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TECHNICAL MEMORANDUM

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NOTES ON LIQUID METAL STUDIES IN FRANCE AND GREAT BRITAIN

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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SUMMARY

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This document is a summary of observations made in laboratories engaged in liquid metal work in Great Britain and France during a visit made in the summer of 1962. Studies in this field abroad are being pursued with vigor and a high degree of competence. Many of the problems being examined are identical with those which have been encountered in U.S. research. Particular attention has been devoted in this effort to (1) presenting names and addresses of British and French workers in this field for the convenience of Americans who wish to communicate with foreign researchers in the same area; and (2) calling attention to ideas and techniques which would appear to be of direct interest and concern to NASA and the U.S. program which have been developed in Europe.

INTRODUCTION

During a visit abroad, during the summer of 1962, the writer had occasion to become acquainted with the work on liquid metals which is currently in progress in France and Great Britain. Information on this activity may be of rather general interest to workers in this country, and for this reason this brief summary is being issued.

A number of general observations are perhaps worth making at this point. In these two countries, liquid metal work at the present time seems largely confined to the alkali metals, sodium and sodium-potassium alloy, for application to fast breeder systems (the Dounreay reactor in Britain, Rapsodie in France). Previous work on liquid bismuth systems, which a few years ago were being very vigorously pursued, has almost totally vanished, abroad as in the United States. No evidence was found of great interest in the use of alkali-metal cooling for thermal neutron spectra, systems like the SRE or Hallam plants in this country. Apparently, the thinking has been that if a group goes to all the trouble of licking the not inconsiderable problems of liquid metal technology, the additional effort to derive the advantages of a fast spectrum will be relatively small. Several aspects of liquid metal technology which are of great interest in the United States at present seem to be relatively untouched in these two countries: boiling liquid metals, mercury systems, the behavior of the more volatile alkali metals rubidium and cesium, and of lithium. It is perhaps easy to understand the reasons for this comparatively more narrow range of interests and activities: The British and French work is pointed towards high temperature power reactor operation, and the special needs of space systems which have been so influential in establishing the direction of the U.S. work have not yet begun to play an important role in the studies of the European workers, so far as could be determined.

Thus the range of interest abroad seems to be much more restricted than it is in this country. But within this narrower framework, the work that is being done seems thoroughly knowledgeable and quite sophisticated. The investigators seem completely familiar with past efforts in the U.S. here, where a substantial part of the world's store of information on liquid metal systems was first derived, and they are currently aware of and struggling with precisely the same problems which are occupying the attention of American workers, e.g., the nature and role of carbon in sodium systems, how to analyze for oxygen at low levels, whether an on-line oxygen meter can practically be developed, etc. Not only are the problems the same, but in many cases precisely the same techniques and tools that U.S. workers have turned to are also being investigated abroad --gas chromatography, electron micro-probe analysis, etc. Some of the approaches used are quite original and ingenious, and are well worth careful consideration (see Appendix A).

In the paragraphs which follow, an attempt will be made to describe the kind of work being carried on at the British and French installations, the places where this activity is centered and perhaps most important and useful of all, the names of the people involved. There is good reason to believe that workers in this field are willing and anxious to exchange ideas and experiences with their American counterparts; and correspondence and other cooperative efforts will probably be most cordially welcomed and gracefully answered.

LIQUID METAL WORK IN FRANCE*

The French work on liquid metals is at the present time being carried out principally at the following sites:

Saclay: Fundamental Studies on Corrosion Processes

Fontenay-aux-Roses: Liquid Metal Technology and Heat Transfer Studies

Grenoble: Engineering Corrosion Work, Large Loops †

Cadarache: Test Facilities for "Rapsodie" **

These are the activities directly under the CEA--the "Commissariat à l' Énergie Atomique", the French equivalent of the AEC, so that these locations correspond essentially to our national laboratories. In addition, there was some indication that liquid metal work was being carried out by EDF, "Electricité de France", the nationalized electric power agency there, at their installation at Chatou in the suburbs of Paris; but no details on the nature and magnitude of the effort in this field could be obtained, except that it is small and concerned with technology and handling.

Saclay

The Saclay laboratory of the CEA is located in a small town called Gif-sur-Yvette (Seine et Oise), about 12 miles almost due south of Paris. This is one of the largest of the French atomic installations, and there are more than 5000 people there. Their interests cover the whole atomic field, fission, fusion, fundamental particles, etc.

The liquid metal studies here are largely devoted to an examination of the fundamental nature of corrosion in Na and NaK. They are under the direction of LOUIS CHAMPEIX, and seems to be proceeding along familiar lines--solubility and solution rate studies, the effects of oxygen, carbon, etc. For oxygen determinations, they use a modification of the Pepkowitz-Judd amalgamation technique. In many of their experiments, they find the residue after removing the sodium by solution in mercury to contain materials other than Na_2O, hydride and carbonate for example. Because of this, after the amalgamation step, they dissolve the mercury-insoluble residue in distilled water under conditions where they can catch and analyze the evolved gas. (NaH would

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* This section has been reviewed by Dr. Vautrey, to whom the writer is indebted for this help. Quotations in the footnotes are from his letter of December 20, 1962.

**See Cadarache, below.

† The information on this work was obtained from French personnel at other sites. No visits were made to Grenoble.

be hydrolyzed by this procedure and yield hydrogen gas; some metallic carbides which might be present, calcium for example, would produce hydrocarbons.) Then the solution is neutralized and acidified, and once more any gases produced in this step are collected, CO_2 from Na_2CO_3 and hydrogen from particulate iron, for example. The residual material in solution is then determined, and on the assumption that it was derived from Na_2O, the oxygen content of the initial Na sample can be calculated. In the corrosion area, attention is largely concentrated on the behavior in Na of stainless steel, and of Nb alloys (for fast reactor operations).

In Champeix's laboratory, a considerable amount of work is being done by JACQUES SANNIER on the determination of both oxygen and carbon in sodium. With respect to carbon, he is using essentially the same method which has become popular in this country, i.e., wet oxidation to produce CO_2 which is determined by gas chromatography. Sannier finds the same problems of reproducibility as have plagued American workers, and spoke of the difficulty of obtaining standard samples for carbon in Na, a dilemma which has caused some concern in the U.S. as well.

The equipment and techniques used at Saclay, and the quality of the results obtained, all look excellent. The scale of the liquid metal work at this laboratory seemed to be quite small, however, perhaps no more than half a dozen people. In France, as in the U.S., the greater part of the effort is expended on technology and applications; fundamental studies on liquid metal behavior, such as are being carried out at Saclay, apparently carry a much lower priority. It may be speculated that a French visitor to American laboratories might make the same remark about us.

Fontenay-aux-Roses

The Fontenay-aux-Roses (Seine) laboratory of the CEA is located about three miles south of Paris, on the road to Saclay, on the site of an old military installation called the Fort de Châtillon. About 1500 people are employed there, only a few of them concerned with liquid metals. As was indicated above, this facility is used largely for engineering tests on Na and NaK systems--heat transfer, corrosion, bearings, seals, pumps, etc. An important function of this laboratory seems to be the back-up support of the large scale work at Cadarache.

The liquid metal studies here are under LOUIS VAUTREY, who has made several visits to the U.S., and is well-known in the liquid metal trade. The scope of the studies at this location is enormous, and the laboratory seems to be concerned with almost every aspect of liquid Na and NaK work which is of interest.

Vautrey and his associates are thoroughly aware of the problems of liquid metal handling, and seem to be in close touch with current thinking and information from the U.S. workers, at least in the unclassified areas.*

Cadarache

Cadarache is located in southern France, about 25 miles from the city of Aix-en-Provence, a famous cultural and educational center, population about 60,000. Aix is

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* It may interest American workers contemplating a visit here, or to the other installations in France, to know that most of the engineers and scientists working in the liquid metal field are quite familiar with English. They of necessity have to read it, and they can follow a talk in English without major difficulty. They prefer French of course, and many of them who have no difficulty in understanding English nevertheless hesitate to try to speak the language--a reaction which was found to be rather common among educated Europeans.

connected with Marseilles, about 20 miles away, by a fine new express highway, one of the very few "Autoroutes" in France. The Cadarache installation seems to have been chosen because of its proximity to the Durance river, which is available for cooling water and is currently being developed for hydroelectric power production. Officially, this laboratory uses a post office address in St. Paul lez Durance (Bouches-du-Rhône), the nearest small town. (Most people who work at Cadarache live either in Aix, or in Manosque, a town of less than 10,000 population, about 16 miles from the site. CEA buses operate between these communities and the installation.)

Cadarache is one of the newest of the CEA installations, and it is still largely under construction. Only a few permanent buildings have been completed, and a visitor in 1962 is impressed by the number of bulldozers and other earth-moving rigs buzzing around the site. Other than construction people, about 600 scientists and technicians are presently employed there; and it is planned eventually to have about 2000 workers.

Administratively, Cadarache comes under Fontenay, for the work on liquid metals, and Louis Vautrey is in charge of this work at both installations. His deputy on the site is JACQUES GOLLION. Although Cadarache and its facilities to date are French, the CEA is now working closely with Euratom on the fast reactor program, and there are a number of citizens of other countries, Euratom employees, who have already moved to Cadarache.

This fast reactor program seems to be the principal concern of the Cadarache installation, and perhaps one of the most important reasons for its existence.* This is where the "Rapsodie" fast breeder reactor is to be built, and the supporting facilities for this project have already been started. These include a plutonium fuel fabrication plant and a large scale liquid metal test facility (of which more later).

A 30 MWt test reactor with a spectrum containing a significant fast component, "Pegase" is under construction and is expected to be available for use in the 1963-4 period.** A critical experiment for the "Pegase" reactor is already on the Cadarache site, and is called "Peggy". "Rapsodie" itself is a sodium cooled 10 megawatt (thermal) reactor, to use Pu and enriched uranium, which is expected to go critical in 1965 or 1966. So far as could be determined, no final decision on the fuel for this reactor has yet been made; it will probably be either a U-Pu-Mo metallic alloy, or ceramic UO_2-PuO_2.

The liquid sodium facilities in support of this reactor are quite impressive. There are two loops, each 14 meters (nearly 46 feet) tall! The first operates at a thermal power of one megawatt, and contains about six tons of sodium. The second, which began operation in August of last year, is a full scale prototype of the "Rapsodie" system, 10 megawatts thermal and containing 16 tons of sodium. These loops appeared to be almost completely automated, with mechanized read-out of their operating characteristics. A continuous record of the system behavior is obtained in the form of tables, pounded out by an automatic typewriter like those on the print-out system of our large computers. Both of these loops are beautifully constructed, and look as though no expense was spared in putting them together.*** They are being used for large scale testing of virtually all of the components to be incorporated into the "Rapsodie" reactor--pumps, seals, bearings, valves, etc. In the selection of these components, the preliminary screening and materials selection appears to have been carried out largely at Fontenay and Saclay, where a considerable amount of the system design is also centered.

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* Work on the land prototype of the future French atomic submarine is reported to be in progress at Cadarache.

** "Pegase is not connected with Rapsodie. It is a swimming pool reactor with experimental gas loops, to check cooling systems for gas cooled reactors."

***One trick that the French seem to like to use is to cover all external heat transfer loops with aluminum sheet. This seems to be put on over pipe lagging and other thermal insulation in a way such that it can readily be removed or replaced. Whether the highly reflective Al sheet is effective in cutting down heat losses from the system is not known; but the gleaming bright shiny surface of the exposed components certainly makes an attractive and impressive appearance. ("It is essentially a better system than others to contain the thermal insulation material.")

Rather surprisingly, no facilities for component testing in sodium under radiation were seen, or seem to have been mentioned during this visit, so far as can be recalled. Considering the obvious care and thoroughness with which the French seem to be proceeding, it is clear that they are aware that sooner or later they will have to set up a sodium cooled test reactor, or a sodium loop in some other system.*

No startlingly new techniques were observed at Cadarache. For oxygen in liquid sodium, Gollion and his people use the amalgamation technique, followed by a flame photometer determination of the Hg-insoluble residue. As has been indicated above, in each step of the solution process after extraction of the sodium with mercury, the addition of water and of acid, the evolved gases are carefully collected and analyzed, by gas chromatography. For loop operation, plugging indicators are used for oxygen control, but with the same doubts and uncertainties about such a secondary technique as are common in the U.S. There are several of the British designed Blake "Rho" meters on hand, which are presently being evaluated, but there seemed to be no great enthusiasm for this instrument. Like everyone else, the French would very much like to have a reliable in-line meter that would read the oxygen content of their systems down to low levels, 10 ppm or less; and again, they have achieved no more success in constructing such an instrument than any one else. Work on this need is currently in progress. One idea that was mentioned as a possible concept on which such an instrument could be designed was the recent report**, by the Russians at the IAEA Salzburg conference, that Na_2O could be electrolyzed, and made to move under an applied electrical field. The French workers seemed quite intrigued by this phenomenon, and some thought on its utilization and application is taking place.

LIQUID METAL WORK IN GREAT BRITAIN***

Liquid metal work in Great Britain, in contrast to the French effort, has a comparatively long and complicated history. A few years ago, there was a large scale effort in this area, and investigations on bismuth and alkali metal systems were carried out at Harwell, Windscale, and several other sites. At about the same time this subject tended to attract diminishing interest in the U.S., roughly the period from 1955 to 1960, there was a parallel decrease in effort in Great Britain. Recently, there has been a revival of this field, due largely to the Dounreay fast reactor, and at the present time a very substantial effort is being devoted to it. During this hiatus, unfortunately, in Great Britain as in the U.S., a large number of the people skilled and experienced in the liquid metal field have been diverted into other areas; and for the most part, this work in Britain is being carried out by a fairly new team. It seems regrettable that greater use is not being made of the pool of manpower experienced in this area, in both Great Britain and the U.S. But the work in England and Scotland seems to be in the hands of extremely able individuals, and they are making good progress after some unfortunate false starts.

At the present time, there is only one laboratory in Great Britain where liquid metal work is carried out, at Culcheth in the town of Warrington (Lancashire), about 28 miles from the important industrial complex of Manchester. Some work, comparatively limited in scope, is also being carried out at Risley, about a mile and a half from the Culcheth site. The objective of this activity, at the present time, seems to be directed

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* "Some small loops of radioactive sodium were and will be tested in the EL3 reactor" --a 17.5 MWt heavy water test reactor at Saclay.

** Nevzorov, B. A.: "The Nature of Oxygen in Liquid Sodium", Paper Number CN-13/40. IAEA Conference on the Corrosion of Reactor Materials. Salzburg, Austria, 4-9 June, 1962. Available in English translation from TID, Oak Ridge as document AEC-tr-5412.

***The section on "Liquid Metal Work in Great Britain" has been reviewed by Dr. Donaldson at Dounreay. His help is gratefully acknowledged. Direct quotes in the footnotes are from his letter, dated December 28, 1962.

largely to support the Dounreay fast reactor, in Scotland. All of the liquid metal work formerly carried out at Harwell and Windscale has now been terminated, and the facilities and people moved to Culcheth and other sites.

Culcheth

The largest liquid metal laboratory in Great Britain is at Culcheth. The work here in this field is carried out largely under the direction of DR. CHRISTOPHER TYZACK. The laboratory studies are being conducted by ALAN THORLEY at this site.* Culcheth is a research installation for the entire United Kingdom Atomic Energy Authority (UKAEA), and the work here includes studies on and for civilian power reactors (mostly of the Calder Hall type), advanced gas-cooled reactors, and fast reactors with liquid metal cooling. In this last category, which is of principal interest, Culcheth supplies design information to Risley, and also carries out investigations in support of Dounreay operations. There are about 400 people at this laboratory, approximately half of them technical, but there are only twelve workers engaged in liquid metal studies. The larger part of the effort, here as in France and the U.S.A., is devoted to engineering tests, the operation of sodium and NaK loops. Work has been going on in this area for about six years now, and at the present time the loops are operated on a continuous schedule, under the direction of four senior scientific assistants.**

The Culcheth people are carrying out some extremely interesting and original studies, and seem to be thoroughly aware of what has been done and is going on. They routinely use the vacuum distillation technique for determining oxygen in Na and NaK (see Appendix A, where this is discussed in detail) and claim to be able to carry out analyses down to 2 ppm. (In this country, using the amalgamation technique, it is rare to find an analyst capable of measuring 10 ppm.) Carbon in alkali metals is also causing them a great deal of concern. Here, like everyone else, they seem still to be groping for techniques and an understanding of the nature of carbon-sodium-oxygen interactions. It is possible that their troubles due to carbon may be somewhat less than those encountered in this country, because of two factors:

1. They use NaK rather than sodium a great deal.*** Since this is normally a distilled product, made by heating metallic Na with KCl, it is probable that a substantial amount of carbon, present in the Na because of the graphite electrodes used in its manufacture, may be left behind in the still pot.

2. A great deal of their metal before use is not only cold-trapped, as is customary here, but passed through high temperature furnaces filled with zirconium chips as well. This hot-trapping procedure has been found not only to accomplish its primary purpose of reducing the oxygen content of the metal to very low levels, but the Zr also seems to remove carbon rather effectively.

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* Other individuals who may be helpful at Culcheth are R. NICHOLS and E. C. W. PERRYMAN, both deputy laboratory heads and extremely hospitable and cordial.

** Who would probably be called laboratory assistants or technicians in the U.S.A.

***Donaldson's comment on this statement is that "...most of the Culcheth work has been carried out using sodium and only a very small proportion of it has been on NaK. Dounreay are, of course, interested in NaK and what little work that has been done here has been with NaK primarily. With respect to the lower carbon content of NaK, it will not be substantially lower as most of the 70/30 NaK used at Dounreay was prepared by mixing sodium with sodium-potassium alloy--mainly eutectic."

This intensive effort on low oxygen sodium and NaK is a direct result of the interest of the British in using niobium in their fast reactor. Nb has quite good corrosion resistance, and mechanical properties at elevated temperatures, but it is extraordinarily sensitive to amounts of oxygen which would be quite tolerable with the ferrous alloys which have been of principal concern in the U.S. Early tests on Nb alloys in static pots looked very good, but later when the same materials were exposed to flowing Na in loops, it had an unhappy tendency to fall apart, a direct consequence of its oxygen sensitivity. The oxide formed on niobium, it seems, tends to be quite non-adherent, and spalls off readily, exposing fresh metal beneath to the ravages of oxygen-containing Na or NaK. (This behavior sounds quite like the experiences in this country with beryllium metal in sodium.) In an effort to combat this, Culcheth has gone on from pure niobium to studies with alloys, containing zirconium and tungsten, and they find somewhat better adherence and protection characteristics. But they appear to be convinced that the ultimate solution to this problem is the reduction of the oxygen content of their liquid metal to extremely low levels. This they feel they can do with their hot traps.

This concern with the effect of oxygen on corrosion as a vitally important factor in fast reactor operation is no doubt responsible for their interest in the fundamentals of the process. Thorley and Tyzack both expressed some doubts about the explanation which has hitherto been advanced, involving in the case of iron, the production of intermediate $Na_2O \cdot x FeO$ compounds . Although some of the strongest evidence in favor of this process was obtained in England some years ago by GEOFFREY HORSLEY (then at Harwell now with the "Dragon" high-temperature gas project at Winfrith Heath in Dorset), they feel a little uneasy about this explanation, and spoke of evidence against it. This information was apparently developed under sub-contract at some university, and they were reluctant to discuss it in detail for fear of pre-empting the rights of the experimenters, and possibly compromising publication in the open literature. For this reason, it was not possible to evaluate the objections to the ferrite concept in detail. Thorley stated that perhaps the compounds postulated are not chemical entities as was assumed, and as was apparently confirmed by Horsley, but some kind of loosely coupled reaction product of Na_2O and oxygen in solid solution in Fe. He admitted that such a complex would have to have many of the characteristics postulated for the compound; and he found it quite difficult to explain the effect of oxygen in iron corrosion in sodium without resorting to some such explanation. The difficulties in understanding this question are compounded by the long standing discrepancy on the solubility of Fe in Na. It will be recalled that in the late 40's and early 50's, measurements were made at both the Knolls Atomic Power Laboratory (KAPL) and the Mine Safety Appliances Company (MSA), in which the equilibrium solubility was found to be virtually independent of the oxygen content of the Na, although the rate of solution depended strongly on the oxygen levels present. Some time later, the Naval Research Laboratory here, using radioactive tracer techniques obtained values for the solubility lower by a factor of 100 to 10,000, depending on temperature (but the slope of their temperature-solubility curve was nearly identical with that previously found). Further, the NRL workers reported that the presence of oxygen does change the equilibrium solubility of Fe in Na. This is a flat and well-defined contradiction in observation, which has remained unresolved for ten years or more. Faced with such profound disagreement on the interactions of the Fe-Na-O system, the British workers find it very difficult to untangle the behavior of the niobium base alloys, whose chemical and metallurgical characteristics are much less well-known or understood.

While the answers have not yet been obtained, the British workers are well aware of what the important questions are; and what is very much to the point, they are conducting fundamental investigations to try to resolve these problems side by side with their engineering test work. The effort along these lines is greater in Great Britain than it is in France, and perhaps even exceeds the amount of work being done here in the U.S., where the principal effort has always tended to be on hardware rather than on understanding. The British attitude cannot but be enthusiastically applauded by American scientists in this field.

Risley

Risley, a short distance from Culcheth, is primarily the administrative headquarters for the UKAEA, and has several thousand people engaged in activities of this kind. It is also the center for design work and engineering tests for the British atomic work. There are no reactors at this site, but about 250 people are employed in laboratory studies here, about 40 in the liquid metal field, mostly on engineering components for Dounreay. There is close contact and intimate liaison with this facility as well as with Culcheth.

One of the most important lines of activity currently being investigated at Risley is the work of DR. W. H. ROBERTS on friction, wear, wetting, and similar factors in liquid alkali metal systems and their close relation to the problems of bearings and lubrication in system components. This is a field in which there was once great activity in the U.S., but which seems to have tapered off markedly (the Lewis Research Center of the National Aeronautics and Space Administration (NASA) in Cleveland is leading the work in this area here).* Roberts and his people find that the behavior of moving parts under sodium or NaK is much more straightforward and well-behaved than was observed here many years ago, by Coffin at KAPL for example. He attributes many of the earlier difficulties in investigation and operation to high oxygen levels in the liquid metal--not at all surprising considering that this work was done when the importance of this factor was only dimly conceived, and sophisticated techniques for the prevention of atmospheric contamination were thought of as a nuisance rather than as a necessity. Roberts is extremely anxious to contact U.S. workers with interests parallel to his own, and invites correspondence and other exchanges of information.

Dounreay

Look at a map of Britain. The most northerly point in Scotland** is called John O'Groats. Almost due south, about 17 miles by road from the tip of the Cape is the town of Wick, a fishing village with a population of about 7000. Wick is where the British European Airways planes land passengers headed for the Dounreay reactor site. A road from Wick skirts the northern coast, and about 20 miles away is the town of Thurso, which formerly existed on fishing and sheep raising, but is now also the place where most of the Dounreay people live. In consequence of this, its population has increased markedly in recent years, and it is now about 8000, the largest inhabited community in this area. Then about 10 miles west of Thurso is the Dounreay Experimental Reactor Establishment (D.E.R.E.), to give it its full title.

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* From a letter received from Harold Hessing, NASA Headquarters, Washington (dated January 7, 1963), it has been learned that there has been a recent surge of activity on liquid metal bearing studies. E. E. Bisson and W. J. Anderson are involved at Lewis. Contracts on this subject have recently been awarded by NASA to:

1. General Electric Company
   Space Power and Propulsion Section
   Evendale, Ohio
   (M. A. Zipkin)

2. Mechanical Technology, Inc.
   Latham, New York
   (Dr. Beno Sternlicht)

**Traditionally, rather than actually. There is a small cape called Dunnet Head which penetrates into the North Sea a little farther than John O'Groats.

This whole section is in the county of Caithness, and has a topography quite different from the traditional image of Scotland. Caithness is essentially a broad coastal plain, with only a few small rolling hills, which in the south begin to merge into the mountainous regions which are normally thought of when the northern Highlands of Scotland are mentioned. The land is poor and rocky, and there is little agriculture. Inland, the only important industry is sheep-grazing. From Dounreay and Thurso, and in fact almost all along the coastal road, the headlands and cliffs of Stroma, the nearest of the Orkney Islands some five miles off-shore, are readily visible. This is one of the picturesque regions of Scotland. The kilt is not infrequently seen. So far as could be determined, the Gaelic is seldom spoken in this area, but the Scottish, or modified English, that is used is heavily accented, and it often takes a rather acute ear to understand what a native is trying to say.

This rather isolated region, then, is where the UKAEA in 1957 set up the D.E.R.E. for the Dounreay fast breeder reactor (D.F.R.). This is a NaK (70/30) cooled system, presently operating* at about 30 MWt, using a very interesting fuel: a core of enriched (47%) U-235, in an annular configuration, with vanadium on the inside and niobium outer tubes. Dounreay is the only operating fast power reactor in the western world** so far as is known; and it will occupy this unique position until Cadarache in France, the Fermi plant in Michigan in the U.S.A., the Argonne EBR-II at Idaho Falls, and possibly some other American fast reactor designs presently being evaluated go into operation. It therefore represents a rather bold and vigorous step forward in the fast reactor area.

To support the DFR, there is a materials testing reactor (DMTR) under the administration of JAMES ATKINSON, and an experimental critical assembly. Facilities for fuel element development, fabrication and testing, and experimental chemical plants for the fast reactor fuel, are also available on the site.

The liquid metal work at Dounreay is administratively associated with Risley, and is supported by the experimental work at Culcheth. On the site, the senior worker in this area is DR. D. M. "DAN" DONALDSON. His group is presently occupied principally with DFR operating problems, but is planning to set up facilities to carry out research and development activities at Dounreay. Work is just beginning on a study of methods of purifying Na and NaK, with particular attention to cold and hot trapping techniques, and the use of diffusion versus by-pass traps.*** When loops and other components are available, this group expects to continue with other types of work: fuel compatibility studies, for example. They are especially interested in plutonium and its compounds, in particular oxides and carbides.

The Dounreay reactor, because of its use of Nb cladding, and the high operating temperature, is extraordinarily sensitive to the oxygen content of the NaK, and levels of oxygen that are acceptable with steel components lead to gross corrosion with niobium. This is, of course, the basis for Dounreay's special interest in oxygen purification and

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* "...It is proposed, within the next few months probably, to increase the power to about 50-60 MWt." In an address to the Northern California Section of the American Nuclear Society, in San Francisco on April 13, 1963, SIR WILLIAM PENNEY of the UKAEA stated that this power level increase was now planned for May, 1963.

** There is a 5 MWt fast breeder reactor, BR-5, at Obninsk in the U.S.S.R. This system uses plutonium oxide fuel, Na as the primary coolant, and NaK in the secondary loop. The reactor went critical in July 1959, and so far as is known is still functioning. No other fast power reactor is known to be operating in the Communist-bloc countries.

***"We will not be doing any work at Dounreay on diffusion traps as a method of liquid metal clean-up. We were interested in diffusion rates as possible mechanisms of blockage or sources of impurity from dead legs."

analysis techniques. They routinely use cold trapping, as does virtually every other reactor with a liquid alkali metal coolant. In addition, they have facilities for gettering their fluid in high temperature zirconium-filled hot traps. One of their most urgent current problems is the evaluation of the efficacy of these components.

For oxygen analysis, Dounreay routinely uses the vacuum distillation technique, and with it obtains reproducibility to ± 2 ppm. Like every other reactor site, they would very much like to have a continuous oxygen monitoring instrument in-line. The only device of this sort that has ever had even a partial success, the Blake "Rho" meter, was developed at Dounreay.* This instrument measures the change in electrical resistivity of a sample of the liquid metal, which is in a very carefully thermostatted conductivity cell (a few hundredths of a degree Centigrade variation in the sample temperature produces changes in the resistivity comparable with the effect of parts per million of oxygen.) Also, the Blake meter, like the plugging indicators so frequently used here, indicates changes in the properties of the liquid metal, but not what the changes are due to. Thus, if impurities other than oxygen (carbon, or gas bubbles for example), are present the apparatus cannot be expected to yield dependable oxygen analyses. For these reasons, there has been a great deal of controversy over the Blake meter, and some workers in the U.S. have expressed some grave doubts about it. Surprisingly enough, the same questions seem to exist in Britain where the instrument was developed. There is general agreement that the meter, like the plugging indicator, is useful in detecting changes in the Na or NaK, providing that the necessary care is taken in the use of this extremely fussy device. But the interpretation of what the changes in resistivity may mean requires rather more experience to evaluate.

The visit to Dounreay on which these comments are based was made at a particularly auspicious occasion: that very time, early in August, 1962, the reactor reached its full power rating, 30 MWt for the first time. It seemed to be operating satisfactorily except for an apparent oxygen build-up in the NaK that seemed to be considerably greater than could be accounted for by air leakage, and this was putting a rather larger burden than was expected on the purification traps.** It will be extremely interesting to watch the future behavior of Dounreay, since so much of the U.S. effort, for both power reactors and space applications, seems to be focussing on fast, alkali metal cooled systems of the same sort.

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* Blake, L. R.: Proc. Inst. Elec. Eng. 107A 383 (August, 1960).

**Since this time, visitors of Vallecitos from Dounreay and Risley have indicated that the mysterious oxygen build-up may have arisen from gases evolved from graphite used in the system. So far as is known, this factor is still under investigation. Donaldson writes, as of December 28, 1962, "I can unfortunately, add nothing to your footnote, it still remains a possibility that the impurity build-up in the NaK arose from outgassing (probably moisture) of the borated graphite, but the situation has still to be resolved."

APPENDIX A

Memo Report: British Techniques for Sampling and Oxygen Analysis in High Temperature Liquid Metal Systems

Dated: September 17, 1962

To: R. W. Lockhart, Mass Transfer Project,
General Electric - Atomic Power Equipment Department

From: Leo F. Epstein

During my recent visit to England, as you requested, I looked into the methods used at Culcheth for sampling high temperature liquid metal loops, which Dr. Christopher Tyzack had mentioned to us during his visit here in May. It turns out that there are two devices which have been developed, and I will try to describe both of them to you in some detail. The incorporation of these concepts into our loops, and in the sodium mass transfer program, it seems to me, might improve our sampling technique significantly, and lead to better reproducibility in the results.

System A. Built-in Inert Atmosphere Boxes

The first, and perhaps most generally useful device used by the British is a small dry box built on as an integral part of their loops, and permanently attached to their sampling port. This is a somewhat miniaturized version of the two chamber steel inert atmosphere boxes of the type we are familiar with, designed so that either inert gas or vacuum can be used. The size of the assembly, as I recall it, was about equal to two cubes, one foot on the side, hitched together. Manipulation was carried out partially through the usual rubber gloves, and also with some rather ingenious remote devices which could be worked from outside the boxes.

With this system, when they want to take a sample of some sort out of the loop, they pull a hard vacuum on the box mounted directly over the port, and flush several times with purified inert gas. Then, either through the gloves or using the external manipulators, they open the flange on the loop and reach down and extract their sample. This is brought into the chamber, cooled, and inserted into a metal container or some similar device, taken out through the second chamber (air lock), and transported to where the analysis or other measurement is to be made, without at any time exposing the sample to the possibility of contact with air. The advantages of this technique will, I am sure, be obvious to you.

This device and method can be used to remove either samples of the liquid metal from the system, or anything else which has been immersed in the liquid metal environment, say a corrosion tab. Such built-on inert atmosphere boxes could be used with almost any kind of liquid metal system, but their application is especially important when the fluid is extremely sensitive to oxygen or the other constituents of air (sodium, for example). But even for relatively inert liquids it is conceivable that a solid sample would be susceptible to change by reaction with air, and this kind of inert atmosphere handling would be desirable. (For example, consider an experiment where a sample of solid CaO ceramic is exposed to liquid mercury, at room temperature. No significant reaction of the Hg and air is to be expected; but reaction of the calcia with atmospheric moisture and CO_2 would be a very definite problem.)

There are some definite disadvantages to this technique. First, the boxes with their associated paraphernalia for evacuation, filling with inert gas, etc., are bulky and complex. It is easy to build one of these into a system, and in fact, I believe the British use only a single sampling opening.* But when, as is true with your loops, there are five or six sampling ports, the complexities introduced become rather formidable, and it is perhaps worth considering alternate techniques, for example the portable box which I believe you have tried, which can be flanged on to any one of the several sampling ports. (This idea is perfectly sound, it seems to me, providing care is taken to insure a completely leak-tight seal for each position.)

A second disadvantage of this system has in fact limited its application in Britain. This arises because at elevated temperatures the liquid metal (Na for them) has a high enough vapor pressure so that there is extensive evaporation when a sample port is opened. This material tends to condense on various parts of the box, and to interact with some of the components. The effect of Na on the glass viewing windows of the box, the rubber gloves, and similar rather sensitive materials, can be quite embarrassing. As a matter of fact, with the Culcheth sodium loops, it is not considered practical, because of this phenomenon, to use the inert atmosphere box technique for hot sampling above about 300 C; it was largely because of this temperature limitation that a great deal of effort went into techniques for remote manipulation (no glass windows, no rubber gloves, etc.) and to the development of the second technique described below.

System B. Integral Oxygen Analysis Sampling Device

This second device is much less flexible in concept and application than the one described above, but for the special purpose for which it was devised has a number of important advantages. It was specifically designed for sampling Na and NaK for oxygen analysis, but presumably could be adapted to other related studies.

To explain how it works, I should remind you that the British do not use the Pepkowitz-Judd amalgamation technique, or the alkyl halide reaction, which are the basic methods of measuring the Na_2O content of Na which we prefer in this country. Instead, they depend largely on the distillation method. In this, the Na sample containing dissolved oxygen is distilled _in vacuo_ at a temperature sufficiently low (500-550 C) so that there is no fear of (a) vaporization of the Na_2O or (b) dissociation of the compound. The Na_2O whose vapor pressure is much less than that of sodium is left behind in the still pot, along with any other non-volatile material which may have been present in the sample initially. After removing this dry sample from the distillation apparatus, it can be treated with H_2O to extract the water soluble material, presumably largely Na_2O, and the amount in solution determined by any one of several techniques, similar to those that are employed with the Hg-insoluble residue from the amalgamation method - weighing, titration with standard acid, spectrographic or flame photometric determination of Na, etc.

In the Culcheth integral sampler, there is a gas and vacuum-tight unit attached to the loop itself into which a small cup can be inserted. Without opening the system in any way, a sample of Na can be withdrawn from the loop and transferred to this cup, which is contained in the sampler unit. This whole assembly can then be isolated physically from the loop itself, and pumped down and heated so as to evaporate off all the sodium. Then the sampler can be opened, the cup removed and the amount of residual material left behind determined by one of the several methods mentioned above. My recollection is that the whole integral sampler assembly is a tube about three inches in diameter and something less than a foot long. A complete description of this device, with drawings, is supposed to be given in the document:

Thacker, R.: _The Determination of the Oxygen Content of Liquid Metals_
IGR-TN/C-609 (Culcheth, 1957)

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*"One rig at Dounreay will have two sampling boxes, but the one unit for evacuation and inert gas filling, etc., is used for both boxes. There is no reason why this should not be extended to a larger number of boxes if required."

I attempted to obtain this paper while I was in Britain, but it is marked "For Official Use Only" and could not be released to me. A request for a copy has been forwarded through regular library channels, and I hope it will reach us shortly. This document should fill in a number of holes in my memory of this equipment: how the sample of sodium is transferred into the unit, how the amount is determined, etc.*

This may be an appropriate point at which to discuss the distillation technique for the determination of oxygen in Na, which is the routine method used by the British, but which has tended to be viewed with some suspicion in this country. It depends, first, on the assumption that Na_2O is (a) non-volatile, and (b) thermally stable. These characteristics are supported by the work of

Brewer, L. and Mastick, D.: J. Am. Chem. Soc. 73 2045 (1951)

so that, in principle, if Na and Na_2O were the only components present, it should be possible to distill away the sodium, and determine the oxygen present. But it should be pointed out, there are many non-volatile materials other than Na_2O which may be present in sodium. First, there may be metals, dissolved off the container walls. Then there is carbon, which we have come to recognize as an almost ubiquitous impurity in Na, and probably in the other alkali metals. This may be present as free C, or possibly as a heavy metal carbide Cr_3C_2 or Fe_3C, for example. A number of common compounds of sodium, the hydride, hydroxide and carbonate for example, should not be stable in the presence of excess Na at elevated temperatures, decomposing or reacting in accordance with reactions like

$$NaH \rightarrow Na + (1/2)H_2\uparrow$$

$$NaOH + Na \rightarrow Na_2O + (1/2)\,H_2\uparrow$$

$$Na_2CO_3 + 2Na \rightarrow 2Na_2O + CO\uparrow$$

or even

$$Na_2CO_3 + 4Na \rightarrow 3Na_2O + C$$

But there is a growing body of evidence that even after prolonged contact (several hundred hours) with Na in huge excess at elevated temperatures, some of these reactions may not go to completion. For this reason, in the amalgamation technique for oxygen in sodium, the residue after removal of the Na by Hg extraction should not be simply dissolved in water without considering the possible presence of some of these materials. A safer procedure is to treat the residue after the extraction with water under conditions where any escaping gases produced can be caught and analyzed (by gas chromatography, for example). In this way, hydride and some of the carbides can be decomposed:

$$NaH + H_2O \rightarrow NaOH + H_2\uparrow$$

$$\text{Heavy Metal Carbides} + H_2O \rightarrow \text{Metal Oxides and Hydroxides} + \text{Volatile Hydrocarbons}$$

Following this step, measured amounts of standard acid should be added, say H_2SO_4. This may result in a further evolution of gas, from reactions like

$$Na_2CO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + CO_2\uparrow$$

or by the decomposition of carbides resistant to neutral water; and the collection and measurement of this gas would appear to be an essential step in the oxygen analysis. Finally, the determination of the oxide present as Na_2O, either from the acid titration or from a flame photometric measurement of the total amount of sodium ion in solution, or otherwise, should take into account the effects of any components present which lead to gas evolution during either the water or acid addition steps.

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*This document has subsequently been received, through normal AEC information channels.

The handling of the unreacted residue after the alkyl halide treatment must be considered with as much care. It should be recalled that this technique also depends on the removal of the bulk of the Na from the oxide (and other contaminants present)--in amalgamation this is done by solution of the Na, in the alkyl halide method by a Wurtz reaction

$$2Na + 2RX \rightarrow 2NaX + R - R$$

$$Na_2O + RX \rightarrow \text{No reaction}$$

In the distillation method for determining oxygen in sodium, virtually all of the problems outlined above on the handling of an Na_2O residue possibly contaminated with other materials are similarly present. But in addition, there is another worry. If there are appreciable amounts of free or carbide carbon present--and for purposes of discussion let it be assumed that there are no other impurities--the reaction between these materials

$$Na_2O + C \rightarrow CO\uparrow + 2Na$$

could result in a loss of oxygen, as CO, in the vacuum system at the elevated temperatures used for the distillation; and this would result in lower apparent oxygen contents than were in fact actually present.*

Since it has now become increasingly and painfully apparent that Na is almost always contaminated with carbon, often in quantities quite large compared with the amount of oxygen present, this is no idle fear, but is based on rather substantial evidence. The claims that have been made for the distillation technique, that it can measure oxygen down to the 2-3 ppm level in sodium (whereas even in the hands of a skillful operator the amalgamation process is seldom good to better than 10 ppm, and the alkyl halide technique is certainly no better) have therefore been questioned.

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* Sodium is known to reduce CO_2 and CO to free carbon, and it might be expected that the reaction

$$Na_2O + C \rightarrow CO\uparrow + 2Na$$

would not go, and in fact, the reverse process should be observed. This concept is supported by the following thermodynamic calculations for the reaction as written here:

Temperature		Free Energy Change	Partial Pressure CO
T(°K)	T(°C)	ΔF° (kcal/mole)	p_{CO}(mm)
300	27	+ 57.1	1.92×10^{-39}
400	127	+ 51.6	4.87×10^{-26}
500	227	+ 46.0	5.94×10^{-18}
600	327	+ 40.3	1.59×10^{-12}
700	427	+ 34.6	1.20×10^{-8}
800	527	+ 29.0	9.08×10^{-6}
900	627	+ 23.4	1.58×10^{-3}
1000	727	+ 17.8	9.79×10^{-2}

(Free energy data for Na_2O and CO obtained from JANAF Interim Thermochemical Tables, prepared at the Dow Chemical Company, Midland, Michigan, and revised to September 30, 1962. Partial pressures computed from relation $\Delta F^\circ = -RT \ln p_{CO}$.)
In spite of this unfavorable thermodynamic consideration the reaction tends to proceed as written because of an important kinetic factor: the escape of the gaseous CO from the condensed phases of the system drives the process to the right, as shown above.

Alan Thorley at Culcheth, who has done extensive work on this distillation process is convinced that it is as good as any other technique at higher oxygen levels, and has the advantage, which he thinks has been demonstrated, that it can be pushed to lower oxygen contents than any other method now employed. He points out that the presence of carbon does not necessarily lead to low results, as described above.* The carbon residue left after distilling away most of the Na could, he thinks, absorb some sodium so as to reduce its vapor pressure and thus keep it from all evaporating off. When this residue is analyzed, either by titration or spectroscopic or flame photometric methods, the entrapped sodium would tend to give high results. He considers that these two diametrically opposite effects of carbon result in an essential stand-off, that is in repeated experiments the low values for oxygen due to loss of materials as CO, are counter balanced by high values arising from absorbed Na, of low volatility under the conditions of his experiment. In any case, Thorley claims to have made comparisons of the results of oxygen analysis by the distillation and amalgamation techniques over a range of temperatures. These data which he plans to publish in the open literature in the near future show good agreement with the curve of solubility of Na_2O in Na against temperature obtained at KAPL, by Salmon and Cashman using the amalgamation method. In contrast to the amalgamation procedure, however, Thorley stated that reproducible results were obtained by distillation down to the 2-3 ppm level. The availability of information on this work will help considerably in the evaluation of the distillation technique for oxygen in Na.

One factor which should be considered in the evaluation of the British work is that their alkali metal may, for one reason or another, be quite low in carbon. Many of their experiments have been done on NaK, rather than sodium.** As is well known, this material is often prepared by treatment of a potassium salt, KCl for example, with metallic Na and distilling off the resulting NaK alloy. This method of preparation, resulting in a distilled metal product, may in itself result in a material sufficiently low in carbon so that interference resulting from the presence of this material is minimized. Many of their other laboratory tests on the distillation technique have been carried out with Na rather more highly purified - by distillation or otherwise - than the usual product used in large scale reactor application, and for this reason also the small amount of carbon present may not cause difficulties. In any case, it would seem that enough information has been developed from the British work so that a very careful examination of the potentialities of the distillation method for determining oxygen in the alkali metals would seem to be justified. With the growing interest in alkalis other than Na and K, it seems particularly appropriate to consider this technique. If it works with these lighter metals, it can perhaps be expected to be even better with the more volatile metals Rb and Cs.

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*Donaldson writes (December 28, 1962): "I spoke to Alan Thorley regarding his views on the effect of carbon on oxygen analyses and he expressed the opinion that values obtained may be high because of the suggested absorption of sodium by carbon. He does not subscribe to the view that low results will be obtained through oxide being reduced by carbon and being removed as CO and quotes the following results in support of his views. Several experiments were carried out in which carbon, to levels of 3, 6 and 12 ppm, was added to sodium containing oxygen at the 10 ppm and at the 40 ppm level. In all cases good carbon recoveries were obtained after distillation." These observations by Thorley raise another most interesting question. It has often been observed that distilled sodium contains a significant amount of oxygen, even when great care has allegedly been taken to prevent contamination by glass, air, etc. Brewer and Mastick suggested that the volatile agent which carried over the oxygen was probably CO. This hypothesis would seem to be open to some doubt in view of Thorley's experiments described above.

**But cf. footnote, p. 6

There is rather more question about its application to lithium, where the presence of stable nitrides and carbides, as well as the very low vapor pressure of Li (compared with Na) may introduce some very formidable problems.*

Conclusions and Recommendations

1. The use of inert atmosphere boxes over the sampling ports in liquid metal systems seems desirable. Efforts to build such devices into operating loops appear to be worthwhile, and may lead to more reproducible results.
2. The use of portable inert atmosphere boxes such as you have previously tried should be re-examined, particularly for systems where there are a large number of sampling points as in your loops.
3. The applicability of the "integral sampler" described above for oxygen determinations in volatile liquid metals depends on establishing the validity of the distillation technique in the presence of carbon and other impurities which may interfere. If the distillation process is a valid one, design of integral samplers into loops seems to be an excellent idea.
4. Enough encouraging information is available from British sources to suggest that previous doubts about the limitations of the distillation process may not be justified. The time has perhaps come for a careful evaluation of this technique. Its simplicity, compared with the amalgamation method, and the promise of dependable oxygen determinations at the 2-3 ppm level would appear to be good reasons for an intensive program on this subject. The possibility of extending it to the alkali metals more volatile than Na would tend to lend further weight and urgency to such a study.
5. The liquid ammonia extraction technique for analyzing alkali metals would also appear to warrant further exploration.

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*It should be mentioned that another method of removing sodium from Na_2O and other solid impurities has recently shown promise here - the extraction of the Na by anhydrous liquid ammonia (see Alter, H. W. and McManus, P.A.: Sodium Mass Transfer: III. <u>The Application of Liquid Ammonia as a Sodium Leaching Agent</u>. Report No. GEAP-4006, General Electric Co., Vallecitos Atomic Laboratory, Pleasanton, California, April, 1962). The solubilities of the most important contaminants that can be expected in sodium - heavy metals, Na_2O, Na_2CO_3, NaH, NaOH, etc., - in this reagent appear to be sufficiently low so that good separations can be achieved. Further studies on the applicability of liquid NH_3 to the analysis of the alkali metals would seem to be desirable.

APPENDIX B

ADDRESSES OF LIQUID METAL INSTALLATIONS MENTIONED IN FRANCE AND GREAT BRITAIN

FRANCE

1. Saclay
Commissariat à l'Énergie Atomique
Laboratoire de Saclay, B.P. No. 2
Gif-sur-Yvette (Seine-et-Oise), FRANCE

2. Fontenay
Commissariat à l' Énergie Atomique
Centre d'Etudes Nucleaires
Fontenay-aux-Roses (Seine), FRANCE

3. Cadarache
Centre d'Etudes Nucleaire de Cadarache
B.P. No. 1
St. Paul Lez Durance (Bouches du Rhône), FRANCE

GREAT BRITAIN

1. Culcheth
UKAEA, Reactor Materials Laboratory
Wigshaw Lane, Culcheth
Warrington (Lancs.), ENGLAND

2. Risley
UKAEA, Reactor Group Headquarters
Risley
Warrington (Lancs.), ENGLAND

3. Dounreay
UKAEA, Dounreay Experimental Reactor Establishment
Thurso (Caithness), SCOTLAND

4. Winfrith Heath
"Dragon" Project Office
A.E.E., Winfrith
Dorchester (Dorset), ENGLAND

NASA-Langley, 1963