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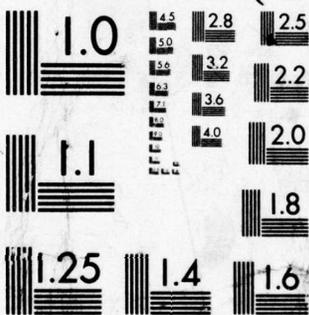
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TECHNIQUES FOR SURFACE WETTING OF NaK TO COPPER
FOR LIQUID METAL SLIPRING HOMOPOLAR MACHINES

by
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Pittsburgh, Pennsylvania 15235

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20. Abstract (cont)

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Several new approaches for establishing and maintaining
wetting, within the naval machine constraints, were discovered.
Two promising techniques recommended for development include
small lithium additions to NaK and ultrasonic encouragement.
Small scale cursory tests were positive for both techniques.
A detailed experimental test plan, to fully develop and
characterize these and other applicable wetting techniques,
is presented.

(Authors)

TABLE OF CONTENTS

TABLE OF CONTENTS (Cont'd)

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High current density homopolar machines employing liquid metal
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were positive for both techniques. A detailed experimental test plan, to fully
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is presented.

1

1. INTRODUCTION

Concepts for new, high current density, liquid metal slipring homopolar machines have been developed for efficient, high power density, naval ship propulsion systems.[1,2,3] These developmental machines employ eutectic NaK-78 (a sodium-potassium alloy) in the rotor-stator slipring annuli, and typically operate at current densities up to 10,000-12,000 apsi. These current densities depend upon the high electrical and thermal conductivity of the liquid metals for good performance.

The utilization of liquid metal sliprings has served to introduce a whole new set of current collection problems and situations. One of these is that of specific contact resistance. A knowledge of the magnitude of the specific contact resistance, ε_k, is necessary for designing a minimum power loss current collector. Johnson, et al.[4] have shown that platings of gold, silver, or nickel on copper significantly affect the contact resistance with NaK, suggesting that surface wetting has a strong influence. The following table, assembled from data from Johnson, et al.,[4] Poulain,[5] D'Albon and Parteni,[6] Sukhanov,[7] and others[8,9] shows that specific contact resistance can vary widely, depending on surface preparations, slipring materials, etc. (Only Cu-NaK data are shown.)

Slipring Material (Coating)	Liquid Metal	ε_k Units(Ωm^2)	Reference
Cu	30 Na-70 K	3.2×10^{-9}	(6)(7)
Cu	22 Na-78 K	$1.0-2.0 \times 10^{-9}$	(4)
Cu(Ni)	22 Na-78 K	0.5×10^{-9}	(4)
Cu(Au)	22 Na-78 K	0.2×10^{-9}	(4)
Cu(Ag)	22 Na-78 K	0.2×10^{-9}	(4)
Cu	30 Na-70 K	4.0×10^{-9}	(5)(7)

Experiments at Westinghouse[1] have shown that the specific contact resistance can vary by two orders of magnitude or more, depending upon whether or not good wetting between NaK-78 and the slipring material or coating has been achieved. There is also evidence that good wetting is conducive to liquid metal retention in high speed sliprings.[1]

The magnitude of the wetting problem can be demonstrated by the following consideration. Poulain[5] gives ϵ_k as $4.0 \times 10^{-9} \Omega\ m^2$ for NaK:Cu, whereas Johnson[4] reports ϵ_k as $0.2 \times 10^{-9}\ \Omega\ m^2$ for NaK:Cu(Au). At 10,000 apsi (or 1.55×10^7 A/m^2) in a typical machine, the contact potential drop ratio per square meter of collector surface would be 20:1 (i.e., 0.062 V: 0.003 V) for poorly-wetted to well-wetted surfaces. For power loss (I^2R), the ratio would be the same, and could amount to 1.2×10^6 watts/m^2 of collector surface for poorly-wetted surfaces. Understanding wetting, its establishment, and its maintenance, therefore, remain essential to efficient machine operation.

The problem of establishing and maintaining good liquid metal-slipring wetting in these advanced design machines is magnified when one realizes that the wetting must be effected at low temperatures (typically less than 100°C), must be repeatable, must be easily re-established in-situ after machine cleanup and reconditioning, and must be accomplished with minimal disruption to presently planned systems.

The problem of liquid metal-solid metal wetting is not new. Kaye[10] reviews the wetting problems of composite structures where tungsten, graphite, or glass fibers must be wetted by a host matrix to insure strengthening. Keeton[11] and Schrock[12] also report the need to wet LMFBR permanent magnet flow meters and electromagnetic pump cells for efficient operation. Walkden[13] reports the need to electroplate Ga-In eutectic to iron sliprings to insure efficient operation of his homopolar generator/motor.

The wetting techniques employed in non-machine applications frequently do not meet the constraints imposed above. A literature review and evaluation were performed to determine which methods of establishing

3

wetting of NaK to copper could be applicable to the new naval propulsion
machines. Methods of measuring and establishing liquid metal wetting, as
well as the theories of wetting, are reviewed. Several new approaches for
establishing and maintaining wetting within the naval machine constraints
were discovered. Two promising techniques recommended for further
development include small lithium additions to NaK and ultrasonic encour-
agement. Small scale cursory tests were positive for both techniques.
A detailed experimental test plan to fully develop and characterize
these and other applicable wetting techniques is presented.

2. <u>CONCLUSIONS</u>

1. The wetting of copper surfaces by eutectic NaK-78 at low temperatures is a complex action, perturbed by many parameters such as surface condition, surface preparation, time, purity control, and fluid actions.

2. Wetting of copper:NaK interfaces can be achieved by certain machine compatible techniques which must be developed and characterized further.

3. Electrical determination of wetting by measuring the specific contact resistance, ε_k, is quantitative and specific to the problem under study and should be preferred over other methods of evaluating wetting.

4. Recently developed techniques of wetting data analysis permit relationships to be developed to predict the onset and degree of wetting as a function of contact time and temperature.

5. Two new wetting techniques, specifically the addition of small amounts of lithium to NaK-78 and ultrasonic encouragement, show positive results in cursory laboratory tests.

3. RECOMMENDATIONS

1. Cursory experimental tests indicate that about 1 wt % lithium addition to eutectic NaK-78 will induce complete wetting of copper in the 80-100°C range. This solution to the problem of minimizing specific contact resistance would not require any changes to presently conceived liquid metal current collection systems. An evaluative program, as described in this report, should be pursued.

2. Cursory experimental tests indicate that ultrasonically induced wetting of copper by NaK-78 is feasible for small solder pot setups. This solution to the problem of minimizing specific contact resistance would only require ultrasonic encouragement for about 60-120 seconds at the initiation of machine operation. Follow-up consultation with experts and additional testing is recommended.

3. Other wetting techniques, such as phosphatizing rinses, electroplating of certain materials, etc., should also be evaluated in a quantitative fashion, since this has not been done historically.

4. The specific contact resistance, ϵ_k, should be employed as a quantitative measure for comparing wetting techniques and their relative performance.

4. METHODS FOR MEASURING WETTING

"A liquid is said to wet a solid surface when the force of adhesion between the molecules or atoms of the liquid and those of the surface layer of the solid is greater than the cohesive force between the molecules of the liquid themselves, consequently, the liquid adheres to the solid surface."[14] Several experimental techniques have been devised to measure liquid metal wetting and include: (1) Sessile Drop; (2) Vertical Plate; (3) Capillary Rise; (4) Visual and Tilting Plate; and (5) Specific Contact Resistance. Each of these techniques has particular advantages and disadvantages, and these are briefly reviewed in the following sections. Since wetting is strongly perturbed by contaminants such as oxygen, adsorbed gases, surface fibers, etc., all of these techniques must be performed under stringent purity (gas) control or vacuum conditions.

4.1 Sessile Drop

The sessile drop test is regarded as the classic liquid metal wetting experiment and is most familiar to the technical field. Small, known aliquots of liquid metal are placed upon a horizontal, flat, solid metal surface. The surface can be heated, can be varied in preparation, and is usually located in a vacuum or controlled atmosphere chamber. The sessile drop is viewed with an optical telescope with a camera attachment. Backlighting is employed to aid in delineating the drop-solid interfacial angle. Good descriptions of sessile drop theory and practice are presented by Maze,[15] Rossington,[16] and Smith.[17] Figure 1 illustrates the geometries and forces involved. The surface tension forces γ_{ij} (where i, j are solid, liquid, vapor) are balanced as

$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} \cos \theta \qquad (1)$$

7

where θ is the wetting angle. The wetting angle θ will be 0° for perfect wetting, $0 < \theta < 90°$ for partial wetting, and $\theta > 90°$ for no wetting. The equilibrium angle θ may be reached rapidly in a good vacuum but slowly in a contaminating atmosphere. Also, θ will vary with time until equilibrium is reached, as well as with temperature, with contamination level, and with liquid metals and different solid metals. Problems also arise if the liquid metal aliquot is too large and major and minor axes change,[15] if back lighting creates a diffraction pattern at the wetting interface, from film shrinkage, chamber vibrations, etc. In short, the sessile drop technique requires careful practice and stringent system control for accurate results. Examples of good experimental practice can be found in Maze,[15] Hodkin, et al.,[18] and Barlow and Planting.[19]

4.2 Vertical Plate

In this method a flat plate is suspended from the arm of a sensitive analytical balance and the plate is partially immersed in the liquid metal under test. At equilibrium, when the plate is partly immersed, the forces acting on the plate can be expressed as:

$$M - F = twx\rho - \frac{2 (t + w)}{g} \gamma \cos \theta \qquad (2)$$

where ρ = liquid density

t, w, x = thickness, width, and depth of immersion

M = mass of the plate

F = weight recorded by the balance

γ = surface tension of liquid

θ = wetting angle

g = gravitation constant

Good presentations of working practice with this technique are presented by Longson and Prescott,[20] Longson and Thorley,[21] and Addison, Iberson, and Pulham.[22] The liquid metal can be heated, circulated through purification traps and filters, and worked to higher temperatures than

in the sessile drop test. However, the liquid metal vapors tend to
condense on the plate suspension cable, and the plate must be immersed
to the same depth for repeat experiments. This technique also requires
pure cover gas, careful temperature control, balance calibration, thermal
corrections, etc.

4.3 Capillary Rise

This method of determining wetting was developed by Achener[23]
and is primarily for high temperature work. A capillary tube of known
radius is dipped into the liquid metal and withdrawn slowly after the
liquid level reaches equilibrium. After cooling, the liquid metal in
the capillary is weighed and the contact angle calculated. Since the
capillary column that is supported is the same as that due to capillary
rise when the tip of the tube just touches the liquid surface, the
weight can be given by

$$\omega = \pi r^2 (h + \frac{r}{3}) \rho \tag{3}$$

where ω = weight of liquid metal

ρ = density of liquid metal

r = internal tube radius

h = capillary rise

The contact angle is found from

$$h = \frac{2 \gamma \cos \theta}{r \rho g} - \frac{r}{3} \tag{4}$$

where γ = surface tension

θ = contact angle

g = gravity constant

Then combining (3) and (4) yields

$$\cos \theta = \frac{\omega g}{2 \pi r \gamma} \tag{5}$$

9

i.e., the contact angle in terms of the weight of liquid metal retained in the capillary. The capillary method can be employed at any temperature, since on cooling the surface tension increases and, therefore, the amount of liquid that can be supported also increases. Problems again occur with atmospheric purity control, maintenance of isothermal capillary surfaces, cleanliness of internal diameters, etc. This technique is intriguing due to its relative simplicity when compared to other techniques.

4.4 Visual and Other

Evaluation of wetting can also be performed qualitatively by visual techniques. Work at Westinghouse has involved placing small drops of NaK on prepared copper surfaces maintained at varying temperatures by a hot plate in a controlled atmosphere glove box. Wetting can be observed by drop spreading, by decrease in drop height, etc. Also, if the surface is tilted, a non-wetted interface permits the droplet to slide off. Wetted interfaces act to retain the droplet. A light brushing with a small soft hair brush sweeps away unwetted combinations, whereas wetted interfaces leave circular wetted zones which cannot be swept away. Another visual technique practiced at Westinghouse employs small copper cylinders which are immersed in glass beakers of NaK heated to varying temperatures. The cylinders are visually examined for wetted surfaces and retention of NaK films.

Other means of evaluating wetting such as the first bubble test[21] (similar to a bubble test for filter pore size calibration) or the tilting plate technique,[24] or the receding contact angle method[21] have not received widespread application or use by researchers in the technical community.

Visual techniques of qualitatively evaluating relative wetting between systems are economic, quick, and remain as good screening methods to employ prior to more costly, quantitative tests.

4.5 Specific Contact Resistance

One method believed to be a good technique of quantitatively measuring wetting is that of specific contact resistance, ε_k. In this technique, a high current density is employed in a copper:NaK:copper couple which simulates the condition of a liquid metal slipring homopolar machine. The better the wetting at the interfaces, the lower the specific contact resistance. Two copper electrodes are separated by a narrow NaK-filled gap (Figure 2). A high density DC current is passed from one electrode to the other through the NaK gap. Leads on the two electrodes are used to measure the potential drop across the couple. The specific contact resistance, ε_k, is found from:

$$\varepsilon_k = \frac{V_{meas} - (V_{SM} + V_{LM})}{J} \quad (\Omega m^2)$$ (5)

where V_{meas} = measured potential across the couple

V_{SM} = calculated potential drop across solid metal part of the couple between instrument leads

V_{LM} = calculated potential drop across NaK filled gap between electrodes

J = current density of electrodes

The ε_k values reported by Johnson, et al.,[4] Poulain,[5] D'Albon and Parteni,[6] Sukhanov,[7] etc., all indicate a quantitative, sensitive, repeatable method of measuring wetting to a high degree. Moreover, the ε_k approach is highly specific to the requirements of this study, that of minimizing NaK:copper resistance. The approach permits the measurement of wetting in flowing systems, between surfaces and fluids that are in contact without the presence of contaminating atmospheres (i.e., are submerged), and in systems which can be easily varied in temperature during testing. The ε_k technique also permits additives to the NaK fluid to be evaluated on the same surface where NaK was evaluated, without system shutdowns, cleanups, or test variations (surface disruption, contamination). The ε_k technique and measurements performed at Westinghouse will be described in more detail in Sections 7.2 and 8.2

11

5. HISTORICAL METHODS OF ESTABLISHING WETTING

Historical practices employed for the establishment and maintenance of wetting have been more qualitative than quantitative. The applications have included soldering and brazing, wetting of liquid metal electromagnetic pumps and flow meters, heat pipe wick wetting, wetting of composite fibers to host matrices, etc. In all of these cases, performance of the product or system was the final evaluation of the wetting levels achieved. Techniques employed to achieve wetting include heating, surface cleaning, protective (wettable) coatings, fluid additives, etc. These techniques and their rationale are reviewed in this section.

5.1 Heating

Mausteller, Tepper, and Rodgers[25] report wetting of sodium-stainless steel electromagnetic pump and flow meter ducts at 315°C. The wetting is observed as a sudden increase in the flow meter millivoltage reading or in the pump performance. Similar results have been experienced at the Westinghouse Research Laboratories Liquid Metal Laboratory[11] and the Westinghouse Advanced Reactors Division.[12] Usually, wetting is induced in these situations by heating the duct wall with a small hand torch or resistance heater rods. Westinghouse has also reported NaK:Cu wetting in the SEGMAG homopolar machine by elevating the machine temperature.[1,4]

In these cases, it is believed that the elevated temperature creates more favorable thermodynamics for the reduction of wetting-inhibiting (protective) surface oxides. Johnson, et al.[4] have reported a critical wetting temperature for the NaK:Cu SEGMAG homopolar current collectors[1] that was repeatable, reproducible, sharp, and associated with machine torque-drag and fluid retention (Figure 3). The critical temperature occurred between 72-76°C for pure copper surfaces and varied with additional surface coatings and geometry treatments. Addison, Iberson, and Pulham[22]

12

also report critical wetting temperatures, as a function of wetting angle, for sodium on cobalt and nickel surfaces (Figure 4). Thermochemical free energy of reaction calculations such as:[26]

$$4 \ Na + O_2 \ = \ 2 \ Na_2 \ O \ ; \ \Delta F_1 \qquad\qquad (6)$$

$$2 \ Me + O_2 \ = \ 2 \ Me \ O \quad ; \ \Delta F_2 \qquad\qquad (7)$$
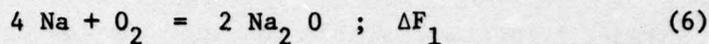
where Me is any metal and ΔF_i is the free energy of reaction,[27] can be combined to show

$$2 \ Na + MeO \ \rightarrow \ Na_2 \ O + Me \ ; \ \Delta F_3 \qquad\qquad (8)$$
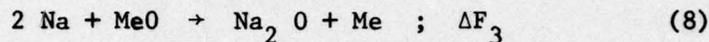
where $\Delta F_3 \ = \ \Delta F_1 - \Delta F_2$ $\qquad\qquad\qquad\qquad\qquad\qquad$ (9)

If ΔF_3 is less than zero, then the reduction of metal oxide MeO by Na is favorable and should occur. The more negative the ΔF_3, the more favorable the reaction. A ΔF_3 greater than zero means the reaction would not occur.

In general, heating should not be regarded as a practical method of establishing wetting in liquid metal slipring machines. If high temperatures are employed, the technique could cause: (1) additional oxides to form on surfaces not covered with a NaK film, (2) thermal degradation of organic insulators and distillation plate-out of organic films (non-wetting), and (3) personnel safety problems.

5.2 Cleaning of Surfaces

It is well recognized that an atomically clean surface is required for intimate and immediate liquid metal-solid metal wetting. The chief problem in achieving wetting is the presence of gaseous and oxide contaminants at the solid-liquid interface. Kaye[10] states that "a single molecular layer of contaminant suffices to change the contact angle". This thought is well supported by Barlow and Planting,[19]

13

Longson and Prescott,[14] Addison, Iberson, and Pulham,[22] and others. Pulham in his work at Westinghouse noted that even under argon at 1 ppm(v) oxygen, freshly abraded copper would not wet with NaK.[28] There was sufficient oxygen at 1 ppm(v) levels for oxygen to oxidize-adsorb on the freshly abraded copper and inhibit wetting. Barlow and Planting[19] report the same situation for copper in a 10^{-5} torr vacuum. Pulham did note that copper abraded beneath the surface of a NaK pool _did_ wet instantly.[28] Thus, surfaces must be absolutely free of oxides, adsorbed gases, etc., for instant and intimate wetting to occur. Obviously, the achieving of these conditions is extremely difficult. The following sections review three methods of cleaning surfaces.

5.2.1 Abrasion

As noted in Pulham's work, abrasion of copper surfaces beneath a NaK pool results in instant wetting.[28] Abrasion in the gaseous atmosphere of an argon glove box with 1 ppm(v) oxygen contamination failed to produce wetting of copper by NaK. Similar results were reported by Klaudy[29] for wetting of steel and molybdenum by mercury. If abrasion were to be employed in a liquid metal slipring machine, it would have to occur beneath the liquid metal at the liquid-solid metal interface. No cover gases or other fluids would be allowed at the abrasion interface. Such a wetting technique could be effected with a retractable abrasion device (drag) in the stator-rotor interface. Shoes, buttons, and liquid metal filled brushes may well be served by this type of device. In fact, the shoe or button surface, which normally rides on a thin fluid film, could be the abrador at machine startup conditions before the fluid film is established. The incorporation of such a device into a machine appears feasible, but would incur problems in rotor wear rates, mechanical movement, disruption to fluid flow patterns, machine penetrations to contaminating atmospheres, abraded materials or filings, etc.

5.2.2 Gaseous Reduction

The Westinghouse homopolar machine was hermetically sealed at all joints, flanges, rotor shaft seals, etc.[1] and could be evacuated

14

to 10^{-3} torr or pressurized. Early program considerations included hydrogen purging and thus oxide reduction of copper collector surfaces prior to machine startup. References 26 and 27 can be used to show that at 100°C (maximum permitted machine temperature due to organic class A or F insulations) the reduction of copper oxides by hydrogen gas is thermodynamically feasible:

$$H_2 + Cu_2O \rightarrow 2\ Cu + H_2O \qquad \Delta F \approx -20,000\ cal.$$
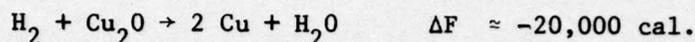
However, the reaction is quite slow, and considerable time would be required for complete reduction of the surface copper oxide. Also, to be successful, the operation would have to proceed without the presence of oxygen, which is highly unlikely for the complex materials combinations and geometries involved. At these low oxygen levels, reoxidation of the copper would occur, in addition to surface contamination caused by the adsorbed gas layers. Barlow and Planting[19] also note that the cleaning of metal surfaces by reduction in hydrogen is insufficient to produce wetting and that temperatures of over 200°C are then required to wet Cu-Na, Ni-Na, Cu-K.

5.2.3 Ion Bombardment

Barlow and Planting[19] performed a series of sessile drop experiments in a 10^{-6} torr vacuum chamber on a hot stage that could be subjected to argon ion-bombardment. The argon ion-bombardment was activated for a few seconds after the sessile drop was placed on the surface to be wetted and caused wetting in every case by driving off adsorbed gases and oxides from the solid surface. The table below presents some of the more pertinent combinations tested under ion-bombardment:

15

Solid Material	Wetted By (at Temperature, °C)
Cu	Na (125°C), K (100°C), Cs (100°C)
Ni	Na (150°C), K (200°C), Cs (at melting)
Ag	Na (150°C)
Pt	Na (at melting)
Zn	Na (at melting)

Hydrogen reduction did not produce wetting of Cu or Ni by Na or K until 200°C was exceeded (without ion-bombardment).

Ion-bombardment will thus cause instant wetting for the Cu:NaK systems under consideration for homopolar machine current collectors. However, incorporating this technique into a machine for in-situ, in-field, shipboard application in a closed machine does not appear feasible. Barlow and Planting[19] do report interesting effects, however, in the lack of low temperature wetting of hydrogen cleaned surfaces. The wetting front without ion bombardment advances slowly with time as surface oxides and adsorbed gases are reacted, while _clean_ surfaces wet instantly.

5.3 Electroplating Surfaces

The electroplating of a dissimilar metal onto a solid surface that is to be wetted by a liquid metal is a common practice. The electroplated material serves several purposes: (1) it protects the substrate material from oxidation or collection of adsorbed gases; (2) the electroplating process usually begins with an off-plate step which strips the substrate surface of oxides, films, etc.; (3) the electroplated material is usually one that is easily wetted by the liquid metal; and (4) the electroplated material is usually quite stable and resists oxidation. Once wetted by a liquid metal, the electroplated material may solutionize and expose a clean, wettable substrate, or it may remain for long periods. Examples of these materials are described in the next section.

Once a plating is employed and wetting is established, the plating material may be entirely removed (dissolved) by the liquid metal. If the substrate material is for any reason re-exposed to inert cover gases

16

(containing even 1 ppm oxygen), machine clean-up cycles, organic insulations outgassing, etc., the electroplating and surface preparation process must be repeated. In-situ bath plating of materials such as Au, Ag, or Ni onto the current collector surfaces of a closed machine is not considered feasible. Brush plating[30] should not be considered since it plates over oxides and thus does not result in good wetting.[31]

5.3.1 Gold, Silver, Platinum, and Others

The noble metals, Au, Ag, and Pt, are easily and readily wet by Na, K, and NaK-78.[1,4,31,32] They resist oxidation at room and low temperatures, are highly soluble in NaK, and dissolve in NaK to expose clean substrate material for continued wetting. Holm[32] reports that a chemisorbed monolayer of oxygen is deposited on gold in air, as on every metal, but does not grow beyond this layer. Such a layer is well penetrable by tunneling electrons and thus is harmless in contacts. Silver oxidizes to Ag_2O at room temperature <u>only</u> in the presence of ozone. Ag_2O is soft, easily removed mechanically, and decomposes at 200°C. Jordon and Lane[33] report instant wetting of Ag-Na, Au-Na, Pt-Na, Ag-K systems. Westinghouse NaK bead tests on copper and on bath plated Ag-Cu and Au-Cu have also shown instant wetting of Au and Ag surfaces at room temperature.[1] Brush plated surfaces also wet instantly, but the plating can be wiped away exposing unwetted Cu surfaces beneath the brush plate.

Although Jordon and Lane report non-wetting of Ni-Na at 250°C, Westinghouse[1] and Johnson, et al.[4] report lower specific contact resistances, ε_k, for Ni-NaK than for Cu-NaK surfaces. Holm[32] resolves this by pointing out that NiO only grows to a few atom layers of thickness in dry atmospheres and is considerably protective. Thus, one can see the ability of electroplated Ni coatings on the copper sliprings of the SEGMAG machine[1,4] to give lower ε_k values than for pure Cu, and the ability of the Ni to remain and give the same ε_k value after machine cleanup and restart processes, since Ni is also quite insoluble in NaK.

17

As can be seen in the work of Johnson, et al.,[4] the ϵ_k values achieved for Ni-NaK are better than for Cu-NaK, but still not as good as could be achieved for Cu (Au)-NaK. Also, Au or Ag plated surfaces dissolve and must be replated for each machine restart following machine cleanup and reconditioning. There is also the danger, for small volume NaK systems, that the Ag or Au could be dissolved in such quantity that the solubility limits would be exceeded[34,35] and the fluidic properties (viscosity, surface tension, etc.) could change substantially. Thus, although electroplated noble metals give instant wetting and low ϵ_k values, they are not long-term solutions to extended wetting maintenance and repeatability problems.

5.3.2 Other Coatings

Other surface coatings exist and, although not widespread or electroplated, are worthy of mention. Westinghouse and others have often considered wetting the copper collector surfaces with a liquid metal that is more stable than NaK. Mercury or Ga-In eutectic have been considered. For instance, the copper surfaces could be electroplated (brush) with Ga-In after the fashion of Walkden,[13] and only a light wipe of the Ga-In with a moist sponge (cloth) would be required to remove contaminants (the copper would not be exposed) before machine assembly, sealing, and startup. This is not an in-situ operation, but the Ga-In may remain in place through several machine operations and permit easy in-situ restart. Hanson[35] reports that Ga forms intermetallic compounds with Na and K, as does Hg. These compounds could form a more viscous solution, and could influence machine operation. The Ga-In eutectic alloy has been reported to be nontoxic[13] and easily handled. This prewetting technique, and protective coating of copper surfaces, may be worth further evaluation. The amount of Ga employed must be small, however, since Hanson[35] reports a high solubility of Cu in Ga which could, in a recirculating system, lead to advanced corrosion processes.

Droste, et al.[37] in a EURATOM patent (Belgium) report the ability to wet stainless steel with sodium after the stainless has been

18

exposed to flowing ammonia (NH_3) gas at 580°C for 2 hours. The wetting is claimed to occur due to nitradation or, through another process, the phosphadation of the stainless surface. Although the temperatures involved by the Droste treatment are too high, Witkowski[38,39] suggests that establishing adsorbed layers of CO gas on a clean copper surface could lead to wetting by NaK.

5.4 Fluid Additives

Fluid additives are used to aid in establishing wetting in liquid metal systems and appear to offer the most promise to resolving the wetting requirements of the NaK:Cu system of interest within the machine constraints imposed. Two major types of additives are employed: (1) getters, and (2) wetters. Getters are defined as those additives which form oxides that are thermodynamically more stable than those of the surface to be wetted. Getters can be soluble (in solution) in the liquid metal, or placed as chips in contact with the liquid metal. The term "getter" is explained by the action of the additive in obtaining or removing (gettering) oxygen from the surface to be wetted by thermodynamic reduction of the surface oxide, and concurrent formation of the more stable getter oxide. Wetters are defined as those additives that form solid solution systems or have high solid solution limits with the materials to be wetted.[35,36] The theory of wetters will be described in greater detail in the next section.

5.4.1 Getters

Deverall[40] has reported adding Mg or Ti chips to a mercury stainless steel heat pipe closed system to encourage wetting. The chips formed highly stable oxides, at the expense of Fe, Cr, and other oxides, and encouraged system wetting. Addition of Zr foils and chips as oxide getters is normal practice in alkali liquid metal loops. High temperature refractory metal alloys of Cb or Ta have getters in their structure, as Cb-1 Zr, Ta-8W-2Hf, etc., to tie up oxygen as getter-oxides and inhibit corrosion. The oxides form by the reduction of the surface oxides of the material to be wetted. Getters have also been

19

added to solders and braze materials to aid in surface wetting.
Kawakatsu, et al.,[41] for instance, report that Li, Na, and P additives
to Sn alloys enhanced wetting of copper by reducing the copper oxide
films. Berghaut and Berben[42] report that the addition of In leads to
wetting of stainless steel by removing the oxide layer. Getters such as
Ba or Ca can be employed in NaK systems to aid in the wetting of copper.
However, cover gas systems would have to be He or A since Ba and Ca are
quite reactive with nitrogen. It is also extremely difficult to obtain
pure Ca or Ba from commercial sources.

One additive that has not received much investigation is lithium.
Li is an alkali metal like Na and K, is readily available, is soluble in
Na to 1-2 weight percent at 100°C,[35,36] and has favorable thermochemical
properties for the reduction of Cu_2O.[26,27] For instance,

$$4Li + O_2 \rightarrow 2Li_2O \qquad\qquad \Delta F = -258 \text{ k cal} \qquad (11)$$

$$2Cu_2O \rightarrow 4Cu + O_2 \qquad\qquad \Delta F = +65 \text{ k cal} \qquad (12)$$

$$4Li + Cu_2O \rightarrow 2Cu + Li_2O \qquad\qquad \Delta F = -193 \text{ k cal} \qquad (13)$$

The reduction capability of Li was dramatically observed recently by the
authors when Li at 200°C was added to a Pyrex breaker contained in an
argon glove box (1 ppm oxygen). The reduction of the SiO_2 was sufficiently
rapid that burning occurred, forming Li_2O and elemental Si.

Tests were made at Westinghouse where 0.5 weight percent Li was
added to eutectic NaK at 50 to 100°C. Oxidized and tarnished copper tubes
and sheet were wetted in the NaK (Li) pool. Wetting occurred within
three minutes in stagnant-to-mildly stirred solutions of NaK with 0.5 wt %
Li, whereas no wetting of copper occurred with NaK and no Li.

The addition of Li in small quantities to the presently conceived
liquid metal loops and support systems of homopolar machines could be
performed with minimal changes to present systems. For these reasons, Li
addition is a prime candidate for solving the wetting problem under the
machine constraints described earlier.

20

5.4.2 Wetters

Wetters are NaK soluble additives which form high solubility
limit systems with the solid surface which is to be wetted. The theory
is that the wetter additive has a lower energy requirement (smaller atomic misfit
or radius ratio) toward the solutionizing of the surface material.[33]
Jordon and Lane[33] show that the system Cu-Li forms solid solutions, and
therefore wets more readily. In fact, the solubility of metals in non-
wetting groups is always lower, much lower, than for those in the wetting
groups. For instance, the solubility of Ni in Na is only 0.004 ppm,
whereas that of Pt and Pd is in the range 1-3 wt %.[33]

Copper forms high solubility systems with Li and is thus easily
wetted by Li. Although a more detailed review of wetters and the radius
misfit ratio will be presented in the next section, the available evidence
for wetters also supports small Li additions to NaK for machine applications.

5.5 Rinses

Certain prerinses have been employed to induce wetting in
sodium/stainless systems. Mausteller, et al.[25] report that prerinses
with Na_3PO_4 (trisodium phosphate) have been found to induce low tempera-
ture wetting successfully. The probable action is the rinse removing
surface oxides and adsorbed gases, leaving a phosphate protective layer.
Wetting then occurs by reactions such as

$$6Na + Zn_3(PO_4)_2 \rightarrow 3Zn + 2Na_3PO_4 \tag{14}$$
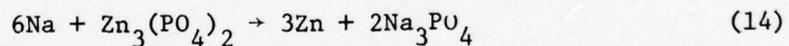
which are exothermic at low temperatures.[43] Whether this reaction would
proceed with Cu is debatable, and may be worthy of evaluation. Mausteller,
et al.[25] still report the necessity of heating to 50°C to cause wetting,
even with the prerinse. This temperature is within the realm of the
stated machine constraints.

21

5.6 Summary of Wetting Requirements

As a review of this section, and the various techniques and mechanisms practiced to induce liquid metal wetting, the following may be considered as requirements for wetting:

1. The solid surface should not have surface films, oxides, etc., which prevent the liquid metal from atomically contacting the solid material.

2. Heating may be used to remove surface oxides through thermochemical reduction.

3. Abrasion may be employed to remove surface oxides if performed beneath the liquid metal surface.

4. Electroplated layers, which resist oxidation, may be employed to protect the substrate from oxidizing.

5. The electroplated layer may be a material which is more easily wetted.

6. Certain pretreatments such as rinses or thermal reactions may aid in wetting.

7. Fluid additives may assist wetting by thermochemically reducing metal surface oxides on the solid, or offering a higher solubility in the liquid for the oxide or solid material.

6. THEORIES OF WETTING

Jordan and Lane[33] have presented a good review of wetting theories, and these views are summarized in this section. The rationale for the practices described in Section 5 becomes clearer when reconsidered in the context of the Jordan and Lane review.

6.1 Oxide Removal

Wetting is instant if the solid is free of protective oxide films. The oxide may be removed by thermochemical reduction, ion bombardment, or abrasion, or it may be prevented from forming with electroplated materials.

6.2 Solubilities

A liquid metal will more easily wet a solid with which it forms a high solubility system than one with which it has very low solubilities.

6.3 Interfacial Tension

Wetting systems may be characterized by an atomic radius ratio term r.* Jordan and Lane[33] report that with liquid sodium the values of r were less than 1.40 for all systems showing wetting and greater than 1.45 for all non-wetting systems. For liquid potassium, wetting occurred at values of r less than 1.56, but not for systems with greater r values. This relationship of wetting to radius ratio is regarded as evidence of the influence of misfit at the solid-liquid interface. The well defined critical values of r obtained for each liquid metal, as the solid metal is changed, are in accordance with the expectation that most of the strain due to misfit occurs in the liquid metal. Also, the critical value of r is higher for K than for Na; K has a lower interatomic binding energy than Na as

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*r is (atomic radius of liquid metal) ÷ (atomic radius of solid metal).

23

shown by lower surface tension and melting point and higher isothermal compressibility. The lower advancing wetting angles for Cu:K also show that the Cu:K interface has a lower energy than the Cu:Na interface. The wetting of Cu by Li is consistent with wetting in terms of interfacial misfit, since r is much lower for the Cu:Li system than for either Cu:K or Cu:Na.

6.4 Intermetallic Compounds

Intermetallic compounds such as Ag-Na, Au-Na, Na-Hg, Zn-K, and Zn-Na show excellent wetting. These intermetallic compound systems have similar radii (i.e., $r \sim 1$) but have large electronegativity differences which can accommodate misfit forces. Also, the intermetallic compound-forming systems have good solubility limits, as seen in Hansen[35] and Elliot.[36]

6.5 Purity of Liquid Metal

Bradhurst and Buchanan[44] have shown that the solution of oxygen in liquid metals lowers the advancing contact angles against solid metal oxides. Copper plates have lower contact angles in K than in Na, and the solubility of oxygen is higher in K than in Na. Pulham[28] also reports that inadvertent oxygen contamination has induced wetting in the NaK:Cu system. This observation is also borne out by the experiences of Hodkin, et al.[18] and Longson and Prescott,[20] wherein a contamination spike of oxygen has induced wetting. The exact mechanism for this effect is still not thoroughly understood.

6.6 Critical Temperature

Johnson, et al.,[4] Addison, Iberson, and Pulham,[22] and others[18] all report a critical temperature indicative of the onset of wetting. Figures 3 and 4 demonstrate this effect. It is thought that this temperature is where the thermochemical reduction of the surface oxides by the liquid metal becomes thermodynamically favorable. It is probable that the

24

critical temperature will vary with fluid additives (i.e., Li to NaK) and/or with fluid turbulence.

6.7 Activation Energy

Various investigators[18] report the wetting angle θ as a function of time t at one temperature T for a liquid metal:solid metal system. Plots of θ vs t are drawn as presented in Figure 5. Thus, wetting occurs slowly, not instantly, and the wetting angle advances at a different rate at each temperature. The rate at which the surface oxides are reduced can be found as $d\theta/dt$, i.e., the slope of the curves of Figure 5. When $\ln (d\theta/dt)$ is plotted against $1/T$, Figure 6, after Hodkin, et al.,[18] the activation energy for the reaction may be found. Since

$$\ln \left(\frac{d\theta}{dt}\right) \, \alpha \, \frac{1}{T} \tag{15}$$

an activation energy Q may be found from the slope of the line in Figure 6, i.e.

$$\frac{d\theta}{dt} = A \, e^{Q/T} \tag{16}$$

The change in the activation energy with fluid additives or turbulence may then be derived. Interestingly, work in the wetting area has not progressed beyond this point. To determine activation energies from plots such as that shown in Figure 6, and to compare the energies found to those required for thermochemical oxide reduction or migration through the oxide (diffusion) of the system components, would seem the next logical step and may be expected in the near future.

7. APPLICATION TO HOMOPOLAR MACHINES

This section reviews the wetting requirements of liquid metal slipring homopolar machines, the historical practice to date (mainly, Westinghouse ARPA work), and then the possible new approaches that may be employed within the constraints imposed. Possible advantages and disadvantages of each of the proposed new wetting techniques are reviewed.

7.1 Wetting Requirements

The major requirements and constraints imposed on the wetting techniques for liquid NaK:Cu slipring surfaces in naval homopolar machines are as follows. The wetting must occur:

1. in-situ
2. aboard a ship
3. with minimal machine disassembly (preferably none)
4. repeatably
5. at low temperatures
6. with minimal disruption to presently planned systems
7. before and after normal machine cleanup and conditioning operations

7.2 Historical Practice

Homopolar machines designed and constructed fifteen to twenty years ago were massive, and no real attempts were made to minimize their size to fit shipboard applications. Treatments to enhance wetting were not attempted. A review of operations at Tullahoma[45] (Arnold Engineering Center) and at NASA Lewis[45] (Cleveland) support these findings. Recent experience with homopolar machines at Garrett[3] and General Electric[2] and Westinghouse[1] has not been extensive, but several attempts to reduce the specific contact resistance ε_k have been reported.

7.2.1 Westinghouse

In the performance of the Advanced Research Projects Agency
(ARPA) SEGMAG contract work,[1] Westinghouse has made several experimental
efforts and evaluations in the area of NaK:Cu wetting. Initial wetting
tests were made by Pulham,[28] wherein wetting between several liquid
metal systems and surface materials was investigated. Pulham's evalua-
tions were mainly qualitative, but they did point out the necessity for
oxide removal, clean surfaces, electroplated assist, etc., as discussed
in earlier sections of this report. Pulham did measure wetting of Hg:
steel and Hg:Cu surfaces by contact resistance in a rotating test rig.
His work supported that of Holm[32] in pointing out the significant
effects of surface oxides on ε_k.

Later, Arcella[46] performed NaK droplet tests on prepared copper
surfaces in an argon glove box. The copper tabs were mounted on a hot
plate and had both bath and brush plated Au and Ag surfaces. The NaK did
not wet as-received or even polished (steel wool) copper at temperatures
to 100°C. The glove box argon was monitored at 1 ppm(v) oxygen as it was
continuously recirculated through the glove box and a purification tower.
Brush plated Au surfaces wetted instantly, whereas brush plated Ag surfaces
wetted more slowly. Wiping the NaK beads away with a soft hair brush re-
vealed that the plating had dissolved (solutionized) in the NaK, and bare
copper was exposed where the NaK had been. The copper beneath the brush
plated Ag surfaces did NOT wet. Apparently, brush plating will not remove
thin oxide films which inhibit wetting. Bath plated Au and Ag surfaces
(0.1 to 0.3 mils thick on copper) wetted well and when brushed away, re-
vealed wetted copper. The off-plating process prior to Au or Ag plating
resulted in oxide stripping. The Au or Ag then acted to protect the copper
from reoxidizing before the NaK could wet the surface. Ni plated surfaces
were also found to wet, but not as quickly.

The first SEGMAG power tests were made with bare copper collector
surfaces. Data analysis indicated that the contact resistance could have
been lower. Concurrent tests by Johnson[4] on a full scale collector

27

simulator (14-inch test stand) indicated by torque measurements that the collectors plated with Au or Ag had lower critical temperatures (Figure 3), filled with NaK more easily, and had better NaK retention (i.e., lack of aerosol and splashing).

The second SEGMAG test series utilized Au bath-plated collector surfaces, and analysis indicated an improved ϵ_k performance. Post-test analysis of surfaces, both in the SEGMAG and in the 14-inch test stand, showed the Au to be entirely dissolved. Rather than replate Au after each machine shutdown, it was decided to Ni plate the collector surfaces. Johnson[4] showed the advantages of Ni surfaces over bare Cu in his current collection program analysis. Post-test analysis of collector surfaces after SEGMAG cleanup operations revealed continuous, protective Ni surfaces, which were restored to operating conditions by a light pass with fine steel wool. The Ni probably wetted because it formed a thinner, more protective oxide than the Cu.[32] The Ni coatings still did not give the same ϵ_k values as Au or Ag, but were factors of 2 to 3 higher.

Concurrent with the SEGMAG tests, a flow cell test program was being conducted.[47] A square, quartz channel with an internal cross-sectional area of 25×10^{-6} m^2 (5 mm x 5 mm) was cavitation bored to admit opposed Cu leads (5 mm x 5 mm) normal to the flow direction of NaK (see Figure 2). The Cu leads were wired to a DC power supply and to a precision millivoltmeter to detect potential drops. Cell test conditions were as follows:

Current (A)	10	20	30	100
Current Density (A/in^2)	256	513	769	2564
Current Density (A/m^2)	4×10^5	8×10^5	1.2×10^6	4.0×10^6
Operating Temp (°C)	30,	60,	90	
NaK Flow Rate (cc/min)	200,	400,	600	
Electrode Separation (mils)	60			

28

The equations employed to resolve ε_k from the cell tests are presented in Figure 2. The <u>best</u> ε_k values for each type of electrode or surface were as follows:

Electrode	Surface	Temp.(°C)	$\varepsilon_k (\Omega\ m^2)$
Cu(OFHC)	-	81	0.3×10^{-9}
Cu(Zr)	-	96	1.14×10^{-9}
Cu(Zr)	Ag	101	0.06×10^{-9}
Cu(OFHC)	Au	101	0.06×10^{-9}
Cu(OFHC)	Ni	80	0.23×10^{-9}

The SEGMAG used Cu(Zr) due to its higher strength and creep resistance. However, as the ε_k values indicate, the small Zr additions may have contributed to the greater ε_k values by forming protective ZrO_2 films. The Au and Ag platings gave the best ε_k values. However, Ni values were also low, and led to the trial of Ni surfaces in the last SEGMAG test.

Johnson, et al.[4] formed the following conclusions from their observations of the flow cell tests:

1. ε_k was found to be time and temperature dependent (much as Hodkin, et al.[19], Longson, et al.[14] Addison, et al.[22] found for wetting angle). Thus it appears that ε_k can be considered as an easily measured electrical value, which indicates the degree of wetting. ε_k vs time and ε_k vs temperature plots both take the form of Figure 5, with ε_k replacing wetting angle.

2. For short time periods, the contact potential is proportional to cell current density for values of NaK flow to 610 cc/min (contact voltage could be approximated as $V \simeq 0.25 \times 10^{-8} J$, where V = volts, $J = A/m^2$).

3. For short time durations, ε_k was noted to be constant for a wide range in J (since ε_k = V/J, and it was noted that V α J, ε_k vs J is expected to be constant).

4. ε_k was shown to be independent of NaK flow rates up to 610 cc/min and current densities to 13.2 $\times 10^5$ A/m^2 (852 apsi) over short time periods.

5. ε_k was shown to be independent of Reynolds number ($\leq$ 4400) over relatively short times.

6. The magnitude and instability of the cell voltage both increased when NaK flow rates > 610 cc/min were used. This may have been caused by:

   a. An impurity of the cell liquid at high flow rate because, when the flow was reduced, a definite time period was required to reach stable, low values again.

   b. Possibly due to secondary fluid flow perturbations at the contact faces, caused by non-streamline flow induced by abrupt electrode projection into the flow channel (Karman Vortex trail). The second cause is not expected for SEGMAG where the flow channel is streamlined with no abrupt obstructions in the flow channel.

7. ε_k values obtained under cell conditions tested were equal to or less than the range of specific contact resistance reported in the literature. The average of all ε_k measured was 2.10 $\times 10^{-9} \Omega$ m^2. The range of ε_k values reported in the literature was 3.2-5.0 $\times$ 10^{-9} Ω m^2 for liquid metal alloy Na(30):K(70) and copper ring material.

From the test data of Johnson, et al.[47] for the ε_k flow cell test, it appears that ε_k measurements are a precise, electrical technique of determining wetting. ε_k values decrease with increasing temperature, as does wetting angle. Finally, ε_k values are directly applicable to

30

homopolar machine slipring related measurements, and for these reasons should be considered a key value for measurement in any machine oriented wetting study.

7.2.2 Others

NaK wetting of Cu is presently under study by other groups,[2,3,48] and the techniques being employed to cause wetting are similar to those described earlier in this text. Also, the importance of understanding and minimizing ϵ_k values has been demonstrated by the same groups, as well as by Westinghouse.[1,4,47]

7.3 New Approaches

Several new approaches to causing intimate NaK:Cu wetting have evolved in the course of preparing this review. These new approaches have not been tried before, or have not been quantitatively evaluated. They will be presented here with minimal analysis, since most considerations and rationale have been presented earlier in this test.

7.3.1 Fluid Additives

The addition of small quantities of Li to NaK should have a very beneficial effect on enhancing the wetting of Cu. Additives of Ba, Mg, or Ca should act in the same fashion. These additives can be made to presently designed systems.

7.3.2 Electroplating

Electroplated surfaces of Ni or Rh on Cu should enhance the wetting of NaK. These electroplated surfaces should not dissolve in the NaK, but should survive repeated cleanup cycles. Electroplated Ga-In eutectic may wet with NaK, yet survive repeated cleanup cycles.

7.3.3 Surface Treatments

Rinsing the cleaned copper surfaces with solutions such as H_3PO_4 (phosphoric acid) or Na_3PO_4 (trisodium phosphate) or purging with CO gas prior to machine startup should setup the Cu collector surfaces for NaK wetting.

31

7.3.4 Ultrasonic Wetting

The Westinghouse Advanced Reactors Division, in evaluating the low temperature wetting of 316 SS by Na for LMFBR pump shaft seals, found that ultrasonic agitation would cause wetting of small 316 SS test pieces at 120°C.[49] A Blackstone ultrasonic soldering pot was used in a dry argon glove box. The principles of ultrasonic soldering are described in References 50 and 51. Basically, an acoustic frequency of around 20 kilocycles is introduced to the liquid metal:solid metal system. The ultrasonic signal causes cavitation to occur in the liquid at the liquid: solid interface. The cavitation breaks up and strips surface oxides from the solid, permitting wetting.

Tests repeated by the authors at the Westinghouse Research Laboratories utilizing a Blackstone ultrasonic soldering pot and NaK:Cu surfaces also resulted in wetting at 80-100°C in 60 to 180 seconds. Consultation with the WRL Ultrasonic Laboratory indicated that an annular, or segmented source could be placed in a SEGMAG-type machine at the copper slipring zones and employed at machine startup to induce wetting. *Employment times would be 60-180 seconds* at startup and perhaps once a week or month thereafter, while the machine is operating. Energy level requirements were not projected. An additional note is worthy of mention. Preliminary evaluation indicates that ultrasonic signals may also be employed to advantage in the in-situ cleanup of liquid metal homopolar machines,[52] perhaps the same ultrasonic system could serve both purposes.

7.4 Advantages-Disadvantages

The new approaches described in Section 7.3 have several advantages to their adaptation. They will operate with minimal disruption to presently conceived systems. They should operate on a repeat basis without machine disassembly. If successful, they will substantially reduce ε_k values and produce more efficient machines, as well as inducing better fluid retention in high speed current collection zones. Almost all of the new approaches will operate with little or no additional machine equipment or processing requirements.

The disadvantage to these new systems is that they are presently untried, hypothetical solutions to a serious ϵ_k problem. Preliminary tests of some of the approaches are quite promising. Quantitative testing and analysis will be required to select the optimum approaches to employ in future machines.

8. EXPERIMENTAL PROGRAM

Previous work by Westinghouse and the Navy has demonstrated that specific surface preparation techniques must be adopted to promote wetting in liquid metal current collectors. However, to date this work has been limited in scope, concerned mainly with attacking the problem on a short term basis, and has resulted only in ad hoc solutions which may be difficult to employ in a practical machine. There is an evident need to focus specifically on the problem of surface wetting in liquid metal current collectors and to investigate plating materials and processes that can promote and maintain wetting at machine operating temperatures.

The authors have investigated and documented a variety of techniques for achieving low temperature wetting in liquid metal current collectors. These techniques are applicable to a wide family of collector geometries and types, and they should yield good electrical contact properties. Several processes for achieving permanent wetting have been identified. The processes include electroplating with various materials, surface preparation techniques, the use of additives in the NaK, and other processes, such as ultrasonic energy.

Experimental work on the next phase of the program will proceed from an initially prepared work plan to a series of carefully performed laboratory tests for screening potential wetting processes. Subsequently, tests will be conducted in small current collector test rigs to demonstrate the best processes in a more realistic machine environment.

The program will be confined to NaK/copper interface studies for the promotion of wetting and, thus, reduced contact resistance. This report has conducted and documented a literature review of historical wetting techniques. These techniques will be conceptually evaluated for

34

machine applicability and incorporated into an experimental program plan. Techniques such as surface preparations (rinses, coatings), surface plating, NaK additives (lithium, barium, calcium), temperature effects (SEGMAG experience, sodium loop experience), and electroplating of the liquid metal onto the collector surface (GaIn experience) will be experimentally evaluated.

The test program will be conducted in three phases: (1) a sessile drop test/screening series wherein only the more successful wetting techniques will be defined and identified for analysis in later phases; (2) a flow cell test wherein the techniques which result in good wetting will be quantitatively evaluated by flowing NaK through an insulated channel between Cu electrodes of different surface preparation and where the specific contact resistance ϵ_k will be measured and employed to delineate the best systems, degree of wetting, etc.; (3) a dynamic rotor system will be employed to simulate a homopolar machine slipring and fluid dynamic pattern, wherein the best wetting systems from Phase 2 will be evaluated.

8.1 Screening Tests

The objective of this task will be to screen quickly all of the recommended new wetting techniques in a qualitative fashion and to select those which look good for further study. The screening tests will consist of placing known aliquot beads of NaK (with and without additives) on copper tabs (of various surface preparation) on a hot plate in an inert gas glove box. Degree of wetting will be qualitatively evaluated by brushing the bead away and examining the interface. Those wetting mechanisms that indicate the best wetting tendencies (subjective evaluation) from the static tests will be carried on to the more quantitative sessile drop test. Table I presents the test matrix for the screening tests.

The sessile drop tests will be performed in the same argon glove box on the same controlled temperature hot plate. High precision sessile drop measurements will not be attempted. Relative qualtitative

35

TABLE I

Screening Tests for Wetting of NaK:Cu

Test Matrix

Test Condition: Argon glove box. Copper tabs on a hot plate.

Test Temperature: Room temperature to 120°C (at least 4 temperatures).

Evaluation: Visual, subjective.

Test Systems: (1) NaK:Cu(OFHC) Control   8 samples

              (2) NaK:Cu(Ni)   Plated   8*
                     :Cu(Rh)   8
                     :Cu(Hg)   8
                     :Cu(GaIn)   8
                     :Cu(In)   8

              (3) Cu:NaK(Li)   Additives   8
                     :NaK(Ba)   8
                     :NaK(Ca)   8

              (4) NaK:Cu(CO adsorbed)   8
                    :Cu(Na_3PO_4 rinse)(H_3PO_4 rinse)   8

              (5) NaK:Cu(ultrasonic)   8
                  Set (2) Ultrasonic   40
                  Set (3) Ultrasonic   24
                  Set (4) Ultrasonic   24
                                                            184
              (6) NSRDC Selection (3 systems)   24

                               TOTAL SAMPLES: 208

*Samples: Two at each temperature, four for each system = 8.

comparisons will be made with an optical cathetometer having a Polaroid attachment. The wetting angle θ will be measured for each system as a function of time and temperature. Plots of θ vs. time (see Figure 5) and θ vs. temperature (see Figure 4) will be derived. From the θ vs. time plots, an attempt will be made to derive a wetting rate:temperature correlation (see Figure 6) to reveal activation energy of wetting. The lower the activation energy, the more readily a system should be wetted.

Table II presents the matrix for the sessile drop test. It is estimated that of the 22 systems screened (Table I), around 8 systems will be satisfactory for sessile drop tests.

8.2 Flow-Cell Evaluation Tests

These parametric tests will be conducted in an insulated cell which will be connected to a high flow rate NaK recirculation system. Multiple Cu electodes will be placed transverse to a flowing NaK stream, as discussed in Figure 2 and presented in Figure 7. The cell will be constructed of heavy wall nylon or polypropylene, and the Cu electrodes will be held in place with Swagelok-to-pipe male adaptors. High density direct current will be passed through the electrodes which will have various surface preparations (or NaK additives, etc.). Possible current flow paths will be A-A', B-B', A-C', C-A', etc. (see Figure 7). Wetting will be quantitatively evaluated by measurement of the contact potential as a function of surface, temperature, current density, NaK flow rate, NaK additive, time, electrode (A-A', A-C', ...) electrode separation distance, conducting areas of each electrode pair, etc. As reported by Johnson,[47] ε_k plots can be made as ε_k vs. time, ε_k vs. temperature, $d\varepsilon_k/dt$ vs. $1/T$, ε_k vs. NaK velocity, $d\varepsilon_k/dt$ vs. NaK velocity, etc. All of these relations wil be searched for trends and reported. A test matrix is presented in Table III. As summarized, four independent variables and two dependent variables can be evaluated in 60 sample runs.

37

TABLE II

Sessile Drop Test for Wetting of NaK:Cu

Test Condition: Argon glove box, copper tabs on hot plate.

Test Temperature: Room temperature to 120°C (At least 4 temperatures).

Evaluation: Optical cathetometer, wetting angle θ, time, temperature.

Test Systems: At least 8 of the 22 systems of Table I.

8 systems x 4 temps x 2 at each = 64 samples

Data Presentation: θ vs time

θ vs temperature (i.e., optimum θ)

$\ln \frac{d\theta}{dt}$ vs $\frac{1}{T}$

TABLE III

Flow Cell Test for the Wetting of NaK:Cu

Test Matrix

Test Conditions: Argon glove box, copper electrodes of various surface treatments in a polypropylene cell through which NaK is flowed.

Test Parameters:
(1) Electrode preparation
(2) NaK preparation
(3) Ultrasonic   (with, without)(2)
(4) Temperature   (3)
(5) NaK flow rate   (4)
(6) Time
(7) DC electrode current (4)
(8) Current density
(9) Electrode separation distance (2)
(10) Repeatability

Test Systems:

Estimated at 5 systems		(I)*
at	3 temperatures each	(I)*
at	4 NaK flow rates each	(D)*
at	4 DC currents each	(D)*
at	2 electrode separations	(I)*
at	2 repeatabilities	(I)*

60 sample runs*

Data Presentation: ε_k vs time (t)

ε_k vs temperature (T)

$d\varepsilon_k/dt$ vs $1/T$

ε_k vs NaK velocity

$d\varepsilon_k/dt$ vs NaK velocity

*I = independent, D = dependent $\therefore$ 5 x 3 x 2 x 2 = 60 tests.

8.3 Rotating Disk Evaluation

The Westinghouse Research Laboratories has several variable speed current collection test devices, operable inside a glove box, to which representative disk and trough geometry machine collectors can be affixed. Presently, 4-1/2 and 7-inch diameter disks, which operate in collectors with batch or recirculating NaK feed, are available. These rotating devices more closely reproduce the fluid dynamic patterns common to typical machines and thus offer the opportunity to explore contact resistance effects (wetting) in a representative, dynamic machine environment.

For the dynamic study, two axially adjacent rotor disks will be machined from one piece of copper. Direct current will be introduced through the stator of one and removed through the stator of the other collector. The net contact resistance of the system will indicate the effectiveness of the wetting promotion technique employed. All of the parameters of the fixed cell parametric tests (previously described) will be evaluated. Table IV presents a test matrix for this test series. As summarized, two independent variables and four dependent variables can be evaluated in 6 sample runs.

8.4 System Interfacing

Throughout the program, questions of interfacing the wetting technique with the total machine systems package will be considered. For instance: for a batch NaK charge operation, will the technique for promoting wetting create amalgams or compounds? For a recirculation NaK system, will the coating become soluable and collect in cold traps or plug filters? Will the wetting technique survive machine cleanup cycles or will reapplication be necessary following machine cleanup? These and other questions will be evaluated with respect to ensuring good machine interfacing.

40

TABLE IV

Rotating Disk Evaluation for the Wetting of NaK:Cu

Test Matrix

Test Conditions: Argon glove box, two copper rotors on a common shaft, various surface treatments of Cu surface or NaK.

Test Parameters: (1) Electrode preparation
    (2) NaK preparation
    (3) Ultrasonic
    (4) Temperature
    (5) RPM (tip speed)
    (6) Time
    (7) DC electrode current
    (8) Current density
    (9) NaK recirculation rate
  (10) Rotor-stator gap
  (11) Repeatability

Test Systems:

Estimated at	3	systems	(I)*
at	3	temperatures each	(D)*
at	4	rpms each	(D)*
at	3	NaK flow rates each	(D)*
at	4	DC currents each	(D)*
at	2	repeatabilities	(I)*
	6	sample runs	

*I = independent, D = dependent ∴ 3 x 2 = 6

41

8.5 Schedule

The schedule for each task is shown in Table V.

8.6 Reporting

The final report will contain the results of all of the experiments and tests. Complete test apparatus descriptions and operating parameters will be described. The optimum means of promoting wetting, compatible with machine requirements, will be recommended. Correlation plots of the specific contact resistance ε_k vs. time, temperature, and ln $d\varepsilon/dt$ vs. $1/T$ will be reported when significant.

TABLE V

Program Schedule
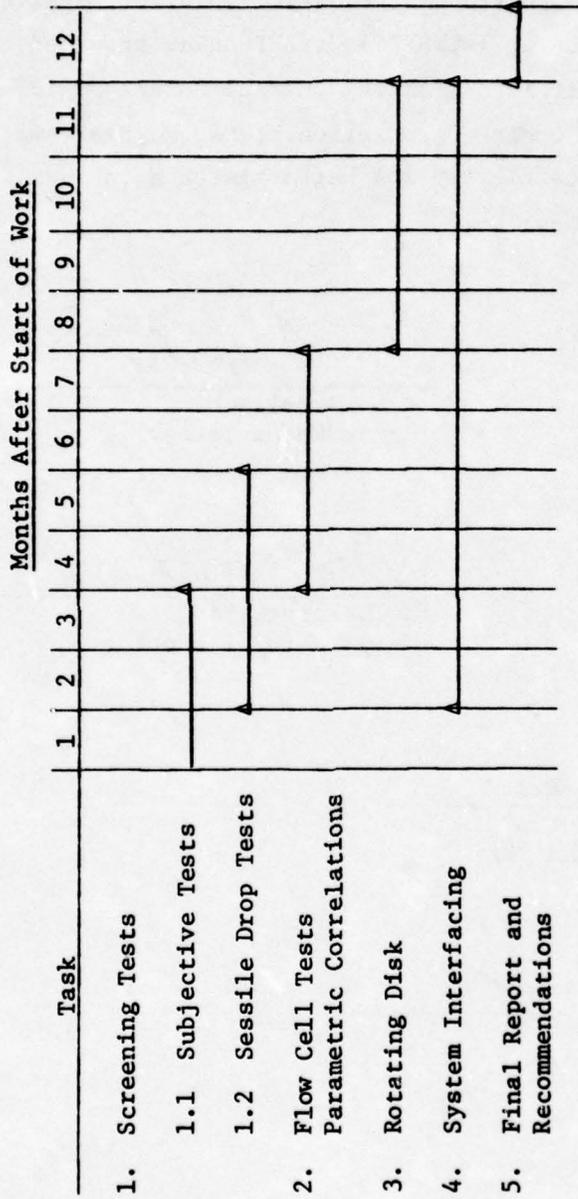
Months After Start of Work

Task	1	2	3	4	5	6	7	8	9	10	11	12
1. Screening Tests												
1.1 Subjective Tests												
1.2 Sessile Drop Tests												
2. Flow Cell Tests Parametric Correlations												
3. Rotating Disk												
4. System Interfacing												
5. Final Report and Recommendations												

43

ACKNOWLEDGMENTS
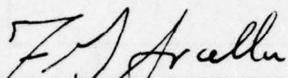
E. G. Arcella
Liquid Metal Technology
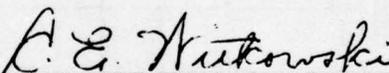
R. E. Witkowski
Liquid Metal Technology

APPROVED: E. Berkey, Manager
Liquid Metal Technology
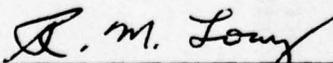
APPROVED: R. M. Lowy, Manager
Materials Chemistry

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    contract for the David Taylor Naval Ship Research and Development
    Center, Annapolis, Maryland.)

Vapor

γ_{LV}

Liquid

γ_{SL}

Θ

γ_{SV}
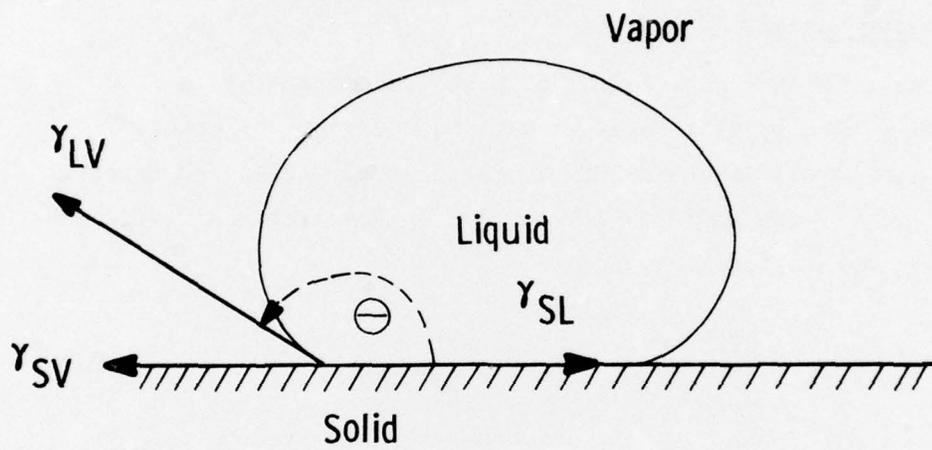
Solid

FIGURE 1. Sessile drop force analysis.

50

NaK Flow

P_1 P_2 I

a

Cu   a   Cu

$|\ell_1|\,\delta\,|\ell_2|$
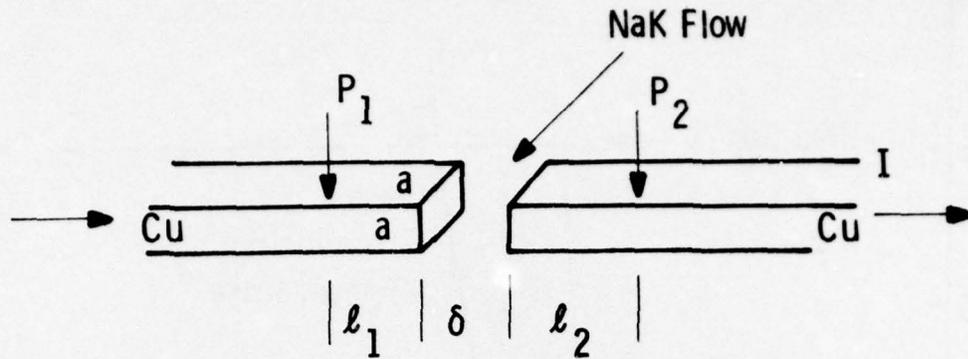
DC Current (Amps)	I
Current Density (I/a^2)	J
NaK Gap Width	δ
Copper Electrode Area	a^2
Couple Potential Drop	$P_1 - P_2$
Specific Contact Potential	ε_k

$$\varepsilon_k = \frac{(P_1 - P_2)_{meas} - (V_{SM} + V_{LM})}{J}$$

where

V_{SM} = Potential Drop in Solid Metal

$$= \frac{I\,(\ell_1 + \ell_2)}{\sigma_{SM}\,a^2}$$

V_{LM} = Potential Drop in Liquid Metal

$$= \frac{I\,\delta}{\sigma_{LM}\,a^2}$$

FIGURE 2. Flow-cell schematic for measurement of specific contact resistance ε_k.

51
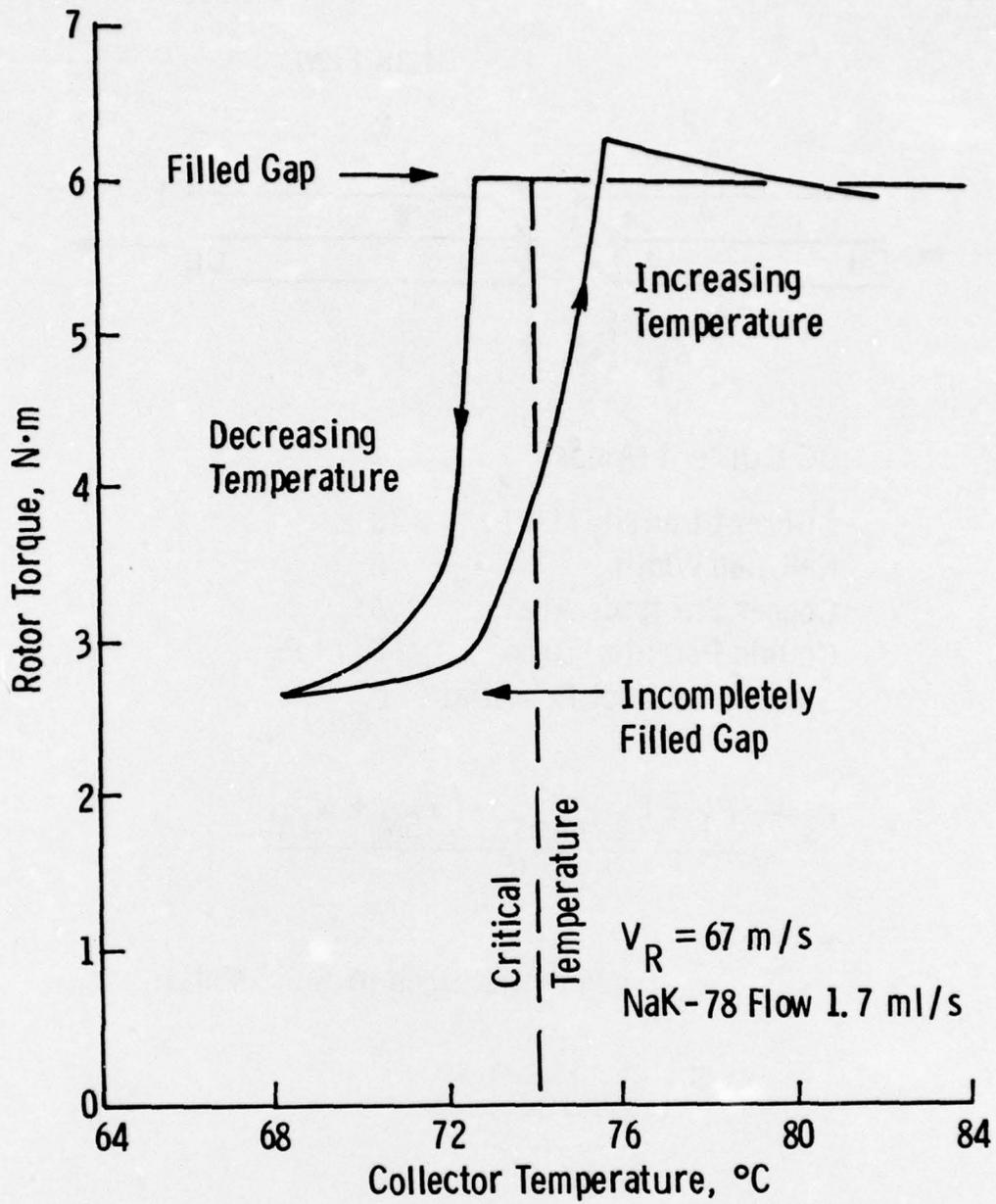
FIGURE 3. Torque-temperature characteristics related to slipring filling
and critical temperature.(4)

52
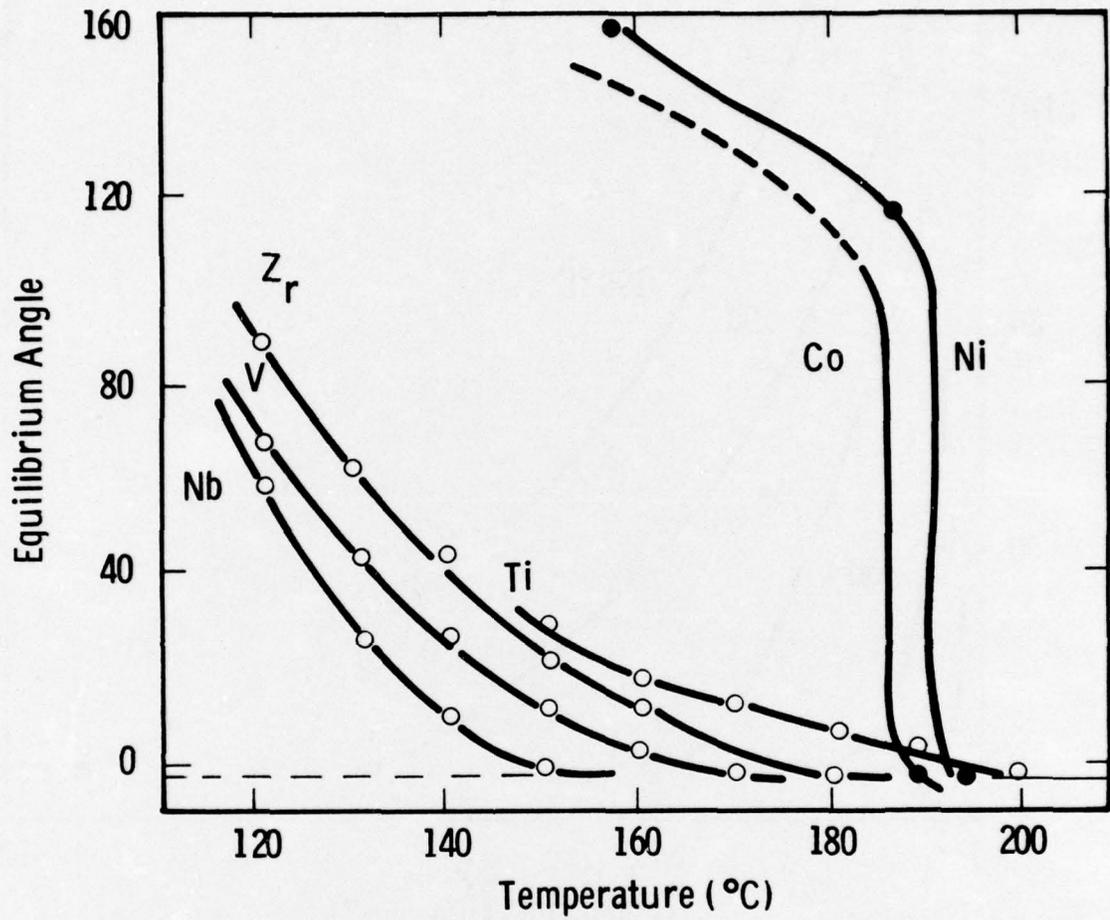
FIGURE 4. Wetting angle and critical wetting temperature for sodium systems.[22]
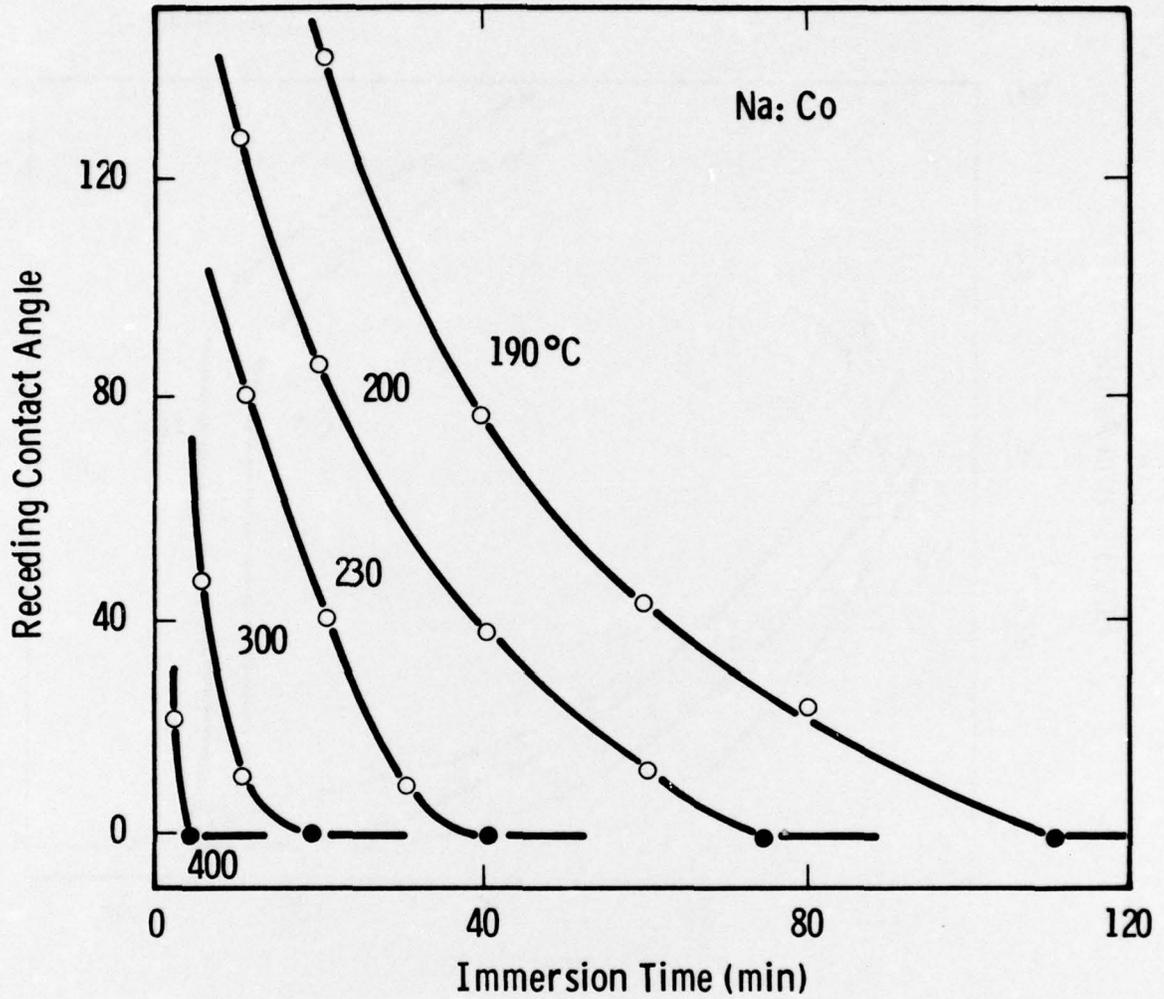
FIGURE 5. Wetting angle decrease with time at a constant temperature.[22]
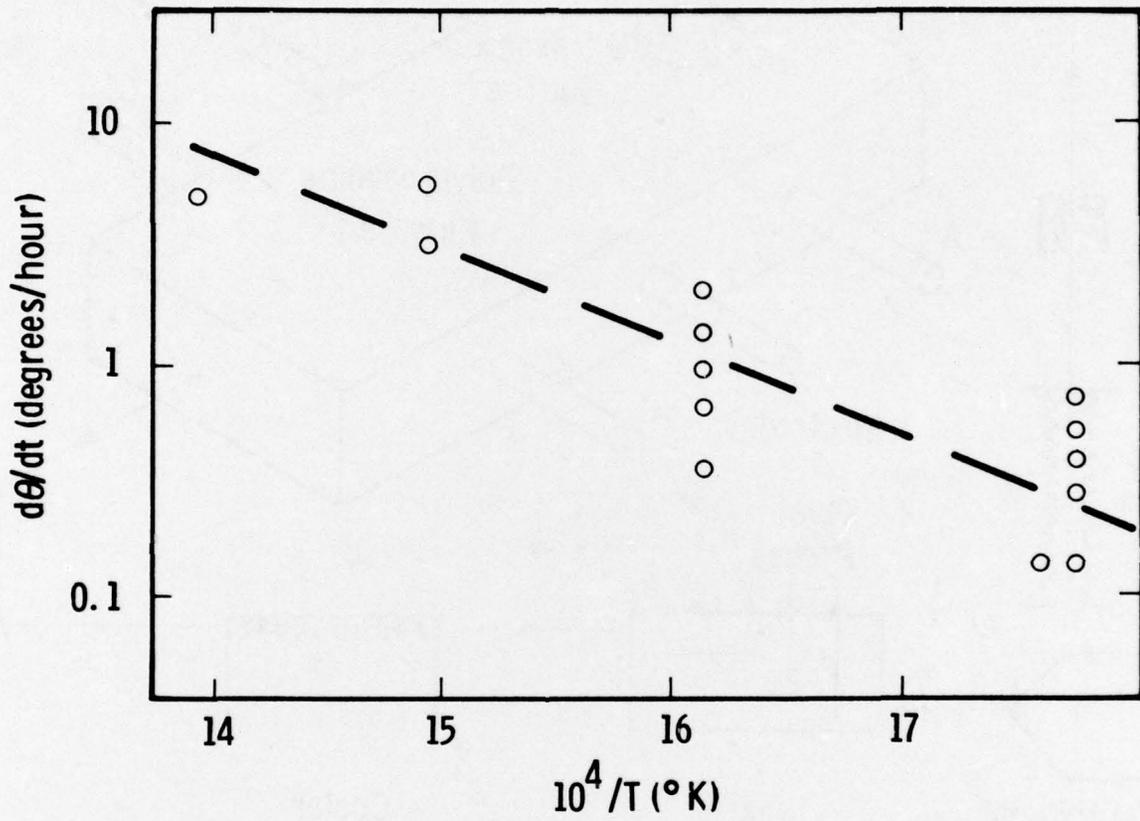
FIGURE 6. Wetting angle decrease rate as a function of temperature for sodium-steel systems.[18]

Dwg. 6376A79
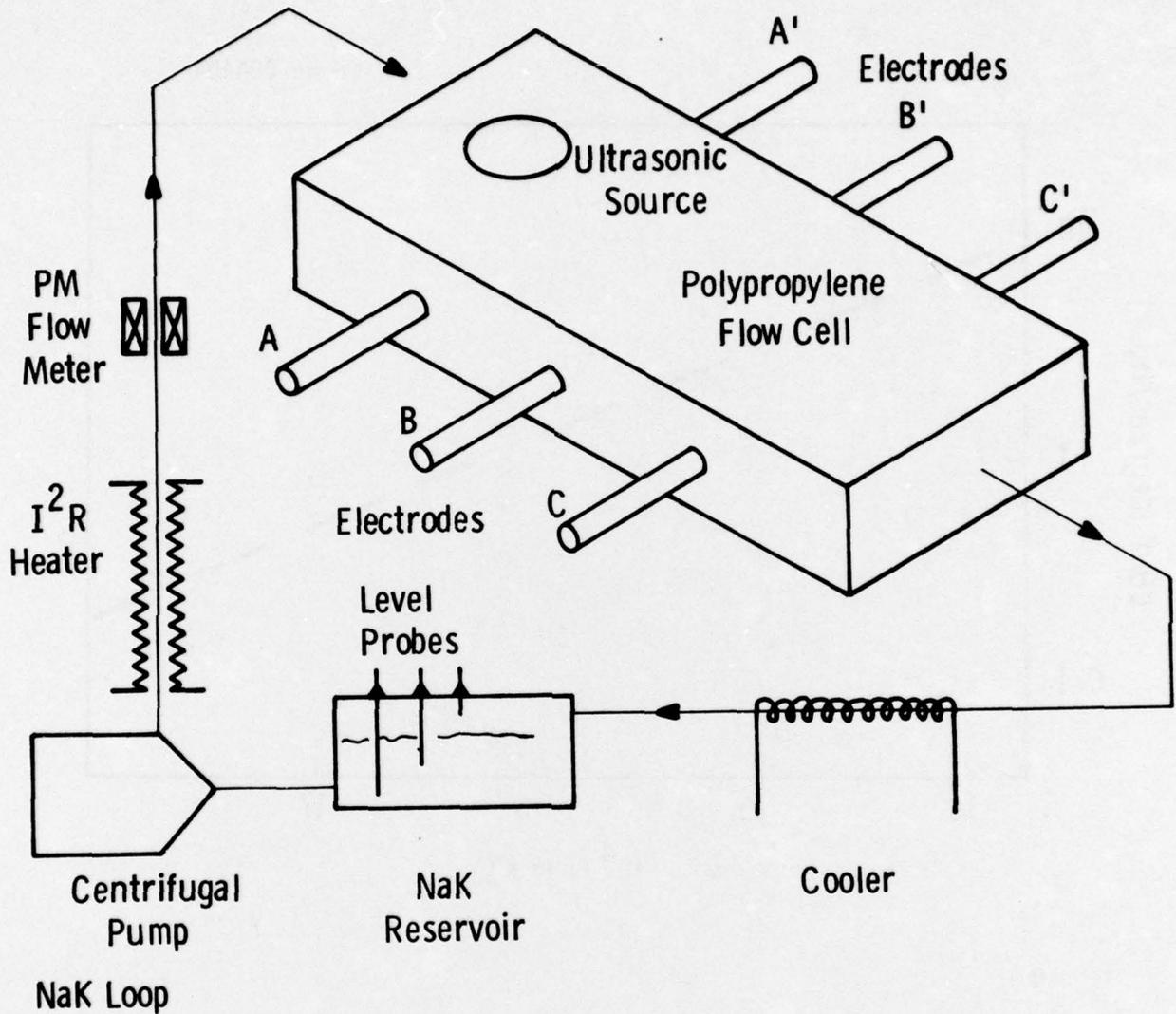
FIGURE 7. Flow-cell test apparatus for the evaluation of specific contact resistance.

56

APPENDIX A

Literature Review

APPENDIX A: Literature Review

The study of techniques for the in-situ wetting of NaK to Cu
was initiated with a literature review. The services of the Westinghouse
Research Laboratories Library staff were employed to conduct and direct
computerized literature searches on keywords in various data banks.

A.1 Data Banks Searched

Table A-1 cites the nine data banks searched, the time period
covered, the citations made from keyword selections, the citations deemed
pertinent after a review of all citations, the percent yield, and the
number of references ordered for detailed review. Of the nearly 200
references cited, almost 20% were deemed pertinent, with the Engineering
Index data bank having the highest yield quotient.

A.2 Keywords/Intersects

Table A-2 presents a typical search sequence of keyword sel-
ections and intersects from one of the data banks searched (Chem. Abstracts).
As seen in Table A-2, "Set" is the sequence step of the search, "Items"
is the number of references available that contain the keywords or
intersect in the "Description". Sets number 1 through 15 search out
keywords such as "NaK", "Na(w)K", "wetting", "wetting(w) angle", etc., where
Items lists the number of references in each data bank that contain or
mention the keyword. The first intersect is Set 16 where "Sodium (2)
Potassium", "NaK", "Na(w)K" are intersected(*) with "Wetting". No items
were cited. Highest yields were for Set 43 which was ordered.

A.2.1 High Yield Words

The computer keyword search routines of citing keywords soon
revealed that tieing a three-part sequence such as (a liquid metal)

TABLE A-1

Literature Review

No.	Source (Data Bank)	Period	Citations	Pertinent	% Yield	Ordered
1	Chem Abstracts	1972-1975	67	14	21%	6
2	Engineering Index	1970-1975	25	8	32%	6
3	Nat'l Tech Inf Serv	1964-1975	19	1	5%	1
4	Nuclear Sci Abstracts	1968-1975	40	11	27%	11
5	Defense Doc Center	1955-1975	10	1	10%	0
6	Aerospace Res Appl Center		36	2	5%	0
	o Sci Tech Aerospace Rept	1962-1975				
	o Internat'l Aerospace	1963-1975				
	o NASA Tech Briefs	1963-1975				
7	Westinghouse Liquid Metal Library		Several	37	On Hand	24
			197	37	18.8%	24

59

User 473   Date: 01/05/76   Time: 11:59:21   File: 3

		Search History			Print Summary		
Set	Items	Description	No.	File	Accn/Set	Fmt	Item-Range
1	27	SODIUM(W)POTASSIUM	1	3	43	2	11-67
2	59	NAK					
3	20	NA(W)K					
4	1339	LIQUID(W)METAL					
5	983	LIQUID(W)METALS					
6	594	ALKALI(W)METAL					
7	478	ALKALI(W)METALS					
8	179	WETTING					
9	0	WETTING(W)ANGLE					
10	0	WETTING					
11	0	WETTING(W)ANGLES					
12	1650	BONDING					
13	2	FLUXING					
14	4636	FLUX?					
15	4066	BOND?					
16	0	(1+2+3)*8					
17	0	SODIUM POTASSIUM					
18	7	(4+5)*8					
19	0	(6+7)*8					
20	12	CONTACT(W)ANGLE					
21	8	CONTACT(W)ANGLES					
22	0	(1+2+3)*(20+21)					
23	55	CONTACT(W)RESISTANCE					
24	0	(1+2+3)*23					
25	0	(4+5+6+7)*23					
26	114	(4+5+6+7)*(14+15)					
27	179	WETTING					
28	0	26*27					
29	29083	MEASUR?					
30	5	29*8					
31	4693	SODIUM(W)POTASSIUM					
32	11	NAK					
33	152	NA(W)K					
34	798	WETTING					
35	4811	(31+32+33)					
36	1	35*34					
37	3906	ALKALI(W)METAL					
38	492	ALKALI(W)METALS					
39	42	COPPER(W)WETTING					
40	21	SODIUM(W)WETTING					
41	8	POTASSIUM(W)WETTING					
42	1	34*(37+38)					
43	67	(39+40+41)					
44	3	COPPER(C)SODIUM(C)WETTING					
45	0	TRISODIUM(W)WETTING(C)SODIUM					
46	0	TRISODIUM(W)PHOSPHATE(C)WETTING					

Srch time   8.86 Print count   57 IF Acc.:   5 Dosc.:
Descs.:   5

(wetting)(a solid metal), for instance NaK:wetting:copper, would not result in a high yield. It became obvious that only a two-word sequence was needed. Sequences such as copper (w) wetting, sodium (w) wetting, potassium (w) wetting, gave the highest yield of citations (items).

A.2.2 Low Yield Words

Low yield words, i.e., zero citations, would result from intersects such as NaK, Na(w)K, etc., intersect contact (w) resistance, or intersect contact (w) angle, or intersect wetting.

A.3 Selected Bibliography

The references cited in this bibliography were considered pertinent to the overall study problem of discovering ways of wetting copper with NaK, but were not cited in the references to the main portion of the paper.

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