinner test unit operated is shown in Figure 1, and consists of a flanged, heated pot with vacuum and inert gas connections. A compression seal permits rotation of a shaft holding the test specimen without introduction of air into the system. Also included is an air lock through which a corrodat sampling device can be introduced into the pot without admitting air. Temperature is measured with a thermocouple immersed in the corrodant and protected from it by a tantalum tube, and an inner tantalum liner is used to contain the corrodant and to keep it from reacting with the walls of
Figure 1. Details of spinner test apparatus
the pot. The pot rests in a tubular resistance furnace and, during early tests, it was flanged to a vacuum-inert gas system containing a small fore pump.

Later, this spinner apparatus was modified and incorporated into another system containing a second spinner test unit. The composite system is shown in Figure 2, with the newer apparatus on the left. Both pots are heated by tubular resistance furnaces and are connected to a centrally located cold trap, below which is mounted an oil diffusion pump. Between the furnace on the right and the diffusion pump is a purification system used to remove oxygen from the inert cover gas. The arrangement of the valves in the inert gas-vacuum system is such that each pot can be maintained under inert gas pressure while the air locks are operated separately. Figure 3 shows details of the newer pot cover, through which protrude a travelling thermocouple on the right, a test specimen in the center, and a graphite sampling crucible on the left.

Spinner tests have been used for two purposes: comparison of the resistances of a number of materials to attack by the eutectic melt of lead-bismuth, and evaluation of various operating conditions on the degree of corrosion resistance exhibited by one of these materials. The operating procedure used in the comparison tests consisted of charging fixed amounts of chemically cleaned lead and bismuth metal to a spinner unit and evacuating the system to a pressure of
Figure 2. Final arrangement of spinner test apparatus
Figure 3. Pot cover from one spinner unit
approximately 20 microns. After the pot had been flushed and re-evacuated, the pressure was increased to 10 psig. Argon of commercial purity was used as the cover gas. The pot then was heated to the test temperature, during which time the test specimen was suspended near the top of the unit. When the desired temperature had been reached the specimen, usually a 3-inch long piece of \( \frac{3}{8} \)-inch, 12 BWG tubing, was lowered into the liquid metal and spun at 200 rpm. The specimens used were received in the annealed condition, and before use were treated in two standard pickling solutions in an attempt to obtain uniform surface conditions. Liquid metal samples were taken before beginning the tests and at intervals during the tests. These samples were analyzed spectrographically for Fe, Cr, and Ni content. After completion of tests, which usually were of 96 hours duration, the specimens were raised from the corrodant and the apparatus allowed to cool. Upon removal from the apparatus, the specimens were sectioned and prepared for metallographic examination. The materials tested in this manner include a mild carbon steel, two alloy steels, four high chromium irons, and an austenitic stainless steel. Compositions of these materials are shown in Table 1.

The procedure used to evaluate the effect of various operating conditions on corrosion resistance differed slightly from that described above in that some precautions were taken to reduce the amount of oxygen and lead-and bismuth oxides
Table 1. Composition of materials tested\textsuperscript{a}

<table>
<thead>
<tr>
<th>Material</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
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<tr>
<td>AISI 347\textsuperscript{b}</td>
<td>0.08</td>
<td>2.00</td>
<td>0.030</td>
<td>0.030</td>
<td>0.75</td>
<td>9.00</td>
<td>17.00</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>max</td>
<td>max</td>
<td>max</td>
<td>max</td>
<td>max</td>
<td>13.00</td>
<td>20.00</td>
<td></td>
</tr>
<tr>
<td>(2\frac{1}{2}) Cr-1 Mo\textsuperscript{c} alloy steel</td>
<td>0.12</td>
<td>0.45</td>
<td>0.013</td>
<td>0.010</td>
<td>0.31</td>
<td>--</td>
<td>2.22</td>
<td>0.96</td>
</tr>
<tr>
<td>(9) Cr\textsuperscript{c} alloy steel</td>
<td>0.10</td>
<td>0.48</td>
<td>0.015</td>
<td>0.010</td>
<td>0.34</td>
<td>--</td>
<td>8.45</td>
<td>0.96</td>
</tr>
<tr>
<td>AISI 410\textsuperscript{c}</td>
<td>0.108</td>
<td>0.69</td>
<td>0.021</td>
<td>0.011</td>
<td>0.38</td>
<td>0.61</td>
<td>12.03</td>
<td>0.11</td>
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<tr>
<td>AISI 430\textsuperscript{c}</td>
<td>0.090</td>
<td>0.40</td>
<td>0.021</td>
<td>0.010</td>
<td>0.34</td>
<td>0.38</td>
<td>16.56</td>
<td>0.02</td>
</tr>
<tr>
<td>AISI 446\textsuperscript{c}</td>
<td>0.12</td>
<td>0.70</td>
<td>0.017</td>
<td>0.009</td>
<td>0.52</td>
<td>0.21</td>
<td>26.48</td>
<td>--</td>
</tr>
<tr>
<td>AISI 440-C\textsuperscript{d}</td>
<td>0.95</td>
<td>1.00</td>
<td>0.040</td>
<td>0.030</td>
<td>1.00</td>
<td>--</td>
<td>16.00</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>1.20</td>
<td>max</td>
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<td>max</td>
<td></td>
<td>18.00</td>
<td>max</td>
</tr>
<tr>
<td>AISI C-1020\textsuperscript{e}</td>
<td>0.18</td>
<td>0.30</td>
<td>0.04</td>
<td>0.05</td>
<td>--</td>
<td>--</td>
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<td></td>
<td>0.23</td>
<td>0.60</td>
<td>max</td>
<td></td>
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</tr>
</tbody>
</table>

\textsuperscript{a}Compositions are given in percentages.

\textsuperscript{b}From (25, p. 43).

\textsuperscript{c}Analysis furnished by supplier.

\textsuperscript{d}From (2, p. 9).

\textsuperscript{e}From (1, p. 307).
present. The corrodatant used was a slug of lead-bismuth eutectic prepared from lead and bismuth by melting the two under a pressure of 0.01 microns of mercury or less. The cylindrical slug produced by furnace cooling of the degassed melt was cut into two parts and the upper part discarded. The bottom section was machined to specified dimensions and immediately transferred to a spinner unit which then was evacuated to 0.01 microns and heated. When the slug had melted, inert cover gas was introduced to prevent distillation of bismuth from the liquid metal. The cover gas first was treated by passing it through heated uranium turnings to remove oxygen. The apparatus then was heated to the operating temperature and from this point the procedure was the same as that followed in the comparison tests.

The second type of equipment used in this work, the thermal convection loop, was operated for three purposes: to test methods of removing corrosion products from flowing liquid metal, to test flanged joints for practicality in lead-bismuth systems, and to determine the effects of thermal gradients and long time exposure on materials previously examined in the spinner units. Three thermal loops were operated and all three consisted of the same basic parts: a melt-charge tank, an expansion tank, a cold trap, a vacuum-inert gas system, and resistance heaters. The piping in all three loops was \( \frac{1}{2} \)-inch nominal, schedule 40 stainless steel pipe. The first loop was
of all welded construction, while the second loop contained two test flanges, one of which is shown in Figure 7a (p. 33). Both loops were constructed primarily from type 347 stainless steel, although small amounts of type 316 stainless steel plate and mesh were used. The third loop was constructed entirely from type 430 steel, and contained a small concentric tube heat exchanger in addition to three test flanges.

Figure 4 is a schematic representation of the second of these loops. The melt and expansion tanks are joined by a flanged line which extends to the bottom of the melt tank and enters the expansion tank just above the intended liquid metal level. The top of the expansion tank contains vacuum-helium connections, a liquid level probe, and a sampling device similar to the ones used in the spinner apparatus. The tank is connected to the loop piping by two experimental ring joint flanges. Below the expansion tank is the cold trap whose effectiveness in removing corrosion products from the flowing metal was being tested. Heat is supplied to the liquid metal by the long resistance heater and is removed from the liquid metal in the cold trap.

The cold trap consists of a stainless steel shell and riser tube, and woven stainless steel mesh packing. The hot liquid metal enters the trap through a tube in the trap cover. As the metal flows downward into the mesh it is cooled and deposits corrosion products which are held by the mesh. The
Figure 4. Arrangement of second thermal convection loop
cool metal then is forced upward through the packed riser tube which traps any precipitated corrosion products that pass through the body of the trap.

Figure 5a is a photograph of the loop described, and illustrates the size of both the first and second loops. Visible are the charge pot, expansion tank, cold trap, and loop piping after partial insulation. Under the insulation are small heating coils used to preheat the loop tanks and piping to about 200°C prior to charging.

The third thermal convection loop is shown schematically in Figure 6 and is pictured in Figure 5b. Two of the three test flanges used in this loop are of a type shown in Figure 7b, and are gasketed with 1/32-inch thick low carbon steel sheet. The faces of these flanges contain either one or two tapered, raised rings which, when the flange is assembled, cause the gasket to deform and form a seal. The third flange is a tongue-and-groove type sealed without a gasket. In addition to the thermocouples that are welded to the loop tanks and piping, two have been inserted into the flowing metal. The first is in the hollow liquid level probe of the expansion tank and the second in the drain tube of the cold trap.

Charging of a loop consisted of evacuating the system, melting the contents of the charge tank while preheating the loop, and then bleeding helium over the surface of the liquid metal in the charge tank to force the metal upward into the
Figure 5. Thermal convection loops

a. second loop

b. third loop
Figure 6. Third thermal convection loop
Figure 7. Experimental flanges

a. ring joint flange removed from second thermal convection loop

b. flange similar to those used in third thermal convection loop and forced convection loop
evacuated loop. Once the loop was charged to the desired level, as indicated by the liquid level probe, the space above the liquid metal in the expansion tank was filled with helium at 10 psig to prevent leakage of air into the loop. The circulating metal was sampled periodically during operation and these samples were analyzed for major corrosion products. In addition, small test specimens of material were inserted into the expansion tank of the third loop and contacted with the flowing liquid metal for periods of 200 to 500 hours. These specimens, after removal from the loop, were examined metallographically for evidence of corrosion. After a loop had failed, it was cut into sections from which were taken lead-bismuth samples for spectrographic analysis and container material specimens for metallographic examination.

Another type of liquid metal circulating system which has been used in this work is a forced circulation loop. This loop, the design of which resulted from the information gained through the literature, the survey of equipment manufacturers, thermal convection loops and spinner tests, and tests of various seals for liquid metal service, is shown schematically in Figure 8. The loop is constructed entirely from type 446 stainless steel, and employs 3/4-inch nominal, schedule 40 piping. The overall height of this unit is 79 inches and the length, excluding the pump, is 70 inches. The components of the loop include a cold trap, a diaphragm pump
Figure 8. Forced convection loop
and its check valve assembly, charge and expansion tanks, three tubular resistance heaters, a vacuum-inert gas system, and preheat coils. The expansion tank and cold trap of this loop are similar to those of the thermal loops described, except that the cold trap is baffled below the inlet tube. The tanks, the cold trap, and the check valve assembly are connected to the piping with flanges similar to that shown in Figure 7b.

The 1 gpm capacity two stage diaphragm pump and the ball check valve assembly to which it is flanged were manufactured by the Lapp Insulator Company. The pump consists of a standard model CPS-2 normally used as a proportioning pump in the chemical industries, and a remote diaphragm assembly capable of high temperature operation. The standard pump operates near room temperature and makes use of a normal hydraulic fluid to transmit the pulse. This fluid fills the gear box, cylinder, and one half of the diaphragm head mounted as part of the pump. The other half of this diaphragm head, as well as the lower half of the remote diaphragm assembly and a tube connecting the two, is filled with a low melting sodium-potassium alloy. The low temperature pump head is of all welded construction, and a 300 series stainless steel has been employed in both the head and the 20 mil thick diaphragm.

The upper half of the remote, high temperature head is filled with the lead-bismuth alloy being circulated in the
loop, and the outlet from this half of the head is connected to the ball check valve assembly in the loop. The entire remote head is constructed of type 446 stainless steel, with the exception of the 20 mil diaphragm which is type 430 stainless steel. A vacuum seal is maintained between the two halves of the remote head by means of polished, raised bearing surfaces on each half. The assembly is similar to a raised face flange, with the diaphragm acting as a gasket.

The remote head operates at the temperature of the loop and is immersed in a heated liquid metal bath for purposes of temperature control. The remote head is connected to the ball check valve assembly and the pump head by the same type flanges as are used in the loop proper. Motion of the low temperature diaphragm in the pump head is transmitted through the sodium-potassium filled connection tube to the high temperature diaphragm, which in conjunction with the check valve assembly causes the pumping action.

Charging and operation of this loop were similar to the procedures used in the thermal convection loops. The forced convection loop and the remote head were evacuated and heated to 200 and 300°C, respectively, at the same time that the metal charge was being melted. Charging the lead-bismuth circuit consisted of transferring the metal from the charge-dump tank to the loop under inert gas pressure. When the desired liquid level had been reached, a frozen seal was formed in the
line connecting the loop and the charge-dump tank. Next, the sodium-potassium sections of the pump were filled by transferring the alloy, under argon pressure, from a dump tank to the evacuated pump. After these sections had been filled, a small bellows sealed needle valve in the charge line was closed so that when the pump was started, hydraulic pressure could be created in the sodium-potassium section.
EXPERIMENTAL RESULTS

Materials Comparison Tests

In the comparison tests no attempt was made to determine absolute rates of corrosion or corrosion product solubility limits. It was thought that the determination of absolute corrosion rates in the spinner units would not be particularly useful, since these same rates were not expected to hold in the circulation systems to be constructed. Corrosion product solubility data, although they would have been helpful in determining the degree of approach of the system to equilibrium, were not judged essential in order to make valid comparisons among the materials being tested.

Operating conditions selected for the comparison tests were comparable to conditions anticipated in loop operation. The liquid metal loops were to contain no provisions for degassing the liquid metal, purifying the inert cover gas, or initially evacuating the flow circuits below pressures obtainable with a fore pump. Accordingly, the comparison tests were conducted under an atmosphere of commercially pure inert gas, rather than gas subjected to additional purification. No attempts were made to degas the liquid metal used in these tests or to evacuate the apparatus below fore pump pressure. In addition, test specimen surface conditions were limited to those which could be promoted conveniently on large quantities of commercially available steel tubing and pipe.
Removal of iron and chromium from the alloys

Some of the data taken during spinner tests with the mild carbon steel are shown in Figure 9, in which the concentration of iron in the melt is expressed as a function of time. The accuracy of all the corrosion product concentration data presented here is plus or minus 20 per cent of the reported value. The precision is somewhat better, being within plus or minus 10 per cent of the values shown except in a few early tests. In general, the data indicate that the iron concentration rises gradually with time, except at 875°C, and that the maximum value is reached after 96 hours.

If Figure 10 the maximum iron concentrations detected during the 96-hour mild carbon steel tests are shown as the logarithm of corrosion product concentration versus the reciprocal of absolute temperature. The data are best represented by a straight line whose position has been estimated by applying the method of least squares. Although Figure 10 suggests that the iron concentrations at the end of 96 hours may represent solubility limits, this cannot be demonstrated satisfactorily. Both the specimen and the thermocouple protection tube are at a slightly lower temperature than the bulk of the liquid metal, because of heat losses through radiation and conduction. Because of this small temperature difference, iron crystallizes out of solution and attaches itself both to the specimen and to the protection tube at the liquid-gas
Figure 9. Variation of iron concentration with time during tests with type C-1020 steel in lead-bismuth eutectic melt.
Figure 10. Effect of temperature on the removal of iron from type C-1020 steel in lead-bismuth eutectic melt after 96 hours.
interface.

An extreme case of this precipitation is illustrated in Figure 11a, which shows the deposit removed from the inside tube wall as well as that adhering to the outside wall. A qualitative analysis of these deposits indicated that the major constituents were lead, bismuth, and iron, with trace amounts of manganese, chromium, and nickel. Figure 11b is a photomicrograph of the deposit which formed during a 900°C test with the 2\( \frac{1}{4} \) chromium-1 molybdenum alloy steel, and it illustrates the dendritic nature of the deposits formed during tests with both the C-1020 steel and the 2\( \frac{1}{4} \) chromium-1 molybdenum alloy steel. The dendrites are iron and the matrix is the lead-bismuth eutectic. Figure 11c shows the deposit formed during a 900°C test with type 446 steel. The white grains are an iron-chromium alloy and the matrix is the lead-bismuth eutectic. The presence of such deposits, in varying amounts, in the majority of the tests conducted makes it seem unlikely that solubility limits were attained.

Data taken during tests with the 2\( \frac{1}{4} \) chromium-1 molybdenum alloy and AISI types 410, 430, and 446 steel are shown in Figures 12, 13, 14, and 15, in which iron and chromium concentrations are expressed as a function of time. The behavior illustrated in Figure 12 is typical of that observed during tests with the 2\( \frac{1}{4} \) chromium-1 molybdenum and the 9 chromium alloy steels. In the lower temperature tests, iron concentra-
Figure 11. Deposits formed at gas-liquid interface during 900°C, 96 hour dynamic tests with ferritic alloys in lead-bismuth eutectic melt

a. Type C-1020 steel specimen and deposit (full size)

b. Deposit formed during test with 2½ chromium-1 molybdenum alloy steel (150x, unetched)

c. Deposit formed during test with type 446 steel (150x, unetched)
Figure 12. Variation of corrosion product concentrations with time during tests with 2% chromium-1 molybdenum alloy steel in lead-bismuth eutectic melt.
Figure 13. Variation of corrosion product concentrations with time during tests with type 410 steel in lead-bismuth eutectic melt.
Figure 14. Variation of corrosion product concentrations with time during tests with type 430 steel in lead-bismuth eutectic melt.
Figure 15. Variation of corrosion product concentrations with time during tests with type 446 steel in lead-bismuth eutectic melt.
tion rises to a maximum within 50 hours and then shows a gradual decrease. At higher temperatures the behavior is more erratic, but in general a maximum is reached within 24 hours, as illustrated by the 900°C curve. Below 850°C the chromium concentration of the melt at the end of 96 hours is less than the detection limit of 5 parts per million. In tests where chromium appears in the melt its concentration increases more slowly than that of iron.

Corrosion products from the high chromium irons, including AISI types 410, 430, and 446 show the same general behavior as did those from the lower chromium alloys. The data of Figures 13 through 15 show that the iron concentration rises more rapidly than does the chromium concentration. In the majority of the tests the iron concentration decreases with increasing time after 50 hours, although the concentration of chromium increases with time. The most noticeable exception to this occurs in the case of the 26 per cent chromium steel.

The rise in iron concentration within the first half of a test followed by a gradual decrease has been noted previously by Grassi (18), and it was thought to be associated either with segregation at the surface of the liquid or with the depression of the solubility of iron by chromium. The former does not seem to offer an adequate explanation. Although surface segregation occurred in tests with all materials, those tests with the C-1020 steel failed to show general decreases
in iron concentration after 50 hours. Yet it was in these tests that the most extensive surface segregation was observed. In view of this, the explanation that chromium in solution depresses the solubility of iron seems more likely.

It appears that the iron concentration rises until, after one or two days depending on the temperature, the accumulation of chromium in the melt is sufficient to displace iron from solution. Such a process accounts both for the decrease in iron concentration with time during tests of iron-chromium alloys, and for the absence of this trend in the C-1020 tests. This explanation is strengthened by work reported in Lane, et al. (24, p. 730) with liquid bismuth. Here it was found that the addition of chromium to bismuth containing dissolved iron decreased, substantially, the amount of iron in solution above 450°C. The chromium solubility was not affected.

Comparison of the maximum corrosion product concentrations for any of the chromium steels (Figure 12, 13, 14, or 15) shows that chromium is present in higher percentages than would have been predicted on the basis of the fraction of the chromium in the steel. This selectivity of the lead-bismuth for chromium perhaps is best illustrated by comparing the fraction of the chromium in the original alloy with the fraction of chromium in the dissolved corrosion products. Figure 12 shows that the maximum amounts of iron and chromium detected in solution during a 900°C test with the 2½ chromium-
molybdenum alloy were 290 and 48 parts per million, respectively. Table 1 gave the fraction of chromium in this alloy as 0.022. Neglecting all corrosion products but iron and chromium (in particular molybdenum, the third major constituent of the steel), it can be seen that the fraction of the corrosion products made up by chromium is 0.142. The ratio of the two fractions, chromium in corrosion products to chromium in alloy steel, is approximately 6.4. Since a value of unity would correspond to a transfer of chromium to the melt roughly in proportion to its concentration in the alloy, it appears even from such a crude analysis that the lead-bismuth selectively removes chromium from the alloy. This selectivity also is apparent in the other alloys; for example, the 900°C tests with types 430 and 446 yield chromium selectivity parameters of 3.22 and 2.24, respectively. At 700°C type 430 yields 1.44 and type 446, 2.16.

Additional information about the corrosion process can be gained from observing the rates of release of iron and chromium to the liquid metal. The relatively rapid rate of iron release, together with the composition and structure of the alloys tested, suggests that iron is immediately available for solution, and that the rate controlling step may be one of solution. On the other hand, the fact that chromium is not as available as iron, together with the slower observed rate of accumulation, suggests that the solution of chromium may be
limited by its availability through solid state diffusion.

The effect of temperature on the removal of iron and chromium from the ferritic steels is illustrated in Figures 16 and 17. The data points are shown in Figure 18 and in Figures 32 through 36 in Appendix A. The data often are best approximated by straight lines whose positions have been estimated by the method of least squares. However, the fact that data are presented in such a manner does not imply that they represent equilibrium solubility values.

That the data do not represent equilibrium solubilities is demonstrated, for the case of type 430 steel, by the chromium concentration data of Figure 18. Here, the results of 96-hour tests are compared with those from the cooling cycle of a 500-hour test in which a specimen was exposed to lead-bismuth at a series of temperatures. The test procedure involved contacting a specimen with the lead-bismuth at a number of temperatures from 930 to 650°C. The temperature of the liquid metal was lowered at 24-hour intervals in increments of 50°C, and at the end of each 24-hour period a sample of the eutectic melt was withdrawn. Figure 18 shows that the chromium concentrations in the melt are much higher, particularly at low temperatures, than the maximum concentrations determined in the 96-hour tests. However, in view of some static tests reported by Grassi, et al. (18) the values from the 500-hour test do not appear to be equilibrium solubilities.
Figure 16. Effect of temperature on the removal of iron from ferritic steels in lead-bismuth eutectic melt after 96 hours.
Figure 17. Effect of temperature on the removal of chromium from ferritic steel in lead-bismuth eutectic melt after 96 hours.
Figure 18. Effect of spinner test operating conditions on chromium concentration of lead-bismuth eutectic melt in contact with type 430 steel.
Grassi equilibrated type 430 steel and the eutectic melt of lead-bismuth, with the result that the amounts of iron and chromium found in solution were substantially in excess of the amounts detected in the 500-hour test. As a result of Grassi's values and those from the 500-hour test, it is clear that the maximum iron and chromium concentrations found during 96-hour tests do not represent equilibrium solubility values. They should be regarded merely as corrosion product accumulations.

Returning to Figure 16 it can be seen that the maximum concentration of iron found in the melt during tests with five of the six ferritic steels lies within a fairly narrow band. The iron concentrations resulting from tests with the sixth material, the mild carbon steel, lie substantially above the band in the lower temperature range. The fact that the mild carbon steel is the only one of the six which contains no chromium seems significant in view of the higher concentration in the low temperature region. It is thought that the addition of small amounts of chromium as an alloying agent has increased the resistance of the steel to dissolution.

The objection may be raised that the difference in iron concentration is not caused by the presence or absence of chromium in the solid alloy, but by its presence or absence in the lead-bismuth melt, i.e., that the addition of small amounts of chromium to the steel does not make it more resist-
ant to attack, but provides a source from which chromium enters the liquid and depresses the solubility of iron. Such an objection may explain small differences in iron concentration but it is not adequate to explain the difference in behavior between the C-1020 steel and the 2½ chromium-1 molybdenum alloy steel. Below 800°C, as illustrated in Figure 32 of Appendix A, the 5 part per million chromium detection limit was not exceeded in 2½ chromium-1 molybdenum alloy steel tests. Less than 5 parts per million chromium in the melt could not have caused the difference in iron concentration evident between the two alloys, so that the assumption of small amounts of chromium imparting corrosion resistance seems reasonable.

Figure 17 shows the effect of temperature on the removal of chromium from the five ferritic steels containing chromium as an alloying element. Comparison of the curves of Figure 17 with the steel analyses previously listed in Table 1 shows that the amount of chromium appearing in the eutectic melt at a given temperature is proportional to the chromium content of the steel. Assuming that the removal of large amounts of chromium from a container material cannot be tolerated, the high chromium alloys appear undesirable as container materials. However, continued reduction in the chromium content of the steel seems to result in the removal of larger amounts of iron, the extreme example of which is the C-1020 steel.
Comparing the steels on the basis of the total corrosion products found in solution (including iron, chromium, and nickel) the one showing the lowest solubility is the 9 chromium alloy. In order of increasing solubility, below 800°C, the remaining materials are type 410, the 2½ chromium-1 molybdenum alloy, types 430, C-1020, and 446.

Although the corrosion product concentration data are useful in comparing the extent to which a component is removed from the various steels, nothing of the degree to which the attacked surfaces deteriorate can be determined from these data. For example, it is possible that a steel showing low solubility of iron and chromium at the same time might undergo extensive intergranular attack resulting in rapid spalling of the container wall. The detection of such behavior can be accomplished only through metallographic examination of the attacked specimens, and it was for this reason that such examinations were performed.

Metallographic examination of corroded specimens

Sections for metallographic examination were removed from specimens at a point which had been 1 inch below the liquid surface during tests. Previous examination of the entire length of several specimens had indicated slight or severe attack, depending on the steel, at the liquid-gas interface. Below this interface, however, the corrosion severity stabilized, and at the depth of interest the only variations were
of a magnitude evident throughout the remainder of the specimen.

Figures 19 through 25 are included to illustrate the type of attack which took place in the various steels, and the increasing severity of this attack with increased temperature.

The 2\% chromium-1 molybdenum alloy steel is attacked intergranularly, as illustrated in Figure 19, and the first significant indication of this appears in a specimen tested at 700°C. At this temperature, attack has advanced to the point where whole grains have been detached from the specimen. The microstructures of the specimens tested at 800 and 900°C reflect the phase transformation which has just begun at 800°C and which is complete at 900°C. The normal microstructure, shown in Figure 19a consists of a ferrite matrix containing chromium carbides or complex iron-chromium carbides. The 800°C specimen consists of ferrite and carbides that have diffused from the grains to the grain boundaries and have become spheroidal. The specimen exhibits grain growth at the surfaces in contact with the eutectic melt, and the intergranular penetration at these surfaces has reached a maximum depth of 6 mils. The specimen tested at 900°C was severely attacked, with only long fingers of ferrite remaining in place of the original material. The depth to which the specimen was attacked reached 9 mils.

The 9 per cent chromium alloy, illustrated in Figure 20,
Figure 19. Attack of 2\({\frac{3}{4}}\) chromium-1 molybdenum alloy steel by the eutectic melt of lead-bismuth

a. Control specimen surface

b. Surface after exposure for 180 hours at 700°C

c. Surface after exposure for 96 hours at 800°C

d. Surface after exposure for 96 hours at 900°C
Figure 20. Attack of 9 chromium alloy steel by the eutectic melt of lead-bismuth (250x)

a. Surface after exposure for 96 hours at 700°C (nital etch)
b. Surface after exposure for 96 hours at 800°C (nital etch)
c. Surface after exposure for 96 hours at 850°C (nital etch)
d. Surface after exposure for 96 hours at 900°C (HCl, HNO₃, glycerine etch)
consists of spheroidal chromium carbide particles in a matrix of ferrite. At 700°C the corrosion involves intergranular attack, reaching depths of 3 mils, followed by removal of surface grains. At 800°C there is a band of material, extending 2 to 3 mils below the surface, from which all carbide has been removed. This removal of chromium carbide is accompanied by depletion of the chromium in solid solution, as reflected by the corrosion product concentration data for this and for the other chromium alloy steels. This depletion of chromium from the surface band is also reflected in microhardness measurements made on the specimen. A Knoop hardness number of 253 with a 100 gram load was recorded for an unattacked portion of the specimen, while the corroded band yielded 180. This band is further damaged by the solution of iron from the chromium depleted grains.

Better evidence of the removal of chromium from the 9 percent chromium alloy is shown in the photomicrograph of the 900°C specimen. At this temperature the steel is austenitic in structure and upon completion of the test it is transformed to martensite due to its alloy content and the cooling procedure used. However, the photomicrograph shows that not all the specimen has transformed during cooling. Bands of metal adjacent to the surfaces were sufficiently depleted in chromium due to the action of the liquid metal that they were rendered non-hardenable under the cooling conditions employed.
The result is an unattacked material showing the needle-like structure characteristic of martensite, along with white surface bands of ferrite. The depth to which the attack has proceeded is clearly marked by the difference in structures, as well as by differences in hardness. The hardened portions yielded Knoop values averaging 488, while the surface bands varied in hardness from 124 to 267. The same hardened areas yielded a diamond pyramid hardness of 413, corresponding to a Rockwell C value of 42.

Corrosion of AISI type 410, another hardenable steel, is illustrated in Figure 21 and involves selective removal of chromium from the steel. This is followed by general attack of the ferrite to produce the surfaces visible in the photomicrographs of the 700 and 850°C specimens. The intergranular nature of the attack is best illustrated by the appearance of the 900°C specimen whose surface region is shown in Figure 21c. Cooling of the specimen at the end of the test resulted in the transformation of the unattacked portion to martensite, the hardness of which was measured as 44.3 on the Rockwell C scale. At the base of the severely corroded, unhardened zone appearing in Figure 21c, there is a narrow band of enlarged grains which can be distinguished by the light rings encircling them. These rings, which are the chromium depleted outer portions of the grains, are more distinct in photomicrograph 21d. As was the case with the 9 per cent chromium steel,
Figure 21. Attack of type 410 steel by the eutectic melt of lead-bismuth (HCl, HNO₃, glycerine etch)

a. Surface after exposure for 97 hours at 700°C (250x)
b. Surface after exposure for 96 hours at 800°C (250x)
c. Surface after exposure for 97 hours at 900°C (250x)
d. Surface after exposure for 97 hours at 900°C (500x)
the depletion of chromium is sufficient to render the attacked sections non-hardenable and these sections are readily distinguished from the unattacked portions.

The behavior of type 430 stainless steel in contact with the eutectic melt is shown in Figure 22. At 700°C the attack is intergranular in nature, and results in the removal of surface grains. At 800°C the first step in the attack seems to have been the removal of chromium and carbides from the surface zones. These chromium depleted zones, which reached a depth of 5 to 6 mils in four days, then seem to have been attacked transgranularly. Solution of iron from the chromium depleted grains is believed to have caused the large voids extending from the surface to the base of the attacked zone. The hardness of this zone is approximately 142 on the Knoop scale while that of the center averages 212. The microstructure of the specimen tested at 900°C reflects the partial phase transformation which takes place at this temperature. The 7-mil surface zone consists of slender stringers of ferrite and illustrates the advanced stages of attack. Just below the surface zone are a number of voids which follow the grain boundaries and extend another 1 to 2 mils into the material.

Although data for accumulation of corrosion products from AISI types 347 and 440-C steel are not reported here, Figure 23 is included to illustrate the manner in which these steels
Figure 22. Attack of type 430 steel by the eutectic melt of lead-bismuth (250x; HCl, HNO₃, glycerine etch)

a. Surface after exposure for 118 hours at 700°C
b. Surface after exposure for 97 hours at 800°C
c. Surface after exposure for 96 hours at 900°C
Figure 23. Attack of types 347 and 440-C steel by the eutectic melt of lead-bismuth (250x)

a. Surface of type 347 after exposure for 96 hours at 600°C (HCl, FeCl₃ etch)

b. Surface of type 347 after exposure for 100 hours at 900°C (HCl, HNO₃, glycerine etch)

c. Surface of type 440-C after exposure for 96 hours at 800°C (HCl, HNO₃, glycerine etch)

d. Surface of type 440-C after exposure for 100 hours at 900°C (HCl, HNO₃, glycerine etch)
corrode. Type 347 is attacked by selective removal of nickel and chromium. At 600°C action of the lead-bismuth is limited to intergranular attack followed by spalling of surface material. At 900°C the intergranular attack, visible at the base of the severely corroded zone, is accompanied by considerable leaching of nickel and chromium from the grains and is followed by deterioration of the whole zone. The depth of the zone illustrated in Figure 23b averages about 9 mils.

The resistance of 440-C to attack was not compared with that of the other alloys because of the much higher carbon content of this steel. Attack of 440-C involves the depletion of chromium and carbides from the material, but the attack does not seem to be intergranular. The normal microstructure of the material, visible in the lower section of Figure 23c, consists of large white areas of primary chromium carbides dispersed in a matrix of ferrite containing smaller secondary carbide particles. Attack at all temperatures is characterized by its lack of uniformity; unattacked areas are found adjacent to material which has been penetrated to depths of 10 mils. The attack which has taken place at 800°C includes removal of chromium carbides and of chromium from solid solution, leaving the white areas visible beneath the specimen surface. At 900°C the attack differs only in degree.

In place of the intergranular attack noted in other alloys, type 440-C exhibits voids that are not connected with
the surface of the specimen. These voids seem to grow with time until they form an interconnecting network linking the specimen surface with the base of the corroded zone. The appearance of these unconnected voids below the surface seems to have resulted from the agglomeration of lattice vacancies formed by the diffusion of chromium from the steel during testing. The continued collection of these lattice vacancies about certain sites eventually results in visible voids.

Attack of type 446 steel, illustrated by Figure 24, is similar to that of type 440-C. The formation of voids is particularly evident in the specimen tested at 800°C. At 900°C the depth of the attacked zone varies irregularly, often exceeding 10 mils, and the surface grains appear very large. The specimens tested at 700 and 800°C contain appreciable amounts of sigma phase within the unattacked areas. However, due to the depletion of chromium in the surface zones, no sigma phase was detected here.

Figure 25, which shows the surfaces of mild carbon steel specimens after testing, is included to illustrate another type of corrosion damage, uniform solution attack. Comparison of the control specimen with the test specimens revealed no changes other than grain growth. Although the surface of the 900°C specimen appeared to have been unattacked when viewed under the microscope, the reduction in specimen wall thickness was evident to the unaided eye. Rough measurements of
Figure 24. Attack of type 446 steel by the eutectic melt of lead-bismuth (250x; HCl, HNO₃, glycerine etch)

a. Control specimen
b. Surface after exposure for 100 hours at 691°C
c. Surface after exposure for 96 hours at 800°C
d. Surface after exposure for 96 hours at 900°C
**Figure 25.** Attack of type C-1020 steel by the eutectic melt of lead-bismuth (250x; nital etch)

- a. Control specimen
- b. Surface after exposure for 96 hours at 700°C
- c. Surface after exposure for 95 hours at 900°C
the wall thickness indicated that a reduction in thickness of about 50 mils had taken place during the 95-hour test.

Selection of container materials

Reviewing the results of the comparison tests from the standpoint of corrosion product accumulation in the liquid metal, it appears that the steels containing small amounts of chromium would be more desirable container materials than those containing large amounts of chromium. The most important reason for this conclusion involves the transfer of corrosion products within a liquid metal circulating system. Material dissolved in the high temperature section of a system is deposited in cooler sections in sufficient quantities to cause complete blockage of the system within short periods of time. In view of this transfer, it appears that the less material removed from the container walls, the less serious the plugging problem. On this basis, the 9 chromium steel is the most desirable material examined, with the remaining steels falling into the order mentioned on page 59.

When the steels are rated on the basis of the extent of corrosive attack, a different order results. Metallographic examinations, which indicate that 700°C is about the useful limit of even the most resistant material tested, demonstrated that the addition of progressively larger amounts of chromium to steel was detrimental to corrosion resistance. This is in agreement with the corrosion product data. However, the
examinations also revealed that two of the materials, the 9 chromium alloy and AISI type 410 steel, were subject to rather extensive intergranular attack and spalling at the lower test temperatures. These examinations, together with measurements made of the depth of attack exhibited by each specimen, suggested another order of resistance.

In rating the materials on the basis of corrosion penetration measurements, both the maximum depths of penetration and the arithmetic average of a number of random measurements were considered. Both sets of measurements showed that the 2½ chromium-1 molybdenum alloy steel was the least severely attacked below 800°C. In the order of increasing severity of attack the remaining materials were types 430, 410, 9 chromium, and 446. The C-1020 steel was not included here, its having been eliminated from further consideration by extensive solution attack and lack of high temperature oxidation resistance.

In making a choice of materials it was decided that rapid intergranular attack followed by extensive spalling was a more important consideration than the amount of chromium or iron released to the liquid metal. By this time it had been demonstrated that corrosion products could be effectively removed from solution in the liquid metal and that plugging of the piping would not present a serious problem. On this basis the 2½ chromium-1 molybdenum alloy represented the best ferritic
container material, with type 430 steel as a second choice.

Additional considerations such as high temperature oxidation resistance, weldability, and availability led to the selection of type 430 steel as the best compromise.

The Effects of Various Operating Conditions on Corrosion

In order to learn more about the manner in which the alloys were attacked, and in order to decrease the rate of attack if possible, several different test conditions were imposed on the spinner units. The complexity of the alloys, the corrosion product precipitation phenomenon, and the limitations in the method of spectrographic analysis discouraged any analytical approach to corrosion mechanisms and rates. It was felt, however, that purely qualitative observations would have some value. The test variables that were examined included specimen surface conditions, liquid metal purity, and relative velocity between specimen surface and liquid metal. The majority of these tests were performed with AISI type 430 steel in the modified apparatus shown in Figure 2 (p. 20).

Specimen surface conditions

In the course of increasing the chromium content of a low carbon steel, a point is reached, near 12 per cent, where the steel exhibits a marked increase in resistance to attack under oxidizing conditions. The cause of this change in behavior, which distinguishes stainless steels and high chromium irons from lower alloy steels, is not fully understood, but it
appears to involve the formation of a protective film (34, p. 35). This film is very likely a chromium oxide surface layer that adheres to the metal tightly and is relatively impene-
trable.

In view of the protection offered by this film against various corrosive media, the question arises as to whether some protection also might be afforded against the action of lead-bismuth. Assuming that the film is a chromium oxide layer, it would be expected to be stable in the presence of lead and bismuth oxides found in the liquid metal test system. For example, at 627°C the reactions

\[ 2\text{Cr} + 3\text{PbO} \rightarrow \text{Cr}_2\text{O}_3 + 3\text{Pb} \]

and

\[ 2\text{Cr} + \text{Bi}_2\text{O}_3 \rightarrow \text{Cr}_2\text{O}_3 + 3\text{Bi} \]

are accompanied by large negative free energy changes. Using data from Glassner (17), the free energy changes for the re-
actions were estimated as -117 Kcal per gram mole and -132 Kcal per gram mole, respectively. In addition, such a film might have self-healing properties in the presence of these lead and bismuth oxides.

In order to determine whether the protective film on a high-chromium iron had any effect on resistance to attack by lead-bismuth, several spinner tests were conducted with type 446 steel. Test temperatures were 600, 700, and 800°C and test conditions were similar to those employed in the
materials comparison tests, except that the new specimens were not pickled.

Comparison of the corrosion product accumulation data from the tests employing untreated steel with data from the comparison tests revealed some differences. In the tests employing untreated specimens the maximum iron concentration of the liquid metal was lower, over the entire temperature range, than the iron concentration detected in tests with pickled specimens. However, the change was of the same magnitude as the analytical error. A considerable reduction in the concentration of chromium in the liquid metal was noticed below 750°C. At 700°C, for example, the concentration of chromium in the melt at the end of 96 hour tests with untreated specimens was one fourth of what it had been after tests with pickled specimens. Metallographic examinations of untreated specimens shows that they were less deeply attacked than the pickled specimens, and that the attack exhibited by the untreated specimens covered a relatively small fraction of the surface.

Additional tests employing several surface conditions were performed with type 430 steel. These tests were carried out at 700, 750, and 800°C for periods of two days. Specimens were tested either in the untreated condition, or after surface treatments including pickling, passivating in nitric acid, and heating to 500°C in air. Analyses of the corrodant
samples taken during these tests failed to reveal any consistent, significant changes in iron concentration with changes in surface conditions. On the other hand, the chromium concentration at the end of the 48-hour test periods was found to change with the various surfaces. The lowest chromium concentration was detected in tests before which the steel had been heated in air. The next higher set of chromium concentrations was associated with the untreated specimens, although the displacement of one curve from the other was not much greater than the precision limits of the analytical technique employed. Chromium concentrations detected in tests with the pickled and passivated specimens were very nearly equal over the temperature range, and were twice as high as those determined in the tests with air oxidized specimens.

An example of these differences in chromium concentration with changes in alloy surface conditions is shown in Figure 26. The data were taken from two 800°C tests with type 430 steel specimens, one of which was air oxidized and the other, pickled. Frequent sampling during the initial stages of the tests revealed that essentially no chromium entered the liquid metal from the oxidized specimen for a period of 6 hours. In contrast to this, the pickled specimen began to release chromium immediately, and the rate of release was higher than that from the oxidized specimen.
Figure 26. Effect of alloy surface conditions on the release of chromium to 800°C lead-bismuth eutectic melt
Photomicrographs of pickled and air oxidized specimens are shown in Figure 27. Neither specimen tested at 700°C seems to have been decarburized, although intergranular penetration was visible along the entire surface of the pickled specimen. The oxidized specimen had been attacked intergranularly but the attack was confined to a very small fraction of the surface.

At 800°C the results of the different surface treatments are more evident. The attacked zone of the pickled specimen, from which large amounts of ferrite have been removed, reaches a maximum depth of 6 mils. The oxidized specimen exhibits several spots where attack has reached a depth of 5.5 mils although the majority of the surface is similar to that shown in Figure 27d, where very little other than decarburization is visible.

The pickled and air oxidized specimens shown in Figure 27 represent the extremes in corrosive attack. Both the untreated surfaces and those passivated with nitric acid exhibited corrosion, the severity of which was bracketed by that of the pickled and air oxidized material.

Both corrosion product concentration data and metallographic examination of specimens indicate that subjection of high chromium irons to oxidizing conditions before exposure to lead-bismuth decreases the rate at which chromium leaves the alloy, and decreases the depth to which the alloy is attacked.
Figure 27. Effect of alloy surface conditions on severity of attack of type 430 steel by lead-bismuth eutectic melt after 48 hours (250x; HCl, HNO₃, glycerine etch)

a. Surface of pickled specimen after exposure at 700°C
b. Surface of air oxidized specimen after exposure at 700°C
c. Surface of pickled specimen after exposure at 800°C
d. Surface of air oxidized specimen after exposure at 800°C
in a given time. An explanation for the results obtained by varying alloy surface conditions is that the surface treatments either destroy or promote a film, very likely a chromium oxide, on the alloy surface. In the absence of this film chromium is removed from the alloy rapidly, and the chromium-depleted zone of the alloy then deteriorates. The presence of this film seems to offer partial protection from attack by decreasing the rate at which chromium is removed from the alloy. Variations in the thickness of this barrier, brought about by changing the severity of the oxidizing conditions, result in different degrees of protection with the most severely oxidized surfaces presenting the best resistance to attack.

Although the surface films provide some resistance to attack by lead-bismuth, this protection is not uniform. Metallographic examination of all specimens with protective films reveals the presence of intergranular attack at a number of points on the surfaces. This attack, although limited to a few points, is almost as severe as that found on specimens where the film has been destroyed prior to tests. In view of this isolated, irregular attack it appears that none of the protective films formed on the high chromium alloys was continuous, and that the ruptured films were not self-healing in the presence of lead and bismuth oxides. If an alloy with a nonuniform surface film were exposed to lead-bismuth for a
long period of time it is very probable that intergranular attack, beginning at flaws in the film, would progress to the stage where the surfaces and film were undercut. Once these surfaces had spalled away, attack similar to that found in the comparison tests would take place.

In view of the nonuniform nature of the protection, it appears that the decrease in corrosion severity noticed would be a temporary condition, and that the deliberate formation of an oxide film at high temperature in air would hold no particular advantages in long time exposures. On the other hand, destruction of the oxide film and the temporary protection it affords seems detrimental. It would be better not to treat the steel surfaces in any manner, except for removal of grease, before contacting them with lead-bismuth.

**Liquid metal impurities**

Three impurities, carbon, iron, and chromium, were added to the liquid lead-bismuth in order to examine their effect on corrosion severity. Carbon was the first to be used, and it was introduced into the melt by substituting a graphite liner for the tantalum liner normally used to contain the lead-bismuth. Tests were conducted with three steels, the 2½ chromium-1 molybdenum alloy and types 430 and 446 steel, over the temperature range 600 to 900°C. Carbon additions to the melt caused an increase in corrosion severity but produced no detectable effect on the decarburization of the specimens.
Additions of iron to the lead-bismuth failed to stop the removal of ferrite from type 430 steel in the 700-800°C range, and had no effect on decarburization.

The effect of additions of chromium to the liquid metal can be seen in Figure 28 where two specimens of type 430 steel are shown. Both specimens were tested for 48 hours at 800°C without having had any previous surface treatment. The first was tested in pure lead-bismuth and the second in a melt to which a large quantity of chromium had been added. Examination of the surface regions of the specimen shown in Figure 28b indicated that there had been some slight removal of chromium carbide, but that there had been no serious intergranular attack.

This reduction in corrosion accompanying the addition of chromium to the liquid metal supports the conclusion, reached through the comparison tests, that lead-bismuth attacks a chromium-containing alloy by selectively removing chromium from the alloy. The addition of large amounts of chromium to the liquid metal reduces the driving force for removal of chromium from the alloy, and has proved more effective in decreasing the corrosion rate than did the promotion of an oxide film.

Although saturation of lead-bismuth with chromium greatly reduces the rate of attack of type 430 steel, such a technique would not be applicable to liquid metal circulation systems.
Figure 28. The effect of chromium additions to the lead-bismuth eutectic melt on removal of chromium from type 430 steel at 800°C (250x; HCl, HNO₃, glycerine etch)

a. Surface of specimen tested for 48 hours in pure lead-bismuth eutectic melt

b. Surface of specimen tested for 48 hours in liquid lead-bismuth-chromium
The temperature gradients present in a loop would cause continual precipitation of chromium in the cold section and lead to eventual plugging of the system.

**Relative velocity of liquid metal and container material**

Several 800°C static and dynamic tests were conducted with type 430 steel to determine whether small velocity changes had an effect on the severity of corrosion. Examination of the specimens from the 24 hour dynamic tests, conducted at 10, 50, 100, and 500 rpm, revealed no differences in depth or type of attack among specimens. However, the specimen tested in static lead-bismuth was less deeply attacked than the others, and the fraction of the surface that had been corroded was substantially smaller. It appears that at low flow rates (below about 1 fps) changes in liquid metal velocity do not affect the corrosion rate, although there is a substantial change in going from a static to a dynamic test.

**Liquid Metal Circulation Systems**

**Thermal convection loops**

The first austenitic stainless steel loop was operated for a period of 250 hours with a cold trap temperature near 260°C and a hot leg temperature that was increased from 500 to 650°C. Under these conditions the nickel concentration of the circulating liquid metal rose steadily from less than 5 parts per million to greater than 500 parts per million. Iron and chromium, which were being removed from the steel along with
the nickel, did not appear in high concentrations in the lead-bismuth but were continuously precipitated in the cold trap as a result of their relatively large temperature coefficients of solubility.

As a result of the severe operating conditions imposed on the loop, an obstruction to flow was formed rapidly in the inlet tube to the cold trap. After 250 hours, this deposit had reached such a size that flow was virtually stopped, resulting in solidification of the lead-bismuth in the cold leg and failure of the heaters. When the loop had cooled it was cut into pieces and examined. The corrosion product deposit found in the cold trap inlet tube was not analyzed, but later experience showed that it very likely was composed of crystals of the intermetallic compound Bi$_3$Ni. Pipe sections removed from the hot leg and the expansion tank exit tube revealed that intergranular attack, reaching a maximum depth of 1.5 mils, had occurred during the 10-day operating period.

The second austenitic stainless steel loop that was constructed is shown in Figure 5a (p. 30) and was operated for a period of 4100 hours, or slightly under six months. During this time the loop temperature was increased in approximately 50°C increments at 200 and 400 hour intervals. The hot leg was operated between 240 and 590°C, and a temperature gradient of 60 to 160°C was maintained between the hot leg and the cold trap. Failure of the loop was caused by burning out of the
main heaters, although the deposits found in the loop would have caused plugging within a short time.

The two sets of ring joint flanges tested in this loop maintained seals against the liquid metal over the entire life of the loop. The liquid metal temperature was lowered about 200°C on two occasions to determine whether any leakage would occur at the flanges, but none was detected. Examination of the joints, one of which was shown in Figure 7a (p. 33), after failure of the loop showed that there had been no leakage of lead-bismuth around the rings. Previous tests with the same type flanges had been conducted for periods as long as 1500 hours and demonstrated that lead-bismuth could be contained at pressures as high as 50 psig over the temperature range 300 to 600°C. Based on these performances, the use of ring joint flanges in small scale experimental liquid metal systems appears practical.

After the second thermal convection loop had failed it was radiographed, sectioned, and examined. During removal of lead-bismuth eutectic from the piping, two large crystalline deposits were found, one near the entrance to the expansion tank and the other near the exit. Both of these deposits, shown in Figure 29, consisted of masses of needle-like crystals mixed with lead-bismuth and fastened to the pipe walls. The crystals have been identified as the intermetallic compound Bi$_3$Ni and were formed with nickel leached from the type
Figure 29. Results of 4100-hour operation of an 18-8 stainless steel thermal convection loop circulating the lead-bismuth eutectic melt

a. Crystalline deposits removed from loop piping

b. Loop cold trap
347 stainless steel container walls.

The cold trap, which is also shown in Figure 29, contained the same type deposits in the entrance and exit tubes. The wire mesh packing in the riser tube and in the upper portion of the trap was covered with a matt of lead-bismuth containing appreciable amounts of nickel and trace amounts of iron and chromium. The mesh near the bottom of the trap and the floor of the trap were covered with small crystals composed principally of iron and chromium, with trace amounts of nickel. From the location of the iron- and chromium-rich deposits it appeared that the trap was functioning satisfactorily, with iron and chromium being removed from the liquid metal and held in the coldest section. The unexpected large deposits of Bi$_3$Ni could not be collected in such a trap, but deposits of this type would not form in a flow system employing nickel-free container materials.

Several sections of loop piping were removed and examined metallographically for evidence of corrosion. A section removed from the hottest section of the loop, at the top of the clamshell resistance furnace, had been attacked irregularly and to a maximum depth of about 17 mils. The attacked zone contained a large number of small, unconnected voids formed by the selective removal of chromium and nickel from the alloy, and was similar in appearance to that of photomicrograph 24c (p. 77). A pipe section removed from a lower temperature area
above the entrance of the cold trap exhibited uniform intergranular penetration and partial spalling of the damaged surface. The depth to which attack had progressed varied from 1.2 to 1.8 mils.

The third thermal convection loop, the largest of the three, was operated for a total of 4300 hours at a minimum hot leg temperature of 300°C and a maximum of 700°C. The temperature gradient across the loop was varied from 130 to 300°C. The operating time was divided into three periods, each of which was ended by the failure of some loop component. The first period of 660 hours was ended by seepage of lead-bismuth from the ungasketed tongue-and-groove flange (Figure 6, p. 31). After the loop had been drained and the cold trap removed it was found that leakage had been caused by misalignment of the flange, resulting in improper seating of the tongue. To avoid further difficulties a gasket was placed in the tongue-and-groove joint.

The second period of operation covered about 1000 hours and was ended by plugging of the cold trap. The loop was drained again and the cold trap removed and examined. The plug that stopped circulation was found in what had been intended as the riser tube of the trap. However, the tube was accidentally welded to the inlet port of the trap and the small cross section tube filled rapidly with material deposited by the liquid metal entering the trap.
A new trap was fabricated and flanged to the loop, and the system was charged for the third time. After 2600 hours of operation a leak developed in the flanged connection of the expansion tank side arm. The system was cooled and dismantled and it was found that the leak had resulted from oxidation of the iron sheet gasket in the joint. During six months at temperatures of 350 to 650°C the gasket had flaked away until there was no longer enough material remaining to hold a seal.

In spite of the failure of the modified tongue-and-groove flange it is felt that joints of this design are entirely satisfactory for use in lead-bismuth systems. The selection of a better high temperature gasket material, such as type 410 or 430 steel, would have eliminated the air oxidation problem. Temperature cycling of 500°C failed to induce leakage in either modified tongue-and-groove flange, and each time after the loop was dumped the flanges were sufficiently tight that a vacuum of 15 microns could be obtained prior to recharging. Removal and replacement of the cold traps in this loop demonstrated that the modified tongue-and-groove flanges could be opened and resealed without any more trouble than that caused by replacement of a gasket.

Examination of the second cold trap, a section of which is shown in Figure 30a, revealed that considerable deposition of corrosion products had taken place. Approximately the lower half of the trap contained crystalline deposits of an
Figure 30. Sections removed from a thermal convection loop in which lead-bismuth eutectic melt was circulated for 4300 hours

a. Cold trap section

b. Pipe sections removed from regions of heavy attack and no attack
iron-chromium alloy, while the upper portion and the inlet and outlet tubes were free of such material. In examining the remainder of the loop no corrosion product deposits could be found, and it appears that all deposition was confined to the lower portion of the trap. The material visible in the trap was accumulated over the 2600-hour period during which the hot leg was operated above 550°C.

An idea of the extent to which the high temperature sections of the loop were attacked is provided by the pipe sections shown in Figure 30b as well as by the mass of iron-chromium deposited in the trap. The corroded section shown in Figure 30b was removed from the hot leg at a point about 4 inches below the top of the vertical heater. The pipe wall has been reduced to less than half its original thickness in places.

The concentric tube heat exchanger incorporated into the loop was operated with water as the coolant but after two short periods of use the outlet tube from the annular section cracked open preventing further tests. During operation of the exchanger at a loop hot leg temperature of 300°C and a cold trap temperature of 192°C, a mass flow rate of 890 pounds per hour was measured. This corresponds to a velocity of 0.18 feet per second in the $\frac{1}{2}$-inch piping.

In order to obtain an idea of the change in corrosion severity in going from a spinner type test to a more realistic
one, a number of small specimens were tested in the third thermal convection loop. After 200- to 500-hour exposure periods these specimens were compared with specimens of the same material tested for the same lengths of time in the spinner units.

Eight of the specimens tested in the expansion tank of the loop were type 430 steel with untreated surfaces. The tests were conducted at expansion tank temperatures between 400 and 600°C with temperature gradients of 100 to 300°C across the loop. Below 550°C the attack which took place, even after 500 hours, was very light and consisted of a general roughening of the steel surfaces. At 550 and 600°C, however, the attack became rather severe, as illustrated by the first two photomicrographs of Figure 31. The attack shown in these photomicrographs was a result of 500-hour exposures and is intergranular in nature and characterized by its nonuniformity. The attack was initiated at a series of points along the surface and it progressed inward and along the surfaces of the steel giving the surfaces a scalloped appearance. These scalloped areas, which are visible in the photomicrographs, reach depths of 4.4 mils at 550°C and 5.3 mils at 600°C.

Specimens tested in the loop for 500 hours at 550°C were compared with type 430 specimens tested in the spinner units and the differences in attack are illustrated, for one case,
Figure 31. Type 430 steel specimens tested in a thermal convection loop or in a spinner unit for periods of 500 hours (250x; HCl, HNO₃, glycerine etch)

a. Specimen surface exposed to lead-bismuth eutectic melt in a thermal convection loop (550°C)

b. Specimen surface exposed to lead-bismuth eutectic melt in a thermal convection loop (600°C)

c. Specimen surface exposed to lead-bismuth eutectic melt in a spinner unit (550°C)
in photomicrographs a and c of Figure 31. The differences are of degree rather than mechanism, and although differences in conditions between spinner and loop tests preclude any but very general qualitative comparisons, one point can be made.

Spinner tests, in which a limited amount of liquid metal is available, are useful for determining differences in behavior between materials. However, when conditions are changed from those employed in such simulated dynamic tests, the materials cannot be expected to behave in exactly the same manner. The differences in behavior illustrated here suggest that a material must be tested using conditions duplicating those under which it is to serve before the limit of its usefulness can be determined. As a result of the loop tests conducted with type 430 steel, the upper limit at which it can be used to contain lead-bismuth appears to be nearer 550°C than 700°C, the limit established as a result of short time spinner tests.

**Forced convection loop**

The loop shown schematically in Figure 8 (p. 35) was constructed as a test system for the experimental diaphragm pump, and its operation has been confined to testing the suitability of the pump for prolonged use with lead-bismuth. The system has been operated continuously for about 2000 hours without serious difficulty.

The operating conditions, which have not been changed
since the loop was charged, include an expansion tank temperature of 500°C and a cold trap temperature of 370°C. The pump is operating at 0.6 gpm, with the remote head at a temperature of 300°C and the ball check valve at 400°C. Discharge pressure is approximately 20 psig.

It has not been possible to maintain an accurate check on pump delivery due to the failure of thermocouples in a heat exchange section, but as far as can be determined there has been no loss in pump capacity with time. Experience to date indicates that once this type of pump is placed in operation it needs little attention other than slight adjustments of oil compensator valves and bleeding of air from the oil side of the low temperature pump head. The operating temperature of the unit is limited only by the ability of the ball check valve assembly material to withstand the corrosive action of the metal being pumped and scoring due to repeated seating and unseating of the balls.

Performance of the pump indicates that it is well suited to the pumping of lead-bismuth at low flow where pulsating flow can be tolerated.
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APPENDIX
Figure 32. Effect of temperature on removal of major constituents from 2 1/2 chromium-1 molybdenum alloy steel in lead-bismuth eutectic melt after 96 hours.
Figure 33. Effect of temperature on removal of major constituents from 9 chromium alloy steel in lead-bismuth eutectic melt after 96 hours.
Figure 34. Effect of temperature on removal of major constituents from type 410 steel in lead-bismuth eutectic melt after 96 hours

AT 700 °C CHROMIUM WAS PRESENT IN AMOUNTS < 5PPM
Figure 35. Effect of temperature on the removal of iron from type 430 steel in lead-bismuth eutectic melt after 96 hours.
Figure 36. Effect of temperature on removal of major constituents from type 446 steel in lead-bismuth eutectic melt after 96 hours.