

NASA-TM-83052

NASA Technical Memorandum 83052

NASA-TM-83052 19830017515

Kinetics of Copper Ion Absorption by Cross-Linked Calcium Polyacrylate Membranes

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February 1983

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DISPLAY 89/2/1
83M25/86*# 1550E 15 PAGE 2360 CATEGORY 23 RPT#: NASA-TM-83052
E-1506 MAS 1.15:83052 83/02/00 11 PAGES UNCLASSIFIED DOCUMENT
KINETICS OF COPPER ION ABSORPTION BY CROSS-LINKED CALCIUM POLYACRYLATE

TITLE: membranes
AUTH: A/PHILIPP, W. H.; B/MAY, C. E.
CORP: National Aeronautics and Space Administration, Lewis Research Center,
Cleveland, Ohio. AVAIL. NTIS SAP: HC A02/MF A01
MAVS: /*CONSTANTS/*ELECTRON IRRADIATION/*ION EXCHANGING/*OXIDATION/*PHASE
TRANSFORMATIONS/*RATES (PER TIME)/*REACTION KINETICS
MINS: /ACETATES/ CALCIUM COMPOUNDS/ CONCENTRATION (COMPOSITION) / COPPER ALLOYS/
MATHEMATICAL MODELS/ PH FACTOR/ STOICHIOMETRY

ABA: Author
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SUMMARY

The absorption of copper ions from aqueous copper acetate solutions by cross-linked calcium polyacrylate membranes was found to obey parabolic kinetics similar to that found for oxidation of metals that form protective oxide layers. For pure calcium polyacrylate membranes the rate constant was essentially independent of copper acetate concentration and film thickness. For a cross-linked copolymer film of polyvinyl alcohol and calcium polyacrylate, the rate constant was much greater and dependent on the concentration of copper acetate. The proposed mechanism in each case involves the formation of a copper polyacrylate phase on the surface of the membrane. The diffusion of the copper ion through this phase appears to be the rate controlling step for the copolymer film. The diffusion of the calcium ion is apparently the rate controlling step for the calcium polyacrylate. At low pH, the copper polyacrylate phase consists of the normal copper salt; at higher pH, the phase appears to be the basic copper salt.

INTRODUCTION

Philipp, et al. (ref. 1) describe an electron irradiation method for making thin water insoluble ion exchange membranes from water soluble polymers, namely polyacrylic acid and polyacrylic salts. Membranes made by casting the aqueous polymer solution and air drying at room temperature were irradiated with 2 MeV electrons to effect cross-linking. The cross-linking mechanism appears to involve abstraction of hydrogen on the alpha carbon atom of the polymer by the radicals from irradiated water. The polymer radicals so produced combine to form a cross-linked structure.

Various salts of the cross-linked polymer have been prepared (ref. 1). The sodium and potassium polyacrylate films swelled extensively in water resulting in poor mechanical strength: in a rapidly stirred solution or with normal handling, these films would tear apart. In contrast, films of the cross-linked calcium polyacrylate had good wet strength. Thus, it was the calcium salt that was tested for ion exchange properties and found to be effective in removing cations such as silver, copper, and cobalt from dilute solutions of these metal ions (ref. 1).

This report describes a kinetic study of copper ion absorption by the calcium polyacrylate membrane. The research involves measuring the copper content of calcium polyacrylate films after immersion of the films in aqueous copper acetate solutions for specified times. The dependences of the rate of copper absorption on film thickness, initial copper acetate concentration, and film composition were determined. A mechanism is proposed which involves the diffusion of copper ion and the formation of a distinct copper polyacrylate phase.

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There are several reasons why our membranes are interesting. The first is that they have a high ion capacity: this is due to their low equivalent weight. Next, our membranes are easily prepared from readily obtainable raw materials. Finally, these membranes can have certain advantages over the usual granular form of ion exchange resins, e.g., ease of handling. Several of these advantages will be emphasized in the Discussion Section of this report.

EXPERIMENTAL DETAILS

The preparation of in situ, radiation cross-linked polyacrylic acid films is described in a previous paper (ref. 1). In brief, this film was made by casting 15 percent aqueous polyacrylic acid onto a smooth glass plate with a Gardner blade. The air dried film was swelled in moist air by placing it in a closed container over water. It was then irradiated with 2 MeV electrons at one microampere per square centimeter for 10 minutes to effect cross-linking. The calcium form of the cross-linked polyacrylate film (CaPA) was made by immersing the irradiated polyacrylic acid film in an aqueous solution of calcium hydroxide. To achieve as close to complete neutralization as possible, about twice the stoichiometric amount of calcium hydroxide was used. The films were stored in the calcium hydroxide solution. Before use in the ion exchange studies, the films were rinsed with distilled water to remove the excess calcium hydroxide. They were then cut into 2 by 8 cm coupons for evaluation.

Two film thicknesses were made by setting the Gardner blade at 100 mils (0.25 cm) for the thick films and 25 mils (0.062 cm) for thin films. The final thicknesses of the respective undried calcium polyacrylate films were 0.35 and 0.09 mm.

Films comprising the cross-linked copolymer of polyacrylic acid (PAA) and polyvinyl alcohol (PVA) (Aldrich, M. W. 14000) were made by the technique described previously for cross-linking PAA films. The aqueous casting solution was prepared by mixing 15 percent solutions of PAA and PVA in the volume ratio of 1:1. Casting was done with the Gardner blade set at 100 mils (0.25 cm). We believe that the electron irradiation converted the polymer blend to a cross-linked copolymer. The final thickness of the undried film in its calcium form was 0.35 mm. The dried film was analyzed quantitatively for calcium with an EDTA titration method. From this analysis and the assumption that all the calcium in the copolymer was in the form of the normal calcium polyacrylate, the ratio of PAA to PVA in the original copolymer was calculated to be 0.96 to 1.

Kinetic studies were performed by exposing the 2 by 8 cm film coupons to a stirred solution of 1 liter of 0.2 M or 3 liters of 0.02 M copper acetate solution for a specified time. The 0.2 M solution contained 0.1 M acetic acid, HAc, to prevent precipitation of basic copper salts formed by hydrolysis of the copper acetate. After removal of the films from the solution, they were rinsed with water, dried at 130° C for 12 hours, and weighed. Next, each dried film was digested in a hot concentrated nitric acid solution; each resultant solution was analyzed for copper by atomic absorption techniques. A separate coupon was used for each time interval.

RESULTS

Figure 1 shows the copper ion absorption per unit sample area by cross-linked CaPA as a function of time. The absorption is seen to be proportional to the square root of time. The significance of this parabolic relationship will be given in the Discussion Section. A nearly identical relationship is seen for both the thick (0.35 mm) and the thin (0.09 mm) membranes. These data indicate no significant variation in absorption kinetics with copper ion concentration, even for the order of magnitude difference in our initial CuAc_2 concentrations (0.2 versus 0.02 M).

Figure 2 is a similar plot for the CaPA - PVA copolymer. The initial part of the curve shows the linear relationship between the copper absorption of the membrane versus the square root of time. But, unlike the CaPA, the copolymer membrane appears to become saturated with copper in several hours as indicated by the leveling off of the copper content versus the square root of time graph. In addition, the initial slopes of the curves for the copolymer membrane ($0.26 \text{ mg/cm}^2/\text{min}^{1/2}$ for 0.2 M CuAc_2 and $0.81 \text{ mg/cm}^2/\text{min}^{1/2}$ for the 0.02 M CuAc_2) are greater than that for the calcium polyacrylate, being respectively about 29 and 9 times those in figure 1. This indicates a considerably higher ion exchange rate for the copolymer over the CaPA. Another dissimilarity between the results of the two membranes is that the copolymer shows a significant CuAc_2 concentration dependence which is not observed for the CaPA polymer. For the copolymer, the saturation point is reached at about 3.25 mg/cm^2 in 0.2 M CuAc_2 and about 1.65 mg/cm^2 in 0.02 M CuAc_2 . These correspond to 25.2 percent Cu and 14.8 percent Cu, respectively, based on the dried film.

DISCUSSION

The slow ion exchange rate of the CaPA and parabolic relationship of copper ion absorption by the membrane with time suggest a diffusion controlled mechanism similar to that for the oxidation of certain metals that form a protective oxide (ref. 2). Here, such a mechanism implies that the ion exchange reaction causes a surface build-up of some material which retards ion transport from the solution to the unreacted CaPA. For absorption of copper ions by our ion exchange membranes, just as for the oxidation of certain metals, the reaction rate is dependent on the sample area and independent of thickness of the specimen. This suggests that the rate controlling process is the diffusion of an ion through a growing barrier layer just as the oxidation rate of a species through a growing oxide coating. The growing barrier in our ion exchange membrane system is probably a phase of copper polyacrylate, CuPA, forming between the CaPA and the solution. This phase would increase in thickness as the ion exchange progresses. The existence of such a phase is supported by our observation that the adherent blue CuPA layer on the film can be removed with fine sandpaper leaving a clear unreacted membrane. For the CaPA - PVA copolymer, such a surface layer was not observed.

The kinetics and mechanism found for the absorption of the copper ion by the cross-linked polyacrylic acid membranes are not those usually expected for the diffusion of ions through an ion exchange membrane. Typically, for ion exchange membrane, absorption is controlled by diffusion through the Nernst layer (ref. 3) which does not grow in thickness as ion exchange

progresses. The resulting kinetics is not parabolic as we have found. Therefore, before we continue with the discussion of our data, let us develop the equations applicable to parabolic kinetics.

If the transport of copper ion through the CuPA layer is the rate controlling step, Fick's law for diffusion in an isotropic substance takes the form

$$\frac{dM}{dT} = D \frac{dC}{dX} \quad (1)$$

where M is the copper content per unit surface area of the CuPA layer, T is time, dC/dX is the copper ion concentration gradient in the CuPA, and D is the diffusion coefficient for the copper through the CuPA layer. Because the copper ion concentration at the CuPA - CaPA boundary should be near zero and the copper ion gradient across the CuPA layer should be uniform, equation (1) may be written as follows:

$$\frac{dM}{dT} = D \frac{C_1}{S} \quad (2)$$

where C_1 is the copper ion concentration in the aqueous solution and S is the thickness of the CuPA layer. Furthermore, the CuPA is assumed to have a flat concentration profile across the thickness, S , so that

$$M = S \cdot C_2 \quad (3)$$

where C_2 is the concentration of the copper species bound in the CuPA layer (not the copper ion concentration). Elimination of S between equations (2) and (3) followed by integration results in

$$M = \frac{2 \cdot D \cdot C_1 \cdot D_2 \cdot t}{\quad} \quad (4)$$

Thus, M should vary with the square root of the time as our data (figs. 1 and 2) show. The value of the quantity $(2 \cdot D \cdot C_1 \cdot C_2)$ can be obtained by squaring the slopes of the curves.

A more quantitative discussion of the diffusion process can be made if an accurate value of C_2 is known. This value can be determined from the actual chemical composition of the CuPA layer as follows:

$$C_2 = \frac{(\% \text{ Cu}) (\text{Wt. of dried Cu-saturated film})}{(\text{Vol. of wet membrane})} \quad (5)$$

Two logical possibilities for the stoichiometric composition of the dried CuPA state exist: namely, the basic salt, $(\text{Cu}(\text{Acry})_2 \cdot \text{CuO})_n$, with 44.6 weight percent copper and the normal salt, $(\text{Cu}(\text{Acry})_2)_n$, containing 30.9 weight percent copper. In the wet state, the basic salt would have the formula $(\text{Cu}(\text{Acry})_2 \cdot \text{Cu}(\text{OH})_2)_n$. For the copolymer

(49 percent PAA), the stoichiometric saturation point for each species, respectively, becomes 21.9 and 15.1 weight percent copper. If the basic salt forms in the more concentrated CuAc_2 without addition of HAC and the normal Cu(PA)_2 forms in the more dilute CuAc_2 containing the 0.1 M HAC, these percent values are consistent with our experimental results. Our experimental results for the PAA - PVA copolymer at the saturation point are 25 weight percent copper in 0.2 M CuAc_2 and 15 weight percent in the 0.02 M CuAc_2 , indicating, respectively, the formation of the basic salt and the formation of the normal salt. We found that when the copolymer film was exposed to the more concentrated 0.2 M CuAc_2 acidified with 0.1 M HAC, the saturation point was reached at about 14 percent indicating that it is the acidity which determines the form of the copper acrylate. These observations lead to the conclusion that the normal salt forms at low pH and the basic salt forms at higher pH in the copolymer.

This behavior may also apply to the pure CaPA membrane; because exposure times were not long enough to attain saturation for the copper absorption in pure CaPA, this could not be substantiated by chemical analysis. However, visible spectra for wet CaPA films exposed to a CuAc_2 solution (pH = 5.1) gave a singlet copper band at 710 millimicrometers while a CaPA film exposed to a 0.1 M CuAc_2 - 0.1 M HAC solution (pH = 4.2) gave a triplet copper band with the maximum at 688 millimicrometers and smaller ones at 652 and 634 millimicrometers. The differences in the spectra indicate differences in the structure, most likely due to the presence of the normal copper polyacrylate at low pH and the basic copper polyacrylate at higher pH. When the optical absorption results were used as a measure of the copper content of the films, the parabolic nature of the copper pick-up was again confirmed.

With the aid of equations (4) and (5), the values of $D \times C_1$ and D were calculated for both the CaPA and CaPA - PVA membranes at both copper acetate concentrations. These are shown in table I. In view of the numerous approximations used in the calculations, the diffusion coefficients calculated for the copper ion through the copolymer are in reasonable agreement with the values of D for other ions through similar polymers: the values of D for Li^+ , Rb^+ , and Mg^{++} through CaPA membranes (Philipp and May; unpublished data) range from $2x$ to $10x 10^{-7} \text{ cm}^2/\text{sec}$. Thus, it can be concluded that the rate of copper pickup by the copolymer membrane is controlled by the copper ion diffusion through the copper polyacrylate phase on the membrane.

However, the values of D calculated for the diffusion of the copper ion through the CaPA membrane are extremely small compared with those obtained for the copolymer. Moreover, the values calculated for D for the CaPA are not the same for the different concentrations of the copper ion in solution. Thus, it is unlikely that the diffusion of copper is the rate controlling step in the pickup of copper ion by the CaPA membrane. Therefore, it appears that the diffusion of the calcium ion out through the copper polyacrylate phase is the rate determining step for the calcium polyacrylate membrane. To explain the difference in rate controlling steps between the two membranes, we present the following hypothesis: the high copper ion concentration inhibits the diffusion of the calcium ion in CuPA (the surface coating layer of the CaPA film). Thus, with the calcium ion being the slower moving ion, its diffusion rate becomes the rate determining step. In contrast, the concentration of copper in CuPA - PVA (the surface layer of the CaPA - PVA) is less, so that the diffusion of the calcium ion is

faster. In this case, the faster diffusion rate of the calcium ion can allow the diffusion of the copper ion to become the rate determining step.

In the present work, the use of membranes exhibited several advantages over the use of granules; if granules had been used the calculations would have been dependent on the granules' effective average diameter which would not have been known as precisely as the thickness of our membranes. Furthermore, the use of a membrane allowed easy confirmation of the existence of the surface layer by sanding of the sample. Moreover, the timing of an experiment was more precise for a single washable membrane than it would have been for a precipitate of granules with occluded solution.

Looking for a moment on the practical side of our work, we reach the following conclusions. The CaPA membrane has a high theoretical capacity for ion exchange with copper; however, because of membrane fouling due to a barrier coating, only a small fraction (12 percent) of the theoretical capacity is reached within 60 hours. Copolymerizing with PVA appears to reduce substantially the effect of membrane fouling so that full ion exchange capacity is reached in a relatively short time (two hours).

CONCLUDING REMARKS

The amount of copper absorbed by a CaPA membrane is proportional to the square root of time. These kinetics result from a growing copper polyacrylate layer on the membrane surface. The continuous growth of this layer is due to the continual exchange of the copper ion in solution with the calcium species at the layer-membrane interface. For the CaPA membrane, the rate determining step appears to be the diffusion of the calcium ion outward through the CuPA layer; while for the CaPA - PVA, the rate determining step appears to be the diffusion of the copper ion inward through the copper-containing layer. The result of this is that the copper ion absorption rate by the copolymer is much greater than that by the calcium polyacrylate. At low pH, the layer formed on a membrane appears to be the normal copper acrylate salt; at high pH, it appears to be the basic copper acrylate salt.

The effect of the formation of the copper polyacrylate layer on the calcium polyacrylate membrane is one of fouling: only a small fraction of the membrane capacity is used even after 60 hours. This fouling is substantially reduced by incorporating the polyvinyl alcohol into the polyacrylate structure. This concept might be carried over and used in conventional carboxylic acid resins.

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TABLE I. - DIFFUSION DATA

Mem-brane	Thick-ness, mm	Cu conc in sol, M	M/\sqrt{t} from figs, $\text{mg}/\text{cm}^2\text{min}^{1/2}$	Cu^b at sat, percent	C_2^c , g/cm^3	$C_1 \times D$, $\text{g}/\text{cm sec}$	D , cm^2/sec
CaPA	0.35	0.2	0.0089	44.6	0.318	2.08×10^{-12}	1.64×10^{-10}
CaPA	.35	.02 ^a	.0089	30.9	.221	2.99×10^{-12}	2.35×10^{-9}
CaPA	.09	.2	.0089	44.6	.318	2.08×10^{-12}	1.64×10^{-10}
CaPA-PVA	.35	.2	.26	21.9	.156	3.61×10^{-9}	2.84×10^{-7}
CaPA-PVA	.35	.02 ^a	.081	15.1	.108	5.06×10^{-10}	3.98×10^{-7}

^aAlso 0.1 M in acetic acid.

^bBased on assumed composition.

^cCalculated from equation (5) with $0.714 \text{ g}/\text{cm}^3$ as the weight of dry membrane divided by the volume of wet membrane.

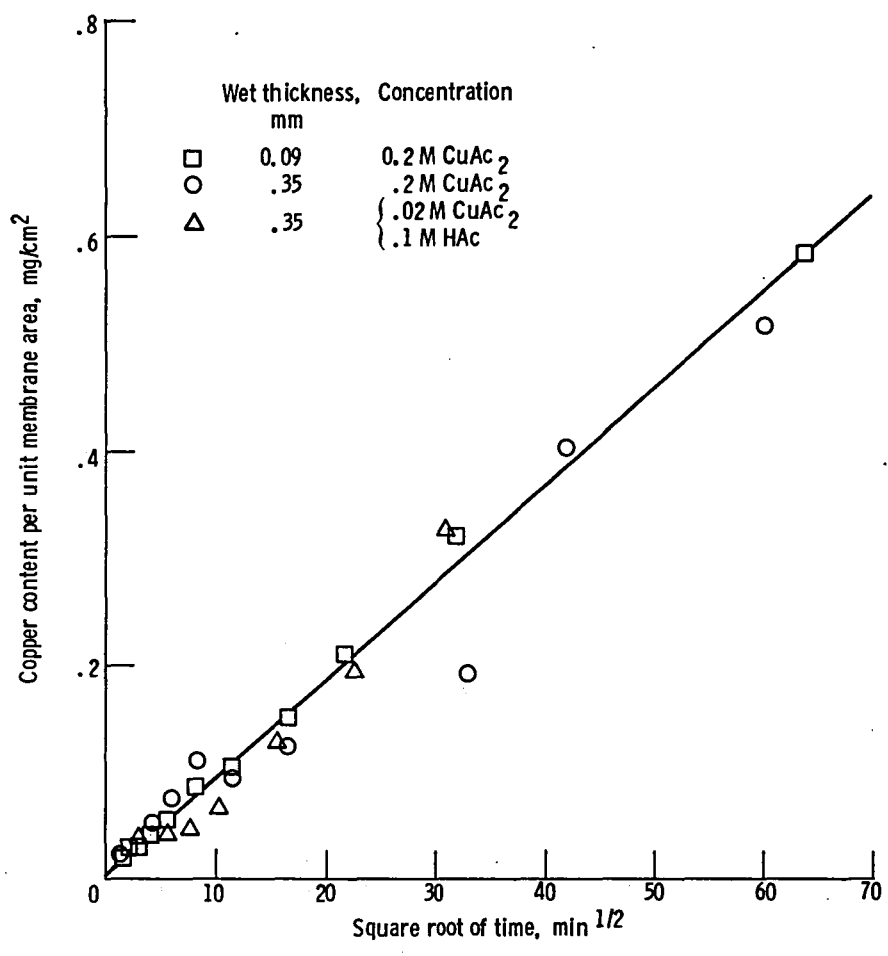


Figure 1. - Kinetics of the absorption of copper ion by a crosslinked CaPA.

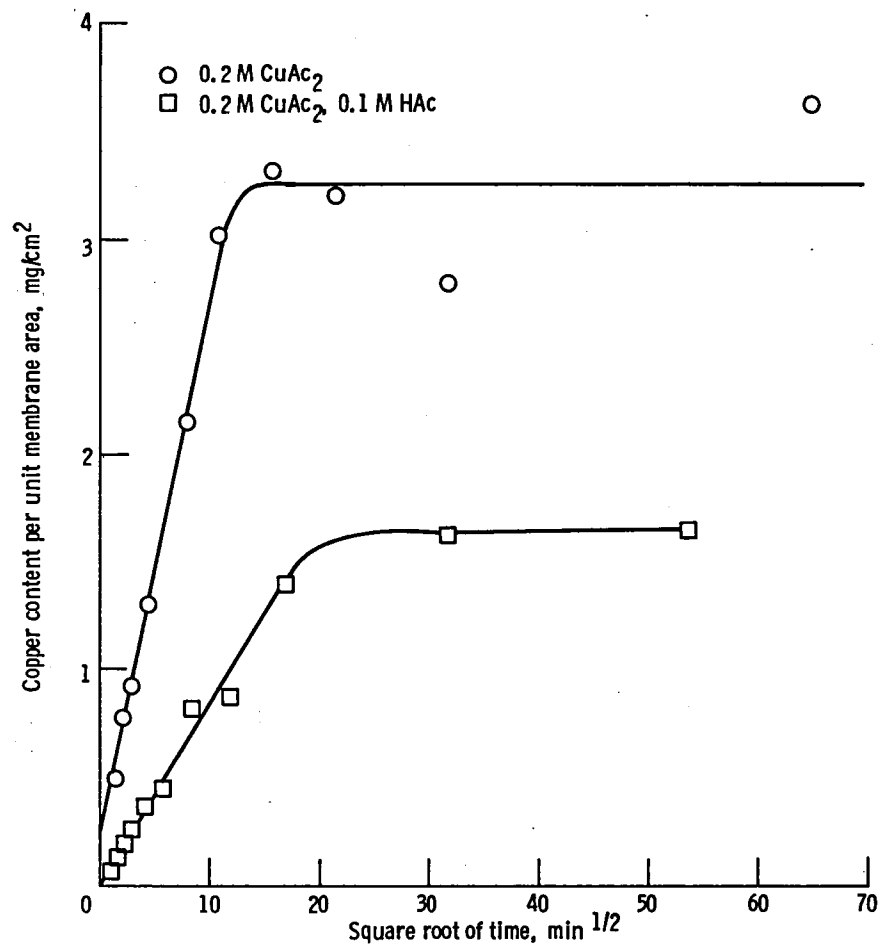


Figure 2. - Kinetics of the absorption of copper ion by the copolymer CaPA-PVA.

1. Report No. NASA TM-83052	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle KINETICS OF COPPER ION ABSORPTION BY CROSS-LINKED CALCIUM POLYACRYLATE MEMBRANES		5. Report Date February 1983	
		6. Performing Organization Code 505-33-1A	
7. Author(s) Warren H. Philipp and Charles E. May		8. Performing Organization Report No. E-1506	
		10. Work Unit No.	
9. Performing Organization Name and Address National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135		11. Contract or Grant No.	
		13. Type of Report and Period Covered Technical Memorandum	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D. C. 20546		14. Sponsoring Agency Code	
		15. Supplementary Notes	
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17. Key Words (Suggested by Author(s)) Ion exchange membranes		18. Distribution Statement Unclassified - unlimited STAR Category 23	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages	22. Price*

* For sale by the National Technical Information Service, Springfield, Virginia 22161

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