General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.

- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.

- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.

- This document is paginated as submitted by the original source.

- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

Produced by the NASA Center for Aerospace Information (CASI)

NASA CONTRACTOR
REPORT

NASA CR-150349

AN INTERIM REPORT ON THE STATUS OF THE ELECTROFORMING SHIELD DESIGN (ESD) PROJECT

By Rondell E. Fletcher
Computer Sciences Corporation
8300 Whitesburg
Huntsville, Alabama 35802

Interim Report

June 1977

Prepared for

NASA - George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama 35812

1. REPORT NO. NASA CR-150349	2. GOVERNMENT ACCESSION NO.	3. RECIPIENT'S CATALOG NO.
4. TITLE AND SUBTITLE An Interim Report on the Status of the Electroforming Shield Design (ESD) Project		5. REPORT DATE June 1977
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Rondell E. Fletcher		8. PERFORMING ORGANIZATION REPORT #
9. PERFORMING ORGANIZATION NAME AND ADDRESS Computer Sciences Corporation 8300 Whitesburg South Huntsville, Alabama 35802		10. WORK UNIT NO.
		11. CONTRACT OR GRANT NO. NAS8-31640
12. SPONSORING AGENCY NAME AND ADDRESS National Aeronautics and Space Administration Washington, D.C. 20546		13. TYPE OF REPORT & PERIOD COVERED Contractor Report
		14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

     This report constitutes a partial completion of an endeavor to research the utilization of a third-generation digital computer to augment electrodeposition/electroforming processes in which nonconducting shielding is employed to effect control of local cathodic current distribution. An exposition of the primary underlying philosophy of the physics of electrodeposition is presented herein. An overview of the technical approach taken to analytically simulate electrolytic tank variables/parameters that are associated with the mechanisms of electrodeposition is also included herein. A Fortran V computer program has been developed and implemented, utilizing the Univac 1108 computer system and the Information International FR 80 graphics display hardware. The Electroforming Shield Design (ESD) program utilized finite-element techniques and electrostatic theory to analytically simulate electropotential fields and ionic transport phenomena associated with specific anode, cathode, electrolytic tank, and nonconducting shield configurations. Graphical depiction of computational output establishes criterion pertinent to size, shape, and location of inert shields to accommodate mechanical specifications for electroforming applications. The initial ESD prototype program is currently being expanded in an attempt to render it amenable to diverse electroforming environments.

17. KEY WORDS Electroforming, Electroplating, Electropotential, Shield Design, Electrostatic, Computerized, and Simulation	18. DISTRIBUTION STATEMENT Unclassified — Unlimited *William H. Fortenberry* William H. Fortenberry, COR

19. SECURITY CLASSIF. (of this report) Unclassified	20. SECURITY CLASSIF. (of this page) Unclassified	21. NO. OF PAGES 26	22. PRICE NTIS

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

AN INTERIM REPORT ON THE STATUS OF THE
ELECTROFORMING SHIELD DESIGN (ESD) PROJECT

INTRODUCTION

This is an interim report related to the current status of an effort to
utilize a digital computer and analytical procedures to provide criterion for
development of a nonconducting shield configuration and its respective place-
ment to augment electroforming activities in terms of local cathodic current
density control. More specifically, the initial phase of the endeavor has been
primarily directed towards an application of theory in an attempt to further the
development of shielding for a Space Shuttle Main Engine (SSME) electroforming
application. At the present time, activities have been associated with a techni-
cal overview of the electroplating technology and its related publications to
ascertain if a similar endeavor has been attempted previously and with the
development of analytical techniques and a Fortran computer program to simu-
late electrodeposition processes involved in electroforming applications.

TECHNICAL REVIEW

The mechanism of electrodeposition is a highly complex physical entity
in terms of the number of variables that are present and the results obtained
when all combinations of variables interact, especially when considered from
an analytical viewpoint. The policy of controlling electrodeposition to facilitate
electroforming is even more complex because of the efforts expended to mani-
pulate variables to accommodate exacting engineering tolerances/mechanical
specifications. One of the primary tasks inherent to the electroforming shield
design (ESD) endeavor is the implicit definition of as many physical phenomena
that contribute to electroforming technology as possible. This is paramount
to the ensuing problem of developing analytical/programming techniques that
are amenable to simulation of electroforming/electrodeposition processes.
Closely associated with this task is the delineation of those electrolytic tank,
anode, and cathode variables whose effects can be controlled in practical
electroforming environments.

When a metal is immersed in an electrolyte, a potential difference develops at the metal-electrolyte interface and is typically referred to as electrode potential, the potentials at anode and cathode, respectively, being denoted as anode/cathode potentials. Through reactions occurring at the anode electrons are liberated and anodic metallic atoms, having lost electrons, are discharged into the electrolyte to constitute positively-charged ionic complexes called cations. Negatively-charged ionic complexes are termed anions. Electrolytes are therefore conductors of the second kind: the constituents thereof are equal quantities of cations and anions. Metallic conductors become conductors of the first kind. Electrons that are liberated at the anode, via oxidation processes, flow through the external circuit of an anode, cathode, electrolytic tank environment and are subsequently consumed at the cathode during the reduction-recombination process. The potential-determining charge carriers in the electrolyte are then the ionic complexes (cations and anions) and possess a dual nature; they are simultaneously chemical individuals and transporters of electrical charge in units of coulombs. Metals are also composed of ions, not neutral atoms, because the free electrons which give rise to metallic conduction do not belong to individual atoms; however, because of their mobility, they belong to all atoms in the solid metal collectively. Metals possess a crystalline structure consisting of ionic lattices, which to a certain extent, are bound by electrostatic forces.

As cationic species are liberated at the anode, they are almost universally encompassed by a hydrated envelope. Application of a specific minimum dc voltage results in the migration/transport of hydrated cation/anion complexes simultaneously towards the anode and cathode. Cations migrate under the influence of the externally supplied field towards the anode. The migration rates of the cation/anion complexes are of the same order of magnitude; only those of hydrogen and hydroxyl ions are significantly greater than those of other ionic complexes. Because of the friction with ambient molecules, mutual ionic attraction, and drag exerted by a hydrated envelope around the specific ionic species, the field-accelerated motion is transformed after a brief acceleration into a finite ionic migration rate defined as the constant ionic drift velocity in cm/sec at a field intensity of 1 V/cm. The drift velocity magnitude is also contingent upon specific external conditions such as pressure, temperature, nature of the solvent/solution, and concentration of ionized complexes, both positive and negative. Since ionic complexes are charge carriers, their migration to anode/cathode creates an electrical double-layer at each respective metal-electrolyte interface. This potential is the result of the equilibrium of chemical and electrical forces. The potential difference existing between the metal and electrolyte becomes the Galvani potential and is dynamic to the extent that in the equilibrium state, the mutual metal-electrolyte interaction does not cease. Although, in a specific time interval, the number of ions deposited on the metal from the electrolyte is equivalent to the number of ions entering the solution from the anode.

2

The electrical double-layer was first postulated by H. Von Helmholtz and is consequently termed the Helmholtz double-layer. When cations are transferred from an electrolyte into the cathodic metal lattice, the Helmholtz inner layer of charge is everywhere contiguous to the cathode surface, opposed to which is a negatively-charged Helmholtz outer layer called the Gouy-Chapman layer. Beyond the Gouy-Chapman layer is the bulk of the electrolyte. A similar situation exists at the electrolyte-anode interface with the Helmholtz inner layer consisting of negatively-charged anions and the Helmholtz outer layer composed of positively-charged cations.

Since the potential-determining ionic complexes resident in an electrolyte move in opposite directions under the influence of an externally supplied electric field, the resulting transport of charge is termed exchange current. However, kinetic inhibition of various types eventually evolves and can result in a variation of the cathode/anode potential. These variations from purely thermodynamic values are typically referred to as overvoltage and are normally independent of the exchange current. If the cathode/anode is indicated, the overvoltage is called polarization. Polarization is produced by potential-inhibiting factors of diverse nature and directly affects cathode/anode reaction processes. Various types of polarization are denoted, depending upon the location of the inhibiting phenomena. The division of total polarization at an electrode into partial polarizations is to a certain extent a matter of definition. Although different reactions at an electrode (cathode/anode) may be quite complex, all systems are related in that the reacting entities must be transferred through the metallic-electrolyte interface (penetration reaction) and must also be transported to or from an electrode (transport processes). The location of the inhibition is usually at the phase boundary itself or is directly associated with transport procedures and can occur simultaneously. Activation polarization is generally caused by inhibition of the transport of potential-determining ionic species through the phase boundary, i.e., the Helmholtz double-layer.

Concentration polarization is due primarily to ionic concentration differences that develop in regions near cathode/anode. This polarization, which is the result of transport inhibition, may be separated into: reaction polarization and diffusion polarization.

Reaction polarization develops when the rate of charged complex generation is hampered.

Diffusion polarization is caused by inhibition of migration of ionic complexes towards phase boundaries. Metal ions are produced at the anode and consumed/discharged at the cathode; therefore, a diffusion (Gouy-Chapman)

layer is formed in regions near anode/cathode. In this layer, ionic concentration is somewhat diverse from the bulk of the electrolyte. In general, at the anode the electrode potential is predominantly positive and at the cathode it is the converse. The transport of ionic complexes to the cathode for subsequent discharge/recombination is influenced by the diffusion layer thickness and the relative concentration with respect to the bulk of the electrolyte itself.

The inhibition of ionic transport through an electrolytic layer which is contiguous to the surface of an electrode is nominally referred to as resistance polarization. It is purely ohmic in nature and may be indicative of a poorly conducting metallic oxide or liquid layer on the metal. It is usually associated with activation polarization.

Determination and categorization of specific types of polarization/ overvoltage are necessary for theoretical interpretation of electrode processes. However, the total overvoltage is of prime consideration in electrolysis voltage which in turn determines electrolytic current and electrode current density. The polarization during electrodeposition is contingent upon the type of metal, type of electrolyte, special additives (buffers, levelers, etc.), and cathodic current density. Polarization generally increases with additional current density and decreases with increasing electrolytic temperature and adequate agitation of the electrolyte.

Reaction mechanisms associated with cathode processes during electrodeposition of metals/hydrogen are then determined by type and properties of electrolyte layers in the vicinity of the cathode through which cations must be transported prior to subsequent discharge/neutralization on the cathode surface.

It is evident that ionic concentration is subject to variation during electroforming activities, especially near electrodes. Ionic complexes that are candidates for electrodeposition evidently are transferred to the cathode by three primary avenues: (1) through transport due to the influence of the imposed electric field, (2) by diffusion processes, and (3) by convection. Two types of convection are inferred: natural and forced convection.

Forced convection is accomplished by an increase in thermal activity and by mechanical agitation. Normal electrolytic convection does not occur in the cathodic diffusion layer although flow is possible within it. The thickness of the diffusion layer is determined by the concentration gradient of the ionic complexes and usually does not form a distinct boundary with the bulk of the electrolyte. It varies somewhat under diverse conditions, i.e., cathode configuration, temperature, quantity of agitation, local cathodic current density, and electrolyte compositions. For example, the diffusion layer during agitation may be of the order of 10μ and may be as much as 500μ in a quiescent state.

4

As previously mentioned, hydrated cationic complexes are transferred to the cathode via the influence of an electric field, diffusion, and convection. Near the cathode, it enters the diffusion layer where its migration velocity is ascertained by the concentration gradient. Cations at this point continue to be bound by their hydrated envelope because the magnitude of the electric field is not large enough to liberate them. However, field alignment of the hydrate dipoles is accomplished in the diffusion layer. Upon entering the Helmholtz double layer, the cations are deprived of their envelope; therefore, the hydrate dipoles become an integral entity of the Helmholtz outer layer. Inside the Helmholtz double layer, the electric field strength approaches 10^7 V/cm. Contemporary cationic neutralization theory states that the cation passes through the double layer normal to the cathode surface and is subsequently discharged on the cathode surface where it is no longer affected by the electric field. Cations which have been neutralized diffuse along the cathode surface to the first crystalline "growth point" available and are incorporated into the metallic lattice.

The distribution of electrodeposit over the surface of a cathode in electroforming operations is determined primarily by the local cathodic current distribution and by the electrolytic bath efficiency in regions contiguous to the effective cathode surface. The local cathodic current density is a function of the primary current distribution and local polarization phenomena. Primary current distribution is typically defined as the distribution over an electrode (cathode/anode) in the absence of disturbing factors (diffusion polarization, convection inhibition, passivation, hydrogen overvoltage/polarization, etc.). Polarization/overvoltage, as denoted earlier, encompasses all phenomena, physical and chemical, which nominally affect properties of the electrolyte near electrode regions and ultimately result in a secondary current distribution diverse from the primary distribution. The secondary current distribution may augment quality/quantity of electrodeposit or may be conversely detrimental. For example, the codeposition of hydrogen is responsible for the formation of pores in electrodeposits. Hydrogen bubbles that are a by-product of electrolysis can adhere to the surface of a cathode, particularly in sulphamate solutions that are amenable to high current densities. The bubbles increase with increasing current density to such an extent that the underlying metallic surface is screened from the current as the electric field is perturbed. As deposition continues, the growth of deposition beneath the bubble is slow or may not exist at all, while adjacent cathode areas receive contrasting electrodeposition. Also, hydrogen protons may be codeposited with certain metallic ions to create hydrogen embrittlement. Electric fields have the unique capability of converging upon corners, sharp points, etc. Indeed, the magnitude of the electric field is approximately inversely proportional to the radius of a point or an entity possessing convex curvature. In the case of a spire/point, the radius can be considered infinitesimally small; therefore, the field magnitude approaches infinity, theoretically. Since the craters, pits, and pores, that occur, due to hydrogen bubble-cathode impingement, possess sharp "lips," the electric field converges upon them and gives impetus to rapid stellite growth. Cathode

5

profiles that exhibit convex curvatures which are closer to an anode than other areas also exhibit higher current densities on the convex curvatures and areas closest to the anode.

The evolution of copious quantities of hydrogen near these convex profiles can interact with the ionic discharge mechanism in such a way as to allow more even cathodic current distribution and electrodepositions on the convex surface. The prediction of this ideal phenomenon would be difficult indeed.

If the temperature of a conductor of the first kind is increased, the free electron mobility is impeded, thereby exhibiting the effects of ohmic resistance. An increase in the temperature of an electrolyte has a converse effect. The mobility of the charge carriers (ions) is increased, and the quantity of charge transported per unit time (current) is increased also. Hence, stratification of electrolytic temperature generates an unpredictable/unstable situation as does stratification of ionic concentration gradients.

The presence of foreign substances that are not a natural by-product of electrolysis (i.e., dust, rust, etc.) frequently adhere to cathode surfaces and are preferentially incorporated into the metallic crystalline structure at normal lattice growth points or at pseudo growth points such as pits/pores which have been caused by hydrogen bubbles. Because of high electric field concentration at these pseudo growth areas, unretarded deposition occasionally occurs. All of the factors that are a consequence of electrolysis/electrodeposition (polarizations, diffusion, convection, stratified thermal/concentration gradients, etc.) are participants of current efficiency. The mutual interactions of these entities precipitate the generation of electrolytic ohmic resistance which usually decreases the quality/quantity of electrodeposit per unit time. In many situations, polarization increases with overall current density and this, in turn, may substantially improve the current efficiency by increasing the particular electrode reaction or product desired. Conversely, polarization also generally causes an ohmic resistance and thereby decreases its energy efficiency. It is of paramount importance that a proper balance between electrode current efficiency, polarization, etc., be considered in electroforming endeavors. Total current efficiency is therefore a function of local and average current densities, electrolyte concentration, polarizations of various types, thermal gradients, electrode composition, additions of external agents and impurities, and the geometry of the electrolytic anode, cathode, and tank configuration. A change in temperature affects the resistivity and viscosity of the cathodic film, ionization rate of complex compounds, ionic hydration and mobility, and general cathode efficiency. Total current efficiency typically denotes the difference between primary and secondary current densities.

6

As previously delineated, the factors that modify primary current density, which are almost entirely a function of anode, cathode, and electroforming tank relative geometry, are many. However, their combined effect, in general, will not dominate the primary current distribution. Furthermore, all of the mutual interactions that can potentially exist are not distinct and not necessarily linear in nature. Consequently, the prediction of the product of their interactions by analytical means is somewhat dubious for a wide spectrum of electroforming activities. Some analytical concepts are primarily based upon empirical results obtained from specific observations and are not necessarily valid for general utilization.

Fortunately, the control of electroforming environments can be accomplished by modern electrodeposition technology.

A quasi-steady-state condition (uniform polarization, temperature, ionic concentration, diffusion layer thickness, etc.) must be attained prior to the introduction of inert shield configurations because if the electric current is unpredictable/unstable, effective shield development to compensate for its anomalies is also unpredictable.

CONCLUSIONS/DECISIONS ASSOCIATED
WITH TECHNICAL APPROACH

Almost all of the known variables that influence current density and related electrodeposit characteristics may be categorized into four distinct classes: (1) those variables governing primary current distribution, (2) those related to the electroforming bath and operating conditions that function to alter primary current distribution, (3) geometrical aspects of the electrolytic bath environment that alter primary current distribution, and (4) the relationship that exists between electrolytic bath efficiency and current density.

In view of Section 2, what quantities, variables, processes, etc., are most likely candidates to be amenable to analytical prediction, depiction, and simulation via utilization of a digital computer? Since the primary current distribution is the dominant influence affecting electrodeposition, and the factors that contribute to secondary current distribution may constitute a quasi-steady-state situation, the electric field configuration, which to a large extent is dictated by relative anode, cathode, and tank geometry, is the entity/mechanism to which attention may be directed. Also, many of the charge transport phenomena

in the secondary current distribution are influenced by the electric field; hence, the electric field is the "common denominator" of the primary and secondary current distributions.

Although the analytical simulation of some electrodeposition processes associated with secondary current distribution might be possible, the measurement of quantities (cationic transport rates, temperature gradients, hydrogen evolution, etc.) for input to a Fortran computer program might prove to be untenable. Analytical procedures have been applied to electropotential problems where geometries were simple to simulate two-dimensional entities by using Conformal Mapping, Fourier Analysis, and the two-dimensional form of Laplace's equation. At the onset of the ESD endeavor, a tacit approach to evaluate/simulate electric field phenomena in two-dimensional vertical/horizontal planes and then superimpose one on the other was attempted. This approach was aborted in favor of three-dimensional analysis through development of another technique.

COMPREHENSIVE OVERVIEW OF CURRENT
ESD PHILOSOPHY/DEVELOPMENT

In an electroforming environment, anions/cations move under the influence of an externally supplied electric potential. Electrons that are liberated from the anode and are transmitted to the cathode via an external circuit also participate in the cationic discharge mechanism. Motion of electrons in most metallic conductors is usually random in nature in the absence of or minimization of internal fields within the metallic structure. When a potential is applied to a cathode, internal fields are established within the conducting metal, causing the free electrons that belong to every metallic atom to move accordingly until the presence of internal fields is minimized or becomes nonexistent. In this steady-state situation, the surface of the cathode constitutes an equipotential surface with the charge carriers (electrons) near the surface to accommodate cationic neutralization and adsorption.

When such a steady-state is achieved, the basic laws of electrostatics, with some qualifying assumptions, are amenable to application to the total anode, cathode, electroforming geometrical arrangement. The transmission of electrical charge, whether in a conductor of the first or second kind, in terms of coulombs per second constitutes current. If a metallic surface is an equipotential, the gradient of the potential is everywhere normal to the surface. Consequently, the

8

gradient of the potential is the analytical analogy to the cathode surface and all subsequent current/charge distributions associated with the electric field enters/leaves equipotential surfaces orthogonally. The basic underlying philosophy of the contemporary ESD Fortran computer program is that of superposition of charge/field associated with classical electrostatic theory. Under quasi-steady-state conditions, the utilization of electrostatic principles yields an approximation to the anode-cathode electropotential situation.

The ESD program employs a technique which is quite similar to finite-element, finite-difference numerical analysis techniques that have applications in modeling fluid flow dynamics, heat transfer, and other physical phenomena. In a similar fashion, anode and cathode surfaces are divided into discrete surface charge elements with each element containing an orthogonal Cartesian coordinate system and unit normal vector at its origin. Each element, if considered to be infinitesimal, functions as a "point charge" distribution whose generated field is analogous to an electrostatic field with its maximum being directed along the element unit vector normal. The total simulated field consists of the vector sum of the positive anode surface charge element and negative cathode surface charge element field contributions, respectively.

In the ESD computer program the simulated analogy of an electric field effect is accomplished by : (1) assuming a representative charged particle/cation contiguous to an anode at the locus of the first anodic surface charge element, and (2) the particle/cation is repeatedly subjected to the composite field that is generated by all anodic and cathodic surface charge elements as it is moved at vector increments, assumed minute enough to constitute mathematical differentials, in the direction of the field gradient. The procedure is continued until mutual orthogonal cation-cathode contact occurs. The location of the cation-cathode contact is computed in a master inertial reference system and also in a cathode-centered reference coordinate system. The cation-cathode contacts are stored in computer memory for subsequent graphical depiction. The representative cation is again repositioned at the locus of the next successive anodic surface charge element, and the previously defined procedure is repeated until the ertire simulated electrolytic tank volume between anode and cathode is effectively "mapped." The recorded positions/motion of the representative cation is in essence a simulation of the influence of an imposed electric field, its flux, and streamline conformation, respectively. The array of stored mutual cation-cathode contact position constitutes the analogy of cathodic primary current density. Theoretically, if the quantity of charge flowing through the external circuit of an electrolytic tank arrangement is known, the number of cation-cathode contacts per unit area, in the sim lation, should be proportional to the local cathodic current density. Since current may flow from all areas normal to an anodic

surface, the flow along tank extremities is necessary to adequately evaluate electrodeposition parameters associated with a specific field conformation. The ESD program contains logic to accommodate the simulation of this physical process. Reflection of current from an electrolyte-atmosphere interface is considered because the permittivity of the atmosphere is less than the permittivity of an electrolytic solution. A similar situation is evident at an electrolyte-tank wall interface. As previously mentioned, during the process of electroforming, projecting areas of a cathode that are closest to an anode and projecting surfaces that exhibit sharp convex curvature are subject to higher local current densities due to convergence of an electric field upon them, in general. The use of nonconducting media to protect these areas from high current density effects is contingent upon dielectric theory.

One of the properties of a dielectric is described as follows. If a dielectric is immersed in an electolyte and subjected to an electric field, the field will be perturbed/reoriented if permittivity of the dielectric is less than the permittivity of the electrolyte. Thus, if a dielectric is placed between an anode and cathodic area that exhibits exorbitant current density, the area under consideration will be "shielded." The electric field/electropotential is decreased near shielded cathode areas; therefore, cathode-contained electrons migrate to areas of higher potential (nonshielded areas) to facilitate electrodeposition. A recorded history of a reconfigured electropotential/electric field is necessary to provide criterion for the evaluation of local cathodic current distribution. The evaluation of electric field flux over a cathode surface is an indication of the probable current distribution and electrodeposit in quasi-steady-state conditions at high current efficiency.

The ESD program contains programmed logic commensurate with analytical techniques to allow the geometric description of anode, cathode, electrolytic tank, and proposed shield configurations in Cartesian, cylindrical, spherical, and polar reference systems. After anode and cathode geometries are described to the program, their respective surfaces are automatically subdivided into surface charge elements. The total bath current is allocated to each element in terms of its relative size and location. The entire geometric arrangement is graphically depicted in three-dimension utilizing the MSFC Univac 1108 computer, FR 80 plotter, and their associated hardware/software facilities. Computed electric field streamlines, emanating normal to anodic surfaces, are depicted in three-dimension also. Their termination on a cathode surface yields the cumulative effect of the cathodic current density. Areas of higher current density can be readily discerned by the depiction of converging streamlines and the frequency of contact per unit area on a cathode. A general survey of mutual cation contact activity subsequently reveals areas that are susceptible to shielding and provides initial criterion as to the size/shape of the same. Upon the introduction of a

10

shielding configuration, via its geometric description in one of the reference systems previously mentioned, perturbed field streamlines are graphically depicted which simulate the effect that shielding has upon cation-cathode positions, i.e , the redistribution of cathodic local current density. The ESD program contains logic to allow an entire environment (anode, cathode, shields, tank extremities, field streamlines, cation-cathode contact positions) to be rotated and viewed from different perspectives to provide a more complete criterion to augment shield design activities.

SELECTED COMPUTER OUTPUT

Copies of FR 80 output (Figs. 1 through 6) may suffice to illustrate some of the present ESD program options/capabilities. Figure 1 presents a geometrical arrangement of a typical nozzle configuration (cathode), a single rectangular anode, and an electrolytic tank whose dimensions are 40 by 40 by 36 in., respectively. Since the cathode is a rigid body of revolution, symmetric about its principal axis, the cylindrical coordinate reference system input option was activated to geometrically define and describe the cathode to the computer. Also, due to the presence of one anode, only a quadrant of the cathode is depicted. The ESD logic incorporates options to depict tank, cathode, anode, shields, etc., in any combination and to sequentially rotate the same through any desired angular displacements. An option to display electric field streamlines and cation cathode contact positions, independent of each other, is also available to engender an optimum clarification of detail. Two modes of electric field streamline depiction are currently available: the standard mode (Mode 1) of successively tracing a field streamline from the locus of each anodic surface element to contact on the cathode, and the scan mode (Mode 2) which involves a computerized scan vertically and horizontally across the face or near proximity of the anode at variable, predetermined increments. Mode 1 would normally be utilized to ascertain the perturbation of the electric field due to shield influences when the option to depict streamlines is active. Mode 2 will, in general, depict as many cation cathode contact positions as are necessary to effectively simulate local cathodic current distribution. For example, if it is desirable to know the ratio of the average number of contacts per cathode surface region, then a large number of contacts per unit area with which to perform the average or to perform a statistical analysis is evidently advantageous. It is possible to select such a small scan increment (vertical/horizontal) that the number of contact positions is quite large and could conceivably exceed Univac 1108 core storage memory. An option to store all computed cation cathode contacts on mass storage devices (tapes, drums, disks, etc.) will be included in the near future. These values

will be available to a generalized local deposition prediction/evaluation technique to determine cathode local area deposit thickness. A general perusal of Figure 1 indicates that a high concentration of electric field is evident at the top and bottom (inlet and exhaust) areas of the nozzle configuration.

The centrally located throat area contains fewer contact points and, hence, under a quasi-steady-state situation is less likely to receive as much electrodeposit. The extreme top and bottom portions, which are possibly characterized by sharp edges, exhibit excessive field concentration and would be subject to "burning." Figure 2 depicts the same configuration as Figure 1 with a nonconducting shield associated with it. The simulated electric field in Figure 1, characterized by the contact distribution on the nozzle, is perturbed by the presence of the shield. The new contact positions are indicative of the new simulated cathodic local current distribution since the contacts per region have in essence been redistributed.

With the advent of a suitable general purpose prediction algorithm, such as a modified form of Faradays laws or utilization of the unmodified form assuming almost 100 percent current efficiency, prediction of local deposit can be effected by evaluation of the number of contacts per unit area or specific region. It should be emphasized at this point that all parameters associated with the mathematical simulation of a specific electroforming process (shield position, anode/cathode position, field strength, etc.) can be output on a high speed line printer if so desired. Currently, shield positions are input and referenced to a cathode centered coordinate system; however, an option to input shields in any of the available reference systems will be incorporated in the ESD logic. Figure 3 illustrates a three-dimensional simulation of a nozzle, anode, and tank environment that is different from Figure 1. It will be readily discerned that the cathode in Figure 3 is "skinnier" than in Figure 1. Again, a single anode is employed and is rectangular in cross sections. It could also be a rectangular basket containing a uniform distribution of anode material. The entire electroplating environment (anode, cathode, tank, etc.) has been rotated to allow a profile of the cathode to be viewed. Options to identify reference coordinate axes, sides of the tank, anode and cathode nomenclature, etc., are contained within the ESD computer program logic but have been suppressed to simplify/explain the basic underlying philosophy of the program. In Figure 1, Mode 2 (scan mode) was employed to generate a relatively large number of contact positions to facilitate the evaluation of relative local cathodic current distribution (i.e., distribution on inlet/exhaust sections relative to throat area).

Mode 1 was employed in Figure 3 to reveal electric field streamlines and probable current flow from the anode surface to the cathode. Flow of current

along the bottom and electrolyte-atmosphere interface are evident. Note also the convergence of the electric field upon the areas closest to the anode and at the inlet/exhaust areas, respectively. Approximately 2 min of Univac 1108 Central Processor Unit (CPU) time was utilized in simulating and depicting Figures 1 and 3. CPU time for Figure 2 was slightly greater and for more complex shield configurations would be greater. Successive simulation of Figure 3 in terms of cathode vertical relationship with respect to tank top and bottom would indicate that the degree of immersion of the cathode in electrolytic solution would vary the electric field concentration on specific cathode areas and could be used to determine an optimum vertical placement of the cathode. As previously mentioned, an algorithm is being developed in an attempt to evaluate local cathodic depositions. The ultimate in three-dimensional simulation would be the utilization of such an algorithm to accommodate time-elapsed depiction (with/without shields) of cathodic growth in terms of satisfaction of input constraints/criteria. Tentatively, the process would be as follows:

1. Computer simulations similar to Figure 3 would be obtained.

2. The number of contacts per unit area or geometric section would be evaluated.

3. A preliminary shield configuration would be described to the ESD program via one of the input reference systems together with input constraints such as desired thickness in specific regions. In the event the cathode possessed symmetry about a principal axis and uniform rotation about the axis is desired, the rotation rate, total bath voltage, etc., would be input.

4. Utilizing a deposition prediction algorithm, the ESD logic would compare simulated electrodeposit thickness in specified regions with input constraints/ criteria to be satisfied and subsequently increment/decrement preliminary shield coordinates in an iterative mode until constraints are satisfied within acceptable limits.

5. The final cathode profile would be output on an FR 80 plotter or advanced graphics terminal screen along with the final coordinates of the "optimized" shield configuration.

Figure 4 illustrates the electric field of Figure 1 as viewed from the top. Figure 5 depicts an alternate shield design simulation in which the shield opening becomes in essence the effective anode. If a prior knowledge of the cathodic deposition growth history is known, the shield opening could be systematically modified per computer run to accommodate changing dimensions of the cathode.

Not considered in the ESD logic are the effects that particular shield placements/ configurations and relative shield-cathode geometry may have upon convection properties and other charge transport inhibition phenomena of an electrolyte. When multiple anode capability is incorporated into the program, it would prove interesting to simulate Figure 5 with an anode in each corner of the tank, each anode being subjected to its respective shielding as is the single node in Figure 6. An effort is being made to utilize the Coons Patch technique for computer-aided design of space form surfaces, developed by Stephen A. Coons, M.I.T., to describe much more intricate cathode, anode, and shield surfaces. An example of these complex surfaces would be a Quadric Saddle Surface associated with blending functions for aircraft fuselage design. It is becoming abundantly evident that there is a practical limit pertinent to utilization of a digital computer in this fashion.

ESD CONCLUSION/SUMMARY

The initial efforts expended in the ESD analysis/development have been primarily directed toward ascertaining if a digital computer could be used to augment nonconducting shield design to facilitate SSME thrust chamber liner electroforming processes. In the interim, SSME engines have been developed which incorporate thrust chamber liners that were electroformed successfully via utilization of appropriate shielding. The ESD Fortran computer program, in its current state, is constrained to function in the capacity of analytically predicting and graphically depicting electric field conformation associated with primary current distribution for relatively uniform geometrical anode/ cathode configurations. The program is being extended to render it amenable to utilization for a larger spectrum of electroforming activities.

The following capabilities are being proposed/incorporated into the existing program logic:

1. Provisions to accommodate geometric description of nonuniform anode/cathode and shield configurations by incorporation of additional input coordinate system options. This should allow versatility for simulation of diversified electroforming efforts.

2. Expansion of ESD logic and computer storage to include additional anodes, since some electroforming requirements dictate multiple-anode usage. Also, the cumulative effect of their respective fields are evidently diverse from single anodic situations; hence, shielding requirements are also different.

14

3. The introduction of additional analytical techniques to accurately predict local cathodic electrodeposit in terms of local current density.

4. The development of the capability to compute and graphically depict a sequential time elapsed history of the "growth" of deposition in the absence of shielding, contrasted with probable effects of shield influence.

5. The introduction of a predictor-corrector numerical integration scheme would be advantageous for solutions of the first-order differential equation that presently describes electric field streamlines, mutual cation cathode contacts, and representative cation motion.

6. The development of additional logic to adopt the Tektronix 4014 advanced graphics display unit in lieu of the FR 80 plotter should enhance the operation of the ESD program by decreasing turnaround time (time elapsed between submission of a computer run and results obtained).

These capabilities will be incorporated into the program logic as time permits, but not necessarily in the order of their appearance in this report. At the conclusion of the ESD development, the program should provide a useful tool to augment diversified electroforming activities. This report is devoid of technical exposition (analytical techniques, theory, programming techniques, etc.) because it is an interim report. The program will be documented according to MSFC Computer Services Office standards, and contemporary development, theory, techniques, etc., will be expounded completely at that time.
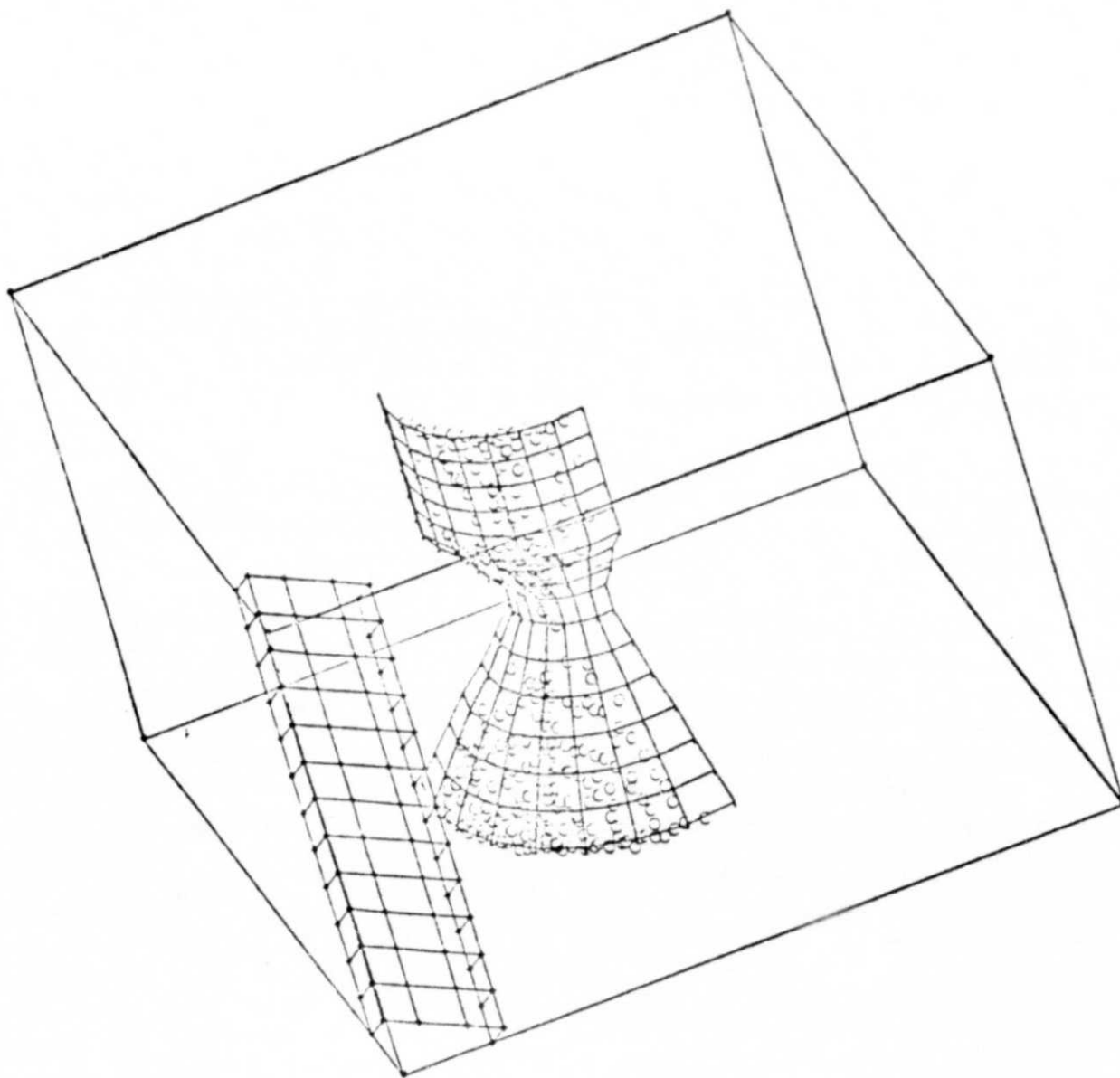
Figure 1. Geometrical arrangement of a typical nozzle configuration (cathode), a single rectangular anode, and an electrolytic tank where dimensions are 101.6 by 101.6 by 91.4 cm, respectively.
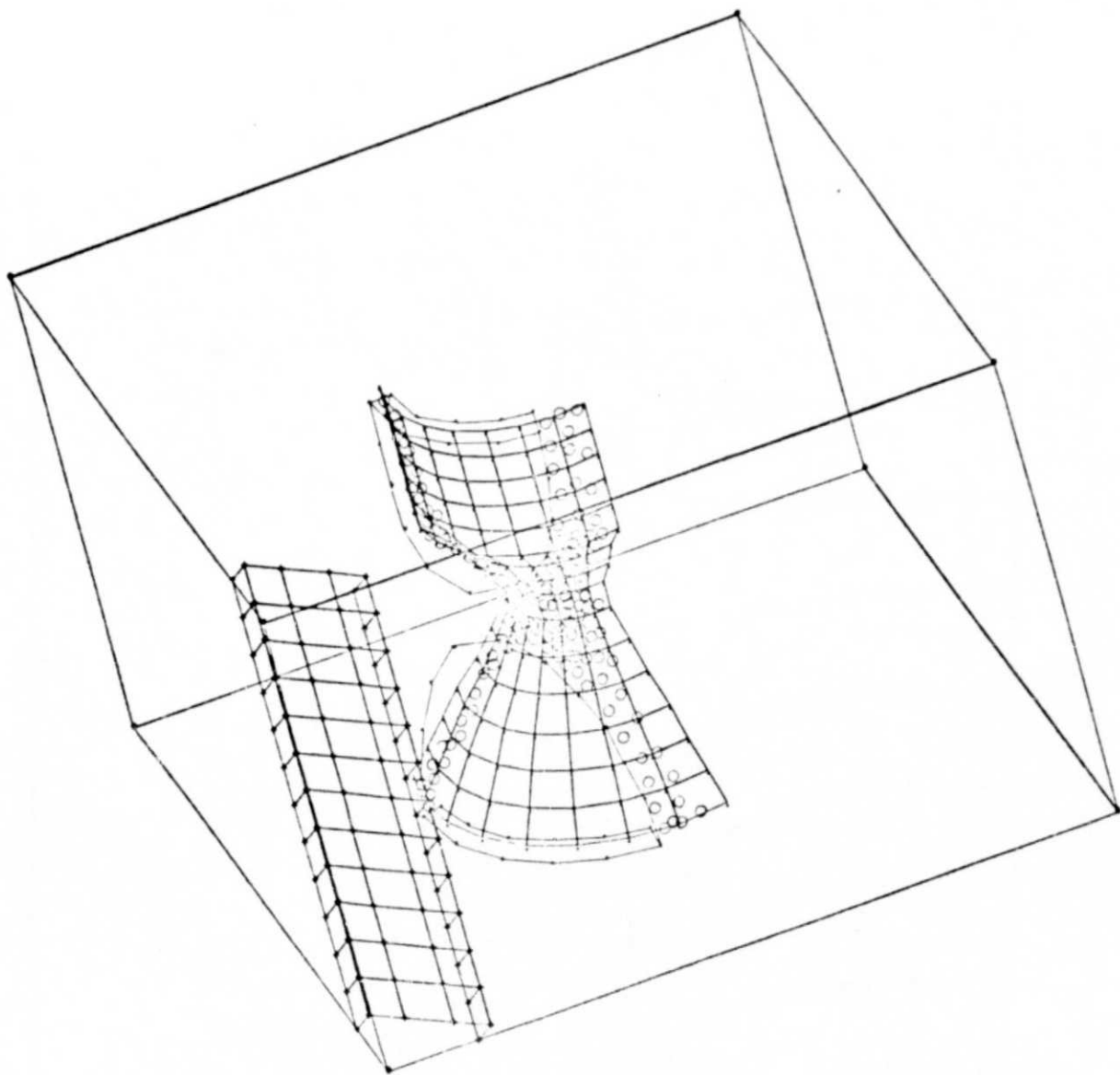
Figure 2. Geometrical arrangement of a typical nozzle configuration (cathode), a single rectangular anode, and an electrolytic tank where dimensions are 101.6 by 101.6 by 91.4 cm, respectively, with a nonconducting shield.
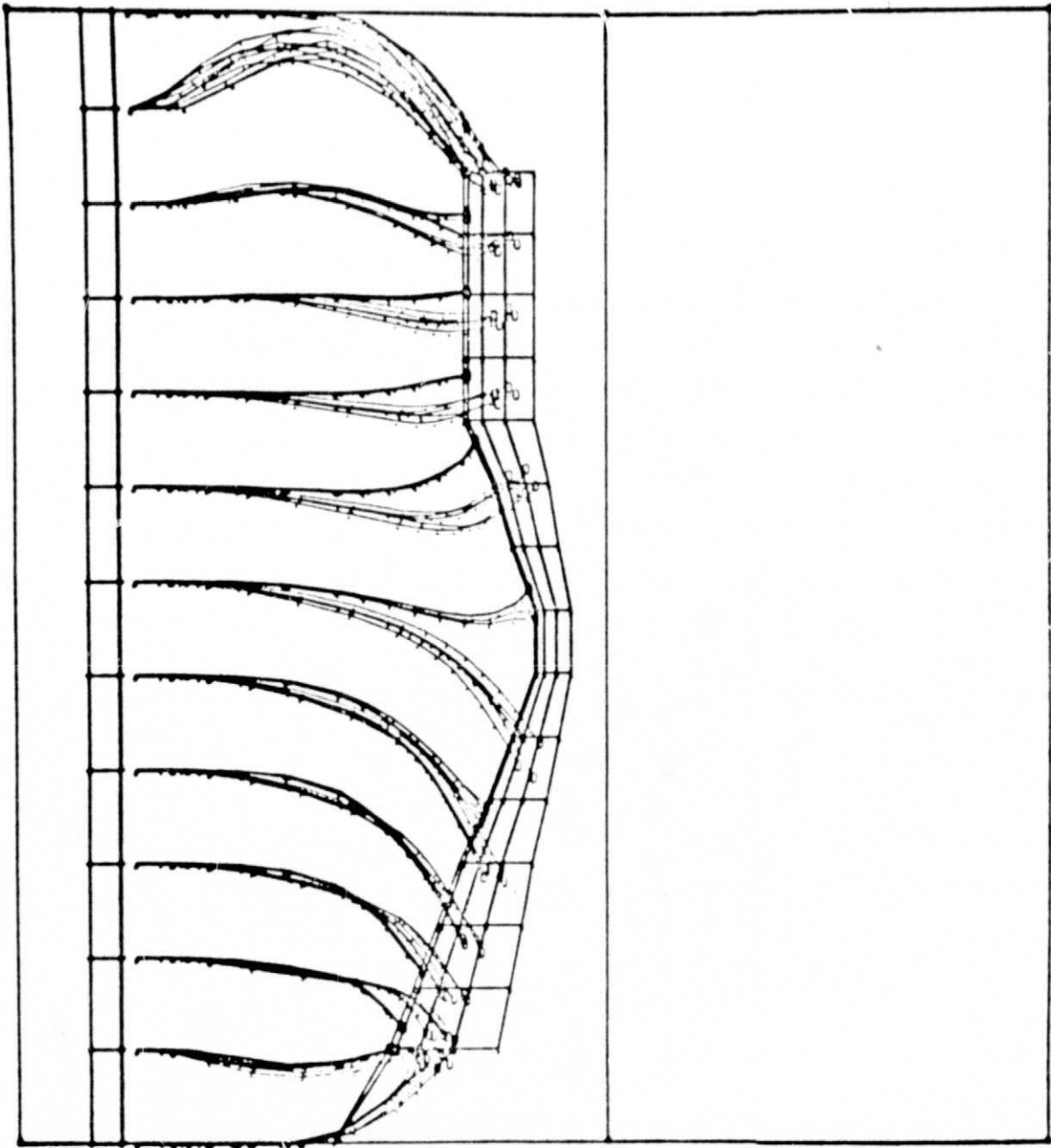
Figure 3. Three-dimensional simulation of a
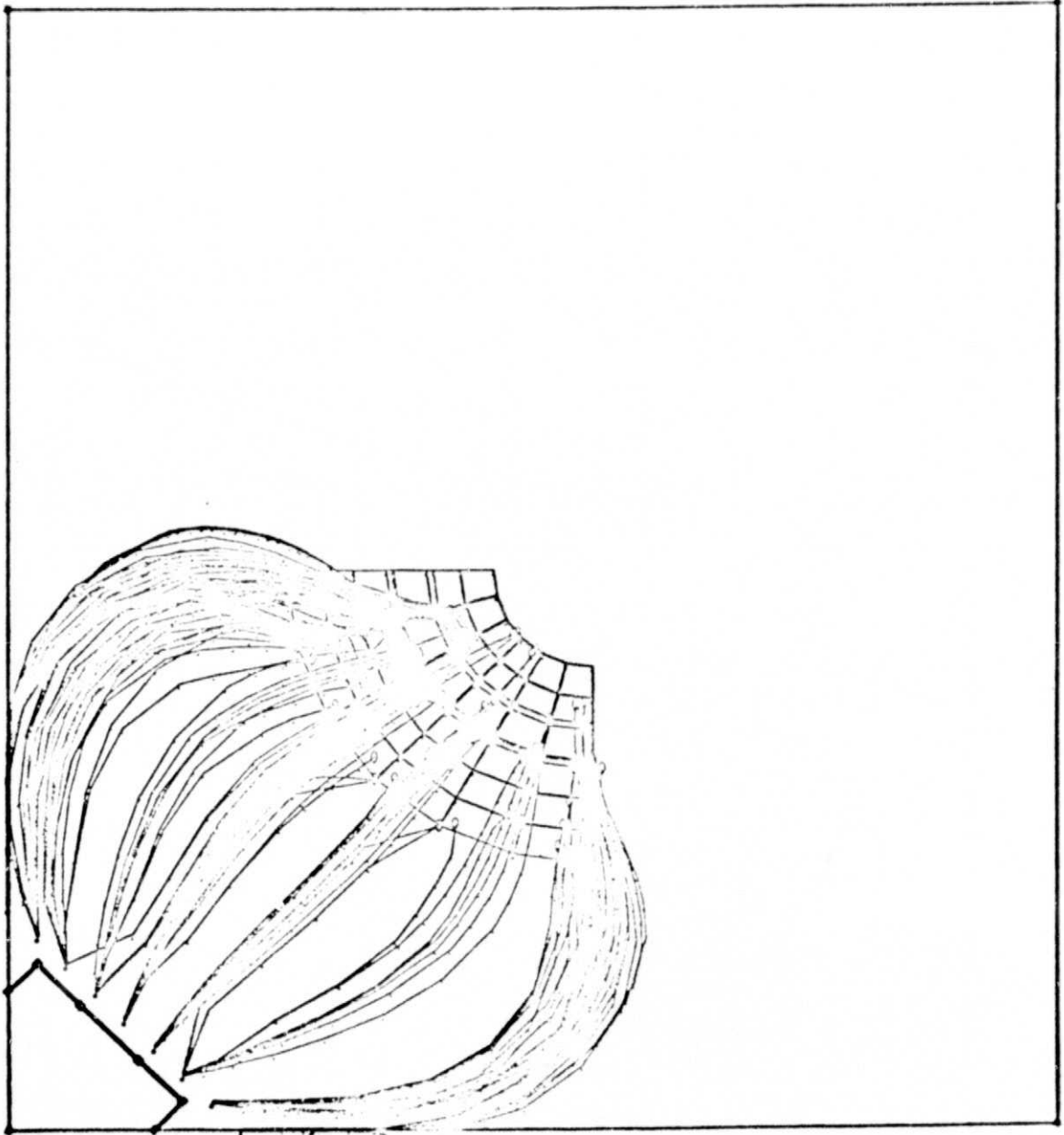nozzle, anode, and tank environment.

18

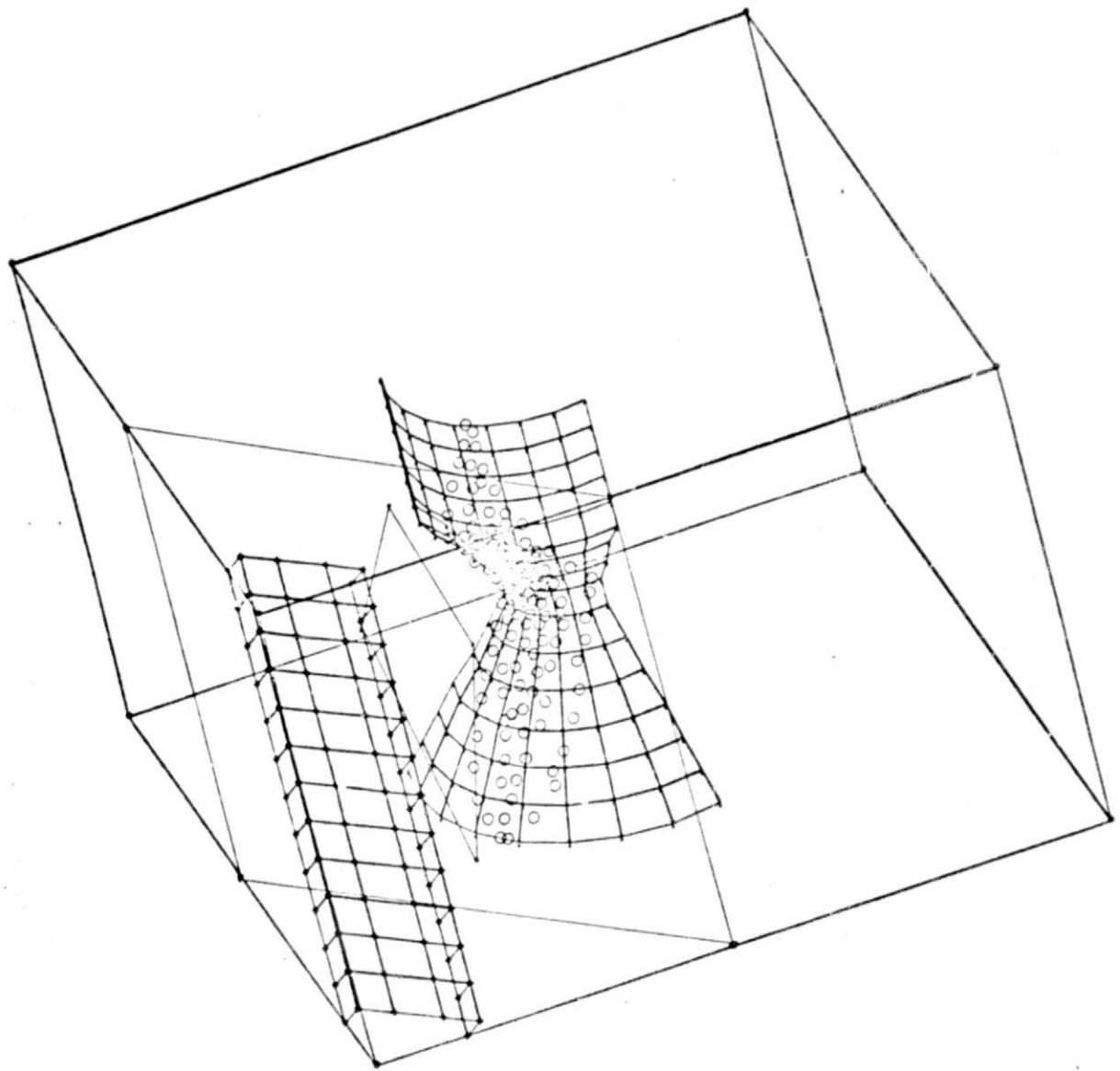Figure 4. Electric field of Figure 1 as viewed from top.
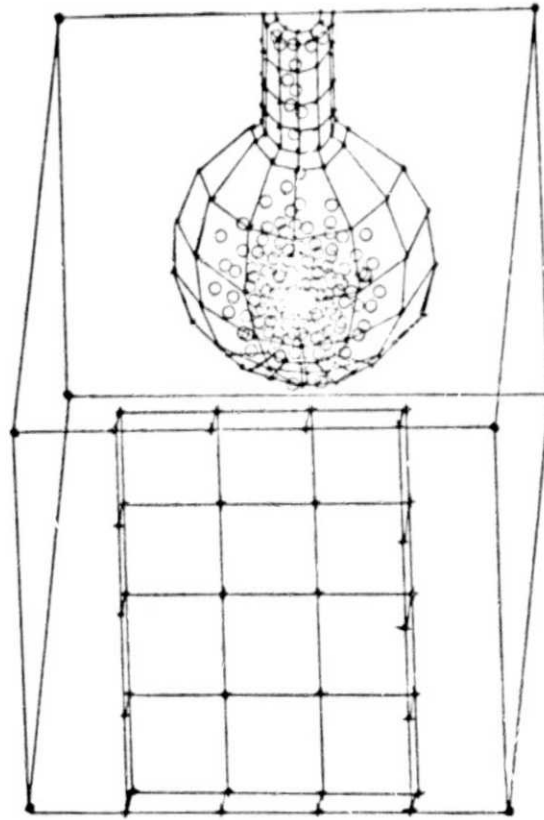
Figure 5. Alternate shield design simulation.

Figure 6. Arbitrary simulation consisting
of rectangular anode and hemisphere-cylinder.